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*Some Chemistry of
Group IVB–Cobalt Carbonyl
Compounds*

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by

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ABSTRACT

The reaction of MeGeH_3 and $\text{Co}_2(\text{CO})_8$ has been reinvestigated. Products obtained from this reaction include $\text{MeGeCo}_3(\text{CO})_{11}$, $\text{Me}_2\text{Ge}_2\text{Co}_4(\text{CO})_{14}$ (or $[\text{MeGeCo}(\text{CO})_4]_2\text{Co}_2(\text{CO})_6$), $\text{MeGeHCo}_2(\text{CO})_x$ ($x = 7$ or 8), $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ and $\text{Co}_4(\text{CO})_{12}$, the relative proportion depending on the ratio of the reactants. Decarbonylation of a mixture of $\text{Me}_2\text{Ge}_2\text{Co}_4(\text{CO})_{14}$, $\text{MeGeCo}_3(\text{CO})_{11}$ and $\text{MeGeHCo}_2(\text{CO})_x$ produced a small amount of $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ together with a new compound $\text{Me}_3\text{Ge}_3\text{Co}_5(\text{CO})_{14}$ (or $(\text{MeGe})_2\text{Co}_4(\text{CO})_{10}(\mu\text{-Ge}(\text{Me})\text{Co}(\text{CO})_4)$) which was characterised by a full crystal structure. The crystal structure of $\text{MeGeCo}_3(\text{CO})_{11}$ was also determined.

A new, convenient and efficient route to $(\text{MeM}')_2\text{Co}_4(\text{CO})_{11}$ ($\text{M}' = \text{Si}, \text{Ge}$) clusters has been developed, based on the reaction of $\text{MeM}'\text{H}_3$ with $\text{Co}_4(\text{CO})_{12}$.

Reactions of RGeH_3 ($\text{R} = \text{Me}, \text{Et}, \text{Ph}$) with $\text{M}'\text{Co}_4(\text{CO})_{14}$ ($\text{M}' = \text{Si}, \text{Ge}$) have been investigated in detail. $(\text{RGeH})_n\text{GeCo}_4(\text{CO})_{14-n}$ ($n = 1$ or 2) were obtained from the $\text{GeCo}_4(\text{CO})_{14}$ system. Further reaction of the products with $\text{Co}_2(\text{CO})_8$ produced two new clusters: $\text{RGe}_2\text{Co}_5(\text{CO})_{15}$ (or $(\text{RGe})\text{Co}_4(\text{CO})_{11}(\text{GeCo}(\text{CO})_4)$) ($\text{R} = \text{Me}, \text{Ph}$) from the $(\text{RGeH})\text{GeCo}_4(\text{CO})_{13}$ reaction and $\text{R}_2\text{Ge}_3\text{Co}_6(\text{CO})_{17}$ (or $(\text{RGe})_2\text{Co}_4(\text{CO})_{10}(\mu\text{-GeCo}_2(\text{CO})_7)$) from the $(\text{RGeH})_2\text{GeCo}_4(\text{CO})_{12}$ reaction. Representative X-ray crystal structures of $\text{MeGe}_2\text{Co}_5(\text{CO})_{15}$ and $\text{Et}_2\text{Ge}_3\text{Co}_6(\text{CO})_{17}$ are described.

With $\text{SiCo}_4(\text{CO})_{14}$, MeGeH_3 produced a mixture of compounds, including the new compound $\text{RGeSiCo}_5(\text{CO})_{15}$ (or $(\text{RGe})\text{Co}_4(\text{CO})_{11}(\text{SiCo}(\text{CO})_4)$, characterised by a full crystal structure), $(\text{RGe})_2\text{Co}_4(\text{CO})_{11}$, $\text{Me}_3\text{Ge}_3\text{Co}_5(\text{CO})_{14}$, $\text{SiCo}_4(\text{CO})_{13}$, $\text{Co}_4(\text{CO})_{12}$ and $\text{Co}_2(\text{CO})_8$.

$RR'GeH_2$ ($R = Me, R' = Me, Cl$) reacted with $GeCo_4(CO)_{14}$ to form $(RR'Ge)GeCo_4(CO)_{13}$ and $(RR'Ge)_2GeCo_4(CO)_{12}$ depending on the reaction conditions. Preliminary studies on the reaction of Me_2GeH_2 with $SiCo_4(CO)_{14}$ indicated that $Me_2GeCo_2(CO)_7$, $Me_2GeCo_2(CO)_8$, $(Me_2Ge)_2Co_2(CO)_6$ and $SiCo_4(CO)_{13}$ were formed.

The reaction of $MeSiH_3$ with $GeCo_4(CO)_{14}$ resulted only in the decarbonylation of $GeCo_4(CO)_{14}$ to $GeCo_4(CO)_{13}$. However, in the reaction of $MeSiH_3$ with $SiCo_4(CO)_{14}$, a number of products were formed. These include $MeSiH_2Co(CO)_4$, $Co_2(CO)_8$, $SiCo_4(CO)_{13}$ and a new product of formula $MeSi_2Co_5(CO)_{15}$ (or $(MeSi)Co_4(CO)_{11}(SiCo(CO)_4)$).

Preliminary studies on the following reactions were also carried out: the reaction of Me_2SiH_2 with $M'Co_4(CO)_{14}$ and the reaction of Me_2SiH_2 with $Co_4(CO)_{12}$. In the $GeCo_4(CO)_{14}$ system no reaction other than the decarbonylation of $GeCo_4(CO)_{14}$ to $GeCo_4(CO)_{13}$ was observed. In both the $SiCo_4(CO)_{14}$ and $Co_4(CO)_{12}$ systems, $Me_2SiHCo(CO)_4$, $Me_2[Co(CO)_4]SiOCCo_3(CO)_9$, $Co_2(CO)_8$ and $Co_4(CO)_{12}$ were obtained.

All new products in this study were fully characterised by infrared, 1H NMR, ^{13}CO NMR and mass spectroscopy, and for most, by X-ray crystallography.

Some ^{13}CO NMR studies on $M'-Co$ carbonyl compounds are also reported.

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TABLE OF CONTENTS

ABSTRACT	i
ACKNOWLEDGEMENTS	ii
TABLE OF CONTENTS	iii
LISTS OF FIGURES	iv
LISTS OF TABLES	v
ABBREVIATIONS	vi

CHAPTER ONE Introduction to Group IVB-Transition metal carbonyls

1.1	Introduction	1
1.2	Syntheses of Group IVB - Cobalt carbonyls	4
1.3	Typology of M'-Co carbonyl compounds	
	(M' = Si, Ge, Sn, Pb)	7
1.3.1	The classification	7
1.3.2	Comments on Types	16

CHAPTER TWO Experimental

2.1	Experimental techniques	30
2.1.1	General techniques	30
2.1.2	Fractionation	30
2.1.3	Toepler pump and associated apparatus for the determination of incondensable gases	31
2.2	Instrumental Techniques	32
2.2.1	Infrared (IR) spectroscopy	32
2.2.2	Nuclear Magnetic Resonance Spectroscopy, (NMR)	33
2.2.3	Mass Spectroscopy	33
2.2.4	Electron Probe Analysis, (EPA)	35
2.2.5	X-Ray Crystallography	35

2.3 Starting Reagents	35
2.3.1 Solvents	35
2.3.2 Chemicals; Storage and Preparation	36
2.4 Preparation of Starting Materials	36
2.4.1 Preparation of Monogermane, GeH_4	36
2.4.2 Preparation of SiH_4 , MeGeH_3 , EtGeH_3 , Me_2GeH_2 , MeSiH_3 and Me_2SiH_2	38
2.4.3 Preparation of PhGeH_3	38
2.4.3.1 preparation of tetraphenylgermane	38
2.4.3.2 preparation of phenylgermanium-trichloride	38
2.4.3.3 reduction of PhGeCl_3 by LiAlH_4	39
2.4.4 Preparation of MeGeH_2Cl	39
2.4.5 Preparation of sodium amalgam	39
2.4.6 Preparation of $\text{NaCo}(\text{CO})_4$	40
2.4.7 Preparation of $\text{M}'\text{Co}_4(\text{CO})_{14}$, $\text{M}' = \text{Si, Ge}$	40
2.4.8 Preparation of $\text{Co}_4(\text{CO})_{12}$	41
2.5 ^{13}C enrichment	41

CHAPTER THREE The Reaction of MeGeH_3 and $\text{Co}_2(\text{CO})_8$

3.1 Introduction	42
3.2 Experimental	44
3.2.1 Experimental Run 1 ($\text{Co}_2(\text{CO})_8 : \text{MeGeH}_3 = 1 : 2$)	45
3.2.2 Observations and Workup	45
3.2.3 Discussion on Run 1	46
3.3 Other runs	48
3.3.1 Observations and workup :	
Run 2 ($\text{Co}_2(\text{CO})_8 : \text{MeGeH}_3 = 1 : 0.9$)	48
Run 3 ($\text{Co}_2(\text{CO})_8 : \text{MeGeH}_3 = 1 : 2$)	53
3.4 Discussion	55

3.5 Thermal Decarbonylation of $\text{Me}_2\text{Ge}_2\text{Co}_4(\text{CO})_{14}$	61
3.5.1 Experimental	61
3.5.2 Results and workup	61
3.5.3 Spectroscopic characterisation of $\text{Me}_3\text{Ge}_3\text{Co}_5(\text{CO})_{14}$	65
3.5.4 X-ray Crystal Structure of $\text{Me}_3\text{Ge}_3\text{Co}_5(\text{CO})_{14}$	72
3.6 Decarbonylation of $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$	81
-- a preliminary study only	
3.6.1 Experimental	81
3.6.2 Results	81
3.7 A brief note on the Si analogue of $\text{Me}_3\text{Ge}_3\text{Co}_5(\text{CO})_{14}$	82
3.7.1 Reactions and workup	82
3.7.2 Characterisation of $\text{Me}_3\text{Si}_3\text{Co}_5(\text{CO})_{14}$	83
3.8 Discussion	85
3.9 Characterisation of $\text{MeGeCo}_3(\text{CO})_{11}$	90
3.9.1 Crystal structure of $\text{MeGeCo}_3(\text{CO})_{11}$	90
3.9.2 Spectroscopic characterisation of $\text{MeGeCo}_3(\text{CO})_{11}$	96

CHAPTER FOUR The Reaction of $\text{Co}_4(\text{CO})_{12}$ with $\text{MeM}'\text{H}_3$ and $\text{Me}_2\text{M}'\text{H}_2$

$\text{M}' = \text{Ge, Si}$ ---- a preliminary study

4.1 Introduction	99
4.2 Reaction of MeGeH_3 with $\text{Co}_4(\text{CO})_{12}$	
4.2.1 Experimental, Run 1	99
4.2.2 Results and workup	99
4.2.3 Incondensable gas measurement and unreacted MeGeH_3	101
4.2.4 Other runs	102
4.2.5 Observations and workup	103
4.2.6 Summary (MeGeH_3 with $\text{Co}_4(\text{CO})_{12}$)	105
4.3 Reaction of MeSiH_3 with $\text{Co}_4(\text{CO})_{12}$	105
4.3.1 Run 1, Sealed tube reaction	105

4.3.2 Run 2 Open tube reaction	107
4.3.4 Summary of results (MeSiH ₃ with Co ₄ (CO) ₁₂)	108
4.4 Characterisation of (MeM') ₂ Co ₄ (CO) ₁₁ (M' = Si, Ge)	108
4.4.1 <i>Infrared spectrum</i>	110
4.4.2 <i>Mass spectrum</i>	111
4.4.3 <i>NMR spectrum</i>	113
4.5 Discussion: the reaction of MeM'H ₃ with Co ₄ (CO) ₁₂	113
4.6 The reaction of Co ₄ (CO) ₁₂ with Me ₂ GeH ₂ (1 : 4 ratio)	116
4.6.1 Experimental	116
4.6.2 Results	116
4.7 The reaction of Co ₄ (CO) ₁₂ + Me ₂ SiH ₂ (1 : 4 ratio)	117
4.7.1 Experimental	117
4.7.2 Results	117
4.8 Discussion : The reaction of Me ₂ M'H ₂ with Co ₄ (CO) ₁₂	119

CHAPTER FIVE The Reaction of RM'H₃ With GeCo₄(CO)₁₄

R = Me, Et, Ph for M' = Ge, and R = Me for M' = Si

5.1 Introduction	121
5.2 Reaction of MeGeH ₃ with GeCo ₄ (CO) ₁₄ (sealed tube)	122
5.2.1 Experimental Run 1	122
5.2.2 Observations and workup	122
5.2.3 Other runs	124
5.3 Sealed tube reaction of EtGeH ₃ with GeCo ₄ (CO) ₁₄	130
5.3.1 Experimental Run 1	130
5.3.2 Observations and workup	130
5.3.3 Run 2	131
5.3.4 Run 3 (a) and 3(b)	132
5.4 Reaction of PhGeH ₃ with GeCo ₄ (CO) ₁₄ (sealed tube)	134
5.4.1 Experimental Run 1	134

5.4.2 Observations and workup	134
5.4.3 Other Runs	136
5.5 Reaction of $(\text{EtGeH})\text{GeCo}_4(\text{CO})_{13}$ with PhGeH_3 (open tube)	140
5.5.1 Experimental	140
5.6 The open tube reaction of MeGeH_3 with $\text{GeCo}_4(\text{CO})_{14}$	143
5.6.1 Experimental, Run 1	143
5.6.2 Results	143
5.6.3 Other run	147
5.7 Characterisation of $(\text{RGeH})\text{GeCo}_4(\text{CO})_{13}$ and $(\text{RGeH})_2\text{GeCo}_4(\text{CO})_{12}$	150
5.7.1 $(\text{RGeH})\text{GeCo}_4(\text{CO})_{13}$	150
5.7.1.1 <i>Infrared spectra</i>	150
5.7.1.2 <i>Mass Spectrum</i>	150
5.7.1.3 <i>NMR spectra</i>	153
5.7.2 $(\text{RGeH})_2\text{GeCo}_4(\text{CO})_{12}$	155
5.7.2.1 <i>Infrared spectrum</i>	155
5.7.2.2 <i>Mass spectrum</i>	156
5.7.2.3 <i>NMR spectra</i>	159
5.7.2.4 <i>Electron probe analysis</i>	159
5.8 The reaction of MeSiH_3 with $\text{GeCo}_4(\text{CO})_{14}$	161
5.8.1 Experimental	161
5.8.2 Observations and workup	161
5.9 Discussion of the reactions of RGeH_3 with $\text{GeCo}_4(\text{CO})_{14}$	161
 CHAPTER SIX The Reaction of $\text{R}_1\text{R}_2\text{M}'\text{H}_2$ with $\text{GeCo}_4(\text{CO})_{14}$ $(\text{R}_1\text{R}_2\text{M}' = \text{Me}_2\text{Ge}, \text{MeClGe} \text{ and } \text{Me}_2\text{Si})$	
6.1 Introduction	168
6.2 The reaction of Me_2GeH_2 with $\text{GeCo}_4(\text{CO})_{14}$	170
6.2.1 Experimental, Run 1	170

6.2.2 Observations and Workup	170
6.2.3 Other runs	172
6.3 Reaction of $(\text{Me}_2\text{Ge})\text{GeCo}_4(\text{CO})_{13}$ with Me_2GeH_2	176
6.3.1 Experimental	176
6.3.2 Observations and workup	176
6.4 Characterisation of $(\text{Me}_2\text{Ge})\text{GeCo}_4(\text{CO})_{13}$	176
6.4.1 <i>Infrared and Raman spectra</i>	176
6.4.2 <i>Mass spectrum</i>	179
6.4.3 <i>NMR data</i>	180
6.4.4 <i>Crystal structure</i>	180
6.5 Characterisation of $(\text{Me}_2\text{Ge})_2\text{GeCo}_4(\text{CO})_{12}$	181
6.5.1 <i>Infrared and Raman spectra</i>	181
6.5.2 <i>Mass spectrum</i>	184
6.5.3 <i>NMR data</i>	184
6.5.4 <i>Crystal Structure</i>	185
6.6 Discussion : The reaction of Me_2GeH_2 with $\text{GeCo}_4(\text{CO})_{14}$ and $(\text{Me}_2\text{Ge})\text{GeCo}_4(\text{CO})_{13}$	186
6.7 Decarbonylation of $(\text{Me}_2\text{Ge})\text{GeCo}_4(\text{CO})_{13}$	188
6.7.1 Decarbonylation of $(\text{Me}_2\text{Ge})\text{GeCo}_4(\text{CO})_{13}$ - incondensable gas and infrared experiment	188
6.7.2 Decarbonylation of $(\text{Me}_2\text{Ge})\text{GeCo}_4(\text{CO})_{13}$ - ^1H NMR experiment	194
6.7.3 Discussion of Decarbonylation of $(\text{Me}_2\text{Ge})\text{GeCo}_4(\text{CO})_{13}$	198
6.8 The reaction of MeGeClH_2 with $\text{GeCo}_4(\text{CO})_{14}$	200
6.8.1 Experimental, Run 1	200
6.8.2 Observations and Workup	200
6.9 Reaction of MeGeClH_2 with $(\text{MeGeCl})\text{GeCo}_4(\text{CO})_{13}$	205
6.9.1 Experimental	205
6.10 Characterisation of $(\text{MeGeCl})\text{GeCo}_4(\text{CO})_{13}$	205
6.10.1 <i>Infrared and Raman spectra</i>	205

6.10.2	<i>Mass spectrum</i>	209
6.10.3	<i>Electron probe analysis</i>	210
6.10.4	<i>NMR data</i>	210
6.11	Characterisation of $(\text{MeGeCl})_2\text{GeCo}_4(\text{CO})_{12}$	213
6.11.1	<i>Infrared spectrum</i>	213
6.11.2	<i>Mass spectrum</i>	213
6.11.3	<i>NMR</i>	214
6.12	The reaction of $(\text{MeGeCl})\text{GeCo}_4(\text{CO})_{13}$ and $(\text{MeGeCl})_2\text{GeCo}_4(\text{CO})_{12}$ with $\text{Co}(\text{CO})_4^-$	215
6.12.1	The reaction of $(\text{MeGeCl})\text{GeCo}_4(\text{CO})_{13}$ with $\text{KCo}(\text{CO})_4$	215
6.12.2	The reaction of $(\text{MeGeCl})_2\text{GeCo}_4(\text{CO})_{12}$ with $\text{KCo}(\text{CO})_4$	216
6.12.3	Characterisation of $\text{MeGe}_2\text{Co}_5(\text{CO})_{17}$	217
6.12.4	Characterisation of $\text{Me}_2\text{Ge}_3\text{Co}_6(\text{CO})_{20}$	220
6.13	Discussion	
6.14	Related reactions -- preliminary studies only	223
6.14.1	The reaction of MeClGeH_2 with $(\text{Me}_2\text{Ge})\text{GeCo}_4(\text{CO})_{13}$	226
6.14.2	The reaction of Me_2SiH_2 with $\text{GeCo}_4(\text{CO})_{14}$	230
6.14.3	The reaction of Me_2SiH_2 with $(\text{Me}_2\text{Ge})\text{GeCo}_4(\text{CO})_{13}$	230
6.15	The effect on the infrared spectrum on replacing $\mu\text{-X}$ by $\mu\text{-R}_2\text{Ge}$ in $\text{Co}_2(\text{CO})_6(\mu\text{-X})_2$ type compounds	231

CHAPTER SEVEN The Reaction of $(\text{RGeH})_n\text{GeCo}_4(\text{CO})_{14-n}$ and $\text{Co}_2(\text{CO})_8$ ($n = 1$ or 2)

7.1	Introduction	238
7.2	Reaction of $(\text{MeGeH})\text{GeCo}_4(\text{CO})_{13}$ with $\text{Co}_2(\text{CO})_8$	238
7.2.1	Experimental, Run 1	239
7.2.2	Observations and Workup	239
7.2.3	Run 2	242
7.3	The Reaction of $(\text{PhGeH})\text{GeCo}_4(\text{CO})_{13}$ with $\text{Co}_2(\text{CO})_8$	243

7.3.1 Experimental	243
7.3.2 Observations and workup	243
7.4 Characterisation of $\text{MeGe}_2\text{Co}_5(\text{CO})_{15}$ and $\text{PhGe}_2\text{Co}_5(\text{CO})_{15}$	245
7.4.1 <i>Infrared spectrum</i>	245
7.4.2 <i>Mass Spectrum</i>	248
7.4.3 <i>NMR</i>	249
7.4.4 <i>Electron probe Analysis</i>	250
7.4.5 <i>Crystal Structure of $\text{MeGe}_2\text{Co}_5(\text{CO})_{15}$</i>	250
7.4.5.1 Experimental	250
7.4.5.2 Preliminary studies and data collection	250
7.4.5.3 Solution and refinement	251
7.4.5.4 Discussion of the structure	251
7.5 Discussion	260
7.6 Reaction of $(\text{RGeH})_2\text{GeCo}_4(\text{CO})_{12}$ with $\text{Co}_2(\text{CO})_8$, R = Me, Et	262
7.6.1 Reaction of $(\text{EtGeH})_2\text{GeCo}_4(\text{CO})_{12}$ with $\text{Co}_2(\text{CO})_8$	262
7.6.1.1 Experimental	262
7.6.1.2 Observations and workup	262
7.6.2 Reaction of $(\text{MeGeH})_2\text{GeCo}_4(\text{CO})_{12}$ with $\text{Co}_2(\text{CO})_8$	265
7.6.2.1 Experimental	265
7.6.2.2 Observations workup and discussion	265
7.7 Characterisation of $\text{Et}_2\text{Ge}_3\text{Co}_6(\text{CO})_{17}$ and $\text{Me}_2\text{Ge}_3\text{Co}_6(\text{CO})_{17}$	267
7.7.1 <i>Infrared spectrum</i>	267
7.7.2 <i>Mass spectrum</i>	270
7.7.3 <i>NMR spectrum</i>	271
7.8 Crystal structure of $\text{Et}_2\text{Ge}_3\text{Co}_6(\text{CO})_{17}$	273
7.8.1 Experimental	273
7.8.2 Preliminary precession studies and data collection	273
7.8.3 Solution and refinement	274
7.8.4 Discussion of the Structure	274
7.9 Discussion	284

7.10 The condensation of extended chain cluster to <i>closo</i> -hexanuclear cluster	285
CHAPTER EIGHT The Reaction of $\text{SiCo}_4(\text{CO})_{14}$ with $\text{R}_x\text{M}'\text{H}_{4-x}$ where $\text{M}' = \text{Ge, Si}$, $\text{R} = \text{Me and Et}$, and $x = 1 \text{ and } 2$	
8.1 Reaction of RGeH_3 with $\text{SiCo}_4(\text{CO})_{14}$	289
8.1.1 Experimental of Run 1	289
8.1.2 Observations and workup	289
8.1.3 Characterisation of $\text{RGeSiCo}_5(\text{CO})_{15}$	299
8.1.4 Crystal structure of $\text{EtGeSiCo}_5(\text{CO})_{15}$	304
8.1.5 Discussion	314
8.2 The Reaction of MeSiH_3 with $\text{SiCo}_4(\text{CO})_{14}$	319
8.2.1 Experimental	319
8.2.2 Observations and workup	320
8.2.3 Characterisation of $\text{MeSi}_2\text{Co}_5(\text{CO})_{15}$	321
8.2.4 Discussion	324
8.3 The Reaction of Me_2GeH_2 with $\text{SiCo}_4(\text{CO})_{14}$	326
8.3.1 Experimental	326
8.3.1 Results	326
8.3.3 Discussion	327
8.4 The Reaction of Me_2SiH_2 with $\text{SiCo}_4(\text{CO})_{14}$	329
8.4.1 Experimental	329
8.4.2 Results	329
8.4.3 Discussion	330

CHAPTER NINE	Infrared, NMR Spectra and Crystal Structures of	
	$(RM')_2Co_4(CO)_{10}(\mu-X)$, $M' = Si, Ge$, $R = \text{alkyl, aryl}$	
	or $Co(CO)_4$, $X = CO$, $GeCo_2(CO)_7$ or $Ge(Me)Co(CO)_4$	
9.1	Infrared spectra	332
9.2	NMR spectra	338
9.3	Crystal structures	341
APPENDICES		
Appendix 1	Structures of compounds (1) to (11)	348
Appendix 2		350
Appendix 3		355
Appendix 4		357
Appendix 5		359
Appendix 6		362
Appendix 7		366
References		369

LIST OF FIGURES

Fig 1.1	$[\text{Ph}_3\text{GeCdNi}(\text{GePh}_3)\text{Cp}]_2$	1
Fig 1.2	$(\text{Cl}_2\text{Ge})_2(\text{CoCpCO})_2\text{Fe}(\text{CO})_4$	1
Fig 1.3	$[\text{Pt}_3\text{Sn}_8\text{Cl}_{20}]^{4-}$	1
Fig 1.4	$(\eta^5\text{-CpFe}(\text{CO})_2\text{Sn})_2\text{Fe}_3(\text{CO})_9$	2
Fig 1.5	$(\text{Me}_2\text{Ge})_3\text{Fe}_2(\text{CO})_6$	2
Fig 1.6	$\text{R}_2\text{M}'[\text{Fe}(\text{CO})_4]_2$	2
Fig 1.7	$\text{R}_2\text{M}'_2\text{Fe}_4(\text{CO})_{16}$	2
Fig 1.8	$\text{Me}_4\text{Sn}_3[\text{Fe}(\text{CO})_4]_4$	2
Fig 1.9	$\text{Ge}[\text{Fe}(\text{CO})_4]_4$	2
Fig 1.10	$(\text{Me}_2\text{Ge})_4[\text{Fe}(\text{CO})_4]_2$	2
Fig 1.11	$\text{R}_3\text{M}'\text{Co}(\text{CO})_4$	14
Fig 1.12	$\text{R}_2\text{M}'[\text{Co}(\text{CO})_4]_2$	14
Fig 1.13	$\text{RM}'[\text{Co}(\text{CO})_4]_3$	14
Fig 1.14	$\text{R}_2\text{M}'\text{Co}_2(\text{CO})_7$	14
Fig 1.15	$\text{RM}'\text{Co}_3(\text{CO})_{11}$	14
Fig 1.16	$(\text{RR}'\text{M}')_2\text{Co}_2(\text{CO})_6$	14
Fig 1.17	$\text{RM}'\text{Co}_3(\text{CO})_9$	14
Fig 1.18	$\text{Ge}[\text{Co}_3(\text{CO})_9][\text{Co}_2(\text{CO})_7]^-$	15
Fig 1.19	$\text{Ge}[\text{Co}_3(\text{CO})_9][\text{Co}_4(\text{CO})_{11}]^-$	15
Fig 1.20	$[\text{Co}(\text{CO})_3(\text{GeCo}_3(\text{CO})_9)_2]^-$	15
Fig 1.21	$[\text{Sn}_2\text{Co}(\text{CO})_3\text{R}_6]^-$	15
Fig 1.22	$[\text{SiCo}_9(\text{CO})_{21}]^{2-}$	15
Fig 1.23	$(\text{acac})_2\text{SnCo}_2(\text{CO})_7$	18
Fig 1.24	$\text{Ge}_2\text{Fe}_2\text{Co}_4(\text{CO})_{21}$	18
Fig 1.25	$\text{Bi}_3(\text{CO})_9$	18

Fig 1.26	$t\text{-BuPFe(CO)}_3[(\text{CoCp})_2\mu\text{-CO}]$	18
Fig 1.27	$\text{MePFe(CO)}_3\text{MoCp(CO)}_2\text{Co(CO)}_3$	18
Fig 1.28	$t\text{-BuPFeCo(CO)}_3\text{NiCp}$	18
Fig 1.29	$[\text{Bi}_2\text{Fe}_2\text{Co(CO)}_{10}]^-$	18
Fig 1.30	$(\text{PPh})_2\text{Co}_4(\text{CO})_{10}$	24
Fig 1.31	$(\text{RP})_2\text{M}_4(\text{CO})_{11}$	24
Fig 1.33	$\text{S}_2\text{Ru}_5(\text{CO})_{14}$	24
Fig 1.34	$\text{S}_2\text{Ru}_6(\text{CO})_{17}$	24
Fig 1.35	$\text{E}_2\text{M}_4(\text{CO})_{12}$	24
Fig 1.36	Orbital interaction diagram for $(\text{HP})_2\text{Fe}_4(\text{CO})_{12}$	26
Fig 1.37	$(\text{RP})_2\text{Fe}_4(\text{CO})_{11}$ and $(\text{RP})_2\text{Fe}_4(\text{CO})_{12}$	27
Fig 1.38	$(\text{PhP})_2\text{Co}_4(\text{CO})_6[\text{P(OMe)}_3]_4$	27
Fig 1.39	$(\text{PhP})_2\text{Co}_4(\text{CO})_8[\text{PPh}_2\text{CH}_2]_2$	27
Fig 1.40	$(\mu_4\text{-PPh})\{\mu_4\text{-}\eta^3\text{-P(Ph)CHCH}\}\text{Ru}_4(\text{CO})_{11}$	28
Fig 1.41	$(\mu_3\text{-PPh})_2\text{Ru}_4(\text{CO})_{12}(\mu_2\text{-H})_2$	28
Fig 1.42	$(\mu_3\text{-PPh})_2\text{Ru}_3(\text{CO})_9\text{Ru(CO)}_4$	28
Fig 1.43	$\{(\text{PhP})_2\text{Fe}_2\text{Co}_2(\text{CO})_{10}(\text{OCMe})\}^-\text{Li}^+$	29
Fig 2.1	Ge isotope patterns	34
Fig 2.2	Isotope patterns of Ge compounds containing Cl, Si	34
Fig 2.3	Monogermane preparation apparatus	37
Fig 2.4	^{13}CO enrichment of $\text{GeCo}_4(\text{CO})_{14}$	41
Fig 3.1	IR spectrum of $\text{Me}_2\text{Ge}_2\text{Co}_4(\text{CO})_{14}$	59
Fig 3.2	Incondensable gas evolution from the decarbonylation of impure $\text{Me}_2\text{Ge}_2\text{Co}_4(\text{CO})_{14}$	62
Fig 3.3	IR spectrum of $\text{Me}_3\text{Ge}_3\text{Co}_4(\text{CO})_{14}$ in CH_2Cl_2	67
Fig 3.4	IR spectrum of $\text{Me}_3\text{Ge}_3\text{Co}_4(\text{CO})_{14}$ in hexane/ CH_2Cl_2	67
Fig 3.5	IR spectrum of $\text{Me}_3\text{Ge}_3\text{Co}_4(\text{CO})_{14}$ as KBr disc	67
Fig 3.6	^1H NMR of $\text{Me}_3\text{Ge}_3\text{Co}_5(\text{CO})_{14}$	70
Fig 3.7	^{13}CO NMR of $\text{Me}_3\text{Ge}_3\text{Co}_5(\text{CO})_{14}$	71
Fig 3.8	Crystal structure of $\text{Me}_3\text{Ge}_3\text{Co}_5(\text{CO})_{14}$	74

Fig 3.9	Another view of $\text{Me}_3\text{Ge}_3\text{Co}_5(\text{CO})_{14}$	75
Fig 3.10	Stereo view of $\text{Me}_3\text{Ge}_3\text{Co}_5(\text{CO})_{14}$	80
Fig 3.11	IR spectrum of $\text{Me}_3\text{Si}_3\text{Co}_5(\text{CO})_{14}$	83
Fig 3.12	Crystal structure of $\text{MeGeCo}_3(\text{CO})_{11}$	92
Fig 3.13	Stereo view of $\text{MeGeCo}_3(\text{CO})_{11}$	93
Fig 4.1	Structure of $(\text{MeM}')_2\text{Co}_4(\text{CO})_{11}$	108
Fig 4.2	IR spectrum of $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ in hexane/ CH_2Cl_2	109
Fig 4.3	IR spectrum of $(\text{MeSi})_2\text{Co}_4(\text{CO})_{11}$ in hexane/ CH_2Cl_2	109
Fig 4.4	IR spectrum of $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ in CH_2Cl_2	109
Fig 4.5	IR spectrum of $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ as CsI disc	109
Fig 4.6	Proposed mechanism for the formation of $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$	115
Fig 4.7a	$\text{Me}_2[\text{Co}(\text{CO})_4]\text{SiOCCo}_3(\text{CO})_9$	120
Fig 4.7b	$\text{Me}_3\text{SiOCCo}_3(\text{CO})_9$	120
Fig 4.8	$(\text{Me}_3\text{SiOC})_4\text{Co}_2(\text{CO})_4$	120
Fig 5.1	Incondensable gas measurement of the reaction of $(\text{EtGeH})\text{GeCo}_4(\text{CO})_{13}$ with PhGeH_3	142
Fig 5.2	Incondensable gas evolution of the open tube reaction of $\text{GeCo}_4(\text{CO})_{14}$ with MeGeH_3 , Runs 1 and 2	145
Fig 5.3	IR spectrum of $(\text{MeGeH})\text{GeCo}_4(\text{CO})_{13}$	149
Fig 5.4	IR spectrum of $(\text{MeGeH})_2\text{GeCo}_4(\text{CO})_{12}$	149
Fig 5.5	IR spectrum of $(\text{EtGeH})(\text{PhGeH})\text{GeCo}_4(\text{CO})_{12}$	149
Fig 5.6	Proposed structure of $(\text{RGeH})\text{GeCo}_4(\text{CO})_{13}$	166
Fig 5.7	Proposed structure of $(\text{RGeH})_2\text{GeCo}_4(\text{CO})_{12}$	166
Fig 6.1	$[(\text{CO})_4\text{CoHgGeCo}_4(\text{CO})_{13}]^-$	169
Fig 6.2	Reaction of Me_2GeH_2 with $\text{GeCo}_4(\text{CO})_{14}$ IR changes and Incondensable gas measurements	173
Fig 6.3	IR spectrum of $(\text{Me}_2\text{Ge})\text{GeCo}_4(\text{CO})_{13}$ in hexane	177
Fig 6.4	IR spectrum of $(\text{Me}_2\text{Ge})\text{GeCo}_4(\text{CO})_{13}$ (CsI disc)	177
Fig 6.5	Raman spectrum of $(\text{Me}_2\text{Ge})\text{GeCo}_4(\text{CO})_{13}$	178
Fig 6.6	Proposed structure of $(\text{Me}_2\text{Ge})\text{GeCo}_4(\text{CO})_{13}$	178

Fig 6.7	IR spectrum of $(\text{Me}_2\text{Ge})_2\text{GeCo}_4(\text{CO})_{12}$ (in hexane)	182
Fig 6.8	IR spectrum of $(\text{Me}_2\text{Ge})_2\text{GeCo}_4(\text{CO})_{12}$ (CsI disc)	182
Fig 6.9	Raman spectrum of $(\text{Me}_2\text{Ge})_2\text{GeCo}_4(\text{CO})_{12}$	183
Fig 6.10	Crystal structure of $(\text{Me}_2\text{Ge})_2\text{GeCo}_4(\text{CO})_{12}$	183
Fig 6.11	Incondensable gas evolution of the decarbonylation $(\text{Me}_2\text{Ge})\text{GeCo}_4(\text{CO})_{13}$	190
Fig 6.12	IR spectrum of the supernatant solution of the decarbonylation of $(\text{Me}_2\text{Ge})\text{GeCo}_4(\text{CO})_{13}$, Run 2	191
Fig 6.13	NMR spectrum of the decarbonylation of $(\text{Me}_2\text{Ge})\text{GeCo}_4(\text{CO})_{13}$	195 196
Fig 6.14	IR spectra of $(\text{MeGeCl})\text{GeCo}_4(\text{CO})_{13}$ (solution)	207
Fig 6.15	IR spectrum of $(\text{MeGeCl})\text{GeCo}_4(\text{CO})_{13}$ (CsI disc)	208
Fig 6.17	NMR spectra of $(\text{MeGeCl})\text{GeCo}_4(\text{CO})_{13}$	212
Fig 6.18	Infrared spectrum of $(\text{MeGeCl})_2\text{GeCo}_4(\text{CO})_{12}$	213
Fig 6.19	Infrared spectrum of $\text{MeGe}_2\text{Co}_5(\text{CO})_{17}$	218
Fig 6.20	Infrared spectrum of $\text{Me}_2\text{Ge}_3\text{Co}_6(\text{CO})_{20}$	221
Fig 6.21	Infrared spectrum of $(\text{Me}_2\text{Ge})(\text{MeGeCl})\text{GeCo}_4(\text{CO})_{12}$	228
Fig 6.22	Possible isomers of $(\text{MeGeCl})\text{GeCo}_4(\text{CO})_{13}$ and $(\text{MeGeCl})_2\text{GeCo}_4(\text{CO})_{12}$	237
Fig 7.1	Incondensable gas evolution of $(\text{MeGeH})\text{GeCo}_4(\text{CO})_{13}$ + $\text{Co}_2(\text{CO})_8$	240
Fig 7.2	Incondensable gas evolution of the reaction of $(\text{PhGeH})\text{GeCo}_4(\text{CO})_{13}$ with $\text{Co}_2(\text{CO})_8$	244
Fig 7.3	Infrared spectrum of $\text{MeGe}_2\text{Co}_5(\text{CO})_{15}$ (CH_2Cl_2)	246
Fig 7.4	Infrared spectrum of $\text{PhGe}_2\text{Co}_5(\text{CO})_{15}$ (Hexane/ CH_2Cl_2)	246
Fig 7.5a	Infrared spectrum of $\text{MeGe}_2\text{Co}_5(\text{CO})_{15}$ (Nujol mull)	247
Fig 7.5b	Infrared spectrum of $\text{PhGe}_2\text{Co}_5(\text{CO})_{15}$ (CsI disc)	247
Fig 7.6	Crystal structure of $\text{MeGe}_2\text{Co}_5(\text{CO})_{15}$	252
Fig 7.7a	View of $\text{MeGe}_2\text{Co}_5(\text{CO})_{15}$ through Ge(1), Ge(2), Co(5)	253

Fig 7.7b	Stereo view of $\text{MeGe}_2\text{Co}_5(\text{CO})_{15}$	253
Fig 7.8	Co-Co bond lengths and the degree of bridging	258
Fig 7.9	Incondensable gas evolution of the reaction of $(\text{EtGeH})_2\text{GeCo}_4(\text{CO})_{12}$ with $\text{Co}_2(\text{CO})_8$	263
Fig 7.10	Infrared spectrum of $\text{Me}_2\text{Ge}_3\text{Co}_6(\text{CO})_{17}$ (CH_2Cl_2)	268
Fig 7.11	Infrared spectrum of $\text{Et}_2\text{Ge}_3\text{Co}_6(\text{CO})_{17}$ (CH_2Cl_2)	268
Fig 7.12	Infrared spectrum of $\text{Et}_2\text{Ge}_3\text{Co}_6(\text{CO})_{17}$ (Hexane)	269
Fig 7.13	Infrared spectrum of $\text{Et}_2\text{Ge}_3\text{Co}_6(\text{CO})_{17}$ (CsI disc)	269
Fig 7.14	Crystal structure of $\text{Et}_2\text{Ge}_3\text{Co}_6(\text{CO})_{17}$	275
Fig 7.15	Crystal structure of $\text{Et}_2\text{Ge}_3\text{Co}_6(\text{CO})_{17}$ (other views)	276
Fig 7.16	Co-Co bonds in the Co_4 plane of $\text{Et}_2\text{Ge}_3\text{Co}_6(\text{CO})_{17}$	281
Fig 7.17	Comparison of bond lengths in $\text{Et}_2\text{Ge}_3\text{Co}_6(\text{CO})_{17}$ and $\text{GeCo}_4(\text{CO})_{14}$	282
Fig 7.18	Possible arrangement of $\text{MeGe}_2\text{Co}_5(\text{CO})_{17}$ to $\text{MeGe}_2\text{Co}_5(\text{CO})_{15}$	287
Fig 7.19	Possible structure of $\text{Et}_2\text{Ge}_3\text{Co}_6(\text{CO})_{20}$	288
Fig 7.20	Speculated product from the condensation of $\text{R}_2\text{Ge}_4\text{Co}_8(\text{CO})_{32}$	288
Fig 8.1	Infrared spectra of $(\text{EtGe})_2\text{Co}_4(\text{CO})_{11}$	292
Fig 8.2	IR spectrum of " $\text{Et}_2\text{Ge}_2\text{SiCo}_6(\text{CO})_{17}$ "	294
Fig 8.3	IR spectrum of $\text{EtGeSiCo}_5(\text{CO})_{15}$ (CH_2Cl_2)	300
Fig 8.4	IR spectrum of $\text{MeGeSiCo}_5(\text{CO})_{15}$ (CH_2Cl_2)	300
Fig 8.5	IR spectrum of $\text{EtGeSiCo}_5(\text{CO})_{15}$ (CsI disc)	300
Fig 8.6	Crystal structure of $\text{EtGeSiCo}_5(\text{CO})_{15}$	306
Fig 8.7a	View of $\text{EtGeSiCo}_5(\text{CO})_{15}$ through Ge(1), Si(1) and Co(5)	307
Fig 8.7b	Stereo view of $\text{EtGeSiCo}_5(\text{CO})_{15}$	307
Fig 8.8	$(\mu_4\text{-PhP})\text{Ru}_4(\text{CO})_{12}(\mu_4\text{-RuCo}(\text{CO})_3)$	311
Fig 8.9	Co-Co bonds in $\text{EtGeSiCo}_5(\text{CO})_{15}$	313
Fig 8.10	Infrared spectrum of $\text{MeSi}_2\text{Co}_5(\text{CO})_{15}$ in hexane/ CH_2Cl_2	322
Fig 9.1	M'-Co bond distances in $(\text{RM}')_2\text{Co}_4(\text{CO})_{11}$	345

LIST OF TABLES

Table 2.1	Constant temperature bath	31
Table 2.2	Solvents and drying agents	35
Table 3.1	Reactant ratios for MeGeH_3 and $\text{Co}_2(\text{CO})_8$	44
Table 3.2	IR bands of the hexane soluble fractions from Runs 2 and 3	49
Table 3.3	Mass Spectrum of the oily product	50
Table 3.4	^1H NMR spectrum of the oily mixture from Run 2	51
Table 3.5	Summary of reactions of MeGeH_3 with $\text{Co}_2(\text{CO})_8$	56
Table 3.6	Incondensable gas evolution from the decarbonylation of $\text{Me}_2\text{Ge}_2\text{Co}_4(\text{CO})_{14}$	63
Table 3.7	IR of the supernatant solution and hexane extracts	63
Table 3.8	Infrared spectra of $\text{Me}_3\text{Ge}_3\text{Co}_5(\text{CO})_{14}$	67
Table 3.9	Mass spectrum of $\text{Me}_3\text{Ge}_3\text{Co}_5(\text{CO})_{14}$	67
Table 3.10	Crystal data of $\text{Me}_3\text{Ge}_3\text{Co}_5(\text{CO})_{14}$	72
Table 3.11	Bond lengths of $\text{Me}_3\text{Ge}_3\text{Co}_5(\text{CO})_{14}$	76
Table 3.12	Bond angles of $\text{Me}_3\text{Ge}_3\text{Co}_5(\text{CO})_{14}$	76
Table 3.13	Infrared spectra of the supernatant solution of the decarbonylation of $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$	82
Table 3.14	Crystal data of $\text{Me}_3\text{Si}_3\text{Co}_5(\text{CO})_{14}$	83
Table 3.15	Infrared spectrum of $\text{Me}_3\text{Si}_3\text{Co}_5(\text{CO})_{14}$	84
Table 3.16	Mass spectrum of $\text{Me}_3\text{Si}_3\text{Co}_5(\text{CO})_{14}$	85
Table 3.17	Crystal data of $\text{MeGeCo}_3(\text{CO})_{11}$	91
Table 3.18	Bond Lengths ($\text{\AA}$) for $\text{MeGeCo}_3(\text{CO})_{11}$	93
Table 3.19	Bond Angles ($^\circ$) of $\text{MeGeCo}_3(\text{CO})_{11}$	94
Table 3.20	Infrared spectrum of $\text{MeGeCo}_3(\text{CO})_{11}$	97

Table 3.21	NMR data of $\text{MeGeCo}_3(\text{CO})_{11}$ (in δ ppm)	97
Table 4.1	Experimental conditions of the reaction of MeGeH_3 and $\text{Co}_4(\text{CO})_{12}$	102
Table 4.2	Incondensable gas evolution of Run 4	104
Table 4.3	Summary of the reactions of MeGeH_3 with $\text{Co}_4(\text{CO})_{12}$	105
Table 4.4	Incondensable gas measurements of MeSiH_3 and $\text{Co}_4(\text{CO})_{12}$	107
Table 4.5	Summary of the reactions of MeSiH_3 with $\text{Co}_4(\text{CO})_{12}$	108
Table 4.6	Infrared spectrum of $(\text{MeM}')_2\text{Co}_4(\text{CO})_{11}$	110
Table 4.7	Mass spectrum of $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$	111
Table 4.8	Mass spectrum of $(\text{MeSi})_2\text{Co}_4(\text{CO})_{11}$	112
Table 4.9	NMR data of $(\text{MeM}')_2\text{Co}_4(\text{CO})_{11}$	131
Table 4.10	IR spectrum of Me_2GeH_2 with $\text{Co}_4(\text{CO})_{12}$	116
Table 4.11	Incondensable data of Me_2SiH_2 with $\text{Co}_4(\text{CO})_{12}$	117
Table 4.12	IR spectrum of the product mixture from $\text{Me}_2\text{SiH}_2 + \text{Co}_4(\text{CO})_{12}$	118
Table 5.1	Infrared spectra of hexane extracts of Run 1	123
Table 5.2	Experimental details and results of Runs 2 and 3	124
Table 5.3	Infrared spectrum of the content of Run 6	128
Table 5.4	Summary of the reaction of $\text{GeCo}_4(\text{CO})_{14}$ with MeGeH_3	129
Table 5.5	Infrared spectrum of the supernatant solution of EtGeH_3 with $\text{GeCo}_4(\text{CO})_{14}$, Run 1	131
Table 5.6	Summary of the reaction of EtGeH_3 with $\text{GeCo}_4(\text{CO})_{14}$	134
Table 5.7	Infrared spectrum of the hexane extracts of the reaction of PhGeH_3 and $\text{GeCo}_4(\text{CO})_{14}$, Run 1	135
Table 5.8	Infrared spectrum of hexane soluble fraction of Runs 2 and 4	137
Table 5.9	Summary of the reaction of PhGeH_3 with $\text{GeCo}_4(\text{CO})_{14}$	140
Table 5.10	Incondensable gas measurement of the reaction of $(\text{EtGeH})\text{GeCo}_4(\text{CO})_{13}$ with PhGeH_3	141

Table 5.11	Incondensable gas measurement of the open tube reaction of $\text{GeCo}_4(\text{CO})_{14}$ with MeGeH_3 , Run 1	144
Table 5.12	Mass spectrum of the CH_2Cl_2 soluble fraction from the open tube reaction of $\text{GeCo}_4(\text{CO})_{14}$ with MeGeH_3	146
Table 5.13	Incondensable gas measurements from the open tube reaction of $\text{GeCo}_4(\text{CO})_{14}$ with MeGeH_3 , Run 2	148
Table 5.14	Infrared spectra of $(\text{RGeH})\text{GeCo}_4(\text{CO})_{13}$ compared to $(\text{Me}_2\text{Ge})\text{GeCo}_4(\text{CO})_{13}$	150
Table 5.15	Mass spectrum of $(\text{EtGeH})\text{GeCo}_4(\text{CO})_{13}$	152
Table 5.16	Mass Spectra of $(\text{PhGeH})\text{GeCo}_4(\text{CO})_{13}$	153
Table 5.17	NMR data of $(\text{RGeH})\text{GeCo}_4(\text{CO})_{13}$	155
Table 5.18	^{13}C NMR of $(\text{MeGeH})\text{GeCo}_4(\text{CO})_{13}$	155
Table 5.19	Infrared spectra of $(\text{RGeH})_2\text{GeCo}_4(\text{CO})_{12}$ compared to $(\text{Me}_2\text{Ge})_2\text{GeCo}_4(\text{CO})_{12}$	156
Table 5.20	Mass spectrum of $(\text{MeGeH})_2\text{GeCo}_4(\text{CO})_{12}$	157
Table 5.21	Mass spectrum of $(\text{EtGeH})_2\text{GeCo}_4(\text{CO})_{12}$	158
Table 5.22	^1H NMR data of $(\text{RGeH})_2\text{GeCo}_4(\text{CO})_{12}$	159
Table 5.23	Cell dimensions of $(\text{EtGeH})_2\text{GeCo}_4(\text{CO})_{12}$	160
Table 6.1	IR spectrum of the supernatant solution of Run 1	173
Table 6.2	Incondensable gas/infrared bands changes for Run 3	174
Table 6.3	Infrared and Raman spectra of $(\text{Me}_2\text{Ge})\text{GeCo}_4(\text{CO})_{13}$	179
Table 6.4	NMR data of $(\text{Me}_2\text{Ge})_2\text{GeCo}_4(\text{CO})_{12}$	180
Table 6.5	Infrared and Raman spectra of $(\text{Me}_2\text{Ge})_2\text{GeCo}_4(\text{CO})_{12}$	181
Table 6.6	Mass spectrum of $(\text{Me}_2\text{Ge})_2\text{GeCo}_4(\text{CO})_{12}$	185
Table 6.7	Summary of results of the reaction of Me_2GeH_2 with $\text{GeCo}_4(\text{CO})_{14}$ and $(\text{Me}_2\text{Ge})\text{GeCo}_4(\text{CO})_{13}$	186
Table 6.8	Incondensable gas evolution of the decarbonylation of $(\text{Me}_2\text{Ge})\text{GeCo}_4(\text{CO})_{13}$, Run 1	189
Table 6.9	Incondensable gas measurement of the decarbonylation of $(\text{Me}_2\text{Ge})\text{GeCo}_4(\text{CO})_{13}$, Run 2	193

Table 6.10	IR spectra of supernatant solution of Run 2	193
Table 6.11	Incondensable gas evolution of the open tube reaction of MeClGeH_2 with $\text{GeCo}_4(\text{CO})_{14}$	204
Table 6.12	Products and approximate yields of the reaction of MeGeClH_2 with $\text{GeCo}_4(\text{CO})_{14}$	205
Table 6.13	Infrared and Raman spectra of $(\text{MeGeCl})\text{GeCo}_4(\text{CO})_{13}$	206
Table 6.14	Mass spectrum of $(\text{MeGeCl})\text{GeCo}_4(\text{CO})_{13}$	209
Table 6.15	NMR data of $(\text{MeGeCl})\text{GeCo}_4(\text{CO})_{13}$	211
Table 6.16	Infrared spectrum of $(\text{MeGeCl})_2\text{GeCo}_4(\text{CO})_{12}$	213
Table 6.17	Mass spectrum of $(\text{MeGeCl})_2\text{GeCo}_4(\text{CO})_{12}$	214
Table 6.18	Infrared spectrum of $\text{MeGe}_2\text{Co}_5(\text{CO})_{17}$	218
Table 6.19	Mass spectrum of $\text{MeGe}_2\text{Co}_5(\text{CO})_{17}$	219
Table 6.20	Infrared spectrum of $\text{Me}_2\text{Ge}_3\text{Co}_6(\text{CO})_{20}$	221
Table 6.21	Mass spectrum of $\text{Me}_2\text{Ge}_3\text{Co}_6(\text{CO})_{20}$	222
Table 6.22	Incondensable gas measurement of the reaction of MeGeClH_2 with $(\text{Me}_2\text{Ge})\text{GeCo}_4(\text{CO})_{13}$	223
Table 6.23	Infrared spectra of $(\text{RR}'\text{Ge})_2\text{GeCo}_4(\text{CO})_{12}$	228
Table 6.24	Mass spectrum of $(\text{Me}_2\text{Ge})(\text{MeGeCl})\text{GeCo}_4(\text{CO})_{12}$	229
Table 6.25	Infrared spectra of 'Bor' type compounds	234
Table 7.1	Experimental conditions of $(\text{MeGeH})\text{GeCo}_4(\text{CO})_{13}$ + $\text{Co}_2(\text{CO})_8$	238
Table 7.2	Incondensable readings of Run 1	239
Table 7.3	Infrared spectrum of hexane fraction, Run 1	241
Table 7.4	Incondensable gas evolution of the reaction of $(\text{PhGeH})\text{GeCo}_4(\text{CO})_{13}$ with $\text{Co}_2(\text{CO})_8$	243
Table 7.5	Solid and solution infrared spectra of $\text{MeGe}_2\text{Co}_5(\text{CO})_{15}$ and $\text{PhGe}_2\text{Co}_5(\text{CO})_{15}$	245
Table 7.6	Mass spectrum of $\text{MeGe}_2\text{Co}_5(\text{CO})_{15}$	248
Table 7.7	NMR data of $\text{MeGe}_2\text{Co}_5(\text{CO})_{15}$ and $\text{PhGe}_2\text{Co}_5(\text{CO})_{15}$	249
Table 7.8	Crystal data for $\text{MeGe}_2\text{Co}_5(\text{CO})_{15}$	251

Table 7.9	Bond Lengths (Å) for $\text{MeGe}_2\text{Co}_5(\text{CO})_{15}$	254
Table 7.10	Bond Angles (°) for $\text{MeGe}_2\text{Co}_5(\text{CO})_{15}$	254
Table 7.11	Incondensable gas evolution of the reaction of $(\text{EtGeH})_2\text{GeCo}_4(\text{CO})_{12}$ with $\text{Co}_2(\text{CO})_8$	262
Table 7.12	Infrared spectrum of reaction mixture on day 26	264
Table 7.13	Incondensable gas evolution of the reaction of $(\text{MeGeH})_2\text{GeCo}_4(\text{CO})_{12}$ with $\text{Co}_2(\text{CO})_8$	265
Table 7.14	Infrared spectrum of the reaction of $(\text{MeGeH})_2\text{GeCo}_4(\text{CO})_{12}$ with $\text{Co}_2(\text{CO})_8$ on the 15 th day	266
Table 7.15	Infrared spectra of $\text{R}_2\text{Ge}_3\text{Co}_6(\text{CO})_{17}$	267
Table 7.16	Mass spectrum of $\text{Et}_2\text{Ge}_3\text{Co}_6(\text{CO})_{17}$	270
Table 7.17	NMR data of $\text{Et}_2\text{Ge}_3\text{Co}_6(\text{CO})_{17}$	272
Table 7.18	Crystal data of $\text{Et}_2\text{Ge}_3\text{Co}_6(\text{CO})_{17}$	273
Table 7.19	Bond Lengths (Å) for $\text{Et}_2\text{Ge}_3\text{Co}_6(\text{CO})_{17}$	277
Table 7.20	Bond Angles (°) for $\text{Et}_2\text{Ge}_3\text{Co}_6(\text{CO})_{17}$	278
Table 8.1	Hexane soluble fraction of Runs 1 and 2	291
Table 8.2	Infrared spectrum of $(\text{EtGe})_2\text{Co}_4(\text{CO})_{11}$	293
Table 8.3	Infrared spectrum of $\text{R}_2\text{Ge}_3\text{Co}_6(\text{CO})_{17}$ type compound	283
Table 8.4	Experimental details of Runs 2 and 3 (at 20°C)	284
Table 8.5	Infrared spectrum of the hexane fraction of Run 2	296
Table 8.6	Infrared spectrum of CH_2Cl_2 fraction	297
Table 8.7	Infrared spectrum of the hexane fraction of Run 3	298
Table 8.8	IR spectra of $\text{EtGeSiCo}_5(\text{CO})_{15}$ and $\text{MeGeSiCo}_5(\text{CO})_{15}$	301
Table 8.9	Mass spectrum of $\text{EtGeSiCo}_5(\text{CO})_{15}$	302
Table 8.10	Mass spectrum of $\text{MeGeSiCo}_5(\text{CO})_{15}$	302
Table 8.11	^1H NMR in CDCl_3 at probe temperature of 27°C	303
Table 8.12	Crystal data of $\text{EtGeSiCo}_5(\text{CO})_{15}$	305
Table 8.13	Bond Lengths (Å) of $\text{EtGeSiCo}_5(\text{CO})_{15}$	308
Table 8.14	Bond Angles (°) of $\text{EtGeSiCo}_5(\text{CO})_{15}$	309
Table 8.15	Infrared spectrum of the hexane soluble fraction	320

Table 8.16	Infrared spectrum of $\text{MeSi}_2\text{Co}_5(\text{CO})_{15}$ compares to those of $\text{MeGe}_2\text{Co}_5(\text{CO})_{15}$ and $\text{Si}_2\text{Co}_6(\text{CO})_{19}$	322
Table 8.17	Mass spectrum of $\text{MeSi}_2\text{Co}_5(\text{CO})_{15}$	323
Table 8.18	Infrared spectrum of hexane washing of the reaction of Me_2GeH_2 with $\text{SiCo}_4(\text{CO})_{14}$	327
Table 8.19	Hexane extracts of the reaction of Me_2SiH_2 with $\text{SiCo}_4(\text{CO})_{14}$	329
Table 8.20	Products from the reaction of $\text{M}'\text{Co}_4(\text{CO})_{14}$ with $\text{R}_n\text{M}'\text{H}_{4-n}$ ($n = 1$ or 2)	331
Table 9.1	IR spectra of $(\text{RM}')_2\text{Co}_4(\text{CO})_{11}$	335
Table 9.2	IR spectra of $(\text{RM}')\text{Co}_4(\text{CO})_{11}(\text{M}''\text{Co}(\text{CO})_4)$	335
Table 9.3	IR spectra of $(\text{RM}')_2\text{Co}_4(\text{CO})_{10}(\mu\text{-X})$	337
Table 9.4	^1H NMR of $(\text{RM}')_2\text{Co}_4(\text{CO})_{10}(\mu\text{-X})$	340
Table 9.5	^{13}C NMR of $(\text{RM}')_2\text{Co}_4(\text{CO})_{10}(\mu\text{-X})$	340
Table 9.6	Crystal structure data of $(\text{RM}')_2\text{Co}_4(\text{CO})_{10}(\mu\text{-X})$	346

Abbreviations and notes

The following abbreviations are used in this thesis:-

M'	Group IVB elements
M	Transition metals
E	Main Group elements
R	usually alkyl or aryl groups unless specified
Me	Methyl
Ethyl	Ethyl
Ph	Phenyl
Pr	Propyl
Bu	Butyl
Np	Naphthyl
Tol	Tolyl
Cp	Cyclopentadienyl
tbd	bis(4-trifluoromethylbutane-2,4,-dionate)
bpd	bis[1,3-bis(trifluoromethyl)propane-1,3-dionate]
bppd	bis(1,3-diphenylpropane-1,3-dionate)
acac	bis(2,4-pentanedionato) ($C_5H_7O_2$)
chtd	bis-(cyclohepta-2,4,6-triene-2,7-dionate)
THF	tetrahydrofuran
int	Intensity

NMR Nuclear magnetic resonance

s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet

all chemical shifts in this work are in δ ppm which equals $10-\tau$

IR Infrared spectroscopy

w = weak, m = medium, s = strong, br = broad, v = very, sh = shoulder

all IR bands in cm^{-1}

CHAPTER ONE

Introduction To Group IVB-Transition Metal Carbonyls

1.1 Introduction

The list of compounds containing a transition metal (M) bonded to a Group IV element (M' = Si, Ge, Sn, Pb) has expanded since the first reports in the 1940s [1-8,10-14].

The types of compounds with M-M' bond(s) range from simple species with single M-M' bonds (e.g. $\text{F}_3\text{SiCo}(\text{CO})_4$) through more complicated polynuclear chain (e.g. $[\text{Ph}_3\text{GeCdNi}(\text{GePh}_3)\text{Cp}]_2$ (Fig 1.1)) and ring complexes (e.g. $(\text{Cl}_2\text{Ge})_2(\text{CoCpCO})_2\text{Fe}(\text{CO})_4$ (Fig 1.2)) to cluster compounds both neutral (e.g. $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ (1a) and ionic (e.g. $[\text{Pt}_3\text{Sn}_8\text{Cl}_{20}]^{4-}$ (Fig 1.3)) with unusual M-M' bondings [6].

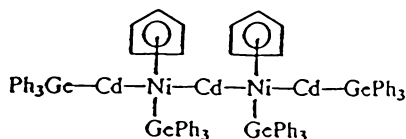


Fig 1.1

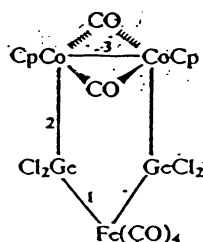
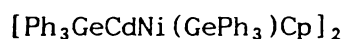


Fig 1.2

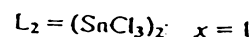
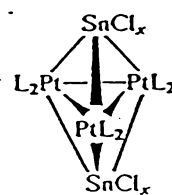
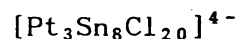


Fig 1.3



The first elements to be studied extensively were those of the iron and chromium groups, followed by manganese, rhenium and cobalt. Characteristically these form M'-M bonds with M in the low oxidation states and with cyclopentadienyl or CO as the commonest ligands [1,6]. The elements of the iron group give rise to a diverse range of structural types and form the most interesting group of M'-M compounds [1,2,4-6,10,13]. Examples of these are shown in Figs 1.4 to 1.10. In contrast, the heavier congeners of cobalt, Rh and Ir together with Pd, Pt and Au form M'-M compounds where the common ligands are tertiary

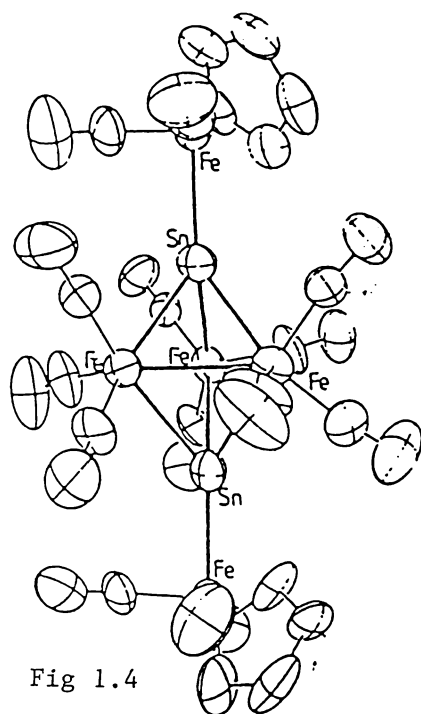


Fig 1.4

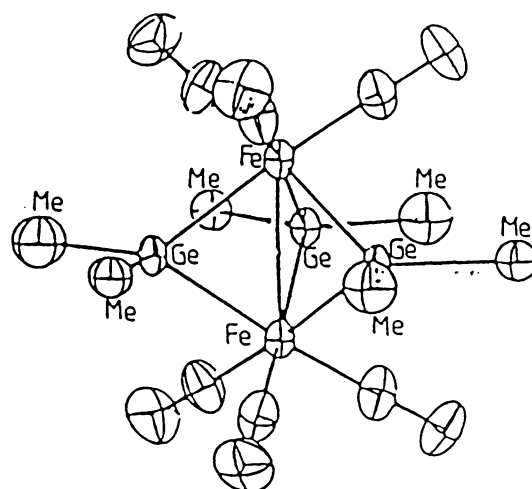
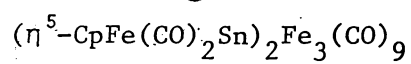
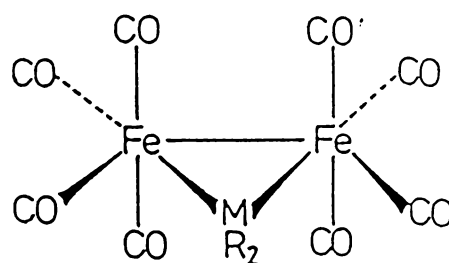
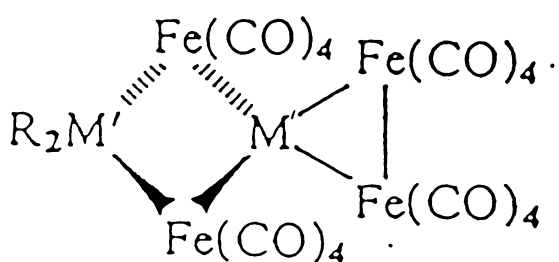
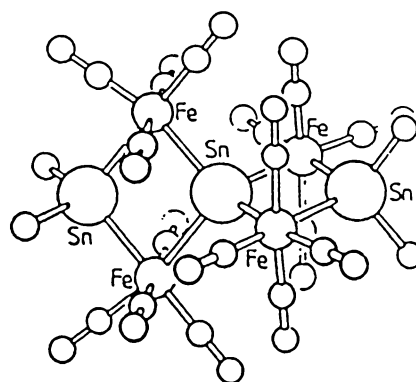
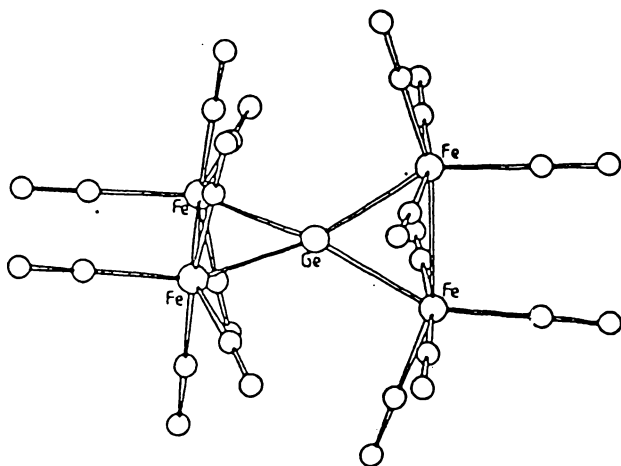
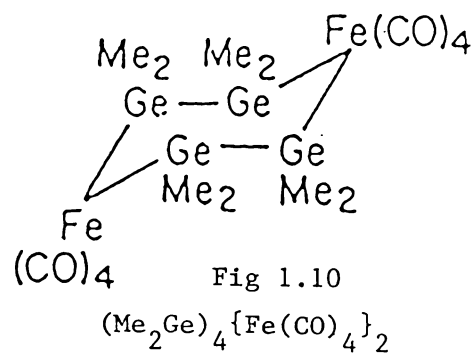
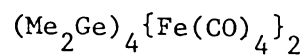
Fig 1.5 $(\text{Me}_2\text{Ge})_3\text{Fe}_2(\text{CO})_6$ Fig 1.6 $\text{R}_2\text{M}'\{\text{Fe(CO)}_4\}_2$ Fig 1.7 $\text{R}_2\text{M}'_2\text{Fe}_4(\text{CO})_{16}$ Fig 1.8 $\text{Me}_4\text{Sn}_3\{\text{Fe(CO)}_4\}_4$ Fig 1.9 $\text{Ge}\{\text{Fe(CO)}_4\}_4$ 

Fig 1.10



phosphines, halogens and carbonyls [1,6] but unlike the cobalt derivatives, no compounds with carbonyls as the only neutral ligand are known. Of the nickel group, the most extensively studied are the four-coordinated platinum-tin complexes. The intensely coloured solutions of $\text{PtCl}_2\text{-SnCl}_2$ complexes were reported as early as 1885, but the actual species were identified much later.

Fewer studies of Group IVB-transition metal compounds are reported for the titanium, vanadium, copper or zinc groups. Reasons for the small number of such compounds include instability of products, difficult purification procedures required, limited synthetic routes and high cost of starting materials. No Group IVB compound of technetium has been made due to handling difficulties (radioactivity).

Of the Group IVB elements, silicon and tin compounds are the most widely explored, followed closely by germanium, while work on lead is more limited.

Early studies on M-M' containing compounds were focussed mainly on comparison with their carbon analogues. There has been considerable interest in the catalytic properties of some M-M' compounds (e.g. the Pt/Sn/Cl system) in hydrogenation and hydroformylation reactions [6,7] and in the possible catalytic capability of some of the other M'-M systems [15]. In the last few years research on M'-M compounds has increased rapidly with interest in their reactions, interconversions, syntheses, structural and spectroscopic properties.

This present work focuses on the studies of germanium and silicon compounds of cobalt carbonyl. Unlike the derivatives of chromium, manganese and iron, these silicon and/or germanium cobalt compounds have the tendency to form clusters [1]. Recent work by highly enthusiastic groups like K.Mackay and B.Nicholson et al, K.Whitmire et al, W.Hermann et al and H.Vahrenkamp et al on extended chain and cluster systems together with the interesting analogues of the

neighbouring iron triad, have served as the main stimulus to the continuing research in this area.

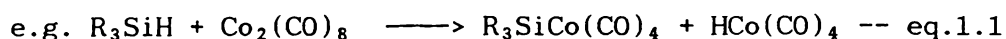
1.2 Syntheses of Group IVB - Cobalt carbonyls

The syntheses of Group IVB - cobalt carbonyl compounds have been extensively reviewed in the past [1-8,14], therefore only the more important methods will be briefly discussed and some key features are noted for each.

1. Reactions of Group IVB hydrides with $\text{Co}_2(\text{CO})_8$:

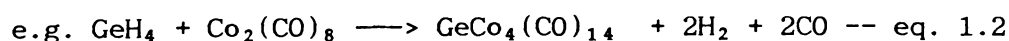
- this is the main synthetic route used in this study.
- most versatile syntheses of Si-Co and Ge-Co compounds.
- not an important route for the preparation of Sn-Co and Pb-Co compounds due to the instability of their hydrides (bond strength decreases in the order $\text{Si-H} > \text{Ge-H} \gg \text{Sn-H} \gg \text{Pb-H}$).
- incondensable gases (H_2 and CO) produced in the reaction are easily removed and may be used to monitor the reaction progress.
- when the starting material contains a number of $\text{M}'\text{-H}$ bonds, polynuclear products are obtained, examples as in equations 1.2 and 1.3.

The reaction is believed to result from the oxidative addition of the $\text{M}'\text{-H}$ bond across a M-M bond, often followed by further reaction of the hydrido complex (equation 1.1).

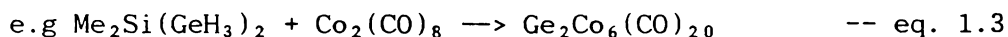


(no solvent, 24 hours in pressure tube, room temperature

yields : $\text{R} = \text{Cl}$, 64%; $\text{R} = \text{Me}$, 38%; $\text{R} = \text{F}$, 60%) [15]



(hexane as solvent, about 3 weeks in pressure tube, room temperature, yield ~90% based on GeH_4 consumed) [16,17].



(in hexane, 2.5 weeks, room temperature, yield 91%, other minor products formed are $\text{GeCo}_4(\text{CO})_{14}$ (**2a**), $\text{Me}_2\text{SiHCo}(\text{CO})_4$) and $\text{Me}_2[\text{Co}(\text{CO})_4]\text{SiOCCo}_3(\text{CO})_9$, [18].

Since a wide range of polyhydrides of Si and Ge are known, this preparative route has great potential.

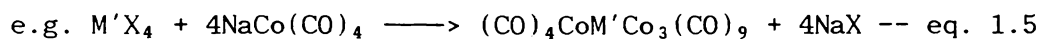
The reaction of Group IVB hydrides with $\text{Co}_2(\text{CO})_8$ may be more complex than shown in the equations above, as yields and products vary greatly depending on the reaction conditions. The reaction of polygermanium hydrides with $\text{Co}_2(\text{CO})_8$ could serve as an example:- the extended chain clusters $\text{Ge}_2\text{Co}_6(\text{CO})_{20}$ (**3**) and $\text{Ge}_3\text{Co}_8(\text{CO})_{26}$ (**4**) were obtained by reacting Ge_2H_6 and Ge_3H_8 with $\text{Co}_2(\text{CO})_8$ respectively. In most reactions a mixture of $\text{GeCo}_4(\text{CO})_{14}$, $\text{Ge}_2\text{Co}_6(\text{CO})_{20}$ and $\text{Ge}_3\text{Co}_8(\text{CO})_{26}$ together with unreacted $\text{Co}_2(\text{CO})_8$ and possibly $\text{Co}_4(\text{CO})_{12}$ were among the observed products. The proportion of each product is a function of both reactant ratio and time, and only under exact control was a specific single product formed [18,19].

2. Reaction of Group IVB metal halides with $\text{Co}(\text{CO})_4^-$

- most widely used method, reactions usually occur rapidly under fairly mild conditions
- reactions are predictable for Ge, Sn and Pb, but for Si there is a tendency to form Si-O species especially when THF is used as solvent.
- $\text{NaCo}(\text{CO})_4$ is easily prepared and the by-product sodium halide is easily removed
- readily extended to polyfunctional species such as Group IVB polyhalides, in this way derivatives with more than one M'-M bond could be prepared (equations 1.5 and 1.6).



(15 minutes at room temperature, 44% yield) [20]



($\text{M}' = \text{Ge}$, $\text{X} = \text{Br}$, in petroleum ether/benzene, 50°C , 20 min,

yield 62%, Fig 1.17) [14,21]

($\text{M}' = \text{Si}$, $\text{X} = \text{I}$, in hexane, 55°C , 2 hours, yield 5%) [14,22]



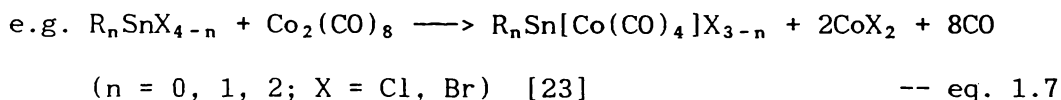
$$x = 1 \text{ to } 3$$

- Complications may arise e.g. in the reactions of GeCl_4 with $\text{NaCo}(\text{CO})_4$, the mercury (from the Hg/Na amalgam) turned up in the product as $\{\text{GeCo}_4(\text{CO})_{13}[\text{HgCo}(\text{CO})_4]\}^-$ [6].

3. Reaction of Group IVB halide with $\text{Co}_2(\text{CO})_8$

(a) using $\text{M}'(\text{IV})$:

- limited to reactions of tin and some germanium halides
- reactions difficult to control



($\text{R} = \text{Ph}$, $n = 1$, $\text{X} = \text{Cl}$, in THF, 2 hours, room temperature, 17% yield)

(b) using $\text{M}'(\text{II})$:

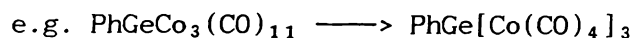
- essentially oxidative addition to $\text{M}'(\text{II})$ halides
- limited to Ge, Sn and Pb which form dihalides
- often require only mild conditions
- require use of excess M' halides



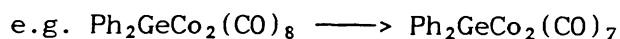
($\text{X} = \text{I}$, in benzene, 3 days, room temperature, 26% yield) [24]

4. Loss of CO from or addition of CO to an existing Group IVB -cobalt carbonyl compound :

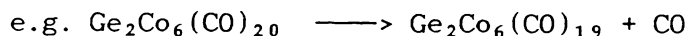
- the number of M'-M bonds does not necessarily change in these interconversions
- leads to the formation or cleavage of M-M bonds
- in many reactions of polyfunctional species, the loss of CO may be involved in the initial reaction to the observed product, especially for Si and Ge derivatives where closed clusters are preferred (e.g. $\text{Co}(\text{CO})_4\text{M}'\text{Co}_3(\text{CO})_9$ was obtained from the reaction of $\text{M}'\text{X}_4$ with $\text{NaCo}(\text{CO})_4$ in equation 1.5 instead of $\text{M}'[\text{Co}(\text{CO})_4]_4$).
- may be initiated by heat, light or pressure.



(300 atm CO) [25]



(hv, 1/2 hr, hexane) [26]



(in hexane, 14 days, 60°C) [27]

1.3 Typology of M'-Co carbonyl compounds (M' = Si, Ge, Sn, Pb)

1.3.1 The classification

The heavier Group IVB - cobalt carbonyl compounds may be classified into 15 (I - XV) different structural types. These are further grouped into 6 tables (Tables 1.1 to 1.6).

Table 1.1 : Types containing terminal $\text{Co}(\text{CO})_4$ units only (Types I-IV)

Table 1.2 : Types containing $\text{Co}_2(\text{CO})_6(\mu\text{-X})_2$ where X = CO or $\text{RR}'\text{M}'$ (Types V - VII)

Table 1.3 : Clusters with linked $\text{M}'\text{Co}_2$ triangles (Types VIII - XI)

Table 1.4 : Types containing a $\text{M}'\text{Co}_3$ trigonal pyramid (Types X - XII)

Table 1.5 : Clusters of $\text{M}'_2\text{Co}_4$ square bipyramid (Type XIII)

Table 1.6 : Miscellaneous types (Types XIV - XV)

Note for Tables 1.1 - 1.6 :

1) * structure determined by X-ray crystallography or electron diffraction.

2) ? tentative assignment : based on partial evidence for an unstable, transient, or minor product.

3) for unmarked compounds - probable structure from close comparison of spectroscopic properties with structurally established analogues.

4) Figs 1.11 to 1.22 are presented on Pages 14 and 15 while structures of commonly mentioned compounds, (I) to (II) are given on two extended pink coloured pages in Appendix 1.

Table 1.1 List of M'- Co carbonyl compounds containing terminal Co(CO)₄ Groups (Types I to IV)

Type I $R_3M'Co(CO)_4$ (Fig 1.11), compounds with one terminal Co(CO)₄ group

R_3/M'	Si	Ge	Sn	Pb
H ₃	[28,29*]	[28,30*]		
D ₃		[28]		
Me ₃	[8,31,32]	[32]	[32-34,38]	[38]
Et ₃	[38,42]	[32,38,41]	[34,38,40]	[38,40]
Ph ₃	[8,38,39,42]	[8,33,38]	[8,33,34,38]	[8,33,38]
(C ₆ F ₅) ₃	[43]	[9*]		[44]
MePh(α -Np)	[7]			
MePh(C ₅ H ₁₁)	[7]			
(OMe) ₃	[38,39]			
(CH ₂ =CH) ₃			[35]	
F ₃	[28,31,45*]	[28]		
Cl ₃	[28,31,38,39,46*-48]	[33,38,47,48,50*]	[8,23,33,34,38,47,48]	
Br ₃	[38,48]	[23,38,48]	[23,34,48,49]	

Table 1.1 List of M'-Co carbonyl compounds containing terminal
Co(CO)₄ Groups (Type I) *cont'd*

I ₃	[48]	[23,38,48]	[23,34,38,48,49]
MeH ₂	[31,51,52]	[80]	
MeF ₂	[52]		
MeCl ₂		[17]	[34,49]
MeBr ₂		[17]	[34,49]
MeI ₂		[33,38]	[34,49]
Ph ₂ H	[42]		
H ₂ Cl	[58]		
Me ₂ H	[58]	[17]	
Me ₂ Cl		[33,38]	[23,34,49]
Me ₂ Br			[34,49]
Me ₂ I			[34,49]
HCl ₂	[58]		
PhCl ₂	[42]	[8,33,38]	[23,34]
PhBr ₂			[23]
PhI ₂		[38]	[23]
Ph ₂ H	[42]		
Ph ₂ Cl		[8,38]	[23,34]
Ph ₂ Br			[23,34]
Ph ₂ I		[33,38]	[23]
n-Bu ₂ Cl			[34]
n-BuCl ₂			[23,34]
(acac) ₂ Cl			[53]
Ph ₂ (Mn(CO) ₅)			[55] [2,56*]
PhCl(Mn(CO) ₅)			[2,57]
HCl(Mn(CO) ₅)		[59]	
Me ₂ (SiHMe ₂)	[54]		
H ₂ (GeH ₃)		[59]	
H ₂ (GeH ₂ Co(CO) ₄)		[59]	
acac			[60]
tbd			[60]
bpd			[60]

Type II $\underline{R_2M'}[Co(CO)_4]_2$ (Fig 1.12), compounds with 2 terminal $Co(CO)_4$ groups

R_2/M'	Si	Ge	Sn	Pb
H_2	[58]			
Cl_2		[33]	[34,63]	
Br_2		[17]	[34,64,63]	
I_2		[64]	[60,64,63]	
Me_2		[20,33,61]	[33,34,36]	
Ph_2		[26,62]	[33,35]	[2,43]
$n-Bu_2$			[34]	
$n-Pr_2$			[34]	
MeH		[20 ⁷]		
$MeCl$		[17,20]	[33,34]	
$MeBr$		[17,20 ⁷]		
MeI		[17,33]		
$PhCl$			[34]	
$(n-Pr)Cl$			[34]	
$(n-Bu)Cl$			[33]	
$(CH=CH)_2$			[35]	
$(CH=CH)Cl$			[33]	
$(CH_3COO)_2$			[23]	
$(acac)_2$			[60,53]	
$(bppd)_2$			[60]	

Type III $\underline{RM'}[Co(CO)_4]_3$ (Fig 1.13a), compounds with three terminal $Co(CO)_4$ groups

R/M'	Si	Ge	Sn	Pb
Me			[34,35,37]	
Et			[34]	
Ph		[25]	[35,37]	
$n-Bu$			[34,35,37]	
F			[23]	
Cl		[17]	[34,35,37,65*]	
Br		[17]	[34,35,37,66*]	
I			[34,35]	
$CH_2=CH$			[37]	
CH_3COO			[23]	

Type IV $\underline{M'[\text{Co}(\text{CO})_4]}_4$ (Fig 1.13b), compounds with 4 terminal $\text{Co}(\text{CO})_4$ groups

$M' =$	Ge	[14,17,67]
	Sn	[14,23,67,68]
	Pb	[14,67,68*]

Table 1.2 Compounds formed by replacing $\mu\text{-CO}$ in one $\text{Co}_2(\text{CO})_8$ unit by M' units (Types V, VI and VII)

Type V Compounds of formula $\underline{R_2M'Co_2(CO)}_7$ (Fig 1.14)

R_2/M'	Si	Ge	Sn
H, Me		[20 ⁷]	
Me_2	[54]	[17,61]	[36]
Ph_2	[25]	[26,62]	
Cl_2	[58]		
$(\text{acac})_2$			[60,53,69*]
$(\text{pbd})_2$			[60]
$(\text{chtd})_2$			[60]

Type VI $\underline{RM'[\text{Co}(\text{CO})_4][\text{Co}_2(\text{CO})_7]}$ (or $\underline{RM'Co_3(CO)}_{11}$) type compound (Fig 1.15)

R/M'	Si	Ge
Me		[20,70,71]
Ph	[25]	[25*,71]
Br		[71]
related species :		
$\text{ClSiMn}(\text{CO})_5[\text{Co}_2(\text{CO})_7]$	[58]	
$\text{MeGeMn}(\text{CO})_5[\text{Co}_2(\text{CO})_7]$	[72]	

Type VII Clusters containing 2 bridging $M'R_2$ groups, $(R_2M')_2Co_2(CO)_6$
(Fig 1.16)

R_2	M'
Me_2	Si [54] Ge [17,61,73,74,75] Sn [36,74]
$Me, [Co(CO)_4]$	Ge [76*]

Table 1.3 Compounds with $M'Co_2$ as building blocks (Type VIII and IX)

Type VIII $M'Co$ compounds with two sets of $Co_2(CO)_7$ groups bridged
by a M' of the formula $M'[Co_2(CO)_7]_2$ (2)

$M' = Si$	[77,78*,79]
Ge	[16*,79]

Type IX Extended chain compound with n number of M' where $n > 1$

n = 2

$(Me_2Ge)(GeCo_4(CO)_{13})$ (5a)	[18,79,81]
$(MeHGe)(GeCo_4(CO)_{13})$ (5b)	[18]
$Ge_2Co_6(CO)_{20}$ (3)	[18,79,81]
$MeGeCo_5(CO)_{17}$ (5c)	[82]

n = 3

$Ge_3Co_8(CO)_{26}$ (4)	[18,79,82-83*]
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n = 4

$(Me_2Ge)_2Ge_2Co_6(CO)_{18}$ (8)	[18]
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Table 1.4 Types containing the $M'Co_3$ trigonal pyramid (Types X to XII)

Type X $RM'[Co_3(CO)_9]$ (Fig 1.17a), compounds with three $Co(CO)_3$ groups forming a $M'Co_3$ core

R/M'	Si	Ge
Me	[85,86,87]	[86]
Ph	[87]	[25,86]
CH ₂ =CH	[85]	
p-Tol	[87]	
Mn(CO) ₅		[72]

Type XI Compounds with a terminal $Co(CO)_4$ group attached to a $M'Co_3$ tetrahedron of the formula $(CO)_4CoM'[Co_3(CO)_9]$ (Fig 1.17b)

M' = Si	[21*,22,67]
Ge	[14,22,67,88*]

Type (XII) Unusual anionic compounds with $M'Co_3$ tetrahedron

1Ge and 5Co : $Ge[Co_3(CO)_9][Co_2(CO)_7]^-$ [89*] (Fig 1.18)

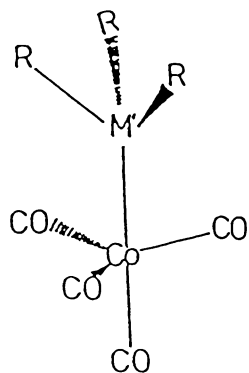
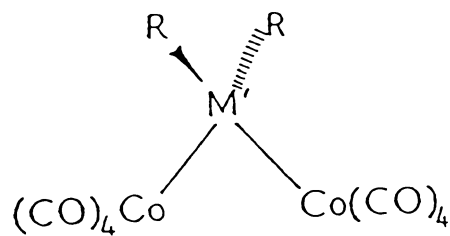
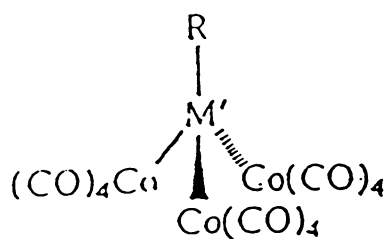
1Ge and 7Co : $Ge[Co_3(CO)_9][Co_4(CO)_{11}]^-$ [90*] (Fig 1.19)

2Ge and 7Co : $\{Co(CO)_3[GeCo_3(CO)_9]_2\}^-$ [79,90*] (Fig 1.20)

Table 1.5 Type containing M'_2Co_4 square pyramid

Type XIII M'_2Co_4 clusters

$(RM')_2Co_4(CO)_{11}$		
M' = Ge	R = Me (1a)	[18,79,84*]
	= Ph (1e)	[91,92]
	= t-Bu (1f)	[91,92]
	= $Co(CO)_4$ (1c)	[18,27*]
	= Me, $Co(CO)_4$ (1g)	[82]
	= Et, $Co(CO)_4$ (1h)	[82]
special :	= Mn(CO) ₅ , $Co(CO)_4$ (1i)	[82]
M' = Si	= $Co(CO)_4$ (1d)	[93*]

Fig 1.11 $R_3M'Co(CO)_4$ Fig 1.12 $R_2M'\{Co(CO)_4\}_2$ Fig 1.13 $RM'\{Co(CO)_4\}_3$

a: R = organic groups
b: R = $Co(CO)_4$

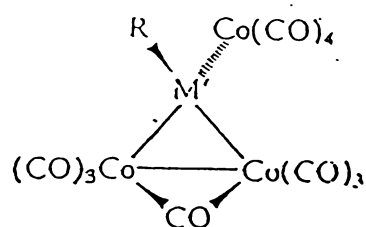
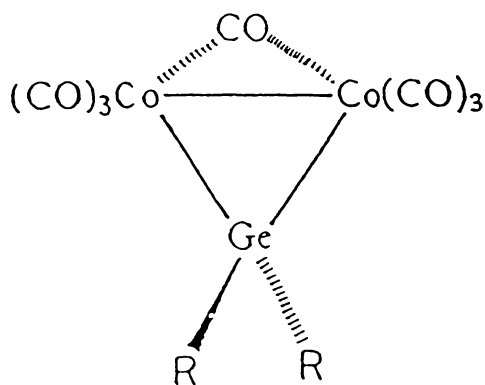
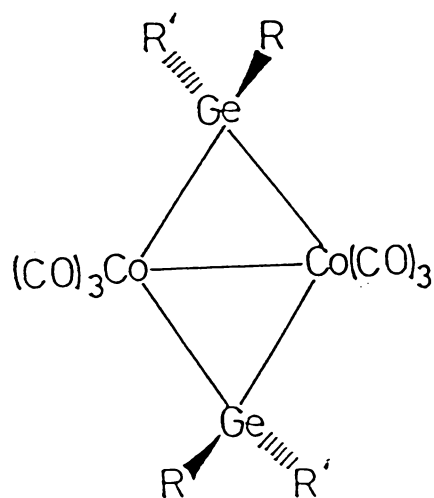
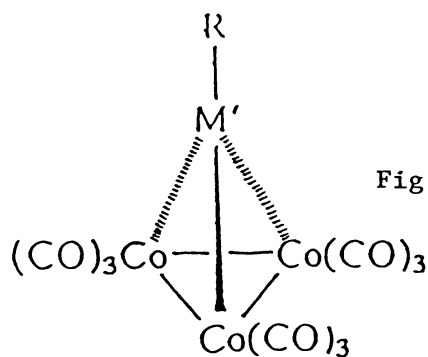


Fig 1.15

$RM'\{Co(CO)_4\}\{Co_2(CO)_7\}$

or $RM'Co_3(CO)_{11}$

Fig 1.14 $R_2M'Co_2(CO)_7$ Fig 1.16 $(RR'M')_2Co_2(CO)_6$ Fig 1.17 $RM'Co_3(CO)_9$

a: R = organic groups
b: R = $Co(CO)_4$

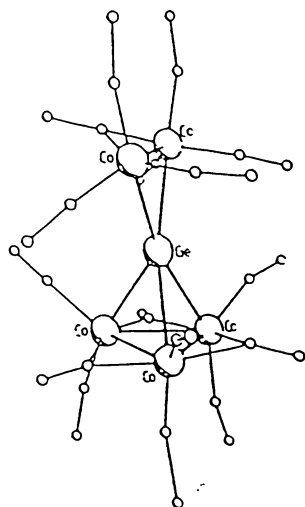


Fig 1.18
 $\{\text{Ge}[\text{Co}_3(\text{CO})_9][\text{Co}_2(\text{CO})_7]\}^-$

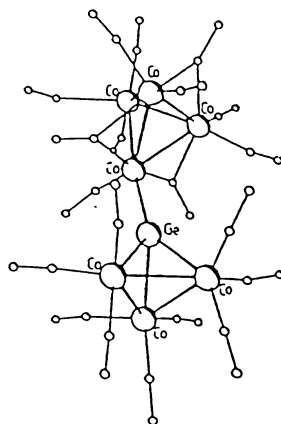


Fig 1.19
 $\{\text{Ge}[\text{Co}_3(\text{CO})_9][\text{Co}_4(\text{CO})_{11}]\}^-$

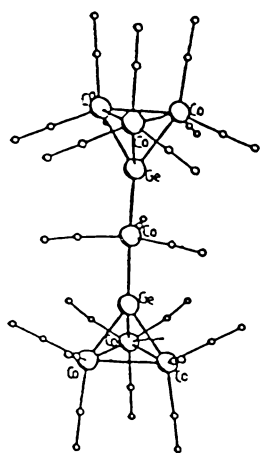


Fig 1.20
 $\{\text{Co}(\text{CO})_3(\text{GeCo}_3(\text{CO})_9)_2\}^-$

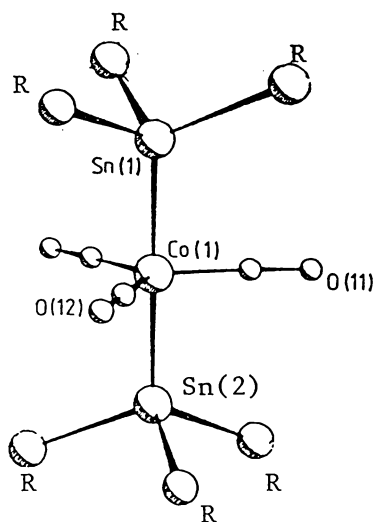


Fig 1.21
 $\{\text{Sn}_2\text{Co}(\text{CO})_3\text{R}_6\}^-$

a: $\text{R}_6 = \text{Cl}_6$

b: $\text{R}_6 = (1,1,2,2-\text{Cl}_4)\{\text{Co}(\text{CO})_4\}_2$

c: $\text{R}_6 = (1,2-\text{Cl}_2)\{\text{Co}(\text{CO})_4\}_4$

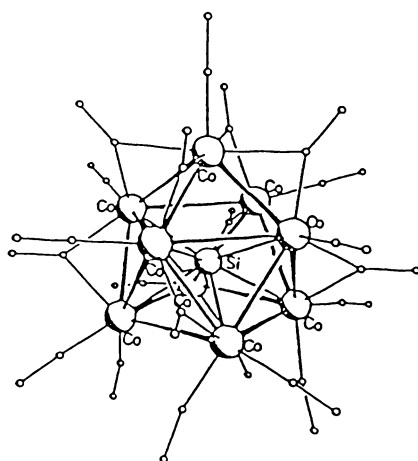


Fig 1.22 $\{\text{SiCo}_9(\text{CO})_{21}\}^{2-}$

Table 1.6 Miscellaneous types

Type XIV Clusters with $M'CoM'$ bonds (Fig 1.21)

2Sn and 1Co : $[Sn_2CoCl_6(CO)_3]^-$ (Fig 1.21a) [94*]

2Sn and 3Co : $[Sn_2Co_3Cl_4(CO)_{11}]^-$ (Fig 1.21b) [94*]

2Sn and 5Co : $[Sn_2Co_5Cl_2(CO)_{19}]^-$ (Fig 1.21c) [94,95*]

2Sn and 7Co : $[Sn_2Co_7(CO)_{27}]^-$ [94?]

Type XV Cluster with encapsulated Si

9Co : $[SiCo_9(CO)_{21}]^{2-}$ (Fig 1.22) [96*]

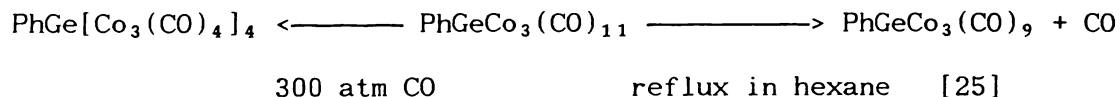
1.3.2 Comments on Types

(a) Simple compounds containing terminal $Co(CO)_4$ groups and $Co_2(CO)_7$ groups (Types I,II and V)

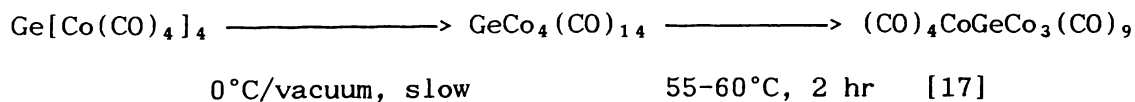
Much has been written about the above groups of simple compounds [1,2,6,8,20,28-61] and therefore no further discussion is necessary here.

(b) Simpler $RM'Co_3$ (Types III,VI,X) and $M'Co_4$ (Types IV,VIII,XI) plus comments on some $M'Co_2(CO)_7$ (Type V) and $(M')_2Co_2(CO)_6$ (Type VII) compounds

The three types of $M'Co_3$ compounds $RM'[Co(CO)_4]_3$, $RM'Co_3(CO)_{11}$ and $RM'Co_3(CO)_9$ are interconvertible via Method 4 in Section 1.2. $PhGeCo_3(CO)_{11}$ serves as a good example :



A similar relationship also exist for the $M'Co_4$ compounds :



The tendency to close down from the open species to form $M'Co_2$ triangles or $M'Co_3$ trigonal pyramids is found in the lighter Group IVB elements (Si, Ge). This can be understood in terms of the size of M' .

For a small M' atom an increase in the number of $Co(CO)_4$ groups would increase the steric congestion around the central M' atom. Formation of a closed cluster is therefore sterically more favourable. For a larger M' atom, a longer $M'-Co$ distance and more acute $Co-M'-Co$ angle are required to maintain a constant $Co-Co$ distance as is required for a closed cluster. Therefore the $Co-Co$ bond in such compounds containing a larger M' would be more strained [36]. This can be seen in the crystal structure of $(acac)_2SnCo_2(CO)_7$ (Fig 1.23) [69] where the $Co-Co$ distance of $2.66\text{\AA}$ is unusually long compared to the $Co-Co$ distance ($2.43-2.55\text{\AA}$) of other cobalt carbonyl cluster compounds containing $\mu-CO$ groups. For example the $Co-Co$ distance in $PhGeCo_3(CO)_{11}$ (Fig 1.15) is $2.546\text{\AA}$ [25]. The bonding is made possible in this tin example by the bulk of the $acac$ ligands and the increase in the coordination number of tin to six [53] as in this case the angle reduction to 61.5° is from 90° (sp^3d^2) instead of from 109.5° (sp^3) (four coordination). The latter reason probably explains the "exceeding instability" found in $Me_2SnCo_2(CO)_7$ which contains a four coordinated tin. Therefore, M' larger than Ge prefer to form compounds of open structure.

An interesting contrast is found in the $M'[Fe_2(CO)_8]_2$ (Fig 1.9) compounds reported for $M' = Si, Ge, Sn$ and Pb . Here $M'Fe_2$ triangles are formed for all four M' cases perhaps because the $Fe-Fe$ distance is less constrained in absence of a bridging CO . The steric argument is reflected in the $Fe-Fe$ distance of these $M'[Fe_2(CO)_8]_2$:

$Ge[Fe_2(CO)_8]_2$ average $Fe-Fe = 2.82\text{\AA}$ [97]

$Sn[Fe_2(CO)_8]_2$ average $Fe-Fe = 2.87\text{\AA}$ [98]

$Pb[Fe_2(CO)_8]_2$ average $Fe-Fe = 2.90\text{\AA}$ [99]

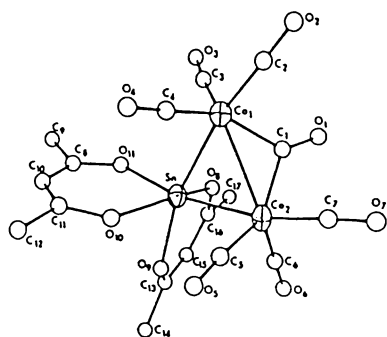
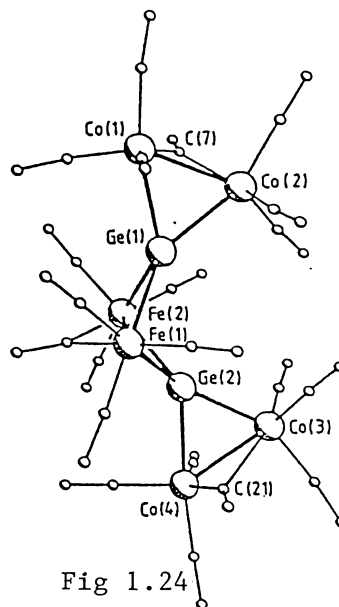
Fig 1.23 $(acac)_2SnCo_2(CO)_7$ 

Fig 1.24

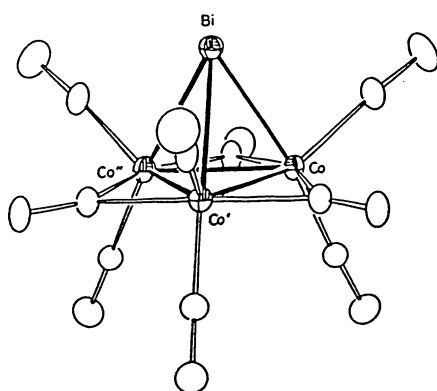
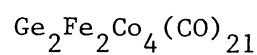
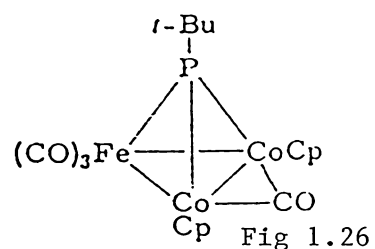
Fig 1.25 $BiCo_3(CO)_9$ 

Fig 1.26

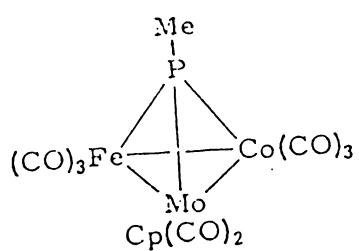
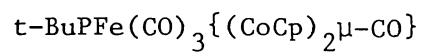


Fig 1.27

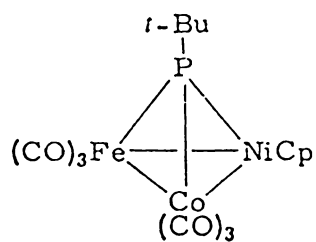
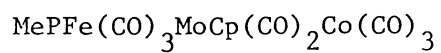


Fig 1.28

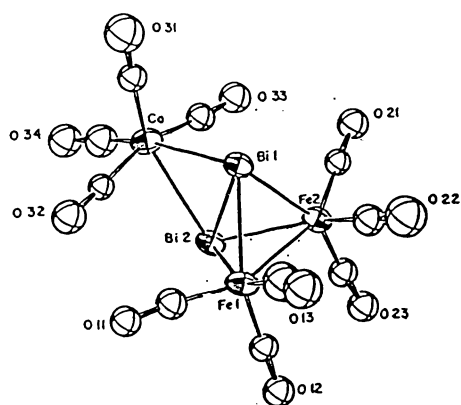
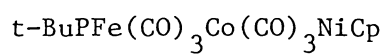
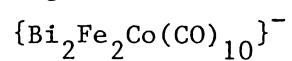


Fig 1.29



These values compare with $\text{Si}[\text{Co}_2(\text{CO})_7]_2$ average Co-Co = 2.528Å [78]

$\text{Ge}[\text{Co}_2(\text{CO})_7]_2$ average Co-Co = 2.565Å [16]

No corresponding Sn or Pb cobalt analogue has been formed. Finally, it is worth noting that in $\text{Ge}_2\text{Fe}_2\text{Co}_4(\text{CO})_{21}$ (Fig 1.24) where the two Fe atoms are bridged by a CO, the Fe-Fe distance is 2.678Å [144].

A small group of clusters of formula $(\text{RR}'\text{M}')_2\text{Co}_2(\text{CO})_6$ (Type VII, Fig 1.16) have both the μ -CO's replaced by M' units. The newest member of this group is $\{\text{Me}[\text{Co}(\text{CO})_4]\text{Ge}\}_2\text{Co}_2(\text{CO})_6$ (or $\text{Me}_2\text{Ge}_2\text{Co}_4(\text{CO})_{14}$) (6). It was only recently synthesised by the reaction of $\text{Fe}(\text{CO})_4(\text{GeH}_2\text{Me})_2$ with $\text{Co}_2(\text{CO})_8$ [76]. Unlike the other members of the group, $\{\text{Me}[\text{Co}(\text{CO})_4]\text{Ge}\}_2\text{Co}_2(\text{CO})_6$ undergoes decarbonylation to form the hexanuclear *closo*-cluster $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ (1a). The heavier member $(\text{Me}_2\text{Sn})_2\text{Co}_2(\text{CO})_6$ is quite stable [36] compared to $\text{Me}_2\text{SnCo}_2(\text{CO})_7$. In $\text{Me}_2\text{SnCo}_2(\text{CO})_7$, the Co-Co bond has the constraints of having to accommodate a small μ -CO on one side and a comparatively large Sn atom on the other. In $(\text{Me}_2\text{Sn})_2\text{Co}_2(\text{CO})_6$, the Co-Co bond is bridged by two Sn atoms on both sides, with no requirement to accommodate a small μ -CO. Therefore the Co-Co bond does not suffer from the strain experienced in $\text{M}'\text{Co}_2(\text{CO})_7$ type compounds with M' bigger than Si or Ge.

The $\text{M}'\text{Co}_3$ clusters are part of the wider group of L_nEM_3 trigonal pyramidal clusters where L = ligand, n = 0 or 1, E = main group element (e.g P, As, S, Se), M = transition metal [14] (Note : E = M' when E is a Group IVB element). The size of M' may again control the formation of the $\text{M}'\text{Co}_3$ trigonal pyramid. Schmid [14] proposed that the maximum covalent radius of M' atoms able to form such $\text{M}'\text{Co}_3$ trigonal pyramids was 1.30Å. Therefore Sn (1.41Å) and Pb (1.47Å) which both exceed this limit are expected to give open structures only. The limit of 1.30Å appeared to be quite critical as titanium (1.32Å) does not form any TiCo_3 cluster compounds. $\text{PhGe}[\text{Co}(\text{CO})_4]_3$ and $\text{Ge}[\text{Co}(\text{CO})_4]_4$ can

decarbonylate to form $\text{PhGeCo}_3(\text{CO})_9$, and $(\text{CO})_4\text{CoGeCo}_3(\text{CO})_9$, respectively while Sn and Pb analogues do not. $(\text{CO})_4\text{CoSiCo}_3(\text{CO})_9$, instead of $\text{Si}[\text{Co}(\text{CO})_4]_4$ was obtained directly from the reaction of SiI_4 with $\text{Co}(\text{CO})_4^-$ [14,100]. Work by Schmid [14], and Patmore and Graham [37] have shown that the earlier claim by Ibekwe and Newlands [101] to have made $n\text{-BuSnCo}_3(\text{CO})_9$, has no support and the explanation based on the size of M' atom seems logical.

This explanation has stood for ten years. However, the recent independent reports of the preparation and crystal structure of $\text{BiCo}_3(\text{CO})_9$, (rather $\text{BiCo}_3(\text{CO})_6(\mu\text{-CO})_3$) (Fig 1.25) by K.Whitmire, J.Leigh and M.Gross [102] and S.Martinengo and G.Ciani [103] have negated the Schmid generalisation. The covalent radius of Bi is 1.46Å, well outside the Schmid limit.

Recent interest in this area has been focussed on compounds that contain mixed transition metal clusters (Fig 1.26-1.28) such as the formation of $t\text{-BuPFe}(\text{CO})_3[\text{Co}(\text{CO})_3]_n[\text{NiCp}]_{2-n}$ where $n = 0$ to 2 [104] and $t\text{-BuGe}[\text{Co}(\text{CO})_3]_n[\text{MCp}(\text{CO})_2]_{3-n}$ where $n = 0$ to 3, $M = \text{Mo}, \text{W}$ [105]. These mixed *closo*- $\text{M}'\text{M}_3$ ($\text{M}' = \text{Group V or Group IV element and } M = \text{transition metal}$) pyramidal clusters have been made by metal exchange reactions as well as from cluster rearrangement and ligand exchange [100,106-111]. Another area of interest has been that of cluster expansion as shown by the formation of RPM_4 and RPM_5 clusters from RPM_3 clusters [111,112] and it is not impossible that such analogous M' clusters could one day be synthesised. The very recently synthesised E_2M_3 anionic cluster of $[\text{Bi}_2\text{Fe}_2\text{Co}(\text{CO})_{10}]^-$ (Fig 1.29) is also based on the L_nEM_3 tetrahedron structure. Its structure, however, differs from the above pyramidal compounds in that it contains two main group atoms (Bi) in the tetrahedron. The $\text{Co}(\text{CO})_4$ group acts as the bridging group between the two Bi atoms [113].

(c) More complex $M'Co_3$ (Type XII) and miscellaneous (Types XIV and XV) compounds

A group of anionic clusters based on the *closo*- $M'Co_3$ framework is shown in Table 1.4. All these anionic clusters are produced by the reaction of $Co(CO)_4^-$ with $M'Co$ clusters [79,89,90,96].

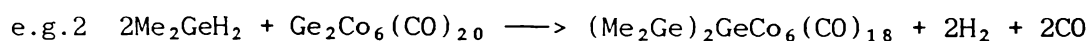
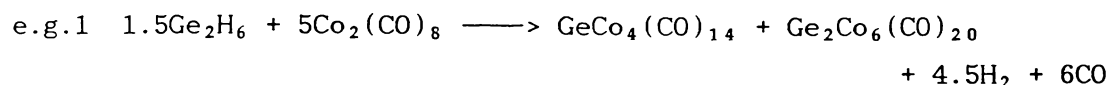
The anionic cluster $\{[GeCo_3(CO)_9][Co_2(CO)_7]\}^-$ was the first example of a five coordinated Ge (Fig 1.18). It was formed by the reaction of $Co(CO)_4^-$ with $GeCo_4(CO)_{14}$. Analogous reaction on $SiCo_4(CO)_{14}$ however yielded the unusual paramagnetic anionic cluster, $[\mu_8-SiCo_9(CO)_{21}]^{2-}$ which contains an interstitial Si (Fig 1.22). The only other Group IVB element which forms such clusters is carbon : where interstitial C is found in carbido clusters such as $[Co_6(CO)_{14}C]^-$ [114], $[Co_8(CO)_{18}C]^{2-}$ [115] and $[Rh_6(CO)_{15}C]^{2-}$ [116].

One of the most interesting $M'Co_3$ pyramid type compound is the anionic $\{[GeCo_3(CO)_9][Co_4(CO)_{11}]\}^-$ which consists of a $GeCo_3$ unit bonded to a tetracobalt group (similar to $Co_4(CO)_{12}$) (Fig 1.19). The anionic cluster $\{Co(CO)_3[GeCo_3(CO)_9]_2\}^-$ however consists of two $GeCo_3$ pyramids linked together by a $Co(CO)_3$ bridge (Fig 1.20). The related compound $[Sn_2Co_7(CO)_{27}]^-$ (believed to exist by infrared spectrum) has the same $M'Co(CO)_3M'$ bond, but is not expected to contain any $M'Co_3$ tetrahedron since its lower homologue $[Sn_2Co_5Cl_2(CO)_{19}]^-$ (Fig 1.21c) was shown to contain two terminal $Co(CO)_4$ groups instead of one $Co_2(CO)_7$ unit on each end.

(d) Extended chain compounds (Type IX)

This group of compounds is built up of a number of $M'Co_2$ triangles formed by substitution of $\mu-CO$ in $Co_2(CO)_8$. $M'Co_2(CO)_7$ and $(M')_2Co_2(CO)_6$ units are combined as building blocks with shared M' apices and Co-Co edges. They are the extension of $R_2M'[Co_2(CO)_6X]$ ($X =$

CO , $\text{R}_2\text{M}'$, $\text{R} = \text{Me}$, $\text{Co}(\text{CO})_4$) and $\text{M}'\text{Co}_4(\text{CO})_{14}$ discussed above. They are usually prepared by the reaction of Group IVB polyhydrides with $\text{Co}_2(\text{CO})_8$ [18,27,82-84], or by the reaction of a Group IVB hydride with an existing open chain cluster [18] :



The recent reaction of $[\text{Fe}(\text{CO})_4\text{GeH}_2]_2$ with $\text{Co}_2(\text{CO})_8$ has produced linked GeFe_2 and GeCo_2 triangles in the extended chain of $\text{Ge}_2\text{Fe}_2\text{Co}_4(\text{CO})_{21}$ (Fig 1.24). Just as the Type V, VI and VII compounds may be seen as substituted $\text{Co}_2(\text{CO})_8$, the central unit of Fig 1.24 is a disubstituted $\text{Fe}_2(\text{CO})_9$. The compound is isoelectronic with $\text{Ge}_2\text{Co}_6(\text{CO})_{20}$ (3). This synthesis has created further interest in this area of work by producing mixed transition metal carbonyl compounds. Further reactions to incorporate Mn and other metals, or Si, into the extended chain appears possible.

Just as the first member of the chain compound series $\text{GeCo}_4(\text{CO})_{14}$ condenses to $(\text{CO})_4\text{CoGeCo}_3(\text{CO})_9$, it was found that the second member, $\text{Ge}_2\text{Co}_6(\text{CO})_{20}$ decarbonylates to form the *closo*-hexanuclear cluster of $\text{Ge}_2\text{Co}_6(\text{CO})_{19}$ [18, 27]. These reactions indicate the potential of these groups of compounds as the precursor of *closo*-multi-nuclear clusters.

(e) *Closo*-hexanuclear $\text{M}'_2\text{Co}_4$ cluster (Type XIII)

Closo-hexanuclear cluster of the type E_2M_4 ($\text{E} = \text{Group III to V elements}$, $\text{M} = \text{transition metals}$) did not appear until 1975 when $(\text{PhP})_2\text{Co}_4(\text{CO})_{10}$ (Fig 1.30) was reported by Ryan et.al. [117]. Though the analogous *closo* cluster of $\text{E}_2\text{Fe}_4(\text{CO})_{11}$ ($\text{E} = \text{PPh or S}$, Fig 1.31(a) and 1.31(b)) and the mixed transition metal cluster of $\text{E}_2\text{Fe}_2\text{Co}_2(\text{CO})_{11}$)

(Fig 1.32) [118,119] were fairly well established, the first Group IVB - transition metal *clos*o cluster of this type was $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ made by S.Foster in 1982 [18, 84]. This was quickly followed by the synthesis of $\text{Ge}_2\text{Co}_6(\text{CO})_{19}$ [27] and its Si analogue [93].

So far, a 'one-off' general method of preparation of $\text{M}'_2\text{Co}_4$ cluster has not been found and methods of synthesis include :

- 1) the reaction of Ge_2H_6 with $\text{Co}_2(\text{CO})_8$ to form $\text{Ge}_2\text{Co}_6(\text{CO})_{20}$ which then decarbonylates to form $\text{Ge}_2\text{Co}_6(\text{CO})_{19}$ (*1c*) [18,27];
- 2) the reaction of Si_2H_6 with $\text{Co}_2(\text{CO})_8$, which gives $\text{SiCo}_6(\text{CO})_{19}$ (*1d*) [93], with only limited evidence for a $\text{Si}_2\text{Co}_6(\text{CO})_{20}$ intermediate;
- 3) the reaction of $\text{Fe}(\text{CO})_4(\text{GeH}_2\text{Me})_2$ with $\text{Co}_2(\text{CO})_8$ [76] which gives $\text{Me}_2\text{Ge}_2\text{Co}_4(\text{CO})_{14}$. This decarbonylates to form $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$;
- 4) the reaction of RGeX_3 with $\text{KCo}(\text{CO})_4$ to form $(\text{RGe})_2\text{Co}_4(\text{CO})_{11}$ [91];

Note : It has been reported [18,84] that prolonged reaction of MeGeH_3 with $\text{GeCo}_4(\text{CO})_{14}$ formed $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ but work reported in this thesis (Chapters Three, Four and Five) makes this reaction unlikely.

Related E_2M_4 clusters containing other main group elements E have been prepared via :

- 1) the reduction of $\text{Co}_2(\text{CO})_8$ in toluene with zinc powder under an atmosphere of carbon monoxide followed by the addition of $\text{C}_6\text{H}_5\text{PCl}_2$ forming $(\text{PhP})_2\text{Co}_4(\text{CO})_{10}$ [117];
- 2) the reaction of $[\text{Fe}(\text{CO})_3\text{PPh}]_2$ with $\text{Co}_2(\text{CO})_8$ to produce the mixed transition metal cluster of $(\text{PPh})_2\text{Fe}_2\text{Co}_2(\text{CO})_{11}$ [118,119]; and
- 3) the reaction of $\text{Ru}_3(\text{CO})_9(\mu\text{-S})_2$ with $\text{Ru}_3(\text{CO})_{12}$ under UV irradiation, produced not only $\text{S}_2\text{Ru}_4(\text{CO})_{11}$ (Fig 1.31(c)), but also other high nuclearity cluster compounds such as $\text{S}_2\text{Ru}_5(\text{CO})_{14}$ (Fig 1.33) and $\text{S}_2\text{Ru}_6(\text{CO})_{17}$ (Fig 1.34) [120].

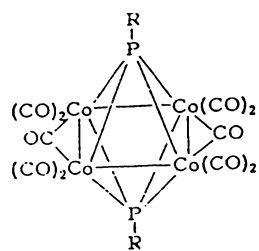
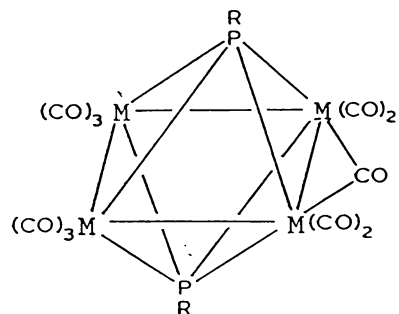
Fig 1.30 $(PPh)_2Co_4(CO)_{10}$ 

Fig 1.31

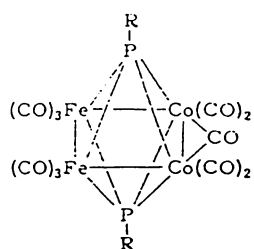
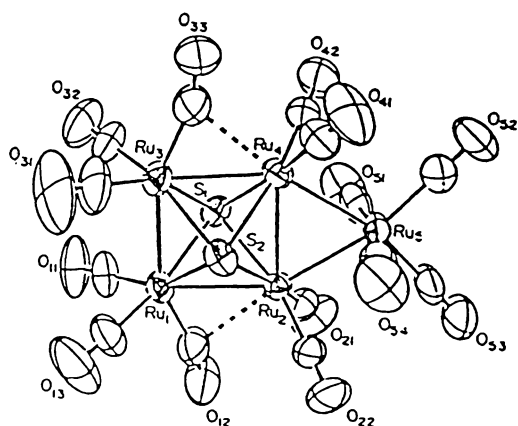
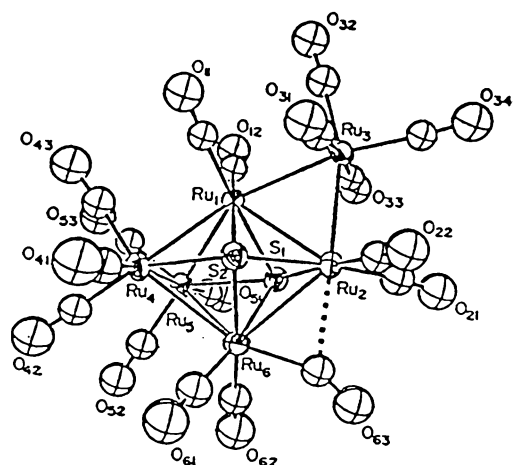
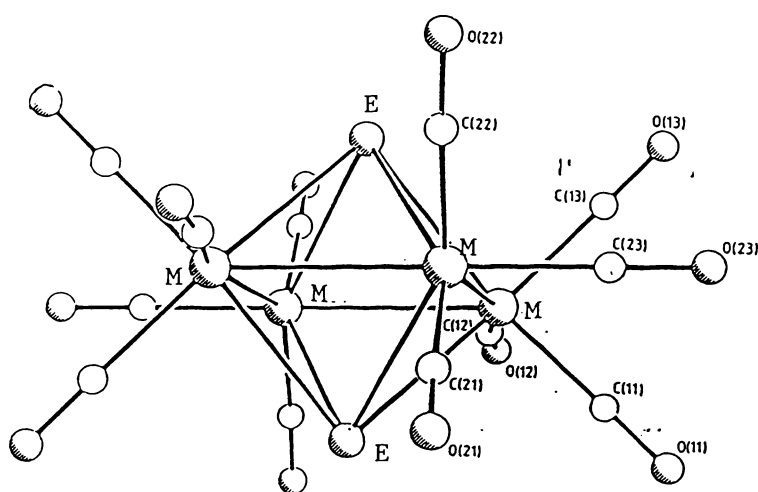
a: $R=PPh$, $M=Fe$ b: $R=S$, $M=Fe$ c: $R=S$, $M=Ru$ 

Fig 1.32

 $(RP)_2Fe_2Co_2(CO)_{11}$ $R = Me, Ph$ Fig 1.33 $S_2Ru_5(CO)_{14}$ Fig 1.34 $S_2Ru_6(CO)_{17}$ Fig 1.35 $E_2M_4(CO)_{12}$ a: $E=Bi$, $M=Ru$ b: $E=PPh$, $M=Ru$

- 4) the reaction of $\text{Ru}_3(\text{CO})_{12}$ with $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ in KOH/MeOH at room temperature followed by treatment on silica produced $\text{Bi}_2\text{Ru}_4(\text{CO})_{12}$ (Fig 1.35a) [121]
- 5) the reaction of $[\text{Me}(\text{C}_5\text{H}_4)(\text{OC})_2\text{Mn}(\text{PPhBr}_2)]$ with $\text{NaCo}(\text{CO})_4$ producing $(\text{PPh})_2\text{Co}_4(\text{CO})_{10}$ which is more easily prepared by 1) [100].
- 6) $[\text{Cp}(\text{OC})_2\text{Mn}(\text{PhPCl}_2)]$ with $\text{Ru}_3(\text{CO})_{12}$ produces $(\text{PPh})_2\text{Ru}_4(\text{CO})_{12}$ (Fig 1.35b) [100].

These six vertex *closo*- E_2M_4 do not conform with the polyhedral skeletal electron pair (PSEP) theory [122] which has been invaluable to the understanding and prediction of the structure of organometallic clusters. According to the PSEP theory, *closo* n -vertex clusters are expected to be stable for $n+1$ skeletal electron pairs. Therefore a normal count of 7 skeletal pairs is anticipated for E_2M_4 compounds, but most of them possess 8. Extended Huckel calculations by Hoffmann et al [123] on $(\text{HP})_2\text{Fe}_4(\text{CO})_{12}$ as a model compound (H for R in Fig 1.35) showed that from the orbital combination of HP--PH and $[\text{Fe}(\text{CO})_3]_4$ the energy gap between the 7 bonding molecular orbitals and the first M-M Π antibonding orbital is small (Fig 1.36). This antibonding orbital is approximately non-bonding and an additional electron pair occupying such an orbital would not impair the stability of the cluster. However studies on a number of representative E_2M_4 clusters had shown that there is a preference for the 8 skeletal electron pairs. With $(\text{HP})_2\text{Fe}_4(\text{CO})_{12}$ as a model again, it was suggested that contribution of the 3d orbitals of the phosphorus provides stabilising effect on the antibonding orbital. This is one of the reasons suggested for the short P--P separation observed. So far only the P_2Fe_4 system has been observed to form stable clusters with either 7 or 8 electron pairs (by adding or losing a CO as in equation 1.9). All other systems possess

8 skeletal electron pairs. Thus, the 8th MO seems to possess a more bonding than the predicted non-bonding or slightly anti-bonding character. Analysis on the electronic structures of these clusters was made by Halet, Hoffmann and Saillard and this showed that systems with 8 skeletal electron pairs are favoured for more electronegative metals such as cobalt while those with 7 skeletal electron pairs are favoured for less electronegative metals such as ruthenium [123].

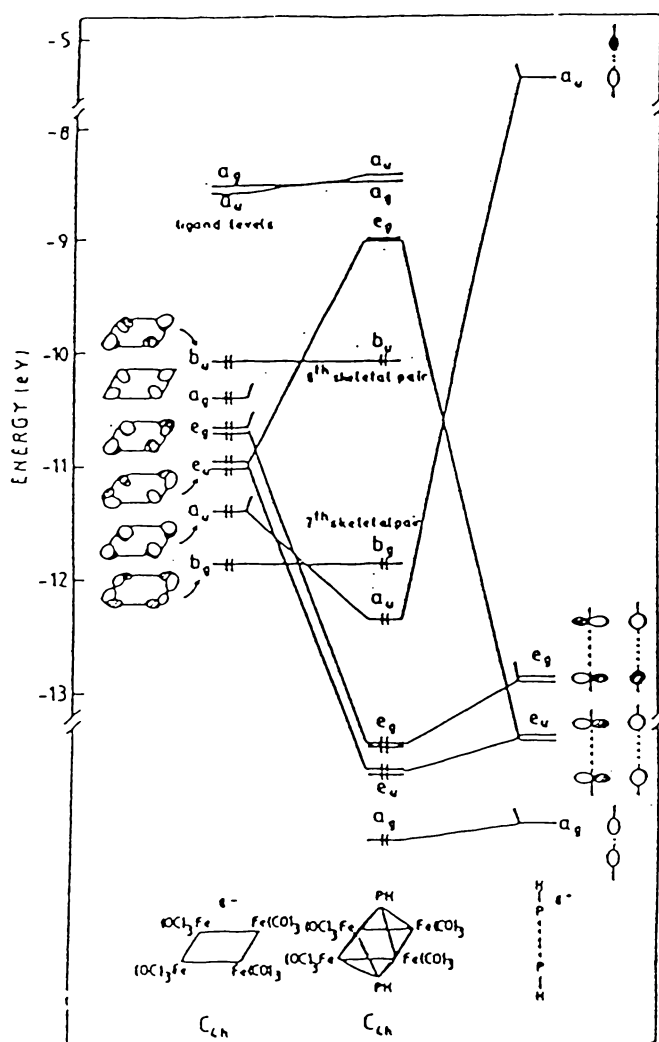
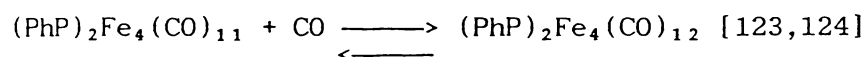


Fig 1.36 Orbital interaction diagram for $(\text{HP})_2\text{Fe}_4(\text{CO})_{12}$ [122]

The more established chemistry of E_2M_4 clusters (some of their reactions as shown in equations 1.9 - 1.15) indicates the extensive chemistry yet to be explored with this group of relatively new M'_2M_4 clusters.

Some reactions of Group VB and Group VIB transition metal clusters of similar skeletal core as M'_2Co_4 cluster :-

CO addition : switch from 7 to 8 electron pair cluster (Fig 1.37)



--- equation 1.9

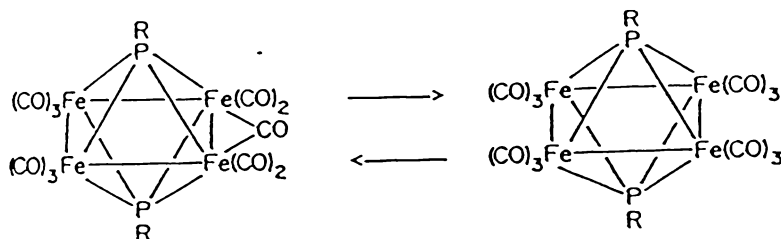


Fig 1.37

Ligand substitution : (Figs 1.38, 1.39)

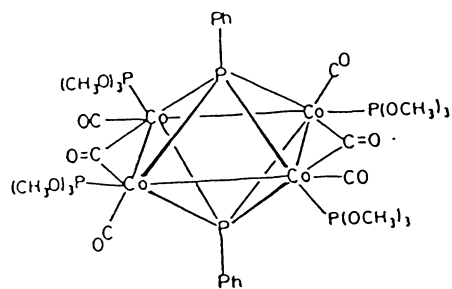
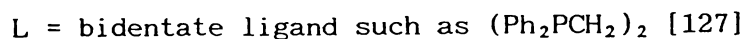
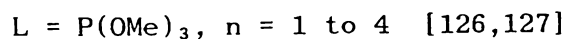
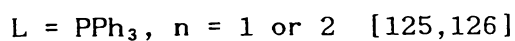
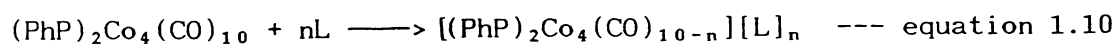


Fig 1.38 $L = P(OMe)_3$

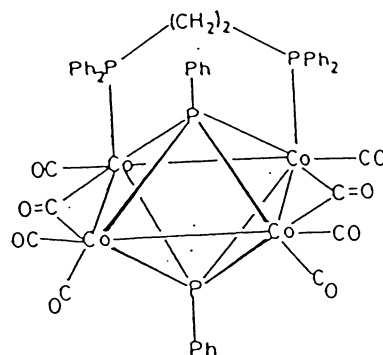
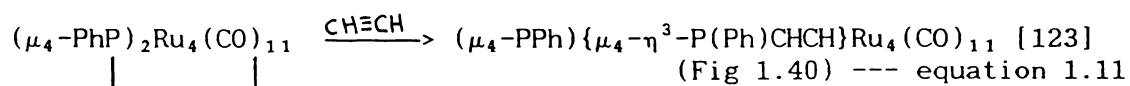


Fig 1.39 $L = PPh_2(CH_2)_2$

Rearrangement reaction :



+ H₂ + CO

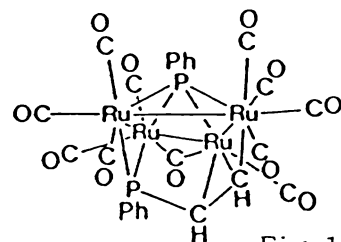
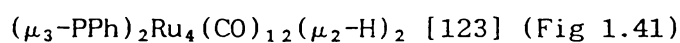


Fig 1.40

+ CO



closo-trigonal prismatic

--- equation 1.12

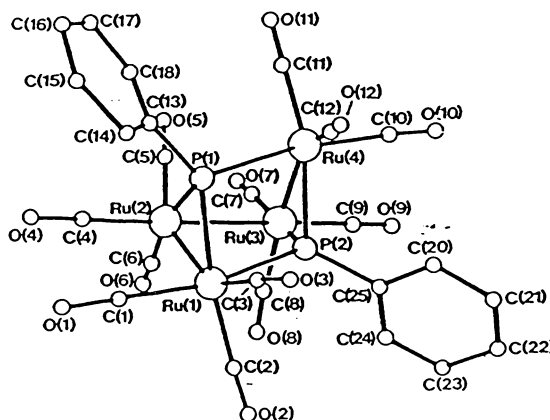


Fig 1.41

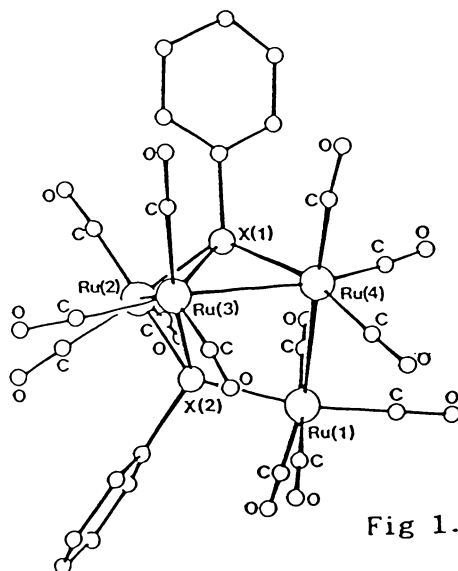
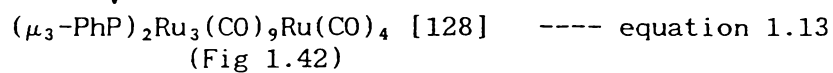


Fig 1.42

Nucleophilic addition :

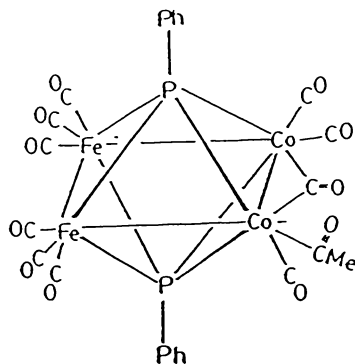
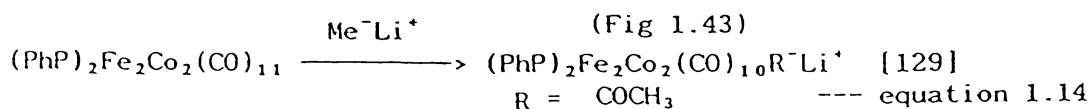
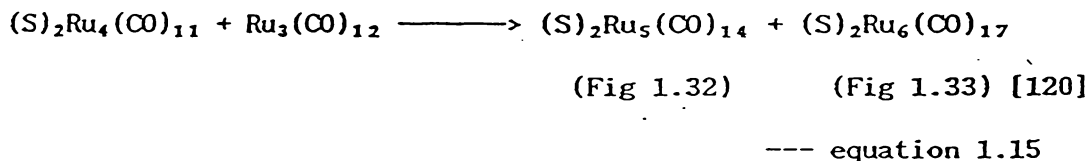


Fig 1.43

Increasing metal skeleton :



The recent report of $(\text{S})_2\text{Ru}_5(\text{CO})_{14}$ and $(\text{S})_2\text{Ru}_6(\text{CO})_{17}$ (Figs 1.32 and 1.33) [120] suggests the possibility of increasing the metal skeleton of $\text{M}_2'\text{Co}_4$ cluster, perhaps by the replacement of $\mu\text{-CO}$ by a further metal carbonyl moiety.

The work reported in this thesis was aimed at further exploring the chemistry of germanium-cobalt carbonyl compounds, together with some studies of related silicon compounds. In Chapter Three, the earlier studies [20,70] of the reaction of MeGeH_3 with $\text{Co}_2(\text{CO})_8$ have been extended and new products identified. Chapter Four describes the synthesis of the *clos*o- cluster $(\text{MeM}')_2\text{Co}_4(\text{CO})_{11}$ ($\text{M}' = \text{Si}, \text{Ge}$) from the reaction of $\text{MeM}'\text{H}_3$ with $\text{Co}_4(\text{CO})_{12}$. More new members are added to Table 1.5 with the syntheses of more *clos*o- hexanuclear clusters from the reaction of $(\text{RGeH})_n\text{GeCo}_4(\text{CO})_{14-n}$ ($n = 1$ or 2) with $\text{Co}_2(\text{CO})_8$ in Chapter Seven and the reaction of RGeH_3 with $\text{SiCo}_4(\text{CO})_{14}$ in Chapter Eight. The number of extended chain compounds (Table 1.3, Type IX) is also expanded from the reactions of $\text{R}_n\text{GeH}_{4-n}$ ($n = 1$ or 2 , $\text{R} = \text{Me}, \text{Et}, \text{Ph}$) with $\text{GeCo}_4(\text{CO})_{14}$ and MeGeClH_2 with $\text{GeCo}_4(\text{CO})_{14}$ in Chapters Five and Six.

CHAPTER TWO

2.1 Experimental techniques

2.1.1 General techniques

The compounds used or prepared in this work were either sensitive to hydrolysis and/or oxidation, so contact with air was avoided whenever possible. Thus, volatile air sensitive compounds were manipulated in a standard vacuum line and involatile compounds were either handled in a Schlenk line or in a nitrogen-flushed glove box. All involatile compounds were either stored in nitrogen-flushed glassware in the refrigerator at 4°C, the freezer at -32°C or the nitrogen-filled glove-box.

All glassware used were stripped of grease (using petroleum spirit) before being base (potassium hydroxide in ethanol) and acid washed (sodium dichromate in sulphuric acid).

2.1.2 Fractionation

Compounds were separated from volatile mixtures by passage through a series of progressively colder traps, which selectively condensed each of the volatile components. Where compounds had high mutual solubility or similar vapour pressures, repeated fractionations were required to obtain enriched fractions. Fractionations were achieved using the constant temperature slush baths listed in Table 2.1.

Table 2.1 Constant temperature (slush) bath

Constituent	Temperature (°C)
ice/water/salt	0 to -20
carbon tetrachloride	-22
chlorobenzene	-45
chloroform	-63
ethyl acetate	-83
toluene	-96
n-propanol	-127
nitrogen	-196

2.1.3 Toepler pump and associated apparatus for the determination

of incondensable gases

CO and H₂ are incondensable at -196°C and they could be measured by the Toepler pump. The total incondensable gas was measured via the gas burette fitted to the Toepler pump, the pressure difference being measured by a cathetometer.

The proportion of H₂ and CO present was calculated from the average molecular weight of a known pressure of the gas contained

within a known volume :

$$H_2 = \frac{28 - w}{26} \times 100\%$$

Unlike the total gas measurement which is reliable to 1%, the accuracy of the measurement of the CO/H₂ ratio is less accurate especially when small weights are involved. It depends on the weight of the gas relative to that of the containing vessel and was optimised by using as high a pressure of gas as possible. For example in the reaction of MeGeH₃ with Co₄(CO)₁₂, with a pressure difference of 13cm, the incondensable gas weighed 0.0063g and the H₂ : CO ratio was

calculated to be 79% : 21% (expected 75% : 25%), with an uncertainty of $\pm 1\%$, when the pressure difference was 0.9cm, the incondensable gas weighed 0.0004g and the H_2 : CO ratio was 81% : 18% with an accuracy of $\pm 13\%$.

The total quantities of H_2 and CO evolved were obtained by relating the proportions of H_2 and CO back to the initial measurement of total gas quantity.

2.2 Instrumental Techniques

2.2.1 Infrared (IR) spectroscopy

Infrared spectroscopy was used to monitor reactions and fractionation, and to identify or characterise samples. Routine infrared spectra were recorded on a Philips Pye Unicam PU 9512 spectrophotometer ($4000-400\text{cm}^{-1}$).

High resolution infrared spectra, to fully characterise a species, were recorded on a Perkin Elmer 180 spectrophotometer. This machine allowed for proper resolution, more operational control and vastly more accurate spectra. The indicated frequencies of bands in the CO region ($2200-1700\text{cm}^{-1}$) were checked against the wavenumber marker which, in turn, was calibrated against NH_3 .

Gas phase infrared spectra were obtained using a gas cell of 10cm path length and 5cm KBr windows.

Liquid phase infrared spectra were run in a standard 0.1mm solution cell with KBr windows. Solutions were usually prepared using hexane or CH_2Cl_2 as solvents.

To obtain solid phase infrared spectra the solid sample was either dispersed as a nujol mull which was held between two KBr windows, or

as CsI or CsBr disk. The latter were prepared by grinding up the solid sample with dried powdered CsI or CsBr, then compressing at 8 tonnes pressure to a disk of 0.1mm thickness.

2.2.2 Nuclear Magnetic Resonance Spectroscopy, (NMR)

^1H and ^{13}C NMR scans were all performed on the 90MHz Jeol FX90 Multinuclear Fourier Transform spectrometer. Various temperature settings were possible and in the case of a weak sample (e.g due to low solubility or only small amount of sample), the spectrum was collected with the aid of the 'Fydax' function. This allowed sample data to be accumulated without being swamped by giant peaks of solvents or impurities (usually grease).

5mm and 8mm outer diameter tubes were used for ^1H and ^{13}C NMR scans respectively with CDCl_3 as solvent. Due to air sensitivity, the samples were sealed under vacuum.

2.2.3 Mass Spectroscopy

This is a useful technique of sample identification and characterisation especially for samples whose molecular weight does not exceed the capable mass range of the machine.

All mass spectra were recorded at the Ruakura Agricultural Research Institute on a Varian CH5 mass spectrometer, of mass range 30-1000 mass units. Air stable solids and solutions were introduced into the spectrometer directly through the solid insertion probe, the solvent being removed by the instrument pump. Air sensitive samples were loaded into the crucibles and onto the probe using protection afforded by a polythene glovebox flushed with nitrogen or argon.

The spectra were computer calibrated, with capability of expansion for weak spectra. Due to the age of the machine, the results were

generally good for the lower m/e values (30-700), but not for the higher m/e values. These were obtained under low resolution conditions, where the values are only accurate to 5-10 units. It is also not possible to determine the number of hydrogen atoms lost when a loss of CH_x ($x = 2, 3$ or 4) is encountered. In this work, the loss of CH_3 is most likely, but CH_2 loss is known and CH_4 may be eliminated between two methyls. It is also not possible to distinguish between the loss of two CH_x (or ethyl group) from the loss of CO or Si.

Characteristic intensity patterns are produced by the presence of naturally occurring isotopes in a compound. Fig 2.1 shows the isotope pattern for Ge_1 , Ge_2 and Ge_3 compounds. Fig 2.2 shows the isotope patterns of Cl and Si and some expected characteristic isotope patterns of Ge compounds containing these two isotopes. Such patterns facilitate identification of compounds.

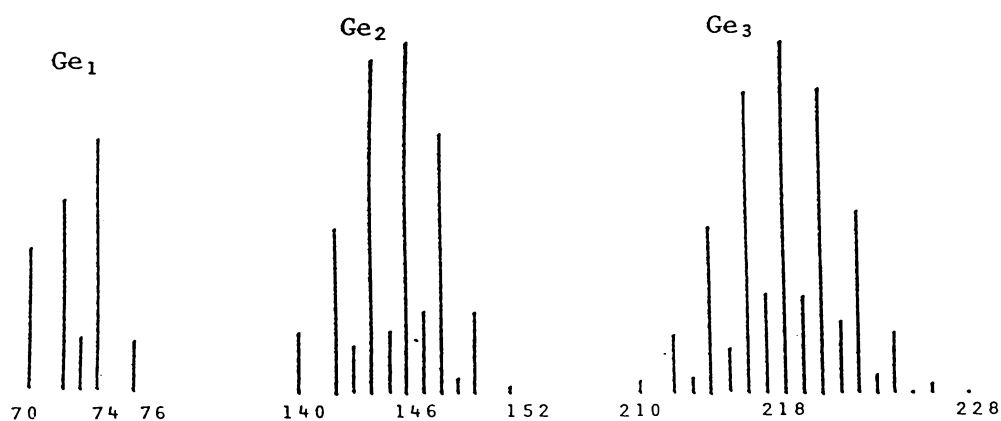


Fig 2.1

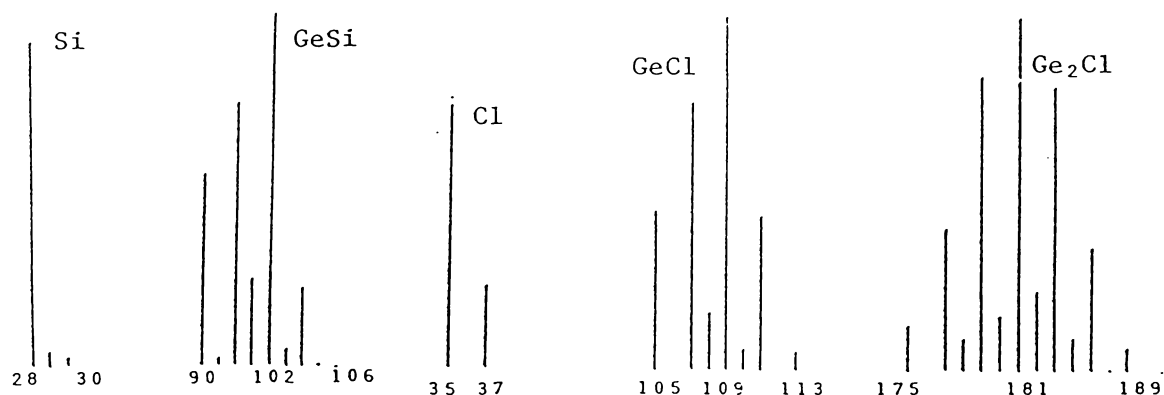


Fig 2.2

2.2.4 Electron Probe Analysis, (EPA)

EPA was used for elemental identification and was useful for determining the metal composition of the sample. It was performed by Dr. C.Beltz and Mr. S.Stokes on an Ortec energy dispersive X-ray analyser attached to a Jeol J.S.M35 scanning electron microscope. The error was about 5%, but with clean samples in the form of crystals, higher accuracy was obtained.

2.2.5 X-Ray Crystallography

Single crystals for studies were mounted sealed in glass capillaries or on glass fibres with Araldite. Preliminary studies were made on a Charles Supper Co. Precession Camera. The final data collection was performed by either the University of Canterbury or the University of Auckland.

2.3 Starting Reagents

2.3.1 Solvents

All common solvents used were dried and degassed by distillation under nitrogen, these are given in Table 2.2.

Table 2.2

Solvent	Drying agent
Dichloromethane	phosphorus pentoxide
Diethyl ether	sodium and benzophenone
THF	sodium and benzophenone
n-Hexane	calcium hydride
Benzene	dried over sodium wire and bubbled with nitrogen
n-Pentane	

2.3.2 Chemicals; Storage and Preparation

$\text{Co}_2(\text{CO})_8$, $\text{Mn}_2(\text{CO})_{10}$ (Pressure Chemicals Ltd.) --- stored in nitrogen flushed bottles in the freezer.

GeO_2 (Koch Light Laboratories), GeCl_4 (Strem Chemicals), LiAlH_4 (M and B Chemicals), MeSiCl_3 , Me_2SiCl_2 and SiCl_4 (Harris and William Chemicals) --- all used as supplied.

Sodium (BDH Chemicals Ltd.) --- stored under paraffin, the oxide layer was removed when used to prepare 1% sodium amalgam.

MeGeCl_3 , EtGeCl_3 and Me_2GeCl_2 (Laramie Chemicals and Strem Chemicals) -- fractionated at -63°C to obtain pure samples, the purity checked by IR spectroscopy [131,132].

SnCl_4 (BDH Chemicals) was manipulated and stored in the fume hood. Samples were initially pumped to remove HCl then condensed away from impurities before use.

Bromobenzene (BDH Chemicals) --- used as supplied, stored in fume hood.

Magnesium turnings --- dried in the oven for 24 hours before used for the Grignard preparation of phenylmagnesium bromide.

2.4 Preparation of Starting Materials

2.4.1 Preparation of Monogermane, GeH_4

Monogermane was prepared by a modification to the technique described by Jolly and Drake [133] using the apparatus as shown in Fig 2.3. A typical preparation involved the addition of GeO_2 (10g, 172.1mmol), NaOH (20g, 500mmol) and sodium borohydride (18g, 476mmol) to distilled water (200-300ml). This suspension was stirred for 24 hours to ensure a thorough dispersion of the relatively insoluble GeO_2 , air was excluded to avoid the formation of sodium carbonate.

Addition of this suspension slowly to 50% orthophosphoric acid provided a vigorous reaction where the monogermane, digermane and higher polygermanes along with water were carried from the reaction mixture by the hydrogen gas produced.

The resultant product gases were passed through a trap containing calcium chloride and then one at -127°C , and three at -196°C . The -127° trap separated the water and polygermanes from the monogermane which was condensed into the -196°C traps. The monogermane was further fractionated through -127°C slush baths to improve its purity. All remains of the -127°C trap were combined and passed through -63°C and -127°C traps, the former yielded trigermane while the latter yielded digermane.

Yields : monogermane 70%, digermane 10%, higher polygermanes 2-3%, all compounds were characterized by their IR spectra [133].

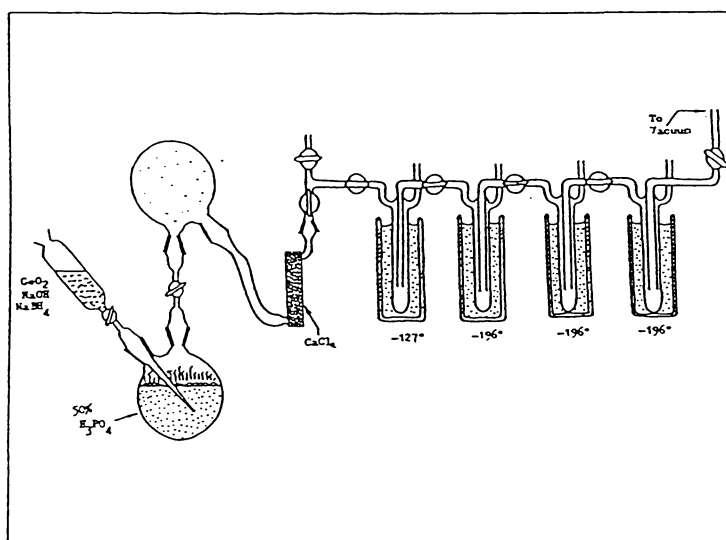


Fig 2.3

Germane preparation apparatus

2.4.2 Preparation of SiH_4 , MeGeH_3 , EtGeH_3 , Me_2GeH_2 , MeSiH_3 and Me_2SiH_2

These were prepared by the reduction of the appropriate chloride using lithium aluminium hydride. A typical preparation involved the condensation of the chloride onto an excess of lithium aluminium hydride in dibutyl ether, the reaction was allowed to proceed at room temperature, with the bleeding off of volatiles when the pressure had built up. The hydride was fractionated at -127°C . The results were generally in the order of 80-90% if the ether was initially dried (over sodium wires and then over lithium aluminium hydride) and an excess of the reducing agent was used. The reduction was vigorous and usually completed within 20 minutes. The purity of the hydrides was checked by IR spectroscopy [134-136].

2.4.3 Preparation of PhGeH_3

This involved the preparation of tetraphenylgermane which was converted to phenylgermanium trichloride. Reduction of the trichloride by lithium aluminum hydride produced PhGeH_3 .

2.4.3.1 preparation of tetraphenylgermane, Ph_4Ge [137]

GeCl_4 (5g) in THF (30 ml) was added in 10 min. to a filtered solution of phenylmagnesium bromide prepared from bromobenzene (44g) and magnesium (7.8g) in THF (90 ml). After 18 hr. under reflux the crude tetraphenylgermane was separated by filtration (without hydrolysis), washed with dilute acetic acid, and crystallised from toluene; the white needle shaped crystals have m.p. $237-238^\circ\text{C}$, yield = 68.7% as compared to 85% reported by Glockling and Hooton [137].

2.4.3.2 preparation of phenylgermanium-trichloride, PhGeCl_3 [138]

Ph_4Ge (2.85g, 7.5mmol) with GeCl_4 (4.83g, 22.5mmol) and freshly sublimed AlCl_3 (0.2g, 1.25mmol) was sealed in an high pressure ampoule

and heated at 120°C for 6.5 hours. Distillation at 60–63°C at 1mm Hg yielded PhGeCl_3 (82%).

2.4.3.3 reduction of PhGeCl_3 by LiAlH_4

PhGeCl_3 (4g, 15.63 mmol) in dried diethyl ether (5 ml) was added dropwise to LiAlH_4 (1.8g, 37 mmol) in dried diethyl ether (20 ml). A white suspension was formed immediately with increase in temperature. This was refluxed for 2 hours after which petroleum spirit (50 – 70°C) was added and the mixture filtered under nitrogen. Distillation at 1mm Hg yielded PhGeH_3 at 40 – 50°C (yield 1.78g, 75%). The purity was checked by IR spectroscopy [139].

2.4.4 Preparation of MeGeH_2Cl

MeGeH_3 was condensed onto SnCl_4 in a large round bottom flask and left to warm up at room temperature for 20 minutes. Fractionation at -63°, -127° and -196°C yielded pure MeGeH_2Cl held at -127°C. The yields were 80 – 90% based on the stannic chloride used. Note : 1) a slight excess (10% more) of MeGeH_3 was used to prevent the formation of dichlorides ; 2) HCl produced in the reaction attacks mercury in the manometer, so care must be taken to prevent their coming into contact. Purity was checked by infrared spectroscopy [132,140].

2.4.5 Preparation of sodium amalgam

A 1% by weight sodium amalgam was prepared by adding small portions of sodium (1g, 43.5mmol) to mercury (100g) held in a separating funnel under a nitrogen atmosphere. Impurities remained on the surface while clean amalgam was removed through the tap. Excess amalgam was inactivated by addition of alcohol and recovering the mercury [141].

2.4.6 Preparation of NaCo(CO)_4

This involved the reduction of $\text{Co}_2(\text{CO})_8$ by sodium amalgam prepared as above. A typical preparation involved the use of 1.0g $\text{Co}_2(\text{CO})_8$ (2.9mmol) dissolved in 30ml THF, and 3-4 ml of sodium amalgam was added at the Schlenk line. The mixture was stirred for an hour under nitrogen. A clear solution with a slight yellowish tint was obtained. This gave a NaCo(CO)_4 solution of approximately 0.18mmol/ml, assuming 90% yield. The clear solution was decanted from the unreacted amalgam.

Note : a cleaner preparation could be obtained via K/Na alloy, but this method require extreme care due to the high inflammability of the alloy.

2.4.7 Preparation of $\text{M}'\text{Co}_4(\text{CO})_{14}$, $\text{M}' = \text{Si, Ge}$ [16,17,18]

In a typical preparation of $\text{GeCo}_4(\text{CO})_{14}$, $\text{Co}_2(\text{CO})_8$ (2.0g, 5.85 mmol) was sealed with GeH_4 ((3.23 mmol which is equivalent to 30 cm of GeH_4 in a 200ml trap on the vacuum line) and left to react in the dark for 2 weeks. The reaction mixture was pumped on the Schlenk line for a day to remove any unreacted $\text{Co}_2(\text{CO})_8$. The involatile fraction was washed several times with hexane to remove $\text{Co}_4(\text{CO})_{12}$ and remaining traces of $\text{Co}_2(\text{CO})_8$. The product was dissolved in CH_2Cl_2 , topped with hexane and placed in the freezer for recrystallisation. Yield ~1.6g (78%) of dark red crystals of $\text{GeCo}_4(\text{CO})_{14}$. Purity was checked by IR spectra.

A similar preparation was used for $\text{SiCo}_4(\text{CO})_{14}$, using SiH_4 instead of GeH_4 . Yields were similar.

2.4.8 Preparation of $\text{Co}_4(\text{CO})_{12}$

Dried benzene (20 ml) was added to $\text{Co}_2(\text{CO})_8$ (2g) in a Schlenk flask under nitrogen. This was placed in the oil bath at 55°C for several hours until gas evolution had ceased and the IR spectrum showed no sign of $\text{Co}_2(\text{CO})_8$. Benzene was removed, the product was dissolved in CH_2Cl_2 and topped with hexane for recrystallisation in the freezer. Black shiny cube shaped crystals of $\text{Co}_4(\text{CO})_{12}$ resulted and almost total conversion of $\text{Co}_2(\text{CO})_8$ to $\text{Co}_4(\text{CO})_{12}$ was obtained. Purity was checked by the infrared spectrum [142].

2.5 ^{13}C enrichment

An atmosphere of highly enriched ^{13}C ($\sim 95\%$) was placed over a solution of the Group IVB cobalt carbonyl compound in a 250ml greaseless tap vessel by the use of the Toepler pump. The exchange was monitored by examination of the IR spectrum (Fig 2.4) and a typical run lasted two weeks. It was noted that CO exchange occurred only when a $\mu\text{-CO}$ group was present (e.g. $(\text{Me}_2\text{Ge})\text{GeCo}_4(\text{CO})_{13}$ (5a) was easily enriched while no enrichment was observed for $(\text{Me}_2\text{Ge})_2\text{GeCo}_4(\text{CO})_{12}$ (9a)).

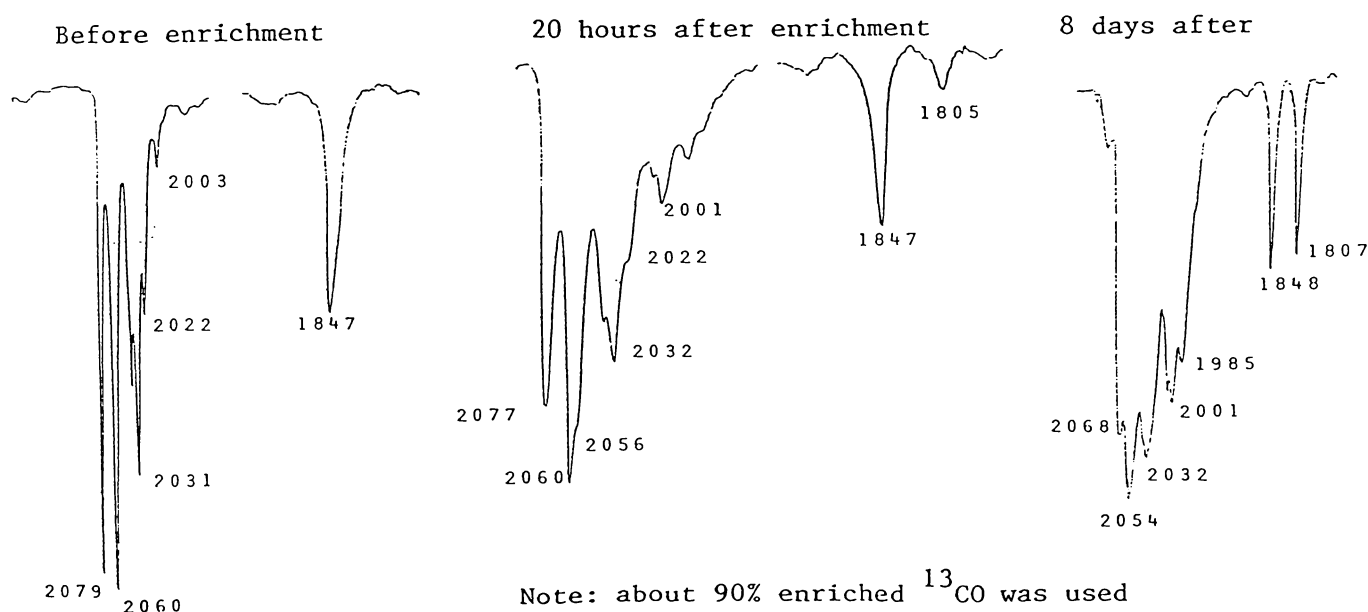


Fig 2.4 ^{13}C enrichment of $\text{GeCo}_4(\text{CO})_{14}$

CHAPTER THREE

The Reaction of MeGeH_3 and $\text{Co}_2(\text{CO})_8$

3.1 Introduction

The reaction of MeGeH_3 with $\text{Co}_2(\text{CO})_8$ (mole ratio of 1 : 1.7 and another at 2 : 1) was first investigated by B.Graham in 1973 [70]. He found that the reaction (followed by ^1H NMR studies) at room temperature was very fast and was complete after about 5 minutes. $\text{MeGeCo}_3(\text{CO})_{11}$, Fig 3.12 was the main product formed, with $\text{HCo}(\text{CO})_4$ observed in the volatile phase.

A number of ^1H NMR reactions (ranging from 2 : 1 to 1 : 2 ratio) at -20°C showed a consistent pattern of change [20]. The initial stage of the reaction (about an hour) could not be fully studied as the signals were very degraded (suggesting a paramagnetic intermediate). When the signal could be resolved, the following were observed: a singlet due to $\text{HCo}(\text{CO})_4$ (21.4τ), two signals due to $\text{MeGeH}_2\text{Co}(\text{CO})_4$ (a triplet at 9.18τ (δ 0.82 ppm) and a quartet at 5.71τ (δ 4.29 ppm)), a doublet at 8.77τ (δ 1.23 ppm) (D_1) together with a quartet at 4.89τ (δ 5.11 ppm), a singlet due to $\text{MeGeCo}_3(\text{CO})_{11}$ (8.07τ (δ 1.93 ppm)) and a singlet at 8.40τ (δ 1.60 ppm). The 8.07τ (δ 1.93 ppm) singlet was observed to increase in intensity as the reaction advanced. Weak signals appeared in the later stages, the most consistent being a second doublet at 8.60τ (δ 1.40 ppm) (D_2) and a singlet at 5.43τ (δ 4.57 ppm). No consistent pattern of the signals with reaction ratio could be concluded. The involatile product was found to be mainly $\text{MeGeCo}_3(\text{CO})_{11}$.

The reaction of $\text{MeGeH}_2\text{Co}(\text{CO})_4$ with $\text{Co}_2(\text{CO})_8$ was also investigated by an ^1H NMR experiment at temperatures ranging from -40°C to 0°C . The

resolution of the signals at the initial stage of the reaction was again poor. The 1 : 1 reaction showed the formation of D_1 which was consumed giving a major $(\text{MeGeCo}_3(\text{CO})_{11}, 8.07\tau (\delta 1.93 \text{ ppm}))$ and minor $(8.40\tau (\delta 1.60 \text{ ppm}) \text{ singlet})$ product. $\text{HCo}(\text{CO})_4$ was formed throughout the reaction. The 1.5 : 1 reaction showed the presence of both D_1 and D_2 . $\text{MeGeCo}_3(\text{CO})_{11}$ appeared only when the temperature was raised to 0°C . When the ratio of $\text{MeGeH}_2\text{Co}(\text{CO})_4$: $\text{Co}_2(\text{CO})_8$ is 0.5 : 1, only D_1 appeared followed by the singlet of $\text{MeGeCo}_3(\text{CO})_{11}$. Two other weak singlets at $8.42\tau (\delta 1.58 \text{ ppm})$ and $8.22\tau (\delta 1.78 \text{ ppm})$ and that of $\text{HCo}(\text{CO})_4$ appeared after 18 hours into the reaction. The singlet at $8.42\tau (\delta 1.58 \text{ ppm})$ appeared early in the reaction while the $8.22\tau (\delta 1.78 \text{ ppm})$ singlet was seen only after long standing. The former was therefore thought to be $\text{MeGe}[\text{Co}(\text{CO})_4]_3$ and the latter to be that of $\text{MeGeCo}_3(\text{CO})_9$. In all runs, the major involatile product was $\text{MeGeCo}_3(\text{CO})_{11}$.

Two further possible products in the reaction of MeGeH_3 with $\text{Co}_2(\text{CO})_8$ are $\text{Me}_2\text{Ge}_2\text{Co}_4(\text{CO})_{14}$ (6) and $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ (1a), though they were not known at the time of the previous work [17,20,70]. $\text{Me}_2\text{Ge}_2\text{Co}_4(\text{CO})_{14}$ has been prepared by the reaction of $(\text{MeGeH}_2)_2\text{Fe}(\text{CO})_4$ with $\text{Co}_2(\text{CO})_8$ [76]. On gentle heating this decarbonylates to form the *closo*-hexanuclear cluster $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$. Both of these compounds are further candidates for the minor products giving the observed singlets in the previous workers' NMR studies [17,20,70]

In both the MeGeH_3 and the $\text{MeGeH}_2\text{Co}(\text{CO})_4$ reaction with $\text{Co}_2(\text{CO})_8$, D_1 was observed in all the runs, but D_2 appeared only when $\text{Co}_2(\text{CO})_8$ was not in excess. D_1 was always stronger than D_2 . From all available information at the time, it was inclined to believe that D_1 belonged to $\text{MeGeHCo}_2(\text{CO})_8$ and D_2 to $\text{MeGeHCo}_2(\text{CO})_7$. These assignments are however only speculative.

Earlier work by Ball, Graham *et al* [25] on the reaction of PhGeH_3 with $\text{Co}_2(\text{CO})_8$ produced $\text{PhGeCo}_3(\text{CO})_{11}$ (**7b**). This is analogous to $\text{MeGeCo}_3(\text{CO})_{11}$. An interesting feature of both compounds is the appearance, in the infrared spectra, of two bridging carbonyl modes at $\sim 1850\text{ cm}^{-1}$ and 1835 cm^{-1} . This was attributed to the two isomers:- one in which the bridging carbonyl lies on the same side as the R group in the molecule, the other with the bridging carbonyl on the same side as the alkyl group.

Both $\text{MeGeCo}_3(\text{CO})_{11}$ and $\text{PhGeCo}_3(\text{CO})_{11}$ were transformed into the *closo*-pyramidal cluster, $\text{RGeCo}_3(\text{CO})_9$ (R = Me, Ph) on refluxing in hexane for several hours [25,71].

All previous reactions of MeGeH_3 and $\text{Co}_2(\text{CO})_8$ were relatively short (not more than 7 days). This Chapter describes the long term (6 months) reaction of MeGeH_3 with $\text{Co}_2(\text{CO})_8$. Each run is followed by a short discussion of the results, while an overall discussion collates all the reaction results. This is then followed by the decarbonylation reaction of $\text{Me}_2\text{Ge}_2\text{Co}_4(\text{CO})_{14}$ which is one of the products from these reactions.

3.2 Experimental

Three sealed tube reactions were carried out for 6 month periods, the details are given in Table 3.1.

Table 3.1 Reactant ratios for MeGeH_3 and $\text{Co}_2(\text{CO})_8$ reaction
(Runs 1 to 3, solvent used = hexane)

Reactants	Run 1	Run 2	Run 3
$\text{Co}_2(\text{CO})_8$ (g)	0.876	1.069	0.675
(mmol)	2.562	3.128	1.975
MeGeH_3 (mmol)	1.306	2.723	3.95
$\text{Co}_2(\text{CO})_8$: MeGeH_3	2 : 1	1 : 0.9	1 : 2

3.2.1 Experimental Run 1 ($\text{Co}_2(\text{CO})_8$: MeGeH_3 = 2 : 1)

$\text{Co}_2(\text{CO})_8$ (0.876g, 2.562 mmoles) was loaded into a 50 ml ampoule under nitrogen. Hexane (10 ml) was added. This was transferred to the vacuum line where it was evacuated and then frozen with liquid nitrogen. MeGeH_3 (1.306 mmoles) was condensed into the ampoule. The ampoule was sealed under vacuum and was left to react for six months in the dark at room temperature.

3.2.2 Observations and Workup

After six months of reaction, a red-brown solution and red solid were observed. The total incondensable gas was found to be 3.18 mmoles, of which 60% was H_2 and 40% CO . The volatiles were removed, but not examined.

The involatile fraction was washed several times with 3-4 ml of hexane each time until a dark red solid of low hexane-solubility was obtained.

The hexane washings were combined together. The infrared spectrum showed this fraction to consist mainly of $\text{MeGeCo}_3(\text{CO})_{11}$ (IR bands at 2080(vs), 2053(s), 2028(vs), 2022(s sh), 1848(mw), 1836(w) in hexane/ CH_2Cl_2) [20,71], $\text{Co}_2(\text{CO})_8$ (IR bands at 2070(s), 2040(vs)) and 2024(vs), and a small amount of $\text{Co}_4(\text{CO})_{12}$ (IR bands at 2065(vs), 2054(vs), 1865(mw)) [142].

Both the fractions were placed under vacuum for a day to remove the $\text{Co}_2(\text{CO})_8$ by sublimation. $\text{MeGeCo}_3(\text{CO})_{11}$ of reasonable purity was obtained on recrystallisation of the hexane fraction. The proportion of $\text{Co}_4(\text{CO})_{12}$ seemed to increase with handling. It was difficult to separate $\text{MeGeCo}_3(\text{CO})_{11}$, $\text{Co}_2(\text{CO})_8$ and $\text{Co}_4(\text{CO})_{12}$ as the solubility differences were small.

The dark red solid was dissolved in CH_2Cl_2 producing a red solution giving an infrared spectrum with bands corresponding to those of $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ (IR bands at 2034(vs), 2016(m), 2006(mw), 1843(w, br), Chapter Four gives a full characterisation) [18,84]. Traces of $\text{MeGeCo}_3(\text{CO})_9$ were also present (IR bands at 2100(w), 2054(s), 2037(vs), 2007(m), 1995(mw,sh)) [71]. Recrystallisation from a CH_2Cl_2 /hexane mixture produced red plates of $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$.

Yield of Run 1:

$\text{MeGeCo}_3(\text{CO})_{11} = 350 \text{ mg (0.61 mmole)} = 47\%^{\wedge}$

$\text{MeGeCo}_3(\text{CO})_{11}$, $\text{Co}_4(\text{CO})_{12}$ and $\text{Co}_2(\text{CO})_8$ (small amount) $\approx 450 \text{ mg}$
(estimated 220mg of $\text{MeGeCo}_3(\text{CO})_{11}$, $\sim 30\%^{\wedge}$ yield from the 450 mg)

pure $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11} = 20 \text{ mg (0.03 mmole)} \approx 2\%^{\wedge}$

$(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ contaminated with $\text{MeGeCo}_3(\text{CO})_9$, $\approx 10 \text{ mg} \approx 1\%$

$\text{Co}_4(\text{CO})_{12} = 50 \text{ mg (0.09 mmole)} \approx 3\%^{*}$

$\text{Co}_2(\text{CO})_8 = 25 \text{ mg (0.07 mmole)} \approx 3\%^{*}$

$^{\wedge}$ based on MeGeH_3 , * based on $\text{Co}_2(\text{CO})_8$ used

3.2.3 Discussion on Run 1 :

Products from Run 1

The major product of this run (where $\text{Co}_2(\text{CO})_8$ was in excess) was $\text{MeGeCo}_3(\text{CO})_{11}$, which is consistent with the previous findings [20]. This was isolated with fairly high purity in 47% yield, while a further 30% (approximately) was inseparable from small amounts of $\text{Co}_4(\text{CO})_{12}$ and $\text{Co}_2(\text{CO})_8$. Errors in weights occur as it is impossible to avoid the introduction of small amounts of tap grease in each purification cycle. As a result, further separation of $\text{MeGeCo}_3(\text{CO})_{11}$ from the mixture was not attempted.

As mentioned earlier, the amount of $\text{Co}_4(\text{CO})_{12}$ obtained at the time of opening the ampoule was fairly small (in region of 5-10% of $\text{MeGeCo}_3(\text{CO})_{11}$) as indicated by an infrared spectrum. The increase in the amount of $\text{Co}_4(\text{CO})_{12}$ after working up is believed to have formed from the decomposition of $\text{Co}_2(\text{CO})_8$ or other unstable products.

One interesting finding in this run is the formation of a measurable quantity of $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$. This, as will be seen in the final discussion, is probably correlated to the formation of $\text{Co}_4(\text{CO})_{12}$. A trace of $\text{MeGeCo}_3(\text{CO})_9$ was also observed.

Incondensable gas: expected and measured

$\text{MeGeCo}_3(\text{CO})_{11} = 350 \text{ mg (0.61 mmole)}$

expect $\rightarrow 0.61 \text{ mmole CO} + 0.92 \text{ mmole H}_2$ (from equation 3.1)

$\text{MeGeCo}_3(\text{CO})_{11} \approx 220 \text{ mg (0.38 mmole)}$

expect $\rightarrow 0.38 \text{ mmole CO} + 0.58 \text{ mmole H}_2$

$(\text{MeGe})_2\text{Co}_4(\text{CO})_{11} = 20 \text{ mg (0.03 mmoles)}$

expect $\rightarrow 0.15 \text{ mmole of CO} + 0.09 \text{ mmole of H}_2$ (eq 3.2, 3.3)

$(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ contaminated with $\text{MeGeCo}_3(\text{CO})_9 \approx 10 \text{ mg}$

expect $\rightarrow \approx 0.07 \text{ mmole of CO} + 0.05 \text{ mmole of H}_2$

$\text{Co}_4(\text{CO})_{12} = 50 \text{ mg (0.09 mmole)}$

expect $\rightarrow 0.35 \text{ mmole of CO}$

The incondensable gases (above) were calculated to check the consistency between the measured incondensable gas with the yields of the products :

total gas = 3.03 mmoles calculated vs 3.18 mmoles measured

gas composition = 51% H_2 calculated vs 60% H_2 measured.

The total incondensable gas figure measured is within 5% error, but the $\text{H}_2\%$ figure is significantly lower. Errors in weighing small amounts of compound (especially $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$) in a large vessel

and in underestimating the yield of $\text{MeGeCo}_3(\text{CO})_{11}$ would result in the low H_2 figure. Of course, errors made while measuring the incondensable gas could not be ignored. The yields obtained in Run 1 tend to favour a lower than 60% H_2 figure due to the formation of $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$, trace amount of $\text{MeGeCo}_3(\text{CO})_9$ and $\text{Co}_4(\text{CO})_{12}$.

3.3 Other runs

Two further runs were carried out. The experimental details of runs 2 and 3 were as in Run 1 (see Table 3.1) except that 1.069g of $\text{Co}_2(\text{CO})_8$ and 2.723 mmoles of MeGeH_3 were used in Run 2, and 0.675g of $\text{Co}_2(\text{CO})_8$ and 3.95 mmoles of MeGeH_3 were used in Run 3.

3.3.1 Observations and workup :

Run 2 ($\text{Co}_2(\text{CO})_8$: MeGeH_3 = 1 : 0.9)

The total incondensable gas was found to be 5.24 mmoles, 68% of which was H_2 and 32% CO . The volatile fraction was removed, but not examined.

The involatile fraction of the product mixture was washed three times with about 3-4 ml of hexane each time. The remaining solid was dissolved in CH_2Cl_2 , the infrared spectrum showed this to consist of $\text{MeGeCo}_3(\text{CO})_{11}$ as the major product. $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ and a trace of $\text{MeGeCo}_3(\text{CO})_9$ were also separated (work up procedures as in Run 1).

The combined hexane washings contained a mixture of compounds. Evaporation gave a brown oil which would not crystallise. Infrared (Table 3.2) and mass spectra of this fraction (Table 3.3) showed that it consisted of $\text{MeGeCo}_3(\text{CO})_{11}$, trace amounts of $\text{Co}_4(\text{CO})_{12}$ (but no $\text{Co}_2(\text{CO})_8$), a compound identified as $\text{Me}_2\text{Ge}_2\text{Co}_4(\text{CO})_{14}$ [76] and a product assigned tentatively as $\text{MeGeHCo}_2(\text{CO})_x$ ($x = 7$ or 8). It was impossible to separate the products as solubility differences were small. The

presence of the bridging carbonyl bands at 1835 and 1847 cm^{-1} of $\text{MeGeCo}_3(\text{CO})_{11}$ made it difficult to determine whether there is a bridging CO band which could be assigned to $\text{MeGeHCo}_2(\text{CO})_7$.

The mass spectrum of the oily mixture (Table 3.3) shows weak parent ions belonging to $\text{Me}_2\text{Ge}_2\text{Co}_4(\text{CO})_{14}$ while the parent ion of $\text{MeGeCo}_3(\text{CO})_{11}$ is reasonably intense. However, there is reasonable indication of the presence of $\text{MeGeHCo}_2(\text{CO})_x$ ($x = 7$ or 8) species in the mass spectrum as another series of overlapping envelopes (assigned as $\text{MeGeHCo}_2(\text{CO})_x^+$, $x = 7$ to 0) in the lower m/e region (from 412 onwards) was observed.

Table 3.2 IR bands of the hexane soluble fractions from Runs 2 and 3 :

Bands (cm^{-1})	Intensities		[20,71]	[76]	Notes
	Run 2	Run 3	$\text{MeGeCo}_3(\text{CO})_{11}$	$\text{Me}_2\text{Ge}_2\text{Co}_4(\text{CO})_{14}$	
2102	w	vw	2105 m		$\text{MeGeHCo}_2(\text{CO})_8 ?$
2094	vw	mw		2097 w	$\text{MeGeHCo}_2(\text{CO})_8 ?$
2083	s	ms		2087 s	
2079	vs	m sh	2082 s		
2070	w	w sh			$\text{MeGeHCo}_2(\text{CO})_x ?$
2065	mw	w		2067 mw	
2053	s	mw	2056 s		
2038	s	s		2039 s	
2029	vs	s	2030 s	2029 s	
2017	vvs br	vs	2020/5m	2017 vs	
2012	vvs	vvs			$\text{MeGeHCo}_2(\text{CO})_x ?$
2004		vvs			unknown
2002		m sh		2002 mw	
1967	vw sh			1970 w	
1847	w	vvw	1850 m		
1835	vw	vvvw	1835 w		

Solvent = CH_2Cl_2 /hexane

Table 3.3 Mass Spectrum of the oily product

m/e	Int	P o s s i b l e A t t r i b u t i o n s		
		$[\text{Me}_2\text{Ge}_2\text{Co}_4(\text{CO})_n]^+$	$[\text{MeGeCo}_3(\text{CO})_y]^+$	$[\text{MeGeHCo}_2(\text{CO})_x]^+$
800-802	vw	n = 14		
772-780	vw	13		
742-758	vw	12		
713-734	vw	11		
685-703	w	10		
658-703	w	9		
629-654	w	8		
600-620	w	7		
562-590	w	6	y = 11	
540-560	w	5	10	
510-530	mw	4	9	
480-503	m	3	8	
450-475	mw	2	7	
430-448	m	1	6	
414-428	vw	0		
400-412	ms		5	x = 7
380-400	w	$[\text{MeGe}_2\text{Co}_4]^+$		
370-385	ms		4	6
358-370	vw		$[\text{GeCo}_3(\text{CO})_4]^+$	
340-352	ms		y = 3	5
330-340	w	$[\text{MeGe}_2\text{Co}_3]^+$	$[\text{GeCo}_3(\text{CO})_3]^+$	
318-328	ms		y = 2	4
300-314	vw		$[\text{GeCo}_3(\text{CO})_2]^+$	
287-300	ms		y = 1	3
270-282	m	$[\text{MeGe}_2\text{Co}_2]^+$	$[\text{GeCo}_3(\text{CO})]^+$	
258-270	vs	$[\text{Ge}_2\text{Co}_2]^+$	y = 0	2
248-253	ms		$[\text{GeCo}_3]^+$	
230-240	w			1
215-224	mw			0
198-210	m		$[\text{MeGeCo}_2]^+$	
188-194	s	$[\text{GeCo}_2]^+$	$[\text{GeCo}_2]^+$	$[\text{GeCo}_2]^+$

A ^1H NMR spectrum was obtained from the cleanest fraction of the oily mixture and its assignment is in Table 3.4.

Table 3.4 ^1H NMR spectrum of the oily mixture from Run 2 and from [20]

Chemical shift, δ (ppm)	Intensity	Assignment
Run 2 (27°C, CDCl_3)		
1.39 distorted doublet	10x	$\text{MeGeHCo}_2(\text{CO})_x$
5.18 multiplet	2x	$\text{MeGeHCo}_2(\text{CO})_x$
5.68 multiplet	1x	$\text{MeGeHCo}_2(\text{CO})_x$
1.71 singlet	3x	$\text{Me}_2\text{Ge}_2\text{Co}_4(\text{CO})_{14}$
1.95 singlet	4x	$\text{MeGeCo}_3(\text{CO})_{11}$

[20] (-20°C, SiCl_4)		
1.25 doublet	$\text{MeGeHCo}_2(\text{CO})_8$ (tentative)	
5.48 quartet $J = 2.2$ Hz	$\text{MeGeHCo}_2(\text{CO})_8$ (tentative)	
1.40 doublet (no GeH signal)	$\text{MeGeHCo}_2(\text{CO})_7$ (tentative)	
1.93 singlet	$\text{MeGeCo}_3(\text{CO})_{11}$	

Note : It should be noted here that the only sharp signals in the spectrum from Run 2 were those at δ 1.71 ppm and 1.95 ppm. The rest were poorly-defined.

The presence of two multiplets due to Ge-H at δ 5.18 and 5.68 ppm with only one distorted methyl-H doublet suggested the possibility of the presence of both $\text{MeGeHCo}_2(\text{CO})_7$ and $\text{MeGeHCo}_2(\text{CO})_8$. The effect of one CO difference in the two compounds probably would not result in any apparent chemical shift in the methyl region. The ratio of peak area indicates that one of them is twice the other's concentration. As the sample was weak and contaminated with $\text{MeGeCo}_3(\text{CO})_{11}$ and $\text{Me}_2\text{Ge}_2\text{Co}_4(\text{CO})_{14}$, the multiplets are likely to be unresolved quartets as seen by earlier workers.

By comparing the above ^1H NMR data with those from [17,20,70], the δ 5.68ppm multiplet is tentatively assigned as that of $\text{MeGeHCo}_2(\text{CO})_8$ and the other at 5.18ppm as that of $\text{MeGeHCo}_2(\text{CO})_7$. (Note that there is an average of about 0.1 ppm difference between some of the chemical shifts obtained in this work and [20]. This may be attributed to the difference in solvent, machine and temperature used).

The above information leads to the belief that $\text{MeGeHCo}_2(\text{CO})_8$ was formed directly from the reaction. Part of this could have been converted to $\text{MeGeHCo}_2(\text{CO})_7$ on pumping on the Schlenk line or general workup procedures.

The singlet at δ 1.71 ppm is tentatively assigned as that of $\text{Me}_2\text{Ge}_2\text{Co}_4(\text{CO})_{14}$. As the infrared and mass spectra obtained from the same sample indicated the presence of $\text{MeGeCo}_3(\text{CO})_{11}$ (1.947ppm), $\text{MeGeHCo}_2(\text{CO})_x$ (1.393ppm) and $\text{Me}_2\text{Ge}_2\text{Co}_4(\text{CO})_{14}$ and as there are only three methyl proton signals present, the assignment is not unreasonable.

Yield of Run 2 :

$\text{MeGeCo}_3(\text{CO})_{11} = 732 \text{ mg} = 1.28 \text{ mmoles} = 47\%$

$(\text{Me}_2\text{Ge})_2\text{Co}_4(\text{CO})_{11} = 31 \text{ mg} = 0.04\text{mmole} = 1.4\%$

Oily mixture of $\text{MeGeCo}_3(\text{CO})_{11}$, $\text{Me}_2\text{Ge}_2\text{Co}_4(\text{CO})_{14}$ + $\text{MeGeHCo}_2(\text{CO})_x = 474\text{mg}$

Comments on Run 2 :

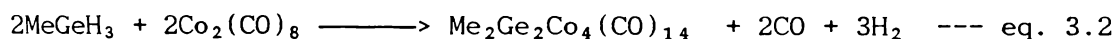
The Products

Run 2 was designed as a reaction with reactants of intermediate ratio between that of Run 1 and Run 3. It is therefore not surprising to find that the products obtained from this run are intermediate : with $\text{MeGeHCo}_2(\text{CO})_x$ and $\text{MeGeCo}_3(\text{CO})_{11}$ as major products and $\text{Me}_2\text{Ge}_2\text{Co}_4(\text{CO})_{14}$ as minor component. The formation of $\text{Me}_2\text{Ge}_2\text{Co}_4(\text{CO})_{14}$

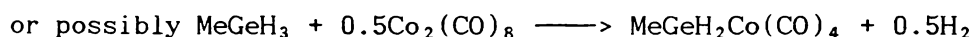
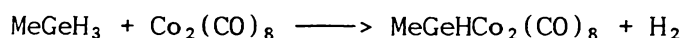
is a totally new observation in such reactions and is believed to be formed due to an excess of MeGeH_3 (see discussion below).

Incondensable gas

The major product in Run 2 was $\text{MeGeCo}_3(\text{CO})_{11}$. If its formation is according to equation 3.1, 60% of the incondensable gases should be H_2 . The formation of $\text{Me}_2\text{Ge}_2\text{Co}_4(\text{CO})_{14}$, via equation 3.2, would also produce incondensable with 60% H_2 :



The actual figure of 68% H_2 is significantly different from 60% (see section 2.13 for discussion of errors). The value observed is consistent with a minor process :



Run 3 ($\text{Co}_2(\text{CO})_8$: MeGeH_3 = 1 : 2)

Unlike run 1 and run 2, the product mixture of run 3 contained very little undissolved solid. It consisted of an orange brown solution with small amount of dark coloured solids. The incondensable gas measurement showed that a total of 3.34 mmoles incondensable gas was evolved, of which 57% was H_2 and 43% CO . The volatile fraction was removed but not examined.

About 10ml of hexane was added to the involatile fraction. This hexane fraction was transferred into another Schlenk flask. Two more extracts with small amounts of hexane were performed. These extracts were added to the first fraction. A small amount of solid residue insoluble in CH_2Cl_2 was left after the washings and this was assumed to be decomposed material.

The hexane fraction was concentrated and left in the freezer overnight. A small amount of $\text{MeGeCo}_3(\text{CO})_9$ (purple red solution in $\text{CH}_2\text{Cl}_2/\text{hexane}$ [71]) was isolated. The remaining hexane soluble fraction was found to be a mixture of products : a high proportion of $\text{Me}_2\text{Ge}_2\text{Co}_4(\text{CO})_{14}$, a considerable amount of $\text{MeGeHCo}_2(\text{CO})_x$, a small amount of $\text{MeGeCo}_3(\text{CO})_{11}$ and an unknown species with a strong IR band at 2004 cm^{-1} with a shoulder at about 2000 cm^{-1} . Attempts to separate the products was unsuccessful. Infrared spectra of the hexane soluble fraction (example in Table 3.2) were very similar to those of Run 2 except that the IR bands due to $\text{MeGeCo}_3(\text{CO})_{11}$ were very low in intensity (with only two tiny weak bands at the bridging carbonyl region), and the presence of the strong 2004 cm^{-1} band accompanied by a shoulder about 4 cm^{-1} away. After pumping under vacuum, the 2004 cm^{-1} band disappeared from the spectrum which indicated a volatile species, perhaps $\text{MeGeH}_2\text{Co}(\text{CO})_4$ (gas phase IR bands at 2106s, 2043vs, 2017vs, 2012vs, 1982m [80]).

Yield of Run 3 :

contaminated $\text{Me}_2\text{Ge}_2\text{Co}_4(\text{CO})_{14}^{\#} = 673\text{mg} \approx 0.84\text{ mmol} = 85\%$ (if pure)

$\text{MeGeCo}_3(\text{CO})_9 = 20\text{mg}$

decomposed material = 13mg

$^{\#}$ $\text{Me}_2\text{Ge}_2\text{Co}_4(\text{CO})_{14}$ contaminated with $\text{MeGeHCo}_2(\text{CO})_x$ (major) and $\text{MeGeCo}_3(\text{CO})_{11}$ (minor)

Comments on Run 3 :

The Products

In Run 3, $\text{Co}_2(\text{CO})_8$ is the limiting reagent. The observation that $\text{Me}_2\text{Ge}_2\text{Co}_4(\text{CO})_{14}$ is the major product reinforces the results obtained in Run 2. Some $\text{MeGeHCo}_2(\text{CO})_x$, a small amount of $\text{MeGeCo}_3(\text{CO})_{11}$ and $\text{MeGeCo}_3(\text{CO})_9$ were also formed.

Incondensable gas measurement

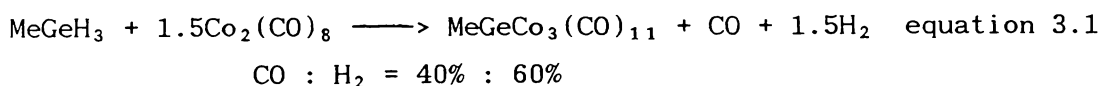
The incondensable gas measurement favours the formation of $\text{Me}_2\text{Ge}_2\text{Co}_4(\text{CO})_{14}$ (equation 3.2) and $\text{MeGeCo}_3(\text{CO})_{11}$ (equation 3.1) which both would give a gas ratio of $\text{H}_2 : \text{CO} = 3 : 2 = 60\% : 40\%$. As $\text{MeGeCo}_3(\text{CO})_{11}$ is produced only in small amount, $\text{Me}_2\text{Ge}_2\text{Co}_4(\text{CO})_{14}$ would seem to be the major product. Formation of $\text{MeGeHCo}_2(\text{CO})_x$ with $x = 8$ would increase the $\text{H}_2 : \text{CO}$ ratio, while formation of $x = 7$ decrease it. Similarly, the formation of $\text{MeGeCo}_3(\text{CO})_9$ and decomposed material would decrease the $\text{H}_2 : \text{CO}$ ratio. The isolation of $\text{MeGeCo}_3(\text{CO})_9$ helps to explain the figure of 57% H_2 obtained (lower than expected).

3.4 Discussion :

The Reaction of MeGeH_3 with $\text{Co}_2(\text{CO})_8$, Runs 1 to 3

The six months reactions of MeGeH_3 with $\text{Co}_2(\text{CO})_8$ at different ratios resulted in different ratio of products as shown in Table 3.5 (next page).

In all the runs, $\text{MeGeCo}_3(\text{CO})_{11}$ was produced, but its yield decreased when the ratio of MeGeH_3 to $\text{Co}_2(\text{CO})_8$ was increased (Run 1 to 3). This is in accordance with the equation :



A small amount of $\text{MeGeCo}_3(\text{CO})_9$ was also produced, presumably from the decarbonylation of $\text{MeGeCo}_3(\text{CO})_{11}$, analogous to $\text{PhGeCo}_3(\text{CO})_{11}$ to $\text{PhGeCo}_3(\text{CO})_9$ [25]. The longer reaction time did not seem to increase the yield of $\text{MeGeCo}_3(\text{CO})_9$ to a great extent, indicating $\text{MeGeCo}_3(\text{CO})_{11}$ is reasonably stable (with respect to decarbonylation) under mild conditions. The ^1H NMR peak at δ 1.58ppm reported from previous studies [17,20,70] was tentatively assigned to this decarbonylated product.

Table 3.5 Summary of reactions of MeGeH_3 with $\text{Co}_2(\text{CO})_8$ for 6 months

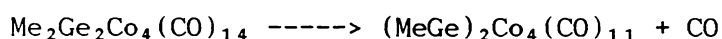
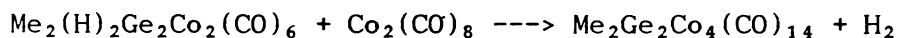
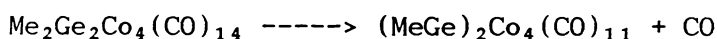
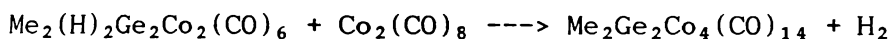
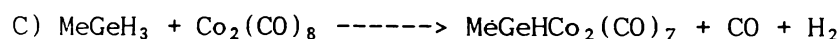
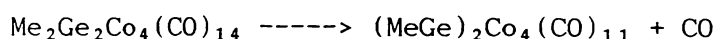
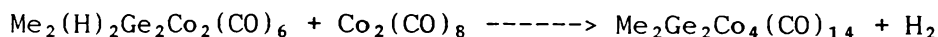
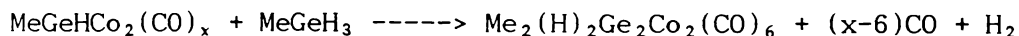
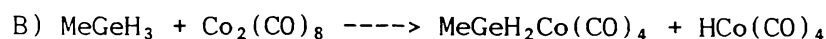
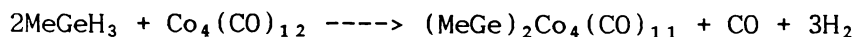
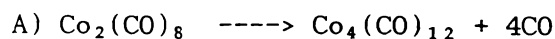
	Run 1	Run 2	Run 3
<u>Reactants :</u>			
$\text{Co}_2(\text{CO})_8$ (g)	0.876	1.069	0.675
(mmoles)	2.562	3.128	1.975
MeGeH_3 (mmoles)	1.31	2.72	3.95
$\text{Co}_2(\text{CO})_8 : \text{MeGeH}_3$	2 : 1	1 : 1	1 : 2
<u>Products :</u>			
$\text{MeGeCo}_3(\text{CO})_{11}$ (%)	~77	>47	trace
$\text{MeGeCo}_3(\text{CO})_9$ (%)	trace	trace	~2
$(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ (%)	~3	1.4	-
$\text{Me}_2\text{Ge}_2\text{Co}_4(\text{CO})_{14}$ (%)	-	cns	~85
$\text{MeGeHCo}_2(\text{CO})_x$ (%)	-	cns	cns
$\text{Co}_4(\text{CO})_{12}$ (%*)	>3	trace	-
$\text{Co}_2(\text{CO})_8$ (%*)	~3	-	-
<u>Incondensable gas :</u>			
Total (mmol)	3.18	5.24	3.34
CO (%)	40	32	43
H_2 (%)	60	68	57

Notes : Only yields of involatile was shown.

All yields were calculated based on limiting reactants unless otherwise stated.

* based on $\text{Co}_2(\text{CO})_8$ used; cns = cannot be separated

$(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ (see Chapter Four for a full characterisation) was obtained as a minor product in Runs 1 and 2. Run 1 produced the highest yield of $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ (~3%, compared to ~3% by S.Foster [18,84]) together with a reasonable amount of $\text{Co}_4(\text{CO})_{12}$ isolated (see Table 3.5). Run 2 gave a small amount of $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ (1.4%) with trace amounts of $\text{Co}_4(\text{CO})_{12}$ while neither was found in Run 3. This seems to indicate that $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ could have been formed via route A) in the following possible routes (these are followed by a short discussion of each route):



Route A :

As will be seen in Chapter Four, MeGeH_3 does react with $\text{Co}_4(\text{CO})_{12}$ cleanly and easily to produce only $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$. The yield of $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ and the presence of $\text{Co}_4(\text{CO})_{12}$ is therefore unlikely to be a coincidence. Probably the excess $\text{Co}_2(\text{CO})_8$ in Run 1 formed $\text{Co}_4(\text{CO})_{12}$ which in turn reacted with MeGeH_3 .

Routes B), C) and D) :

These routes require the presence of excess MeGeH_3 which means that run 3 would be expected to produce the most $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$, but this is not the case. Moreover, it has been found that $\text{Me}_2\text{Ge}_2\text{Co}_4(\text{CO})_{14}$ decarbonylates to form $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ only at $\sim 45^\circ\text{C}$ [76]. With the high incondensable gas pressure already present in the sealed

ampoules, it is unlikely that decarbonylation of $\text{Me}_2\text{Ge}_2\text{Co}_4(\text{CO})_{14}$ would occur. Therefore the formation of $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ via these routes is improbable.

The results obtained from runs 2 and 3 are consistent with the input:- the higher the $\text{MeGeH}_3 : \text{Co}_2(\text{CO})_8$ ratio, the less $\text{MeGeCo}_3(\text{CO})_{11}$ is expected to be produced and the more $\text{Me}_2\text{Ge}_2\text{Co}_4(\text{CO})_{14}$ and $\text{MeGeHCo}_2(\text{CO})_x$ are expected. With more MeGeH_3 in run 3 than in run 2 the likelihood of disubstituting the $\text{Co}_2(\text{CO})_8$ is higher and more $\text{Me}_2\text{Ge}_2\text{Co}_4(\text{CO})_{14}$ is therefore expected in run 3.

No previous report on the ^1H NMR data of $\text{Me}_2\text{Ge}_2\text{Co}_4(\text{CO})_{14}$ has been published. The singlet at δ 1.71 ppm in the ^1H NMR spectrum obtained in run 2 (Table 3.4) is tentatively assigned to $\text{Me}_2\text{Ge}_2\text{Co}_4(\text{CO})_{14}$ which was clearly present in the infrared and mass spectra of the same sample (Tables 3.2 and 3.3).

$\text{Me}_2\text{Ge}_2\text{Co}_4(\text{CO})_{14}$ was first made by the reaction of $(\text{MeGeH}_2)_2\text{Fe}(\text{CO})_4$ with $\text{Co}_2(\text{CO})_8$ [76]. The crystal structure 6 shows that the molecule is a derivative of $\text{Co}_2(\text{CO})_8$ where both the $\mu\text{-CO}$'s are replaced by the $\text{MeGeCo}(\text{CO})_4$ units (in $\text{MeGeCo}_3(\text{CO})_{11}$ and $\text{PhGeCo}_3(\text{CO})_{11}$ only one bridging CO has been replaced). Crystallographically, it shows C_{2v} symmetry which would give rise to 12 infrared active bands. The observed solution infrared spectrum shows 10 clearly resolved bands with no bridging CO as expected (Fig 3.1).

In all previous studies of the reaction of MeGeH_3 with $\text{Co}_2(\text{CO})_8$ [17,18,20,70], neither $\text{Me}_2\text{Ge}_2\text{Co}_4(\text{CO})_{14}$ nor $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ were detected. Similarly, no phenyl analogues were seen in the related reaction of PhGeH_3 with $\text{Co}_2(\text{CO})_8$ [25]. Their presence in this work and not in any of the earlier studies indicates they required the

appropriate reaction ratio and a long reaction time for their formation.

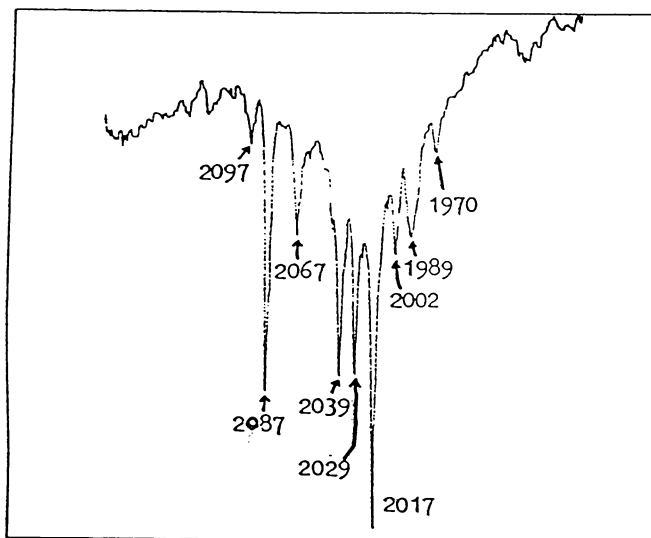
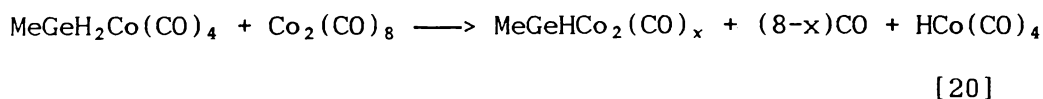
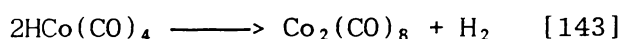


Fig 3.1 IR spectrum of $\text{Me}_2\text{Ge}_2\text{Co}_4(\text{CO})_{14}$ [76]

The existence of a dicobalt species of likely formula $\text{MeGeHCo}_2(\text{CO})_x$ was indicated by the infrared as well as the ^1H NMR spectra. However, the number of CO groups remained speculative. The infrared spectra showed that the involatile fractions were always contaminated with $\text{MeGeCo}_3(\text{CO})_{11}$ and $\text{Me}_2\text{Ge}_2\text{Co}_4(\text{CO})_{14}$ in this study. The infrared spectrum of Run 3 (contains only a small amount of $\text{MeGeCo}_3(\text{CO})_{11}$) showed no sign of any bridging carbonyl bands that could have belonged to a dicobalt species with a bridging carbonyl if the formula is $\text{MeGeHCo}_2(\text{CO})_7$. By comparison with the analogues $\text{MeGeXCo}_2(\text{CO})_8$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$ and Me [17]), R.Gerlach tentatively assigned the dicobalt species as $\text{MeGeHCo}_2(\text{CO})_8$. The analogous compounds $\text{Me}_2\text{GeCo}_2(\text{CO})_8$ [33,61] and $\text{Ph}_2\text{GeCo}_2(\text{CO})_8$ [62] have been synthesised and shown to be of reasonable stability despite the two bulky phenyl groups on $\text{Ph}_2\text{GeCo}_2(\text{CO})_8$. The stability of $\text{MeGeHCo}_2(\text{CO})_8$ (with much smaller Me and H) is therefore not a problem. The incondensable gas measurement in Run 2 favours the value of x in

MeGeHCo₂(CO)_x to be 8 (if x = 7, the %CO would have to be higher than 40%). However, working up procedures may result in the decarbonylation (x = 7). The ¹H NMR spectrum of the sample which gave the same infrared spectrum in Run 2, showed the presence of signals that correspond to those of MeGeHCo₂(CO)_x detected by both B.Graham and R.Gerlach [20]. However, a second multiplet at δ 5.18 ppm was also recorded. By comparing the results with those obtained from [17,20,71], the δ 5.68ppm multiplet seems to be that of MeGeHCo₂(CO)₈ and the second multiplet at δ 5.18 ppm seems to be that of MeGeHCo₂(CO)₇. The latter is probably the result of the decarbonylation of MeGeHCo₂(CO)₈ by pumping under vacuum.

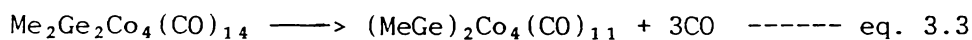
The compound with a strong band at 2004 cm⁻¹ in Run 3 remains unassigned. Its disappearance on pumping under vacuum indicates volatility and hence small molecular weight type compound. One candidate is MeGeH₂Co(CO)₄ [80], but no solution infrared spectrum of this compound is available for comparison. The volatiles of Runs 1 to 3 were not examined, but from previous studies with short reaction time [20], HCo(CO)₄ constitutes the main proportion of volatiles together with a small quantity of MeGeH₂Co(CO)₄. 80% of the reacted hydrogen in one study [20] was found to remain as HCo(CO)₄. With the long reaction time involved, not much of these volatiles would be expected to remain, as :-



Also, the mass balance in all the three runs indicated that if HCo(CO)₄ was formed at all, no more than only minor quantity of it could be included. HCo(CO)₄ was probably the precursor to the Co₄(CO)₁₂.

3.5 Thermal Decarbonylation of $\text{Me}_2\text{Ge}_2\text{Co}_4(\text{CO})_{14}$

$\text{Me}_2\text{Ge}_2\text{Co}_4(\text{CO})_{14}$ decarbonylated to $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ when heated in solution at 45°C [76] as in equation 3.3 :



The substantial rearrangement taking place at this relatively low temperature might leave scope for other interesting transformations under more forcing conditions. Although a pure sample was not available, it was thought worthwhile to carry out an exploratory study on the mixed fraction produced in Run 3 (Page 53).

3.5.1 Experimental

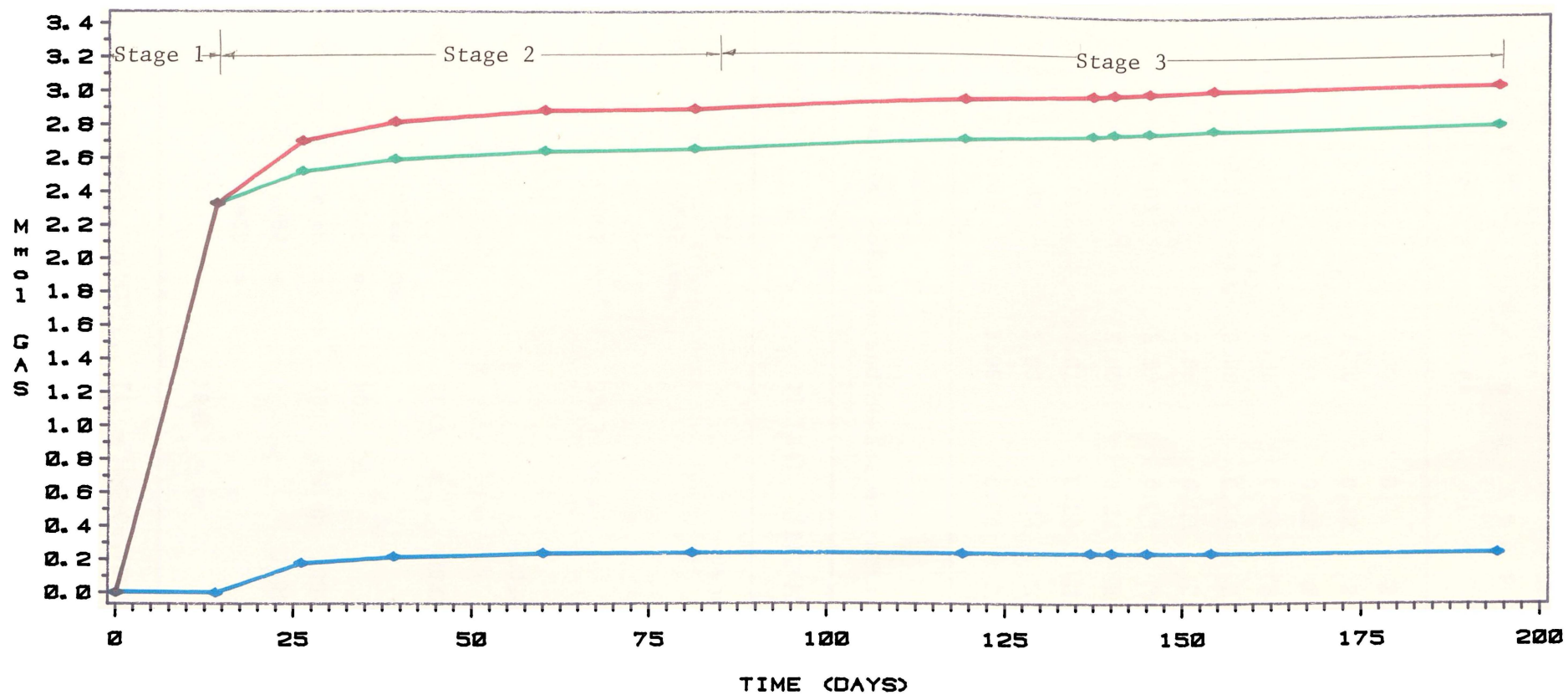
$\text{Me}_2\text{Ge}_2\text{Co}_4(\text{CO})_{14}$ (major component), containing $\text{MeGeHCo}_2(\text{CO})_x$ (minor component) plus $\text{MeGeCo}_3(\text{CO})_{11}$ (trace) (673mg, approximately 0.84 mmole) and hexane (50 ml) were placed in a 200 ml reaction vessel with a greaseless tap. This was heated at 55°C in an oil bath and incondensable gas measurement was carried out at suitable intervals. The temperature of the oil bath was then increased to 75°C after 154 days of reaction.

3.5.2 Results and workup:

The incondensable gas evolved is given in Table 3.6 and Fig 3.2.

After heating for 194 days, the product mixture consisted of a black powdery solid and a dark brown supernatant solution. The brown hexane solution was decanted from the solid. The infrared spectrum of the solution showed that no starting material remained (Table 3.7).

Fig 3.2
Incondensable Gas Evolution
From The Decarbonylation Of
 $\text{Me}_2\text{GeCo}_4(\text{CO})_{14}$



TOTAL GAS ———
HYDROGEN ———
CARBON MONOXIDE ———

Table 3.6 Incondensable gas evolution from the decarbonylation of
 $\text{Me}_2\text{Ge}_2\text{Co}_4(\text{CO})_{14}$ (in mmoles)

Days	Gas evolved			accumulated gas		
	total	H ₂	CO	total	H ₂	CO
14	2.33	0	2.33	2.33	0	2.33
26	0.37	0.18	0.19	2.70	0.18	2.52
39	0.11	0.04	0.07	2.81	0.22	2.59
60	0.07	0.02	0.05	2.88	0.24	2.64
81	0.01	0.00(2)	0.01	2.89	0.24	2.65
119	0.07	0	0.07	2.96	0.24	2.72
137	0.03	0	0.03	2.99	0.24	2.75
140	0.01	0	0.01	3.00	0.24	2.76
145	0.01	0	0.01	3.01	0.24	2.77
154	0.02	0	0.02	3.03	0.24	2.79
194	0.02	0	0.02	3.05	0.24	2.81

Table 3.7 IR of the supernatant solution and hexane extracts

Supernatant	Extracts	I	II [84]	III [71]
	2100 vw			2100 w
2090 w	2090 vw	2092 mw		
2080 w				
2068 w	2068 w	2062 ms	2063 vw sh	
2061 m				
2054 mw sh	2050 m			2054 s
2047 m				
2031 ms sh	2035 ms		2034 vs	2037 vs
2025 ms		2023 ms		
2012 vs		2016 vs	2016 m	
	2008 m	2010 ms sh	2005 mw sh	2007 m
		1994 w		1995 mw sh
1978 m		1980 w		
1844 vv			1843 w br	

I = $\text{Me}_3\text{Ge}_3\text{Co}_5(\text{CO})_{14}$, II = $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$, III = $\text{MeGeCo}_3(\text{CO})_9$,

Two possible components of the supernatant solution were $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ and a new compound characterised as $\text{Me}_3\text{Ge}_3\text{Co}_5(\text{CO})_{14}$ in Section 3.5.3 and 3.5.4. The black solid fraction was extracted with hexane, the infrared spectrum of the extracts (Table 3.7) indicated a mixture of compounds, with evidence for $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ and $\text{MeGeCo}_3(\text{CO})_9$.

CH_2Cl_2 was added to the remaining solid, the red solution formed was left to stand to allow the undissolved black powder-like material to settle down. The CH_2Cl_2 solution was decanted into a clean flask. The solution was concentrated and on recrystallisation produced dark square plates. These were identified as $\text{Me}_3\text{Ge}_3\text{Co}_5(\text{CO})_{14}$. The characterisation is presented in Section 3.5.3 while the full crystal structure is presented in Section 3.5.4.

A nujol mull infrared spectrum of the black solid powder residue gave a very weak spectrum with bands at 2069 cm^{-1} m, 2015 cm^{-1} s, and 1972 cm^{-1} ms, sh. This was very similar to the spectrum of $\text{Me}_3\text{Ge}_3\text{Co}_5(\text{CO})_{14}$ (Table 3.8). It is likely that the bands (if any at all in this region) of the solid residue were weak and were swamped by those of $\text{Me}_3\text{Ge}_3\text{Co}_5(\text{CO})_{14}$.

Yield :

$\text{Me}_3\text{Ge}_3\text{Co}_5(\text{CO})_{14}$ (as pure crystals) = $\approx 85\text{ mg} = 0.089\text{ mmol}$

(as dark red solid) = $\approx 250\text{mg} = 0.262\text{ mmol}$

mixture of $\text{Me}_3\text{Ge}_3\text{Co}_5(\text{CO})_{14}$ + $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ (approximately 2 : 1)

$\approx 100\text{mg}$

unidentified black insoluble powder $\approx 150\text{mg}$

3.5.3 Spectroscopic characterisations of $\text{Me}_3\text{Ge}_3\text{Co}_5(\text{CO})_{14}$

Infrared spectra

The infrared spectrum of $\text{Me}_3\text{Ge}_3\text{Co}_5(\text{CO})_{14}$ (Table 3.8) is discussed in terms of the structure determined crystallographically.

A total of 14 infrared bands are predicted for $\text{Me}_3\text{Ge}_3\text{Co}_5(\text{CO})_{14}$ based on a C_s symmetry: $(8A' + 6A'')$. Like species containing the $\text{Ge}_2\text{Co}_4(\text{CO})_{11}$ unit, fewer bands are observed than predicted (see Tables 9.1-9.3 in Chapter Nine). In the solution infrared spectrum in Fig 3.4, only 7 bands (all terminal) are observed, with no indication of the semi-bridging CO. Compounds such as $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ (*1a*) and $\text{Ge}_2\text{Co}_6(\text{CO})_{19}$ (*1c*) each with a fully bridging CO and two semi-bridging CO's show only a very weak bridging CO band at about 1835 cm^{-1} . The two semi-bridging CO's in $\text{Me}_3\text{Ge}_3\text{Co}_5(\text{CO})_{14}$ are not expected to be observed at this level of resolution.

The infrared spectrum of the solid (Fig 3.5) showed only six bands. A weak band at 2043 cm^{-1} not seen in the solution infrared spectrum was observed. Except for the 2097 cm^{-1} band, all other bands were shifted to the lower wavenumber.

In $(\text{RM}')_2\text{Co}_4(\text{CO})_{11}$ compounds the strongest and the most significant band appears at $2033\text{--}2040\text{ cm}^{-1}$ with a shoulder at $\sim 2015\text{ cm}^{-1}$. $\text{Me}_3\text{Ge}_3\text{Co}_5(\text{CO})_{14}$ however lacks this distinct feature, with the strongest band at 2016 cm^{-1} . A comparison and discussion of the infrared spectra of $\text{Me}_3\text{Ge}_3\text{Co}_5(\text{CO})_{14}$ and $\text{M}'_2\text{Co}_4(\text{CO})_{11}$ type compounds is detailed in Chapter Nine.

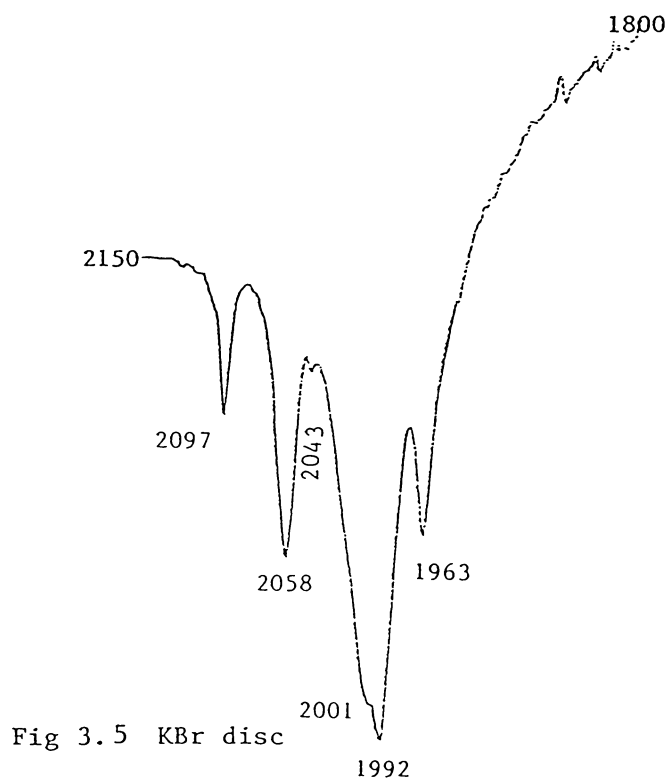
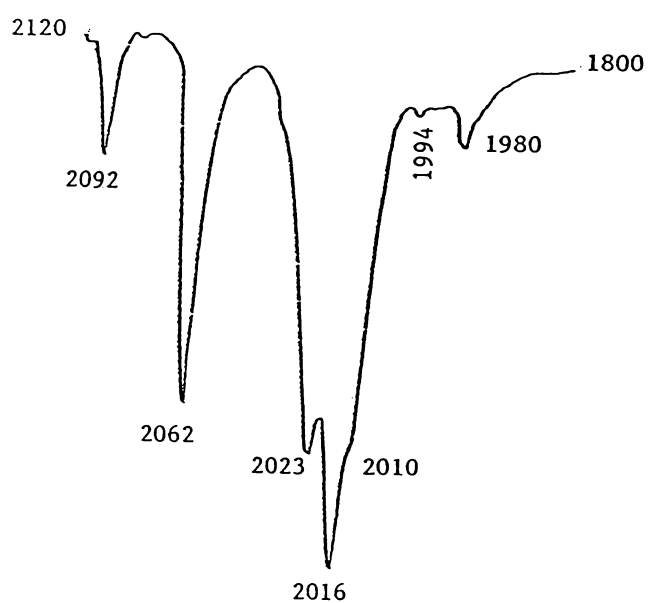
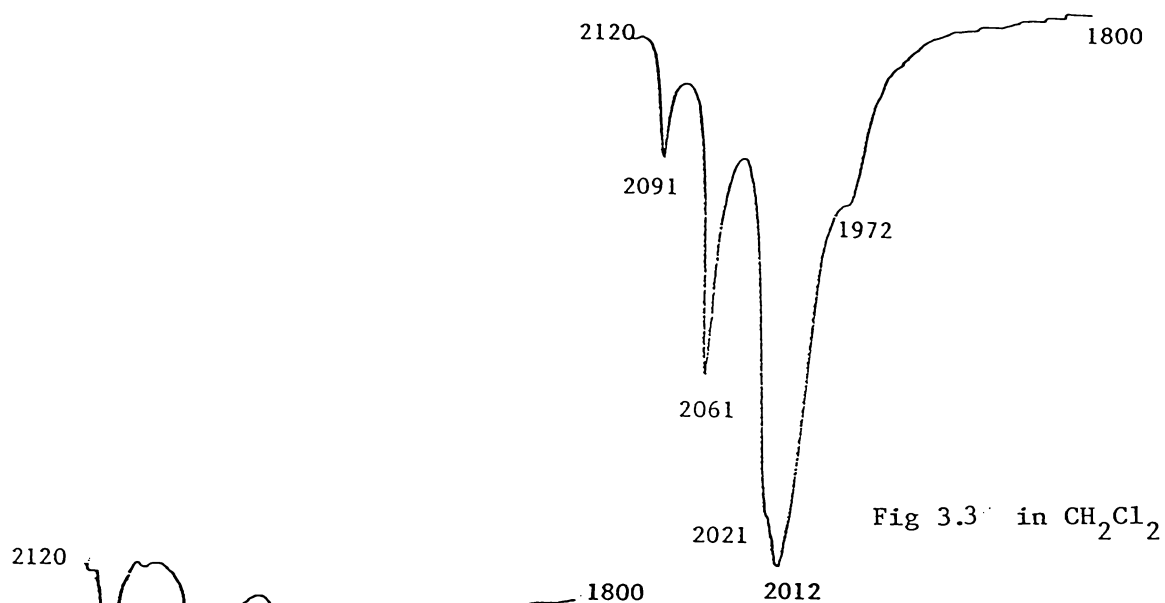


Fig 3.3 to Fig 3.5 Infrared spectra of $\text{Me}_3\text{Ge}_3\text{Co}_5(\text{CO})_{14}$

Table 3.8 Infrared spectra of $\text{Me}_3\text{Ge}_3\text{Co}_5(\text{CO})_{14}$

Bands	Intensity	Bands	Intensity	Bands	Intensity
In CH_2Cl_2		In hexane/ CH_2Cl_2		KBr disc	
2091	mw	2092	mw	2097	mw
2061	ms	2062	ms	2058	ms
				2043	w
2021	s sh	2023	ms		
2012	vs	2016	vs	2001	vs sh
		2010	ms sh		
		1994	w	1992	vs
1972	mw sh	1980	w	1963	m

Mass spectrum

The parent ion envelope calculated at 954 was not observed in the mass spectrum of $\text{Me}_3\text{Ge}_3\text{Co}_5(\text{CO})_{14}$ (Table 3.9). The highest envelope observed is assigned to that of $[\text{P-CO}]^+$. Unlike $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ where the loss of Me group occurred only after the loss of all the CO's, $\text{Me}_3\text{Ge}_3\text{Co}_5(\text{CO})_{14}$ loses its first Me group after the loss of four CO's. The last two methyl groups were lost after the loss of 13 CO's. All envelopes of strong enough intensity showed a distinct Ge_3 pattern.

Table 3.9 Mass spectrum of $\text{Me}_3\text{Ge}_3\text{Co}_5(\text{CO})_{14}$

m/e	Int	Possible assignments
923-929	vvw	$[\text{P-CO}]^+$ for $\text{P} = [\text{Me}_3\text{Ge}_3\text{Co}_5(\text{CO})_{14}]^+$
870-879	mw	$[\text{P-3CO}]^+$
848-852	vvw	$[\text{P-4CO}]^+$
823-830	vw	$[\text{P-4CO-Me}]^+$
794-803	w	$[\text{P-5CO-Me}]^+$
770-781	s	$[\text{P-6CO-Me}]^+$

Table 3.9 *cont'd...*

746-750	s	[P-7CO-Me] ⁺
717-730	vs	[P-8CO-Me] ⁺
691-702	m	[P-9CO-Me] ⁺
660-673	m	[P-10CO-Me] ⁺
630-645	mw	[P-11CO-Me] ⁺
603-613	w	[P-12CO-Me] ⁺
578-589	vvw	[P-13CO-Me] ⁺
550-564	w	[P-13CO-2Me] ⁺ or [P-14CO] ⁺
520-545	vs	[P-14CO-2Me] ⁺
505-520	vw	[P-14CO-3Me] ⁺
450-472	vw	[P-14CO-2Me-Co] ⁺
449-460	vw	[P-14CO-3Me-Co] ⁺

*NMR Data:*¹H NMR :

The peaks listed below are the observed ¹H NMR signals for Me₃Ge₃Co₅(CO)₁₄ : δ 1.97, 2.47, 2.56 ppm. As shown in Figure 3.6, the three singlets are of almost equal intensity. The δ 1.97 ppm singlet probably belongs to the methyl group on the μ-Ge(Me)Co(CO)₄ unit. The presence of a Me and a Co(CO)₄ group on the bridging unit creates different environments for the two apical Me groups, therefore two singlets instead of one were observed (δ 2.47 and 2.56 ppm), as compared to the ¹H NMR signal of (MeGe)₂Co₄(CO)₁₁ (δ 2.75 ppm).

¹³CO NMR :

Four ¹³CO NMR singlets at δ 203.4 ppm, 200.5 ppm, 199.6 ppm and 196.8 ppm with a relative ratio of approximately 3 : 1 : 1 : 2 were observed (Fig 3.7a). This is quite unexpected, as ¹³CO NMR of (RM')₂Co₄(CO)₁₁ type compounds indicated that all the CO's were in equivalent positions in solution even at -50°C (see Section 9.2). Studies of (PPh)₂Co₄(CO)₁₀ [129] at 0°C showed that the eight

terminal and two bridging CO's were equivalent in the NMR study. The environment of the two groups of CO's was only differentiated at -100°C at which two ^{13}C O resonances at 238 and 204 ppm with a relative intensity of 1 : 4 [129]. The presence of a $\mu\text{-Ge}$ unit in $\text{Me}_3\text{Ge}_3\text{Co}_5(\text{CO})_{14}$ seems to have prevented the fast exchange of CO's in the Ge_2Co_4 core at -50°C , thus resulting in the differentiation of CO's in different environments. With reference to the results in Section 9.2, the four signals are assigned as follows :

singlet at δ 203.4 ppm: due to the four terminal CO's and two semi-bridging CO's on Co(1) and Co(1'). The crystal structure of $\text{Me}_3\text{Ge}_3\text{Co}_4(\text{CO})_{14}$ (Fig 3.8) has shown that the two semi-bridging CO's have short C-Co(1) distance (1.776Å) and long C-Co(2) distance (2.480Å). Therefore they could almost be considered as terminal CO's on Co(1) and Co(1') giving a total of six CO on these two Co's.

singlets at δ 200.5 ppm and 199.6 ppm: assigned to the four terminal CO's on Co(2) and Co(2'). These four CO's are in two different environments : two of them in the proximity of the methyl group of the $\mu\text{-Ge}(\text{Me})\text{Co}(\text{CO})_4$ unit and the other two nearer to the $\text{Co}(\text{CO})_4$ group. The slightly different environments resulted in two singlets very close to each other.

singlet at δ 196.8 ppm: assigned to the four terminal CO's on the apical $\text{Co}(\text{CO})_4$ group, i.e. on Co(3). The observation of only one singlet indicates that the axial and equatorial CO's in the $\text{Co}(\text{CO})_4$ are still exchanging rapidly at -50°C .

As the temperature was raised to room temperature (Fig 3.7b), the singlets at δ 203.4 ppm, 200.5 ppm and 199.6 ppm merged to form a broad peak at 201.9 ppm. A sharp singlet at δ 197 ppm was also observed, indicating that the CO's in the $\text{Co}(\text{CO})_4$ unit (197 ppm) do not exchange with those on the central Co_4 unit at room temperature.

A singlet at δ 31.4 ppm was also observed in both the -50°C and room temperature spectra. No assignment has been made to this singlet as, if any resonance due to the methyl carbon is observed at all, there should be three singlets due to the three different methyl carbon environments indicated by the crystal structure. Also, the Me-Ge signals are expected to be close to $\delta = 0$ ppm, so this 31.4 ppm peak is presumably from the tap grease.

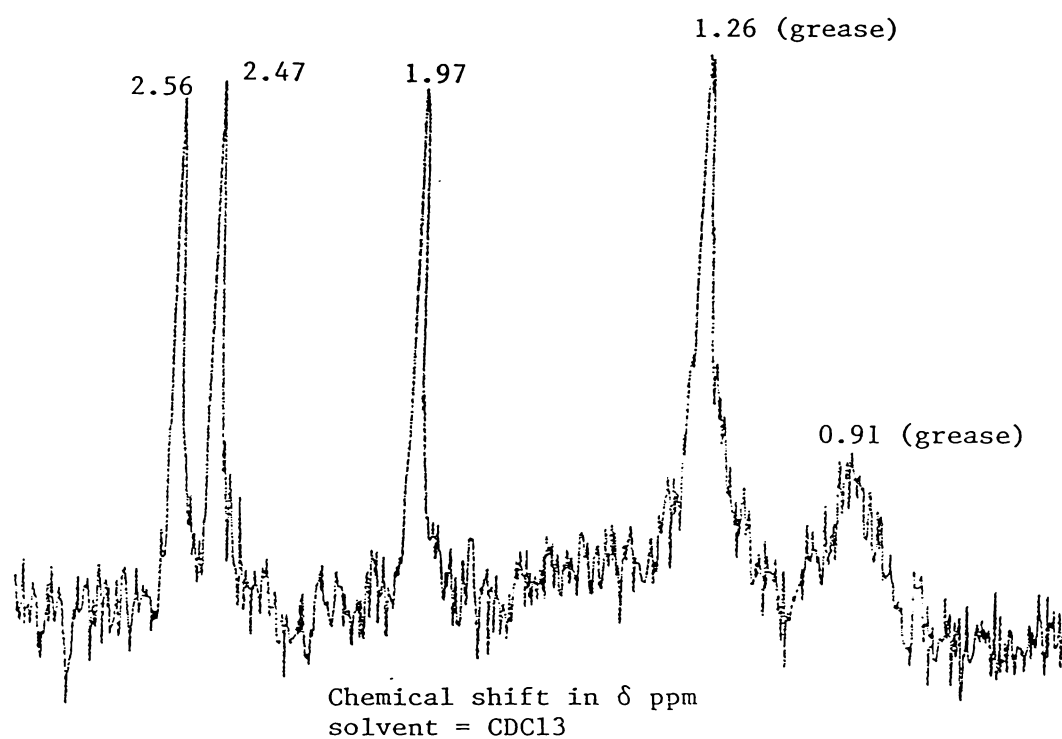


Fig 3.6 ^1H NMR spectrum of $\text{Me}_3\text{Ge}_3\text{Co}_5(\text{CO})_{14}$ at 27°C

Solvent = CDCl_3

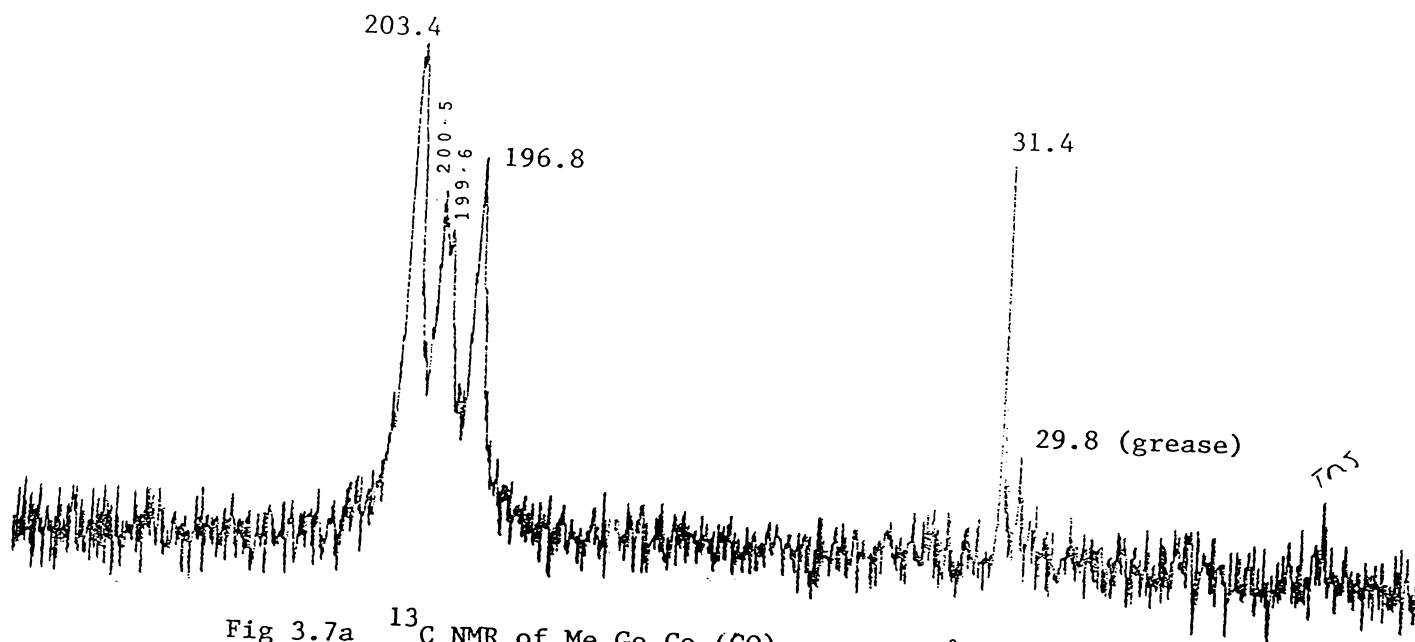


Fig 3.7a ^{13}C NMR of $\text{Me}_3\text{Ge}_3\text{Co}_5(\text{CO})_{14}$ at -50°C

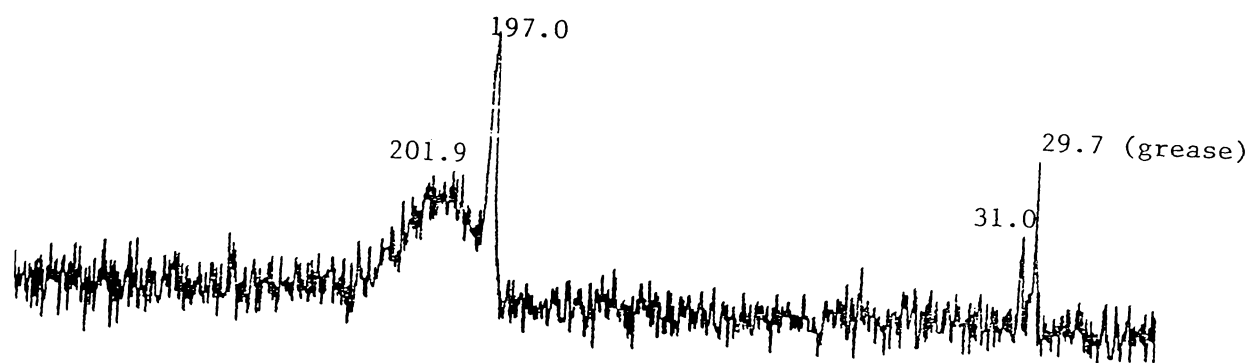


Fig 3.7b ^{13}C NMR spectrum of $\text{Me}_3\text{Ge}_3\text{Co}_5(\text{CO})_{14}$ at 27°C

3.5.4 X-ray Crystal Structure of $\text{Me}_3\text{Ge}_3\text{Co}_5(\text{CO})_{14}$

(Note : This is a joint study with S.G.Anema)

Experimental:

Crystals of $\text{Me}_3\text{Ge}_3\text{Co}_5(\text{CO})_{14}$ were readily formed from a hexane/ CH_2Cl_2 (40:60) solution at -30°C . Many crystals were grossly twinned, though the smaller crystals proved suitable for a full X-ray structure. A dark red square plate-shaped crystal (size about 0.5mm x 0.3mm x 0.1mm) was mounted on a glass fibre for preliminary studies.

Preliminary studies and data collection:

Initial precession photographs, using nickel filtered CuK_α X-radiation, indicated the crystal was monoclinic in the space group C2, C2/m or Cm. The structure was successfully determined in the C2/m space group.

Data collection was performed by Dr. C.Rickard at the University of Auckland on an Enraf-Nonius CAD 4 Diffractometer. The crystal data is given in Table 3.10 :

Table 3.10 Crystal data of $\text{Me}_3\text{Ge}_3\text{Co}_5(\text{CO})_{14}$

Formula : $\text{C}_{17}\text{H}_9\text{O}_{14}\text{Ge}_3\text{Co}_5$
Mr = 949.8
Space group : Monoclinic, C2/m
a = 12.330(6)Å, b = 12.302(3)Å, c = 18.815(4)Å,
$\beta = 92.93(3)^\circ$
U = 2850.14Å ³ , $D_{\text{calc}} = 2.21 \text{ g/ml}$
Z = 4
F(000) = 1816
$\mu(\text{MoK}\alpha) = 58.31\text{cm}^{-1}$
T = 21°C (294K)

A total of 2418 reflections were collected in the range of $1 \leq \theta \leq 24$ which corresponded to 1884 unique reflections. Empirical absorption corrections and Lorentz and polarisation corrections were applied. Of the data 1215 had $F^2 > 2\sigma(F^2)$ and were used for all calculations.

Solution and refinement:

The six heavy metal atoms were readily located using the TREF routine of SHELXS86. Subsequent difference maps phased on this skeleton using SHELX76 revealed the positions of all 8 unique carbonyls and the three methyl carbons. The hydrogens of the three methyl groups were placed in the calculated positions using the AFIX subroutine of SHELX, but they did not settle on the mirror plane suggesting near free rotation or disorder of all these groups. In the final cycle of full-matrix least squares refinement, all non-hydrogen atoms were assigned anisotropic temperature factors. Convergence gave $R = 0.0361$, $R_w = 0.0347$, $w = [\sigma^2(F) + 0.0004F^2]^{-1}$.

The maximum final electron density was less than $0.569 \text{ e/\AA}^3$ and no non-hydrogen parameters shifted by more than 0.035 its esd.

A variance analysis showed little dependence on $\sin \theta$ or $(F/F_{\text{max}})^{1/2}$.

Discussion of the structure:

Diagrams of the full molecule are given in Figs 3.8 to 3.10. Bonded and selected non-bonded distances are given in Table 3.11 while interatomic angles and dihedral angles are given in Table 3.12. Final positional parameters and thermal parameters are in Appendix 3.

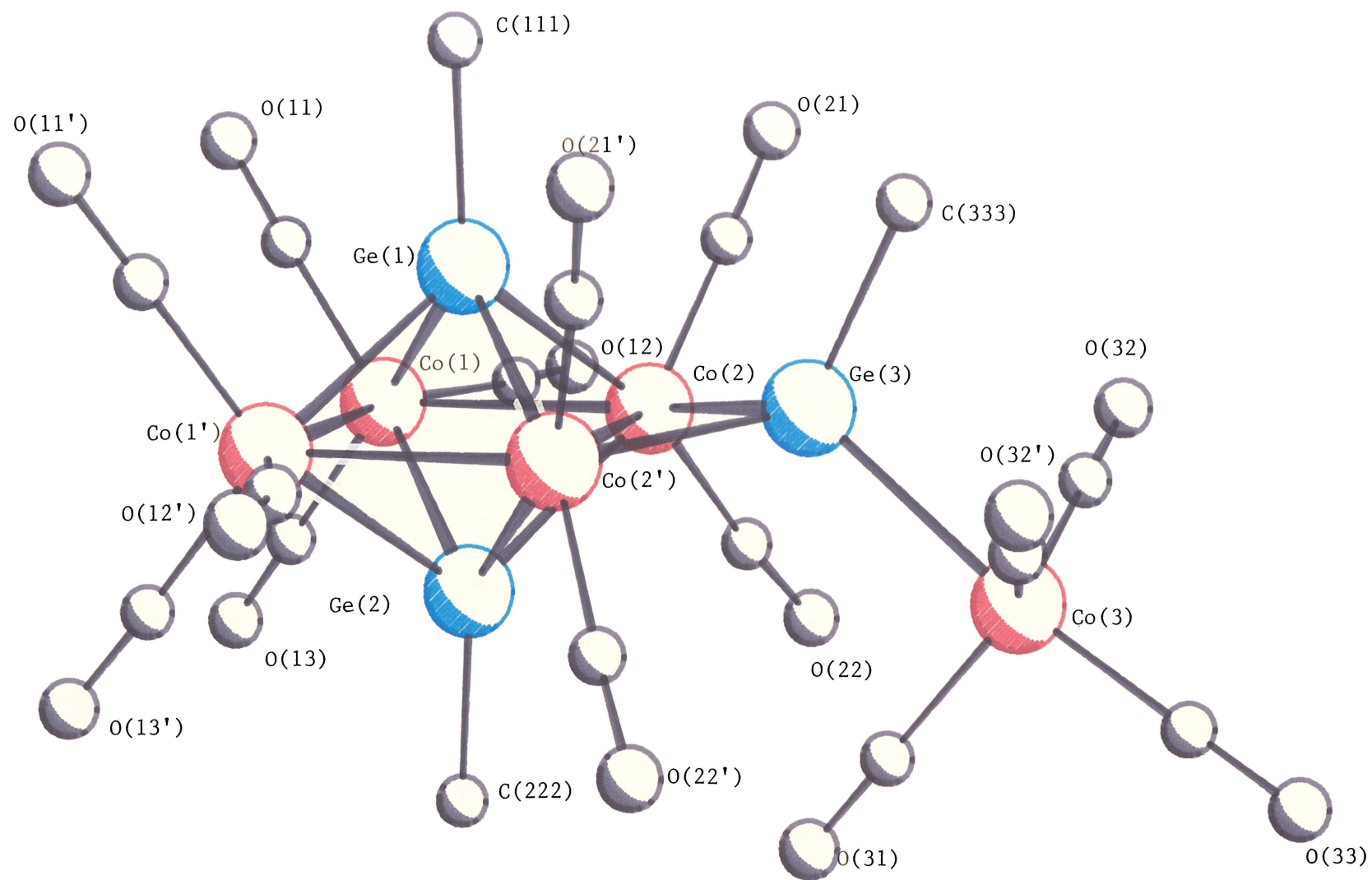


Fig 3.8 Crystal structure of $\text{Me}_3\text{Ge}_3\text{Co}_5(\text{CO})_{14}$

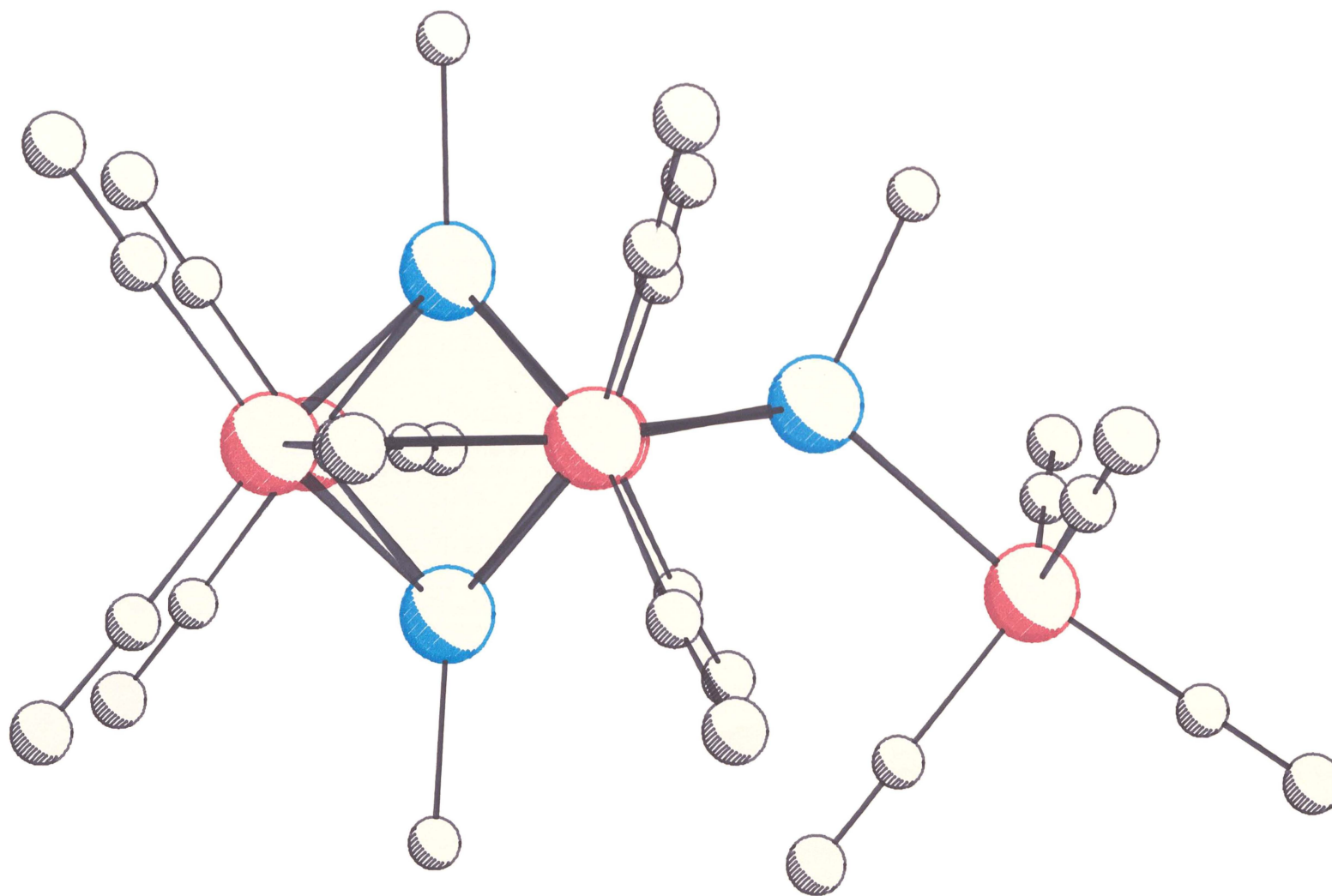


Fig 3.9 Another view of $\text{Me}_3\text{Ge}_3\text{Co}_5(\text{CO})_{14}$

Table 3.11 Bond Lengths (Å)

Bond	Length (Å)	Bond	Length (Å)
Ge(1) ---Ge(2)	2.882(2)	Co(2) ---Co(2)	2.734(3)
Ge(1) ---Co(1)	2.401(2)	Co(2) ---C(12)	2.48(1)
Ge(1) ---Co(2)	2.372(2)	Co(2) ---C(21)	1.78(1)
Ge(1) ---C(111)	1.93(1)	Co(2) ---C(22)	1.80(1)
Ge(2) ---Co(1)	2.407(2)	Co(3) ---C(31)	1.83(2)
Ge(2) ---Co(2)	2.389(2)	Co(3) ---C(32)	1.82(2)
Ge(2) ---C(222)	1.93(1)	Co(3) ---C(33)	1.78(2)
Ge(3) ---Co(2)	2.339(2)	C(11) ---O(11)	1.13(1)
Ge(3) ---Co(3)	2.440(3)	C(12) ---O(12)	1.15(1)
Ge(3) ---C(333)	1.95(1)	C(13) ---O(13)	1.14(1)
Co(1) ---Co(1)	2.722(3)	C(21) ---O(21)	1.15(1)
Co(1) ---Co(2)	2.673(2)	C(22) ---O(22)	1.13(1)
Co(1) ---C(11)	1.80(1)	C(31) ---O(31)	1.12(2)
Co(1) ---C(12)	1.78(1)	C(32) ---O(32)	1.09(2)
Co(1) ---C(13)	1.79(1)	C(33) ---O(33)	1.15(2)

Table 3.12 Bond Angles (°)

Bonds	Angle (°)	Bonds	Angle (°)
Ge(2)-Ge(1)-Co(1)	53.30(0)	Ge(1)-Co(2)-Co(1)	56.5(1)
Ge(2)-Ge(1)-Co(2)	53.00(0)	Ge(1)-Co(2)-C(12)	87.5(3)
Ge(2)-Ge(1)-C(111)	178.7(5)	Ge(1)-Co(2)-C(21)	86.7(4)
Co(1)-Ge(1)-Co(2)	68.1(1)	Ge(1)-Co(2)-C(22)	165.3(3)
Co(1)-Ge(1)-C(111)	125.8(4)	Ge(2)-Co(2)-Ge(3)	100.5(1)
Co(1)-Ge(1)-Co(1)	69.1(1)	Ge(2)-Co(2)-Co(1)	56.4(1)
Co(2)-Ge(1)-C(111)	127.8(4)	Ge(2)-Co(2)-C(12)	86.3(3)
Co(2)-Ge(1)-Co(2)	70.4(1)	Ge(2)-Co(2)-C(21)	159.4(4)
Ge(1)-Ge(2)-Co(1)	53.10(0)	Ge(2)-Co(2)-C(22)	91.6(4)
Ge(1)-Ge(2)-Co(2)	52.50(0)	Ge(3)-Co(2)-Co(1)	143.2(1)
Ge(1)-Ge(2)-C(333)	176.5(5)	Ge(3)-Co(2)-C(12)	172.7(3)
Co(1)-Ge(2)-Co(2)	67.7(1)	Ge(3)-Co(2)-C(21)	88.1(4)
Co(1)-Ge(2)-C(333)	124.4(3)	Ge(3)-Co(2)-C(22)	95.4(4)

Table 3.12 *cont'd...*

Co(1)-Ge(2)-Co(1)	68.9(1)	Co(1)-Co(2)-C(12)	40.1(3)
Co(2)-Ge(2)-C(333)	129.9(3)	Co(1)-Co(2)-C(21)	106.1(4)
Co(2)-Ge(2)-Co(2)	69.8(1)	Co(1)-Co(2)-C(22)	111.9(3)
Co(2)-Ge(3)-Co(3)	122.3(1)	C(12)-Co(2)-C(21)	84.6(5)
Co(2)-Ge(3)-C(222)	116.9(3)	C(12)-Co(2)-C(22)	86.9(4)
Co(2)-Ge(3)-Co(2)	71.5(1)	C(21)-Co(2)-C(22)	106.3(5)
Co(3)-Ge(3)-C(222)	104.8(5)	Ge(3)-Co(3)-C(31)	90.9(5)
Ge(1)-Co(1)-Ge(2)	73.7(1)	Ge(3)-Co(3)-C(32)	81.3(5)
Ge(1)-Co(1)-Co(2)	55.4(1)	Ge(3)-Co(3)-C(33)	173.8(6)
Ge(1)-Co(1)-C(11)	84.7(4)	C(31)-Co(3)-C(32)	115.4(5)
Ge(1)-Co(1)-C(12)	106.0(4)	C(31)-Co(3)-C(33)	95.4(8)
Ge(1)-Co(1)-C(13)	151.8(5)	C(32)-Co(3)-C(33)	96.0(5)
Ge(2)-Co(1)-Co(2)	55.8(1)	C(32)-Co(3)-C(32)	126(1)
Ge(2)-Co(1)-C(11)	150.7(4)	Co(1)-C(11)-O(11)	177(1)
Ge(2)-Co(1)-C(12)	104.6(4)	Co(1)-C(12)-Co(2)	75.8(4)
Ge(2)-Co(1)-C(13)	87.1(4)	Co(1)-C(12)-O(12)	164(1)
Co(2)-Co(1)-C(11)	125.5(4)	Co(2)-C(12)-O(12)	119.8(9)
Co(2)-Co(1)-C(12)	64.1(4)	Co(1)-C(13)-O(13)	176(1)
Co(2)-Co(1)-C(13)	128.5(4)	Co(2)-C(21)-O(21)	177(1)
C(11)-Co(1)-C(12)	100.2(5)	Co(2)-C(22)-O(22)	174(1)
C(11)-Co(1)-C(13)	104.6(5)	Co(3)-C(31)-O(31)	179(1)
C(12)-Co(1)-C(13)	98.6(6)	Co(3)-C(32)-O(32)	178(2)
Ge(1)-Co(2)-Ge(2)	74.5(1)	Co(3)-C(33)-O(33)	179(2)
Ge(1)-Co(2)-Ge(3)	91.8(1)		

Dihedral angles :

Ge(3)-Co(2)-Co(2') to Co(1)-Co(1')-Co(2)-Co(2') = 171.4°

Ge(3)-Co(2)-Co(2') to Ge(2)-Co(2)-Co(2') = 132.6°

Ge(3)-Co(2)-Co(2') to Ge(1)-Co(1)-Co(2) = 133.0°

Co(1)-Co(1')-Co(2)-Co(2') to Ge(1)-Co(2)-Co(2') = 47.6°

Co(1)-Co(1')-Co(2)-Co(2') to Ge(2)-Co(2)-Co(2') = 47.8°

Co(1)-Co(1')-Co(2)-Co(2') to Ge(2)-Co(1)-Co(2) = 46.8°

Co(1)-Co(1')-Co(2)-Co(2') to Ge(1)-Co(1)-Co(2) = 46.4°

Co(1)-Co(1')-Co(2)-Co(2') to Ge(1)-Co(1)-Co(1') = 46.3°

Co(1)-Co(1')-Co(2)-Co(2') to Ge(2)-Co(1)-Co(1') = 46.9°

The molecule lies on a crystallographic mirror plane which passes through all the three Ge's, Co(3), the 3 methyl groups, C0(31) and C0(33).

The structure consists of a distorted square plane of cobalt atoms quadruply bridged on each face by μ_4 -GeMe. μ -Ge(Me)Co(CO)₄ bridges one of the Co-Co bonds. Of the ten carbonyls on the square plane of Co atoms, 8 are terminal and 2 are semi-bridging opposite cobalt-cobalt bonds.

The (MeGe)₂Co₄(CO)₁₀ unit

The different Co-Co bond lengths found in the distorted square Co₄ plane can be explained by the degree of bridging and the type of bridging groups. The longest bond is that of Co(2)-Co(2') (2.734(3)Å) which contains the μ -GeMeCo(CO)₄. This is consistent with the lengthening of a Co-Co bond when the μ -CO is replaced by a μ -Ge group, presumably to accommodate the larger μ -Ge atom [156]. This length is comparable to that in Me₂Ge₂Co₄(CO)₁₄ (2.733(2)Å) (6) [76] where the central Co-Co bond is bridged by two Ge(Me)Co(CO)₄ groups. The next longest Co-Co bond is the Co(1)-Co(1') (2.722(3)Å) which does not contain any bridging groups, while the shortest bond Co(1)-Co(2) (2.673(2)Å) contains the semi-bridging carbonyl C0(12) which is consistent with the observation of the shortening of metal-metal bonds which are bridged by a CO.

The average Ge-Co bond length in the Ge₂Co₄ unit is 2.392(3)Å while those of Ge₂Co₆(CO)₁₉ [27] and (MeGe)₂Co₄(CO)₁₁ [84] are 2.413(5)Å and 2.386(2)Å respectively. This can be explained in terms of the size of the bulky terminal Co(CO)₄ groups. Like Ge₂Co₆(CO)₁₉, the two Ge atoms in Me₃Ge₃Co₅(CO)₁₄ are inclined slightly towards the

Co(2)-Co(2') bond : (Ge(1)-Co(1) = 2.401(2)Å, Ge(1)-Co(2) = 2.372(2)Å, Ge(2)-Co(1) = 2.407(2)Å, Ge(2)-Co(2) = 2.389(2)Å ($\Delta \sim 6$ e.s.d).

The steric effect of the $\text{Co}(\text{CO})_4$ group is reflected by the dihedral angle between the plane Co(2)-Ge(3)-Co(2') and the Co_4 plane. This is skewed 8.6° towards the Co(2)-Co(2')-Ge(1) plane on the Me side of the $\mu\text{-Ge}(\text{Me})\text{Co}(\text{CO})_4$ group (as obvious in Fig 3.9).

All the terminal carbonyls in the $(\text{MeGe})_2\text{Co}_4(\text{CO})_{10}$ unit are normal and in the expected positions with the average bond lengths of Co-C 1.79(1)Å and C-O 1.14(1)Å.

A comparison of the Ge-Co and Co-Co bond lengths of various $\text{M}'_2\text{Co}_4(\text{CO})_{11}$ type clusters and related compounds such as $\text{Me}_3\text{Ge}_3\text{Co}_5(\text{CO})_{14}$ is discussed in Chapter Nine.

The $\mu\text{-Ge}(\text{Me})\text{Co}(\text{CO})_4$ unit

The $\mu\text{-Ge}(\text{Me})\text{Co}(\text{CO})_4$ group is symmetrically positioned, Ge(3)-Co(2) and Ge(3)-Co(2') = 2.339(2)Å as required by the mirror symmetry. They are significantly shorter than the Ge-Co bonds in the $(\text{MeGe})_2\text{Co}_4(\text{CO})_{10}$ unit (ave 2.392(2)Å). They are also shorter than those of $\text{GeCo}_4(\text{CO})_{14}$ (ave 2.361(3)Å) [80] and those in $\text{PhGeCo}_3(\text{CO})_{11}$ (2.375(3)Å, 2.392(3)Å) [25] (Fig 3.2.b). The Co(2)-Ge(3)-Co(2') angle of $71.5(1)^\circ$ is larger than those in $\text{Me}_2\text{Ge}_2\text{Co}_4(\text{CO})_{14}$ ($69.5(0)^\circ$), $\text{PhGeCo}_3(\text{CO})_{11}$ ($64.6(1)^\circ$) and $\text{GeCo}_4(\text{CO})_{14}$ ($66.0(1)^\circ$). This is expected due to the longer Co(2)-Co(2') bond.

The effect of the acute Co(2)-Ge(3)-Co(2') angle ($71.5(1)^\circ$) is the opening of the Co(2)-Ge(3)-Co(3) angle (122.3°) and Co(2')-Ge(3)-C_{Me} angle (116°) and the slight closing of the Co(3)-Ge(3)-C_{Me} (104.8°). This is consistent with the values for $\text{Me}_2\text{Ge}_2\text{Co}_4(\text{CO})_{14}$ (120.8° , $120.0(2)^\circ$ and $104.0(3)^\circ$ respectively), $\text{MeGeCo}_3(\text{CO})_{11}$ ($121.9(1)^\circ$,

116.4(6)° and 107.1(5)°) and $\text{PhGeCo}_3(\text{CO})_{11}$ (121.9(1)°, 117.5(3)° and 107.0(3)° respectively).

The $\text{Ge}(3)\text{--Co}(3)$ (2.440(3)Å) distance is significantly longer than those in the $(\text{MeGe})_2\text{Co}_4(\text{CO})_{10}$ unit ($\text{Ge}(1)\text{--Co}(1)$ = 2.401(2)Å, $\text{Ge}(1)\text{--Co}(2)$ = 2.372(2)Å, $\text{Ge}(2)\text{--Co}(1)$ = 2.407(2)Å, $\text{Ge}(2)\text{--Co}(2)$ = 2.389(2)Å) as expected. The $\text{Ge}(3)\text{--Co}(3)$ bond length is also longer than that in $\text{GeCo}_4(\text{CO})_{13}$ (2.35Å) [88] and $\text{Ge}_2\text{Co}_6(\text{CO})_{19}$ (2.405(4)Å). The $\text{Ge}(3)\text{--Co}(3)$ distance however is shorter when compared to those in $\text{PhGeCo}_3(\text{CO})_{11}$ (2.456(3)Å) and $\text{Me}_2\text{Ge}_2\text{Co}_4(\text{CO})_{14}$ (2.455(1)Å). Terminal $\text{Co}(\text{CO})_4$ groups attached to a Ge generally have longer Ge-Co bond. A short Ge-Co bond is possible in molecules with little steric interference from other ligand(s) as in $\text{GeCo}_4(\text{CO})_{13}$.

All the carbonyls in the $\text{Co}(\text{CO})_4$ are normal with average Co-C distance of 1.80(1)Å and C-O 1.12(1)Å.

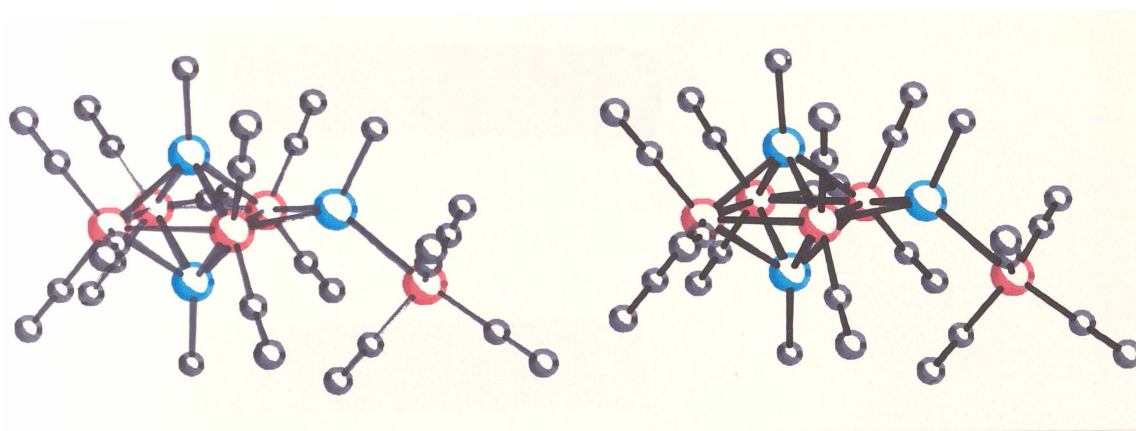


Fig 3.10 Stereo view of $\text{Me}_3\text{Ge}_3\text{Co}_5(\text{CO})_{14}$

3.6 Decarbonylation of $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ -- a preliminary study only

This short study was carried out only after the new compound $\text{Me}_3\text{Ge}_3\text{Co}_5(\text{CO})_{14}$ was synthesised. The main objective of this experiment was to determine if $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ would rearrange to $\text{Me}_3\text{Ge}_3\text{Co}_5(\text{CO})_{14}$ on heating or whether the $\text{Me}_3\text{Ge}_3\text{Co}_5(\text{CO})_{14}$ came from some other rearrangement or reaction. Due to time constraint, this reaction was not carried to completion.

3.6.1 Experimental:

$(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ (77 mg, 0.107 mmole) was loaded into a 15ml reaction tube with hexane (5ml). This was heated at 75°C for 45 days. Incondensable gas measurements were taken at suitable intervals.

3.6.2 Results:

Only three incondensable gas measurements were carried out :

Days	Total mmole
6	0.08
20	0.18
45	0.27

The average molecular weight of the incondensable gas measured on the first gas taking indicated no H_2 . But due to the large error associated with small amount of gas measured (see Chapter Two) no further attempts were made to measure the molecular weight of the incondensable gas.

The dark red solution of $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ darkened on heating. Infrared spectra (Table 3.13) of the supernatant solution taken on the 20th and 45th day of heating showed the appearance of bands corresponding to those of $\text{Me}_3\text{Ge}_3\text{Co}_5(\text{CO})_{14}$. A very dark coloured solid was observed after 45 days into the reaction. About 70mg of total solid was left.

Table 3.13 Infrared spectra of the supernatant solution of the decarbonylation of $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$

Starting material	20 th day	45 th day	$\text{Me}_3\text{Ge}_3\text{Co}_5(\text{CO})_{14}$
		2091 vw	2092 mw
	2060 vw	2060 w	2062 ms
2034 vs	2034 vs	2034 vs	
		2023 w sh	2023 ms
2016 m	2016 m	2016 vs	2016 vs
2006 mw	2006 mw	2010 ms sh	2010 ms sh
		1994 w sh	1994 w
			1980 w
1843 w, br	1834 vw, br	1834 vw, br	

Due to time constraint, the reaction was stopped at this stage and no attempt was made to separate the components.

3.7 A brief note on the Si analogue of $\text{Me}_3\text{Ge}_3\text{Co}_5(\text{CO})_{14}$

3.7.1 Reactions and workup

A reaction of MeSiH_3 with $\text{Co}_2(\text{CO})_8$ sealed by a previous worker in an ampoule dating at least two years was opened. The solution in the ampoule was deep red and dark regular diamond shaped crystals were noted. A total of 1.36 mmoles of incondensable was measured, 84% of which was H_2 , 16% CO . As the ratio and purity of the starting materials was not known it was only worked up qualitatively.

On working up, the sample was separated into two fractions : the supernatant and the crystals. The supernatant was found to be a mixture of products most remaining unidentified, while the crystals were found to be pure $\text{Me}_3\text{Si}_3\text{Co}_5(\text{CO})_{14}$ (or $[(\text{MeSi})_2\text{Co}_4(\text{CO})_{10}\{\mu_2\text{-Si}(\text{Me})\text{Co}(\text{CO})_4\}]]$) by comparison of properties with $\text{Me}_3\text{Ge}_3\text{Co}_5(\text{CO})_{14}$. The infrared spectrum and unit cell dimensions

and mass spectrum were all consistent with the formulation. The preliminary crystal data of $\text{Me}_3\text{Si}_3\text{Co}_5(\text{CO})_{14}$ is given in Table 3.14, the infrared spectrum in Table 3.15 and Fig 3.11, and the mass spectrum in Table 3.16.

A possible formation of $\text{Me}_3\text{Si}_3\text{Co}_5(\text{CO})_{14}$ is through an excess of MeSiH_3 with a mixture of $\text{Co}_2(\text{CO})_8$ and $\text{Co}_4(\text{CO})_{12}$ (assuming impure $\text{Co}_2(\text{CO})_8$). MeSiH_3 with $\text{Co}_2(\text{CO})_8$ is known to form $\text{MeSiH}_2\text{Co}(\text{CO})_4$ [51] while $\text{Co}_4(\text{CO})_{12}$ with MeSiH_3 forms pure $(\text{MeSi})_2\text{Co}_4(\text{CO})_{11}$ (Chapter Four). The reaction of these two products together could form $\text{Me}_3\text{Si}_3\text{Co}_5(\text{CO})_{14}$. All this obviously is only speculative as the reaction conditions are unknown. Unfortunately, the lack of time prevents further investigation of this reaction.

3.7.2 Characterisation of $\text{Me}_3\text{Si}_3\text{Co}_5(\text{CO})_{14}$

Preliminary crystal data:

The crystal data of $\text{Me}_3\text{Si}_3\text{Co}_5(\text{CO})_{14}$ is very similar to that of $\text{Me}_3\text{Ge}_3\text{Co}_5(\text{CO})_{14}$ and is given in Table 3.14. The molecular weight of 817 gave a calculated density of 2.02 g/ml which is expected for such Si compounds (see Chapter Eight, Section 8.2.3).

Table 3.14 Crystal data of $\text{Me}_3\text{Si}_3\text{Co}_5(\text{CO})_{14}$

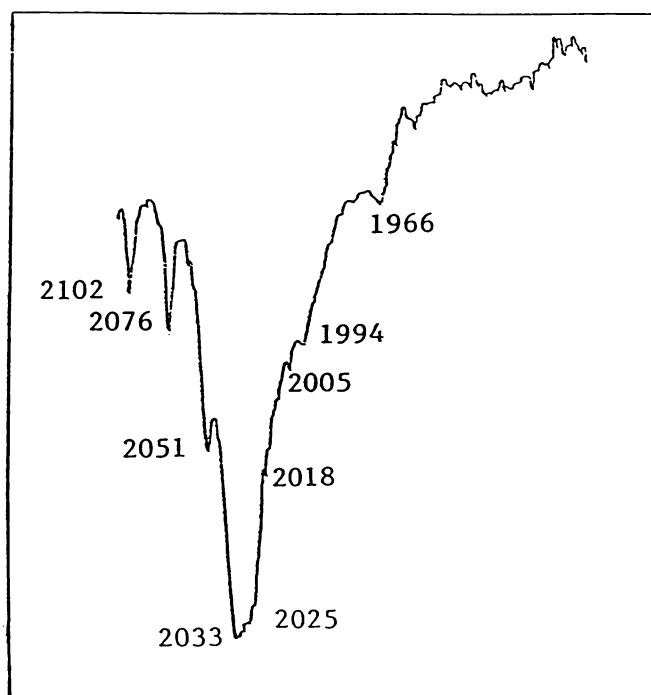
Formula : $\text{C}_{17}\text{H}_9\text{O}_{14}\text{Si}_3\text{Co}_5$
Mr = 817
Space group : Monoclinic, C2/m
$a = 12.138\text{\AA}$, $b = 12.121\text{\AA}$, $c = 18.894\text{\AA}$
$\beta = 93^\circ$
$U = 2775.95\text{\AA}^3$, $D_{\text{calc}} = 2.02 \text{ g/ml}$
$Z = 4$

Solution infrared spectrum:

The solution infrared spectrum of $\text{Me}_3\text{Si}_3\text{Co}_5(\text{CO})_{14}$ in CH_2Cl_2 (Table 3.15) showed more bands than those of $\text{Me}_3\text{Ge}_3\text{Co}_5(\text{CO})_{14}$. Nine out of the predicted fourteen bands ($8A' + 6A''$) were observed. No bridging carbonyl band was present. A discussion of the infrared spectrum of $\text{Me}_3\text{Si}_3\text{Co}_5(\text{CO})_{14}$ in comparison with $(\text{RM}')_2\text{Co}_4(\text{CO})_{11}$ type clusters is given in Chapter Nine.

Table 3.15 Infrared spectrum in CH_2Cl_2 :

Bands	Int
2102	w
2076	mw
2051	m
2033	vs
2025	vs, br
2018	m, sh
2005	mw
1994	w
1966	w

Fig 3.11 IR spectrum of $\text{Me}_3\text{Si}_3\text{Co}_5(\text{CO})_{14}$ *Mass spectrum:*

The mass spectrum of $\text{Me}_3\text{Si}_3\text{Co}_5(\text{CO})_{14}$ is given in Table 3.16. The highest envelope in the mass spectrum of $\text{Me}_3\text{Si}_3\text{Co}_5(\text{CO})_{14}$ was very weak, with a m/e value of 807 which is 10 units lower than that of the parent ion peak (817) (see Chapter Two). A subsequent loss of 14 CO's from m/e 807 was observed. Methyl loss was observed after the loss of almost all the CO's.

Table 3.16 Mass spectrum of $\text{Me}_3\text{Si}_3\text{Co}_5(\text{CO})_{14}$

m/e	Int	Possible assignments
807	vw	$[\text{P}]^+?$
759-760	w	$[\text{P-CO}]^+$
732-733	m	$[\text{P-2CO}]^+$
704	w	$[\text{P-3CO}]^+$
676-677	m	$[\text{P-4CO}]^+$
645-650	vs	$[\text{P-5CO}]^+$
618-622	vs	$[\text{P-6CO}]^+$
589-592	vs	$[\text{P-7CO}]^+$
560-564	s	$[\text{P-8CO}]^+$
532-536	ms	$[\text{P-9CO}]^+$
504-506	ms	$[\text{P-10CO}]^+$
476-478	s	$[\text{P-11CO}]^+$
447-452	m	$[\text{P-12CO}]^+$
420-425	ms	$[\text{P-13CO}]^+$
402-406	vs	$[\text{P-13CO-Me}]^+$
390-393	mw	$[\text{P-14CO}]^+$
379-381	w	$[\text{P-14CO-Me}]^+$
351-357	w	$[\text{P-14CO-3Me}]^+$ or $[\text{P-14CO-Me-Si}]^+$
320-321	w	$[\text{P-14CO-3Me-Si}]^+$

3.8 Discussion :

Reaction of $\text{Me}_2\text{Ge}_2\text{Co}_4(\text{CO})_{14}$ on heating

Prior to this work, $\text{Me}_2\text{Ge}_2\text{Co}_4(\text{CO})_{14}$ was heated in hexane in an open tube reaction at $\sim 45^\circ\text{C}$ to yield predominantly $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ [144]. An uncharacterised minor product was reported whose IR spectrum was similar to that of $\text{Me}_3\text{Ge}_3\text{Co}_5(\text{CO})_{14}$ as characterised in this study. Preliminary precession photographic studies on some of the crystals confirmed these products were the same.

In Section 3.5.1, impure $\text{Me}_2\text{Ge}_2\text{Co}_4(\text{CO})_{14}$ was initially heated at 55°C and 3 moles equivalent of CO and a small amount of H_2 were released after 26 days of reaction. As incondensable gas continued to

evolve, the reaction was allowed to proceed. When the temperature was raised to 75°C, the amount of gas evolved did not increase significantly. The reaction was then stopped. The total gas evolution was 3.3 moles per mole of starting material.

When the solids were examined, the major product was the new compound shown to be $\text{Me}_3\text{Ge}_3\text{Co}_5(\text{CO})_{14}$ together with a small amount of $(\text{Me}_2\text{Ge})_2\text{Co}_4(\text{CO})_{11}$. This novel product, $\text{Me}_3\text{Ge}_3\text{Co}_5(\text{CO})_{14}$, is the first example of an extended skeleton built on a closed germanium-cobalt cluster.

Analysis of the incondensable gas evolved showed that the first 14 days (Stage 1) of heating produced the bulk of the gas. Very close to 3CO per mole of $\text{Me}_2\text{Ge}_2\text{Co}_4(\text{CO})_{14}$ was obtained, as expected from equation 3.3.

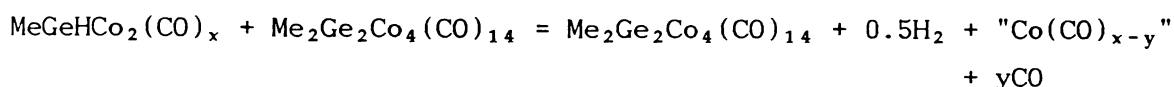
However, the average molecular weight of the incondensable gas evolved in the 14 to 81 day period (Stage 2) was found to be lower than the initial 14 day period. This may be attributed to the release of H_2 from $\text{MeGeHCo}_2(\text{CO})_x$ (see Table 3.2) or even $\text{MeGeH}_2\text{Co}(\text{CO})_4$ (2004 cm^{-1} species ?). These compounds could have attacked $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ formed in Stage 1 to form $\text{Me}_3\text{Ge}_3\text{Co}_5(\text{CO})_{14}$ (see analogous reactions in equations 3.4 to 3.6 below). If this was in fact true and the hydrogen figures in Table 3.6 were correct, then the amount of $\text{MeGeHCo}_2(\text{CO})_x$ (or/and $\text{MeGeH}_2\text{Co}(\text{CO})_4$) formed was higher than earlier interpreted in Run 3. The reaction may be analysed by the following steps :

(1) The H_2 evolution of 0.24 mmol, suggests 0.43 to 0.53 mmol of $\text{MeGeHCo}_2(\text{CO})_x$ was present in the mixture (assuming 10% error in the incondensable gas measurement). This accounts for 180–220 mg of the mixture. Thus the $\text{Me}_2\text{Ge}_2\text{Co}_4(\text{CO})_{14}$ content was approximately 0.55 to 0.60 mmol.

(2) The formation of ~ 0.05 mmol of $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ by equation 3.3 requires 0.05 mmol of $\text{Me}_2\text{Ge}_2\text{Co}_4(\text{CO})_{14}$.

(3) The remaining 0.5 to 0.55 mmol $\text{Me}_2\text{Ge}_2\text{Co}_4(\text{CO})_{14}$ was available to form $\text{Me}_3\text{Ge}_3\text{Co}_5(\text{CO})_{14}$ (estimated to be 0.45 mmol which matches well with the above figures).

(4) Thus it was tempting to interpret the approximate 1 : 1 : 1 ratio of $\text{Me}_2\text{Ge}_2\text{Co}_4(\text{CO})_{14}$: $\text{MeGeHCo}_2(\text{CO})_x$: $\text{Me}_3\text{Ge}_3\text{Co}_5(\text{CO})_{14}$ as implying that $\text{MeGeHCo}_2(\text{CO})_x$ was the source of the added $\text{MeGeCo}(\text{CO})_4$ unit :



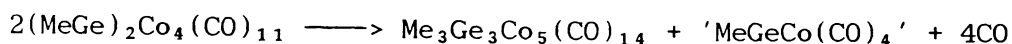
If the undefined cobalt carbonyl species was the black residue, its weight should be less than that of $\text{MeGeHCo}_2(\text{CO})_x$, and this was observed. The number of CO evolved, less that in (2) and divided by the number of moles of $\text{MeGeHCo}_2(\text{CO})_x$ gives the value of y as ~ 6 , indicating this as a reasonable value ($x = 7$ or 8).

It should be emphasised that, although these figures seem to fit quite well, there are significant experimental uncertainties, especially in the hydrogen determination and hence in the number derived from this.

(5) The pattern of CO evolution in Table 3.6 and Fig 3.2 indicated that most of the CO was evolved before the H_2 formation started. This suggests that the first step was decarbonylation of $\text{Me}_2\text{Ge}_2\text{Co}_4(\text{CO})_{14}$, and its transformation into $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ by equation 3.3 is already established. Although time was short, it was felt that the decarbonylation of $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ was worth a brief examination as a comparison.

The preliminary study on the decarbonylation of $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ at 75°C in Section 3.6 however showed that $\text{Me}_3\text{Ge}_3\text{Co}_5(\text{CO})_{14}$ was in fact

formed, but very slowly (compared to the decarbonylation of impure $\text{Me}_2\text{Ge}_2\text{Co}_4(\text{CO})_{14}$). 2.5 mole CO per mole of $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ was evolved. The following reaction may have occurred :



but this only accounts for 2 moles CO per mole $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$. Decomposition of some of the 'MeGeCo(CO)₄' fragments may made up for the remaining 0.5 mole CO per mole $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ observed. The other 'MeGeCo(CO)₄' fragment then replaced the bridging CO in $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ to form $\text{Me}_3\text{Ge}_3\text{Co}_5(\text{CO})_{14}$ -- compare with the above suggestion that the required 'MeGeCo(CO)₄' unit may have derived from $\text{MeGeHCo}_2(\text{CO})_x$ as discussed in the five steps described above.

The findings in Section 3.6 indicate that in the absence of $\text{MeGeHCo}_2(\text{CO})_x$, $\text{Me}_3\text{Ge}_3\text{Co}_5(\text{CO})_{14}$ may still be formed from $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ if the time and/or temperature were sufficient. The reaction in Stage 3 in Section 3.5 might be similar to that described in equation 3.4 with a slow release of CO.

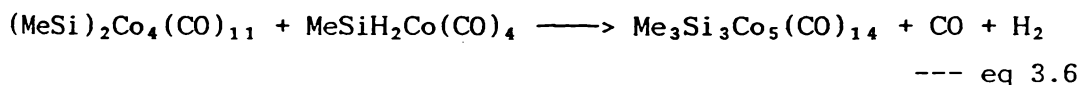
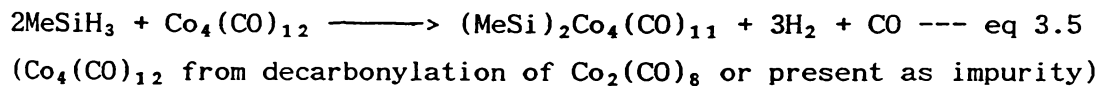
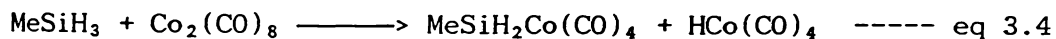
Another reaction route that could have lead to the formation of $\text{Me}_3\text{Ge}_3\text{Co}_5(\text{CO})_{14}$ may be the breaking up of $\text{MeGeCo}_3(\text{CO})_{11}$ to provide MeGeCo(CO)_4 unit which reacted with $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$. As $\text{MeGeCo}_3(\text{CO})_{11}$ was present in a very small quantity (IR spectrum Table 3.2), this route is not expected to contribute much to the formation of $\text{Me}_3\text{Ge}_3\text{Co}_5(\text{CO})_{14}$.

Products other than $\text{Me}_3\text{Ge}_3\text{Co}_5(\text{CO})_{14}$ and $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ could not be determined. Beside the black residue, one other possible product is $\text{MeGeCo}_3(\text{CO})_9$. This could be a product from the breaking up of $\text{Me}_2\text{Ge}_2\text{Co}_4(\text{CO})_{14}$ or $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ to produce a MeGeCo(CO)_4 unit. The high temperature of 75°C would also have forced any $\text{MeGeCo}_3(\text{CO})_{11}$ into

$\text{MeGeCo}_3(\text{CO})_9$. The infrared spectrum of the unidentified compounds does show some indication of $\text{MeGeCo}_3(\text{CO})_9$.

The MeSiH_3 and $\text{Co}_2(\text{CO})_8$ reaction

The formation of $\text{Me}_3\text{Si}_3\text{Co}_5(\text{CO})_{14}$ from the long term reaction of MeSiH_3 with $\text{Co}_2(\text{CO})_8$ may present another possible route to the formation of such compounds. The unknown reactant ratio prevented the reaction being examined quantitatively. A possible route to its formation could be through the coupling of $\text{MeSiH}_2\text{Co}(\text{CO})_4$ and $(\text{MeSi})_2\text{Co}_4(\text{CO})_{11}$ (parallel to the $\text{MeGeH}_2\text{Co}(\text{CO})_4$ attack on $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ to form $\text{Me}_3\text{Ge}_3\text{Co}_5(\text{CO})_{14}$ as mentioned above).



Alternatively, excess MeSiH_3 may react with $(\text{MeSi})_2\text{Co}_4(\text{CO})_{11}$ to form a ' $(\text{MeSi})_2\text{Co}_4(\text{CO})_{10}(\mu_2\text{-Si}(\text{Me})\text{H})$ ' species. Replacement of the hydrogen site by a $\text{Co}(\text{CO})_4$ group provided by unreacted $\text{Co}_2(\text{CO})_8$ or $\text{HCo}(\text{CO})_4$ would result in $\text{Me}_3\text{Si}_3\text{Co}_5(\text{CO})_{14}$.

It should be stressed that the formation of $\text{Me}_3\text{Ge}_3\text{Co}_5(\text{CO})_{14}$ from $\text{Me}_2\text{Ge}_2\text{Co}_4(\text{CO})_{14}$ and $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ requires further investigation as does the reaction of MeSiH_3 and $\text{Co}_2(\text{CO})_8$: e.g. repeat the decarbonylation reaction of 3.4.1 using pure $\text{Me}_2\text{Ge}_2\text{Co}_4(\text{CO})_{14}$, and taking infrared spectra at intervals. Decarbonylation of $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ and $\text{Me}_2\text{Ge}_2\text{Co}_4(\text{CO})_{14}$ at various temperatures will also provide a better understanding of the reactions. However, no method of

getting suitable quantities of completely pure $\text{Me}_2\text{Ge}_2\text{Co}_4(\text{CO})_{14}$ is yet available.

3.9 Characterisation of $\text{MeGeCo}_3(\text{CO})_{11}$

3.9.1 Crystal structure of $\text{MeGeCo}_3(\text{CO})_{11}$

It was decided in the later part of this work that the crystal structure of $\text{MeGeCo}_3(\text{CO})_{11}$ would be useful for comparison with some of the more complex structures determined in this thesis.

Experimental :

A pure hexane solution of $\text{MeGeCo}_3(\text{CO})_{11}$ (from Section 3.2.1 Run 1) was concentrated and placed in the freezer overnight. Orange diamond plates and some needles were obtained. Most of them were twinned. A single needle shaped crystal was found and mounted with Araldite for preliminary investigation.

Preliminary study and data collection :

Preliminary precession photographs using Ni filtered $\text{Cu-K}\alpha$ X-radiation indicated the crystal was triclinic. As $Z = 2$, the space group was assumed as $P\bar{1}$ which was confirmed by the successful solution of the structure.

The refined lattice parameters and intensity data were collected at the University of Canterbury using a Nicolet XRD P3 four-circle automatic diffractometer. A thin plate shaped crystal of size 1mm x 0.8mm x 0.16mm was used in the data collection. The cell parameters were calculated using $\text{Mo-K}\alpha$ X-rays from 25 high angle reflections. The crystal data is given in Table 3.17.

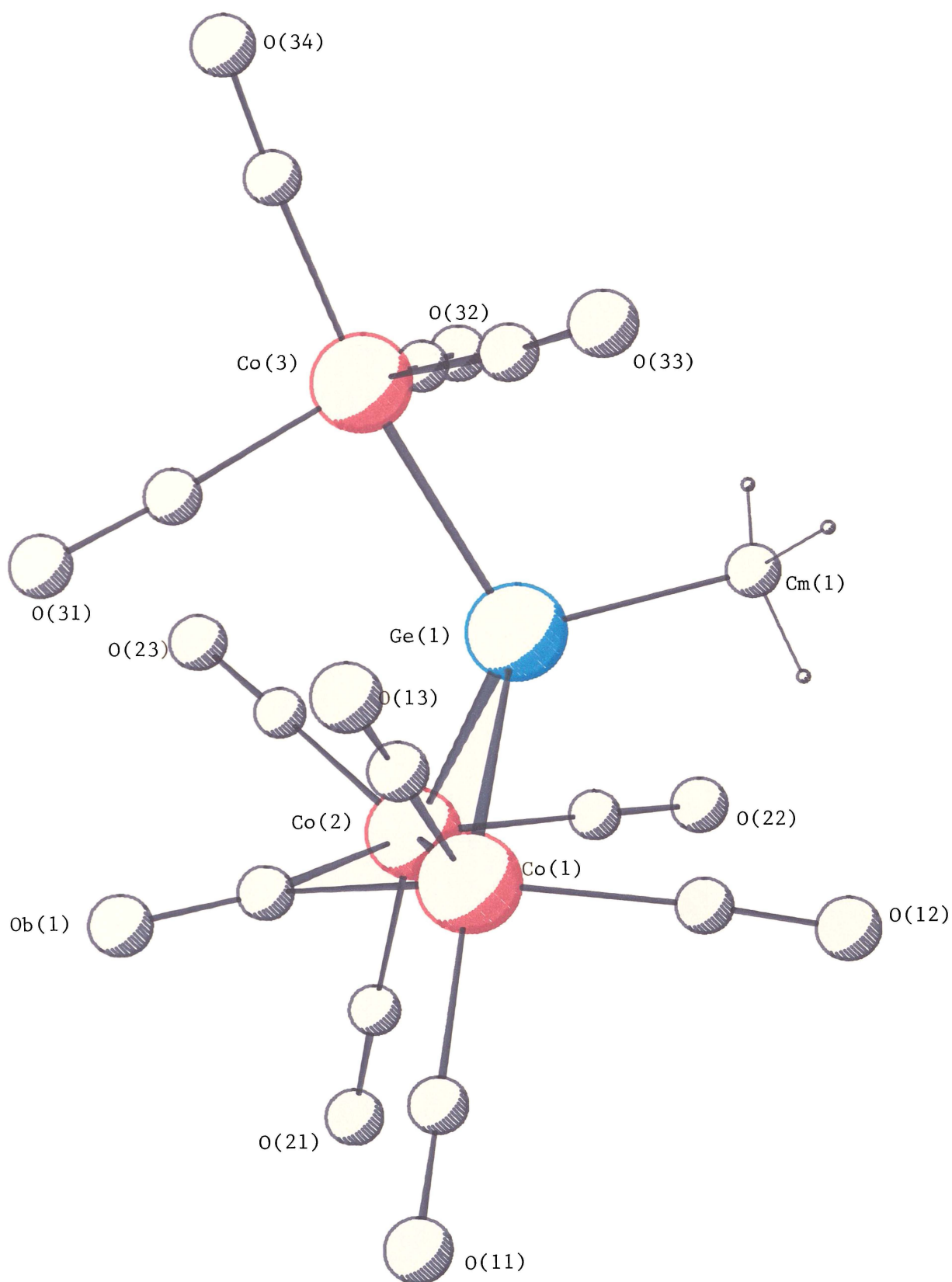
Table 3.17 Crystal data of $\text{MeGeCo}_3(\text{CO})_{11}$

Formula $\text{C}_{12}\text{H}_3\text{O}_{11}\text{Ge}_1\text{Co}_3$
 Mr = 572.54
 Triclinic, space group $P\bar{1}$
 A = 8.626(6)Å, B = 8.656(5)Å, C = 13.381(9)Å,
 $\alpha = 88.25(5)^\circ$, $\beta = 84.72(5)^\circ$, $\gamma = 66.26(4)^\circ$
 Unit cell volume = 910.7Å³
 Density = 2.09g/cm³
 Z = 2
 F(000) = 552, $\mu(\text{MoK}\alpha) = 43.5\text{cm}^{-1}$, T = 173K

A total of 2171 unique reflexions in the range of $4^\circ \leq 2\theta \leq 45^\circ$ were collected. 1614 reflexions had $F^2 > 3\sigma(F^2)$ and these were used for all calculations. The data were corrected for Lorentz and polarisation effects. The data was also corrected with a very large linear absorption corection factor using an empirical method (transmission factors 0.962 maximum, 0.047 minimum). This large absorption correction was needed because the crystal used for the data collection was a very thin plate.

Solution and refinement :

The metal atoms were located using the TREF routine of SHELXS86. The coordinates of the heavy metal atoms were used in SHELX76 program and subsequent refinement and difference maps located all 11 CO's and the methyl carbon. In the final cycles of full-matrix least-squares refinement, all atoms were assigned anisotropic temperature factors, with the hydrogens placed in calculated positions using the AFIX routine of SHELX76. The final refinement converged with $R = 0.0649$, $R_w = 0.0636$ where $w = 1.137/(\sigma^2 F + 0.001 F^2)$.

Fig 3.12 Crystal structure of $\text{MeGeCo}_3(\text{CO})_{11}$ 

A final difference map shows a small amount of residual electron density of about 1.49 eÅ^{-3} close to the Ge atom, but otherwise no more than 1.1 residual eÅ^{-3} was achieved which was considered acceptable in view of the large absorption correction involved. No non-hydrogen parameter shifted by more than 0.1 times its standard deviation in the final cycle.

Discussion of structure :

The bond lengths and bond angles of $\text{MeGeCo}_3(\text{CO})_{11}$ are presented in Tables 3.18 and 3.19, and the views of the molecule are presented in Figs 3.12 and 3.13.

Table 3.18 Bond Lengths (Å) for $\text{MeGeCo}_3(\text{CO})_{11}$

Ge(1) ---Co(1)	2.378(2)	Co(3) ---C(32)	1.76(2)
Ge(1) ---Co(2)	2.373(2)	Co(3) ---C(33)	1.78(2)
Ge(1) ---Co(3)	2.421(2)	Co(3) ---C(34)	1.82(2)
Ge(1) ---Cm(1)	2.00(1)	C(12) ---O(12)	1.13(2)
Co(1) ---Co(2)	2.582(3)	C(13) ---O(13)	1.16(2)
Co(1) ---C(11)	1.82(2)	C(21) ---O(21)	1.13(2)
Co(1) ---C(12)	1.82(2)	C(22) ---O(22)	1.15(2)
Co(1) ---C(13)	1.76(2)	C(23) ---O(23)	1.14(2)
Co(1) ---Cb(1)	1.93(2)	Cb(1) ---Ob(1)	1.16(2)
Co(2) ---C(21)	1.80(1)	C(31) ---O(31)	1.18(2)
Co(2) ---C(22)	1.80(2)	C(32) ---O(32)	1.14(2)
Co(2) ---C(23)	1.79(2)	C(33) ---O(33)	1.13(2)
Co(2) ---Cb(1)	1.97(2)	O(34) ---C(34)	1.12(2)
Co(3) ---C(31)	1.77(2)		

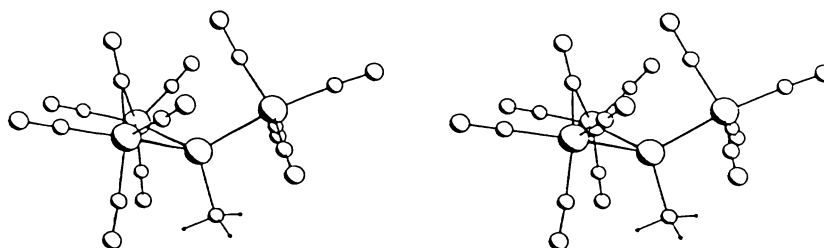


Fig 3.13 Stereo View of $\text{MeGeCo}_3(\text{CO})_{11}$

Table 3.19 Bond Angles (°) of $\text{MeGeCo}_3(\text{CO})_{11}$

Co(1)-Ge(1)-Co(2)	65.8(1)	Co(1)-Co(2)-Cb(1)	47.8(5)
Co(1)-Ge(1)-Co(3)	123.1(1)	C(21)-Co(2)-C(22)	94.1(7)
Co(1)-Ge(1)-Cm(1)	116.5(6)	C(21)-Co(2)-C(23)	102.8(7)
Co(2)-Ge(1)-Co(3)	121.9(1)	C(21)-Co(2)-Cb(1)	88.2(6)
Co(2)-Ge(1)-Cm(1)	118.2(5)	C(22)-Co(2)-C(23)	109.0(7)
Co(3)-Ge(1)-Cm(1)	107.0(5)	C(22)-Co(2)-Cb(1)	154.4(7)
Ge(1)-Co(1)-Co(2)	57.0(1)	C(23)-Co(2)-Cb(1)	95.3(7)
Ge(1)-Co(1)-C(11)	168.6(4)	Ge(1)-Co(3)-C(31)	89.9(5)
Ge(1)-Co(1)-C(12)	85.1(4)	Ge(1)-Co(3)-C(32)	82.2(5)
Ge(1)-Co(1)-C(13)	89.9(4)	Ge(1)-Co(3)-C(33)	81.5(4)
Ge(1)-Co(1)-Cb(1)	87.2(5)	Ge(1)-Co(3)-C(34)	171.5(5)
Co(2)-Co(1)-C(11)	112.6(4)	C(31)-Co(3)-C(32)	117.6(7)
Co(2)-Co(1)-C(12)	100.2(5)	C(31)-Co(3)-C(33)	116.0(7)
Co(2)-Co(1)-C(13)	132.4(5)	C(31)-Co(3)-C(34)	98.6(7)
Co(2)-Co(1)-Cb(1)	49.1(5)	C(32)-Co(3)-C(33)	123.5(8)
C(11)-Co(1)-C(12)	92.9(6)	C(32)-Co(3)-C(34)	93.0(7)
C(11)-Co(1)-C(13)	101.2(6)	C(33)-Co(3)-C(34)	95.5(7)
C(11)-Co(1)-Cb(1)	88.3(6)	Co(1)-C(12)-O(12)	176(1)
C(12)-Co(1)-C(13)	110.8(6)	Co(1)-C(13)-O(13)	176(1)
C(12)-Co(1)-Cb(1)	146.1(6)	Co(2)-C(21)-O(21)	178(2)
C(13)-Co(1)-Cb(1)	102.1(7)	Co(2)-C(22)-O(22)	175(1)
Ge(1)-Co(2)-Co(1)	57.2(1)	Co(2)-C(23)-O(23)	178(1)
Ge(1)-Co(2)-C(21)	162.8(5)	Co(1)-Cb(1)-Co(2)	83.1(7)
Ge(1)-Co(2)-C(22)	83.8(4)	Co(1)-Cb(1)-Ob(1)	138(1)
Ge(1)-Co(2)-C(23)	94.1(5)	Co(2)-Cb(1)-Ob(1)	138(1)
Ge(1)-Co(2)-Cb(1)	86.5(4)	Co(3)-C(31)-O(31)	176(1)
Co(1)-Co(2)-C(21)	107.9(5)	Co(3)-C(32)-O(32)	178(2)
Co(1)-Co(2)-C(22)	107.8(5)	Co(3)-C(33)-O(33)	175(1)
Co(1)-Co(2)-C(23)	129.5(5)	Co(3)-C(34)-O(34)	176(2)

The crystal structure of the Ph analogue of $\text{MeGeCo}_3(\text{CO})_{11}$, $\text{PhGeCo}_3(\text{CO})_{11}$ was carried out by Graham *et al* in 1970 [25]. Like $\text{PhGeCo}_3(\text{CO})_{11}$, $\text{MeGeCo}_3(\text{CO})_{11}$ may be considered as a derivative of $\text{Co}_2(\text{CO})_8$ where one of the $\mu\text{-CO}$'s was replaced by a $\mu\text{-Ge(Me)Co(CO)}_4$

group. The two molecules are similar in that the μ -CO in both structures lies on the $\text{Co}(\text{CO})_4$ side of the Ge-Co(1)-Co(2) plane. This is unexpected, as the μ -CO might have been expected to be on the same side as the Me group which is sterically less bulky.

Co-Co bonds

The Co(1)-Co(2) bond (2.581(3)Å) is significantly longer than those of $\text{Co}_2(\text{CO})_8$ (2.529(1)Å) and $\text{PhGeCo}_3(\text{CO})_{11}$ (2.546(3)Å), but shorter than those in $\text{Me}_2\text{Ge}_2\text{Co}_4(\text{CO})_{14}$ (2.733(2)Å) (6) and $\text{Me}_3\text{Ge}_3\text{Co}_5(\text{CO})_{14}$ (2.734(3)Å). The long Co-Co distances in the latter two compounds are due to the replacement of both the μ -CO's by μ -M' units [156].

Ge-Co

Like the two Ge-Co bond distances (2.397(1)Å), 2.397(1)Å of the GeCo_2 triangles in $\text{Me}_2\text{Ge}_2\text{Co}_4(\text{CO})_{14}$, the two Ge-Co bond distances (2.378(2)Å, 2.373(2)Å) in $\text{MeGeCo}_3(\text{CO})_{11}$ are almost equal. Those in $\text{PhGeCo}_3(\text{CO})_{11}$ however show considerable asymmetry : 2.375(3)Å, 2.392(3)Å.

The Ge-Co(3) bond length (2.421(2)Å) is longer than the bridged Ge-Co distances as expected and this length is significantly longer than that in $\text{GeCo}_4(\text{CO})_{13}$ (2.349(1)Å [88], but shorter than those in $\text{PhGeCo}_3(\text{CO})_{11}$ (2.456(3)Å), $\text{Me}_2\text{Ge}_2\text{Co}_4(\text{CO})_{14}$ (2.455(1)Å) and $\text{Me}_3\text{Ge}_3\text{Co}_5(\text{CO})_{14}$ (2.440(3)Å).

CO groups

The terminal carbonyls of the $\text{Co}_2(\text{CO})_6$ and $\text{Co}(\text{CO})_4$ units are normal and in the expected positions. Average Co-C and C-O distances in the $\text{Co}_2(\text{CO})_6$ unit are 1.80(2)Å and 1.14(2)Å respectively, and those in the $\text{Co}(\text{CO})_4$ unit are 1.78(2)Å and 1.14(2)Å respectively.

The bridging CO in $\text{MeGeCo}_3(\text{CO})_{11}$ is slightly asymmetric with Co-C bonds of 1.928(2)Å and 1.966(2)Å and a C-O distance of 1.16(2)Å, all of which are normal for such bonds [25,78,80]

Ge-C

The Ge-C(M) bond distance of 2.00(1)Å is comparable to that in $\text{Me}_2\text{Ge}_2\text{Co}_4(\text{CO})_{14}$ (1.978(7)Å) but appears to be at the longer end of a normal σ bond (Ge-C in Me_4Ge = 1.95Å [11]). It is slightly longer than that in $\text{Me}_3\text{Ge}_3\text{Co}_5(\text{CO})_{14}$ (Ge(3)-C(222) = 1.95(1)Å).

Dihedral angle

The dihedral angle between the Ge-Co(1)-Co(2) plane and the μ -CO-Co(1)-Co(2) plane in $\text{MeGeCo}_3(\text{CO})_{11}$ ($119.5(2)^\circ$) is as expected. It is large compared to that in $\text{PhGeCo}_3(\text{CO})_{11}$ (95°). The large dihedral angle is possible in $\text{MeGeCo}_3(\text{CO})_{11}$ as the methyl group is sterically less demanding compared to the phenyl group (a bulky group which tends to 'push' the μ -CO group toward the $\text{Co}(\text{CO})_4$ group, thus reducing the dihedral angle). The dihedral angle between the two Ge-Co(1)-Co(2) planes in $\text{Me}_2\text{Ge}_2\text{Co}_4(\text{CO})_{14}$ is 113.09° , indicating a small change in the dihedral angle (from 119.5°) with the replacement of the μ -CO (in $\text{MeGeCo}_3(\text{CO})_{11}$) by the more bulky bridging $\text{Ge}(\text{Me})\text{Co}(\text{CO})_4$ unit in $\text{Me}_2\text{Ge}_2\text{Co}_4(\text{CO})_{14}$.

3.9.2 Spectroscopic characterisation of $\text{MeGeCo}_3(\text{CO})_{11}$

This has been carried out by a number of workers including G.Schmid, B.G.Graham and R.Gerlach [6,20,70,71]. The aim of this small section is to summarise very briefly all available data obtained to-date for the convenience of further workers.

*Infrared spectrum :*Table 3.20 Infrared spectrum of $\text{MeGeCo}_3(\text{CO})_{11}$

This work hex/ CH_2Cl_2 [71] in cyclohexane	
2103 m	2105 m
2079 s	2082 s
2054 s	2056 s
2029 s	2030 s
2017 m	2020/5 m
2011 mw sh	2007 w sh
1994 w sh	1998 w sh
1847 m	1850 m
1835 w	1833 w

Mass spectrum :

The mass spectrum of $\text{MeGeCo}_3(\text{CO})_{11}$ [71] showed a consecutive loss of eleven CO's from the parent ion. Me loss was observed after the loss of all CO's.

NMR spectrum :

The ^1H NMR spectrum (27°C) of $\text{MeGeCo}_3(\text{CO})_{11}$ shows only a singlet at δ 1.95 ppm (Table 3.21) indicating a single Me proton environment despite two isomers indicated in the solution infrared spectra (1847 and 1835 cm^{-1}) (see Table 3.20 above and [25]).

Table 3.21 NMR data of $\text{MeGeCo}_3(\text{CO})_{11}$ (in δ ppm)

	This work	[20,70]
^1H NMR	1.95 (27°C, CDCl_3)	1.93 (-20°C, SiCl_4)
^{13}C NMR	203.5, 195.4 (-40°C) ~ 2x : 1x (CDCl_3)	

The ^{13}C NMR spectrum was obtained from a ^{13}C enriched sample. The two singlets obtained were in the approximate intensity ratio of

2:1. The δ 203.5 ppm singlet is assigned as that of the six terminal and the bridging CO's of the $\text{Co}_2(\text{CO})_7$ unit while the δ 195.4 singlet due to those in the $\text{Co}(\text{CO})_4$ unit. Like the ^{13}C NMR of $\text{M}'\text{Co}_4(\text{CO})_{14}$ ($\text{M}' = \text{Si}, \text{Ge}$) in Appendix 2, no differentiation of the bridging CO from the six terminal CO's is observed.

CHAPTER FOUR

The Reaction of $\text{Co}_4(\text{CO})_{12}$ with $\text{MeM}'\text{H}_3$ and $\text{Me}_2\text{M}'\text{H}_2$, $\text{M}' = \text{Ge}, \text{Si}$

---- a preliminary study

4.1 Introduction

The studies reported in Chapter Five did not confirm the original proposal by Foster [84] that $(\text{MeGeH})\text{GeCo}_4(\text{CO})_{13}$, formed from the reaction of MeGeH_3 with $\text{GeCo}_4(\text{CO})_{14}$ (see Chapter One), condensed to the *closo*-hexanuclear cluster $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ (*1a*). However, the observation of small yields of $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ in the experiments reported in Chapter Three where $\text{Co}_4(\text{CO})_{12}$ was also present in the product mixture, suggested that the reaction of MeGeH_3 with $\text{Co}_4(\text{CO})_{12}$ might have been the source of the $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ found in [84]. The work reported in this Chapter was undertaken to examine this possibility, and to explore the reactivity of $\text{Co}_4(\text{CO})_{12}$ with other Group IVB hydrides such as MeSiH_3 , Me_2GeH_2 and Me_2SiH_2 .

Both sealed tube and open tube reactions of $\text{MeM}'\text{H}_3$ and $\text{Me}_2\text{M}'\text{H}_2$ with $\text{Co}_4(\text{CO})_{12}$ were carried out ($\text{M}' = \text{Si}, \text{Ge}$).

4.2 Reaction of MeGeH_3 with $\text{Co}_4(\text{CO})_{12}$

4.2.1 Experimental

Run 1 ($\text{MeGeH}_3 : \text{Co}_4(\text{CO})_{12} = 2.2 : 1$)

$\text{Co}_4(\text{CO})_{12}$ (0.255g, 0.445 mmol) was loaded into a 50 ml ampoule at the Schlenk line. Hexane (10 ml) was added. The ampoule was transferred to the vacuum line where it was degassed and the contents frozen down by liquid nitrogen. MeGeH_3 (0.962 mmoles) was condensed in

and the ampoule sealed under vacuum. The reaction was allowed to proceed in the dark at room temperature for 4 months.

4.2.2 Results and workup

About 2 months into the reaction, red, square, platelike crystals were observed to have formed along with black rhombohedral crystals. After about 4 months, the reaction mixture consisted of a dark reddish brown supernatant solution and lots of dark crystals, some of which looked red under light.

The reaction was stopped and worked up. The incondensable gases were measured. The total incondensable gas was 1.06 mmol of which 79% was H_2 , and 21% CO .

The volatile phase (and some solvent) was removed, the infrared spectrum indicated unreacted $MeGeH_3$ and hexane. Due to the difficulty in separating $MeGeH_3$ from hexane, the amount of unreacted $MeGeH_3$ was not measured (but see Section 4.2.3).

The remaining hexane supernatant solution (less than 2 ml) was separated from the solid. The infrared spectrum of this fraction showed unreacted $Co_4(CO)_{12}$ (IR bands at 2065(vs), 2054(vs), 1865(mw) [142]). A weak band at 2035 cm^{-1} was also observed which corresponds to the strongest band of $(MeGe)_2Co_4(CO)_{11}$ [84].

The solid fraction was washed several times with hexane (3-4 ml each time). These washings showed predominantly $Co_4(CO)_{12}$ (by IR) and were added to the supernatant solution. The remaining red solid was dissolved in CH_2Cl_2 and the infrared spectrum showed bands due to $Co_4(CO)_{12}$ and $(MeGe)_2Co_4(CO)_{11}$ [84].

On recrystallisation from CH_2Cl_2 /hexane, red square plates were obtained which IR showed to be pure $(MeGe)_2Co_4(CO)_{11}$. Preliminary X-ray crystallographic studies confirmed this as the unit cell dimensions and space group were identical to those reported. Though

$(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ has been characterized previously [18,84], an improved mass spectrum and infrared spectrum, plus NMR data are given in Section 4.4.

4.2.3 Incondensable gas measurement and unreacted MeGeH_3

The amount of MeGeH_3 used in the reaction could be estimated quantitatively from the hydrogen measurement in the incondensable gas (using equation 4.1 in Discussion). Thus, 0.84 mmol of H_2 in the incondensable gas measured came from the reaction of 0.56 mmol of MeGeH_3 (therefore 0.4 mmol of MeGeH_3 remained unreacted) and of 0.28 mmole of $\text{Co}_4(\text{CO})_{12}$. This should yield 0.28 mmol of $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ (63% yield) and 0.28 mmol of CO. These quantities compare well with those observed of 0.22 mmol of CO and 0.29 mmole of $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ (plus those inseparable from the $\text{Co}_4(\text{CO})_{12}$). As all the H_2 was accounted for in the reaction, it could be assumed that there was little or no hydrogen in the form of $\text{HCo}(\text{CO})_4$.

In Runs 2 and 4, where all the $\text{Co}_4(\text{CO})_{12}$ reacted, the agreement between the yield obtained from the weighing of the product and that calculated from the incondensable gas measurement was good. Hence the amount of MeGeH_3 used in the reaction could be estimated from the incondensable gas measurement.

Yield of Run 1 :

Weight of pure $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ = 0.188g = 0.292 mmol = 59%

Weight of $\text{Co}_4(\text{CO})_{12}$ (contaminated with $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$) = 0.123g

From incondensable gas measurement = 63%

Note : all yields in this Chapter are based on $\text{Co}_4(\text{CO})_{12}$

Material balance :

Input	Output
$\text{Co}_4(\text{CO})_{12} = 0.255\text{g}$	$(\text{MeGe})_2\text{Co}_4(\text{CO})_{11} = 0.188\text{g}$
$\text{MeGeH}_3 = 0.051\text{g}$	$\text{Co}_4(\text{CO})_{12} \text{ (impure)} = 0.123\text{g}$
	$\text{CO} = 0.006\text{g}$
	$\text{H}_2 = 0.002\text{g}$
Total = 0.306g	Total = 0.319g

4.2.4 Other runs

Three other runs were carried out. Details of the reactant ratio of all four runs are given in Table 4.1 and a brief discussion of the results of each run is given. Workup procedures for each run were the same as Run 1, except Run 4 where the incondensable gases were measured intermittently as the reaction proceeded. Run 3 was carried out at 30°C (oil bath).

Table 4.1 Experimental conditions of the reaction of MeGeH_3 and $\text{Co}_4(\text{CO})_{12}$

Conditions / Run	1	2	3	4
$\text{Co}_4(\text{CO})_{12}$ (g)	0.2545	0.015	0.012	0.0234
(mmol)	0.445	0.026	0.021	0.041
MeGeH_3 (mmol)	0.962	0.152	0.084	0.141
$\text{MeGeH}_3 : \text{Co}_4(\text{CO})_{12}$	2.2 : 1	5.8 : 1	4 : 1	3.5 : 1
Sealed/open tube	sealed	sealed	sealed	open
Tube size (ml)	50	50	20	200
Reaction temperature	Room	Room	28–30°C	Room
Reaction time	120 days	60 days	7 days	13 days
Solvent (hexane)	10 ml	10 ml	5 ml	30 ml

4.2.5 Observations and workup

Run 2 (MeGeH_3 : $\text{Co}_4(\text{CO})_{12}$ = 5.8 : 1)

As in Run 1, dark red crystals, some of them distinct square plates were noted in a dark red supernatant solution at the end of the reaction. The total incondensable gas measured was 0.101 mmol, 77% of the gas composition was H_2 , and 22% CO . On working up, no $\text{Co}_4(\text{CO})_{12}$ remained and total conversion to $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ was achieved.

Yield of Run 2:

Weight of $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ = 0.019g = 100% $\pm$ 5%

Prediction from incondensable gas measurement = 97% $\pm$ 5%

Run 3 (MeGeH_3 : $\text{Co}_4(\text{CO})_{12}$ = 4 : 1)

The yellowish brown solution of $\text{Co}_4(\text{CO})_{12}$ changed to reddish brown after 4 days of reaction in the 30°C oil bath. Dark crystals which appeared red under light were formed at the side of the ampoule.

After 7 days of reaction, no further change was observed and the reaction was worked up. The total incondensable gas measured was 0.079 mmol, 81% consisted of H_2 and 19% CO . The volatile fraction was removed but not examined.

The involatile fraction was separated into hexane and CH_2Cl_2 soluble fractions as in Run 1. The infrared spectrum of the hexane fraction showed the presence of $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ along with bands due to unreacted $\text{Co}_4(\text{CO})_{12}$. On recrystallisation from CH_2Cl_2 /hexane, square plates of $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ were obtained. The infrared spectrum of the CH_2Cl_2 fraction showed the only product to be $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$.

Yield of Run 3 :

Weight of $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ = 0.0113g = 0.016 mmol = 75% $\pm$ 5% yield

From incondensable gas measurement, yield = 94% $\pm$ 5%

Difference in the two values is due to incomplete separation of $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ from the $\text{Co}_4(\text{CO})_{12}/(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ mixture, only pure $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ was weighed.

Run 4 (MeGeH_3 : $\text{Co}_4(\text{CO})_{12}$ = 3.45 : 1)

This run was followed by the evolution of incondensable gas, the results of which are shown in Table 4.2.

Table 4.2 Incondensable gas evolution of Run 4

Days	Gas evolved (mmoles)	Total gas evolved (mmoles)	% H_2	% CO
4	0.130	0.130	69	31
8	0.022*	0.152	78	22
9	0.005	0.157	not determined	
13	0.001	0.158	not determined	
Total (mmol)		0.158	0.111	0.047

* readings not accurate due to mistake incurred during measurement

The total gas evolution was expected to be 0.164 mmol (75% H_2 , 25% CO) for complete reaction of $\text{Co}_4(\text{CO})_{12}$ with MeGeH_3 (according to equation 4.1). 0.158 mmol (96% of expected gas) was measured after 13 days. The loss of some of the gas on day 8 was minor and probably within the $\pm 10\%$ error on the yield obtained. On working up, the volatiles were removed but not examined. The infrared spectrum of the involatile fraction (dissolved in CH_2Cl_2) showed no indication of any remaining $\text{Co}_4(\text{CO})_{12}$. The only product was $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$, which indicated a quantitative conversion to $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ (based on equation 4.1).

Yield of Run 4 :

Weight of $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ = 0.031g = 0.043 mmol = 105% $\pm$ 10%

From incondensable gas measurement = 96% $\pm$ 5%

4.2.6 Summary

Table 4.3 gives a summary of the conditions and results for all four runs of MeGeH_3 and $\text{Co}_4(\text{CO})_{12}$.

Table 4.3 Summary of the reactions of MeGeH_3 with $\text{Co}_4(\text{CO})_{12}$

	Run 1	Run 2	Run 3	Run 4
$\text{Co}_4(\text{CO})_{12}$ (mmoles)	0.445	0.026	0.021	0.041
Ratio MeGeH_3 : $\text{Co}_4(\text{CO})_{12}$	2.2:1	5.8:1	~4:1	3.5:1
Temperature	room	room	28-30°C	room
Reaction time	120 days	60 days	7 days	13 days
Sealed / open tube	sealed	sealed	sealed	open
Ampoule size	50 ml	50 ml	20 ml	200 ml
Yield of $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$:				
from incondensable data	63%	97%	94%	96%
from recrystallisation	59%	100%	75%	100%
$\text{Co}_4(\text{CO})_{12}$ recovered	~40%	0	detectable	0

4.3 Reaction of MeSiH_3 with $\text{Co}_4(\text{CO})_{12}$

4.3.1 Run 1, sealed tube reaction (MeSiH_3 : $\text{Co}_4(\text{CO})_{12}$ = 2 : 1)

Experimental

$\text{Co}_4(\text{CO})_{12}$ (0.1217g, 0.213 mmol) and hexane (10 ml) were loaded into a 50 ml ampoule at the Schlenk line. The ampoule was transferred to the vacuum line, degassed and the contents frozen down by liquid nitrogen. MeSiH_3 (0.425 mmol) was condensed into the ampoule and then sealed under vacuum. The ampoule of reactants was allowed to react in the dark at room temperature for 160 days.

Observations and workup

After 160 days, tiny red crystals and some red powder were observed on the side and in the bottom of the ampoule. The supernatant solution was very dark reddish brown in colour.

The reaction was worked up at this stage. The volatile fraction showed some unreacted MeSiH_3 , but this could not be separated from the solvent. 0.47 mmoles of total incondensable gases were obtained with an overall $\text{H}_2 : \text{CO}$ ratio of 74 : 26.

The small amount of supernatant solution (left after the removal of most of the volatiles) was removed. The solid was washed several times with small amounts of hexane (3-4 ml). The hexane washings were added to the supernatant solution. The remaining solid was dissolved in CH_2Cl_2 .

Infrared spectrum showed that the hexane fraction consisted of unreacted $\text{Co}_4(\text{CO})_{12}$ and a product with a strong 2034 cm^{-1} band.

Recrystallisation yielded the only new product identified as $(\text{MeSi})_2\text{Co}_4(\text{CO})_{11}$ (some as red plates, some came down as a red powder, characterisations in Section 4.4). This compound had just been recently synthesised via the reaction of $(\text{MeSiH}_2)_2\text{Fe}(\text{CO})_4$ with $\text{Co}_2(\text{CO})_8$ and its crystal structure determined [144]. Not all $(\text{MeSi})_2\text{Co}_4(\text{CO})_{11}$ could be isolated from the unreacted $\text{Co}_4(\text{CO})_{12}$ (see yield from weighing compares to that from incondensable gas).

Yield of Run 1 :

from weighing = 51mg = 0.083 mmol = 39% (isolated)

from total incondensable gas measurement = 55%

4.3.2 Run 2 Open tube reaction (MeSiH_3 : $\text{Co}_4(\text{CO})_{12}$ = 2 : 1)

Experimental

$\text{Co}_4(\text{CO})_{12}$ (0.045g, 0.079 mmol) and hexane (10 ml) were loaded into a 200 ml greaseless tap reaction vessel. The reaction vessel was transferred to the vacuum line, degassed and the contents frozen down by liquid nitrogen. MeSiH_3 (0.166 mmol) was condensed into the vessel and the tap closed. The reaction was allowed to proceed at 30°C for 49 days. Measurement of the incondensable gas was carried out intermittently.

Results :

The colour of the $\text{Co}_4(\text{CO})_{12}$ solution gradually changed from dark brown to dark reddish brown with the deposit of red powder and some dark coloured crystals. The incondensable gas measurements are presented in Table 4.4. On working up after 49 days, only $(\text{MeSi})_2\text{Co}_4(\text{CO})_{11}$ was obtained.

Table 4.4 Incondensable gas measurements of MeSiH_3 and $\text{Co}_4(\text{CO})_{12}$, Run 2

Days	Total gas evolved (mmoles)	$\text{H}_2:\text{CO}$ % : %	Accumulated gas (mmoles)
11	0.228	71:29	0.228
20	0.059	80:20	0.287
27	0.010	*	0.297
35	0.008	*	0.305
49	0.03	*	3.08

* not determined as amount of gas is too small

Yield of Run 2 : Weight of $(\text{MeSi})_2\text{Co}_4(\text{CO})_{11} \approx 0.05\text{g} \approx 100\%$

from incondensable gas $\approx 95\%$

4.3.4 Summary of results of the reaction of MeSiH_3 with $\text{Co}_4(\text{CO})_{12}$

Table 4.5 gives a summary of the conditions and results for the reaction of MeSiH_3 with $\text{Co}_4(\text{CO})_{12}$.

Table 4.5 Summary of the reactions of MeSiH_3 with $\text{Co}_4(\text{CO})_{12}$

	Run 1 sealed tube	Run 2 open tube
$\text{Co}_4(\text{CO})_{12}$ (mmoles)	0.213	0.079
MeSiH_3 (moles)	0.425	0.166
Ratio MeSiH_3 : $\text{Co}_4(\text{CO})_{12}$	2 : 1	2 : 1
Temperature	room	30°C
Reaction time (days)	160	49
Vessel size	50 ml	200 ml
Hexane (ml)	10	30
Yield of $(\text{MeSi})_2\text{Co}_4(\text{CO})_{11}$	55%	100%

4.4 Characterisation of $(\text{MeM}')_2\text{Co}_4(\text{CO})_{11}$ ($\text{M}' = \text{Si}, \text{Ge}$) :

The crystal structures of $(\text{MeM}')_2\text{Co}_4(\text{CO})_{11}$ ($\text{M}' = \text{Si}$ [144], Ge [18,84]) have been determined. Both the molecules were shown to consist of two M' atoms quadruply bridging a distorted square planar array of Co atoms. Of the eleven CO's, eight were completely terminal, two semi-bridging and one fully bridging. The molecule possessed a mirror plane through the two M' atoms and the bridging CO which is planar. The structure of $(\text{MeM}')_2\text{Co}_4(\text{CO})_{11}$ is shown in Fig 4.1.

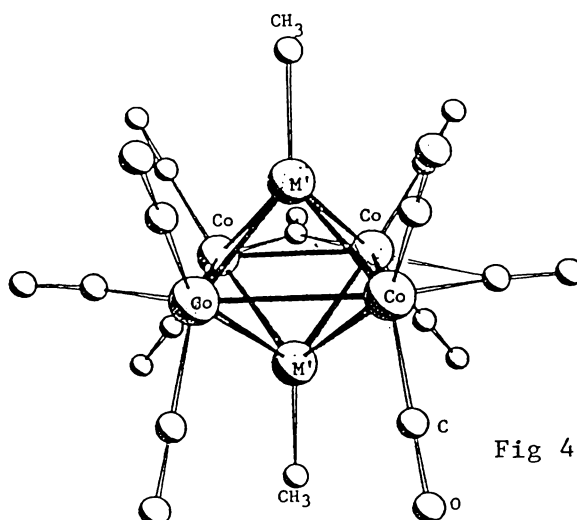


Fig 4.1 $(\text{MeM}')_2\text{Co}_4(\text{CO})_{11}$

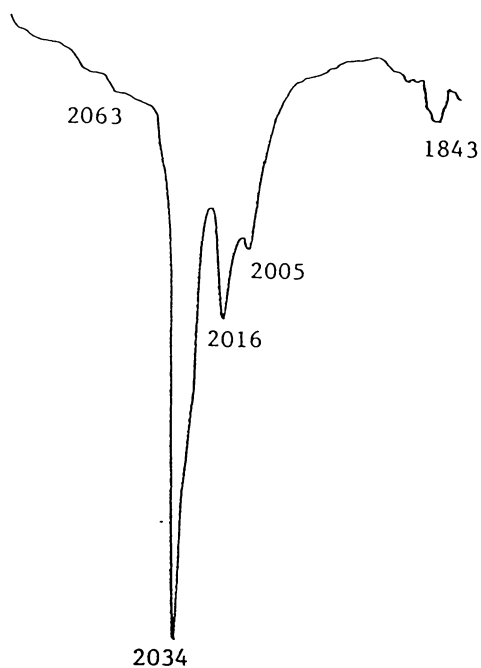


Fig 4.2 IR spectrum of $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ in hexane/ CH_2Cl_2

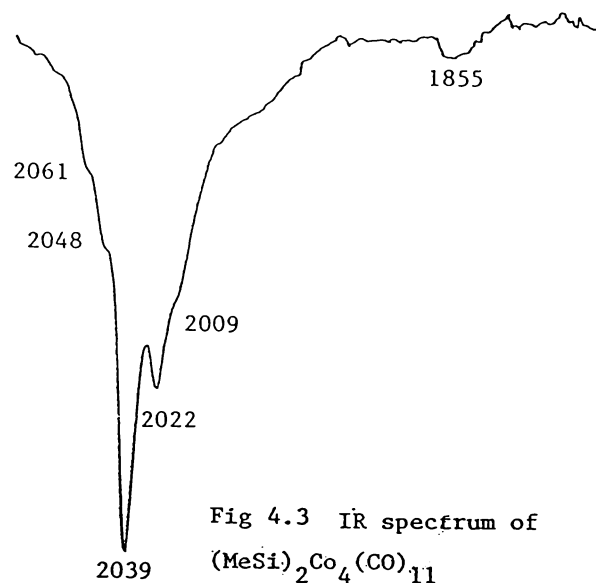


Fig 4.3 IR spectrum of $(\text{MeSi})_2\text{Co}_4(\text{CO})_{11}$ in hexane/ CH_2Cl_2

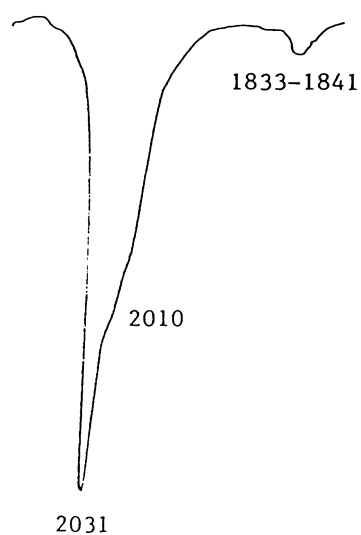


Fig 4.3 IR spectrum of $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ in CH_2Cl_2

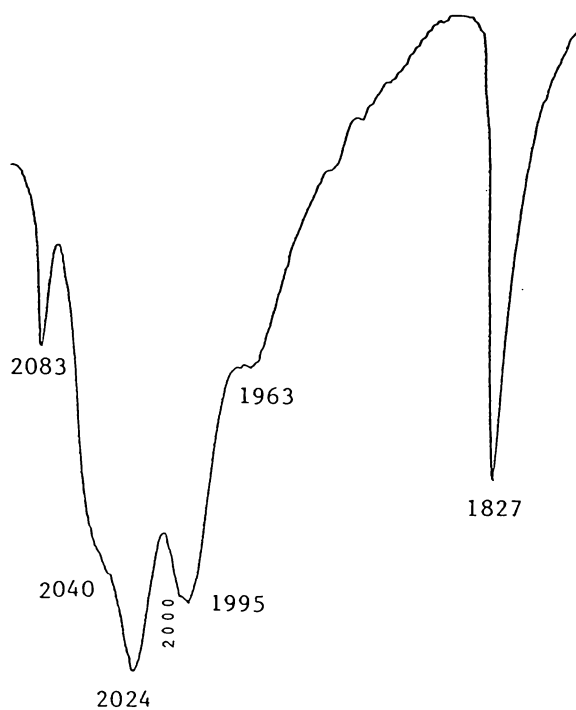


Fig 4.5 Solid IR spectrum of $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ (CsI disc)

4.4.1 Infrared spectrum:

A total of eight infrared bands ($3A_1 + 3B_1 + 2B_2$) and a bridging CO band (A_1) are expected for $(MeM')_2Co_4(CO)_{11}$ assuming C_{2v} symmetry. Only four obvious bands and a very weak bridging mode were observed in the solution infrared spectrum of $(MeGe)_2Co_4(CO)_{11}$ (Table 4.6, Figs 4.2 and 4.3). The solution infrared spectrum of $(MeSi)_2Co_4(CO)_{11}$ (Fig 4.4) shows up to six bands. Most of the bands of $(MeSi)_2Co_4(CO)_{11}$ are shifted by 4-5 wavenumbers higher than those of $(MeGe)_2Co_4(CO)_{11}$. The infrared spectrum of solid $(MeGe)_2Co_4(CO)_{11}$ showed a total of seven out of the nine predicted bands. A discussion of the infrared bands of $(RM'_2)Co_4(CO)_{11}$ compounds is given in Chapter Nine.

Table 4.6 Infrared spectrum of $(MeM')_2Co_4(CO)_{11}$

$(MeGe)_2Co_4(CO)_{11}$				$(MeSi)_2Co_4(CO)_{11}$	
Solution			Solid	Solution	
CH_2Cl_2	hex/ CH_2Cl_2	[84]	CsI	CH_2Cl_2	hex/ CH_2Cl_2
			2083w		
2063vw sh				2058w sh	2061w sh
				2047m sh	2048m sh
2031vs	2034vs	2034vs	2040s sh	2038vs	2039vs
2010s sh	2016m	2016m	2024vs	2020ms	2022ms
	2005mw sh	2004sh	2000s sh		2009mw
			1995s		
			1963w sh		
1833-41vw	1843w br	1853w br	1827s	1847vw br	1855w

4.4.2 Mass spectrum :

The mass spectrum of $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ (Table 4.7) obtained in this work is an improvement over that obtained previously [18,84] showing the presence of the parent ion at 713-722 (calculated value of 722). An isotope intensity pattern appropriate to Ge_2 atoms (see Chapter Two) was observed for most of the envelopes. The loss of eleven CO's from the parent ion was observed, consistent with the formulation as $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$.

Table 4.7 Mass spectrum of $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$

m/e	Int	Possible assignments
713-725	vw	$n = 11$ for $P = [(\text{MeGe})_2\text{Co}_4(\text{CO})_n]^+$
685-695	m	10
657-672	m	9
629-638	w	8
601-611	m	7
571-583	s	6
543-553	m	5
516-528	w	4
490-500	mw	3
460-472	m	2
431-443	mw	1
403-415	ms	$0 = [\text{Me}_2\text{Ge}_2\text{Co}_4]^+$
388-399	ms	$[\text{MeGe}_2\text{Co}_4]^+$
374-383	ms	$[\text{Ge}_2\text{Co}_4]^+$
328-340	w	$[\text{MeGe}_2\text{Co}_3]^+$
316-326	w	$[\text{GeCo}_3]^+$
272-279	w	$[\text{MeGe}_2\text{Co}_2]^+$
258-268	w	$[\text{Ge}_2\text{Co}_2]^+$
212-221	vw	$[\text{MeGe}_2\text{Co}]^+$
200-210	m	$[\text{MeGeCo}_2]^+$
188-194	vw	$[\text{GeCo}_2]^+$

The highest m/e peak of $(\text{MeSi})_2\text{Co}_4(\text{CO})_{11}$ (see Table 4.8) is that of $[\text{P-CO}]^+$ instead of the parent ion, P^+ . Unlike $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ which loses Me after the loss of all the CO's, $(\text{MeSi})_2\text{Co}_4(\text{CO})_{11}$ loses its first Me after the loss of 3CO. As Si and CO have the same m/e value, it is quite possible that the loss of Si-Me is simultaneous with that of the loss of CO e.g. the envelope at m/e 504-507 could be assigned as that of $[\text{P-4CO-Me}]^+$ or $[\text{P-3CO-Me-Si}]^+$.

Table 4.8 Mass spectrum of $(\text{MeSi})_2\text{Co}_4(\text{CO})_{11}$

m/e	Int	Assignment
590-600	vw	$[\text{P-CO}]^+$
575	vw	$[\text{P-2CO}]^+$
553-554	mw	$[\text{P-3CO}]^+$
531-533	m	$[\text{P-3CO-Me}]^+$
507-509	w	$[\text{P-4CO-Me}]^+$
484-487	w	$[\text{P-5CO}]^+$
460-462	m	$[\text{P-6CO}]^+$
431-435	s	$[\text{P-7CO}]^+$
400-406	m	$[\text{P-8CO}]^+$
373-378	m	$[\text{P-9CO}]^+$
347-350	m	$[\text{P-10CO}]^+$
317-322	ms	$[\text{P-11CO}]^+$
292-294	m	$[\text{P-11CO-2Me}]^+$
261-264	m	$[\text{P-11CO-Si-2Me}]^+$
231-236	ms	$[\text{P-11CO-2Si-2Me}]^+$
174-177	m	$[\text{P-11CO-2Si-2Me-Co}]^+$
116-120	ms	$[\text{P-11CO-2Si-2Me-2Co}]^+$

4.4.3 NMR spectrum :

The ^1H NMR signal of the methyl proton in $(\text{MeM}')_2\text{Co}_4(\text{CO})_{11}$ appeared at $\sim\delta$ 2.5 ppm as a singlet (see Table 4.9, also see Table 9.4 for NMR of such compounds). All the six methyl protons are in equivalent positions in solution as only a singlet was observed.

The observations of only one ^{13}C NMR signal indicated that the terminal and bridging CO's were in one ^{13}C environment even at -50°C . The ^1H NMR and ^{13}C NMR of $(\text{RM}')_2\text{Co}_4(\text{CO})_{11}$ type compounds are discussed in detail in Chapter Nine.

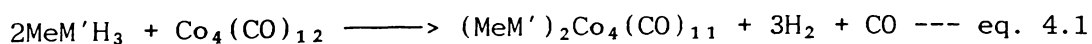
Table 4.9 NMR data of $(\text{MeM}')_2\text{Co}_4(\text{CO})_{11}$

	$\text{M}' = \text{Ge}$	$\text{M}' = \text{Si}$
^1H NMR (RT)	2.75 (s)	2.73 (s)
^{13}C NMR (RT)	203.2 (s)	-
	(-50°C) 202.6 (s)	202.6 (s)

CDCl_3 as solvent, chemical shift in δ ppm

4.5 Discussion: the reaction of $\text{MeM}'\text{H}_3$ with $\text{Co}_4(\text{CO})_{12}$

The experiments on the reaction of $\text{MeM}'\text{H}_3$ ($\text{M}' = \text{Si}, \text{Ge}$) with $\text{Co}_4(\text{CO})_{12}$ gave a single product, $(\text{MeM}')_2\text{Co}_4(\text{CO})_{11}$, which is consistent with the equation :



This suggests that the formation of $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ in the experiments with $\text{Co}_2(\text{CO})_8$ (Chapter Three), probably arose via the initial formation of $\text{Co}_4(\text{CO})_{12}$ from $\text{Co}_2(\text{CO})_8$. It also makes it probable that the original formation of $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ in the prolonged reaction of MeGeH_3 with $\text{GeCo}_4(\text{CO})_{14}$ [18,84] was indeed a side reaction involving $\text{Co}_4(\text{CO})_{12}$ which was adventitiously present -

either from decomposition of $\text{GeCo}_4(\text{CO})_{14}$ or from $\text{Co}_2(\text{CO})_8$ or $\text{Co}_4(\text{CO})_{12}$ carried over from the preparation of $\text{GeCo}_4(\text{CO})_{14}$.

Tables 4.3 and 4.5 show that the rate of reaction of MeGeH_3 with $\text{Co}_4(\text{CO})_{12}$ was increased by the following factors :- at low concentration of $\text{Co}_4(\text{CO})_{12}$ the reaction proceeded more rapidly when all the $\text{Co}_4(\text{CO})_{12}$ was in solution. This may be due to the possible maintenance of a low incondensable gas pressure over the reaction. Gentle heating also increased the reaction rate. With favourable conditions, the reaction has been shown to go to completion in 13 days (for the reaction of MeGeH_3 with $\text{Co}_4(\text{CO})_{12}$).

The other reported method of preparing $(\text{RGe})_2\text{Co}_4(\text{CO})_{11}$ is by the reaction of RGeX_3 ($\text{X} = \text{halide}$) with $\text{KCo}(\text{CO})_4$, for $\text{R} = \text{t-Bu}$ or Ph (7% and 47% yield respectively) [114,115] (see also Chapter One). There is no published report of any $(\text{RSi})_2\text{Co}_4(\text{CO})_{11}$ species for $\text{R} = \text{alkyl}$ or phenyl groups, but both $(\text{MeM}')_2\text{Co}_4(\text{CO})_{11}$ ($\text{M}' = \text{Si, Ge}$) have been made recently via the reaction of $(\text{MeM}'\text{H}_2)_2\text{Fe}(\text{CO})_4$ with $\text{Co}_2(\text{CO})_8$ (unpublished result [144]). The results obtained in this Chapter provide a clean, easy and efficient way of obtaining $(\text{MeM}')_2\text{Co}_4(\text{CO})_{11}$, and could probably be used to prepare similar clusters with different R groups such as Et , Ph and $n\text{-butyl}$. R groups such as halide could possibly be incorporated. Replacement of halide groups by metal carbonyl anions (e.g. $\text{Co}(\text{CO})_4^-$, $\text{Mn}(\text{CO})_5^-$ and possibly $\text{Fe}(\text{CO})_4^{2-}$) could produce clusters with higher molecular weight and also those with mixed transition metals.

The mechanism by which $(\text{MeM}')_2\text{Co}_4(\text{CO})_{11}$ is formed from $\text{MeM}'\text{H}_3$ and $\text{Co}_4(\text{CO})_{12}$ is not known. A proposed mechanism is shown in Fig 4.6. It should be noted that this is only a very simplified version of the actual mechanism and alternative approaches are certainly feasible. It

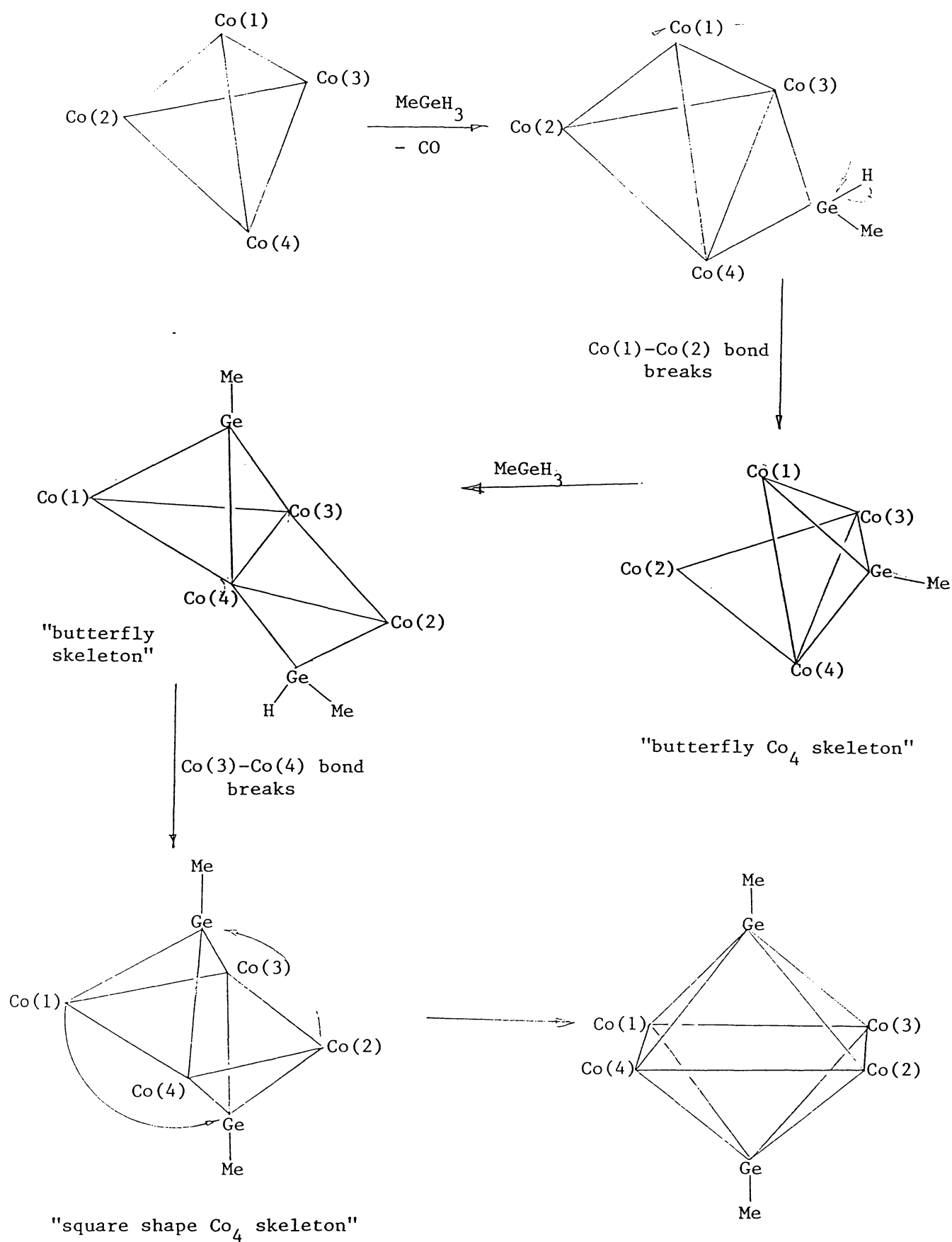


Fig 4.6 Possible mechanism for the formation of $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ (also for $\text{M}' = \text{Si}$)

only shows the rearrangement of the metal atoms and not the carbonyl groups, which are undoubtedly intimately involved.

4.6 The reaction of $\text{Co}_4(\text{CO})_{12}$ with Me_2GeH_2 (1 : 4 ratio)

4.6.1 Experimental :

$\text{Co}_4(\text{CO})_{12}$ (0.383g, 0.67 mmol) and hexane (10ml) were loaded into a 50ml ampoule. This was transferred to the vacuum line where it was frozen and degassed. Me_2GeH_2 (2.88 mmol) was condensed in and the ampoule sealed under vacuum. This was left to react for 3 months.

4.6.2 Results :

After 3 months, a dark solution with some brownish coloured crystals was obtained. The incondensable gas was not measured, and the volatile fraction was collected but not examined. The infrared spectrum showed that the involatile fraction consisted of unreacted $\text{Co}_4(\text{CO})_{12}$ [143], $\text{Me}_2\text{GeCo}_2(\text{CO})_7$ and $(\text{Me}_2\text{Ge})_2\text{Co}_2(\text{CO})_6$ [17,18,61] (Table 4.10).

Table 4.10 Infrared spectrum of the product of Me_2GeH_2 with $\text{Co}_4(\text{CO})_{12}$

Product mixture (C_6H_{14})	$\text{Me}_2\text{GeCo}_2(\text{CO})_7$ (C_6H_{12}) [61]	$(\text{Me}_2\text{Ge})_2\text{Co}_2(\text{CO})_6$ (C_6H_{12}) [61]	$\text{Co}_4(\text{CO})_{12}$ (C_7H_{16}) [143]
2054 w			2054 vs
2043 m	2047 s		
2029 vs	2024 s	2028 s	
2009 s	2006 s	2008 s	
1997 s sh	1998 sh		
1994 s			
1989 s		1989 s	
1980 mw sh	1971 w	1980 m	
1950 vw sh		1945 vw	
1865 vw			1865 mw
1841 vw	1844 ms		

solvent = CH_2Cl_2 /hexane

The products were similar to those formed in the reaction of Me_2GeH_2 with $\text{Co}_2(\text{CO})_8$ by Foster [18] and the reaction of $\text{Me}_2\text{GeHCo}(\text{CO})_4$ with $\text{Co}_2(\text{CO})_8$ by Gerlach [17]. The reaction of Me_2GeH_2 and $\text{SiCo}_4(\text{CO})_{14}$ in Chapter Eight also produced similar products. Attempts to separate the products proved to be time consuming and unsuccessful as was experienced by other workers [17,18]. The yield of each of the products is therefore not known, but they appeared to be in similar proportion from the infrared spectrum.

4.7 The reaction of $\text{Co}_4(\text{CO})_{12}$ + Me_2SiH_2 (1 : 4 ratio)

4.7.1 Experimental :

$\text{Co}_4(\text{CO})_{12}$ (0.1524g, 0.267 mmol) was loaded into a 200 ml reaction vessel with a greaseless tap. Hexane (30ml) was added. Air was then evacuated from the vessel at the vacuum line. The contents were frozen down by liquid nitrogen. Me_2SiH_2 (0.107 mmol) was condensed into the vessel. Incondensable gas was measured at intervals.

4.7.2 Results :

The incondensable gas measurement for the first 48 days is presented in Table 4.11.

Table 4.11 Incondensable data of Me_2SiH_2 with $\text{Co}_4(\text{CO})_{12}$

Days	Total mmole gas	% H_2
3	0.280	99.7
23	0.315	90.89
48	0.123	not measured

The infrared spectrum sampled at day 23 (Table 4.12) showed that the major part of the product was likely to be

$\text{Me}_2[\text{Co}(\text{CO})_4]\text{SiOCCo}_3(\text{CO})_9$ [18], along with $\text{Me}_2\text{SiHCo}(\text{CO})_4$, $\text{Co}_2(\text{CO})_8$ and $\text{Co}_4(\text{CO})_{12}$ in decreasing order of abundance.

The infrared spectrum of the soluble fraction of the reaction mixture taken after 48 days, was very similar to that taken on day 23, but the bands corresponding to $\text{Me}_2[\text{Co}(\text{CO})_4]\text{SiOCCo}_3(\text{CO})_9$ were stronger.

The reaction was stopped after 48 days as no further products were formed. The volatiles were removed but not examined. The products could not be separated due to the small difference in solubility. The products identified in order of decreasing quantity are $\text{Me}_2[\text{Co}(\text{CO})_4]\text{SiOCCo}_3(\text{CO})_9$, $\text{Me}_2\text{SiHCo}(\text{CO})_4$ and $\text{Co}_2(\text{CO})_8$ (based on the IR spectrum).

Table 4.12 IR spectrum of the product mixture from $\text{Me}_2\text{SiH}_2 + \text{Co}_4(\text{CO})_{12}$

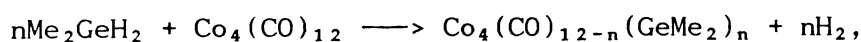
Bands	Int.	Possible assignments
2098	vw	$\text{Me}_2[\text{Co}(\text{CO})_4]\text{SiOCCo}_3(\text{CO})_9$ [18]
2091	w	$\text{Me}_2\text{SiHCo}(\text{CO})_4$ [18]
2067	mw	$\text{Co}_2(\text{CO})_8$, $\text{Me}_2[\text{Co}(\text{CO})_4]\text{SiOCCo}_3(\text{CO})_9$
2063	m	$\text{Co}_4(\text{CO})_{12}$
2053	vs	$\text{Co}_4(\text{CO})_{12}$, $\text{Me}_2[\text{Co}(\text{CO})_4]\text{SiOCCo}_3(\text{CO})_9$
2051	vs	$\text{Me}_2[\text{Co}(\text{CO})_4]\text{SiOCCo}_3(\text{CO})_9$
2043	s (sh)	$\text{Me}_2[\text{Co}(\text{CO})_4]\text{SiOCCo}_3(\text{CO})_9$
2041	vs	$\text{Co}_2(\text{CO})_8$
2037	s (sh)	?
2029	s	$\text{Me}_2\text{SiHCo}(\text{CO})_4$, $(\text{Me}_2\text{Si})_2\text{Co}_2(\text{CO})_6$? [54]
2022	ms	$\text{Co}_2(\text{CO})_8$, $\text{Me}_2[\text{Co}(\text{CO})_4]\text{SiOCCo}_3(\text{CO})_9$
2016	m (sh)	$\text{Me}_2[\text{Co}(\text{CO})_4]\text{SiOCCo}_3(\text{CO})_9$
2007	mw	$\text{Me}_2\text{SiHCo}(\text{CO})_4$, $(\text{Me}_2\text{Si})_2\text{Co}_2(\text{CO})_6$?
1994	m	$\text{Me}_2\text{SiHCo}(\text{CO})_4$, $(\text{Me}_2\text{Si})_2\text{Co}_2(\text{CO})_6$?
1972	w	?
1865	w	$\text{Co}_4(\text{CO})_{12}$, $\text{Co}_2(\text{CO})_8$
1856	w	$\text{Co}_2(\text{CO})_8$

solvent = CH_2Cl_2 /hexane

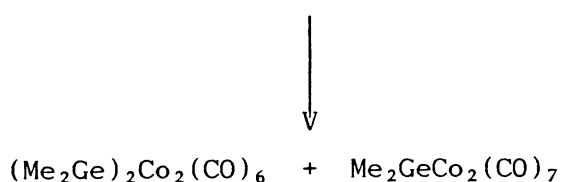
4.8 Discussion : The reaction of $\text{Me}_2\text{M}'\text{H}_2$ with $\text{Co}_4(\text{CO})_{12}$

$\text{Me}_2\text{GeCo}_2(\text{CO})_7$ and $(\text{Me}_2\text{Ge})_2\text{Co}_2(\text{CO})_6$ were previously obtained from the reaction of Me_2GeH_2 with $\text{Co}_2(\text{CO})_8$ [17,18]. $\text{Me}_2\text{GeCo}_2(\text{CO})_8$ was also produced in the reaction carried out by [18] but was not observed in this work.

The reaction of Me_2GeH_2 with $\text{Co}_4(\text{CO})_{12}$ was conducted to test the possibility of replacing some or all of the bridging CO's in $\text{Co}_4(\text{CO})_{12}$ by Me_2Ge units. Such products were not obtained as the $\text{Co}_4(\text{CO})_{12}$ molecule was found to break down to $\text{Co}_2(\text{CO})_x$ and possibly $\text{Co}(\text{CO})_4$ units. As the volatile fraction was not examined, it is not known how much of the Me_2GeH_2 had reacted, nor whether $\text{HCo}(\text{CO})_4$ was formed. As $\text{Me}_2\text{GeCo}_2(\text{CO})_7$ and $(\text{Me}_2\text{Ge})_2\text{Co}_2(\text{CO})_6$ were formed in similar amounts, from the infrared intensities, a reaction might be envisaged which started by the replacement of $\mu\text{-CO}$ by $\mu\text{-GeMe}_2$ as found in other systems :



where n is 0 to 4



The formation of $(\text{Me}_2\text{Ge})_2\text{Co}_2(\text{CO})_6$ is not unexpected as Me_2GeH_2 is present in four times excess. Studies of the reaction of Me_2GeH_2 with $\text{Me}_2\text{GeCo}_2(\text{CO})_7$ [18] showed that the replacement of the bridging CO in $\text{Me}_2\text{GeCo}_2(\text{CO})_7$ to form $(\text{Me}_2\text{Ge})_2\text{Co}_2(\text{CO})_6$ was very slow compared to similar reaction with $\text{Co}_2(\text{CO})_8$.

The IR band at 1994cm^{-1} remains unassigned, but one possible candidate is $\text{Me}_2\text{GeHCo}(\text{CO})_4$. R.Gerlach has found that $\text{Me}_2\text{GeHCo}(\text{CO})_4$ reacted with $\text{Co}_2(\text{CO})_8$ to produce $\text{Me}_2\text{GeCo}_2(\text{CO})_7$, $(\text{Me}_2\text{Ge})_2\text{Co}_2(\text{CO})_6$ and

$\text{Me}_2\text{GeCo}_2(\text{CO})_8$ [17]. Though $\text{Me}_2\text{GeCo}_2(\text{CO})_8$ was not observed in this work, its formation would be unfavourable in the low CO environment of this reaction.

Unlike the reaction of Me_2GeH_2 with $\text{Co}_4(\text{CO})_{12}$, the reaction of Me_2SiH_2 with $\text{Co}_4(\text{CO})_{12}$ produced the methylidyne cluster $\text{Me}_2[\text{Co}(\text{CO})_4]\text{SiOCCo}_3(\text{CO})_9$ (Fig 4.7a) as the major product (see Table 4.12). Some $\text{Me}_2\text{SiHCo}(\text{CO})_4$, and a small amount of $\text{Co}_2(\text{CO})_8$ was also observed. The results are very similar to those of the reaction of Me_2SiH_2 or Ph_2SiH_2 with $\text{Co}_2(\text{CO})_8$ [18].

The formation of $\text{Me}_2[\text{Co}(\text{CO})_4]\text{SiOCCo}_3(\text{CO})_9$ is not surprising as Si was known to have a high affinity for oxygen forming SiO products such as $\text{Me}_3\text{SiOCCo}_3(\text{CO})_9$ (Fig 4.7b) [146,147] and $(\text{Me}_3\text{SiOC})_4\text{Co}_2(\text{CO})_4$ (Fig 4.8) [147].

The incondensable gas measurement showed that three days into the reaction, almost no CO was measured, and after 23 days, less than 10% of the gas was CO. This is expected for the formation of $\text{Me}_2[\text{Co}(\text{CO})_4]\text{SiOCCo}_3(\text{CO})_9$, which takes up two CO for every mole formed from $\text{Co}_4(\text{CO})_{12}$.

The evidence for the presence of $(\text{Me}_2\text{Si})_2\text{Co}_2(\text{CO})_6$ is weak as its strong infrared bands [54] occur at similar positions to those of $\text{Me}_2\text{SiHCo}(\text{CO})_4$. The presence of 2 unassigned infrared bands indicates that further products are present but remain uncharacterised.

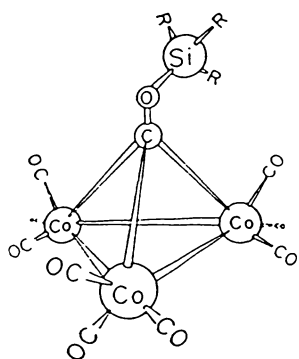


Fig 4.7 $\text{R}_3\text{SiOCCo}_3(\text{CO})_9$

a: $\text{R}_3 = \text{Me}_2\{\text{Co}(\text{CO})_4\}$

b: $\text{R}_3 = \text{Me}_3$

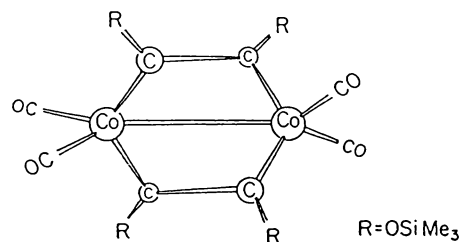


Fig 4.8 $(\text{Me}_3\text{SiOC})_4\text{Co}_2(\text{CO})_4$

$\text{R} = \text{OSiMe}_3$

CHAPTER FIVE

The Reaction of $\text{RM}'\text{H}_3$ With $\text{GeCo}_4(\text{CO})_{14}$

$\text{R} = \text{Me, Et, Ph}$ for $\text{M}' = \text{Ge}$, and $\text{R} = \text{Me}$ for $\text{M}' = \text{Si}$

5.1 Introduction

The reaction of MeGeH_3 and $\text{GeCo}_4(\text{CO})_{14}$ (**2a**) was first investigated by S. Foster in 1982 [18]. In a run using a ratio of $\text{MeGeH}_3 : \text{GeCo}_4(\text{CO})_{14} = 1.4 : 1$ and a 10 weeks reaction time, the sole product was $(\text{MeGeH})\text{GeCo}_4(\text{CO})_{13}$ (**5b**). However, in another run using a 0.93 : 1 ratio and 6 months reaction time, the hexa-nuclear cluster, $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ (**1a**) [84] was isolated in low yields along with the major product $(\text{MeGeH})\text{GeCo}_4(\text{CO})_{13}$.

$(\text{MeGeH})\text{GeCo}_4(\text{CO})_{13}$ was characterised by infrared and mass spectroscopy [18]. The structure is believed to be like that of $\text{GeCo}_4(\text{CO})_{14}$ with one of the $\mu\text{-CO}$'s replaced by a $\mu\text{-Ge}(\text{Me})\text{H}$ unit.

In this Chapter, the reactions of MeGeH_3 and also EtGeH_3 , PhGeH_3 and MeSiH_3 with $\text{GeCo}_4(\text{CO})_{14}$ were investigated. The possibility of replacing the second $\mu\text{-CO}$ in $\text{GeCo}_4(\text{CO})_{14}$ by a $\mu\text{-Ge}(\text{R})\text{H}$ group was also studied. The formation of $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ is reinvestigated in this work.

A series of sealed and open tube reactions were examined with and without heating.

5.2 Reaction of MeGeH_3 with $\text{GeCo}_4(\text{CO})_{14}$ (sealed tube)

Run 1 (MeGeH_3 : $\text{GeCo}_4(\text{CO})_{14}$ = 1 : 1)

5.2.1 Experimental :

$\text{GeCo}_4(\text{CO})_{14}$ (0.848g, 1.211mmol) and hexane (10 ml) were loaded into a 50 ml ampoule at the Schlenk line. The ampoule was transferred to the vacuum line where the gases were removed and the ampoule frozen down by liquid nitrogen. MeGeH_3 (1.2mmol) was condensed in and the ampoule sealed under vacuum. The reaction was allowed to proceed in the dark, at room temperature for 196 days.

5.2.2 Observations and workup :

After 196 days of reaction, the solution had become darker brown in colour, but the solid fraction remained reddish brown. On opening the ampoule, a total of 1.514 mmoles of incondensable gas was measured, 60% was H_2 and 40% CO .

The volatile fraction was condensed into a trap at -196°C . The infrared spectrum of these volatiles showed the presence of MeGeH_3 and hexane. The amount of MeGeH_3 recovered was not known due to the difficulty in separating small quantities of MeGeH_3 from the relatively large amount of hexane.

The solid was extracted several times with 3-4 ml of hexane each time. The extracts were combined, the infrared spectrum (Table 5.1) showed the presence of both $(\text{MeGeH})\text{GeCo}_4(\text{CO})_{13}$ and $\text{GeCo}_4(\text{CO})_{14}$, and a shoulder at 2086 cm^{-1} (Note : this shoulder was found to be one of the infrared bands of $(\text{MeGeH})_2\text{GeCo}_4(\text{CO})_{12}$ which was isolated pure in Section 5.6, Run 2 and characterised in Section 5.7.2). The hexane extracts were concentrated and cooled in the freezer. Dark brownish red crystals were obtained. These were found to be $\text{GeCo}_4(\text{CO})_{14}$. This fractional crystallization procedure was repeated several times which

removed most of the $\text{GeCo}_4(\text{CO})_{14}$. After this, dark brown conglomerates began to form. These were found to be $(\text{MeGeH})\text{GeCo}_4(\text{CO})_{13}$ with small amounts of $\text{GeCo}_4(\text{CO})_{14}$ (by infrared spectrum). Attempts to grow crystals of $(\text{MeGeH})\text{GeCo}_4(\text{CO})_{13}$ failed.

The remaining solid fraction was dissolved in CH_2Cl_2 . The infrared spectrum of this solution showed mainly $\text{GeCo}_4(\text{CO})_{14}$ and a very small amount of $(\text{MeGeH})\text{GeCo}_4(\text{CO})_{13}$.

Comparing the results obtained in this run and that of [18] under the same conditions, this run produced mainly $(\text{MeGeH})\text{GeCo}_4(\text{CO})_{13}$ with a detectable amount of $(\text{MeGeH})_2\text{GeCo}_4(\text{CO})_{12}$, and no $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ was obtained.

Table 5.1 Infrared spectra of hexane extracts of Run 1

Bands	Intensity	Possible assignment
2098	w	$(\text{MeGeH})\text{GeCo}_4(\text{CO})_{13}$
2086	vw, sh	$(\text{MeGeH})_2\text{GeCo}_4(\text{CO})_{12}$?
2079	s	$\text{GeCo}_4(\text{CO})_{14}$
2067	vs	$(\text{MeGeH})\text{GeCo}_4(\text{CO})_{13}$
2061	vs	$\text{GeCo}_4(\text{CO})_{14}$
2056	vs, sh	$(\text{MeGeH})\text{GeCo}_4(\text{CO})_{13}$
2047	s	$(\text{MeGeH})\text{GeCo}_4(\text{CO})_{13}$
2030	m	$(\text{MeGeH})\text{GeCo}_4(\text{CO})_{13}$ + $\text{GeCo}_4(\text{CO})_{14}$
2021	m	$(\text{MeGeH})\text{GeCo}_4(\text{CO})_{13}$ + $\text{GeCo}_4(\text{CO})_{14}$
2004	mw	$\text{GeCo}_4(\text{CO})_{14}$
1847	mw	$\text{GeCo}_4(\text{CO})_{14}$

Due to the difficulty in separating the $(\text{MeGeH})\text{GeCo}_4(\text{CO})_{13}$ from $\text{GeCo}_4(\text{CO})_{14}$, the approximate yield of the $(\text{MeGeH})\text{GeCo}_4(\text{CO})_{13}$ was obtained by weight difference before and after the reaction.

Yield of Run 1 :

Weight of $\text{GeCo}_4(\text{CO})_{14}$ used = 0.848g

Total weight of involatile reaction mixture = 0.8895g

Increase in weight = 0.0415g

≈ 57% conversion

From the total incondensable gas measurement, the percentage conversion to $(\text{MeGeH})\text{GeCo}_4(\text{CO})_{13}$ = 63% assuming that the reaction proceeded via equation 5.1.



5.2.3 Other runs

Five other runs were carried out: two room temperature reactions (Runs 2 and 3) and three runs at 30–35°C (Run 4 to 6).

Runs 2 and 3:

The experimental procedures were as in Run 1 except that the reaction time was shorter. The experimental conditions and results are summarized in Table 5.2. The results obtained were very similar to Run 1 except for the absence of $(\text{MeGeH})_2\text{GeCo}_4(\text{CO})_{12}$.

Due to the difficulty in separating the $(\text{MeGeH})\text{GeCo}_4(\text{CO})_{13}$ from $\text{GeCo}_4(\text{CO})_{14}$, the yield is not known, but was estimated from the infrared spectra. Details of these runs are given in Table 5.2.

Table 5.2 Experimental details and results of Runs 2 and 3

Room temperature reaction	Run 2	Run 3
MeGeH_3 (mmol)	0.562	0.149
$\text{GeCo}_4(\text{CO})_{14}$ (g)	0.313	0.105
(mmol)	0.446	0.146
Reaction time (days)	70	42
$(\text{MeGeH})\text{GeCo}_4(\text{CO})_{13}$ (yield)	~10–20%	~10–20%

Run 4 (MeGeH_3 : $\text{GeCo}_4(\text{CO})_{14}$ = 2 : 1)

Experimental :

$\text{GeCo}_4(\text{CO})_{14}$ (0.247g, 0.354mmol) and hexane (10 ml) were loaded into a 50 ml ampoule at the Schlenk line. The ampoule was transferred to the vacuum line where the ampoule was degassed and frozen down by liquid nitrogen. MeGeH_3 (0.71 mmol) was condensed in and the ampoule sealed under vacuum. The reaction was carried out in an oil bath set at 35°C for a period of 11 days.

Observations and workup :

The red brown solution became darker in colour. After 11 days, only a small amount of dark red brown solid was observed.

As this run was only a preliminary study, the volatile fraction and the incondensable gases of this run were removed but not examined.

The involatile solid was extracted several times with 3-4 ml of hexane each time. The hexane extracts were combined together, the infrared spectrum of these showed the presence of $(\text{MeGeH})\text{GeCo}_4(\text{CO})_{13}$ and $\text{GeCo}_4(\text{CO})_{14}$. The remaining solid fraction consisted of $\text{GeCo}_4(\text{CO})_{14}$, and a small amount of $\text{GeCo}_4(\text{CO})_{13}$ (infrared bands at 2112 w, 2083 s, 2045 vs, 2029 m, 2008 vw [22]).

The hexane extracts were concentrated and cooled in the freezer. Small dark lumps of $(\text{MeGeH})\text{GeCo}_4(\text{CO})_{13}$ of reasonable purity were obtained. This purification cycle was repeated several times.

Yield of Run 4 :

$$\begin{aligned} (\text{MeGeH})\text{GeCo}_4(\text{CO})_{13} \text{ (impure)} &= 0.105\text{g} = 1.383 \text{ mmoles} \\ &= 39\% \end{aligned}$$

Run 5 (MeGeH_3 : $\text{GeCo}_4(\text{CO})_{14}$ = 1.7 : 1)

Experimental :

$\text{GeCo}_4(\text{CO})_{14}$ (0.26g, 0.383mmol) was reacted with MeGeH_3 (0.629mmol) in hexane (5ml) in a 20 ml ampoule for 16 days at a temperature of 30°C.

In this reaction, the reactants were shaken for a day and then heated at 30°C for 16 days with occasional shaking (about 4 to 5 times per day). A smaller sized ampoule (20 ml) was used. This procedure was adopted to prevent the formation of $\text{GeCo}_4(\text{CO})_{13}$ and to hasten the reaction of $\text{GeCo}_4(\text{CO})_{14}$ with MeGeH_3 .

Observations and workup :

Only a very small amount of solid was observed after 16 days at 30°C. The solution was dark brown in colour. The ampoule was cooled in ice water for several hours before opening (to crystallize the $\text{GeCo}_4(\text{CO})_{14}$ for easier separation on working up). Red needle shaped crystals appeared on cooling (found to be $\text{GeCo}_4(\text{CO})_{14}$). 0.402mmol of incondensable gas was measured, of which 51% was H_2 . Part of the volatiles were removed, leaving about 3 ml of solution in the ampoule. The infrared spectrum of the volatiles showed the presence of unreacted MeGeH_3 and hexane.

The small amount of hexane supernatant solution was separated from the solid fraction. The solid was extracted three times with about 2-3 ml of hexane. The extracts were added to the supernatant solution. Infrared spectrum of the remaining solid fraction (dissolved in CH_2Cl_2 and hexane) showed this to consist largely of $\text{GeCo}_4(\text{CO})_{14}$ with a very small amount of $(\text{MeGeH})\text{GeCo}_4(\text{CO})_{13}$. No $\text{GeCo}_4(\text{CO})_{13}$ or $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ was formed.

The infrared spectrum of the hexane extracts indicated only the presence of $\text{GeCo}_4(\text{CO})_{14}$ and $(\text{MeGeH})\text{GeCo}_4(\text{CO})_{13}$. It was very similar to

that showed in Table 5.1 except that no band at 2081 cm^{-1} was noted. Repeated purification as in Run 1 from CH_2Cl_2 and hexane yielded a small quantity of almost pure $(\text{MeGeH})\text{GeCo}_4(\text{CO})_{13}$.

Yield of Run 5 :

Weight of $(\text{MeHGe})\text{GeCo}(\text{CO})_{13}$ (nearly pure) = $0.127\text{g} = 0.167\text{mmol}$
 = 44%

Calculation of yield from incondensable data :

moles of MeGeH_3 used = moles $(\text{MeGeH})\text{GeCo}_4(\text{CO})_{13}$ produced
 = 51% of 0.402mmol
 = $0.211\text{ mmol} = 53\%$

Run 6 (MeGeH_3 : $\text{GeCo}_4(\text{CO})_{14} = 7 : 1$)

Experimental :

$\text{GeCo}_4(\text{CO})_{14}$ (0.082g , 0.117mmol) was reacted with MeGeH_3 (0.772 mmol) in hexane (10ml) in a 50ml ampoule. The reaction was allowed to proceed at room temperature for 90 days with occasional shaking and then heated at 30°C for 14 days.

Observations and workup :

After 90 days, no solid was observed and the solution has changed from a red brown to a yellow brown colour. After 14 days of gentle warming, the colour of the solution had become a lighter yellow.

0.302mmol of total incondensable gas was measured. 48% of this was H_2 , 52% CO . The volatile fraction was removed but not examined.

The infrared spectrum of involatile fraction (Table 5.3) consisted of $(\text{MeGeH})\text{GeCo}_4(\text{CO})_{13}$ and $(\text{MeGeH})_2\text{GeCo}_4(\text{CO})_{12}$. No $\text{GeCo}_4(\text{CO})_{14}$ remained.

Table 5.3 Infrared spectrum of the content (hexane solution) of Run 6

Bands (cm^{-1})	Int	Assignments
2098	w	$(\text{MeGeH})\text{Co}_4(\text{CO})_{13}$
2086	vw	$(\text{MeGeH})_2\text{Co}_4(\text{CO})_{12}$
2069	s	$(\text{MeGeH})\text{Co}_4(\text{CO})_{13}$
2059	s	$(\text{MeGeH})_2\text{Co}_4(\text{CO})_{12}$
2056	s	$(\text{MeGeH})\text{Co}_4(\text{CO})_{13}$
2047	s	$(\text{MeGeH})\text{Co}_4(\text{CO})_{13}$
2043	vs	$(\text{MeGeH})_2\text{Co}_4(\text{CO})_{12}$
2031	m	$(\text{MeGeH})\text{Co}_4(\text{CO})_{13}$
2021	ms	$(\text{MeGeH})\text{Co}_4(\text{CO})_{13}$
2011	m	$(\text{MeGeH})_2\text{Co}_4(\text{CO})_{12}$
1843	w	$(\text{MeGeH})\text{Co}_4(\text{CO})_{13}$

Yield of Run 6 :

The difficulty in separating the products meant that the percentage conversion into each products could only be estimated by the increase in weight after the reaction.

Weight of $\text{GeCo}_4(\text{CO})_{14}$ used = 82mg

Total weight of product mixture = 92mg

Increase in weight = 10mg

As no $\text{GeCo}_4(\text{CO})_{14}$ was left, it could be assumed that 0.117 mmol of $(\text{MeGeH})\text{GeCo}_4(\text{CO})_{13}$ had been formed.

Weight increase due to $(\text{MeGeH})\text{GeCo}_4(\text{CO})_{13}$ formation =

$$(60.6 \times 0.117)/1000 \text{ mg} = 7.1\text{mg}$$

Therefore 2.9mg of weight increase was due to $(\text{MeGeH})_2\text{GeCo}_4(\text{CO})_{12}$ formation = 0.05mmol of $(\text{MeGeH})_2\text{GeCo}_4(\text{CO})_{12}$

The amount of $(\text{MeGeH})\text{GeCo}_4(\text{CO})_{13}$ left after the di-substitution process = 0.07mmol

Proportion of $(\text{MeGeH})\text{GeCo}_4(\text{CO})_{13}$: $(\text{MeGeH})_2\text{GeCo}_4(\text{CO})_{12} \approx 60\% : 40\%$

From total incondensable gas measurement :

0.15mmol of H_2 was evolved = mmole of $MeGeH_3$ used

0.117mmol H_2 was due to the formation of $(MeGeH)GeCo_4(CO)_{13}$ and 0.033

mmol H_2 was due to the formation of $(MeGeH)_2GeCo_4(CO)_{12}$

Proportion of $(MeGeH)GeCo_4(CO)_{13}$: $(MeGeH)_2GeCo_4(CO)_{12} \approx 70\% : 30\%$

These two values are in general agreement as there is at least 10% error in the above calculations where a small weight and small amount of gas were being measured.

The reactions of $MeGeH_3$ and $GeCo_4(CO)_{14}$ are summarized in Table 5.4.

Table 5.4 Summary of the reaction of $GeCo_4(CO)_{14}$ with $MeGeH_3$

Run	$GeCo_4(CO)_{14}$ (mmol)	$MeGeH_3$ (^x)	Days	Products	Yield
<u>Sealed tube without heat</u>					
1	1.211	1	196	$(MeGeH)GeCo_4(CO)_{13}$ $(MeGeH)_2GeCo_4(CO)_{12}$	57% [@] , 63% [#] trace
2	0.446	1.3	70	$(MeGeH)GeCo_4(CO)_{13}$ $(MeGeH)_2GeCo_4(CO)_{12}$	10-20% [^] trace
3	0.146	1.3	42	$(MeGeH)GeCo_4(CO)_{13}$ $(MeGeH)_2GeCo_4(CO)_{12}$	10-20% [^] trace
<u>Sealed tube with heat</u>					
4	0.354	2	11	$(MeGeH)GeCo_4(CO)_{13}$ $GeCo_4(CO)_{13}$	39% [@]
5	0.371	1.7	16	$(MeGeH)GeCo_4(CO)_{13}$	44% [@] 53% [#]
6	0.117	7	90	$(MeGeH)GeCo_4(CO)_{13}$ $(MeGeH)_2GeCo_4(CO)_{12}$	60% [@] 70% [#] 40% [@] 30% [#]

^x number of times that of $GeCo_4(CO)_{14}$, [@] from actual weighing

[^] estimated from infrared spectra, [#] from incondensable data

5.3 Sealed tube reaction of EtGeH_3 with $\text{GeCo}_4(\text{CO})_{14}$

Run 1 (EtGeH_3 : $\text{GeCo}_4(\text{CO})_{14}$ = 1.3 : 1)

5.3.1 Experimental :

$\text{GeCo}_4(\text{CO})_{14}$ (0.3325g, 0.475mmol) and hexane (10 ml) were loaded into a 50 ml ampoule at the Schlenk line. The ampoule was transferred to the vacuum line where the gases were removed and then the ampoule frozen down by liquid nitrogen. EtGeH_3 (0.617mmol) was condensed in and the ampoule sealed under vacuum. The reaction was allowed to proceed in the dark, at room temperature for 65 days, and then reacted at 30°C for 5 days.

5.3.2 Observations and workup :

The contents of the ampoule, after 70 days, consisted of a reddish brown solid in a dark brown solution with a yellowish tint. The reaction was worked up. The incondensable gas was not measured, and the volatile fraction was not examined.

The supernatant solution was separated from the solid fraction. The supernatant solution (infrared spectrum in Table 5.5) was found to contain $(\text{EtGeH})\text{GeCo}_4(\text{CO})_{13}$ and $(\text{EtGeH})_2\text{GeCo}_4(\text{CO})_{12}$, both identified by comparing the infrared spectra with those of the methyl analogues (Section 5.7). The characterisation of both $(\text{EtGeH})\text{GeCo}_4(\text{CO})_{13}$ and $(\text{EtGeH})_2\text{GeCo}_4(\text{CO})_{12}$ are in Section 5.7.

The solid fraction was dissolved in hexane and infrared spectrum indicated this to be mainly $\text{GeCo}_4(\text{CO})_{14}$ along with a small amount of $(\text{EtGeH})\text{GeCo}_4(\text{CO})_{13}$ and $(\text{EtGeH})_2\text{GeCo}_4(\text{CO})_{12}$. The hexane was removed and the remaining solid was extracted 2 times with ~2 ml of hexane. The extracts were added to the supernatant solution. The hexane solution was concentrated and cooled in the freezer. The dark brown conglomerates obtained was found to be almost pure $(\text{EtGeH})\text{GeCo}_4(\text{CO})_{13}$. The remaining solution contained $(\text{EtGeH})\text{GeCo}_4(\text{CO})_{13}$,

$(\text{EtGeH})_2\text{GeCo}_4(\text{CO})_{12}$ and $\text{GeCo}_4(\text{CO})_{14}$ which could not be separated easily due to the small differences in solubility.

As no further products were formed, the reaction was likely to proceed via equations 5.3 and 5.4.

Yield of Run 1 :

$(\text{EtGeH})\text{GeCo}_4(\text{CO})_{13} = 0.1895\text{g} = 51\%$ based on $\text{GeCo}_4(\text{CO})_{14}$

The weight of the mixture of $(\text{EtGeH})\text{GeCo}_4(\text{CO})_{13}$, $(\text{EtGeH})_2\text{GeCo}_4(\text{CO})_{12}$ and $\text{GeCo}_4(\text{CO})_{14}$ was not known due to the contamination by grease.

Table 5.5 Infrared spectrum of the supernatant solution of EtGeH_3 with $\text{GeCo}_4(\text{CO})_{14}$ Run 1 :

Bands	Intensity	Assignment
2097	w	$(\text{EtGeH})\text{GeCo}_4(\text{CO})_{13}$
2086	vw	$(\text{EtGeH})_2\text{GeCo}_4(\text{CO})_{12}$
2079	m	$\text{GeCo}_4(\text{CO})_{14}$
2067	s	$(\text{EtGeH})\text{GeCo}_4(\text{CO})_{13}$
2061	sh ms	$\text{GeCo}_4(\text{CO})_{14}$
2056	s	$(\text{EtGeH})\text{GeCo}_4(\text{CO})_{13}$
2047	vs	$(\text{EtGeH})\text{GeCo}_4(\text{CO})_{13}$
2042	sh s	$(\text{EtGeH})_2\text{GeCo}_4(\text{CO})_{12}$
2030	m	$(\text{EtGeH})\text{GeCo}_4(\text{CO})_{13}$
2019	ms	$(\text{EtGeH})\text{GeCo}_4(\text{CO})_{13}$
2010	mw	$(\text{EtGeH})_2\text{GeCo}_4(\text{CO})_{12}$
1842	w	$(\text{EtGeH})\text{GeCo}_4(\text{CO})_{13}$

5.3.3 Run 2 (EtGeH_3 : $\text{GeCo}_4(\text{CO})_{14} = 1.3 : 1$)

$\text{GeCo}_4(\text{CO})_{14}$ (0.2154g, 0.308mmol) and hexane (10 ml) were loaded into a 50 ml ampoule at the Schlenk line. The ampoule was transferred to the vacuum line where the gases were removed and then the ampoule frozen down by liquid nitrogen. EtGeH_3 (0.398mmol) was condensed in

and the ampoule sealed under vacuum. The ampoule was wrapped in Al foil and shaken at room temperature for 70 days.

Observations and workup :

A reddish brown solid with dark brown solution was obtained. On working up, the total incondensable gas measured was 0.319mmol, of which 42% was H₂ and 58% CO.

The infrared spectrum of the volatile fraction showed only the presence of residual EtGeH₃ and hexane.

The involatile fraction was dissolved in hexane and infrared spectrum of the solution indicated mainly (EtGeH)GeCo₄(CO)₁₃ and GeCo₄(CO)₁₄. On removal of the solvent, the involatile solid was extracted several times with hexane (3-4ml each time) as in Run 1 until a very small amount of solid (EtGeH)GeCo₄(CO)₁₃ was left. The hexane extracts consisted of (EtGeH)GeCo₄(CO)₁₃ and a small amount of GeCo₄(CO)₁₃ [22] and GeCo₄(CO)₁₄ (shown by infrared spectrum). The extracts were combined, concentrated and cooled in the freezer. Small amounts of dark purple crystals of GeCo₄(CO)₁₃ were isolated on the first cooling in the freezer. Dark brown (almost black) 'droplet like' solids of (EtGeH)GeCo₄(CO)₁₃ were obtained on the subsequent purification cycles using a mixture of CH₂Cl₂/hexane.

Yields of Run 2 :

$$(\text{EtGeH})\text{GeCo}_4(\text{CO})_{13} = 0.096\text{g} = 0.124\text{mmol} = 40\%$$

$$\text{GeCo}_4(\text{CO})_{13} = 0.0112\text{g} = 0.017\text{mmol} = 5.6\%$$

Calculation of yield from incondensable data :

$$\text{moles of } (\text{EtGeH})\text{GeCo}_4(\text{CO})_{13} = 0.134\text{mmol} = 44\%$$

5.3.4 Run 3 (a) and 3(b)

The aim of these runs is to produce (EtGeH)₂GeCo₄(CO)₁₂ directly from GeCo₄(CO)₁₄ using a large excess of EtGeH₃.

Run 3(a) ($\text{GeCo}_4(\text{CO})_{14}$: EtGeH_3 = 1 ; 3)

$\text{GeCo}_4(\text{CO})_{14}$ (0.2327g, 0.332mmol) and hexane (10 ml) were loaded into a 50 ml ampoule at the Schlenk line. The ampoule was transferred to the vacuum line where the gases were removed and then the ampoule frozen down by liquid nitrogen. EtGeH_3 (1.329mmol) was condensed in and the ampoule sealed under vacuum. The ampoule was wrapped in Al foil and shaken at room temperature for 30 days.

A yellowish brown solution with brown solid material was obtained. On working up, the infrared spectrum of the solution showed a mixture of $(\text{EtGeH})\text{GeCo}_4(\text{CO})_{13}$ and $(\text{EtGeH})_2\text{GeCo}_4(\text{CO})_{12}$. This was confirmed by the incondensable gas measurement which showed that the total incondensable gas obtained was 0.924mmol, of which 49% was H_2 and 51% CO. If the reaction proceeded via eq 5.3 and 5.4, page 161, then the total gases expected would be 1.329mmol, H_2 : CO = 50% : 50%. Therefore the reaction was only 71% completed (equation 5.3 and 5.4).

Run 3(b)

The involatile fraction of run 3(a) was resealed with the volatile fraction collected in Run 3(a) plus an additional 0.332mmol of EtGeH_3 . The ampoule was shaken for 2 months and then heated at 30°C for 5 days.

A yellow solution was obtained. The incondensable gas was not measured and the volatile fraction showed only the presence of unreacted EtGeH_3 with hexane (by infrared spectrum). The infrared spectrum of the solution was that of pure $(\text{EtGeH})_2\text{GeCo}_4(\text{CO})_{12}$. On recrystallisation from CH_2Cl_2 /hexane, yellow rectangular plates of $(\text{EtGeH})_2\text{GeCo}_4(\text{CO})_{12}$ were obtained, but almost all of them were twinned.

Yield of Run 3 :

Weight of crystals of $(\text{EtGeH})_2\text{GeCo}_4(\text{CO})_{12} \approx 0.27\text{g} = 96\%$

The reactions of EtGeH_3 with $\text{GeCo}_4(\text{CO})_{14}$ are summarized in Table 5.6.

Table 5.6 Summary of the reaction of EtGeH_3 with $\text{GeCo}_4(\text{CO})_{14}$

Run	$\text{GeCo}_4(\text{CO})_{14}$ (mmoles)	EtGeH_3 (x^*)	Time (days)	Products	Yield
1	0.475	1.3	65 5dy/30°C	$(\text{EtGeH})\text{GeCo}_4(\text{CO})_{13}$ $(\text{EtGeH})_2\text{GeCo}_4(\text{CO})_{12}$	51% [@] not determined
2	0.308	1.3	70 shaking	$(\text{EtGeH})\text{GeCo}_4(\text{CO})_{13}$ $\text{GeCo}_4(\text{CO})_{13}$	40% [@] , 44% [#] 5.6% [@]
3(a)	0.332	3	30 shaking	$(\text{EtGeH})\text{GeCo}_4(\text{CO})_{13}$ $(\text{EtGeH})_2\text{GeCo}_4(\text{CO})_{12}$	71% [#]
3(b)	from 3(a)	4	60 5dy/30°C	$(\text{EtGeH})_2\text{GeCo}_4(\text{CO})_{12}$	

x^* = number of times that of $\text{GeCo}_4(\text{CO})_{14}$, [@] from weighing

[#] % conversion from total incondensable gas measurement

5.4 Reaction of PhGeH_3 with $\text{GeCo}_4(\text{CO})_{14}$ (sealed tube)

Run 1 (PhGeH_3 : $\text{GeCo}_4(\text{CO})_{14}$ = 1.5 : 1)

5.4.1 Experimental :

$\text{GeCo}_4(\text{CO})_{14}$ (0.309g, 0.441mmol), PhGeH_3 (0.0914g, 0.65mmol) and hexane (10 ml) were loaded into a 50 ml ampoule at the Schlenk line. The ampoule was transferred to the vacuum line where the ampoule was frozen down by liquid nitrogen and degassed. The ampoule was sealed under vacuum. The reaction was allowed to proceed in the dark, at room temperature for 120 days (4 months).

5.4.2 Observations and workup :

A brown solution with a brownish red solid was observed after 120 days.

On working up, the volatiles were removed but not examined.

The involatile fraction was extracted several times with hexane (3 to 4 ml each time). The brown coloured hexane extracts were added together and the infrared spectrum (Table 5.7) showed it to consist of mainly $\text{GeCo}_4(\text{CO})_{14}$ with a small amount of a new product identified as $(\text{PhGeH})\text{GeCo}_4(\text{CO})_{13}$ (by comparing the infrared bands with those of $(\text{MeGeH})\text{GeCo}_4(\text{CO})_{13}$). Characterisation of $(\text{PhGeH})\text{GeCo}_4(\text{CO})_{13}$ is in Section 5.7. Recrystallisation of the hexane extracts yielded a small amount of pure $(\text{PhGeH})\text{GeCo}_4(\text{CO})_{13}$. The remaining $(\text{PhGeH})\text{GeCo}_4(\text{CO})_{13}$ was difficult to separate from the $\text{GeCo}_4(\text{CO})_{14}$.

Table 5.7 Infrared spectrum of the hexane extracts of the reaction of PhGeH_3 and $\text{GeCo}_4(\text{CO})_{14}$, Run 1

Bands	Int.	Assignments
2097	w	$(\text{PhGeH})\text{GeCo}_4(\text{CO})_{13}$
2079	ms	$\text{GeCo}_4(\text{CO})_{14}$
2068	s	$(\text{PhGeH})\text{GeCo}_4(\text{CO})_{13}$
2061	vs	$\text{GeCo}_4(\text{CO})_{14}$
2056	vs	$(\text{PhGeH})\text{GeCo}_4(\text{CO})_{13}$
2048	vs	$(\text{PhGeH})\text{GeCo}_4(\text{CO})_{13}$
2043	sh s	$\text{GeCo}_4(\text{CO})_{14}$?
2031	ms	$(\text{PhGeH})\text{GeCo}_4(\text{CO})_{13}$
2020	ms	$(\text{PhGeH})\text{GeCo}_4(\text{CO})_{13}$
1847	w	$\text{GeCo}_4(\text{CO})_{14}$
1843	w	$(\text{PhGeH})\text{GeCo}_4(\text{CO})_{13}$

The remaining solid fraction was dissolved in hexane and infrared spectrum of this indicated the presence of mainly of $\text{GeCo}_4(\text{CO})_{14}$ and a very small amount of $(\text{PhGeH})\text{GeCo}_4(\text{CO})_{13}$ which could not be separated.

Yield of Run 1 :

Weight of clean $(\text{PhGeH})\text{GeCo}_4(\text{CO})_{13} = \sim 0.03\text{g} = \sim 8\%$

Weight of $(\text{PhGeH})\text{GeCo}_4(\text{CO})_{13} + \text{GeCo}_4(\text{CO})_{14} = 0.295\text{g}$

Total weight increase = $\sim 0.016\text{g}$

Therefore 0.016g weight increase = 0.131mmol of $(\text{PhGeH})\text{GeCo}_4(\text{CO})_{13}$

= $\sim 30\%$ yield

5.4.3 Other Runs :

Three other runs were carried out. Run 2 described a reaction using similar reactant ratio to Run 1, but the reaction was carried out in an oil bath at a temperature of 30°C . Run 3 had similar experimental conditions as Run 1, but with a higher PhGeH_3 to $\text{GeCo}_4(\text{CO})_{14}$ ratio. Run 4 described the reaction of $(\text{PhGeH})\text{GeCo}_4(\text{CO})_{13}$ with PhGeH_3 , which was an attempt to obtain the di-substituted product $(\text{PhGeH})_2\text{GeCo}_4(\text{CO})_{12}$. The details and results of these experiments are presented below.

Run 2 ($\text{PhGeH}_3 : \text{GeCo}_4(\text{CO})_{14} = 1.7 : 1$)

$\text{GeCo}_4(\text{CO})_{14}$ (0.205g , 0.29mmol), PhGeH_3 (0.075g , 0.49mmol) and hexane (10 ml) were sealed in a 50 ml ampoule as in Run 1. The ampoule was wrapped in Al foil and shaken at room temperature for 90 days (3 months). It was then heated at 30°C for 60 days (2 months).

The contents of the ampoule consisted of a brown solution with brown deposits on the side of the ampoule. The total incondensable gas measured 0.736mmol , of which 41% was H_2 and 59% CO (this indicated that 62% of PhGeH_3 was being consumed). The volatile fraction was condensed into a flask and the solution infrared spectrum of this showed the presence of hexane and PhGeH_3 .

On working up, the involatile fraction was separated into two fractions, a hexane soluble fraction and a CH_2Cl_2 soluble fraction.

Infrared spectrum (Table 5.8) of the hexane soluble product showed mainly $(\text{PhGeH})\text{GeCo}_4(\text{CO})_{13}$ and a new compound later characterised as $(\text{PhGeH})_2\text{GeCo}_4(\text{CO})_{12}$ (Section 5.7.2). No $\text{GeCo}_4(\text{CO})_{14}$ was indicated.

The CH_2Cl_2 fraction remained unidentified. Its infrared spectrum was very poorly resolved, and showed only weak bands of $(\text{PhGeH})\text{GeCo}_4(\text{CO})_{13}$ (present as contaminant).

Table 5.8 Infrared spectrum of hexane soluble fraction of Runs 2 and 4

Bands	Intensity		Possible assignments
	Run 2	Run 4	
2097	w	w	$(\text{PhGeH})\text{GeCo}_4(\text{CO})_{13}$
2085	vw	mw	$(\text{PhGeH})_2\text{GeCo}_4(\text{CO})_{12}$
2068	ms	s	$(\text{PhGeH})\text{GeCo}_4(\text{CO})_{13}$
2057	s	ms	$(\text{PhGeH})\text{GeCo}_4(\text{CO})_{13}$
2061	s	vs	$(\text{PhGeH})_2\text{GeCo}_4(\text{CO})_{12}$
2048	sh vs	s	$(\text{PhGeH})\text{GeCo}_4(\text{CO})_{13}$
2043	vs	vs	$(\text{PhGeH})_2\text{GeCo}_4(\text{CO})_{12}$
2030	m	mw	$(\text{PhGeH})\text{GeCo}_4(\text{CO})_{13}$
2020	ms	s	$(\text{PhGeH})\text{GeCo}_4(\text{CO})_{13}$ + $(\text{PhGeH})_2\text{GeCo}_4(\text{CO})_{12}$
2008	m	ms	$(\text{PhGeH})_2\text{GeCo}_4(\text{CO})_{12}$
2004	sh m		$(\text{PhGeH})_2\text{GeCo}_4(\text{CO})_{12}$?
1842	w		$(\text{PhGeH})\text{GeCo}_4(\text{CO})_{13}$

Yield of Run 2 :

$$(\text{PhGeH})\text{GeCo}_4(\text{CO})_{13} = 0.074\text{g} (0.091\text{mmol}) = 24\%$$

$$\text{Mixture of } (\text{PhGeH})\text{GeCo}_4(\text{CO})_{13} \text{ and } (\text{PhGeH})_2\text{GeCo}_4(\text{CO})_{12} = \sim 0.26\text{g}$$

$$\text{CH}_2\text{Cl}_2 \text{ fraction} = \sim 0.05\text{g (unidentified).}$$

Run 3 Ratio of PhGeH_3 : $\text{GeCo}_4(\text{CO})_{14}$ = 3 : 1

$\text{GeCo}_4(\text{CO})_{14}$ (0.205g, 0.29mmol), PhGeH_3 (0.120g, 0.867mmol) and hexane (10 ml) were reacted in a 50 ml ampoule as in Run 1 for 120 days (4 months) at room temperature.

A brown solution and a very small amount of brownish red solid was observed after 120 days of reaction.

The volatile fraction was removed and its infrared spectrum showed only the presence of hexane and PhGeH_3 . The incondensable gas measurement was not taken due to a leak in the Toepler pump.

The involatile fraction was extracted several times with small amounts of hexane (3-4 ml each time). The infrared spectrum of these hexane extracts showed the presence of $(\text{PhGeH})\text{GeCo}_4(\text{CO})_{13}$ and $(\text{PhGeH})_2\text{GeCo}_4(\text{CO})_{12}$ as in Run 2, (Table 5.8). The infrared spectrum of the remaining solid fraction was very similar to that of the hexane extracts except for the presence of a small amount of $\text{GeCo}_4(\text{CO})_{14}$.

The hexane extracts were combined and recrystallised. Pure $(\text{PhGeH})\text{GeCo}_4(\text{CO})_{13}$ was obtained as a light orange solid. The amount of pure $(\text{PhGeH})\text{GeCo}_4(\text{CO})_{13}$ decreased on subsequent recrystallisation from the supernatant solution.

Yield of Run 3 :

Pure $(\text{PhGeH})\text{GeCo}_4(\text{CO})_{13}$ = 0.1179g (0.16 mmoles) = 55%

The yield of $(\text{PhGeH})_2\text{GeCo}_4(\text{CO})_{12}$ could not be obtained by weighing, it was estimated to be about 10% from the infrared spectrum.

Run 4 (PhGeH₃ : (PhGeH)GeCo₄(CO)₁₃ = 3.4 : 1)

(PhGeH)GeCo₄(CO)₁₃ (0.171g, 0.208mmol), PhGeH₃ (0.119g, 0.78 mmol) and hexane (10 ml) were reacted in a 50 ml ampoule as in Run 1 for 90 days at room temperature with constant shaking. The ampoule was then heated at 30°C for 60 days.

Like run 2, a brown solution with a brown deposit on the side of the ampoule was noted. On working up, the total incondensable gas measured was 0.362 mmol of which 46% was H₂ and 54% CO. A hexane soluble and a CH₂Cl₂ soluble fraction was obtained.

The infrared spectrum of the hexane soluble fraction (Table 5.8) showed the presence of (PhGeH)GeCo₄(CO)₁₃ and (PhGeH)₂GeCo₄(CO)₁₂. 'Recrystallisation' from CH₂Cl₂/hexane yielded a small amount of pure (PhGeH)₂GeCo₄(CO)₁₂ (yellow coloured powder). The rest of the solution was too difficult to separate into components.

The CH₂Cl₂ soluble products remained uncharacterised. A poorly resolved infrared spectrum showing bands at 2068 m, 2056 s, 2042 vs, and 2012 ms was obtained. However, these bands corresponded to the strong bands of (PhGeH)GeCo₄(CO)₁₃ and (PhGeH)₂GeCo₄(CO)₁₂ (Tables 5.14 and 5.19).

Yield of Run 4 :

(PhGeH)₂GeCo₄(CO)₁₂ = ~0.02g = 0.021 mmol = ~10%

mixture of (PhGeH)GeCo₄(CO)₁₃ and (PhGeH)₂GeCo₄(CO)₁₂ = ~0.15g

unidentified CH₂Cl₂ product = ~0.02g

From the incondensable gas measurement, the percentage conversion of (PhGeH)GeCo₄(CO)₁₃ to (PhGeH)₂GeCo₄(CO)₁₂ was 79%.

The reactions of PhGeH_3 with $\text{GeCo}_4(\text{CO})_{14}$ are summarized in Table 5.9.

Table 5.9 Summary of the reactions of PhGeH_3 with $\text{GeCo}_4(\text{CO})_{14}$

Run	$\text{GeCo}_4(\text{CO})_{14}$ (mmoles)	PhGeH_3 ($\times$)	Time (days)	Temperature	Products	Yield
1	0.441	1.5	120	room	$(\text{PhGeH})\text{GeCo}_4(\text{CO})_{13}$	~30% [@]
2	0.29	1.7	90 60	room 30°C	$(\text{PhGeH})\text{GeCo}_4(\text{CO})_{13}$ $(\text{PhGeH})_2\text{GeCo}_4(\text{CO})_{12}$ + unidentified product	24% [@] not known
3	0.29	3	120	room	$(\text{PhGeH})\text{GeCo}_4(\text{CO})_{13}$ $(\text{PhGeH})_2\text{GeCo}_4(\text{CO})_{12}$	55% [@] 10% [^]
4	0.208*	~4	90 60	room 30°C	$(\text{PhGeH})_2\text{GeCo}_4(\text{CO})_{12}$ + unidentified product	~79% [#]

keys : [@] from weighing , [^] from IR, [#] from incondensable gas measurement,
^x number of times that of $\text{GeCo}_4(\text{CO})_{14}$, *0.208 mmol of $(\text{PhGeH})\text{GeCo}_4(\text{CO})_{13}$

5.5 Reaction of $(\text{EtGeH})\text{GeCo}_4(\text{CO})_{13}$ with PhGeH_3 (open tube)

5.5.1 Experimental :

At the Schlenk line, $(\text{EtGeH})\text{GeCo}_4(\text{CO})_{13}$ (0.1495g, 0.193mmol), PhGeH_3 (0.0605g, 0.430mmol) and hexane (10 ml) were loaded into a 20ml reaction tube fitted with a greaseless tap. All gases were removed at the vacuum line at -196°C . The mixture was allowed to react at room temperature for 35 days, then heated at 30°C for 156 days. Incondensable gases were measured at intervals.

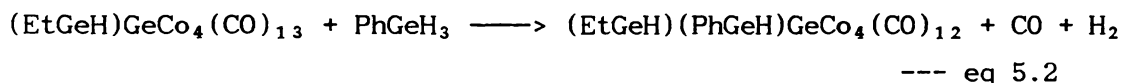
5.5.2 Results :

A brown solution with some brown solid was obtained at the end of the reaction. The incondensable gas measurements are presented in Table 5.10 and Fig 5.1.

Table 5.10 Incondensable gas measurement of the reaction of
 $(\text{EtGeH})\text{GeCo}_4(\text{CO})_{13}$ with PhGeH_3

Days	moles gases (mmoles)	total gases (mmoles)	composition (%)
32	0.116	0.116	52% H_2 , 48% CO
77	0.143	0.259	40% H_2 , 60% CO
81	0.024	0.283	not measured
91	0.019	0.302	not measured
122	0.019	0.321	not measured
156	0.008	0.329	not measured

The reaction expected was the replacement of the remaining bridging CO by a bridging PhGeH group via:

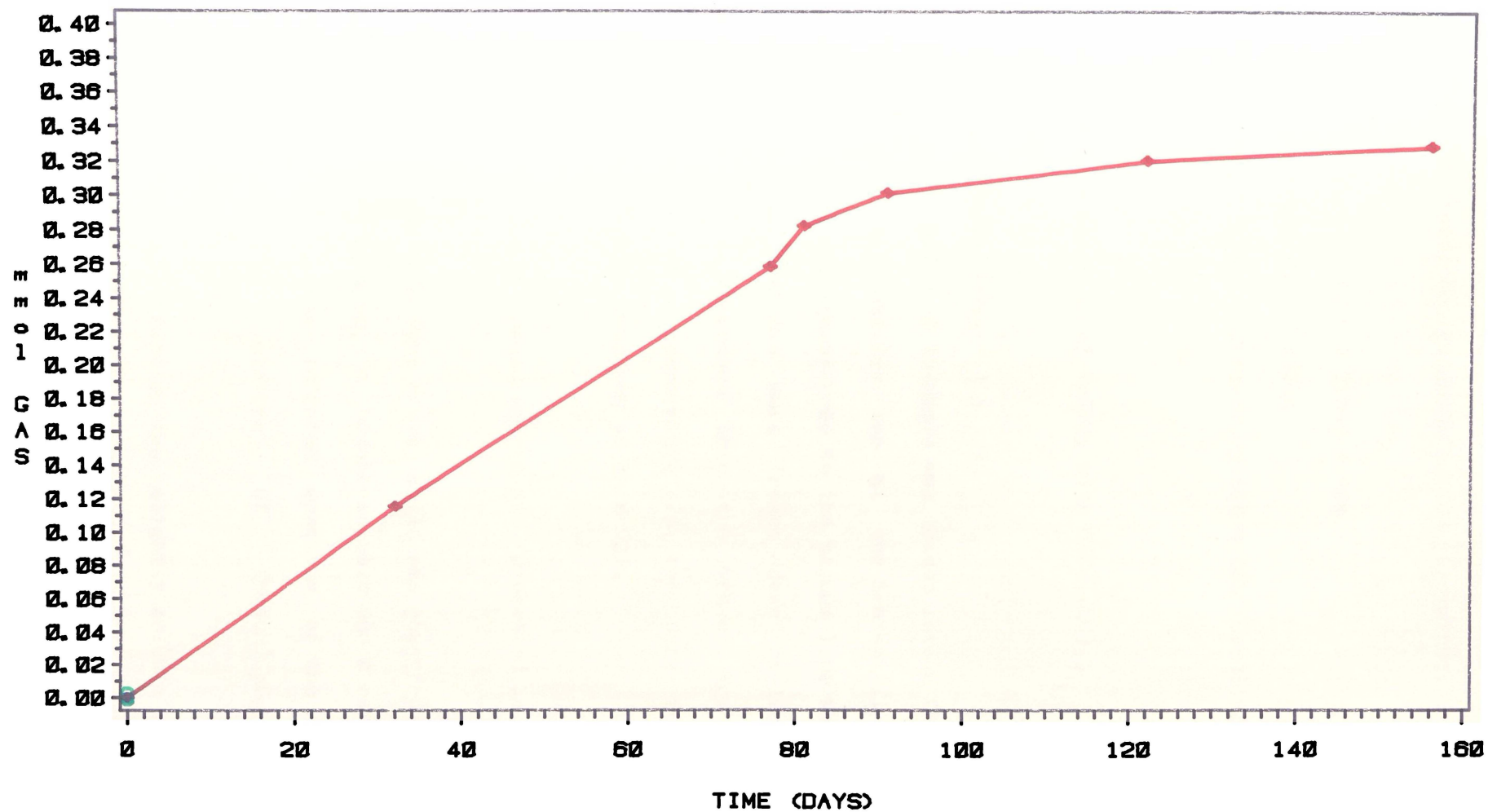


Therefore the incondensable gas expected was 0.385mmol with H_2 : CO = 1 : 1. The incondensable gas readings give an average of 46% H_2 and 54% CO with a total of 0.329mmol of gas. Considering the small amount of gas measured (therefore higher errors incurred), this figure is reasonable to assume that the expected reaction had occurred.

On working up, two involatile products were obtained: - a hexane soluble light brown compound and a dark brown hexane insoluble and CH_2Cl_2 soluble compound.

The hexane soluble fraction, on purification by recrystallisation from CH_2Cl_2 /hexane, yielded a yellow compound. This was later characterised as $(\text{EtGeH})(\text{PhGeH})\text{GeCo}_4(\text{CO})_{12}$ (characterisation in Section 5.7).

Figure 5.1
Incondensable Gas Evolution Of The Reaction
Of $(\text{EtGeH})\text{GeCo}_4(\text{CO})_{13} + \text{PhGeH}_3$



The CH_2Cl_2 soluble fraction has an infrared spectrum with bands at 2050cm^{-1} s (sh), 2039cm^{-1} s, 2002cm^{-1} ms, 1830cm^{-1} vw. It could not be further characterised. No $(\text{EtGeH})\text{GeCo}_4(\text{CO})_{13}$ remained.

Yield :

$(\text{EtGeH})(\text{PhGeH})\text{GeCo}_4(\text{CO})_{12} = 0.1196\text{g} = 69\%$

CH_2Cl_2 soluble compound = 0.0381g

from incondensable gas measurement, yield = 85% (assuming $\text{H}_2 = 50\%$)

5.6 The open tube reaction of MeGeH_3 with $\text{GeCo}_4(\text{CO})_{14}$

5.6.1 Experimental :

Run 1 ($\text{MeGeH}_3 : \text{GeCo}_4(\text{CO})_{14} = 1.4 : 1$)

$\text{GeCo}_4(\text{CO})_{14}$ (0.3064g, 0.438mmol) was loaded into a 250 ml reaction vessel fitted with a greaseless tap at the Schlenk line. Hexane (30 ml) was added. This was transferred to the vacuum line where all gases were evacuated. The contents were frozen down by liquid nitrogen. MeGeH_3 (0.613mmol) was condensed into the vessel. The contents were left to react at room temperature in the dark for 145 days. Incondensable gases were measured at intervals.

5.6.2 Results :

The incondensable gas measurements are presented as in Table 5.11 and Fig 5.2.

A brown solution with some brown solid was observed at the end of the reaction. On working up, a hexane soluble and a hexane insoluble fraction were obtained. The infrared spectrum of the hexane soluble fraction showed a mixture of $(\text{MeGeH})\text{GeCo}_4(\text{CO})_{13}$ and $(\text{MeGeH})_2\text{GeCo}_4(\text{CO})_{12}$.

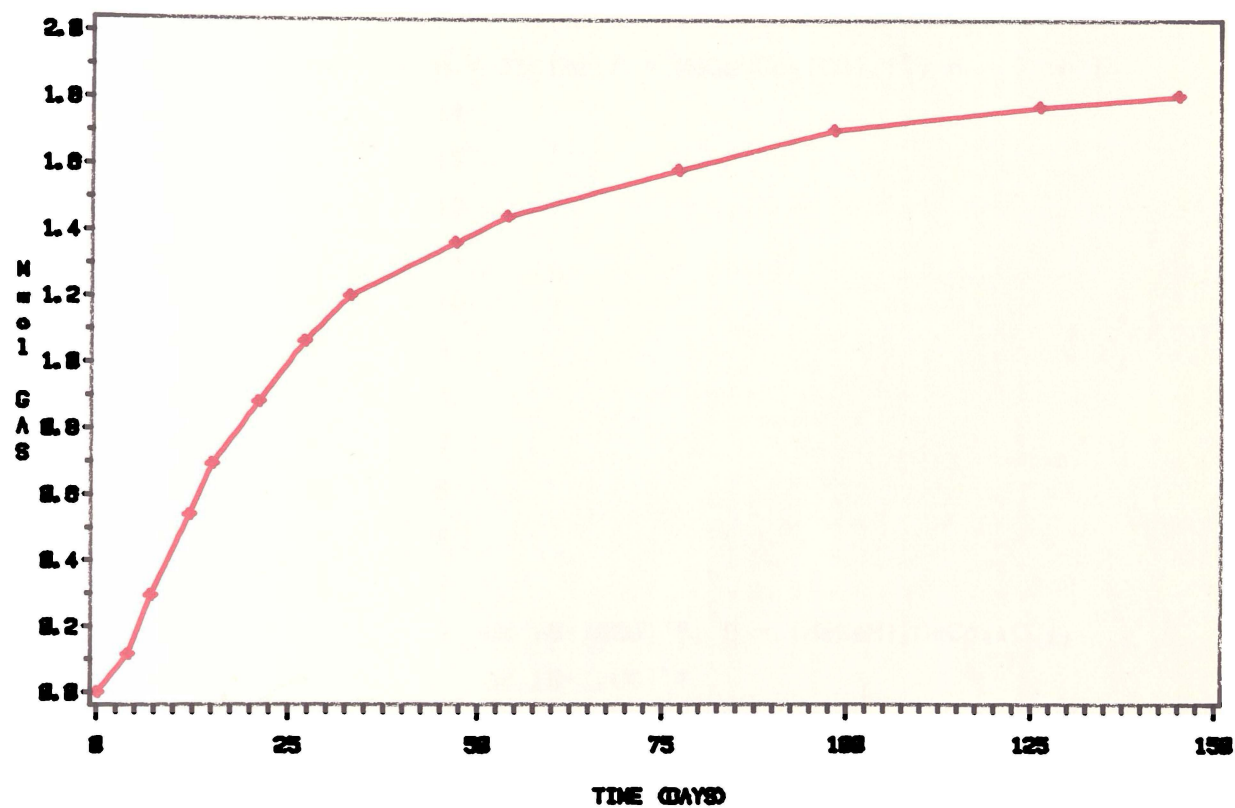
The hexane insoluble fraction was slightly soluble in CH_2Cl_2 . Its infrared spectrum showed $(\text{MeGeH})\text{GeCo}_4(\text{CO})_{13}$ and $(\text{MeGeH})_2\text{GeCo}_4(\text{CO})_{12}$.

Any new products present were either very insoluble in CH_2Cl_2 or were heavily contaminated by $(\text{MeGeH})\text{GeCo}_4(\text{CO})_{13}$ and $(\text{MeGeH})_2\text{GeCo}_4(\text{CO})_{12}$. A mass spectrum of this fraction gave the highest envelope at $m/e = 865$ (Table 5.12). This and a series of envelopes that followed were remarkably similar to that of $\text{MeGe}_2\text{Co}_5(\text{CO})_{15}$ in Chapter Seven except that the envelopes were very weak in this spectrum. The absence of infrared bands belonging to $\text{MeGe}_2\text{Co}_5(\text{CO})_{15}$ and the failure to recrystallise it for further characterisation leaves this compound uncharacterised.

Table 5.11 Incondensable gas measurement of the open tube reaction of $\text{GeCo}_4(\text{CO})_{14}$ with MeGeH_3 , Run 1

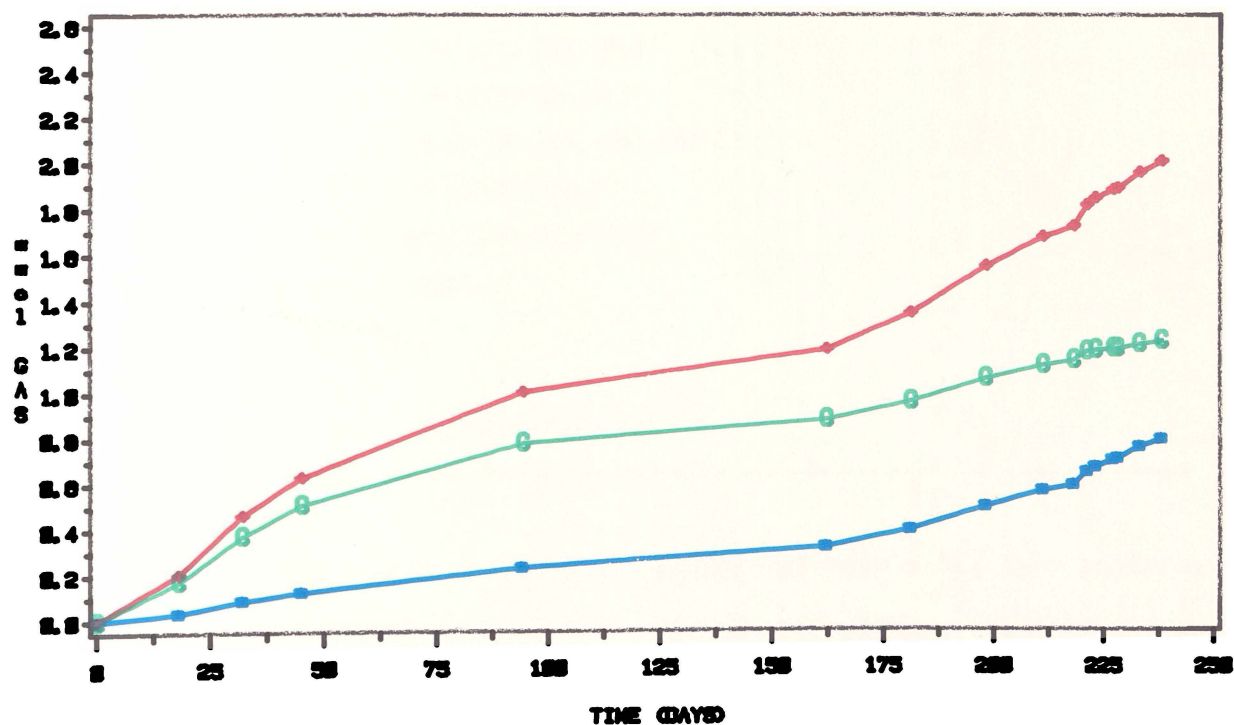
Day	Gas evolved (mmol)	Cumulative gas (mmol)
4	0.116	0.116
7	0.180	0.296
12	0.245	0.541
15	0.154	0.695
21	0.188	0.883
27	0.182	1.065
33	0.137	1.202
47	0.163	1.365
54	0.081	1.446
77	0.140	1.586
98	0.121	1.707
126	0.073	1.780
145	0.031	1.811

Fig 5. 2
Incondensables From $\text{MeGaH}_3 + \text{GaCo}(\text{CO})_4$
Run 1



TOTAL GAS = —

Run 2



TOTAL GAS = —
 HYDROGEN = —
 CARBON MONOXIDE = —

Table 5.12 Mass spectrum of the CH_2Cl_2 soluble fraction from the open tube reaction of $\text{GeCo}_4(\text{CO})_{14}$ with MeGeH_3 , Run 1

m/e	Int	Possible assignments
865-868	vw	$n = 15$ for $\text{P} = \text{MeGe}_2\text{Co}_5(\text{CO})_n]^+$, $n = 0$ to 15
835-842	vw	14
810-818	w	13
788-790	vw	12
758-763	vw	11
728-737	w	10
701-712	w	9
672-683	w	8
641-657	w	7
614-626	w	6
587-597	w	5
558-569	vw	4
530-542	vw	3 or $[\text{B}-10\text{CO}]^{+?}$, $\text{B} = (\text{MeGeH})_2\text{GeCo}_4(\text{CO})_{12}$
500-517	vw	2 or $[\text{B}-11\text{CO}]^{+?}$
472-489	w	1
443-459	m	0
385-404	mw	$[\text{P}-15\text{CO}-\text{Co}]^+$ or $[\text{B}-12\text{CO}-\text{Co}]^{+?}$, $[\text{B}-12\text{CO}-\text{Ge}-\text{Me}-\text{H}]^{+?}$
350-358	s	$[\text{P}-14\text{Co}-2\text{Co}-\text{Me}]^+$ or $[\text{B}-12\text{CO}-2\text{Co}]^{+?}$
340-350	w	$[\text{B}-12\text{CO}-2\text{Co}-\text{Me}]^+$
328-337	w	$[\text{P}-15\text{CO}-2\text{Co}]^+$
311-325	w	$[\text{P}-15\text{CO}-2\text{Co}-\text{Me}]^+$
298-308	w	$[\text{P}-15\text{CO}-\text{Ge}-\text{Me}]^+$
282-297	w	$[\text{B}-12\text{CO}-2\text{Ge}-2\text{Me}-2\text{H}]^{+?}$
270-281	mw	$[\text{P}-15\text{CO}-3\text{Co}]^+$
255-270	mw	$[\text{P}-15\text{CO}-3\text{Co}-\text{Me}]^+$
242-255	mw	$[\text{GeCo}_3]^+$
230-240	ms	?
212-228	ms	?
190-206	s	$[\text{P}-15\text{CO}-3\text{Co}-\text{Ge}]^+$

Only the envelopes at 530-542 and 500-517 have a Ge_3 type pattern, these could be due to ions from $(\text{MeGeH})_2\text{GeCo}_4(\text{CO})_{12}$, as this was an

impurity in this fraction (as seen in the infrared spectrum). But this assignment is tentative due to the absence of envelope higher than 530-542.

5.6.3 Other run :

One other run was carried out using $\text{GeCo}_4(\text{CO})_{14}$ (0.3271g, 0.467mmol), MeGeH_3 (0.588mmol) and hexane (30ml). The experimental procedures were as in Run 1, except that further MeGeH_3 (1.13mmol) was added after 226 days of reaction. Small samples were drawn for infrared studies as the reaction proceeded.

A yellowish brown solution and a brown solid were observed at the end of the reaction. The incondensable gas measurements are presented in Table 5.13.

As only very small amount of sample was drawn for infrared spectra (less than 0.3ml each time) this would have little effect on the reaction.

On working up, three fractions were obtained :- a hexane soluble fraction, a hexane insoluble but slightly CH_2Cl_2 soluble fraction (as observed in run 1) and a small amount of insoluble solid (assumed as decomposed material). The hexane soluble fraction consisted of only $(\text{MeGeH})_2\text{GeCo}_4(\text{CO})_{12}$.

The infrared spectrum of the CH_2Cl_2 fraction was very poorly resolved, showing only a broad band at 2042 cm^{-1} . The mass spectrum of this fraction was also poorly resolved. The highest m/e peak was at m/e 735 which could either be that of $[(\text{MeGeH})_2\text{GeCo}_4(\text{CO})_9]^+$ or the parent ion of $(\text{MeGeH})\text{GeCo}_4(\text{CO})_{13}$. Weak envelopes due to successive loss of 28-30 m/e units were observed, but no definite Ge pattern could be assigned due to overlapping of envelopes and poor resolution of the spectrum.

Table 5.13 Incondensable gas measurements from the open tube reaction of $\text{GeCo}_4(\text{CO})_{14}$ with MeGeH_3 , Run 2

Day	(all gas measured in mmol)				Peaks ratio
	H_2	CO	total	cumulative	
18	0.034	0.171	0.205	0.205	S(6.4), M(1)
32	0.053	0.203	0.256	0.461	S(5.5), M(1)
45	0.035	0.131	0.166	0.627	S(2.9),M(1),B(.3)
94	0.105	0.267	0.372	0.999	S(2.7),M(1),B(.36)
162	0.084	0.101	0.185	1.184	S(0.7),M(1),B(.5)
181	0.078	0.081	0.159	1.343	S(0.6),M(1),B(.6)
198	0.102	0.102	0.204	1.547	
211	0.070	0.057	0.127	1.674	M(1),B(1.1)
218	0.023	0.022	0.045	1.719	M(1), B(3.1)
221	0.056	0.037	0.093	1.812	
223	0.023	0.007	0.030	1.842	
227	0.031 ₊	0.005	0.036	1.878	
228	0.006	0.001	0.007	1.885	M(1),B(12)
233	0.051 ₊	0.019	0.070	1.955	
238	0.034	0.014	0.048	2.003	B
238	0.785	1.218	2.003	2.003	

Note : Peak ratio is obtained by the peak height of each compound against that of $(\text{MeGeH})\text{GeCo}_4(\text{CO})_{13}$, M in the hexane soluble fraction.

peak used : M = $(\text{MeGeH})\text{GeCo}_4(\text{CO})_{13}$: 2098 cm^{-1}

B = $(\text{MeGeH})_2\text{GeCo}_4(\text{CO})_{12}$: 2086 cm^{-1}

S = $\text{GeCo}_4(\text{CO})_{14}$: 2079 cm^{-1}

Yield of Run 2 :

Weight of $(\text{MeGeH})_2\text{GeCo}_4(\text{CO})_{12}$ = $\sim 0.3\text{g} \approx 78\%$

Weight of CH_2Cl_2 soluble = $\sim 0.02\text{g}$

Weight of CH_2Cl_2 insoluble material = $\sim 0.02\text{g}$

Fig 5.3 Infrared spectrum of $(\text{MeGeH})\text{GeCo}_4(\text{CO})_{13}$ (hexane)

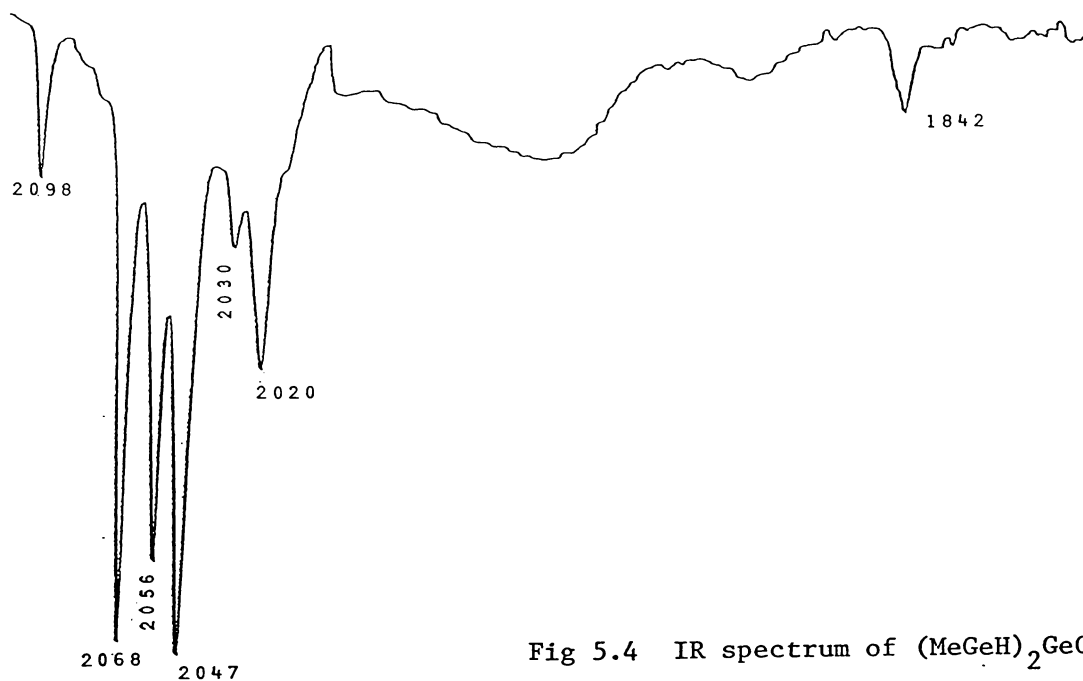


Fig 5.4 IR spectrum of $(\text{MeGeH})_2\text{GeCo}_4(\text{CO})_{12}$ (hexane)

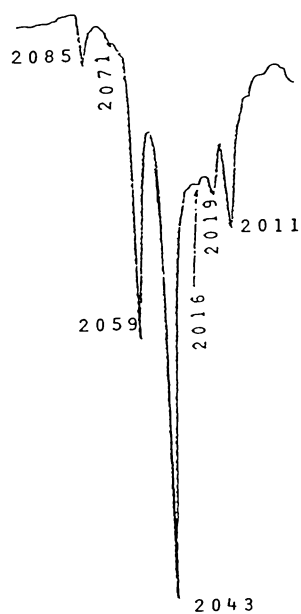
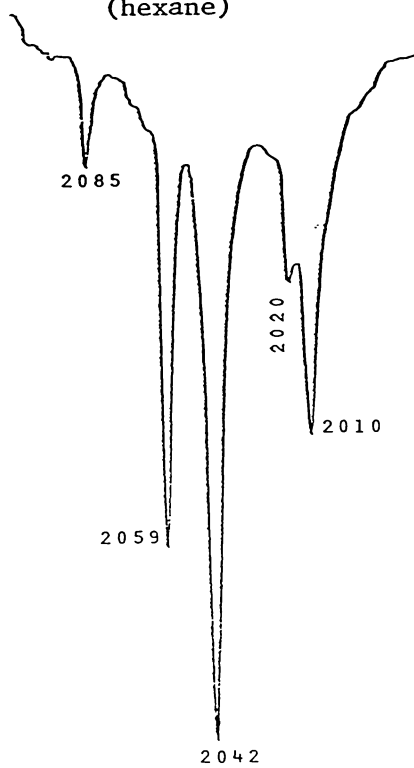


Fig 5.5 IR spectrum of $(\text{EtGeH})(\text{PhGeH})\text{GeCo}_4(\text{CO})_{12}$ (hexane)

5.7 Characterisation of $(\text{RGeH})\text{GeCo}_4(\text{CO})_{13}$ and $(\text{RGeH})_2\text{GeCo}_4(\text{CO})_{12}$

5.7.1 $(\text{RGeH})\text{GeCo}_4(\text{CO})_{13}$

5.7.1.1 *Infrared spectrum :*

The incorporation of a single RGeH group into $\text{GeCo}_4(\text{CO})_{14}$ lowers the symmetry from C_2 to C_s . Twelve terminal CO bands (6A' and 6A'') and one bridging CO bands are predicted, but all $(\text{RGeH})\text{GeCo}_4(\text{CO})_{13}$ showed only 7 bands in solution, as shown in Table 5.14 and Fig 5.2.

Table 5.14 Infrared spectra of $(\text{RGeH})\text{GeCo}_4(\text{CO})_{13}$
compared to $(\text{Me}_2\text{Ge})\text{GeCo}_4(\text{CO})_{13}$ [81]

R = Me	R = Et	R = Ph	cf $(\text{Me}_2\text{Ge})\text{GeCo}_4(\text{CO})_{13}$
2098w	2097w	2097w	2096w
			2093w
2068vs	2068vs	2068vs	2064s
2056s	2057s	2056s	2054ms
			2049ms sh
2047vs	2046vs	2048vs	2043vs
2030mw	2030mw	2031mw	2026m
2020m	2019m	2020m	2021m sh
			2017ms
			2003mw
1842w	1842w	1842w	1843w

5.7.1.2 *Mass Spectrum :*

The mass spectra of $(\text{RGeH})\text{GeCo}_4(\text{CO})_{13}$ compounds all showed a parent ion envelope at 770–782 for R = Me, 771–796 for R = Et and 820–823 for R = Ph. A systematic loss of all 13 CO's before the loss

of any other groups was observed. For well resolved mass spectra of these compounds, a clear Ge_2 isotope pattern was observed. Overlapping weak envelopes of $\text{GeCo}_4(\text{CO})_n^+$ ($n = 8$ to 0) was also observed. Details of the mass spectrum of each compound were presented below :

$(\text{MeGeH})\text{GeCo}_4(\text{CO})_{13}$: The mass spectrum of $(\text{MeGeH})\text{GeCo}_4(\text{CO})_{13}$ was collected by Foster [18] and therefore was not repeated in this work. His spectrum gave a parent ion envelope at m/e 770-782 followed by a series of envelopes corresponding to the loss of all 13 CO's. As $(\text{MeGeH})\text{GeCo}_4(\text{CO})_{13}$ was not isolated pure, the mass spectrum also showed envelopes due to $\text{GeCo}_4(\text{CO})_n$ ($n = 0$ to 14).

$(\text{EtGeH})\text{GeCo}_4(\text{CO})_{13}$: the mass spectrum of $(\text{EtGeH})\text{GeCo}_4(\text{CO})_{13}$ (Table 5.15) was poorly resolved. This was likely to be due to a fault in the mass spectrometer. The first CH_3 loss was observed after a consecutive loss of 8 CO's and this was unexpected. After this, two series of Ge_2 type envelopes were seen : one of $[\text{P}-n\text{CO}]^+$ and the other of $[\text{P}-n\text{CO}-\text{CH}_3]^+$. The loss of the whole C_2H_5 fragment occurred after the loss of all the 13 CO's. Overlap due to $\text{GeCo}_4(\text{CO})_n^+$ ($n = 7$ to 0) was also observed.

Table 5.15 Mass spectrum of $(\text{EtGeH})\text{GeCo}_4(\text{CO})_{13}$

m/e	Int	Possible assignments
771-796	w	$[\text{P}]^+$ where $\text{P} = (\text{EtGeH})\text{GeCo}_4(\text{CO})_{13}$
746-755	w	$[\text{P-CO}]^+$
682-695	w	$[\text{P-3CO}]^+$
635-645	w	$[\text{P-5CO}]^+$
600-615	w	$[\text{P-6CO}]^+$
580-592	w	$[\text{P-7CO}]^+$
554-556	w	$[\text{P-8CO}]^+$
538-548	w	$[\text{P-8CO-Me}]^+$
520-528	w	$[\text{P-9CO}]^+$
504-514	m	$[\text{P-9CO-Me}]^+$, $\text{GeCo}_4(\text{CO})_7^+$
490-503	m	$[\text{P-10CO}]^+$
475-485	mw	$[\text{P-10CO-Me}]^+$, $\text{GeCo}_4(\text{CO})_6^+$
469-473	mw	$[\text{P-11CO}]^+$
444-456	mw	$[\text{P-11CO-Me}]^+$, $\text{GeCo}_4(\text{CO})_5^+$
440-447	mw	$[\text{P-12CO}]^+$
422-432	mw	$[\text{P-12CO-Me}]^+$, $\text{GeCo}_4(\text{CO})_4^+$
405-419	mw	$[\text{P-13CO}]^+$
397-400	w	$[\text{P-13CO-Me}]^+$, $\text{GeCo}_4(\text{CO})_3^+$
362-370	m	$\text{GeCo}_4(\text{CO})_2^+$
343-355	m	$[\text{P-13CO-Co}]^+$
332-340	m	$\text{GeCo}_4(\text{CO})^+$
313-323	m	$[\text{P-13CO-Et}]^+$
302-310	ms	GeCo_4^+
285-300	ms	$[\text{P-13CO-2Co}]^+$
260-269	ms	$[\text{P-13CO-Et-2Co}]^+$

$(\text{PhGeH})\text{GeCo}_4(\text{CO})_{13}$: the mass spectrum (Table 5.16) shows a weak parent ion envelope at 820-823, followed by the loss of 13 CO groups. This is quite similar to that of $(\text{MeGeH})\text{GeCo}_4(\text{CO})_{13}$. The fragmentation of the phenyl group did not appear until all the CO's were lost. The $\text{Ge}_2\text{Co}_4(\text{CO})_n^+$ ($n = 13$ to 0) metal skeleton constitutes the strongest

envelopes of the spectrum. Overlapping by weak envelopes due to $\text{GeCo}_4(\text{CO})_n^+$ ($n = 8$ to 0) was observed.

Table 5.16 Mass Spectrum of $(\text{PhGeH})\text{GeCo}_4(\text{CO})_{13}$

m/e	Int	Possible assignments
818-822	mw	P^+ $\text{P} = (\text{PhGeH})\text{GeCo}_4(\text{CO})_{13}$
792-798	m	$[\text{P-CO}]^+$
762-772	s	$[\text{P-2CO}]^+$
734-744	ms	$[\text{P-3CO}]^+$
706-714	mw	$[\text{P-4CO}]^+$
678-688	mw	$[\text{P-5CO}]^+$
652-658	vw	$[\text{P-6CO}]^+$
622-632	m	$[\text{P-7CO}]^+$
594-604	s	$[\text{P-8CO}]^+$
568-576	m	$[\text{P-9CO}]^+$
532-548	m	$[\text{P-10CO}]^+$, $\text{GeCo}_4(\text{CO})_8^+$
512-520	m	$[\text{P-11CO}]^+$
502-510	w	$\text{GeCo}_4(\text{CO})_7^+$
478-492	m	$[\text{P-12CO}]^+$, $\text{GeCo}_4(\text{CO})_6^+$
450-464	s	$[\text{P-13CO}]^+$, $\text{GeCo}_4(\text{CO})_5^+$
422-440	w	$[\text{P-13CO-2C-6H}]^+$, $\text{GeCo}_4(\text{CO})_4^+$
392-412	mw	$[\text{P-13CO-5C-6H}]^+$, $\text{GeCo}_4(\text{CO})_3^+$
376-388	vs	$[\text{Ge}_2\text{Co}_4]^+$
360-372	w	$\text{GeCo}_4(\text{CO})_2^+$
332-345	w	$\text{GeCo}_4(\text{CO})^+$
318-328	ms	$[\text{Ge}_2\text{Co}_3]^+$
302-317	vw	GeCo_4^+
258-264	mw	$[\text{Ge}_2\text{Co}_2]^+$

5.7.1.3 NMR spectra :

Because of the high solubility of $(\text{RGeH})\text{GeCo}_4(\text{CO})_{13}$ in hexane (especially when $\text{R} = \text{Et}$), it was difficult to free the compound from grease. As a result, their ^1H NMR spectra were exceptionally difficult

to run. Peaks in the region of δ 0.8 to 1.3 ppm were usually obscured by the grease peaks.

The NMR peaks (Table 5.17) of the products are observed in the expected region: methyl and ethyl protons in the alkyl region of $\sim \delta$ 1.5 ppm and phenyl proton in the aromatic region of $\sim \delta$ 7.5 ppm. The Ge-H proton signal occurs at around δ 5.5 ppm for the methyl and ethyl analogues, and approximately δ 6 ppm for the phenyl compounds. In a clean and concentrated enough sample, the expected multiplicity is observed : e.g a methyl doublet at δ 1.36 ppm and a quartet at δ 5.72 ppm are observed for $(\text{MeGeH})\text{GeCo}_4(\text{CO})_{13}$. For all phenyl containing compounds, both the phenyl proton multiplets ($\sim \delta$ 7.5 ppm and δ 7.7 ppm) seem to have derived from a doublet overlapping unsymmetrically over a triplet and the Ge-H signal appears as a poorly resolved triplet.

The presence of only one set of proton signals in each compound (e.g only one singlet at δ 1.37 ppm and a multiplet at δ 5.72 ppm) indicated that if the isomers proposed in Fig 5.6 do exist, then the molecule is fluxional in solution, giving only one proton environment (see Section 6.5.3 for discussion on fluxional process).

The ^{13}C O signals of the mono-substituted compounds consisted of a broad singlet at around δ 200 ppm which was very similar to the parent compound, $\text{GeCo}_4(\text{CO})_{14}$ at δ 201.4ppm (Appendix 2). In the NMR spectrum of $(\text{EtGeH})\text{GeCo}_4(\text{CO})_{13}$ a small peak at δ 203 ppm was observed as well as the strong singlet at δ 200.7 ppm. This may be attributed to the presence of an impurity, the most likely one being $\text{GeCo}_4(\text{CO})_{13}$ (see yield of Run 2 in Section 5.3). The NMR study of $(\text{MeGeH})\text{GeCo}_4(\text{CO})_{13}$ (Table 5.18) at various temperature settings showed a small but definite shift to the lower field with drop in temperature. No resolution into bridging and terminal CO environments was observed.

Table 5.17 NMR data of $(RGeH)GeCo_4(CO)_{13}$

	R = Me	R = Et	R = Ph	$(Me_2Ge)GeCo_4(CO)_{13}$
1H : R	1.37 (d, 3x)	1.39 (t, 3x)	7.49 (m, 3x)	1.31
		1.90 (d of q, 2x)	7.79 (m, 2x)	
: Ge-H	5.72 (t, 1x)	5.55 (t, 1x)	6.04 (s, br)	-
^{13}CO	203.6	200.7 [^]	not collected	199.8

1H NMR collected at room temperature ($\sim 27^\circ C$), ^{13}CO NMR at 0 to $-50^\circ C$
 Solvent = $CDCl_3$, [^] small peak at ~ 203 ppm was observed

Table 5.18 ^{13}CO NMR of $(MeGeH)GeCo_4(CO)_{13}$ at various temperature

Temp	signal
^{13}CO ($-60^\circ C$)	δ 203.80 ppm (s, br)
$-56^\circ C$	δ 203.80 ppm (s, br)
$-50^\circ C$	δ 203.61 ppm (s, br)
$-45^\circ C$	δ 203.48 ppm (s, br)
$-40^\circ C$	δ 203.22 ppm (s, br)
$-30^\circ C$	$\delta \sim 203.02$ ppm (s, br)
$-20^\circ C$	δ 202.83 ppm (s, br)
$-10^\circ C$	δ 202.83 ppm (s, br)
$0^\circ C$	δ 202.83 ppm (s, br)

5.7.2 $(RGeH)_2GeCo_4(CO)_{12}$

5.7.2.1 Infrared spectrum :

All $(RGeH)_2GeCo_4(CO)_{12}$ (except $(EtGeH)(PhGeH)GeCo_4(CO)_{12}$, Fig 5.4) showed a simple infrared pattern with only five infrared bands in solution (Table 5.19 and Fig 5.3). Their infrared spectra were very similar to that of $(Me_2Ge)_2GeCo_4(CO)_{12}$ which possesses an idealized C_2

symmetry. A discussion of the infrared spectra of $(RR'Ge)GeCo_4(CO)_{13}$ and $(RR'Ge)_2GeCo_4(CO)_{12}$ is given in Section 6.15 in Chapter Six.

Table 5.19 Infrared spectra of $(RGeH)_2GeCo_4(CO)_{12}$
compared to $(Me_2Ge)_2GeCo_4(CO)_{12}$

R = Me	R = Et	R = Ph	R = Et, Ph	cf $(Me_2Ge)_2GeCo_4(CO)_{12}$
2085w	2086w	2085mw	2085vw 2071vw sh	2081w
2059s	2059s	2061vs	2059m	2054s
2042vs	2042vs	2042vs	2043vs 2026w sh	2037vs
2019m	2019mw	2020m	2019w	2015m
2010ms	2009ms	2008ms	2011mw	2003ms

5.7.2.2 Mass spectrum :

The mass spectra of $(RGeH)_2GeCo_4(CO)_{12}$ compounds showed a parent ion envelope, $(RGeH)_2GeCo_4(CO)_{12}^+$. A systematic loss of 12 CO's before the loss of any other groups was observed except in the case of $(EtGeH)_2GeCo_4(CO)_{12}$ where one CH_3 of the ethyl group is lost at the very beginning. This early loss of methyl group is not expected. For well resolved mass spectra of these compounds, a clear Ge_3 isotope pattern was observed. Details of the mass spectrum of each compound are presented below.

$(MeGeH)_2GeCo_4(CO)_{12}$: The mass spectrum of $(MeGeH)_2GeCo_4(CO)_{12}$ (Table 5.20) was poorly resolved due to instrumental difficulties. A consecutive loss of twelve CO's from the parent ion was observed before loss due to the Me group. A total of twelve CO's and two Me's was indicated.

Table 5.20 Mass spectrum of $(\text{MeGeH})_2\text{GeCo}_4(\text{CO})_{12}$

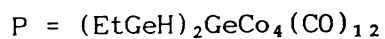
m/e	Int	Assignments
820-825	mw	$\text{P}^+ = [(\text{MeGeH})_2\text{GeCo}_4(\text{CO})_{12}]^+$
791-800	ms	$[\text{P-CO}]^+$
763-780	m	$[\text{P-2CO}]^+$
740-746	w	$[\text{P-3CO}]^+$
710-725	w	$[\text{P-4CO}]^+$
682-698	w	$[\text{P-5CO}]^+$
652-666	mw	$[\text{P-6CO}]^+$
632-640	w	$[\text{P-7CO}]^+$
597-606	w	$[\text{P-8CO}]^+$
572-589	w	$[\text{P-9CO}]^+$
542-546	w	$[\text{P-10CO}]^+$
513-519	w	$[\text{P-11CO}]^+$
498-516	w	$[\text{P-11CO-Me}]^+$
484-492	w	$[\text{P-12CO}]^+$ or $[\text{P-11CO-2Me}]^+$
454-493	w	$[\text{P-12CO-2Me}]^+$
441-448	s	$[\text{P-11CO-Me-Co}]^+$
425-437	m	$[\text{P-11CO-2Me-Co}]^+$
411-421	s	$[\text{P-12CO-Me-Co}]^+$
401-407	s	$[\text{P-12CO-2Me-Co}]^+$

$(\text{EtGeH})_2\text{GeCo}_4(\text{CO})_{12}$: The mass spectrum of $(\text{EtGeH})_2\text{GeCo}_4(\text{CO})_{12}$ was obtained earlier than those of $(\text{EtGeH})\text{GeCo}_4(\text{CO})_{13}$ and $(\text{MeGeH})_2\text{GeCo}_4(\text{CO})_{12}$, when the mass spectrometer was working properly and was very well resolved. The envelopes were of distinct Ge_3 isotope pattern except for those which were overlapped by $\text{GeCo}_4(\text{CO})_n^+$ envelopes. The parent ion envelope was not observed and the highest m/e envelope was that of $[\text{P-Me}]^+$ (unexpected). A total loss of 12CO's was observed from the parent ion. The envelope due to the Ge_3Co_4^+ skeleton ion was the second strongest envelope.

Overlap due to weak $\text{GeCo}_4(\text{CO})_n^+$ ($n = 12$ to 0) was observed.

Table 5.21 Mass spectrum of $(\text{EtGeH})_2\text{GeCo}_4(\text{CO})_{12}$

ion peak	Int	Assignment
836-838	vw	12 for $[(\text{P-Me})(\text{CO})_n]^+$
809-811	w	11 $n = 12 \text{ to } 0$
783-785	w	10
755-758	m	9
727-730	vw	8
700-706	vs	7
672-679	m	6
642-651	ms	5, $\text{GeCo}_4(\text{CO})_{12}^+$
613-623	mw	4, $\text{GeCo}_4(\text{CO})_{11}^+$
585-593	ms	3, $\text{GeCo}_4(\text{CO})_{10}^+$
557-565	m	2, $\text{GeCo}_4(\text{CO})_9^+$
531-537	mw	1, $\text{GeCo}_4(\text{CO})_8^+$
502-509	mw	0, $\text{GeCo}_4(\text{CO})_7^+$
476-487	mw	$\text{EtGe}_3\text{Co}_4^+$, $\text{GeCo}_4(\text{CO})_6^+$
448-456	s	Ge_3Co_4^+ , $\text{GeCo}_4(\text{CO})_5^+$
390-399	mw	Ge_3Co_3^+ , $\text{GeCo}_4(\text{CO})_3^+$
334-340	vw	$\text{GeCo}_4(\text{CO})^+$
309-313	w	GeCo_4^+



$(\text{PhGeH})_2\text{GeCo}_4(\text{CO})_{12}$: The mass spectrum of $(\text{PhGeH})_2\text{GeCo}_4(\text{CO})_{12}$ was very poorly resolved, with a weak parent ion envelope (P) at $m/e = 918$. This is slightly lower than calculated. Only envelopes corresponding to P-3CO, P-5CO, P-7CO, P-9CO, P-11CO and P-12CO were clear enough to be identified.

5.7.2.3 NMR spectra :

The difficulty encountered in obtaining well resolved ^1H NMR spectra and the comments on the chemical shifts mentioned in $(\text{RGeH})\text{GeCo}_4(\text{CO})_{13}$ also applied to $(\text{RGeH})_2\text{GeCo}_4(\text{CO})_{12}$.

^{13}C NMR could not be obtained for the di-substituted products due to the absence of bridging CO to facilitate the ^{13}C exchange in the enrichment process. Table 5.22 presents the ^1H NMR data of $(\text{RGeH})_2\text{GeCo}_4(\text{CO})_{12}$ (all chemical shifts in δ ppm, solvent = CDCl_3)

Table 5.22 ^1H NMR data of $(\text{RGeH})_2\text{GeCo}_4(\text{CO})_{12}$

	R = Me	R = Et*	R = Ph	R = Ph, Et
^1H : alkyl	1.36 (d, 3x)	1.38 (t)		1.38 (m [#] , 3x)
		1.90 (m)		1.85 (m, 2x)
: phenyl			7.48 (m, 3x)	7.48 (m, 3x)
			7.78 (m, 2x)	7.78 (m, 2x)
: Ge-H	5.70 (q, 1x)	5.55 (m)		5.52 (s, br, 1x)
			6.10 (s, br)	6.10 (m, 1x)

* Due to the high solubility of $(\text{EtGeH})_2\text{GeCo}_4(\text{CO})_{12}$ in solvent, removal of grease was difficult, the ^1H NMR spectrum was swamped by grease peaks, and the values above are only estimates of the badly resolved peaks.

- unresolved triplet?

^1H NMR of $(\text{Me}_2\text{Ge})_2\text{GeCo}_4(\text{CO})_{12}$: singlet at δ 1.34 ppm

5.7.2.4 *Electron probe analysis* : only the EPA of $(\text{EtGeH})_2\text{GeCo}_4(\text{CO})_{12}$ was carried out as this was the only one that was obtained pure as crystals. The result was :

Atomic % of Co:Ge = 56.82:43.18 = 3.95:3 $\approx$ 4 : 3 as expected

5.7.2.5 XRD study (of $(\text{EtGeH})_2\text{GeCo}_4(\text{CO})_{12}$)

A single crystal (thin yellow rectangular plate) of $(\text{EtGeH})_2\text{GeCo}_4(\text{CO})_{12}$ was mounted for X-ray preliminary studies (section 2.2.5). The crystal data is presented in Table 5.23.

Table 5.23 Cell dimensions of $(\text{EtGeH})_2\text{GeCo}_4(\text{CO})_{12}$:

Formula $\text{C}_{16}\text{H}_{12}\text{O}_{12}\text{Co}_4\text{Ge}_3$
Mr = 849.8
Space group triclinic
$a = 12.89\text{\AA}$, $b = 22.93\text{\AA}$, $c = 9.12\text{\AA}$
$\alpha = 99.45^\circ$, $\beta = 94.53^\circ$, $\gamma = 93.19^\circ$
$U = 2644.23\text{\AA}^3$
$Z = 4$, $\rho = 2.13 \text{ g/cm}^3$
(2 independent molecules in asymmetric unit)

However, this crystal did not survive the full data collection, and all other crystals examined were twinned. A full data set could not be obtained. The preliminary data does seem to conform to that expected for this type of compound (densities of Ge-Co carbonyl compounds with ethyl group are between 1.8 to 2.2 g/cm^3).

5.8 The reaction of MeSiH_3 with $\text{GeCo}_4(\text{CO})_{14}$

5.8.1 Experimental :

$\text{GeCo}_4(\text{CO})_{14}$ (0.1708g, 0.244 mmoles) and hexane (10 ml) were loaded into a 50 ml ampoule at the Schlenk line. The ampoule was transferred to the vacuum line where the contents were evacuated of gas and then frozen down by liquid nitrogen. MeSiH_3 (0.838 mmoles) was condensed in and the ampoule sealed under vacuum. The ampoule of reactants was allowed to react in the dark at room temperature for 8 weeks.

5.8.2 Observations and workup :

The solution changed from a red brown to a purple brown colour. The total amount of incondensable gas measured was 0.168 mmol, and all of this was CO.

The volatiles were removed, but not studied. The involatile fraction was washed several times with small amounts of hexane (3-4 ml/time).

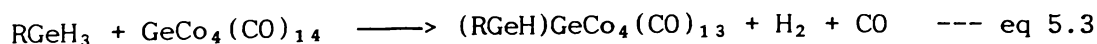
The remaining solid fraction was dissolved in hexane. The infrared spectrum of the solution showed that the starting material, $\text{GeCo}_4(\text{CO})_{14}$, was recovered along with $\text{GeCo}_4(\text{CO})_{13}$ (2081 s, 2043 vs, 2026 m in CH_2Cl_2 /hexane) [22]. The hexane washings were combined and the infrared spectrum of this showed that $\text{GeCo}_4(\text{CO})_{13}$ was the major component (with a small amount of $\text{GeCo}_4(\text{CO})_{14}$).

Like the reaction of Me_2SiH_2 with $\text{GeCo}_4(\text{CO})_{14}$ (Chapter Six), no substitution reaction occurred. Only the decarbonylation of $\text{GeCo}_4(\text{CO})_{14}$ was observed. This is consistent with the incondensable gas measurement which showed that only CO was measured. Calculations based on the amount of CO evolved showed that about 69% of the $\text{GeCo}_4(\text{CO})_{14}$ had been converted into $\text{GeCo}_4(\text{CO})_{13}$.

5.9 Discussion of the reactions of RGeH_3 with $\text{GeCo}_4(\text{CO})_{14}$

Sealed tube reaction :

Sections 5.2 - 5.4 described the sealed tube reactions of RGeH_3 with $\text{GeCo}_4(\text{CO})_{14}$ (for R = Me, Et, Ph). The reactions appeared to follow equations 5.3 and 5.4 :



The volatile fraction of the reaction showed that no products such as $\text{HCo}(\text{CO})_4$ or $\text{RGeH}_2\text{Co}(\text{CO})_4$ were formed indicating that $\text{GeCo}_4(\text{CO})_{14}$ probably did not break up into smaller fragments. The composition of the incondensable gas consistently showed a near equal amount of H_2 and CO when the only products were $(\text{RGeH})\text{GeCo}_4(\text{CO})_{13}$ and $(\text{RGeH})_2\text{GeCo}_4(\text{CO})_{12}$. A higher proportion of CO was obtained in the systems where decarbonylation of $\text{GeCo}_4(\text{CO})_{14}$ [17] had occurred. In Run 2 of the reaction of EtGeH_3 with $\text{GeCo}_4(\text{CO})_{14}$ for instance, the percentage CO measured was 58% and 5.6% of $\text{GeCo}_4(\text{CO})_{13}$ was obtained. Decarbonylation of $\text{GeCo}_4(\text{CO})_{14}$ to $\text{GeCo}_4(\text{CO})_{13}$ could, in most cases be prevented by the use of lower temperatures and smaller ampoules as in Section 5.2 Run 5.

The incondensable gas measurement usually gave a better estimate of the yield of products as not all the $(\text{ReGeH})\text{GeCo}_4(\text{CO})_{13}$ produced could be separated from $\text{GeCo}_4(\text{CO})_{14}$. For example in 5.2, Run 5 of the sealed tube reaction of MeGeH_3 with $\text{GeCo}_4(\text{CO})_{14}$ (at 30°C), the estimated yield of $(\text{MeGeH})\text{GeCo}_4(\text{CO})_{13}$ was 53% from the incondensable gas measurement. The amount of $(\text{MeGeH})\text{GeCo}_4(\text{CO})_{13}$ isolated nearly pure was only 44%.

The type of involatile products obtained ($(\text{RGeH})\text{GeCo}_4(\text{CO})_{13}$ or $(\text{RGeH})_2\text{GeCo}_4(\text{CO})_{12}$) is dependent on the ratio of reactants, reaction time, temperature and the type of R groups (Tables 5.4, 5.6 and 5.9). Higher ratio of RGeH_3 to $\text{GeCo}_4(\text{CO})_{14}$ and longer reaction times resulted in the formation of more $(\text{RGeH})_2\text{GeCo}_4(\text{CO})_{12}$.

Of the three R groups, the ethyl analogue is the easiest to prepare and purify. This is illustrated by the following reactions : for the same reaction time of 70 days under similar reaction conditions the yield of $(\text{MeGeH})\text{GeCo}_4(\text{CO})_{13}$ was about 10-20% (estimated from infrared spectrum) while that of $(\text{EtGeH})\text{GeCo}_4(\text{CO})_{13}$ was 40%. A

similar $\text{PhGeH}_3 : \text{GeCo}_4(\text{CO})_{14}$ reaction but with a longer reaction time of 120 days produced only about 24% $(\text{PhGeH})\text{GeCo}_4(\text{CO})_{13}$.

Gentle heating at 30°C was found to speed up the reaction as shown in the reaction of EtGeH_3 with $\text{GeCo}_4(\text{CO})_{14}$ (compare Runs 1 and 2 in Section 5.3). Heating for only 5 out of the 70 days improved the yield of $(\text{EtGeH})\text{GeCo}_4(\text{CO})_{13}$ by 11%. This however (Run 1) led to the production of mono- as well as the di- substituted product. Gentle heating of the PhGeH_3 reaction was observed to produce a hexane insoluble CH_2Cl_2 soluble brown solid which could not be characterised.

The reaction of MeGeH_3 or EtGeH_3 with $\text{GeCo}_4(\text{CO})_{14}$ at low ratio, if left for a long enough time, will produce the di-substituted species e.g. for $\text{MeGeH}_3 : \text{GeCo}_4(\text{CO})_{14}$ of 1.3 : 1 ratio, a reaction time of 196 days indicated a trace of $(\text{MeGeH})_2\text{GeCo}_4(\text{CO})_{12}$ had formed. A shorter reaction time of 70 days was required for the di-substituted species to be formed in the $\text{EtGeH}_3 : \text{GeCo}_4(\text{CO})_{14}$ reaction under similar conditions. But in the reaction of $1.5 \times \text{PhGeH}_3 : 1 \times \text{GeCo}_4(\text{CO})_{14}$, a long reaction time of 120 days did not result in the formation of any $(\text{PhGeH})_2\text{GeCo}_4(\text{CO})_{12}$.

Though the di-substituted species appeared at low $\text{RGeH}_3 : \text{GeCo}_4(\text{CO})_{14}$ as early as 70 days into the reaction for EtGeH_3 , total conversion to $(\text{RGeH})_2\text{GeCo}_4(\text{CO})_{12}$ was difficult. As long as up to 90 days plus heat for a $4 \times \text{EtGeH}_3 : 1 \times \text{GeCo}_4(\text{CO})_{14}$ reaction was required for total conversion to $(\text{EtGeH})_2\text{GeCo}_4(\text{CO})_{12}$. Similar reaction conditions but with a higher $\text{MeGeH}_3 : \text{GeCo}_4(\text{CO})_{14}$ of 7 : 1 resulted in only 60 to 70% yield of $(\text{MeGeH})_2\text{GeCo}_4(\text{CO})_{12}$. More difficulty was encountered for the PhGeH_3 reaction. A long reaction time of 150 days plus heat only managed to convert about 79% of $(\text{PhGeH})\text{GeCo}_4(\text{CO})_{13}$ to the disubstituted species.

No $(\text{RGe})_2\text{Co}_4(\text{CO})_{11}$ was observed in any of the runs.

Open tube reactions :

As shown in Section 5.5, replacement of the remaining bridging CO in $(\text{EtGeH})\text{GeCo}_4(\text{CO})_{13}$ by a $\mu\text{-Ge(Ph)H}$ unit was achieved by using PhGeH_3 in an open tube reaction. The di-substituted product $(\text{EtGeH})(\text{PhGeH})\text{GeCo}_4(\text{CO})_{12}$ was the major product together with an unidentified product which was less soluble than the major product. A similar reaction should be feasible with the reaction of $(\text{PhGeH})\text{GeCo}_4(\text{CO})_{13}$ with PhGeH_3 to achieve total conversion to $(\text{PhGeH})_2\text{GeCo}_4(\text{CO})_{12}$ in a shorter time. This method has the advantage of both economy in time and PhGeH_3 . This, however was not carried out due to the shortage of starting material and time.

The open tube reaction of $\text{GeCo}_4(\text{CO})_{14}$ with MeGeH_3 produced $(\text{MeGeH})\text{GeCo}_4(\text{CO})_{13}$ and the formation of $(\text{MeGeH})_2\text{GeCo}_4(\text{CO})_{12}$ was indicated after about 45 days.

The infrared spectra taken at intervals during the reaction indicated a stepwise reaction as in equations 5.3 and 5.4.

The incondensable gas evolution in Run 2 indicated that more CO than expected from the equations was released. A high proportion of CO was evolved at the initial stages of reaction. Because the volatiles of the reaction were not examined, the explanation for the high initial CO evolution could only be speculative : the trapping of the H_2 in the form of $\text{HCo}(\text{CO})_4$ or some reaction intermediates. The major product in the open tube reaction of MeGeH_3 with $\text{GeCo}_4(\text{CO})_{14}$ is $(\text{MeGeH})_2\text{GeCo}_4(\text{CO})_{12}$ and/or $(\text{MeGeH})\text{GeCo}_4(\text{CO})_{13}$ depending on the reactant ratio and the reaction time (as in the sealed tube reaction). A hexane insoluble fraction not observed in the sealed tube reactions was obtained in both runs of the open tube reaction. In Run 1, the mass spectrum of this compound was very similar to that of

$\text{MeGe}_2\text{Co}_5(\text{CO})_{15}$ (see Chapter Seven), but its evidence was lacking in Run 2. Its solubility in CH_2Cl_2 however was too low compared to $\text{MeGe}_2\text{Co}_5(\text{CO})_{15}$ (the colour was wrong too -- $\text{MeGe}_2\text{Co}_5(\text{CO})_{15}$ forms a dark red solution in CH_2Cl_2 while this gave a brown solution with brown suspension). It could not be characterised by any other means. This hexane insoluble fraction remained unassigned and may be a compound with formula similar to $\text{MeGe}_2\text{Co}_5(\text{CO})_{15}$.

Again no $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ was formed in the open tube reaction of MeGeH_3 with $\text{GeCo}_4(\text{CO})_{14}$.

Structure of $(\text{RGeH})\text{GeCo}_4(\text{CO})_{13}$ and $(\text{RGeH})_2\text{GeCo}_4(\text{CO})_{12}$

The products were characterised solely by spectroscopic means as attempts to obtain the crystals of most of the products failed. $(\text{RGeH})\text{GeCo}_4(\text{CO})_{13}$ does not crystallize even in high purity. They formed round disc shaped amorphous solids. $(\text{PhGeH})_2\text{GeCo}_4(\text{CO})_{12}$ forms round yellow conglomerates. $(\text{MeGeH})_2\text{GeCo}_4(\text{CO})_{12}$ does crystallize, but the thin needles dissolve too quickly in hexane when brought up to room temperature. $(\text{EtGeH})_2\text{GeCo}_4(\text{CO})_{12}$ forms thin plates, but majority of these are badly twinned. The only single crystal from which the unit cell dimensions in Table 5.23 was obtained did not survive the data collection procedure in the University of Auckland.

The structures of $(\text{RGeH})\text{GeCo}_4(\text{CO})_{13}$ and $(\text{RGeH})_2\text{GeCo}_4(\text{CO})_{12}$ can be related to be those of $(\text{Me}_2\text{Ge})\text{GeCo}_4(\text{CO})_{13}$ and $(\text{Me}_2\text{Ge})_2\text{GeCo}_4(\text{CO})_{12}$ through the very similar infrared pattern observed (Tables 5.14 compares to Table 6.3 and Table 5.19 compares to Table 6.5). The crystal structure of $(\text{Me}_2\text{Ge})_2\text{GeCo}_4(\text{CO})_{12}$ has been done [148] while the crystal structure of $(\text{Me}_2\text{Ge})\text{GeCo}_4(\text{CO})_{13}$ was only partially determined. Based on the known structures of the Me_2Ge analogues, the proposed

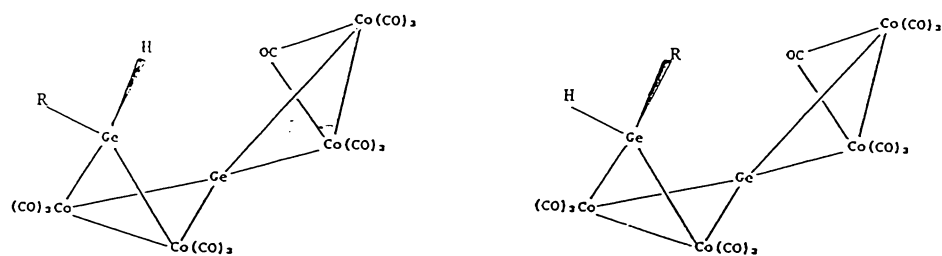


Fig 5.6 Proposed structure of $(\text{MeGeH})\text{GeCo}_4(\text{CO})_{13}$
(2 possible isomers)

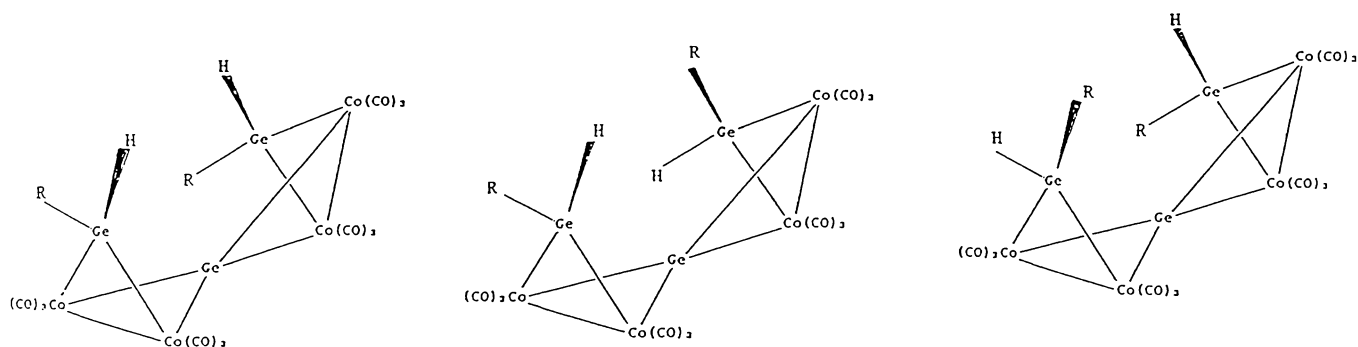


Fig 5.7 Proposed structure of $(\text{MeGeH})_2\text{GeCo}_4(\text{CO})_{12}$
(3 possible isomers)

structures (plus their isomers) of $(RGeH)GeCo_4(CO)_{13}$ and $(RGeH)_2GeCo_4(CO)_{12}$ are shown in Figs 5.6 and 5.7.

The crystal structures of these compounds are of interest as the isomeric form of these compounds cannot be determined by any other methods. It is likely that all isomers would exist in solution and that the crystal structure merely represents the most sterically favoured position.

Related reaction :

Unlike its Ge analogue, $MeSiH_3$ did not react with $GeCo_4(CO)_{14}$. The unreacted $GeCo_4(CO)_{14}$ decarbonylated to form $GeCo_4(CO)_{13}$.

CHAPTER SIX

The Reaction of $R_1R_2M'H_2$ with $GeCo_4(CO)_{14}$



6.1 Introduction

The reaction of Me_2GeH_2 with $GeCo_4(CO)_{14}$ (2a) was first investigated by Foster [18,81]. The mono-substituted product $(Me_2Ge)GeCo_4(CO)_{13}$ (5a) was obtained and characterised by infrared and mass spectroscopy. The attempt to determine the crystal structure managed only to locate the heavy metal skeleton and one methyl group [18], probably due to a twinned crystal. The reaction of $RGeH_3$ with $GeCo_4(CO)_{14}$ in Chapter Five showed that both mono- and di-substituted species could be formed, the major product dependent on the reaction conditions. The corresponding di-substituted product of the Me_2GeH_2 with $GeCo_4(CO)_{14}$ reaction was not observed [18]. The di-substituted product, $(Me_2Ge)_2Ge_2Co_6(CO)_{18}$ (8) however, was synthesised from the reaction of Me_2GeH_2 with $Ge_2Co_6(CO)_{20}$ (3) [18,81]. This di-substitution of $Ge_2Co_6(CO)_{20}$ and not $GeCo_4(CO)_{14}$ was explained by Foster [18] as : substitution of Me_2Ge group on one end of $GeCo_4(CO)_{14}$ would result in the shortening of the other Co-Co bond, thus making the second substitution less favourable. This reasoning seems to be supported by the crystal structure of $[(CO)_4CoHgGeCo_4(CO)_{13}]^+$ (Fig 6.1) [6] where the Hg bridged Co-Co bond is 2.75Å and the other Co-Co bond is 2.54Å, while the average Co-Co bond in $GeCo_4(CO)_{14}$ is 2.57Å. $Ge_2Co_6(CO)_{20}$ on the other hand contains three sets of Co-Co bonds, the lengthening of a Co-Co bond on one end would cause a shortening in the central set, which in turn would result in the lengthening of the Co-Co bond on the other end. Thus substitution can occur on both ends.

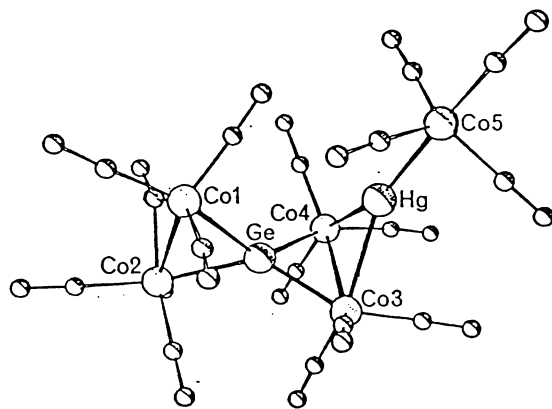


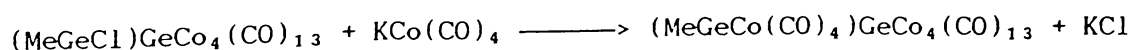
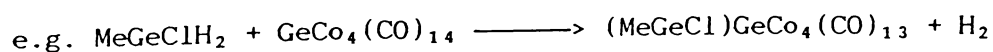
Fig 6.1 $[(\text{Co})_4\text{CoHgGeCo}_4(\text{CO})_{13}]^-$

Examination of the experimental conditions used by Foster [18] shows that those in the reaction of Me_2GeH_2 and $\text{Ge}_2\text{Co}_6(\text{CO})_{20}$ would encourage di-substitution while those used for the corresponding Me_2GeH_2 and $\text{GeCo}_4(\text{CO})_{14}$ reaction were less favourable for di-substitution:-

	Run 1	Run 2
$\text{Me}_2\text{GeH}_2 : \text{Ge}_2\text{Co}_6(\text{CO})_{20}$	15.5 : 1	6.7 : 1
Reaction time	20 weeks	5 weeks
$\text{Me}_2\text{GeH}_2 : \text{GeCo}_4(\text{CO})_{14}$	2.3 : 1	1.5 : 1
Reaction time	12 weeks	7 weeks

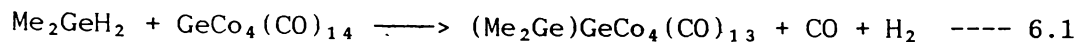
It was therefore felt worthwhile to investigate the reaction of Me_2GeH_2 with $\text{GeCo}_4(\text{CO})_{14}$ to see whether further substitution was possible. The results are reported in this Chapter. The reaction of Me_2SiH_2 with $\text{GeCo}_4(\text{CO})_{14}$ is also attempted.

This Chapter also discusses the reaction of $\text{GeCo}_4(\text{CO})_{14}$ with MeGeClH_2 . If the reaction proceeds in a similar fashion to MeGeH_3 or Me_2GeH_2 with $\text{GeCo}_4(\text{CO})_{14}$, then this could be a convenient route to chain extension by salt elimination reactions of the resulting product using metal carbonyl anions :

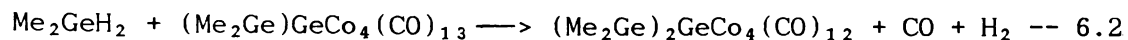


6.2 The reaction of Me_2GeH_2 with $\text{GeCo}_4(\text{CO})_{14}$

The reaction of Me_2GeH_2 with $\text{GeCo}_4(\text{CO})_{14}$ was reported to proceed as in equation 6.1 [18,81] :



It is the aim of this Section to attempt the second substitution, as shown in equation 6.2 :



- either by (1) direct reaction with excess Me_2GeH_2 or (2) by reaction of isolated $(\text{Me}_2\text{Ge})\text{GeCo}_4(\text{CO})_{13}$ with Me_2GeH_2 .

Run 1 ($\text{Me}_2\text{GeH}_2 : \text{GeCo}_4(\text{CO})_{14} = 1.5 : 1$)

6.2.1 Experimental :

$\text{GeCo}_4(\text{CO})_{14}$ (0.2318g, 0.331mmol) was loaded into a 50 ml ampoule at the Schlenk line. Hexane (10ml) was added and the ampoule was transferred to the vacuum line where the contents were degassed then frozen down by liquid nitrogen. Me_2GeH_2 (0.497mmol) was condensed into the ampoule and then sealed under vacuum. The reaction was allowed to proceed in the dark at room temperature for 30 days.

6.2.2 Observations and Workup :

The colour of the solution became slightly lighter as the reaction proceeded. After two weeks, big red pyramidal shaped crystals appeared on the side of the ampoule. The reaction was stopped after 30 days.

On working up, incondensable gases were not measured due to a Toepler pump fault. The volatile fraction was collected and its IR spectrum showed only Me_2GeH_2 (measurement not taken) and hexane solvent.

The involatile solid was washed several times with small amounts of hexane (2-3 ml each time). The washings were combined together.

Infrared spectrum (Table 6.1) showed this hexane fraction to be a mixture of $(\text{Me}_2\text{Ge})\text{GeCo}_4(\text{CO})_{13}$, $\text{GeCo}_4(\text{CO})_{14}$ and a new product (found to be $(\text{Me}_2\text{Ge})_2\text{GeCo}_4(\text{CO})_{12}$, characterisation in Section 6.5). $(\text{Me}_2\text{Ge})\text{GeCo}_4(\text{CO})_{13}$ was separated by recrystallisation, the yield obtained pure was 0.096g (0.126mmol) or 38%, significantly more still remained in solution. The remaining $(\text{Me}_2\text{Ge})\text{GeCo}_4(\text{CO})_{13}$, $\text{GeCo}_4(\text{CO})_{14}$ and $(\text{Me}_2\text{Ge})_2\text{GeCo}_4(\text{CO})_{12}$ could not be separated quantitatively. Characterisation of $(\text{Me}_2\text{Ge})\text{GeCo}_4(\text{CO})_{13}$ is given in Section 6.4.

The remaining red crystals were dissolved in hexane/ CH_2Cl_2 the infrared spectrum showed it to be pure $(\text{Me}_2\text{Ge})\text{GeCo}_4(\text{CO})_{13}$.

Yield of Run 1 :

Weight of $(\text{Me}_2\text{Ge})\text{GeCo}_4(\text{CO})_{13}$ = 0.096g = 38% (minimum yield)

Table 6.1 Infrared spectrum of the supernatant solution of Run 1

Bands	Int	Assignments
2096	w	$(\text{Me}_2\text{Ge})\text{GeCo}_4(\text{CO})_{13}$
2081	w sh	$(\text{Me}_2\text{Ge})_2\text{GeCo}_4(\text{CO})_{12}$
2079	w	$\text{GeCo}_4(\text{CO})_{14}$
2065	s	$(\text{Me}_2\text{Ge})\text{GeCo}_4(\text{CO})_{13}$
2054	s	$(\text{Me}_2\text{Ge})\text{GeCo}_4(\text{CO})_{13}$
2043	s	$(\text{Me}_2\text{Ge})\text{GeCo}_4(\text{CO})_{13}$ + $\text{GeCo}_4(\text{CO})_{14}$?
2037	ms	$(\text{Me}_2\text{Ge})_2\text{GeCo}_4(\text{CO})_{12}$
2027	m	$(\text{Me}_2\text{Ge})\text{GeCo}_4(\text{CO})_{13}$ + $\text{GeCo}_4(\text{CO})_{14}$?
2020	m	$(\text{Me}_2\text{Ge})\text{GeCo}_4(\text{CO})_{13}$
2015	ms	$(\text{Me}_2\text{Ge})\text{GeCo}_4(\text{CO})_{13}$
2002	mw	$(\text{Me}_2\text{Ge})\text{GeCo}_4(\text{CO})_{13}$
1985	vw	$(\text{Me}_2\text{Ge})\text{GeCo}_4(\text{CO})_{13}$
1844	mw	$(\text{Me}_2\text{Ge})\text{GeCo}_4(\text{CO})_{13}$

6.2.3 Other runs:

Two further runs were carried out. Run 2 was carried out as in Run 1 except that a higher ratio of Me_2GeH_2 to $\text{GeCo}_4(\text{CO})_{14}$ was used. Run 3 was carried out as an open tube reaction, the progress of which was monitored by incondensable gas measurements.

Run 2 (Me_2GeH_2 : $\text{GeCo}_4(\text{CO})_{14}$ = 2.7 : 1)

$\text{GeCo}_4(\text{CO})_{14}$ (0.301g, 0.4299mmol) was reacted with Me_2GeH_2 (1.161 mmol) in hexane (10 ml) in a sealed tube reaction. The reaction was allowed to proceed as in Run 1. The reaction was stopped after 60 days.

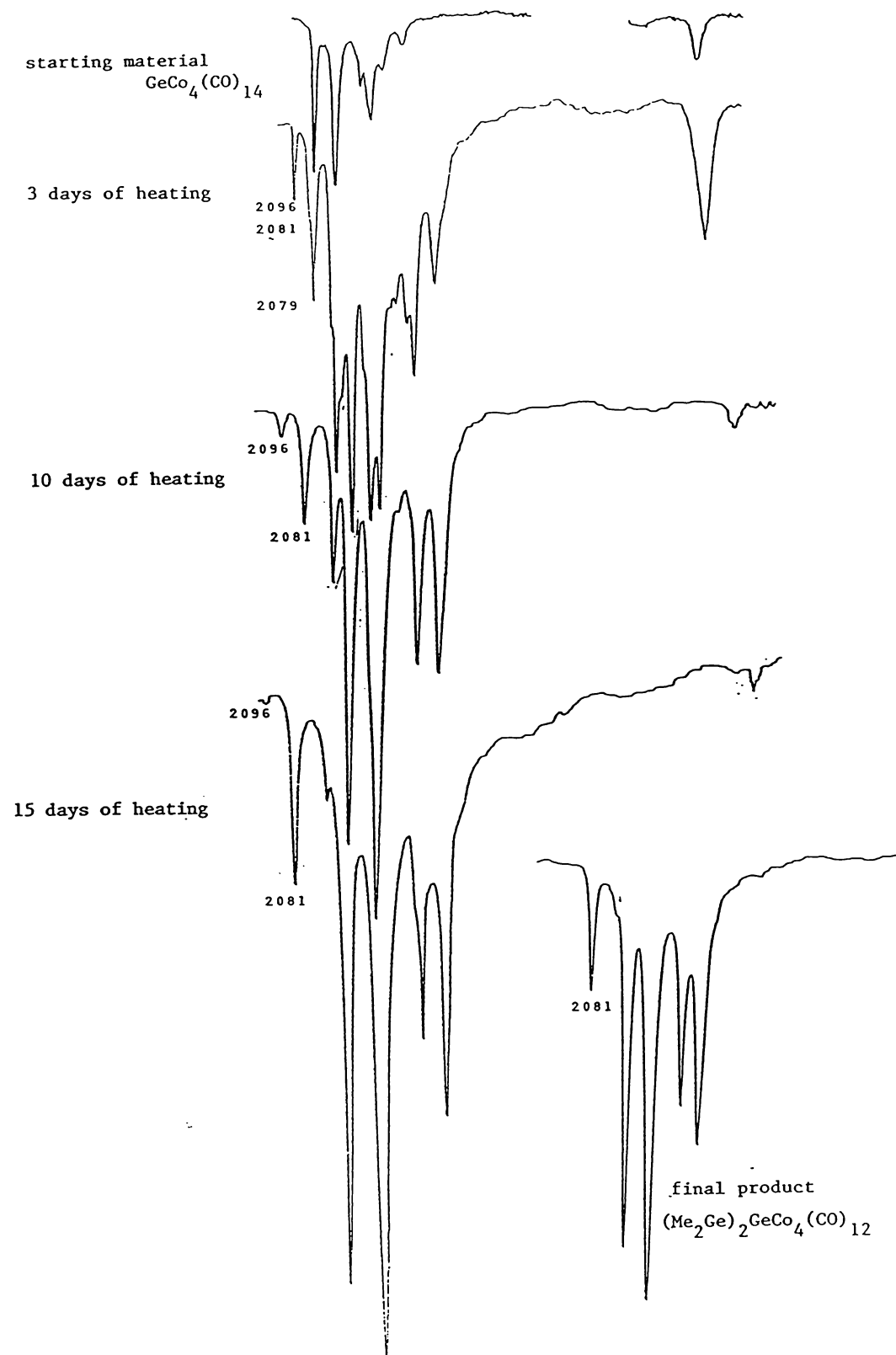
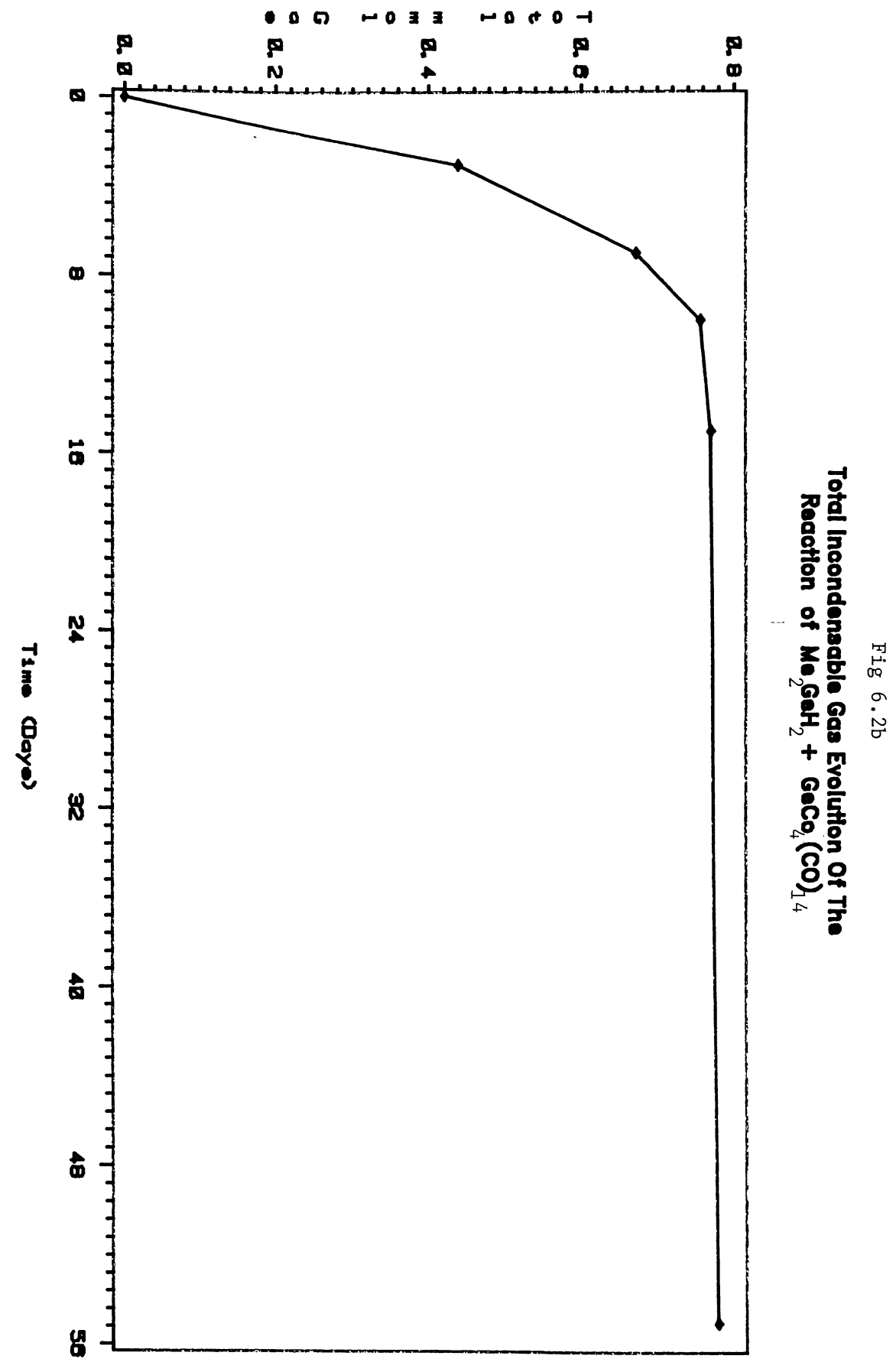
Red crystals were observed on the side of the ampoule and a red solution was formed. It was worked up as in Run 1. The incondensable gases were not measured, and the volatiles were removed, but not examined.

The hexane washings consisted of mainly $(\text{Me}_2\text{Ge})\text{GeCo}_4(\text{CO})_{13}$ together with small amount of $\text{GeCo}_4(\text{CO})_{14}$ and $(\text{Me}_2\text{Ge})_2\text{GeCo}_4(\text{CO})_{12}$. The intensity of the bands due to $(\text{Me}_2\text{Ge})_2\text{GeCo}_4(\text{CO})_{12}$ were more pronounced than those in Run 1.

The red crystals remaining were pure $(\text{Me}_2\text{Ge})\text{GeCo}_4(\text{CO})_{13}$. Although a greater percentage of $(\text{Me}_2\text{Ge})\text{GeCo}_4(\text{CO})_{13}$ was crystallised pure compared to Run 1, the yield of $(\text{Me}_2\text{Ge})_2\text{GeCo}_4(\text{CO})_{12}$ appeared to be enhanced based on infrared spectrum. Accurate yields of $(\text{Me}_2\text{Ge})_2\text{GeCo}_4(\text{CO})_{12}$ however could not be obtained as it could not be separated.

Yield of Run 2 :

Weight of $(\text{Me}_2\text{Ge})\text{GeCo}_4(\text{CO})_{13}$ = 0.172g = 0.222mmol
= 52%

Fig 6.2 a IR changes in the reaction of Me_2GeH_2 with $\text{GeCo}_4(\text{CO})_{14}$ (Run 3)

Run 3 (Me_2GeH_2 : $\text{GeCo}_4(\text{CO})_{14}$ = 1.5 : 1)

$\text{GeCo}_4(\text{CO})_{14}$ (0.137g, 0.195mmol) and hexane (5 ml) were loaded into a 25 ml open tube vessel. The contents were evacuated at the vacuum line and frozen by liquid nitrogen. Me_2GeH_2 (0.292mmol) was condensed into the reaction tube. The reaction was left to react at 30°C. The incondensable gas was measured intermittently as the reaction proceeded. A small amount of the hexane solution of the reaction was drawn for IR studies after the incondensable gas measurement (shown in Table 6.2). After 15 days, when the incondensable gas evolution dwindled, a further 0.604mmol of Me_2GeH_2 was added to the reactants and the reaction was continued for a further 40 days.

Table 6.2 Incondensable gas/infrared bands changes for Run 3

Days	Gas evolved (mmol)	Total gas evolved (mmol)	Intensity ratio of bands at 2079 : 2096 : 2081 cm^{-1}
3	0.439	0.439	1.83 : 0.73 : 1
7	0.235	0.674	did not run I.R.
10	0.084	0.758	0 : 0.39 : 1
15	0.013	0.771	0 : 0.04 : 1
55	0.008	0.779	0 : 0 : 1

2079 cm^{-1} = representative band of $\text{GeCo}_4(\text{CO})_{14}$

2096 cm^{-1} = representative band of $(\text{Me}_2\text{Ge})\text{GeCo}_4(\text{CO})_{13}$

2081 cm^{-1} = representative band of $(\text{Me}_2\text{Ge})_2\text{GeCo}_4(\text{CO})_{12}$

The colour of the reaction mixture changed from dark red to orange as reaction progressed. This was accompanied by the decrease in intensity of the band at 2079 cm^{-1} and the appearance of bands at 2096 cm^{-1} and 2081 cm^{-1} (Fig 6.2). The band at 2079 disappeared completely after 10 days, while the band at 2096 decreased relative to the band at 2081. After 55 days, the band at 2096 disappeared completely.

As only the supernatant solution of the reaction mixture was used in obtaining the infrared spectra, the more soluble species would be over represented. Therefore the band intensity ratio is only a rough guide to the concentration of the species at any stage.

The incondensable gas evolution slowed down rapidly after 10 days of reaction, and all the $\text{GeCo}_4(\text{CO})_{14}$ was consumed by this stage as indicated by infrared spectrum. However, it took 45 more days to release the last 2.5% of gas. Near quantitative evolution of incondensable gas was measured if the reaction proceeded according to equations 6.1 and 6.2. The composition of the incondensable gas at the first gas measurement was 46% H_2 : 54% CO . This compares well to those expected in equation 6.1 and 6.2 (within 10% experimental errors). No measurement of the gas composition was made on the subsequent readings due to the small volume of gas evolved (therefore high error).

At end of the reaction, tiny yellow diamond shape crystals of $(\text{Me}_2\text{Ge})_2\text{GeCo}_4(\text{CO})_{12}$ were formed on the side of the reaction tube. The resulting hexane solution was light orange in colour. On working up, the volatile fraction was separated. The infrared spectrum of this indicated the presence of Me_2GeH_2 and hexane. The involatile fraction was dissolved in hexane, and its infrared spectrum indicated a single new product, $(\text{Me}_2\text{Ge})_2\text{GeCo}_4(\text{CO})_{12}$. 0.16g (97%) of the product was isolated, the rest remained unseparated from grease. The characterisation of $(\text{Me}_2\text{Ge})_2\text{GeCo}_4(\text{CO})_{12}$ is given in Section 6.5.

Yield of Run 3 :

Weight of $(\text{Me}_2\text{Ge})_2\text{GeCo}_4(\text{CO})_{12} \approx 0.16\text{g} = 97\%$

6.3 Reaction of $(\text{Me}_2\text{Ge})\text{GeCo}_4(\text{CO})_{13}$ with Me_2GeH_2 (1 : 2.5)

6.3.1 Experimental :

$(\text{Me}_2\text{Ge})\text{GeCo}_4(\text{CO})_{13}$ (0.112g, 0.145 mmol) was sealed with Me_2GeH_2 (0.361 mmol) and hexane (10 ml) in an ampoule. This was left to react at room temperature for 90 days with constant shaking.

6.3.2 Observations and workup :

After 3 months of reaction, the reddish orange solution of $(\text{Me}_2\text{Ge})\text{GeCo}_4(\text{CO})_{13}$ had become yellow. A few yellow diamond shaped crystals were observed on the neck of the ampoule. The reaction was stopped and worked up. No incondensable gas measurement was performed. The volatile fraction showed only unreacted Me_2GeH_2 (not measured) and hexane. The involatile phase was pure $(\text{Me}_2\text{Ge})_2\text{GeCo}_4(\text{CO})_{12}$ as shown by infrared spectrum.

Yield :

Weight of $(\text{Me}_2\text{Ge})_2\text{GeCo}_4(\text{CO})_{12}$ = 0.124g = 0.145mmol = ~100%

6.4 Characterisation of $(\text{Me}_2\text{Ge})\text{GeCo}_4(\text{CO})_{13}$

6.4.1 Infrared and Raman spectra:

The solution and solid IR spectra of $(\text{Me}_2\text{Ge})\text{GeCo}_4(\text{CO})_{13}$ are shown in Figs 6.3 and 6.4 and the details are given in Table 6.3. The solid Raman spectrum is given in Table 6.3 and Fig 6.5.

$(\text{Me}_2\text{Ge})\text{GeCo}_4(\text{CO})_{13}$ has idealised C_s symmetry. 13 infrared bands are predicted : 12 for the terminal CO stretches ($6A' + 6A''$) and a bridging CO stretch (A'). The solution spectrum was well resolved, but showed only 11 bands while the solid state spectrum showed all 13 bands, indicating lower site symmetry in the crystal.

The Raman spectrum (solid) showed 12 of the 13 expected peaks. It corresponds well with the solid state infrared spectrum.

IR spectra of $(\text{Me}_2\text{Ge})\text{GeCo}_4(\text{CO})_{13}$

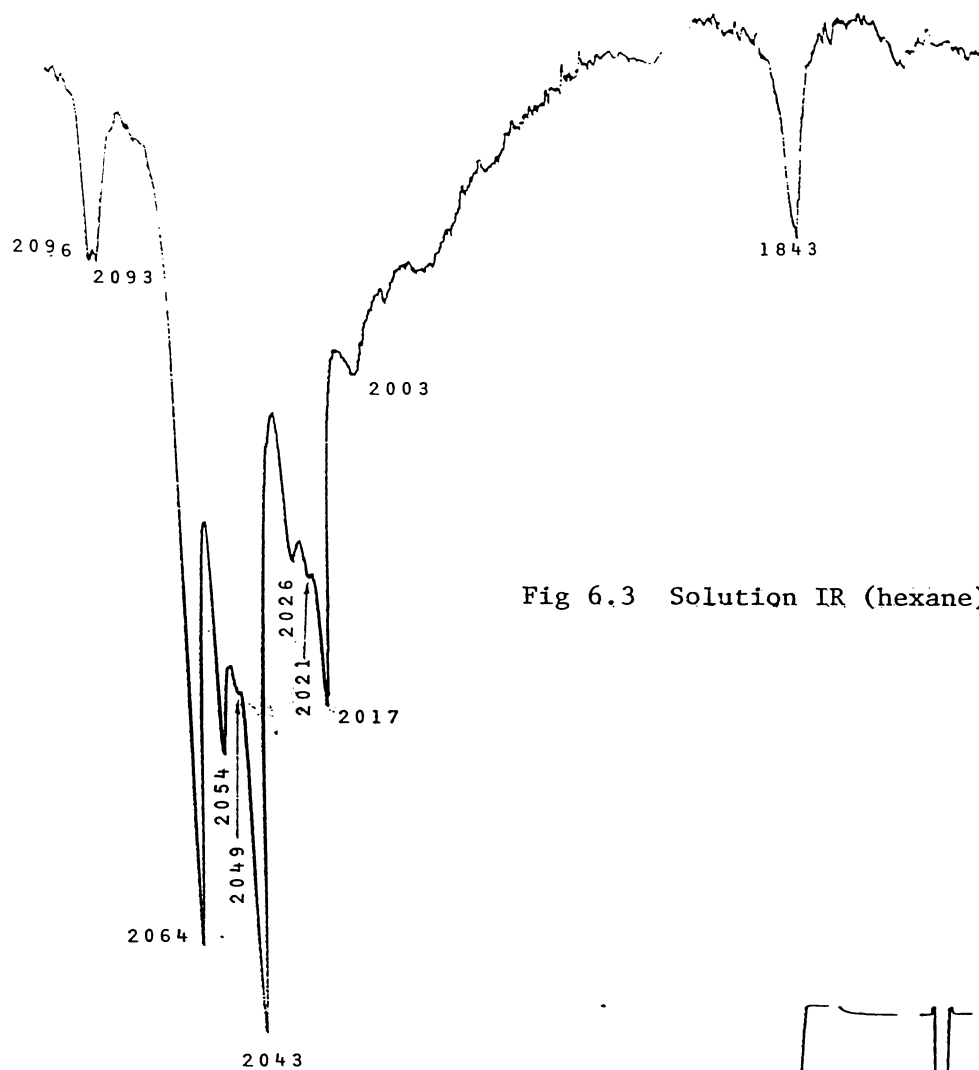
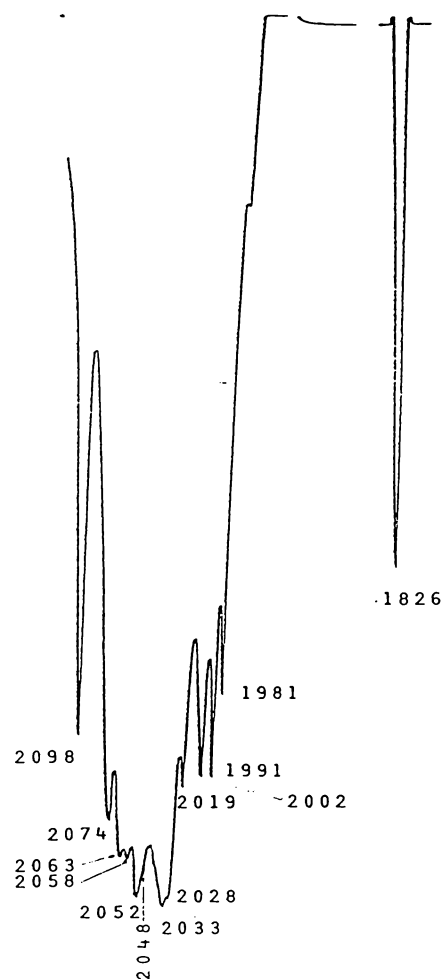


Fig 6.3 Solution IR (hexane)

Fig 6.4 Solid IR (CsI disc)



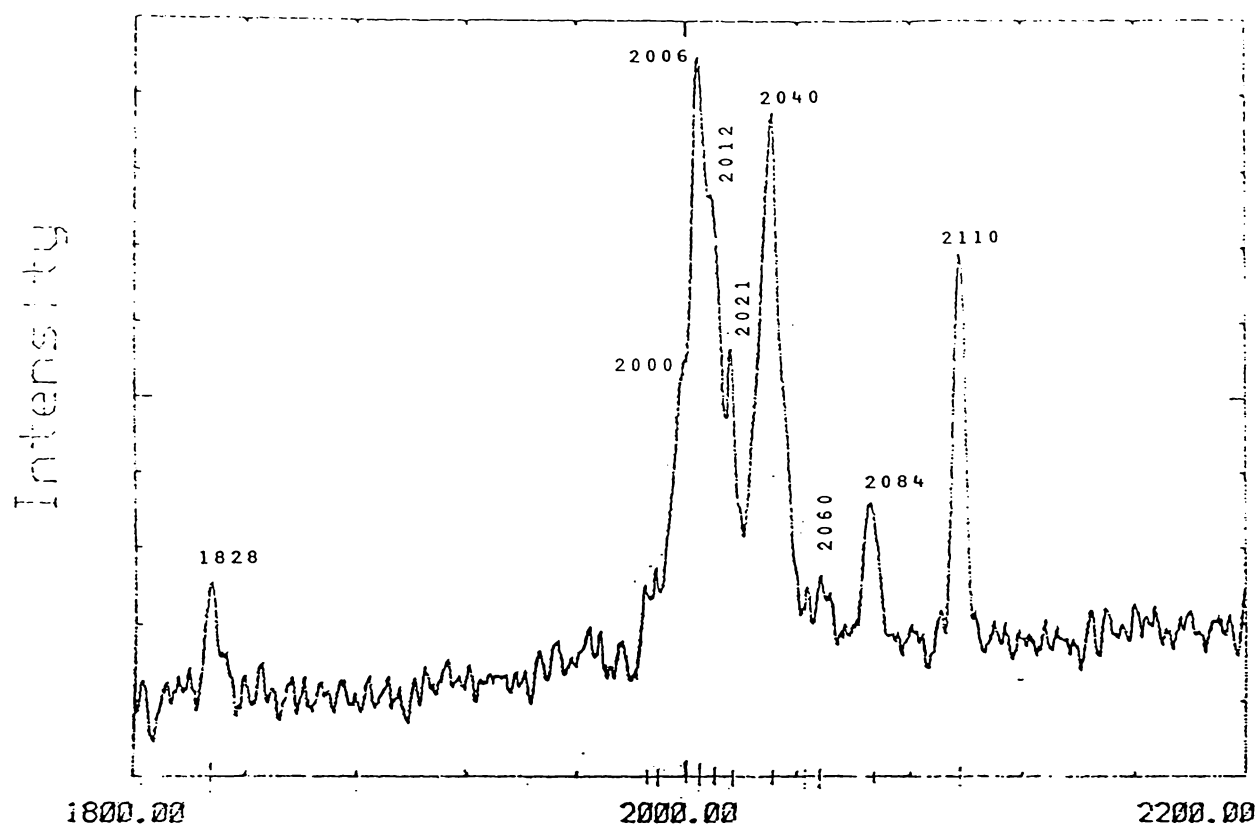


Fig 6.5 Raman Spectrum of $(\text{Me}_2\text{Ge})\text{GeCo}_4(\text{CO})_{13}$ (single crystal)

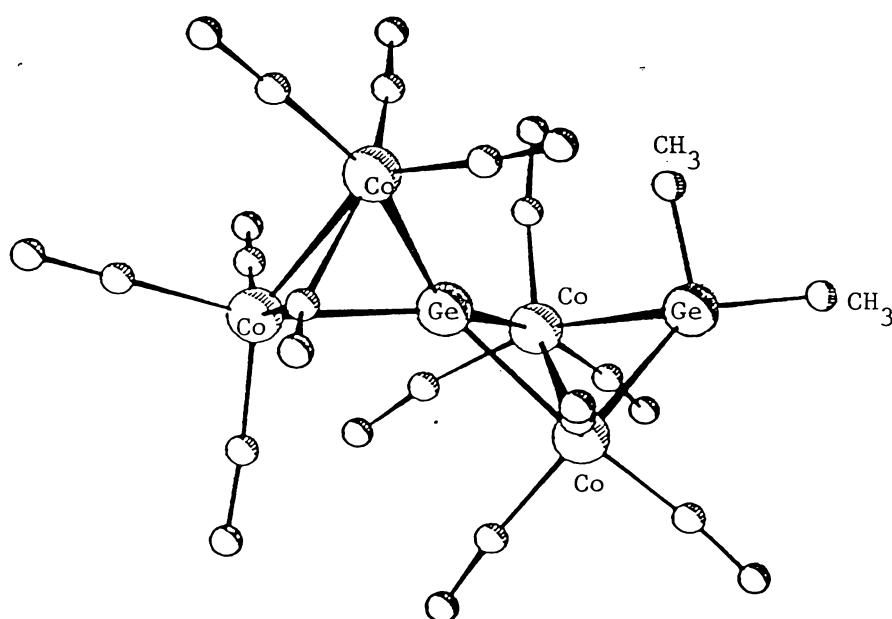


Fig 6.6 Proposed structure of $(\text{Me}_2\text{Ge})\text{GeCo}_4(\text{CO})_{13}$

A discussion on the infrared spectra of $(RR'Ge)GeCo_4(CO)_{13}$ type compounds is given in Section 6.15.

Table 6.3 Infrared and Raman spectra of $(Me_2Ge)GeCo_4(CO)_{13}$

Solution IR In Hexane		Solid IR CsI disc		Raman single crystal	
2096	w	2098	m	2110	ms
2093	w				
		2074	s	2084	w
2064	s	2063	s	2062	vw
		2058	s	2060	vw
2054	ms	2052	vs	2054	vw
2049	ms sh				
2043	vs	2048	s sh	2040	s
		2033	vs		
2026	m	2028	s sh		
2021	m sh			2021	m
2017	ms	2019	ms	2012	ms sh
2003	mw	2002	vs	2006	vs
		1991	ms	2000	m sh
				1990	vw
		1981	m	1986	vw
1843	w	1826	m	1828	w

6.4.2 Mass spectrum

The mass spectrum of $(Me_2Ge)GeCo_4(CO)_{13}$ has previously been reported [18,81] and therefore was not attempted in this work. The reported spectrum showed the major current carrier is $[P-(CO)_n]^+$ ($n = 0$ to 13). Weak $[P-Me-(CO)_n]^+$ ($n = 0$ to 13) envelopes were also present. A prominent $Ge_2Co_4^+$ envelope was observed.

6.4.3 NMR data

The NMR resonance of $(\text{Me}_2\text{Ge})\text{GeCo}_4(\text{CO})_{13}$ is summarised in Table 6.4 :

Table 6.4 NMR data of $(\text{Me}_2\text{Ge})\text{GeCo}_4(\text{CO})_{13}$ (in CDCl_3)

^1H NMR	δ 1.31 ppm at 27°C
^{13}C NMR	δ 202.5 ppm at -5°C
	δ 199.8 ppm at -50°C

The structure of $(\text{Me}_2\text{Ge})\text{GeCo}_4(\text{CO})_{13}$ in Fig 6.6 requires that one of the methyl groups is nearer to the μ -CO than the other. The observations of only one singlet indicated that the molecule is fluxional in solution resulting in both the methyl groups (therefore the six protons) in an equivalent position. Similarly, only a broad ^{13}C singlet was obtained for the 13 CO's, though at least three environments are expected : one for the six CO's on the two Co's with the μ -GeMe₂ unit, one for the six CO's on the two Co's containing the μ -CO and one for the μ -CO. A discussion of the NMR spectra of $(\text{Me}_2\text{Ge})\text{GeCo}_4(\text{CO})_{13}$ and related compounds is given in Section 6.10.4.

6.4.4 Crystal structure :

The preliminary cell dimensions of a number crystals of $(\text{Me}_2\text{Ge})\text{GeCo}_4(\text{CO})_{13}$ ($a = b = 12\text{\AA}$, $c = 34\text{\AA}$, $\alpha = \beta = \gamma = 90^\circ$, tetragonal) indicated that this compound was the same one investigated by Foster [18,81]. A full crystal structure of $(\text{Me}_2\text{Ge})\text{GeCo}_4(\text{CO})_{13}$ was not obtained as the data was collected on a twinned crystal (this problem was again encountered in all the crystals studied in this work). The heavy metal skeleton was obtained and this confirmed the expected arrangement shown in Fig 6.6. Further attempts at obtaining single crystals of $(\text{Me}_2\text{Ge})\text{GeCo}_4(\text{CO})_{13}$ in this work failed. All samples tested were found to be twinned. With the successful solution of the crystal

structure of $(\text{Me}_2\text{Ge})_2\text{GeCo}_4(\text{CO})_{12}$ [148], it was deemed unnecessary to pursue this structure any further.

6.5 Characterisation of $(\text{Me}_2\text{Ge})_2\text{GeCo}_4(\text{CO})_{12}$

6.5.1 Infrared and Raman spectra:

The solution and solid state infrared and the solid state Raman spectra of $(\text{Me}_2\text{Ge})_2\text{GeCo}_4(\text{CO})_{12}$ are shown in Figs 6.7 to 6.9, the details are in Table 6.5.

Table 6.5 Infrared and Raman spectra of $(\text{Me}_2\text{Ge})_2\text{GeCo}_4(\text{CO})_{12}$

Solution hexane		Solid CsI disc		Raman single crystal	
2081	w	2082	mw	2081	ms
		2058	ms	2056	w
2054	s	2053	ms sh		
2037	vs	2041	s sh	2036	w
		2031	vs sh	2034	w
		2029	vs sh		
2015	m	2018	m sh	2010	s sh
		2008	m	2006	vs
2003	ms	2002	m sh	2000	w
		1996	ms	1997	s
		1988	mw	1990	s
		1982	mw	1982	s
				1976	w
				1973	w

$(\text{Me}_2\text{Ge})_2\text{GeCo}_4(\text{CO})_{12}$ has idealised C_2 symmetry with a two fold axis passing through the central Ge atom and bisecting the angle between the two $\mu\text{-GeMe}_2$ units. The predicted number of bands based on this symmetry is 12 (6A and 6B), but only five bands were observed in the solution infrared spectrum. The solid state infrared and Raman

Infrared spectra of $(\text{Me}_2\text{Ge})_2\text{GeCo}_4(\text{CO})_{12}$

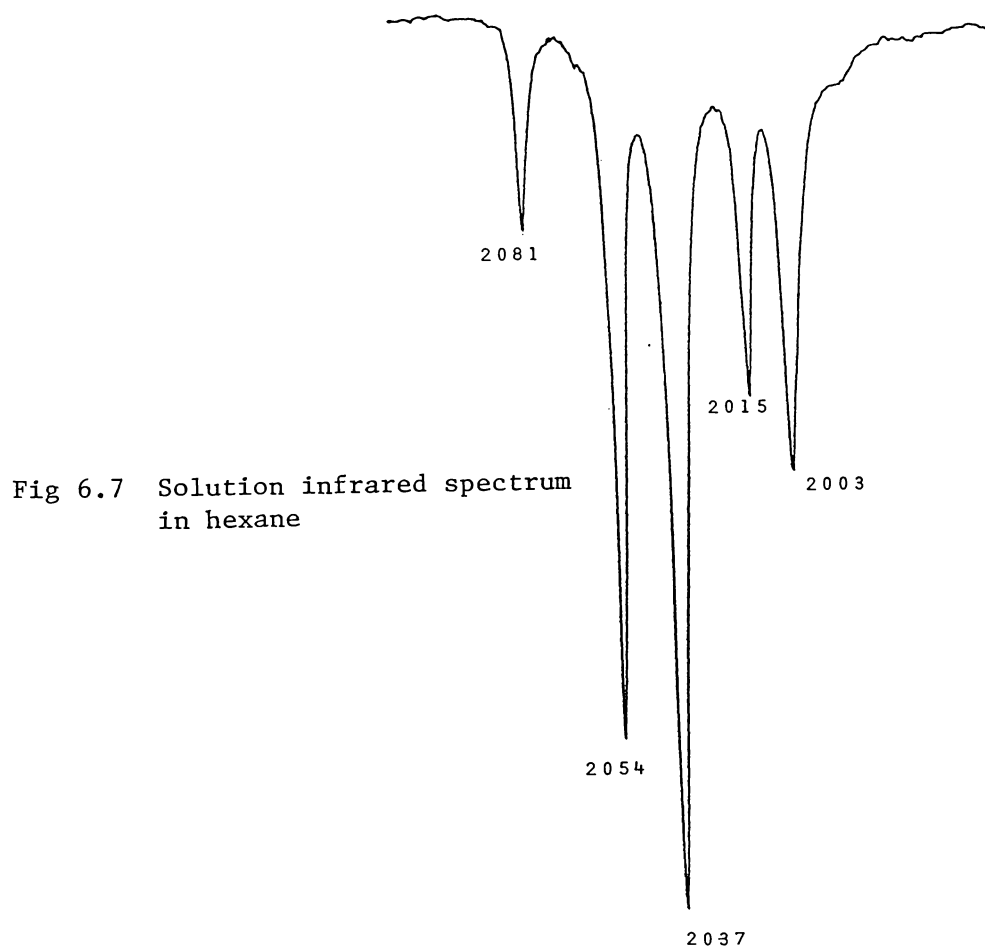


Fig 6.7 Solution infrared spectrum
in hexane

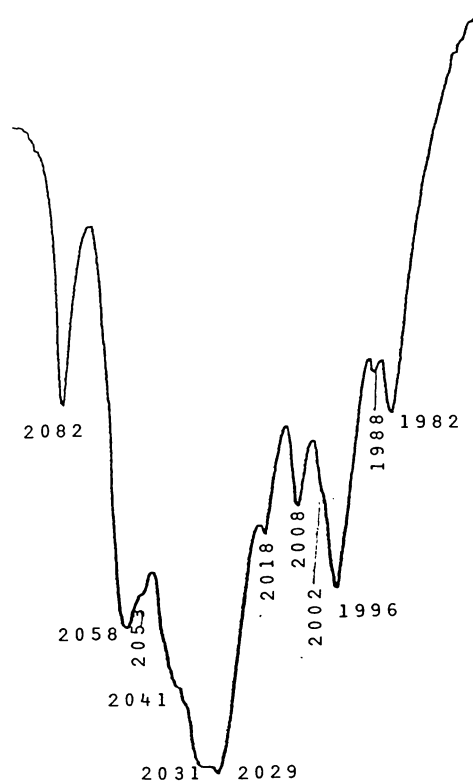


Fig 6.8 Solid IR spectrum
(CsI disc)

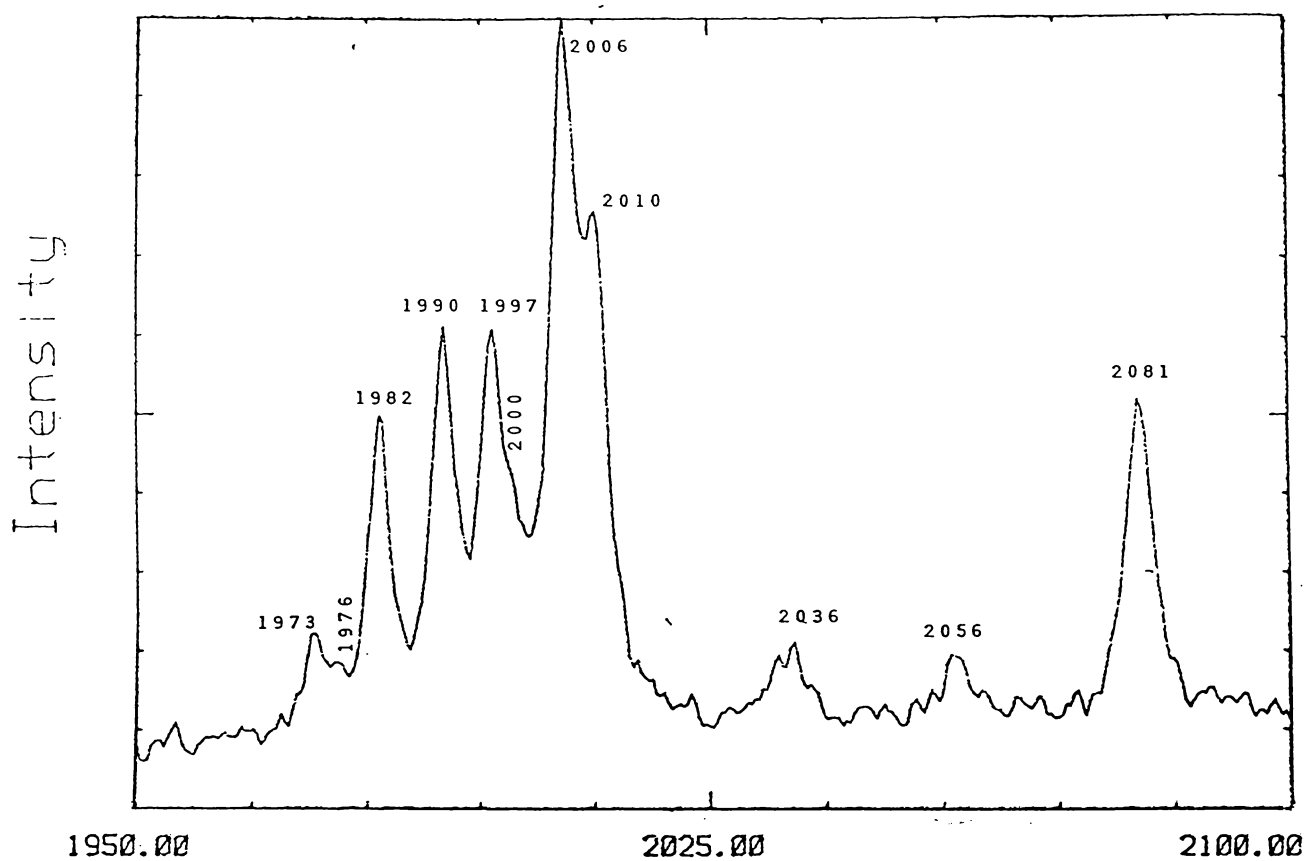


Fig 6.9 Raman spectrum of $(\text{Me}_2\text{Ge})_2\text{GeCo}_4(\text{CO})_{12}$

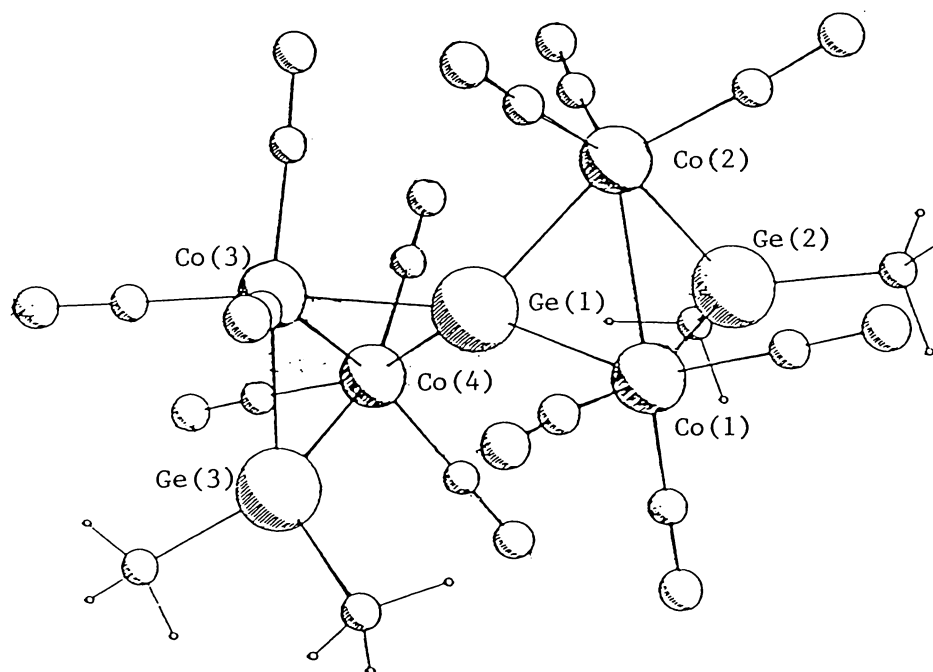


Fig 6.10 Crystal structure of $(\text{Me}_2\text{Ge})_2\text{GeCo}_4(\text{CO})_{12}$ [148]

spectra, however, showed all 12 predicted bands indicating lower site symmetry in the crystal (see Section 6.15 for discussion).

6.5.2 Mass spectrum :

The mass spectrum of $(\text{Me}_2\text{Ge})_2\text{GeCo}_4(\text{CO})_{12}$ was performed on pure crystals. This showed the highest envelope as that of $m/e = [\text{P-Me}]^+$. Overlapping of envelopes ($[\text{P-nCO}]^+$ and $[\text{P-(Me}_2\text{Ge)-n(CO)}]^+$) was observed. A total of 12 CO losses were recorded. The loss of a methyl group before $[\text{P-3CO}]^+$ (compare to $(\text{Me}_2\text{Ge})\text{GeCo}_4(\text{CO})_{13}$) was unexpected, and not normally observed. Most other compounds of this type lose all CO's first, then the methyl groups. The reason for this anomaly is uncertain.

A distinct Ge_2 pattern was apparent in some of the envelopes e.g. in 590-606 when the $[\text{P-(CO)}_n]^+$ envelope was weak. Envelopes due to $\text{GeCo}_4(\text{CO})_n^+$ were very weak and could only be picked up on the lower scale of the mass spectrum where interference from other envelopes was minimal. Details of the mass spectrum of $(\text{Me}_2\text{Ge})_2\text{GeCo}_4(\text{CO})_{12}$ is given in Table 6.6.

6.5.3 NMR data :

The ^1H NMR spectrum of $(\text{Me}_2\text{Ge})_2\text{GeCo}_4(\text{CO})_{12}$ (at 27°C , in CDCl_3) showed a singlet at δ 1.34 ppm.

The crystal structure of $(\text{Me}_2\text{Ge})_2\text{GeCo}_4(\text{CO})_{12}$ (Fig 6.10) showed two methyl proton environments. However, only a singlet was observed, indicating that all the methyl groups were equivalent in solution. This indicates that the molecule is fluxional in solution resulting in a single proton environment. A discussion on the NMR of $(\text{RR}'\text{Ge})\text{GeCo}_4(\text{CO})_{13}$ and $(\text{RR}'\text{Ge})_2\text{GeCo}_4(\text{CO})_{12}$ is given in Section 6.10.4.

Table 6.6 Mass spectrum of $(\text{Me}_2\text{Ge})_2\text{GeCo}_4(\text{CO})_{12}$

m/e	Int	Possible assignments
833-843	vw	$[\text{P-Me}]^+$
809-818	m	$[\text{P-Me-CO}]^+$
783-794	ms	$[\text{P-Me-2CO}]^+$
759-768	ms	$[\text{P-3CO}]^+$
745-757	vw	$[\text{P-Me-3CO}]^+$, $[\text{P-(Me}_2\text{Ge)}]^+$
732-744	ms	$[\text{P-4CO}]^+$
702-716	ms	$[\text{P-5CO}]^+$, $[\text{P-(Me}_2\text{Ge)-CO}]^+$
674-686	vs	$[\text{P-6CO}]^+$, $[\text{P-(Me}_2\text{Ge)-2CO}]^+$
646-660	ms	$[\text{P-7CO}]^+$, $[\text{P-(Me}_2\text{Ge)-3CO}]^+$
614-630	s	$[\text{P-8CO}]^+$, $[\text{P-(Me}_2\text{Ge)-4CO}]^+$
602-616	vw	$[\text{P-Me-8CO}]^+$
590-602	m	$[\text{P-9CO}]^+$, $[\text{P-(Me}_2\text{Ge)-5CO}]^+$
575-590	mw	$[\text{P-Me-9CO}]^+$
560-570	m	$[\text{P-10CO}]^+$, $[\text{P-(Me}_2\text{Ge)-6CO}]^+$
532-540	w	$[\text{P-11CO}]^+$, $[\text{P-(Me}_2\text{Ge)-7CO}]^+$
508-518	m	$[\text{P-12CO}]^+$, $[\text{P-(Me}_2\text{Ge)-8CO}]^+$
549-561	w	$[\text{P-Me-10CO}]^+$
476-490	m	$[\text{P-12CO-2Me}]^+$, $[\text{P-(Me}_2\text{Ge)-9CO}]^+$
465-472	m	$[\text{P-12CO-3Me}]^+$
448-459	s	$[\text{P-12CO-4Me}]^+$, $[\text{P-(Me}_2\text{Ge)-10CO}]^+$
432-448	vw	$\text{Ge}_2\text{Co}_4(\text{CO})_2^+$
415-430	w	$[\text{P-(Me}_2\text{Ge)-11CO}]^+$
405-412	mw	$\text{Ge}_2\text{Co}_4(\text{CO})^+$
390-400	m	$[\text{P-(Me}_2\text{Ge)-12CO}]^+$
378-385	w	Ge_2Co_4^+

6.5.4 Crystal Structure :

The preliminary studies of a single crystal of $(\text{Me}_2\text{Ge})_2\text{GeCo}_4(\text{CO})_{12}$ indicated that the unit cell dimensions ($a = 9.7\text{\AA}$, $b = 15.0\text{\AA}$, $c = 9.6\text{\AA}$, $\alpha = 97^\circ$, $\beta = 92^\circ$, $\gamma = 100^\circ$ and space group, $P\bar{1}$) of the crystal were identical to those of $(\text{Me}_2\text{Ge})_2\text{GeCo}_4(\text{CO})_{12}$ determined crystallographically by M.Service [148]. The crystal structure

consists of two $\text{Co}_2(\text{CO})_6$ groups bridged by a central germanium atom, and two Me_2Ge groups bridging both ends of the Co-Co bonds (Fig 6.10). One interesting feature of the crystal structure of $(\text{Me}_2\text{Ge})_2\text{GeCo}_4(\text{CO})_{12}$ is, like $\text{GeCo}_4(\text{CO})_{14}$, the central Ge atom does not bridge either of the Co-Co bond symmetrically. The corresponding $\mu\text{-GeMe}_2$ group is also unsymmetric, being displaced toward the Co with the long Ge-Co bond. The Co-Co bonds (av 2.642Å) are also longer than those of $\text{GeCo}_4(\text{CO})_{14}$ (2.567Å). This is expected as the Co-Co bonds are bridged by two Ge atoms.

6.6 Discussion : The reaction of Me_2GeH_2 with $\text{GeCo}_4(\text{CO})_{14}$ and $(\text{Me}_2\text{Ge})\text{GeCo}_4(\text{CO})_{13}$

The reactions of Me_2GeH_2 with $\text{GeCo}_4(\text{CO})_{14}$ and $(\text{Me}_2\text{Ge})\text{GeCo}_4(\text{CO})_{13}$ are summarised in Table 6.7. The products from Me_2GeH_2 and $\text{GeCo}_4(\text{CO})_{14}$ were characterised as $(\text{Me}_2\text{Ge})\text{GeCo}_4(\text{CO})_{13}$ and $(\text{Me}_2\text{Ge})_2\text{GeCo}_4(\text{CO})_{12}$ by spectroscopic means and X-ray crystallography (Sections 6.4, 6.5, [18,81,148]).

Table 6.7 Summary of results of the reaction of Me_2GeH_2 with $\text{GeCo}_4(\text{CO})_{14}$ and $(\text{Me}_2\text{Ge})\text{GeCo}_4(\text{CO})_{13}$

Reaction of Me_2GeH_2 with $\text{GeCo}_4(\text{CO})_{14}$			
	Run 1	Run 2	Run 3
$\text{GeCo}_4(\text{CO})_{14}$ (mmol)	0.331	0.4299	0.195
Me_2GeH_2 : $\text{GeCo}_4(\text{CO})_{14}$	1.5 : 1	2.7 : 1	1.5 : 1 then 3 : 1
Reaction temperature (°C)	20	20	28-34
Reaction time (days)	30	60	55
sealed/opened tube	sealed	sealed	open
Yield* $(\text{Me}_2\text{Ge})\text{GeCo}_4(\text{CO})_{13}$	38% (wt)	52% (wt)	0
$(\text{Me}_2\text{Ge})_2\text{GeCo}_4(\text{CO})_{12}$	&	&	97%

Table 6.7 *cont'd...*Reaction of $(\text{Me}_2\text{Ge})\text{GeCo}_4(\text{CO})_{13}$ with Me_2GeH_2

$(\text{Me}_2\text{Ge})\text{GeCo}_4(\text{CO})_{13}$ (mmol)	0.145
$\text{Me}_2\text{GeH}_2 : (\text{Me}_2\text{Ge})\text{GeCo}_4(\text{CO})_{13}$	2.5 : 1
Reaction temperature	20
Reaction time (days)	90
shaking	yes
sealed/opened tube	sealed
Yield $(\text{Me}_2\text{Ge})_2\text{GeCo}_4(\text{CO})_{12}$	100%

& could not be isolated

The incondensable gas measurements and the infrared spectra obtained in the reaction of Me_2GeH_2 with $\text{GeCo}_4(\text{CO})_{14}$ (see 6.2 Run 3) indicated that the reaction proceeds via equations 6.1 and 6.2. It is believed that one of the bridging CO groups in $\text{GeCo}_4(\text{CO})_{14}$ is first replaced by a Me_2Ge with the release of CO and H_2 to form $(\text{Me}_2\text{Ge})\text{GeCo}_4(\text{CO})_{13}$. The replacement of the second bridging CO by a second Me_2Ge group then occurred, and requires only mild conditions. The di-substituted product appeared as early as 3 days into the reaction in Run 3 (open tube) where the incondensable gases were constantly removed. A 97% conversion to $(\text{Me}_2\text{Ge})_2\text{GeCo}_4(\text{CO})_{12}$ was achieved in 10 days.

In the sealed tube reaction, small amounts of $(\text{Me}_2\text{Ge})_2\text{GeCo}_4(\text{CO})_{12}$ were indicated in the infrared spectrum of the supernatant solution of the product mixture of Run 1 ($\text{Me}_2\text{GeH}_2 : \text{GeCo}_4(\text{CO})_{14} = 1.5 : 1$) with a short reaction time of 30 days, and it is quite surprising that it was not observed in the previously reported reactions by Foster [18] with a higher $\text{Me}_2\text{GeH}_2 : \text{GeCo}_4(\text{CO})_{14}$ ratio and longer reaction times (7 and 12 weeks). A reaction time of 60 days and a 2.7 : 1 ratio of $\text{Me}_2\text{GeH}_2 : \text{GeCo}_4(\text{CO})_{14}$ showed an improved yield of $(\text{Me}_2\text{Ge})_2\text{GeCo}_4(\text{CO})_{12}$, though it

could not be separated due to a small solubility difference with $(\text{Me}_2\text{Ge})\text{GeCo}_4(\text{CO})_{13}$ and $\text{GeCo}_4(\text{CO})_{14}$. Similar reactions by M. Service using five time excess of Me_2GeH_2 with $\text{GeCo}_4(\text{CO})_{14}$ at room temperature produced only $(\text{Me}_2\text{Ge})_2\text{GeCo}_4(\text{CO})_{12}$ with a reaction time of 90 days [148]. Pure $(\text{Me}_2\text{Ge})_2\text{GeCo}_4(\text{CO})_{12}$ was obtained in a 90 days reaction of $(\text{Me}_2\text{Ge})\text{GeCo}_4(\text{CO})_{13}$ with Me_2GeH_2 (1:2.5 ratio) at room temperature. It appears that the best procedure of obtaining $(\text{Me}_2\text{Ge})_2\text{GeCo}_4(\text{CO})_{12}$ is by the open tube reaction demonstrated by Run 3, while the best method of preparing $(\text{Me}_2\text{Ge})\text{GeCo}_4(\text{CO})_{13}$ is by using a lower ratio of Me_2GeH_2 to $\text{GeCo}_4(\text{CO})_{14}$ as in Runs 1 and 2.

The above experiments are in marked contrast to the previous assertion that only one of the bridging CO's of $\text{GeCo}_4(\text{CO})_{14}$ can be replaced by Me_2Ge groups [18].

6.7 Decarbonylation of $(\text{Me}_2\text{Ge})\text{GeCo}_4(\text{CO})_{13}$

6.7.1 Decarbonylation of $(\text{Me}_2\text{Ge})\text{GeCo}_4(\text{CO})_{13}$ - incondensable gas and infrared experiment

Run 1

Experimental :

$(\text{Me}_2\text{Ge})\text{GeCo}_4(\text{CO})_{13}$ (0.073g, 0.094 mmol) and hexane (5 ml) were placed in a 20 ml reaction tube and heated at 30°C for 50 days. The temperature was then raised to 50°C. Incondensable gases were measured intermittently as the reaction proceeded (Table 6.8, Fig 6.11). Samples were also drawn for infrared spectra as the reaction proceeded.

Observations and Workup :

The colour of the $(\text{Me}_2\text{Ge})\text{GeCo}_4(\text{CO})_{13}$ solution changed from orange/red to yellow/brown and then to dark red/brown. The composition of the gas evolved was not determined in most samplings because of the

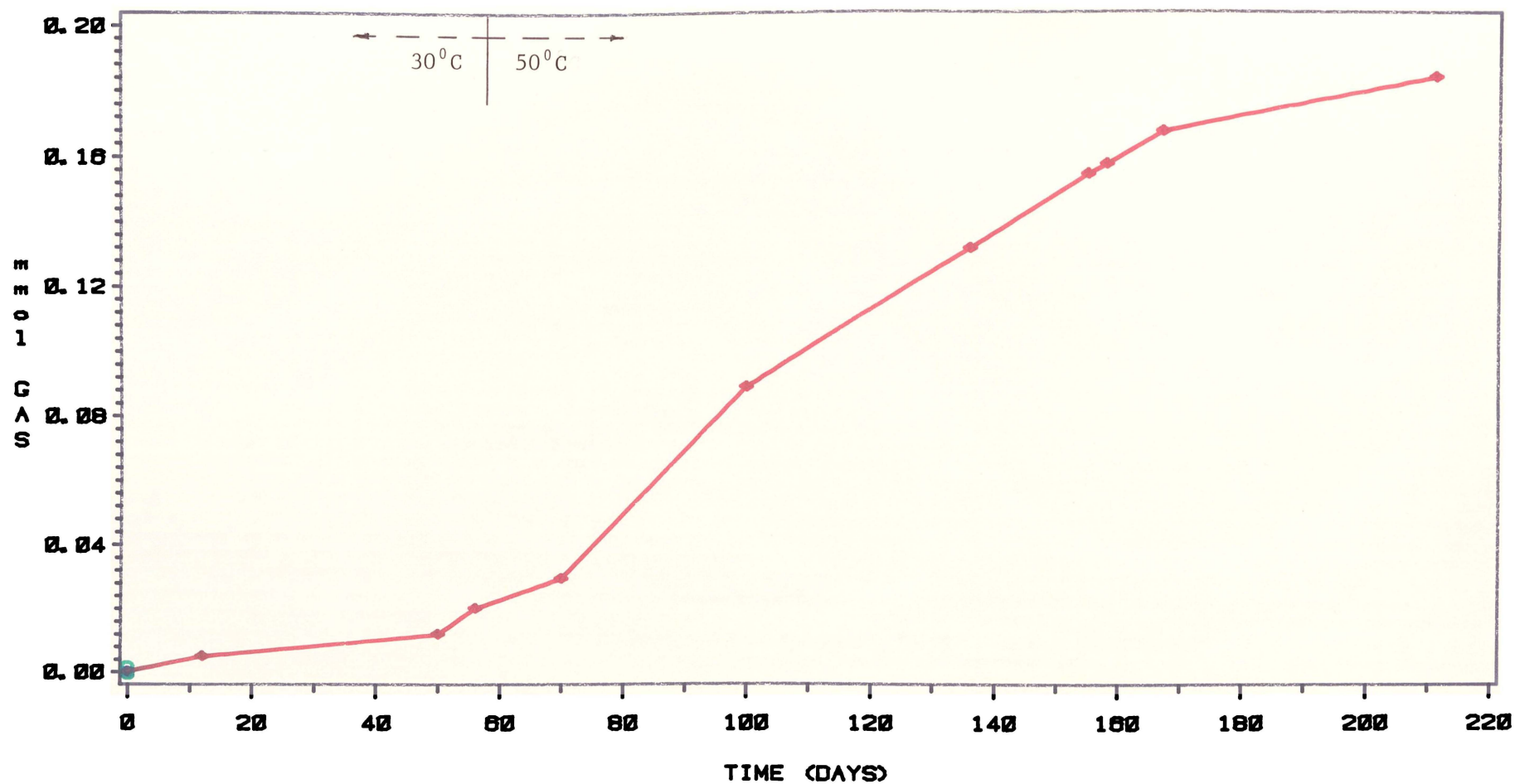
small amount of incondensable gas evolved (therefore low accuracy). Two samplings (day 100, and day 155) indicated no H_2 in the incondensable gas. The gas evolution was very slow in the initial stages (Table 6.8). A sudden 'burst' of gas was observed on the 100th day of reaction when the temperature was raised to 50°C.

Table 6.8 Incondensable gas evolution of the decarbonylation of $(Me_2Ge)GeCo_4(CO)_{13}$, Run 1

Time (days)	Gas evolved (mmol)	Total gas evolved (mmol)	Remarks
12	0.005	0.005	at 30°C
50	0.007	0.012	
56	0.008	0.020	at 50°C
70	0.009	0.029	
100	0.059	0.088	100% CO
136	0.043	0.131	intermediate work up
155	0.023	0.154	100% CO
158	0.003	0.157	
167	0.010	0.167	
211	0.016	0.184	

After 136 days, the incondensable gas evolved exceeded the amount for 1 CO evolution. The contents of the reaction tube were worked up. The infrared of the supernatant solution indicated not only $(Me_2Ge)GeCo_4(CO)_{13}$, but also $(Me_2Ge)_2GeCo_4(CO)_{12}$ and $GeCo_4(CO)_{14}$. The intensity ratio was approximately 3 : 4 : 3 respectively (note : due to different solubilities of each compound in hexane, the intensity ratio does not represent the concentration level of each compound in solution). The dark solid fraction was dissolved in CH_2Cl_2 and hexane. The infrared spectrum of this indicated the presence of mainly

Figure 6.11
Incondensable Gas Evolution Of The
Decarbonylation of $(Me_2Ge)GeCo_4(CO)_{13}$



TOTAL GAS = -----

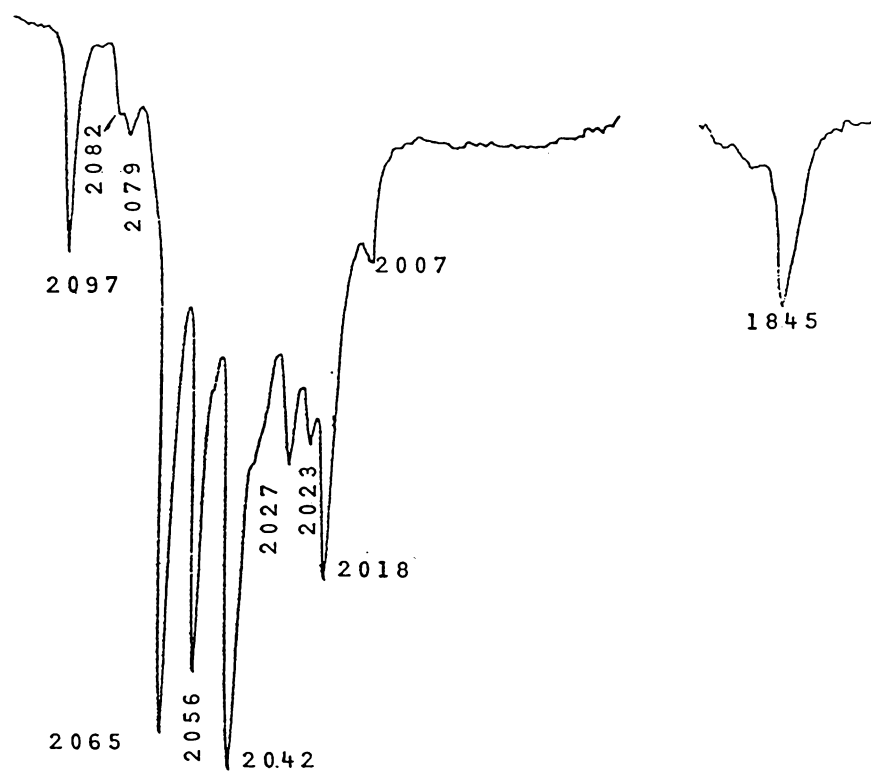


Fig 6.12 IR spectrum of the supernatant solution of the decarbonylation of $(\text{Me}_2\text{Ge})\text{GeCo}_4(\text{CO})_{13}$ on day 34, Run 2

$(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ plus a small amount of $\text{GeCo}_4(\text{CO})_{14}$ and $(\text{Me}_2\text{Ge})_2\text{GeCo}_4(\text{CO})_{12}$. The solvent was removed, and the remaining solid washed with a small amount of hexane. The residual solid was dissolved in CH_2Cl_2 forming a red solution. This has an infrared spectrum identical to that of $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ (2063sh, 2031vs, 2010m sh, 1833-1841vw br) [18,84] (see also Chapter Three and Four, Section 4.2.3 for characterisation of $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$).

All the fractions were returned to the reaction tube for further heating until a total of approximately 2 mole of incondensable gas per mole $(\text{Me}_2\text{Ge})\text{GeCo}_4(\text{CO})_{13}$ (211 days) were released. Some dark solid and a red brown solution were formed. The infrared spectrum of the red brown solution indicated the presence of only $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$. The solid fraction was dissolved in CH_2Cl_2 forming a red solution. The infrared spectrum of the CH_2Cl_2 fraction indicated that the only product was $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$. A small amount of dark solid remained undissolved (possibly undissolved $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$).

The weight of the final product was not recorded due to the accumulation of a large amount of grease at this stage.

Run 2

Reaction procedures were as in Run 1, using $(\text{Me}_2\text{Ge})\text{GeCo}_4(\text{CO})_{13}$ (0.084g, 0.109mmol) and a temperature of 50°C was used throughout the reaction.

Results :

The incondensable gas measurements are presented in Table 6.9.

Similar colour changes were observed as in Run 1. Samples of the supernatant solution were withdrawn for infrared studies on day 34 and 59 (Table 6.10). On day 34 $(\text{Me}_2\text{Ge})\text{GeCo}_4(\text{CO})_{13}$, $(\text{Me}_2\text{Ge})_2\text{GeCo}_4(\text{CO})_{12}$ and $\text{GeCo}_4(\text{CO})_{14}$ were present in the approximate ratio (IR intensity of

band 2097 : 2081 : 2079 cm^{-1}) : 3 : 1 : 1 (Fig 6.12). On day 59, the intensity ratio (IR spectrum not as well resolved as on day 34) was approximately 8 : 1 : 1. The reaction was then worked up. The hexane soluble fraction was a mixture of $(\text{Me}_2\text{Ge})\text{GeCo}_4(\text{CO})_{13}$, $(\text{Me}_2\text{Ge})_2\text{GeCo}_4(\text{CO})_{12}$ and $\text{GeCo}_4(\text{CO})_{14}$ as shown by IR. The infrared spectrum of the CH_2Cl_2 fraction consisted of only $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$.

Table 6.9 Incondensable gas measurement of the decarbonylation of $(\text{Me}_2\text{Ge})\text{GeCo}_4(\text{CO})_{13}$, Run 2

Days	Gas (mmol)	Total gas (mmol)
18	0.05	0.05
24	0.02	0.07
34	0.02	0.09
59	0.05	0.15

Note : this reaction was stopped before completion of reaction due to the inavailability of the Toepler pump and time

Table 6.10 IR spectra of supernatant solution of Run 2

Day 34	Day 59	Possible assignments
2097 mw	2097 m	$(\text{Me}_2\text{Ge})\text{GeCo}_4(\text{CO})_{13}$
2082 w	2081 w br	$(\text{Me}_2\text{Ge})_2\text{GeCo}_4(\text{CO})_{12}$
2079 w		$\text{GeCo}_4(\text{CO})_{14}$
2065 vs	2063 s	$(\text{Me}_2\text{Ge})\text{GeCo}_4(\text{CO})_{13} + \text{GeCo}_4(\text{CO})_{14}?$
2056 s	2054 vs	$(\text{Me}_2\text{Ge})\text{GeCo}_4(\text{CO})_{13} + (\text{Me}_2\text{Ge})_2\text{GeCo}_4(\text{CO})_{12}$
2042 vs	2042 vs	$(\text{Me}_2\text{Ge})\text{GeCo}_4(\text{CO})_{13}$
2039 m sh	2039 s sh	$(\text{Me}_2\text{Ge})_2\text{GeCo}_4(\text{CO})_{12} + \text{GeCo}_4(\text{CO})_{14}$
	2034 ms	$\text{GeCo}_4(\text{CO})_{14}$
2027 m	2027 ms sh	$(\text{Me}_2\text{Ge})\text{GeCo}_4(\text{CO})_{13}$
2023 m		$\text{GeCo}_4(\text{CO})_{14}$
2018 ms	2016 s	$(\text{Me}_2\text{Ge})\text{GeCo}_4(\text{CO})_{13} + (\text{Me}_2\text{Ge})_2\text{GeCo}_4(\text{CO})_{12}$
2007 mw sh	2004 m	$(\text{Me}_2\text{Ge})\text{GeCo}_4(\text{CO})_{13} + \text{GeCo}_4(\text{CO})_{14}$
1845 mw	1844 m	$(\text{Me}_2\text{Ge})\text{GeCo}_4(\text{CO})_{13} + \text{GeCo}_4(\text{CO})_{14}$

Yield :

Weight of $(\text{Me}_2\text{Ge})\text{GeCo}_4(\text{CO})_{13}$ mixture* = 0.05g

Weight of $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ = 0.034g = 0.047 mmol = 43% yield

* mixture of $(\text{Me}_2\text{Ge})\text{GeCo}_4(\text{CO})_{13}$, $(\text{Me}_2\text{Ge})_2\text{GeCo}_4(\text{CO})_{12}$, $\text{GeCo}_4(\text{CO})_{14}$ and possibly some $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$

6.7.2 Decarbonylation of $(\text{Me}_2\text{Ge})\text{GeCo}_4(\text{CO})_{13}$ -- ^1H NMR experiment

Run 1

Experimental :

$(\text{Me}_2\text{Ge})\text{GeCo}_4(\text{CO})_{13}$ crystals (of unknown weight) were sealed in 5mm NMR tube with a small amount of CDCl_3 . ^1H NMR spectra was run during the heating process (at 49°C). The ^1H NMR spectra are presented in Fig 6.13.

Observations and workup :

At the start of the reaction, a singlet at δ 1.31 ppm was observed. After 3 days of heating, the most obvious change in the spectrum was that signal to noise level was very poor. It was also difficult to lock on the signal. The chemical shift of the signal did not appear to have changed but the signal had broadened. The relative height of the signal versus that of solvent had dropped from 9.5 : 1 (before heating) to 5 : 1.

After another week of heating, a noisy spectrum was again obtained. Two very close peaks were observed : one at δ 1.34 ppm, another at δ 1.31 ppm plus a shoulder at δ 1.29 ppm. The first peak was assigned as that of $(\text{Me}_2\text{Ge})_2\text{GeCo}_4(\text{CO})_{12}$ (δ 1.34 ppm) and the second peak as that of $(\text{Me}_2\text{Ge})\text{GeCo}_4(\text{CO})_{13}$ (δ 1.31 ppm). The relative height of the broad signal to that of the solvent was now 3.4 : 1. Some dark deposit had accumulated at the bottom of the NMR tube.

All chemical shifts in δ ppm

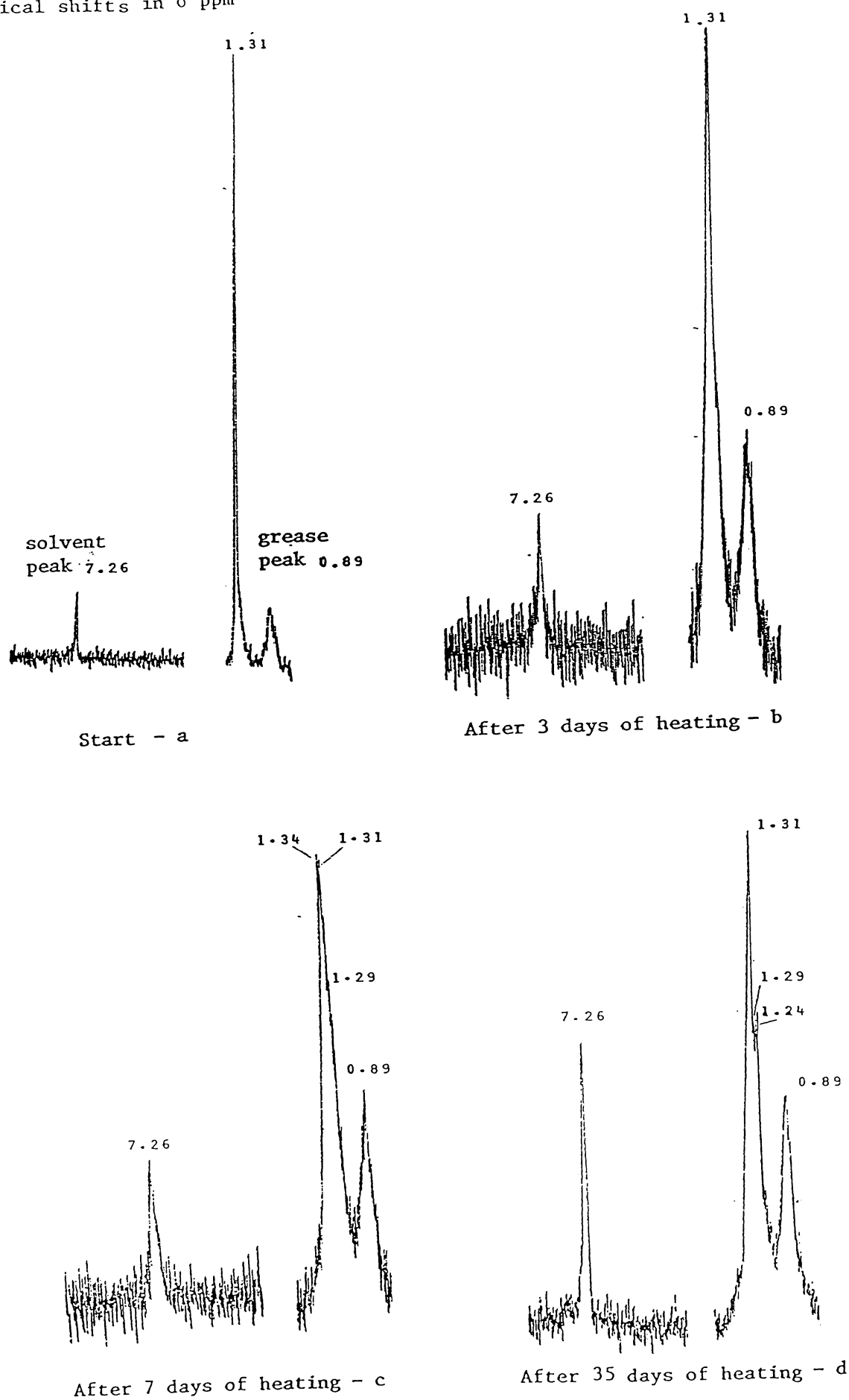
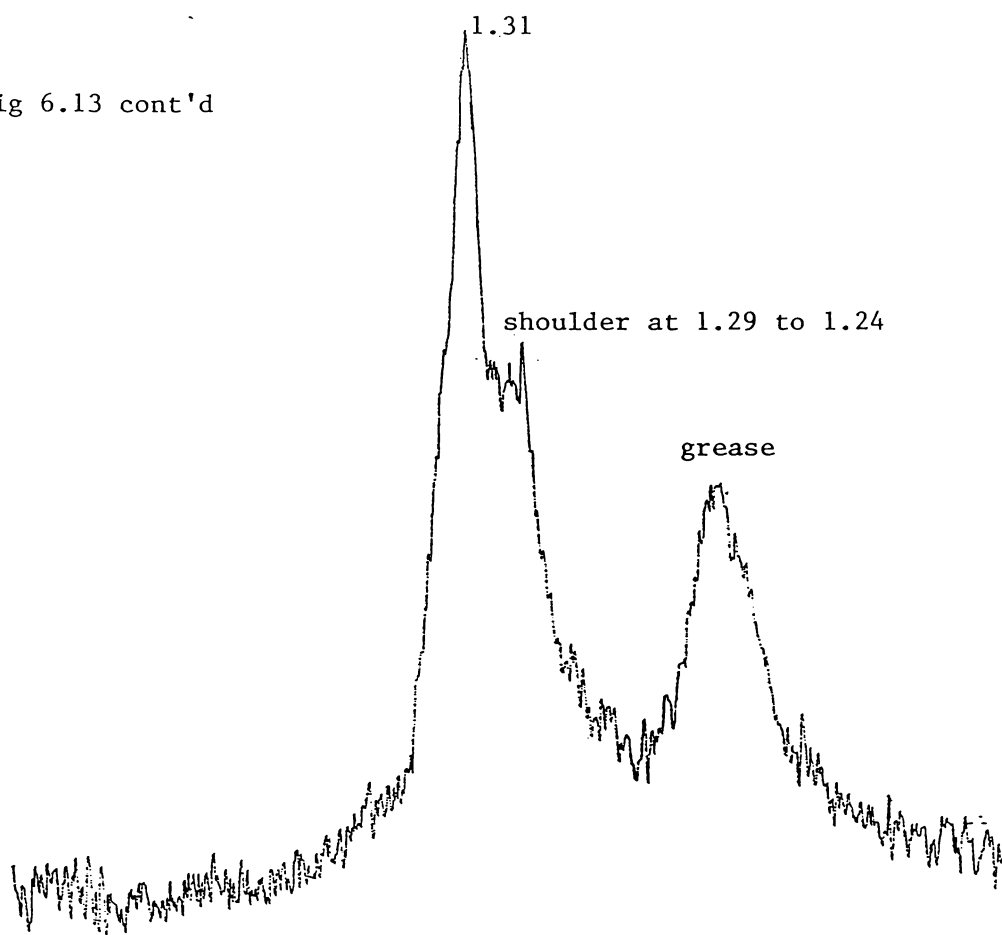


Fig 6.13 NMR spectra of the decarbonylation of $(\text{Me}_2\text{Ge})\text{GeCo}_4(\text{CO})_{13}$

Fig 6.13 cont'd



e -- expanded view of methyl peak in d

A further 18 days of heating showed that the most prominent peak was the one at δ 1.31 ppm with a broad shoulder between δ 1.29 to 1.24 ppm (see Fig 6.13e). As the noise level was high it was not certain if the peak at δ 1.34 ppm was still present. On further heating, the noise level was very high and the solvent signal could not be locked on.

The NMR tube was left in the oil bath for about two months. A yellow brown solution with a brown deposit (looked powdery) at the bottom of the tube^{were observed}. Attempt to run the ^1H NMR spectrum again failed. The NMR tube was opened and an infrared spectrum of the supernatant solution was obtained from Philips Pye Unicam Pu 9512 spectrophotometer as the Perkin Elmer 180 was down. The IR bands (which were only about $\pm 5\text{ cm}^{-1}$ accurate), indicated the presence of $(\text{Me}_2\text{Ge})_2\text{GeCo}_4(\text{CO})_{12}$, $\text{GeCo}_4(\text{CO})_{14}$ and $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$. The latter compound seemed to be the major component. The remaining brown solid fraction however decomposed to a purple colour on working up (had to worked up in the presence of air) and could not be further identified.

Run 2

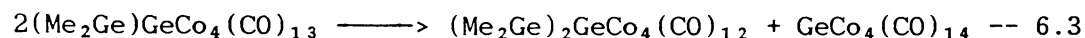
Experimental procedures were as in Run 1 except that about half the concentration of $(\text{Me}_2\text{Ge})\text{GeCo}_4(\text{CO})_{13}$ was used.

At the start of the reaction, a singlet at 1.31 ppm was observed. After heating for 14 days, a dark brown solution with a black residue was obtained. Like the first sample, the ^1H NMR spectrum could not be obtained due to difficulty in locking in the solvent signal.

A possible cause for the deterioration of the NMR signal is the production of paramagnetic species. This was confirmed by an ESR spectrum of the contents of both NMR samples which gave a strong signal with a g value of 4.33, which is consistent with a $3d^7$ ion in an octahedral field [150].

6.7.3 Discussion of Decarbonylation of $(\text{Me}_2\text{Ge})\text{GeCo}_4(\text{CO})_{13}$

The results from 6.7.1 and 6.7.2 suggested that on heating, $(\text{Me}_2\text{Ge})\text{GeCo}_4(\text{CO})_{13}$ disproportionated to form $(\text{Me}_2\text{Ge})_2\text{GeCo}_4(\text{CO})_{12}$ and $\text{GeCo}_4(\text{CO})_{14}$ (based on infrared spectrum). A possible balanced equation is in equation 6.3.



One of these three compounds or a combination of all three of them then goes to form $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$.

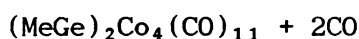
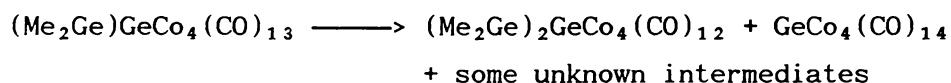
The results obtained from Section 6.7 were most unexpected as the formation of $(\text{Me}_2\text{Ge})_2\text{GeCo}_4(\text{CO})_{12}$ from $(\text{Me}_2\text{Ge})\text{GeCo}_4(\text{CO})_{13}$ would necessarily involve a Me_2Ge transfer. The formation of $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ was again unexpected as this would require a second Me_2Ge plus a Me transfer if it was derived from $(\text{Me}_2\text{Ge})_2\text{GeCo}_4(\text{CO})_{12}$ and $\text{GeCo}_4(\text{CO})_{14}$; or a Me transfer if it formed from $(\text{Me}_2\text{Ge})\text{GeCo}_4(\text{CO})_{13}$.

In Run 2, the intensity ratio of $(\text{Me}_2\text{Ge})\text{GeCo}_4(\text{CO})_{13}$: $(\text{Me}_2\text{Ge})_2\text{GeCo}_4(\text{CO})_{12}$: $\text{GeCo}_4(\text{CO})_{14}$ IR bands (see Table 6.10) was 3 : 1 : 1 and 8 : 1 : 1 on the 34th and 59th day of the reaction respectively. This was unexpected as the concentration of $(\text{Me}_2\text{Ge})\text{GeCo}_4(\text{CO})_{13}$ was expected to decrease with time. This may be due to the build up of the concentration of $(\text{Me}_2\text{Ge})_2\text{GeCo}_4(\text{CO})_{12}$ and $\text{GeCo}_4(\text{CO})_{14}$ to a certain level before they were consumed to form $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$.

The ^1H NMR experiment indicated the formation of a paramagnetic intermediate which was confirmed by an ESR spectrum. The broad shoulder between δ 1.29 ppm and δ 1.24 ppm could be due to the intermediates associated with the Me or Me_2Ge transfer. Unfortunately, the whole reaction could not be followed to completion by ^1H NMR experiments due

to high noise level. Similar difficulties had been reported earlier by B.Graham and R.Gerlach in the reaction of MeGeH_3 with $\text{Co}_2(\text{CO})_8$ [20]. Though $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ was indicated in the infrared spectrum of the supernatant solution of Run 1 after further heating, similar results could not be confirmed in the solid fraction due to decomposition. Also, in both the NMR runs, no peak due to $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ was observed.

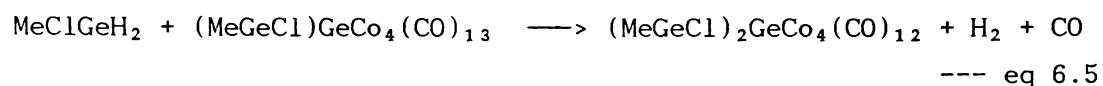
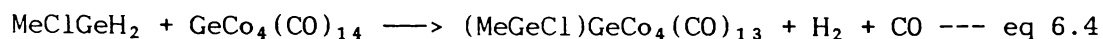
The actual mechanism of the formation of $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ still remains unknown. The formation of $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ from each mole of $(\text{Me}_2\text{Ge})\text{GeCo}_4(\text{CO})_{13}$ with the evolution of approximately 2 moles of gas (Run 1) seems to indicate that the following reaction has taken place:



It should be stressed here that this work (the decarbonylation of $(\text{Me}_2\text{Ge})\text{GeCo}_4(\text{CO})_{13}$) is only a preliminary study and it deserves a more detailed study. A larger scale experiment should be attempted so that the composition of the incondensable gas could be more accurately determined and for samplings for IR and perhaps NMR studies (of both supernatant solution and solid fraction). The heating together of $\text{GeCo}_4(\text{CO})_{14}$ and $(\text{Me}_2\text{Ge})_2\text{GeCo}_4(\text{CO})_{12}$ in a decarbonylation reaction would help to ascertain if the two compounds rearranged to form $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$. This experiment could be compared to the heating of $(\text{Me}_2\text{Ge})_2\text{GeCo}_4(\text{CO})_{12}$ and $\text{GeCo}_4(\text{CO})_{13}$. Lastly, it would be interesting to compare the decarbonylation of $(\text{Me}_2\text{Ge})\text{GeCo}_4(\text{CO})_{13}$ with those in which the one or both of the methyl groups are replaced by other organic groups or halides i.e. $(\text{RR}'\text{Ge})\text{GeCo}_4(\text{CO})_{13}$ and with that of $(\text{Me}_2\text{Ge})_2\text{GeCo}_4(\text{CO})_{12}$.

6.8 The reaction of MeGeClH_2 with $\text{GeCo}_4(\text{CO})_{14}$

The reaction of MeGeClH_2 with $\text{GeCo}_4(\text{CO})_{14}$ was expected to be analogous to that of Me_2GeH_2 with $\text{GeCo}_4(\text{CO})_{14}$, and should follow equations 6.4 and 6.5 :



6.8.1 Experimental

Run 1 ($\text{MeGeClH}_2 : \text{GeCo}_4(\text{CO})_{14} = 2 : 1$)

$\text{GeCo}_4(\text{CO})_{14}$ (0.2978g, 0.425mmol) was loaded into a 50 ml ampoule at the Schlenk line, with hexane (10ml). The ampoule was transferred to the vacuum line where the contents were degassed and then frozen down by liquid nitrogen. MeGeClH_2 (0.857mmol) was condensed in and the ampoule sealed under vacuum. The ampoule was wrapped in Al foil and placed on a shaker at room temperature for 14 days.

6.8.2 Observations and Workup :

After 2 weeks, red needle-shaped crystals were observed on the side of the ampoule together with a red solution. The reaction was stopped and the incondensable gas measured. This showed a total of 0.726mmol gas evolved, of which 59% was H_2 (0.428mmol) and 41% CO (0.298mmol).

The volatiles were not examined. The involatile fraction was fairly soluble in hexane and very soluble in CH_2Cl_2 . It was found to consist of $(\text{MeGeCl})\text{GeCo}_4(\text{CO})_{13}$ (characterised in Section 6.10) and a small amount of unreacted $\text{GeCo}_4(\text{CO})_{14}$. $(\text{MeGeCl})\text{GeCo}_4(\text{CO})_{13}$ was isolated without difficulty by recrystallisation from hexane/ CH_2Cl_2 solution in the freezer. The red crystals were pure $(\text{MeGeCl})\text{GeCo}_4(\text{CO})_{13}$.

Some black insoluble lumps which were most likely decomposed material was also obtained.

Yield of Run 1:

$(\text{MeGeCl})\text{GeCo}_4(\text{CO})_{13} \approx 0.3\text{g} = 0.38 \text{ mmol} = 89\% \text{ yield.}$

Estimation from the incondensable gas measurement indicated a yield of 100.3%. This was an overestimation because a small amount of $\text{GeCo}_4(\text{CO})_{14}$ was recovered. This may be attributed to the error incurred by the Toepler pump or from the decomposition of MeGeClH_2 which was not taken into account.

Other runs :

Three other runs were completed. Runs 2, 3 and 4 were carried out as in Run 1 except for the different ratio of reactants used and slightly different conditions (stated in each run). Run 4 was carried out as an open tube reaction so that incondensable gas could be measured at intervals. Workup procedures were as in Run 1.

Run 2 ($\text{MeGeClH}_2 : \text{GeCo}_4(\text{CO})_{14} = 1.3 : 1$)

$\text{GeCo}_4(\text{CO})_{14}$ (0.6466g, 0.923mmol) was reacted with MeGeClH_2 (0.147g, 1.175mmol) in hexane (10ml) in a 50ml ampoule. The ampoule was shaken for the first 30 days and left to react in the dark for another 30 days.

As in Run 1, a red solution was formed and red crystals were observed after 2 weeks of reaction. After 60 days the reaction was stopped. 2.02mmol of incondensable gas was measured, of which 45% was H_2 and 55% CO .

Similar products to that in Run 1 were obtained, except for the presence of an orange oil. This was found at the bottom of the flask containing the hexane solution of $(\text{MeGeCl})\text{GeCo}_4(\text{CO})_{13}$ after

recrystallisation in the freezer. The orange oil was not particularly soluble in hexane and quite soluble in CH_2Cl_2 . Due to its presence, it was difficult to crystallise all the $(\text{MeGeCl})\text{GeCo}_4(\text{CO})_{13}$ giving isolated yield less than 50%.

An attempt to obtain the infrared spectrum of the orange oil, showed only a poorly resolved one similar to that of $(\text{MeGeCl})\text{GeCo}_4(\text{CO})_{13}$.

Yield of Run 2 :

Weight of pure $(\text{MeGeCl})\text{GeCo}_4(\text{CO})_{13}$ crystals = 0.356g = 0.448mmol = 49%

Weight of $(\text{MeGeCl})\text{GeCo}_4(\text{CO})_{13}$ with orange liquid = 0.303g

Weight of impure $\text{GeCo}_4(\text{CO})_{14}$ = 0.036g (about 5%)

Estimated yield from incondensable gas data = 97%

Run 3 (MeGeClH_2 : $\text{GeCo}_4(\text{CO})_{14}$ = 1.6 : 1)

$\text{GeCo}_4(\text{CO})_{14}$ (0.6144g, 0.876mmol) was reacted with MeGeClH_2 (0.170g, 1.43mmol) as a sealed tube reaction for 75 days in the dark.

On working up, a total of 2.195mmol of incondensable gas was measured, of which 44% was H_2 . The volatile fraction was not examined.

The red involatile fraction was dissolved in hexane/ CH_2Cl_2 and its infrared spectrum indicated the presence of $(\text{MeGeCl})\text{GeCo}_4(\text{CO})_{13}$ and also a new compound characterised as $(\text{MeGeCl})_2\text{GeCo}_4(\text{CO})_{12}$ (characterisation in Section 6.11). No $\text{GeCo}_4(\text{CO})_{14}$ was left. The solvent was removed, and the involatile solid was separated into hexane and CH_2Cl_2 fractions. $(\text{MeGeCl})\text{GeCo}_4(\text{CO})_{13}$ was obtained by recrystallisation from the hexane fractions. $(\text{MeGeCl})_2\text{GeCo}_4(\text{CO})_{12}$ was obtained as a yellow solid from the CH_2Cl_2 solution. The residual solution from both fractions contained a mixture of $(\text{MeGeCl})_2\text{GeCo}_4(\text{CO})_{12}$ and $(\text{MeGeCl})\text{GeCo}_4(\text{CO})_{13}$.

A small amount of CH_2Cl_2 insoluble material was also observed.

Yield of Run 3 :

Weight of $(\text{MeGeCl})\text{GeCo}_4(\text{CO})_{13} = 0.55\text{g} = 79\%^*$

Weight of $(\text{MeGeCl})_2\text{GeCo}_4(\text{CO})_{12} = 0.13\text{g} = 16\%$ yield

Weight of decomposed material = 0.012g

* infrared spectra indicated the presence of small amount of $(\text{MeGeCl})_2\text{GeCo}_4(\text{CO})_{12}$

The incondensable gas reading showed that 0.435mmol more gas than expected from equation 6.4 was evolved. This can be attributed to the formation of $(\text{MeGeCl})_2\text{GeCo}_4(\text{CO})_{12}$. Calculations from the incondensable gas evolution indicated that 0.191 mmol (21%) of $(\text{MeGeCl})_2\text{GeCo}_4(\text{CO})_{12}$ was formed (cf 16% isolated).

Run 4 $(\text{MeGeClH}_2 : \text{GeCo}_4(\text{CO})_{14} = 1.2 : 1 \text{ then } 2.8 : 1)$

$\text{GeCo}_4(\text{CO})_{14}$ (0.2756g, 0.394mmol) was reacted with MeGeClH_2 (0.061g, 0.488mmol) with hexane (5 ml) in a 25ml greaseless tap reaction tube. The incondensable gas measurements are presented in Table 6.11. After 32 days of reaction more MeGeClH_2 (0.135g, 1.1mmol) was added. The reaction was stopped after 67 days.

The percentage of H_2 evolved (measured when the total gas evolved was large enough) was consistently lower than would be expected from equations 6.4 and 6.5.

The colour of the reaction changed to red which slowly darkened as reaction proceeded. A red solid was formed.

The addition of more MeGeClH_2 resulted in an increase in the evolution of gas. At the end of the reaction, spots of red liquid were observed to be accumulating on the side of the reaction tube.

On working up after 67 days, the infrared spectra of the involatiles (dissolved in hexane and CH_2Cl_2) showed the presence of both $(\text{MeGeCl})_2\text{GeCo}_4(\text{CO})_{12}$ and $(\text{MeGeCl})\text{GeCo}_4(\text{CO})_{13}$ (separation

procedures as in Run 3). A red oil was also obtained and its poorly resolved infrared spectrum in CH_2Cl_2 showed the following bands (cm^{-1}) : 2050, 2045, 2034 and 1973.

Table 6.11 Incondensable gas evolution of the open tube reaction of MeClGeH_2 with $\text{GeCo}_4(\text{CO})_{14}$

Days	moles of gas (mmol)	Total gas (mmol)	% H_2
1	0.064	0.064	not measured
4	0.135	0.199	"
6	0.107	0.306	"
10	0.241	0.547	25%
16	0.093	0.645	not measured
26	0.133	0.778	34%
32	0.039	0.817 add more MeGeClH_2 after 32 th day	
41	0.284	1.101	40%
45	0.190	1.291	45%
58	0.266	1.556	41%
67	0.078	1.634	not measured

Though more than 4 moles of incondensable gas per mole of $\text{GeCo}_4(\text{CO})_{14}$ was obtained, total conversion of $\text{GeCo}_4(\text{CO})_{14}$ to $(\text{MeGeCl})_2\text{GeCo}_4(\text{CO})_{12}$ did not occur.

Yield of Run 4 :

$(\text{MeGeCl})_2\text{GeCo}_4(\text{CO})_{12}$ (not clean) = 0.2414g (0.271mmol) = 69% yield
mixture of $(\text{MeGeCl})_2\text{GeCo}_4(\text{CO})_{12}$ and $(\text{MeGeCl})\text{GeCo}_4(\text{CO})_{13}$ = 0.0771g
(infrared spectrum indicated $(\text{MeGeCl})\text{GeCo}_4(\text{CO})_{13}$ and $(\text{MeGeCl})_2\text{GeCo}_4(\text{CO})_{12}$ in the mixture to be of similar proportion)
oily mixture = 0.2152g

6.9 Reaction of MeGeClH_2 with $(\text{MeGeCl})\text{GeCo}_4(\text{CO})_{13}$ (ratio = 4.2 : 1)

6.9.1 Experimental :

$(\text{MeGeCl})\text{GeCo}_4(\text{CO})_{13}$ (0.2706g, 0.341mmol) was reacted with MeGeClH_2 (0.176g, 1.41mmol) hexane (10 ml) as a sealed tube reaction for 2 months at room temperature.

6.9.2 Observations and Workup :

The red solution of $(\text{MeGeCl})\text{GeCo}_4(\text{CO})_{13}$ lightened very slightly as reaction proceeded. At the end of the reaction, the red solution had a yellowish tint. On working up, the infrared spectrum of the red hexane solution showed the presence of both $(\text{MeGeCl})\text{GeCo}_4(\text{CO})_{13}$ and $(\text{MeGeCl})_2\text{GeCo}_4(\text{CO})_{12}$. The products could not be separated. The percentage conversion was estimated to be about 50%.

Table 6.12 Products and approximate yields of
the reaction of MeGeClH_2 with $\text{GeCo}_4(\text{CO})_{14}$

Compounds	Run 1	Run 2	Run 3	Run 4	6.9*
$(\text{MeGeCl})\text{GeCo}_4(\text{CO})_{13}$:	89% ^w	>49% ^w	79% ^w	~15% ^{i r}	
	100.3% ⁱ	97% ⁱ	79% ⁱ		50% ^{i r}
$(\text{MeGeCl})_2\text{GeCo}_4(\text{CO})_{12}$:		-	16% ^w	69% ^w	
			21% ⁱ	~85% ^{i r}	
red oil	-	yes	-	yes	
decomposed material	yes	-	yes	-	
Unreacted $\text{GeCo}_4(\text{CO})_{14}$	yes	yes	no	no	

^w by weight, ⁱ by incondensable gas measurement, ^{i r} by infrared

* $(\text{MeGeCl})\text{GeCo}_4(\text{CO})_{13}$ used instead of $\text{GeCo}_4(\text{CO})_{14}$

6.10 Characterisation of $(\text{MeGeCl})\text{GeCo}_4(\text{CO})_{13}$

6.10.1 Infrared and Raman spectra :

The symmetry of $(\text{MeGeCl})\text{GeCo}_4(\text{CO})_{13}$ is C_s . 13 infrared and 13 Raman bands are predicted ($7A' + 6A''$). Only 10 infrared bands are

observed in both the solution and solid infrared spectra (Tables 6.13 and Figs 6.14 and 6.15). The solid infrared spectrum is not as well resolved as would be expected. A total of 13 Raman peaks are observed (Table 6.13 and Fig 6.16), though some of them are fairly weak.

An upward shift in the average carbonyl stretching frequency is observed when the Cl group in $(\text{MeGeCl})\text{GeCo}_4(\text{CO})_{13}$ and $(\text{MeGeCl})_2\text{GeCo}_4(\text{CO})_{12}$ replaces Me in $(\text{Me}_2\text{Ge})\text{GeCo}_4(\text{CO})_{13}$ and $(\text{Me}_2\text{Ge})_2\text{GeCo}_4(\text{CO})_{12}$. This is observed in halide containing $\text{M}'\text{-Co}$ carbonyls [8,17,28,33,38]. The electron withdrawing effect of the chlorine transmits through the molecule to reduce π^* CO electron population, increasing the CO bond strength, hence increasing the magnitude of the force constant and therefore increasing the CO stretching frequency.

Table 6.13 Infrared and Raman spectra of $(\text{MeGeCl})\text{GeCo}_4(\text{CO})_{13}$ in CH_2Cl_2 /hexane in hexane Solid IR in CsI Raman spectrum

Bands	Int	Bands	Int	Bands	Int	Bands	Int
				2099	w	2103.5	ms
2097	w	2097	w	2097	ms		
2075	m	2076	ms	2076	s	2076.5	m
2069	s	2070	s				
		2059	vs				
2056	vs	2054	vs sh	2052	vs	2052	m
		2049	m sh	2046	vs sh	2041.0	vs
2035	m	2032	s	2028	m	2035.0	ms sh
						2030	ms sh
		2029	ms	2026	s	2027.5	ms
2022	m	2022	s	2017	s	2015.5	ms
						2009	m
						2008	m sh
				2004	s sh	2005	m sh
				2003	s	1999	mw
1841	w	1842	w	1827	ms	1836	w

Infrared spectra of $(\text{MeGeCl})\text{GeCo}_4(\text{CO})_{13}$

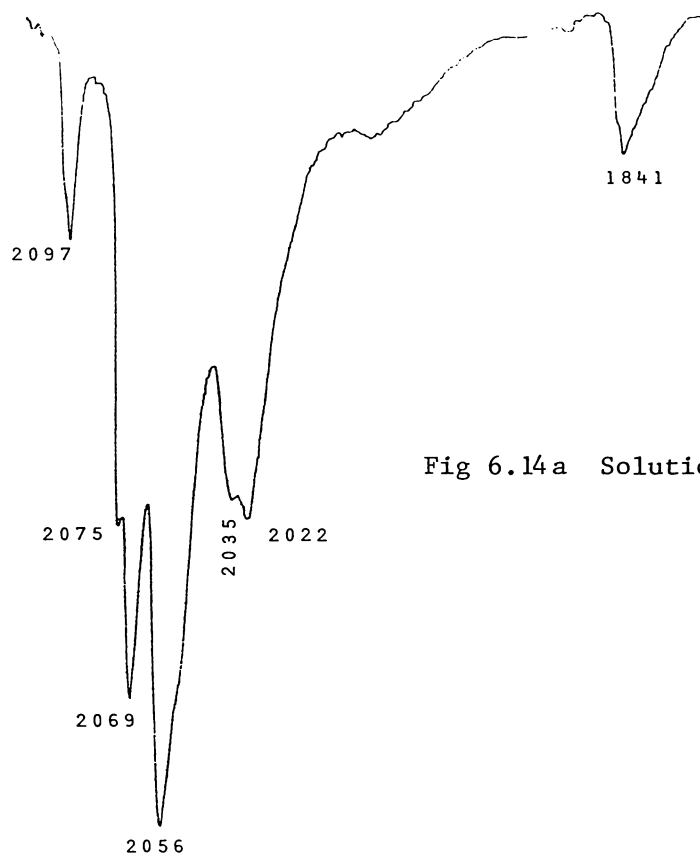


Fig 6.14a Solution IR in hexane/ CH_2Cl_2

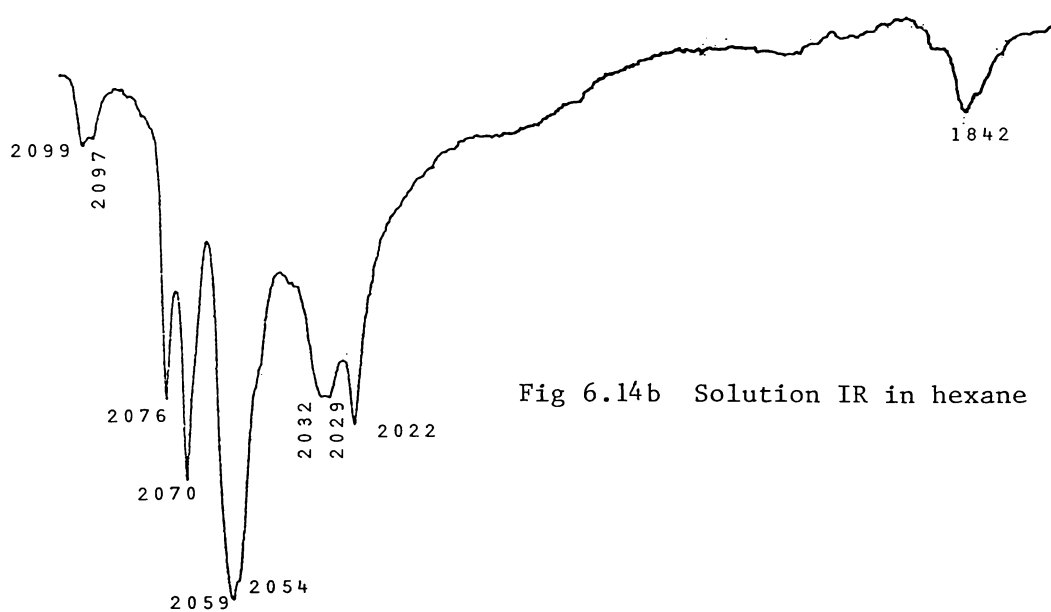


Fig 6.14b Solution IR in hexane

Fig 6.15 Solid IR spectrum of $(\text{MeGeCl})\text{GeCo}_4(\text{CO})_{13}$ (CsI disc)

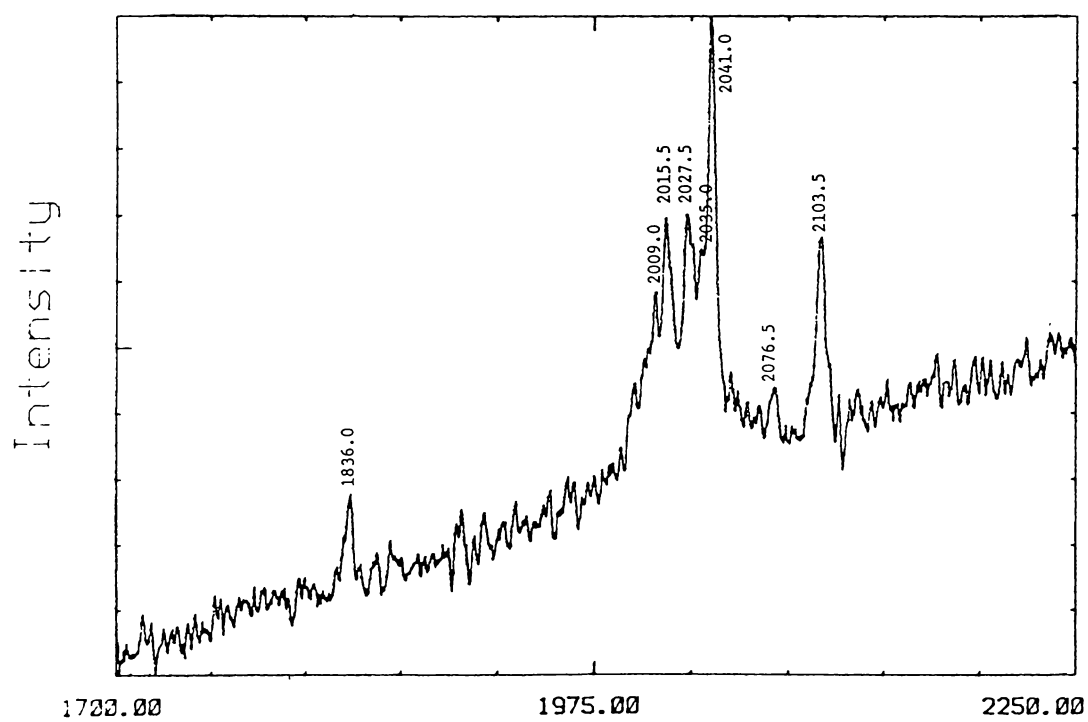
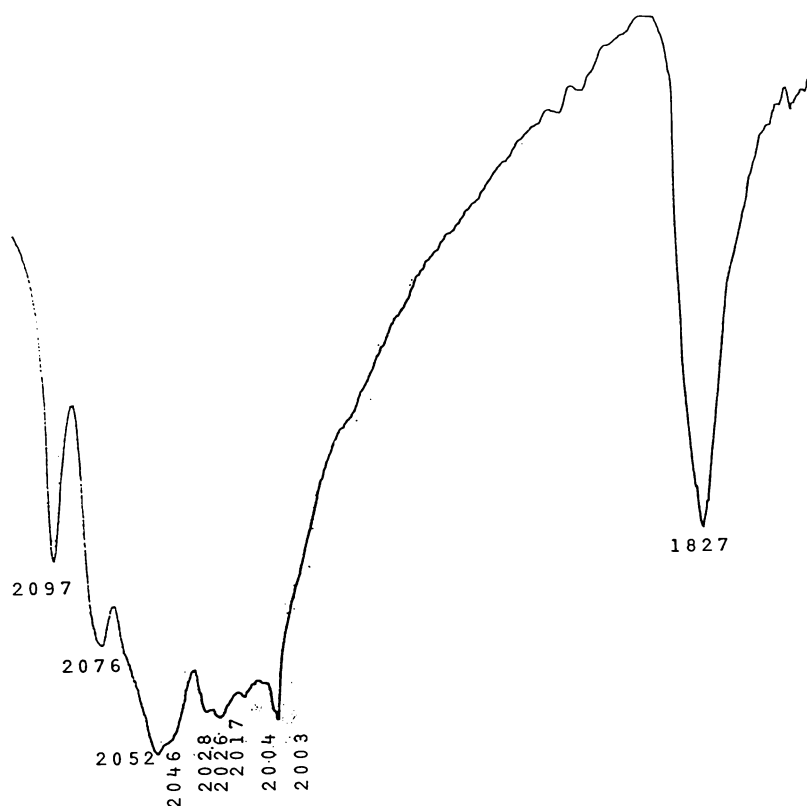


Fig 6.16 Raman spectrum of $(\text{MeGeCl})\text{GeCo}_4(\text{CO})_{13}$ (single crystal)

6.10.2 Mass spectrum :

The parent ion envelope of $(\text{MeGeCl})\text{GeCo}_4(\text{CO})_{13}$ was not observed, the highest m/e envelope being that of $[\text{P}-2\text{CO}]^+$ (Table 6.14). A stepwise loss of 11CO 's from the $[\text{P}-2\text{CO}]^+$ was followed by the loss of the Me and Cl fragments. Weak overlapping envelopes from $\text{MeClGeCo}_2(\text{CO})_n^+$ and $\text{GeCo}_4(\text{CO})_n^+$ ($n = 0$ to 8) was observed at the lower m/e range where envelopes due to $[\text{P}-(\text{CO})_n]^+$ faded out, and when the Ge_1 isotope pattern can be distinguished. Details of the mass spectrum are given in Table 6.14.

Table 6.14 Mass spectrum of $(\text{MeGeCl})\text{GeCo}_4(\text{CO})_{13}$

m/e	Int	Assignments and possible overlaps
770	vw	$[\text{P}-\text{CO}]^+$ where $\text{P} = (\text{MeGeCl})\text{GeCo}_4(\text{CO})_{13}$
735-740	mw	$[\text{P}-2\text{CO}]^+$
707-717	ms	$[\text{P}-3\text{CO}]^+$
680-688	mw	$[\text{P}-4\text{CO}]^+$
651-660	mw	$[\text{P}-5\text{CO}]^+$
623-632	mw	$[\text{P}-6\text{CO}]^+$
593-606	vs	$[\text{P}-7\text{CO}]^+$
567-578	ms	$[\text{P}-8\text{CO}]^+$
539-550	ms	$[\text{P}-9\text{CO}]^+$
510-520	m	$[\text{P}-10\text{CO}]^+$
482-492	ms	$[\text{P}-11\text{CO}]^+$
454-464	mw	$[\text{P}-12\text{CO}]^+$
422-436	ms	$[\text{P}-13\text{CO}]^+$
410-423	mw	$[\text{P}-13\text{CO}-\text{Me}]^+$
395-405	mw	$[\text{P}-13\text{CO}-\text{Cl}]^+$
385-395	w	$[\text{P}-13\text{CO}-\text{Cl}-\text{Me}]^+$, $\text{GeCo}_4(\text{CO})_4^+$
365-374	w	$\text{GeCo}_4(\text{CO})_3^+$
352-362	w	$\text{MeClGeCo}_2(\text{CO})_4^+$
332-340	vw	$\text{GeCo}_4(\text{CO})_2^+$
325-336	w	$\text{MeClGeCo}_2(\text{CO})^+$
308-310	vw	GeCo_4^+

6.10.3 *Electron probe analysis :*

The electron probe analysis of $(\text{MeGeCl})\text{GeCo}_4(\text{CO})_{13}$ indicated that the compound consisted of chlorine, cobalt and germanium in the approximate ratio of 0.8 : 4 : 2 compared to the expected 1 : 4 : 2 ratio. The proportion of chlorine was slightly less than expected as it is on the lower limit of the detection scale of the machine.

6.10.4 *NMR data :*

At 27°C, a singlet in the methyl region was obtained for the proton NMR spectrum of $(\text{MeGeCl})\text{GeCo}_4(\text{CO})_{13}$ (Table 6.15, Fig 6.17a). But this broadened with decreasing temperature and at -30°C, two peaks were visible. At -50°C, the two peaks sharpened : δ 1.87 ppm and δ 1.74 ppm in the relative ratio of 2 : 1.

The chemical shift of $(\text{MeGeCl})\text{GeCo}_4(\text{CO})_{13}$ is on the lowfield side compared to those of $(\text{Me}_2\text{Ge})\text{GeCo}_4(\text{CO})_{13}$ as expected due to the presence of the Cl atom. A lowfield shift was also observed with a decrease in temperature.

At -50°C, two broad ^{13}C O singlets (δ 197.4 ppm and 202.7 ppm) were observed (Fig 6.17b). These however, collapsed into a broad singlet at δ 202.4 ppm at 27°C.

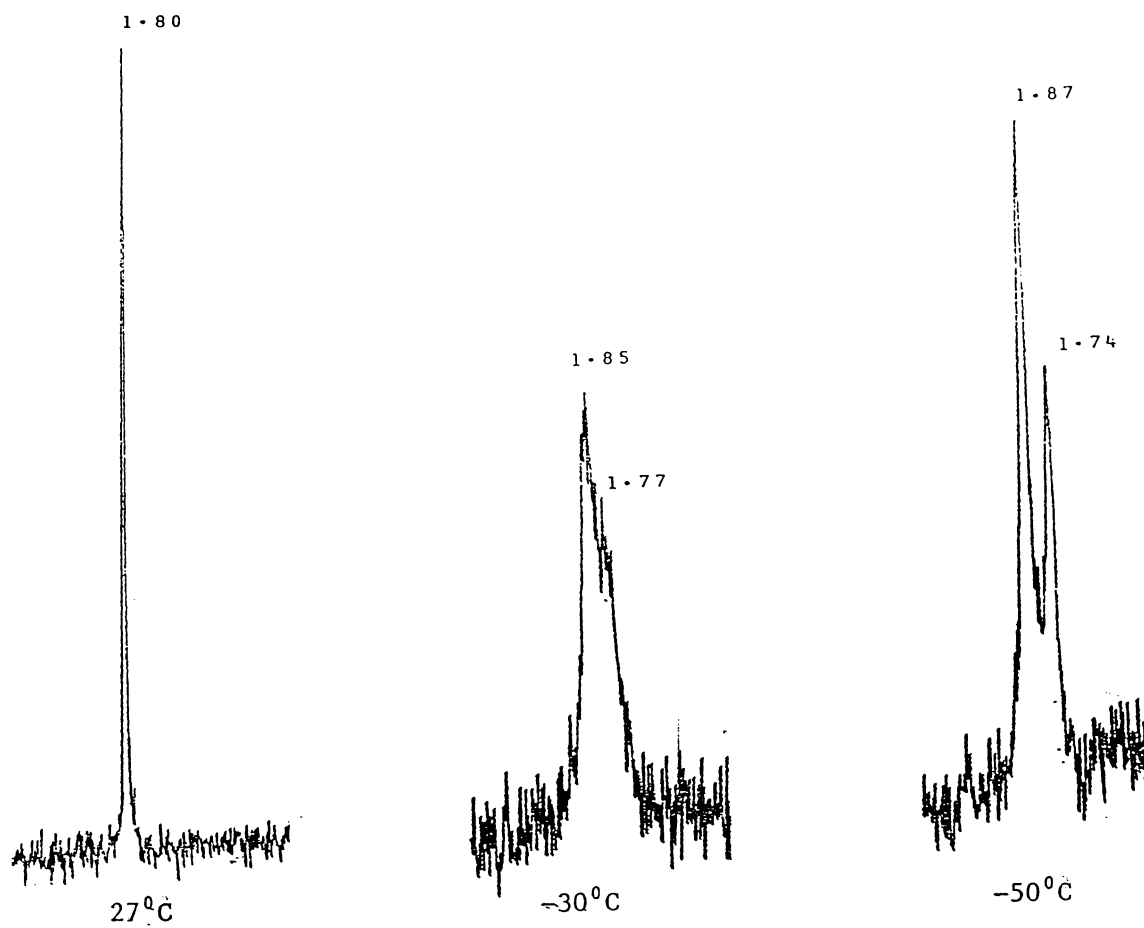
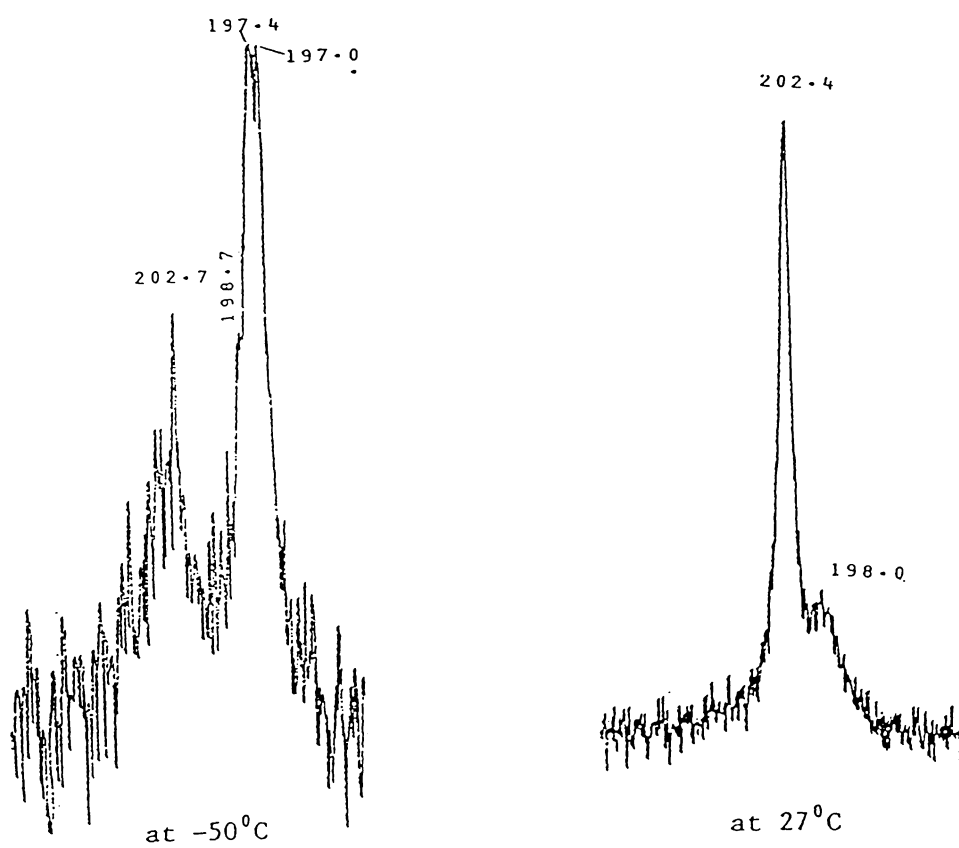
The observed NMR spectra of $(\text{RR}'\text{Ge})\text{GeCo}_4(\text{CO})_{13}$ and $(\text{RR}'\text{Ge})_2\text{GeCo}_4(\text{CO})_{12}$ ($\text{RR}' = \text{Me}_2, \text{MeH}$ and EtH) of a single proton or CO environment indicate that two fluxional processes are conceivable. The first involves an 'inside-out' flapping about the Co-Co bonds which makes the two methyl groups equivalent and would also average some of the CO terminal positions. The second process is CO exchange between

the bridging and terminal positions - which would also be involved in the exchange with external CO's. This may explain the unsuccessful attempt to ^{13}C enrich $(\text{Me}_2\text{Ge})_2\text{GeCo}_4(\text{CO})_{12}$ under the same conditions as those of $(\text{Me}_2\text{Ge})\text{GeCo}_4(\text{CO})_{13}$. The ^{13}C NMR spectra of $(\text{Me}_2\text{Ge})\text{GeCo}_4(\text{CO})_{13}$, $(\text{MeGeH})\text{GeCo}_4(\text{CO})_{13}$ and $(\text{EtGeH})\text{GeCo}_4(\text{CO})_{13}$ showed a single broad peak even at -50°C indicating that the exchange processes are taking place even at low temperature.

The observed NMR spectra of $(\text{MeGeCl})\text{GeCo}_4(\text{CO})_{13}$ (both ^1H and ^{13}C) at low temperature were different from those of $(\text{RR}'\text{Ge})\text{GeCo}_4(\text{CO})_{13}$ and $(\text{RR}'\text{Ge})_2\text{GeCo}_4(\text{CO})_{12}$ mentioned above. This may be explained in two ways : firstly, the presence of the electronegative Cl atom in the molecule increases the force constant of the Co-CO bond and reduces the ease of rapid exchanging at low temperature; secondly, the two isomers (Fig 6.22) become distinguishable at low temperature due to slower fluxional processes. The intensity of the two peaks (δ ppm) at 197.7 : 202.7 $\approx$ 2 : 1 may indicate that one of the isomers (likely the one with the methyl group towards the $\mu\text{-CO}$) is twice the concentration of the other.

Table 6.15 NMR data of $(\text{MeGeCl})\text{GeCo}_4(\text{CO})_{13}$

NMR	Temp ($^\circ\text{C}$)	Chemical shifts (δ ppm)
^1H	27	1.80 (s)
	-20	singlet, δ not recorded
	-30	1.85 (s), 1.77 (shoulder)
	-50	1.87 (s, 2x), 1.74 (s, 1x)
^{13}C	27	202.4 (s, br), 198.0 (shoulder)
	-50	197.4 (s, 2x, br), 202.7 (s, 1x, br)

Fig 6.17a ^1H NMR spectra of $(\text{MeGeCl})\text{GeCo}_4(\text{CO})_{13}$ Fig 6.17b ^{13}C NMR spectra of $(\text{MeGeCl})\text{GeCo}_4(\text{CO})_{13}$ 

6.11 Characterisation of $(\text{MeGeCl})_2\text{GeCo}_4(\text{CO})_{12}$

6.11.1 Infrared spectrum :

The infrared pattern in Table 6.16 and Fig 6.18 (though poorly resolved) of $(\text{MeGeCl})_2\text{GeCo}_4(\text{CO})_{12}$ is very similar to that of $(\text{Me}_2\text{Ge})_2\text{GeCo}_4(\text{CO})_{12}$, with only five observed bands. Theoretically, the symmetry of $(\text{MeGeCl})_2\text{GeCo}_4(\text{CO})_{12}$ should be C_2 and 12 bands are expected. Like $(\text{MeGeCl})\text{GeCo}_4(\text{CO})_{13}$, the positions of the infrared bands are about 5 cm^{-1} higher than those of $(\text{Me}_2\text{Ge})_2\text{GeCo}_4(\text{CO})_{12}$ due to the electron withdrawing property of the Cl group.

Table 6.16 Infrared spectrum of $(\text{MeGeCl})_2\text{GeCo}_4(\text{CO})_{12}$

In $\text{CH}_2\text{Cl}_2/\text{hexane}$	
Bands	Int
2092	w
2066	ms
2050	vs
2026	m, sh
2018	ms

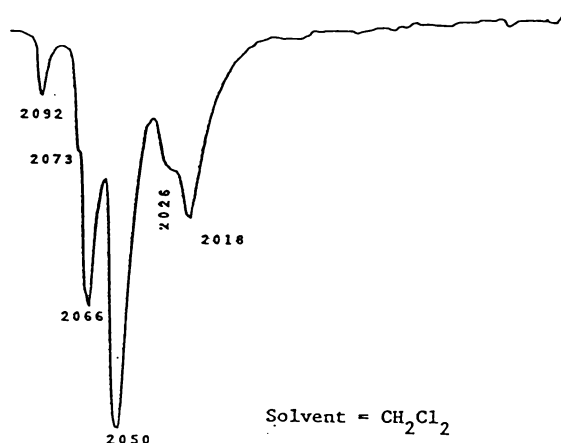


Fig 6.18 Solution IR of $(\text{MeGeCl})_2\text{GeCo}_4(\text{CO})_{12}$

6.11.2 Mass spectrum :

The parent envelope peak (891) of $(\text{MeGeCl})_2\text{GeCo}_4(\text{CO})_{12}$ was not observed (Table 6.17). The highest m/e envelope observed was a very weak and narrow one at 848–850 which was assigned as that of $[\text{P-Cl-CO}]^+$. The envelopes observed were likely those of $[\text{P-Cl-(CO)}_n]^+$ possibly overlapped by $[\text{P-2Cl-(CO)}_n]^+$. The Ge_3 pattern was difficult to pick out due to overlapping envelopes. The envelopes in the lower region were assigned tentatively as those of $\text{GeCo}_4(\text{CO})_n^+$ and $\text{MeGe}_2\text{Co}_4(\text{CO})_n^+$.

Table 6.17 Mass spectrum of $(\text{MeGeCl})_2\text{GeCo}_4(\text{CO})_{12}$

m/e	Int	Assignments and possible overlaps
848-850	vw	$[\text{P-Cl-CO}]^+$
818-828	m	$[\text{P-Cl-2CO}]^+$, $[\text{P-2Cl}]^+$
794-782	mw	$[\text{P-Cl-3CO}]^+$, $[\text{P-2Cl-CO}]^+$
768-803	w	$[\text{P-Cl-4CO}]^+$, $[\text{P-2Cl-2CO}]^+$
740-750	m	$[\text{P-Cl-5CO}]^+$, $[\text{P-2Cl-3CO}]^+$
715-724	mw	$[\text{P-Cl-6CO}]^+$, $[\text{P-2Cl-4CO}]^+$
687-701	vs	$[\text{P-Cl-7CO}]^+$, $[\text{P-2Cl-Me-4CO}]^+$
658-672	m	$[\text{P-Cl-8CO}]^+$, $[\text{P-2Cl-Me-5CO}]^+$
630-643	ms	$[\text{P-Cl-9CO}]^+$, $[\text{P-2Cl-Me-6CO}]^+$
603-620	mw	$[\text{P-Cl-10CO}]^+$, $[\text{P-2Cl-Me-7CO}]^+$
575-588	m	$[\text{P-Cl-11CO}]^+$, $[\text{P-2Cl-Me-8CO}]^+$
545-561	ms	$[\text{P-Cl-12CO}]^+$, $[\text{P-2Cl-Me-9CO}]^+$
530-540	vw	$[\text{P-Cl-Me-12CO}]^+$
520-529	m	$\text{MeGeCo}_4(\text{CO})_7^+$, $[\text{P-2Cl-Me-10CO}]^+$
496-503	w	$[\text{P-2Cl-Me-11CO}]^+$
485-487	vw	$[\text{P-2Cl-2Me-11CO}]^+$
462-465	w	$\text{Ge}_2\text{Co}_4(\text{CO})_3^+$
425-438	mw	$\text{MeGe}_2\text{Co}_4(\text{CO})^+$
400-410	w	MeGe_2^+ , $\text{Ge}_2\text{Co}_4(\text{CO})^+$
389-398	s	$\text{MeGe}_2\text{Co}_4^+$

$\text{P} = (\text{MeGeCl})_2\text{GeCo}_4(\text{CO})_{12}$

6.11.3 NMR :

The ^1H NMR spectrum of $(\text{MeGeCl})_2\text{GeCo}_4(\text{CO})_{12}$ (in CDCl_3) showed a singlet at δ 1.82 ppm at 27°C. This indicated that all the six protons in the molecule are equivalent in solution (as in $(\text{MeGeH})_2\text{GeCo}_4(\text{CO})_{12}$). The chemical shift is on the lowfield side compare to those of $(\text{Me}_2\text{Ge})_2\text{GeCo}_4(\text{CO})_{12}$ (δ 1.34 ppm) due to the presence of the two Cl atoms.

Though the shortage of time prevented the low temperature NMR to be collected, the results from $(\text{MeGeCl})\text{GeCo}_4(\text{CO})_{13}$ indicated that at

least two peaks would be expected as three isomers are possible for $(\text{MeGeCl})_2\text{GeCo}_4(\text{CO})_{12}$ (Fig 6.22).

6.12 The reaction of $(\text{MeGeCl})\text{GeCo}_4(\text{CO})_{13}$ and $(\text{MeGeCl})_2\text{GeCo}_4(\text{CO})_{12}$ with $\text{Co}(\text{CO})_4^-$

6.12.1 The reaction of $(\text{MeGeCl})\text{GeCo}_4(\text{CO})_{13}$ with $\text{KCo}(\text{CO})_4$

Experimental :

$(\text{MeGeCl})\text{GeCo}_4(\text{CO})_{13}$ (0.284g, 0.357mmol) was dissolved in CH_2Cl_2 (20ml). This was added to $\text{KCo}(\text{CO})_4$ (prepared from 0.081g, 0.236mmol of $\text{Co}_2(\text{CO})_8$) and the mixture was stirred vigorously for 15 minutes. The solvent was removed and the product was extracted with hexane.

Observations and workup :

The colour of the solution did not change significantly from red. A white precipitate was observed (believed to be KCl). The solvent was removed leaving a red solid.

On extracting with hexane, two fractions were obtained. The first was dark red. Its infrared spectrum showed that it contained a small amount of $\text{Co}_4(\text{CO})_{12}$ and all the bands associated with $\text{MeGe}_2\text{Co}_5(\text{CO})_{17}$ [82] (Table 6.18), see also Chapter Seven. The second fraction consisted of clean $\text{MeGe}_2\text{Co}_5(\text{CO})_{17}$. There was no evidence of any remaining starting material.

Yield :

Weight of clean $\text{MeGe}_2\text{Co}_5(\text{CO})_{17}$ = 0.127g (0.136 mmol) = 38%

Weight of contaminated $\text{MeGe}_2\text{Co}_5(\text{CO})_{17}$ = 0.207g

6.12.2 The reaction of $(\text{MeGeCl})_2\text{GeCo}_4(\text{CO})_{12}$ with $\text{KCo}(\text{CO})_4$

Experimental :

The experimental procedures were as in Section 6.12.1. $\text{Co}_2(\text{CO})_8$ (0.092g, 0.269mmol) was reduced to form $\text{KCo}(\text{CO})_4$ (0.43mmol assuming 80% yield).

$(\text{MeGeCl})_2\text{GeCo}_4(\text{CO})_{12}$ (0.1901g, 0.213 mmol) was reacted with the prepared $\text{Co}(\text{CO})_4^-$ in CH_2Cl_2 (20 ml) for 15 minutes.

Note : This $(\text{MeGeCl})_2\text{GeCo}_4(\text{CO})_{12}$ sample was contaminated with a small amount $(\text{MeGeCl})\text{GeCo}_4(\text{CO})_{13}$ which could not be separated.

Results :

The colour of the solution after the reaction was only very slightly darker. A white deposit (KCl) was observed.

The hexane extracts consisted mainly of $\text{MeGe}_2\text{Co}_5(\text{CO})_{17}$ (resulting possibly from the presence of $(\text{MeGeCl})\text{GeCo}_4(\text{CO})_{13}$ as an impurity), and $\text{Co}_4(\text{CO})_{12}$ from the infrared spectrum.

The residue was not very soluble in hexane. It was extracted with CH_2Cl_2 and hexane (1 : 1). It has an infrared spectrum that showed no bridging carbonyl frequencies (Fig 6.20 and Table 6.20). This compound was later characterised as $\text{Me}_2\text{Ge}_3\text{Co}_6(\text{CO})_{20}$ by its mass spectrum and by comparing its infrared spectrum to similar compounds such as $(\text{MeGe})_2\text{GeCo}_4(\text{CO})_{12}$ (see Section 6.5). No starting material was left.

Yield :

Weight of $\text{Me}_2\text{Ge}_3\text{Co}_6(\text{CO})_{20}$ = 0.1815g (0.156 mmol) = 85%

Weight of $\text{MeGe}_2\text{Co}_5(\text{CO})_{17}$ + $\text{Co}_4(\text{CO})_{12}$ = 0.077g

6.12.3 Characterisation of $\text{MeGe}_2\text{Co}_5(\text{CO})_{17}$ (**5c**)

The formula of this compound is assigned as $\text{MeGe}_2\text{Co}_5(\text{CO})_{17}$ based on the similar infrared spectrum with that made by L. McLeod by the reaction of MeGe_2H_5 with $\text{Co}_2(\text{CO})_8$ [82] (IR spectrum of $\text{MeGe}_2\text{Co}_5(\text{CO})_{17}$ by McLeod : 2104w, 2089s, 2066s, 2056s, 2046vs, 2026s, 2006sh, 1998w and 1843mw (in hexane)). In the mass spectrum, though the parent ion was not observed, many of the envelopes correspond to those obtained by [82], and a loss of 17 CO's and a Me group was indicated. A compound of similar infrared spectrum was also obtained in the hydride replacement reaction of $(\text{MeGeH})\text{GeCo}_4(\text{CO})_{13}$ with $\text{Co}_2(\text{CO})_8$ which was expected to produce $\text{MeGe}_2\text{Co}_5(\text{CO})_{17}$ (see Chapter Seven). In one of the runs, $\text{MeGe}_2\text{Co}_5(\text{CO})_{17}$ was obtained along with $\text{MeGe}_2\text{Co}_5(\text{CO})_{15}$. As the decarbonylation of $\text{MeGe}_2\text{Co}_5(\text{CO})_{17}$ resulted in $\text{MeGe}_2\text{Co}_5(\text{CO})_{15}$ by [82], it is very likely that this compound obtained from the $(\text{MeGeCl})\text{GeCo}_4(\text{CO})_{13}$ reaction with $\text{KCo}(\text{CO})_4$ is $\text{MeGe}_2\text{Co}_5(\text{CO})_{17}$.

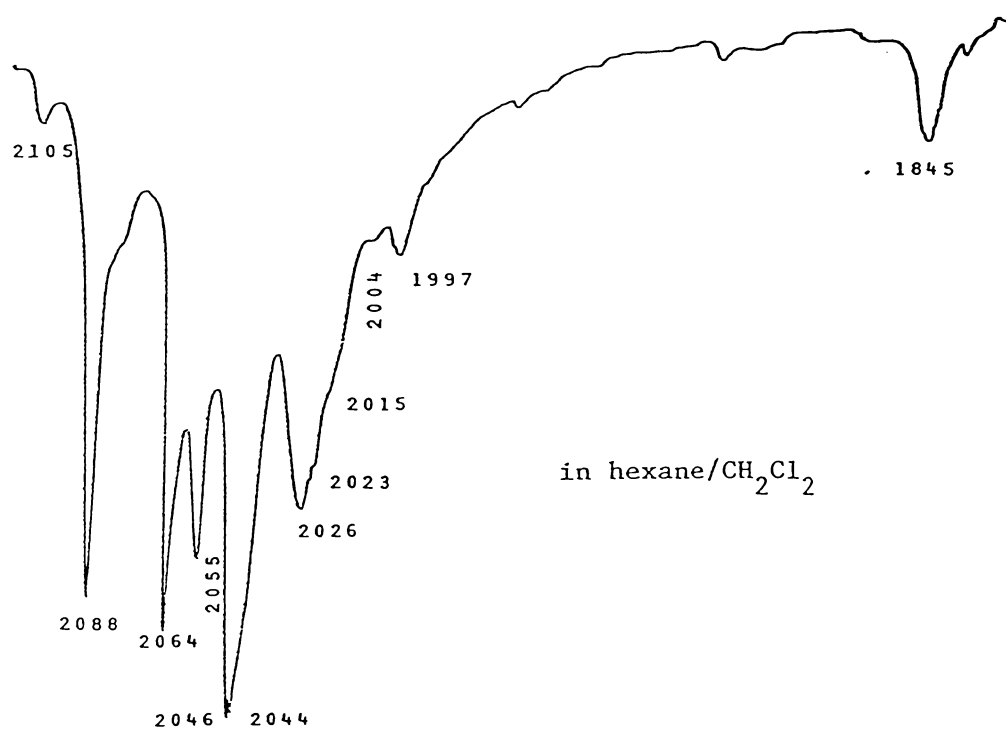
Infrared spectrum :

The structure of $\text{MeGe}_2\text{Co}_5(\text{CO})_{17}$ (**5c**) is most likely to be an open chain cluster very similar to that of $(\text{Me}_2\text{Ge})\text{GeCo}_4(\text{CO})_{13}$ (Fig 6.5). This structure belongs to C_s symmetry. The number of predicted CO bands is sixteen with a bridging CO band. Of these only twelve were observed as shown in Table 6.18 and Fig 6.19. The infrared spectrum of $\text{MeGe}_2\text{Co}_5(\text{CO})_{17}$ is very similar to that of $(\text{MeGeH})\text{GeCo}_4(\text{CO})_{13}$ except for the two bands at 2105w and 2088s.

Table 6.18 Infrared spectrum of $\text{MeGe}_2\text{Co}_5(\text{CO})_{17}$
(in hexane/ CH_2Cl_2)

Bands	Int
2105	w
2088	vs
2064	s
2055	ms
2046	vs
2044	vs
2026	ms
2023	ms, sh
2015	ms, sh
2004	m, sh
1997	mw
1845	w

Fig 6.19 Infrared spectrum of $\text{MeGe}_2\text{Co}_5(\text{CO})_{17}$



Mass spectrum :

In this study, the parent ion envelope P^+ was not observed in the mass spectrum of $\text{MeGe}_2\text{Co}_5(\text{CO})_{17}$ (Table 6.19) which presents the series $[\text{P}-(\text{CO})_n]^+$ for $n = 0$ to 17. A similar series together with a weak parent ion envelope at 926-938 were observed by McLeod [82].

Table 6.19 Mass spectrum of $\text{MeGe}_2\text{Co}_5(\text{CO})_{17}$

m/e	Int	Assignments
890	w	$[\text{P-CO-Me}]^+$
865-870	s	$[\text{P-2CO}]^+$
835-843	vs	$[\text{P-3CO}]^+$
815-820	w	$[\text{P-4CO}]^+$
789-794	m	$[\text{P-5CO}]^+$
762-766	m	$[\text{P-6CO}]^+$
734-738	m	$[\text{P-7CO}]^+$
703-715	ms	$[\text{P-8CO}]^+$
677-682	s	$[\text{P-9CO}]^+$
648-654	mw	$[\text{P-10CO}]^+$
622-625	m	$[\text{P-11CO}]^+$
592-600	m	$[\text{P-12CO}]^+$
579-586	s	$[\text{P-12CO-Me}]^+$
567-572	vw	$[\text{P-13CO}]^+$
538-550	vw	$[\text{P-14CO}]^+$
522-530	w	$[\text{P-15CO-Me}]^+$
509-517	vw	$[\text{P-15CO}]^+$
450-460	vw	$[\text{P-17CO}]^+$
446	m	$[\text{P-17CO-Me}]^+$
340-342	m	$[\text{P-17CO-2Co}]^+$
325-327	w	$[\text{P-17CO-2Co-Me}]^+$

6.12.4 Characterisation of $\text{Me}_2\text{Ge}_3\text{Co}_6(\text{CO})_{20}$ (*9g*)

The compound obtained from the reaction of $(\text{MeGeCl})_2\text{GeCo}_4(\text{CO})_{12}$ with $\text{KCo}(\text{CO})_4$ is very likely to be $\text{Me}_2\text{Ge}_3\text{Co}_6(\text{CO})_{20}$. Its infrared spectrum is similar to the product obtained from the reaction of $(\text{MeGeH})_2\text{GeCo}_4(\text{CO})_{12}$ with $\text{Co}_2(\text{CO})_8$. The product obtained from the latter reaction was found to decarbonylate under vacuum to form $\text{Me}_2\text{Ge}_3\text{Co}_6(\text{CO})_{17}$. The ethyl analogue, $\text{Et}_2\text{Ge}_3\text{Co}_6(\text{CO})_{17}$ (*11*), was made by the same route and was fully characterised in Chapter Seven (including a crystal structure). As the formula of $\text{R}_2\text{Ge}_3\text{Co}_6(\text{CO})_{17}$ is different from $\text{Me}_2\text{Ge}_3\text{Co}_6(\text{CO})_{20}$ by three CO's, and as the mass spectrometer is reliable up to only 900-1000 m/e unit, the mass spectrum of $\text{Me}_2\text{Ge}_3\text{Co}_6(\text{CO})_{20}$ should be closely related to the observed mass spectrum of $\text{R}_2\text{Ge}_3\text{Co}_6(\text{CO})_{17}$. Comparison of the mass spectrum of $\text{Me}_2\text{Ge}_3\text{Co}_6(\text{CO})_{20}$ with $\text{Et}_2\text{Ge}_3\text{Co}_6(\text{CO})_{17}$ showed that the two spectra were very similar (in terms of appearance of the envelopes and their intensity).

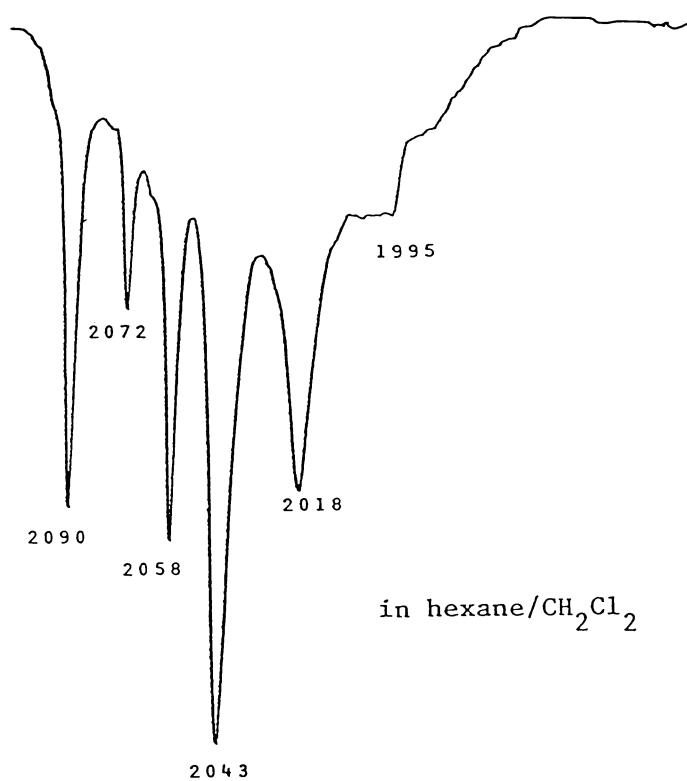
Infrared spectrum :

The structure of $(\text{MeGeCo}(\text{CO})_4)_2\text{GeCo}_4(\text{CO})_{12}$ is most likely an open chain cluster (*9g*). This is closely related to the structure of $(\text{Me}_2\text{Ge})_2\text{GeCo}_4(\text{CO})_{12}$ except that one Me group on each end is replaced by a $\text{Co}(\text{CO})_4$ group. This should ideally assume a C_2 symmetry. Therefore twenty infrared bands are predicted : $10\text{A}' + 10\text{A}''$. However, only six infrared bands were observed (Table 6.20, Fig 6.20). The absence of a bridging CO is consistent with the predicted structure. Discussion of the infrared spectrum of $\text{Me}_2\text{Ge}_3\text{Co}_6(\text{CO})_{20}$ in relation to closely related compounds such as $(\text{Me}_2\text{Ge})_2\text{GeCo}_4(\text{CO})_{12}$ is given in Section 6.15.

Table 6.20 Infrared spectrum of $\text{Me}_2\text{Ge}_3\text{Co}_6(\text{CO})_{20}$
(in hexane/ CH_2Cl_2)

Bands	Int
2090	ms
2072	mw
2058	ms
2043	vs
2018	s
1995	w, sh

Fig 6.20 Infrared spectrum of $\text{Me}_2\text{Ge}_3\text{Co}_6(\text{CO})_{20}$



Mass Spectrum :

As the molecular weight of $\text{Me}_2\text{Ge}_3\text{Co}_6(\text{CO})_{20}$ (1151g/mol) exceeded the capability limit of the mass spectrometer, the highest mass unit recorded was that due to $[\text{P}-5\text{CO}]^+$ where P = parent ion (Table 6.21). The $[\text{P}-n\text{CO}]^+$ series was succeeded by the $[\text{P}-n\text{CO}-\text{Me}]^+$ series after the loss of 8 CO's. The second Me loss did not occur until the loss of all the CO's. A definite Ge_3 pattern was observed.

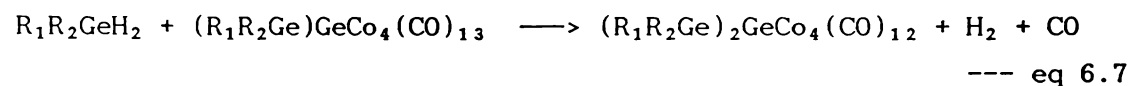
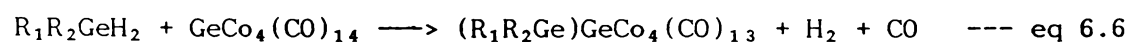
Table 6.21 Mass spectrum of $\text{Me}_2\text{Ge}_3\text{Co}_6(\text{CO})_{20} = \text{P}$

m/e	Int	Assignments
1024-1032	mw	$[\text{P}-5\text{CO}]^+$
998-1002	vw	$[\text{P}-6\text{CO}]^+$
969-976	mw	$[\text{P}-7\text{CO}]^+$
946-950	w	$[\text{P}-8\text{CO}]^+$
919-923	vw	$[\text{P}-8\text{CO}-\text{Me}]^+$
889-897	mw	$[\text{P}-9\text{CO}-\text{Me}]^+$
853-873	s	$[\text{P}-10\text{CO}-\text{Me}]^+$
837-850	vs	$[\text{P}-11\text{CO}-\text{Me}]^+$
812-823	mw	$[\text{P}-12\text{CO}-\text{Me}]^+$
790-797	m	$[\text{P}-13\text{CO}-\text{Me}]^+$
761-771	m	$[\text{P}-14\text{CO}-\text{Me}]^+$
731-742	mw	$[\text{P}-15\text{CO}-\text{Me}]^+$
707-712	mw	$[\text{P}-16\text{CO}-\text{Me}]^+$
677-687	mw	$[\text{P}-17\text{CO}-\text{Me}]^+$
648-656	mw	$[\text{P}-18\text{CO}-\text{Me}]^+$
621-631	mw	$[\text{P}-19\text{CO}-\text{Me}]^+$
589-603	m	$[\text{P}-20\text{CO}-\text{Me}]^+$
578-587	mw	$[\text{P}-20\text{CO}-2\text{Me}]^+$
567-572	w	$[\text{P}-19\text{CO}-\text{Me}-\text{Co}]^+$
578-587	mw	$[\text{P}-20\text{CO}-2\text{Me}]^+$
522-530	w	$[\text{P}-20\text{CO}-2\text{Me}-\text{Co}]^+$

6.13 Discussion : The reactions of MeClGeH_2 with $\text{GeCo}_4(\text{CO})_{14}$; plus the reactions of $\text{Co}(\text{CO})_4^-$ with $(\text{MeGeCl})\text{GeCo}_4(\text{CO})_{13}$ and $(\text{MeGeCl})_2\text{GeCo}_4(\text{CO})_{12}$

The reaction of MeClGeH_2 with $\text{GeCo}_4(\text{CO})_{14}$

The reactions of MeGeClH_2 with $\text{GeCo}_4(\text{CO})_{14}$ proceeded in a manner very similar to that of Me_2GeH_2 with $\text{GeCo}_4(\text{CO})_{14}$ i.e. via equations :



for $\text{R}_1\text{R}_2 = \text{Me}_2$ or MeCl

The equations are supported by incondensable gas data, infrared spectra and the products obtained. The open tube reaction however showed a consistently low H_2 evolution. It was not certain if this was related to the formation of a red unidentified oily liquid. This red oil was found to interfere with the recrystallisation of $(\text{MeGeCl})\text{GeCo}_4(\text{CO})_{13}$ and $(\text{MeGeCl})_2\text{GeCo}_4(\text{CO})_{12}$.

The mono-substituted product in both the MeClGeH_2 and Me_2GeH_2 reactions with $\text{GeCo}_4(\text{CO})_{14}$ was obtained very easily by sealed tube reaction (compare Section 6.8, Run 2 with Section 6.2, Run 1 where the same reaction time and reactant ratio were used). Both $(\text{MeGeCl})\text{GeCo}_4(\text{CO})_{13}$ and $(\text{Me}_2\text{Ge})\text{GeCo}_4(\text{CO})_{13}$ were easily isolated, and this is unlike the RGeH_3 with $\text{GeCo}_4(\text{CO})_{14}$ system in Chapter Five.

The tendency to form the di-substituted product was higher in the Me_2GeH_2 reaction than the MeGeClH_2 reaction. $(\text{Me}_2\text{Ge})_2\text{GeCo}_4(\text{CO})_{12}$ was formed only 3 days into the reaction described in 6.2 Run 3. In the reaction of MeGeClH_2 with $\text{GeCo}_4(\text{CO})_{14}$ no $(\text{MeGeCl})_2\text{GeCo}_4(\text{CO})_{12}$ was observed until after 2 mole ratio of incondensable gas had evolved

(after 26 days). With the addition of excess MeGeClH_2 , only partial conversion to $(\text{MeGeCl})_2\text{GeCo}_4(\text{CO})_{12}$ was observed after 67 days. This cannot be rationalised in terms of the lower reactivity of MeGeClH_2 because there is no obvious difference in the formation of the mono-substituted product. This difficulty in di-substitution was again observed in the reaction of $(\text{MeGeCl})\text{GeCo}_4(\text{CO})_{13}$ with MeClGeH_2 where a higher $\text{MeGeClH}_2 : (\text{MeGeCl})\text{GeCo}_4(\text{CO})_{13}$ was used compared to the corresponding Me_2GeH_2 reaction.

This reluctance to di-substitution may be due to both steric and electronic effects. The inclusion of Cl in the molecule could lead to increased $d-d \pi$ bonding in Ge-Co bonds and overall deactivation of the molecule to further substitution. This discussion is supported by the shortening of the Ge-Co bond observed in the crystal structure of $\text{Cl}_3\text{GeCo}(\text{CO})_4$ [50]. Ge-Co bond length as 2.31Å compares to the expected covalent bond length of 2.56Å. The bond length shortening effect is also observed in $\text{F}_3\text{SiCo}(\text{CO})_4$ and $\text{Cl}_3\text{SiCo}(\text{CO})_4$ [8]. As well as the electronic effect, any shortening of Ge-Co bonds may bring about steric congestion and therefore a resistance to di-substitution.

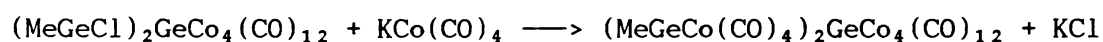
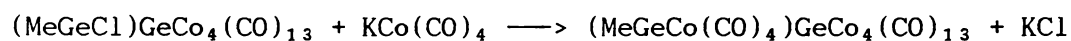
The other possible reason could be due to the repulsion of the δ^- charge on the two chloride atoms in one (Isomer III) of the three possible isomers in the di-substituted species (Fig 6.22). This repulsion problem would be intensified by the Ge-Co bond shortening mentioned above.

The products $(\text{MeClGe})\text{GeCo}_4(\text{CO})_{13}$ and $(\text{MeClGe})_2\text{GeCo}_4(\text{CO})_{12}$ are characterised by spectroscopic means. Crystal structures could not be obtained for the former since the crystals survived for only three hours under X-rays, while single crystals of $(\text{MeClGe})_2\text{GeCo}_4(\text{CO})_{12}$ were not obtained. Despite this, the structures of $(\text{MeClGe})\text{GeCo}_4(\text{CO})_{13}$ and $(\text{MeClGe})_2\text{GeCo}_4(\text{CO})_{12}$ are expected to be very similar to those of their

Me₂Ge analogues (5a) and (9a). (MeGeCl)GeCo₄(CO)₁₃ and (MeGeCl)₂GeCo₄(CO)₁₂ are new members of a now extensive family of open clusters with formula (R₁R₂Ge)GeCo₄(CO)₁₃ and (R₁R₂Ge)₂GeCo₄(CO)₁₂ for R₁R₂ = Me₂, MeH, EtH, PhH, MeCl and MeCo(CO)₄ (see Section 6.15) of basic structures (5) and (9) respectively.

The reactions of (MeClGe)GeCo₄(CO)₁₃ and (MeClGe)₂GeCo₄(CO)₁₂ with KCo(CO)₄

The reactions of (MeGeCl)GeCo₄(CO)₁₃ and (MeGeCl)₂GeCo₄(CO)₁₂ with KCo(CO)₄ produced the extended chain products MeGe₂Co₅(CO)₁₇ and Me₂Ge₃Co₆(CO)₂₀ respectively according to the equations :



KCl was obtained as a white deposit on the side of the reaction flask while the products MeGe₂Co₅(CO)₁₇ and Me₂Ge₃Co₆(CO)₂₀ were extracted as hexane soluble compounds.

The reactions were rapid compared to the hydride replacement reaction, (MeGeH)GeCo₄(CO)₁₃ or (EtGeH)₂GeCo₄(CO)₁₂ with Co₂(CO)₈ (Chapter Seven). In these two latter reactions, the extended chain compounds were isolated pure only with difficulty (see Chapter Seven). MeGe₂Co₅(CO)₁₇ has been previously prepared by the reaction of MeGe₂H₅ with Co₂(CO)₈ by McLeod [82]. This preparation however also produced MeGeCo₃(CO)₁₁ and GeCo₄(CO)₁₄ which were not easily separated. The halide replacement reaction of (MeGeCl)GeCo₄(CO)₁₃ and (MeGeCl)₂GeCo₄(CO)₁₂ in comparison with the other two methods is quick and easy and gives relatively pure products.

The crystal structure of these compounds have not yet been obtained, but the structures could be predicted from the comparison of properties with those of known structures such as $(\text{Me}_2\text{Ge})_2\text{GeCo}_4(\text{CO})_{12}$ and $\text{MeGeCo}_3(\text{CO})_{11}$.

$\text{MeGe}_2\text{Co}_5(\text{CO})_{17}$ has been shown to close down to form $\text{MeGe}_2\text{Co}_5(\text{CO})_{15}$ (*1g*) at 55°C [82]. Preliminary studies on the reaction of $(\text{MeGeH})_2\text{GeCo}_4(\text{CO})_{12}$ with $\text{Co}_2(\text{CO})_8$ in Chapter Seven have indicated the formation of $\text{Me}_2\text{Ge}_3\text{Co}_6(\text{CO})_{20}$ which decarbonylated to form $\text{Me}_2\text{Ge}_3\text{Co}_6(\text{CO})_{17}$ (structure as in (*11*)).

6.14 Related reactions -- preliminary studies only

6.14.1 The reaction of MeClGeH_2 with $(\text{Me}_2\text{Ge})\text{GeCo}_4(\text{CO})_{13}$

Experimental :

$(\text{Me}_2\text{Ge})\text{GeCo}_4(\text{CO})_{13}$ (0.04g, 0.052mmol) and MeGeClH_2 (0.03g, 0.24mmol), hexane (30 ml) were loaded into a 200 ml reaction vessel as an open tube reaction. The reaction was allowed to proceed in the dark at room temperature and the incondensable gas was measured at intervals.

Results :

Table 6.22 Incondensable gas measurement of the reaction of MeGeClH_2 with $(\text{Me}_2\text{Ge})\text{GeCo}_4(\text{CO})_{13}$:

Days	Gas evolved (mmol)	Gas composition
5	0.079	59% CO, 41% H_2
8	0.008	
26	0.007	
34	0.001	

The majority of the gas was released in the first five days (see Table 6.22). The colour of the solution changed from reddish orange to light yellow which was very similar to the colours of $(\text{Me}_2\text{Ge})_2\text{GeCo}_4(\text{CO})_{12}$ and $(\text{MeGeCl})_2\text{GeCo}_4(\text{CO})_{12}$. The reaction was stopped after 34 days when the evolution of gas tailed off.

A yellow solid soluble in hexane was obtained. It was characterised as $(\text{Me}_2\text{Ge})(\text{MeGeCl})\text{GeCo}_4(\text{CO})_{12}$ by mass spectrum and by comparing its infrared spectrum to those of $(\text{Me}_2\text{Ge})_2\text{GeCo}_4(\text{CO})_{12}$ and $(\text{MeGeCl})_2\text{GeCo}_4(\text{CO})_{12}$. No other compounds were present.

Yield :

Weight of product : 0.049g = 0.056 mmol --> 100% yield

From incondensable gas measurement = 81%

Characterisation of $(\text{Me}_2\text{Ge})(\text{MeGeCl})\text{GeCo}_4(\text{CO})_{12}$

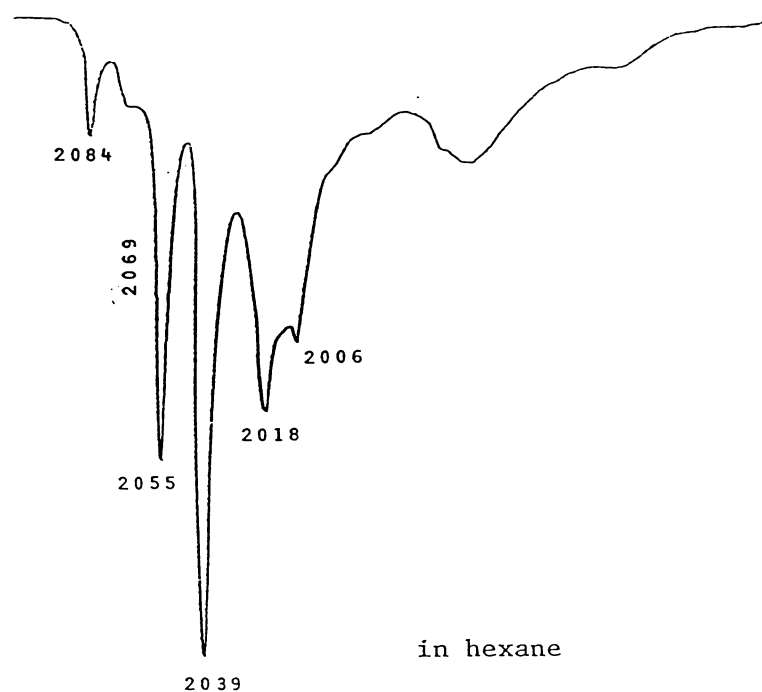
Infrared spectrum :

The infrared spectrum of $(\text{Me}_2\text{Ge})(\text{MeGeCl})\text{Co}_4(\text{CO})_{12}$ (Fig 6.21) can be related to those of $(\text{Me}_2\text{Ge})_2\text{GeCo}_4(\text{CO})_{12}$ and $(\text{MeGeCl})_2\text{GeCo}_4(\text{CO})_{12}$ as shown in Table 6.23. Its structure is expected to be very similar to that of $(\text{Me}_2\text{Ge})_2\text{GeCo}_4(\text{CO})_{12}$ except that one of the methyl groups has been replaced by a Cl atom. Twelve infrared bands are predicted if the symmetry is regarded as C_s . Like $(\text{EtGeH})(\text{PhGeH})\text{GeCo}_4(\text{CO})_{12}$ (Chapter Five), its infrared spectrum is remarkably similar (except for one extra weak band at 2069 cm^{-1}) to those of $(\text{RR}'\text{Ge})\text{GeCo}_4(\text{CO})_{12}$ (see Section 6.15) despite the differing bridging groups.

The absence of a $\mu\text{-CO}$ band is consistent with the predicted structure.

Table 6.23 Infrared spectra of $(RR'Ge)_2GeCo_4(CO)_{12}$

$(RR')_2 = (Me_2)(MeCl)$		$(Me_2)_2$		$(MeCl)_2$	
Bands	Int	Bands	Int	Bands	Int
2081	w	2084	w	2092	w
2069	vw sh			2066	ms
2054	s	2055	ms		
2037	vs	2039	vs	2050	vs
2015	m	2018	ms	2026	m sh
2003	ms	2006	m sh	2018	ms

Fig 6.21 Infrared spectrum of $(Me_2Ge)(MeGeCl)Co_4(CO)_{12}$ *Mass Spectrum :*

The mass spectrum of $(Me_2Ge)(MeGeCl)Co_4(CO)_{12}$ (poorly resolved, Table 6.24) showed two series of weak envelopes : one of $[P-nCO]^+$ and the other with $[P-Me-nCO]^+$ for $n = 12$ to 0. The loss of the chlorine atom occurred after the loss of eleven COs. The second Me group was fragmented only after the loss of all other ligands. The late loss of Cl was also observed in the mass spectrum of $(MeGeCl)GeCo_4(CO)_{13}$.

Table 6.24 Mass spectrum of $(\text{Me}_2\text{Ge})(\text{MeGeCl})\text{Co}_4(\text{CO})_{12}$

m/e	Int	Possible assignments
865-875	w	P^+
855-865	w	$[\text{P-Me}]^+$
838-848	m	$[\text{P-CO}]^+$
825-836	m	$[\text{P-Me-CO}]^+$
812-823	m	$[\text{P-2CO}]^+$
802-808	m	$[\text{P-Me-2CO}]^+$
785-795	ms	$[\text{P-3CO}]^+$
775-785	ms	$[\text{P-Me-3CO}]^+$
761-770	w	$[\text{P-4CO}]^+$
741-751	w	$[\text{P-Me-4CO}]^+$
725-735	w	$[\text{P-5CO}]^+$
712-722	mw	$[\text{P-Me-5CO}]^+$
690-710	w	$[\text{P-6CO}, \text{P-Me-6CO}]^+$
675-680	w	$[\text{P-7CO}]^+$
660-670	w	$[\text{P-Me-7CO}]^+$
630-655	w	$[\text{P-8CO}]^+, [\text{P-Me-8CO}]^+$
615-625	w	$[\text{P-9CO}]^+$
604-615	w	$[\text{P-Me-9CO}]^+$
578-602	w	$[\text{P-10CO}]^+, [\text{P-Me-10CO}]^+$
560-579	w	$[\text{P-11CO}]^+$
550-560	mw	$[\text{P-Me-11CO}]^+$
520-535	w	$[\text{P-11CO-Cl}]^+, [\text{P-Me-12CO}]^+$
499-510	w	$[\text{P-12CO-Cl}]^+$
481-495	w	$[\text{P-Me-12CO-Cl}]^+$
470-480	w	$[\text{P-2Me-12CO-Cl}]^+$
445-458	mw	$[\text{P-2Me-12CO-Cl}]^+ = [\text{Ge}_3\text{Co}_4]^+$
325-340	ms	$[\text{MeGeCo}_4]^+?$



NMR data : this was not obtained as the sample was highly contaminated by grease.

6.14.2 The reaction of Me_2SiH_2 with $\text{GeCo}_4(\text{CO})_{14}$

Experimental :

$\text{GeCo}_4(\text{CO})_{14}$ (0.544g, 0.777mmol) was loaded into a 50 ml ampoule with hexane (10 ml). This was transferred to the vacuum line where all the gases were removed. The contents were frozen down by liquid nitrogen and Me_2SiH_2 (3.1mmol) was condensed in and the ampoule sealed. The reaction was allowed to proceed for 2 months at room temperature in the dark.

Observations and Workup :

The reddish brown solution changed to a purple colour after two weeks. The incondensable gas were not measured on opening the ampoule and the volatiles were not examined.

The involatile fraction was washed with hexane. The hexane washings were shown to consist mainly of $\text{GeCo}_4(\text{CO})_{13}$ [17,22] which is the decarbonylated product of $\text{GeCo}_4(\text{CO})_{14}$. The infrared spectrum of the solid fraction showed that most of the solid residue consisted of virtually pure $\text{GeCo}_4(\text{CO})_{14}$. No other compounds were observed.

6.14.3 The reaction of Me_2SiH_2 with $(\text{Me}_2\text{Ge})\text{GeCo}_4(\text{CO})_{13}$

Experimental :

$(\text{Me}_2\text{Ge})\text{GeCo}_4(\text{CO})_{13}$ (0.102g, 0.132mmol) and Me_2SiH_2 (0.66mmol) were sealed in an ampoule as in 6.14.2. The reaction was allowed to proceed at room temperature with shaking for 8 months.

Observations and workup :

No change in colour of the reactants was observed. After 8 months, about 0.3 mmoles of incondensable gas were measured and this was found to be mainly H_2 (presumably from the decomposition of Me_2SiH_2 e.g reaction with any OH groups on the ampoule). The involatile material was dissolved in hexane. The infrared spectrum of this solution showed

no bands other than those of $(\text{Me}_2\text{Ge})\text{GeCo}_4(\text{CO})_{13}$ --- i.e. no reaction had taken place.

6.15 The effect on the infrared spectrum on replacing $\mu\text{-X}$ by $\mu\text{-R}_2\text{Ge}$ in $\text{Co}_2(\text{CO})_6(\mu\text{-X})_2$ type compounds

The infrared spectra of $\text{Co}_2(\text{CO})_8$ (bridged form), $\text{Me}_2\text{GeCo}_2(\text{CO})_7$ and $(\text{Me}_2\text{Ge})_2\text{Co}_2(\text{CO})_6$ conform to the idealised 'Bor spectrum' or infrared spectrum of the type $\text{M}_2(\text{CO})_6(\mu\text{-X})_2$ [149]. This 'Bor spectrum' for $\text{Co}_2(\text{CO})_8$ based on a C_{2v} symmetry exhibits five infrared bands ($2\text{A}_1 + 2\text{B}_1 + \text{B}_2$) and an infrared inactive A_2 mode. All five predicted bands of $(\text{Me}_2\text{Ge})_2\text{Co}_2(\text{CO})_6$ (C_{2v} symmetry, $2\text{A}_1 + 2\text{B}_1 + \text{B}_2$) and seven bands of $\text{Me}_2\text{GeCo}_2(\text{CO})_7$ (C_s symmetry, $4\text{A}' + 3\text{A}''$) are observed. Ten terminal CO bands and one bridging CO band are predicted for $\text{MeGeCo}_3(\text{CO})_{11}$ based on C_s symmetry ($7\text{A}' + 4\text{A}''$). Only nine are observed (excluding one bridging CO due to isomerism). With a mixture of terminal $\text{Co}(\text{CO})_4$ groups and $\text{Co}_2(\text{CO})_7$ groups in the same molecule, assignment becomes difficult. Without interference from the $\text{Co}_2(\text{CO})_7$ carbonyls, the $\text{Co}(\text{CO})_4$ group is expected to show three bands (C_{3v} symmetry, $2\text{A}_1 + \text{E}$). Though no specific reference for these carbonyl stretches is available, results from [17,20,23] indicate that they may be expected in the region of 2100-2120 cm^{-1} , 2050-2070 cm^{-1} , 2030-2010 cm^{-1} . Table 6.25 shows that the following three bands may be assigned to the $\text{Co}(\text{CO})_4$ group : 2105, 2056 and 2030 cm^{-1} . Mixing and overlapping of bands from the $\text{Co}_2(\text{CO})_7$ and $\text{Co}(\text{CO})_4$ groups no doubt has occurred. Nevertheless, the infrared spectrum of $\text{MeGeCo}_3(\text{CO})_{11}$ can be described as one consisting of bands of a terminal $\text{Co}(\text{CO})_4$ group superimposed on the spectrum of $(\mu\text{-X})_2\text{Co}_2(\text{CO})_6$ unit, where X is a bridging $\text{MeGeCo}(\text{CO})_4$ unit and a bridging CO. The infrared spectrum of $\text{Me}_2\text{Ge}_2\text{Co}_4(\text{CO})_{14}$ may

similarly be described as one consisting of bands from $\text{Co}(\text{CO})_4$ groups superimposed upon that of $(\text{Me}_2\text{Ge})_2\text{Co}_2(\text{CO})_6$.

The effect of successive replacement of the $\mu\text{-CO}$ by a bridging GeMe_2 is the shift to low frequency in the spectra of $\text{Me}_2\text{GeCo}_2(\text{CO})_7$ and $(\text{Me}_2\text{Ge})_2\text{Co}_2(\text{CO})_6$ (Table 6.25). As shown, this shift ranges from an average of 17 to 35 cm^{-1} on the first replacement and by about 16 to 21 cm^{-1} on the second replacement.

The molecules $[\{(\mu\text{-X})(\text{Co}_2(\text{CO})_6)_2\text{Ge}\}]$ for $\text{X} = \text{CO}$, R_2Ge can be regarded as 'double Bor' units. The vibrational modes may be interpreted in terms of the 'Bor vibrational modes' if the coupling of the vibrations of the two $\text{Co}_2(\text{CO})_6$ units across the central germanium is moderate or small. Many compounds synthesised in Chapter Five and Six can be regarded as 'double Bor' units and they are shown in Table 6.25.

If the two $\mu\text{-CO}$'s in $\text{GeCo}_4(\text{CO})_{14}$ or $[\{(\mu\text{-CO})(\text{Co}_2(\text{CO})_6)_2\text{Ge}\}]$ are ignored, the $\text{GeCo}_4(\text{CO})_{12}$ unit assumes a D_{2d} symmetry, giving five predicted infrared bands ($2\text{B}_2 + 3\text{E}$) -- a close resemblance to the 'Bor spectrum' of $(\mu\text{-X})_2\text{Co}_2(\text{CO})_6$. The observed infrared spectra of $(\text{RR}'\text{Ge})_2\text{GeCo}_4(\text{CO})_{12}$ seems to conform to this idealised symmetry except when the bridging groups on both ends are different : $(\text{Me}_2\text{Ge})(\text{MeGeCl})\text{GeCo}_4(\text{CO})_{12}$ shows six IR bands and $(\text{EtGeH})(\text{PhGeH})\text{GeCo}_4(\text{CO})_{12}$ shows seven IR bands. The infrared spectrum of $(\text{Me}_2\text{Ge})(\text{MeGeCl})\text{GeCo}_4(\text{CO})_{12}$ is better regarded as that of the 'Bor spectrum' (C_{2v} symmetry) and the extra band (2069 cm^{-1} , sh) as the A_2 inactive mode while the symmetry of $(\text{EtGeH})(\text{PhGeH})\text{GeCo}_4(\text{CO})_{12}$ is better regarded as C_s .

Replacement of one $\mu\text{-CO}$ in $\text{GeCo}_4(\text{CO})_{14}$ by a $\mu\text{-GeRR}'$ group reduces the symmetry of the molecule to C_s . Therefore the number of infrared bands observed were more than five -- an average of nine were observed

(IIa to IIId in Table 6.25). The successive replacement of a μ -CO by a Me_2Ge unit or $\text{MeR}'\text{Ge}$ unit in $\text{GeCo}_4(\text{CO})_{14}$ again displays a shift an average of 20 to 30 cm^{-1} to the lower frequency.

The infrared spectra of $\text{MeGe}_2\text{Co}_5(\text{CO})_{17}$ and $\text{Me}_2\text{Ge}_3\text{Co}_6(\text{CO})_{20}$, like that of $\text{MeGeCo}_3(\text{CO})_{11}$ may be described as one in which the bands of a terminal $\text{Co}(\text{CO})_4$ groups are superimposed on the spectrum of a $[\{(\mu\text{X})(\text{Co}_2(\text{CO})_6)_2\text{Ge}\}]$ unit. Four extra bands (2105, 2055, 2015 and 1997) presumably to account for the $\text{Co}(\text{CO})_4$ group in $\text{MeGeCo}_5(\text{CO})_{17}$ were observed, but in $\text{Me}_2\text{Ge}_3\text{Co}_6(\text{CO})_{20}$, only one band (2090) more than that of $\text{GeCo}_4(\text{CO})_{14}$ was observed. This indicates that $\text{Me}_2\text{Ge}_3\text{Co}_6(\text{CO})_{20}$ may be regarded as a idealised 'double Bor' unit in solution despite the bridging $\mu\text{-Ge}(\text{Me})\text{Co}(\text{CO})_4$ groups on both ends.

There is little or no effect on the frequency when Me is being replaced by H, Et or Ph. There is however, a shift of 2 to 3 cm^{-1} to higher frequency when one of the R groups is Cl. This effect has been explained in Section 6.10.

The higher homologues of $[\{(\mu\text{X})(\text{Co}_2(\text{CO})_6)_2\text{Ge}\}]$, $[\{(\mu\text{X})(\text{Co}_2(\text{CO})_6\text{Ge})_2\text{Co}_2(\text{CO})_6\}]$ and $[\{(\mu\text{X})(\text{Co}_2(\text{CO})_6\text{GeCo}_2(\text{CO})_6)_2\text{Ge}\}]$, may be regarded as the 'triple Bor' and 'quadruple Bor' units. As the totally symmetric mode is not observed in these compounds, the effect of substitution of the μ -CO by $\mu\text{-GeMe}_2$ group could not be directly assessed in the same manner as the lower homologues. However, a relationship between the substitution of a μ -CO by a μGeMe_2 group and a shift to the higher frequency of the out-of-phase combination of the symmetric mode seems to exist : 2079 cm^{-1} in $\text{GeCo}_4(\text{CO})_{14}$ to 2081 cm^{-1} in $(\text{Me}_2\text{Ge})_2\text{GeCo}_4(\text{CO})_{12}$, and 2085 cm^{-1} in $\text{Ge}_2\text{Co}_6(\text{CO})_{20}$ to 2087 cm^{-1} in $(\text{Me}_2\text{Ge})_2\text{Ge}_2\text{Co}_6(\text{CO})_{18}$. It would be interesting to see if the highest observed frequency in $(\text{Me}_2\text{Ge})_2\text{Ge}_3\text{Co}_8(\text{CO})_{24}$ (if synthesised) would be in the region of 2095 cm^{-1} .

Table 6.25 Infrared spectra of 'Bor' type compounds

(I)	(Ia)	(Ib)	(Ic)	(Id)
[149]	[61]	[17,61]	[76]	[20,71]
2112vw			2097w	2105w
	2085s		2087s	2082s
2071s		2066s	2067mw	
				2056s
	2047vs			2046sh
2044vs				
2042vs			2039s	
	2024vs	2029vs	2029s	2030s
			2017vs	2020/5m
	2006vs	2006vs	2002mw	2007w
	1998sh, w		1989w	1998w
		1990vs		
		1981mw		
	1971sh, w		1970w	
1866w				
1857m				1850w
	1844s			1835w sh

(I) = Co_2Co_8 , (Ia) = $\text{Me}_2\text{GeCo}_2(\text{CO})_7$, (Ib) = $(\text{Me}_2\text{Ge})_2\text{Co}_2(\text{CO})_6$,
(Ic) = $\text{Me}_2\text{Ge}_2\text{Co}_4(\text{CO})_{14}$, (Id) $\text{MeGeCo}_3(\text{CO})_{11}$

Table 6.25 *cont'd...*

(II)	(IIa)	(IIb)	(IIc)	(IIId)
2105w				2105w
	2098w	2096w	2099w	
		2093w	2093w	2088vs
2079s			2076ms	
2061vs	2068vs	2064s	2070s	2064s
	2056s	2054ms	2059vs	2055ms
		2049ms sh	2054vs sh	
2040m	2047vs	2043vs		2046vs
				2044vs
2032m	2030mw		2035ms	
2023w	2020m	2026m	2029ms	2026ms
		2021m sh	2022ms	2023ms sh
		2017ms		2015ms sh
2005w		2003mw		2004m sh
				1997mw
1848m	1842w	1843w	1842w	1845w

(II) $\text{GeCo}_4(\text{CO})_{14}$, (IIa) $(\text{MeGeH})\text{GeCo}_4(\text{CO})_{13}$,
 (IIb) $(\text{Me}_2\text{Ge})\text{GeCo}_4(\text{CO})_{13}$, (IIc) $(\text{MeGeCl})\text{GeCo}_4(\text{CO})_{13}$,
 (IIId) $\text{MeGe}_2\text{Co}_5(\text{CO})_{17}$

(IIe)	(IIIf)	(IIIg)	(IIH)	(IIi)	(IIj)
			2090ms		
2085w	2081w	2092w	2072mw	2084w	2085vw
		2066ms		2069vw sh	2071vw sh
2059s	2054s		2058ms	2055ms	2059m
2042vs	2037vs	2050vs	2043vs	2039vs	2043vs
		2026m sh			2026w sh
2019ms	2015m		2018s	2018ms	2019w
2010ms	2003ms	2018ms		2006m sh	2011mw
			1995w, sh		

(IIe) $(\text{MeGeH})_2\text{GeCo}_4(\text{CO})_{12}$, (IIIf) $(\text{Me}_2\text{Ge})_2\text{GeCo}_4(\text{CO})_{12}$
 (IIIg) $(\text{MeGeCl})_2\text{GeCo}_4(\text{CO})_{12}$, (IIH) $\text{Me}_2\text{Ge}_3\text{Co}_6(\text{CO})_{20}$
 (IIi) $(\text{Me}_2\text{Ge})(\text{MeGeCl})\text{GeCo}_4(\text{CO})_{12}$, (IIj) $(\text{EtGeH})(\text{PhGeH})\text{GeCo}_4(\text{CO})_{12}$

Table 6.25 *cont'd...*

(III)	(IIIa)	(IV)
[18,27]	[18]	[18,83]
>2105?		>2105?
		2094s
2085s	2087w	2073s
2068vs	2065s-vs	2065vs
2054s	2053vs	2053s
2050sh		
2040w	2041vs	2038m
2033wm	2034sh w	
2027m		2027m
	2013sh	2011w, sh
	2008ms	
2003w	1985vw, sh	
1848sh		1853w, br
1844wm		

(III) $\text{Ge}_2\text{Co}_6(\text{CO})_{20}$, (IIIa) $(\text{Me}_2\text{Ge})_2\text{Ge}_2\text{Co}_6(\text{CO})_{18}$

(IV) $\text{Ge}_3\text{Co}_8(\text{CO})_{26}$

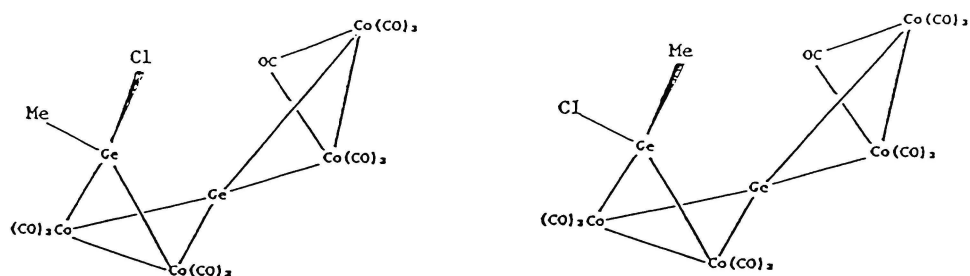
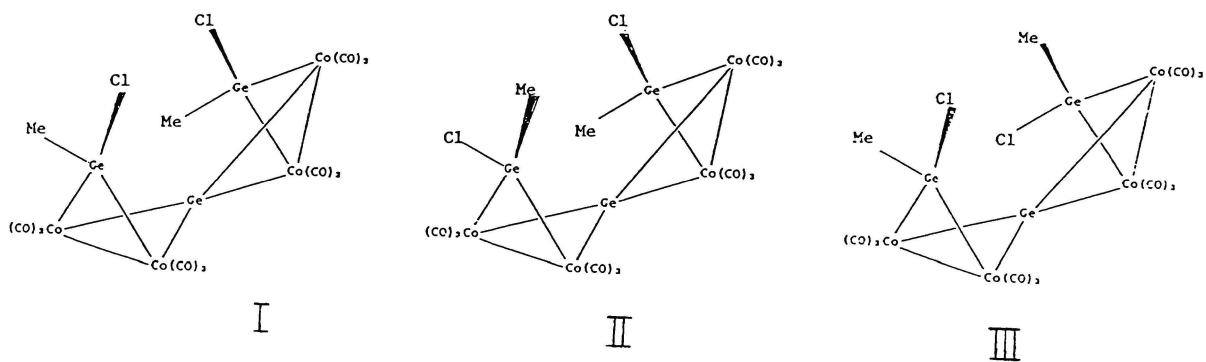


Fig 6.22 Possible isomers of $(\text{MeGeCl})\text{GeCo}_4(\text{CO})_{13}$ (above)
and $(\text{MeGeCl})_2\text{GeCo}_4(\text{CO})_{12}$ (below)



CHAPTER SEVEN

The Reaction of $(RGeH)_nGeCo_4(CO)_{14-n}$ and $Co_2(CO)_8$ ($n = 1$ or 2)

7.1 Introduction :

The reaction of Group IVB hydrides with $Co_2(CO)_8$ is an important preparative route, but has generally been limited to simpler systems such as GeH_4 with $Co_2(CO)_8$. This Chapter describes the reaction of some larger compounds (which contain functional hydrogens) with $Co_2(CO)_8$ to see how versatile this preparative route is. $(RGeH)GeCo_4(CO)_{13}$ and $(RGeH)_2GeCo_4(CO)_{12}$ contain one, and two functional H respectively and the reaction of these with $Co_2(CO)_8$ is examined.

7.2 Reaction of $(MeGeH)GeCo_4(CO)_{13}$ with $Co_2(CO)_8$

The experimental conditions of two runs of this reaction are given in Table 7.1.

Table 7.1 Experimental conditions of $(MeGeH)GeCo_4(CO)_{13} + Co_2(CO)_8$

	Run 1	Run 2
$(MeGeH)GeCo_4(CO)_{13}^*$ (g)	0.21	0.127
(mmol) [#]	~0.22	~0.13
$Co_2(CO)_8$ (g)	~0.05	~0.03
(mmol)	0.15	0.08
Reaction time	45 days	21 days

* $(MeGeH)GeCo_4(CO)_{13}$ was contaminated with $GeCo_4(CO)_{14}$ and was estimated to be of about 80% purity. [#] based on 80% purity

7.2.1 Experimental :

Run 1 ((MeGeH)GeCo₄(CO)₁₃ : Co₂(CO)₈ = 1.5 : 1)

(MeGeH)GeCo₄(CO)₁₃* (0.21g, 0.22mmol) and Co₂(CO)₈ (0.05g, 0.15 mmol) together with hexane (5 ml) were loaded into a 25 ml greaseless tap reaction vessel under nitrogen. The contents were cooled with liquid nitrogen and evacuated to remove all incondensable gas. This was closed and left to react for 45 days at room temperature with intermittent measurement of incondensable gas (given in Table 7.2).

7.2.2 Observations and Workup :

Table 7.2 Incondensable readings of Run 1 :

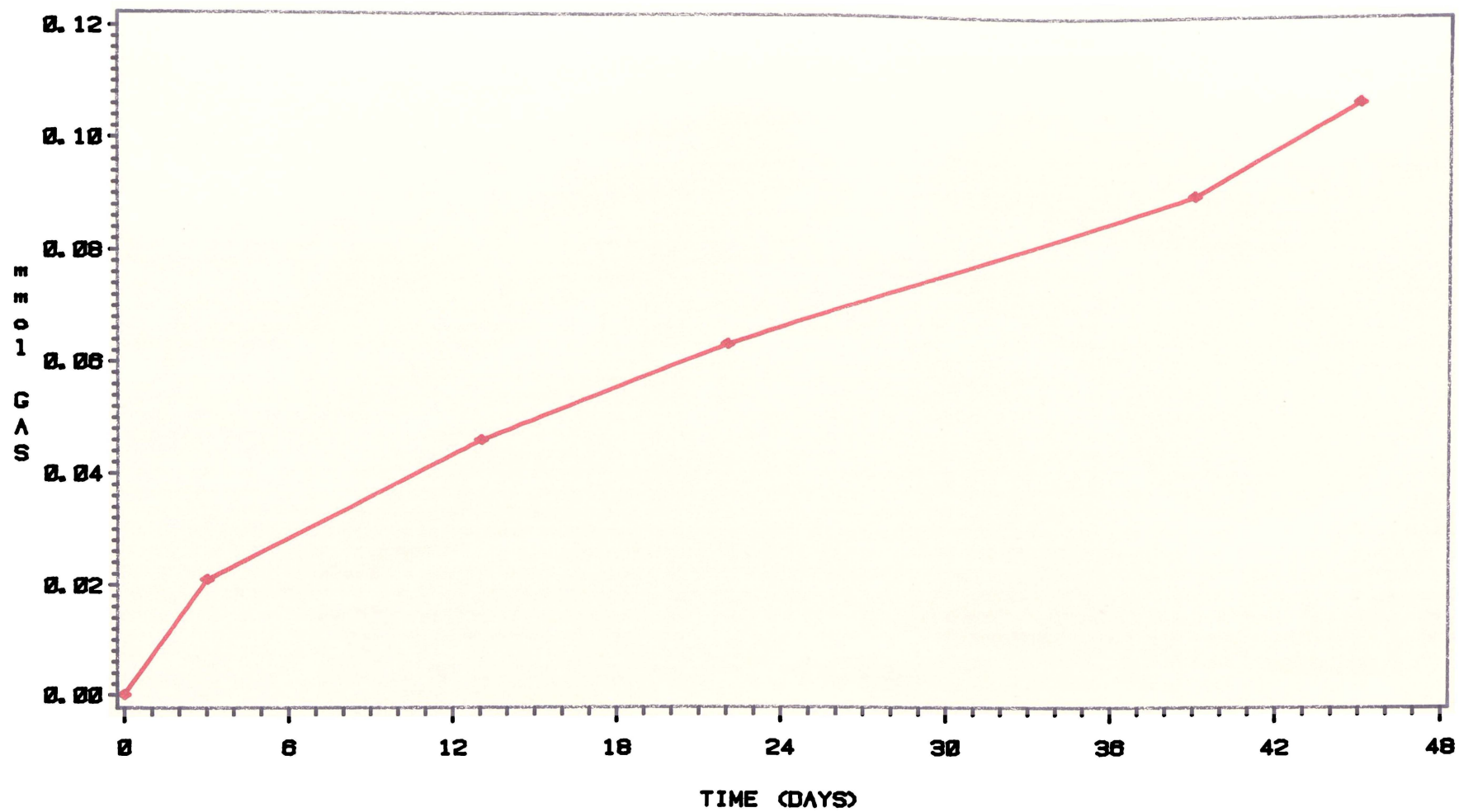
Days	mmol of gas	Total mmol of gas	%H ₂
3	0.021	0.021	0
13	0.025	0.046	0
22	0.017	0.063	0
39	0.027	0.090	0
45	0.017	0.107	0

By 45 days, the reaction produced a brown solution with some dark solid at the bottom of the reaction tube. On working up, 3 fractions were obtained :- a brown hexane soluble fraction, a reddish brown CH₂Cl₂ soluble fraction and a CH₂Cl₂ insoluble fraction.

Hexane soluble fraction

The infrared spectrum of this fraction (Table 7.3) showed a mixture of compounds ; GeCo₄(CO)₁₄, GeCo₄(CO)₁₃, a small amount of Co₄(CO)₁₂ and Co₂(CO)₈ plus a compound previously characterised (Chapter Six) as MeGe₂Co₅(CO)₁₇ (5c). The mixture was placed under vacuum for half a day to sublime away any unreacted Co₂(CO)₈. The residual solid was crystallised from CH₂Cl₂/hexane to give a small

Figure 7.1
Incondensable Gas Evolution Of The Reaction
Of $(\text{MeGeH})\text{GeCo}_4(\text{CO})_{13} + \text{Co}_2(\text{CO})_8$



TOTAL GAS = -----

amount of dark red crystals, characterised (in Section 7.4) as $\text{MeGe}_2\text{Co}_5(\text{CO})_{15}$ (1g). Note : $\text{MeGe}_2\text{Co}_5(\text{CO})_{17}$ and $\text{MeGe}_2\text{Co}_5(\text{CO})_{15}$ were both independently prepared via another route and characterised spectroscopically by L.McLeod [82].

CH_2Cl_2 fraction

The CH_2Cl_2 fraction was dark red. The infrared spectrum indicated it to be solely $\text{MeGe}_2\text{Co}_5(\text{CO})_{15}$.

CH_2Cl_2 insoluble fraction

This consisted of some dark purplish coloured solid (which indicates decomposed material) and some colourless solid. The mass spectrum of this showed the highest m/e peak to be at 446 (single peak) and the highest intensity 'envelope' at m/e 354 (two peaks). No specific Ge or CO loss patterns were observed.

Table 7.3 Infrared spectrum (in cm^{-1}) of hexane fraction, Run 1

Bands Int		Possible assignments				
		$\text{MeGe}_2\text{Co}_5(\text{CO})_{17}$ [Chapter Five, 82]	$\text{GeCo}_4(\text{CO})_{14}$ [16]	$\text{GeCo}_4(\text{CO})_{13}$ [22]	$\text{Co}_4(\text{CO})_{12}$ [142]	$\text{Co}_2(\text{CO})_8$ [142]
2102	w	2102 w				
2088	m	2088 s				
2082	m			2083 s		
2079	sh m		2079 s			
2065	ms	2064 s			2063 s	2068 s
2061	m		2061 vs			
2055	m	2055 ms			2055 vs	
2045-43	vvs	2043 vs		2045 vvs		2042 vs
2027	m	2026 m		2029 m		2030 m
2004	w	2004 w	2005 w			
1865	vw				1867 w	1866 vw
1845	w	1845 w				

Yield of Run 1 :

Weight of $\text{MeGe}_2\text{Co}_5(\text{CO})_{15} = \sim 0.08\text{g}$ (0.092 mmol) = 42%

$\text{MeGe}_2\text{Co}_5(\text{CO})_{17}$ mixture* = $\sim 0.15\text{g}$

Decomposed material = $\sim 0.02\text{g}$

* contains $\text{MeGe}_2\text{Co}_5(\text{CO})_{17}$, $\text{GeCo}_4(\text{CO})_{14}$, $\text{GeCo}_4(\text{CO})_{13}$ and $\text{Co}_4(\text{CO})_{12}$

7.2.3 Run 2 ($(\text{MeGeH})\text{GeCo}_4(\text{CO})_{13} : \text{Co}_2(\text{CO})_8 = 1.6 : 1$)

This run was not followed by incondensable gas measurement due to a leak in the sealing ring of the tap. As a result, the reaction tube was capped with a small round bottom flask to reduce leakage. This was then left in the refrigerator to react for 21 days.

On working up, only a hexane soluble fraction was obtained. The infrared spectrum (similar to that in Table 7.3) indicated that the major product was $\text{MeGe}_2\text{Co}_5(\text{CO})_{17}$ but the bands due to $\text{GeCo}_4(\text{CO})_{14}$, $\text{GeCo}_4(\text{CO})_{13}$ and a small amount of $\text{Co}_4(\text{CO})_{12}$ were present. These were probably introduced as impurity rather than rising from the breakdown of $(\text{MeGeH})\text{GeCo}_4(\text{CO})_{13}$. On standing in the freezer, a red solid separated out, leaving $\text{GeCo}_4(\text{CO})_{14}$, $\text{GeCo}_4(\text{CO})_{13}$ and $\text{Co}_4(\text{CO})_{12}$ in the supernatant solution. The red solid was virtually pure $\text{MeGe}_2\text{Co}_5(\text{CO})_{17}$.

Yield of Run 2 :

Weight of $\text{MeGe}_2\text{Co}_5(\text{CO})_{17} = \sim 0.1\text{g} = 0.11\text{ mmol} = 85\%$

Weight of $\text{GeCo}_4(\text{CO})_{14} + \text{GeCo}_4(\text{CO})_{13} + \text{Co}_4(\text{CO})_{12} = \sim 0.05\text{g}$

7.3 The Reaction of $(\text{PhGeH})\text{GeCo}_4(\text{CO})_{13}$ with $\text{Co}_2(\text{CO})_8$ (only one run)

7.3.1 Experimental :

$(\text{PhGeH})\text{GeCo}_4(\text{CO})_{13}$ (~0.121g, 0.146 mmol) and $\text{Co}_2(\text{CO})_8$ (~0.03g, 0.088 mmol) were reacted via an open tube according to the procedures described in 7.2 Run 1.

7.3.2 Observations and workup :

The reaction was followed by incondensable gas evolution. The results are given in Table 7.4 and Fig 7.2.

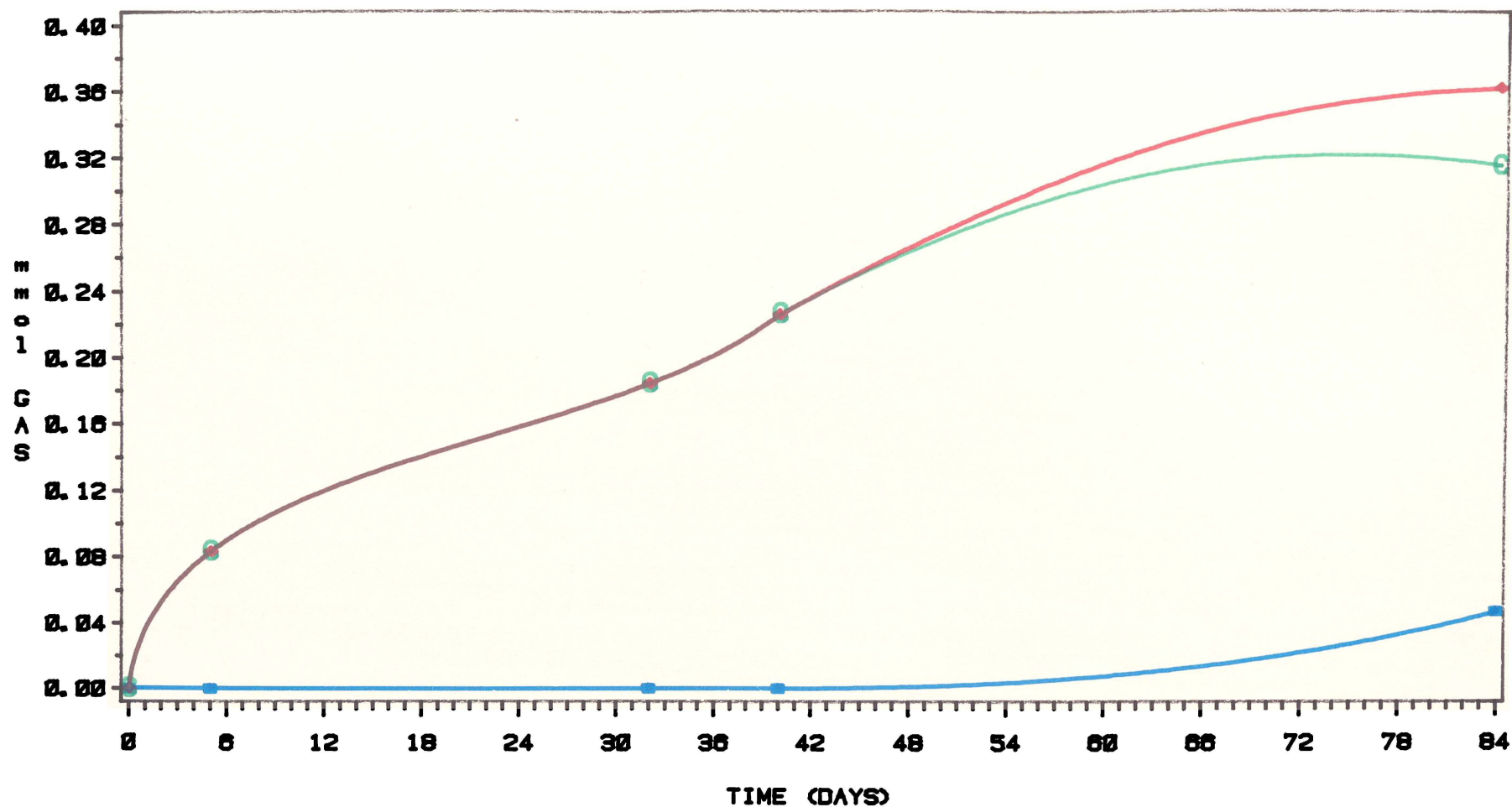
Table 7.4 Incondensable gas evolution of the reaction of $(\text{PhGeH})\text{GeCo}_4(\text{CO})_{13}$ with $\text{Co}_2(\text{CO})_8$:

Days	mmol gas	total mmol gas	mmol H_2	mmol CO
5	0.084	0.084	0	0.084
32	0.110	0.184	0	0.184
40	0.041	0.225	0	0.225
84	0.137	0.362	0.047	0.315

After 84 days, the reaction was stopped and worked up. The infrared spectrum of the volatile fraction indicated the presence of mainly hexane and a very weak absorption at about 2050 cm^{-1} , probably arising from $\text{HCo}(\text{CO})_4$ (2116vw, 2052m, 2030s, 1993 vw) [142].

Extracting with hexane gave a dark brown solution leaving a hexane-insoluble red brown solid. The solid was dissolved in CH_2Cl_2 to form a red solution. The infrared spectrum of the CH_2Cl_2 solution (Table 7.5) is very similar to that of $\text{MeGe}_2\text{Co}_5(\text{CO})_{15}$ obtained in Section 7.3 and characterised in Section 7.4. Based on the similarity of the infrared spectrum and the reaction, this product is likely to be $\text{PhGe}_2\text{Co}_5(\text{CO})_{15}$. The dark brown hexane solution consisted of $\text{Co}_4(\text{CO})_{12}$ and $\text{PhGe}_2\text{Co}_5(\text{CO})_{15}$. No $\text{PhGe}_2\text{Co}_5(\text{CO})_{17}$ was observed.

Figure 7.2
Incondensable Gas Evolution Of The Reaction
Of $(\text{PhGeH})\text{GeCo}(\text{CO})_4$ + $\text{Co}_2(\text{CO})_8$



TOTAL GAS - - - -
 HYDROGEN - - - -
 CARBON MONOXIDE - - - -

Yield :

Weight of $\text{PhGe}_2\text{Co}_5(\text{CO})_{15} = 0.051\text{g} = 0.0544 \text{ mmol} = 37\%$

Weight of $\text{Co}_4(\text{CO})_{12} + \text{PhGe}_2\text{Co}_5(\text{CO})_{15}$ mixture = $\sim 0.1\text{g}$

7.4 Characterisation of $\text{MeGe}_2\text{Co}_5(\text{CO})_{15}$ and $\text{PhGe}_2\text{Co}_5(\text{CO})_{15}$

7.4.1 Infrared spectrum

The solution and solid infrared spectra of $\text{MeGe}_2\text{Co}_5(\text{CO})_{15}$ and $\text{PhGe}_2\text{Co}_5(\text{CO})_{15}$ are given in Figs 7.3 to 7.5 and details in Table 7.5.

Table 7.5 Solid and solution infrared spectra :

$\text{MeGe}_2\text{Co}_5(\text{CO})_{15}$ [82]				$\text{PhGe}_2\text{Co}_5(\text{CO})_{15}$			
Solid (nujol mull)		Solution (CH_2Cl_2)		Solution (CH_2Cl_2)		Solid (CsI)	
2106	m	2106	m	2105	mw	2106	m
2072	m	2067	m	2061	mw	2071	mw
2051	sh	2050	m sh	2050	m sh	2054	m sh
2040	sh					2043-2039	s sh
2037	sh	2037	vvs	2038	vvs	2032	s sh
2029	vs					2029	vs
2015	ms	2013	ms	2015	m	2016	s
2012	sh					2008	s
2001	s	2004	ms sh	2005	m sh	2000	s
1994	sh					1995	s sh
1991	sh						
1966	sh	1965	w sh	1969	w sh	1970	w sh
1854	m	1843	vw br	1845	vw br	1853	mw

The solid infrared of $\text{PhGe}_2\text{Co}_5(\text{CO})_{15}$, though not as well resolved as that of $\text{MeGe}_2\text{Co}_5(\text{CO})_{15}$, was very similar. A full discussion on the infrared spectra of these *closo*-hexanuclear clusters is given in Chapter Nine.

Solution infrared spectra of $R\text{Ge}_2\text{Co}_5(\text{CO})_{15}$

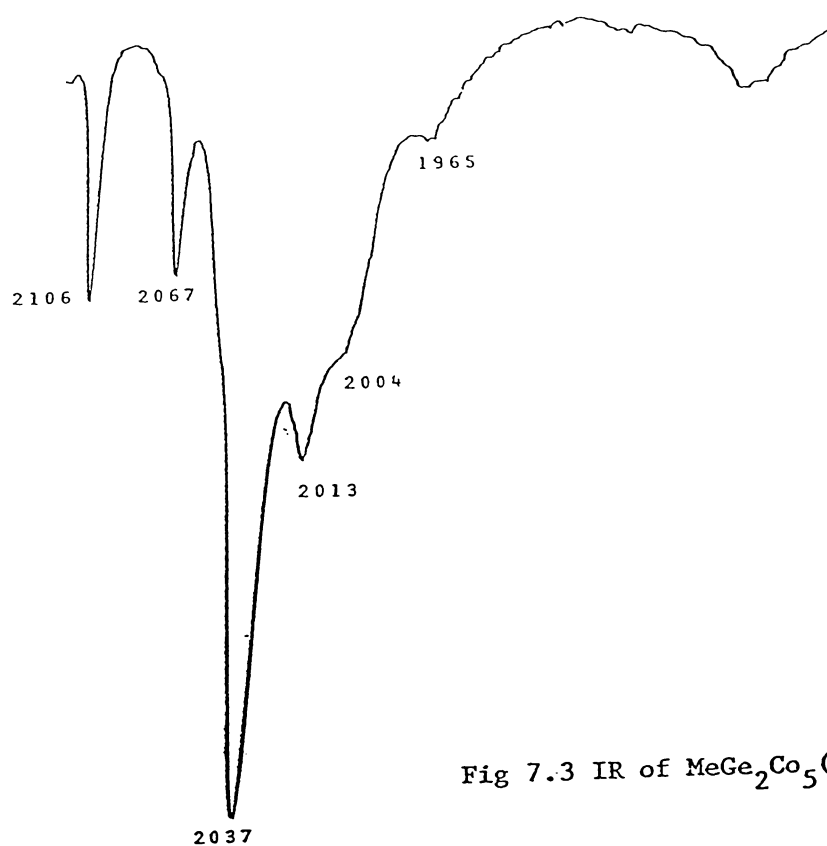


Fig 7.3 IR of $\text{MeGe}_2\text{Co}_5(\text{CO})_{15}$ (CH_2Cl_2)

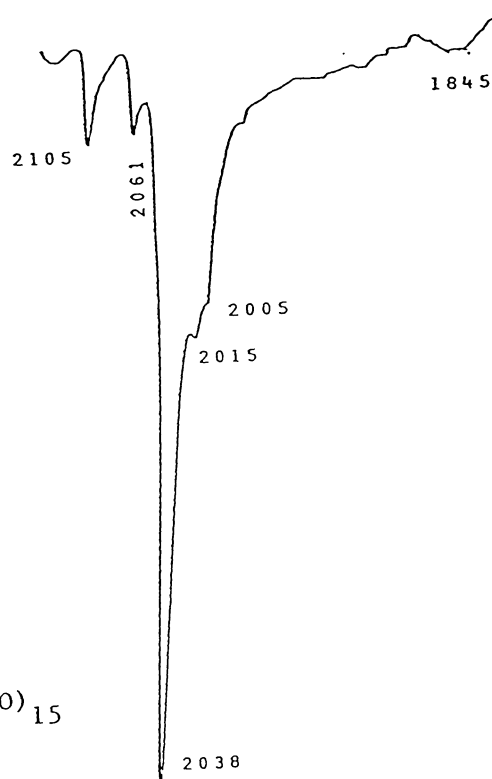


Fig 7.4 IR of $\text{PhGe}_2\text{Co}_5(\text{CO})_{15}$
(hexane/ CH_2Cl_2)

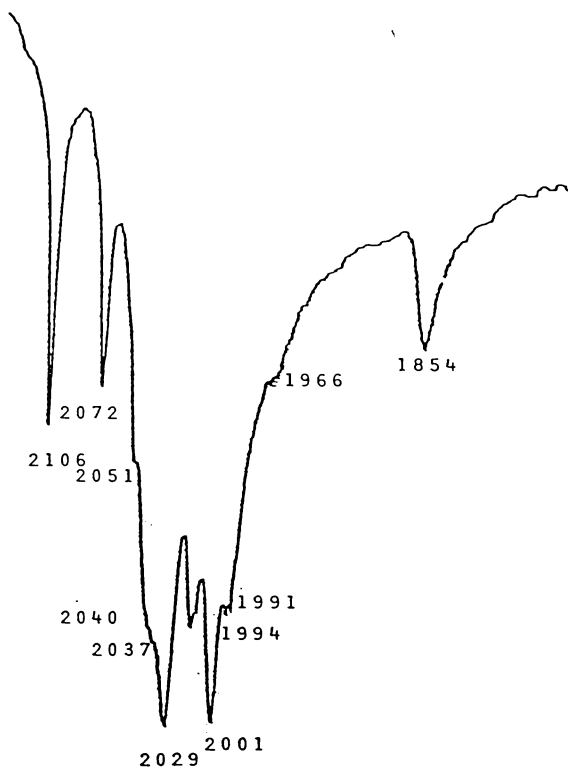


Fig-7. 5a Solid infrared spectrum of $\text{MeGe}_2\text{Co}_5(\text{CO})_{15}$ (in Nujol mull) [82]

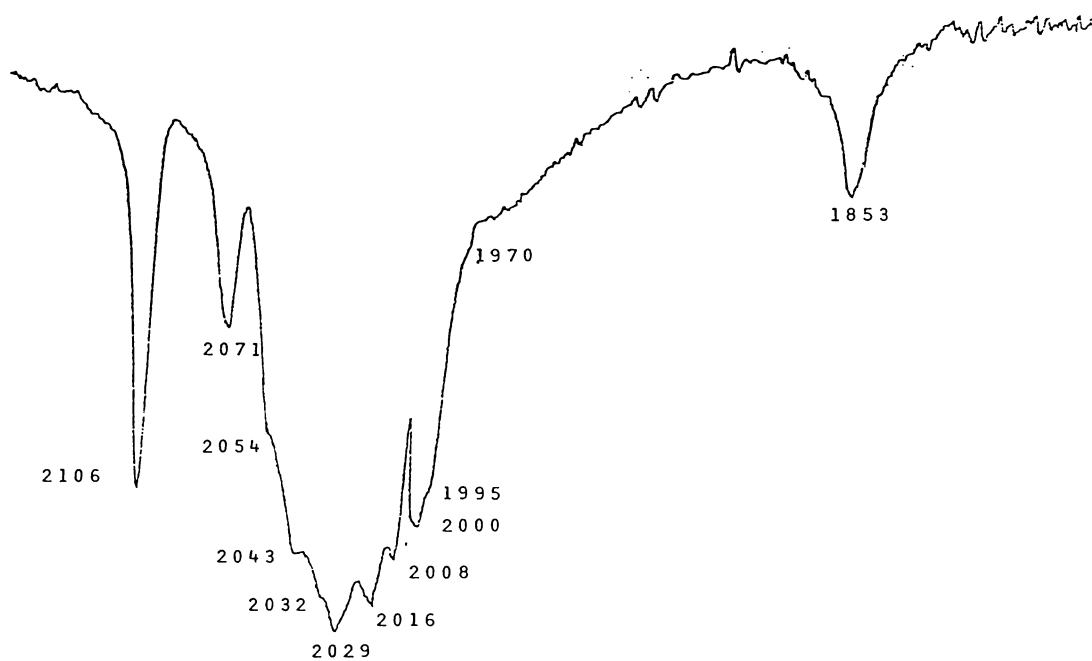


Fig 7.5b Solid infrared spectrum of $\text{PhGe}_2\text{Co}_5(\text{CO})_{15}$ (CsI disc)

7.4.2 Mass Spectrum :

The mass spectrum of $\text{MeGe}_2\text{Co}_5(\text{CO})_{15}$ showed a series of envelopes of formula $\text{MeGe}_2\text{Co}_5(\text{CO})_n^+$ ($n = 0$ to 15) with a distinct Ge_2 isotope pattern. In the lower m/e region, overlapping by $\text{MeGeCo}_3(\text{CO})_x^+$ ($x = 0$ to 9) was observed. The envelopes due to latter ions were also observed previously [82]. The details of the mass spectrum of $\text{MeGe}_2\text{Co}_5(\text{CO})_{15}$ are given in Table 7.6.

Table 7.6 Mass spectrum of $\text{MeGe}_2\text{Co}_5(\text{CO})_{15}$

m/e	Intensity	Possible assignments
868-875	m	$(\text{MeGe})\text{GeCo}_5(\text{CO})_n^+$, $n=15$
849-842	mw	$n=14$
822-812	ms	13
793-790	vvw	12
766-760	vvw	11
740-730	m	10
713-702	vs	9
683-673	ms	8
655-648	m	7
627-616	m	6
597-538	m	5
570-560	m	4
542-532	m	3
515-502	mw	2, $\text{MeGeCo}_3(\text{CO})_9^+$
490-478	m	1, $\text{MeGeCo}_3(\text{CO})_8^+$
460-448	s	0, $\text{MeGeCo}_3(\text{CO})_7^+$
442-435	vw	$\text{MeGeCo}_3(\text{CO})_6^+$, Ge_2Co_5^+
428-420	vw	$\text{MeGe}_2\text{Co}_4(\text{CO})^+$
401-390	m	$\text{MeGe}_2\text{Co}_4^+$
385-375	mw	$\text{MeGeCo}_3(\text{CO})_4^+$, Ge_2Co_4^+
353-351	s	$\text{MeGeCo}_3(\text{CO})_3^+$
325-320	w	$\text{MeGeCo}_3(\text{CO})_2^+$, MeGeCo_4^+

7.4.3 NMR

The ^1H NMR resonance of $\text{MeGe}_2\text{Co}_5(\text{CO})_{15}$ (singlet at δ 2.77 ppm, Table 7.7) is very similar to that of $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ (δ 2.75 ppm). Two multiplets at δ 7.71 and 8.24 ppm of relative intensity 3 : 2 were obtained for $\text{PhGe}_2\text{Co}_5(\text{CO})_{15}$.

In the ^{13}C NMR spectrum of $\text{MeGe}_2\text{Co}_5(\text{CO})_{15}$, two ^{13}C singlets were obtained, one at δ 195.9 ppm and the other at δ 202.6 ppm (-50°C), the latter was about three times the intensity of the former. These values are comparable to those obtained from $\text{Ge}_2\text{Co}_6(\text{CO})_{19}$ (δ 202.9 ppm and δ 195.6 ppm) (see Section 9.2). The 195.9 ppm peak is assigned as that due to the ^{13}C 's in the apical $\text{Co}(\text{CO})_4$ group on $\text{MeGe}_2\text{Co}_5(\text{CO})_{15}$ and the 202.7 ppm peak to be due to those on the $\text{Co}_4(\text{CO})_{11}$ unit. The latter peak is very similar to the ^{13}C NMR spectrum of $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$, which also contains the $\text{Co}_4(\text{CO})_{11}$ unit (202.6ppm).

The 202.6ppm peak showed a slight lowfield shift with increase in temperature while the 195.9 ppm peak shifted towards the high field. No resolution into bridging and terminal CO's was observed. Attempts to obtain the ^{13}C signal of the methyl group at different temperatures and different relaxation times were not successful.

Table 7.7 NMR data of $\text{MeGe}_2\text{Co}_5(\text{CO})_{15}$ and $\text{PhGe}_2\text{Co}_5(\text{CO})_{15}$

	$\text{MeGe}_2\text{Co}_5(\text{CO})_{15}$	$\text{PhGe}_2\text{Co}_5(\text{CO})_{15}$
^1H NMR (27°C)	2.77 ppm (s)	7.71 (m,3x), 8.24 (m,2x)
^{13}C NMR		
0°C	203.2ppm (s, 3x), 195.3ppm (s, 1x)	
-5°C	203.1ppm (s, 3x), 195.7ppm (s, 1x)	
-50°C	202.6ppm (s, 3x), 195.9ppm (s, 1x)	

7.4.4 *Electron probe Analysis*

The electron probe analysis of a crystalline sample of $\text{MeGe}_2\text{Co}_5(\text{CO})_{15}$ gave a Ge : Co ratio of 2 : 5.2, which is in accordance with the formulation (2 : 5).

7.4.5 *Crystal Structure of $\text{MeGe}_2\text{Co}_5(\text{CO})_{15}$*

7.4.5.1 Experimental :

Plate-shaped crystals of $\text{MeGe}_2\text{Co}_5(\text{CO})_{15}$ were grown from a CH_2Cl_2 solution into which hexane slowly diffused at -30°C . A suitable crystal was mounted on a glass fibre with Araldite for preliminary precession photographic studies.

7.4.5.2 Preliminary studies and data collection :

Initial precession photographs showed the crystal to be monoclinic C-centred. The systematic absences were consistent with the space group of C2/c (note: L.McLeod [82] attempted this crystal structure determination prior to this work, working in a unit cell in C2/m with cell parameters of $a = 12.722\text{\AA}$, $b = 14.498\text{\AA}$, $c = 13.234\text{\AA}$, $\beta = 90^\circ$, no solution was obtained. With hindsight it is obvious that complete rows of reflections were missed along the c axis resulting in the assignment of an incorrect space group).

Intensity data and refined lattice parameters were obtained at the University of Canterbury using a Nicolet XRD P3 four-circle automatic diffractometer. Crystallographic details are given in Table 7.8.

The data was collected in the space group I2/a (a non-standard setting of C2/c). A total of 3692 reflections were collected in the range $4^\circ \leq 2\theta \leq 45^\circ$ which corresponded to 3252 unique reflections. 1346 reflections had $F^2 > 3\sigma(F)^2$ and were used in the refinement. The data

was corrected for Lorentz and polarisation effects and for linear absorptions, based on a series of ϕ scans.

Table 7.8 Crystal data for $\text{MeGe}_2\text{Co}_5(\text{CO})_{15}$

Molecular formula : $\text{C}_{16}\text{H}_3\text{O}_{15}\text{Ge}_2\text{Co}_5$
Molecular weight : 875.2
Monoclinic, space group C2/c
$a = 12.852(3)\text{\AA}$, $b = 14.528(5)\text{\AA}$, $c = 26.566(8)\text{\AA}$
$\beta = 90.32(2)^\circ$
Volume = $4960.29\text{\AA}^3$
$D_{\text{calc}} = 2.34\text{gcm}^{-3}$
$Z = 8$
$F(000) = 3344$, $\mu(\text{MoK}\alpha) = 111.15\text{ cm}^{-1}$, $T = 173\text{K}$

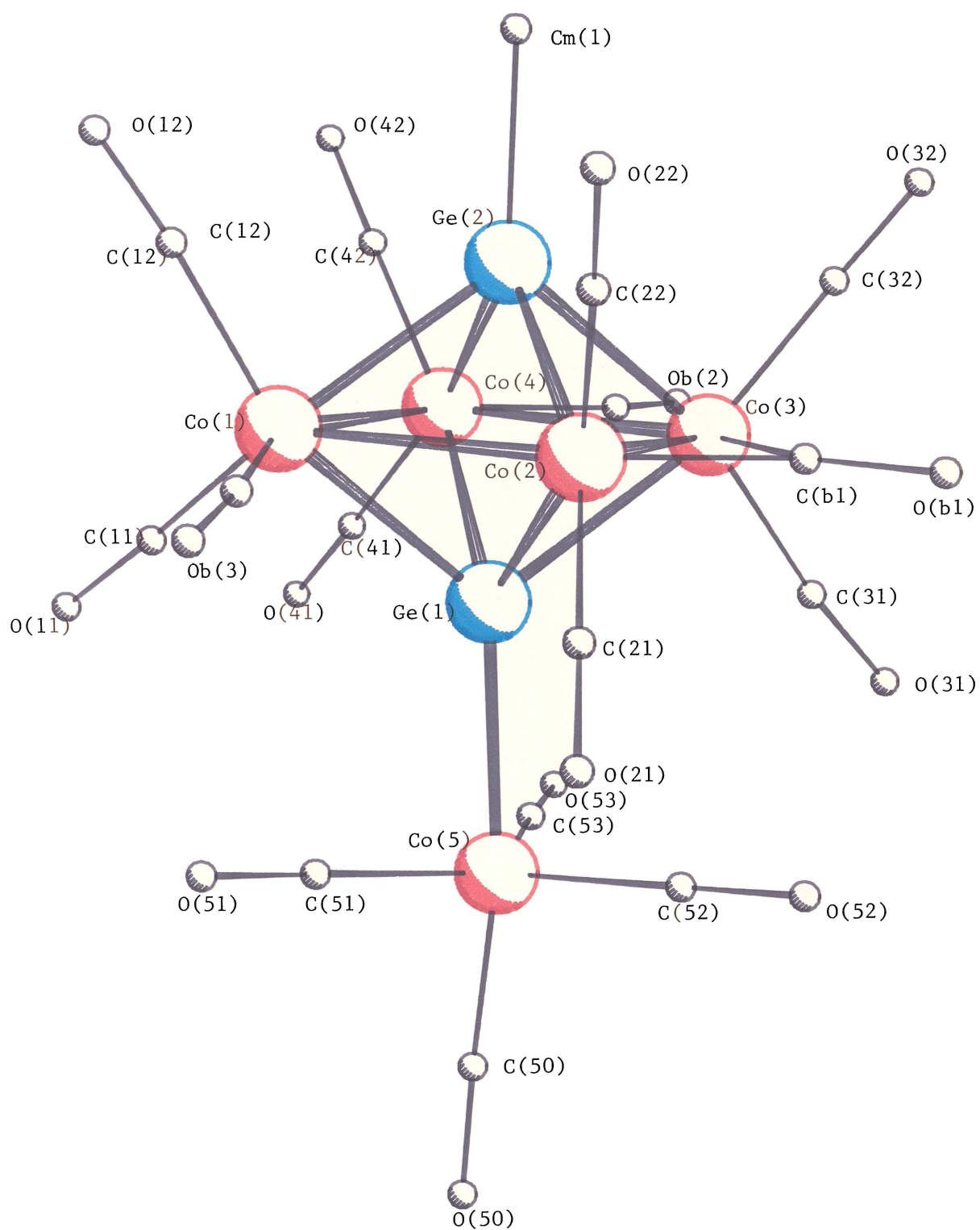
7.4.5.3 Solution and refinement :

The metal atoms were located using the TREF routine of SHELXS86. The coordinates of these heavy metal atoms were used as a base set for SHELX76 and subsequent refinements and difference maps located all 15 unique CO's and the methyl carbon. In the final cycles of full matrix least-squares refinement, the metal atoms were assigned anisotropic temperature factors with all other atoms isotropic. Refinement converged with $R = 0.0524$ and $R_w = 0.0502$ where $w = 1.4470/(\sigma^2 F + 0.000559F^2)$. Hydrogen atoms were not included.

A final difference map showed no residual electron density more than $0.83\text{ e \AA}^{-3}$. No parameter shifted by more than 0.01σ and a variance analysis showed no dependence on $\sin\theta$ or F/F_{max} .

7.4.5.4 Discussion of the structure :

The crystal structure of $\text{MeGe}_2\text{Co}_5(\text{CO})_{15}$ is shown in Figs 7.6 and 7.7, the bond lengths and bond angles in Tables 7.9 and 7.10. The final

Fig 7.6 Crystal structure of $\text{MeGe}_2\text{Co}_5(\text{CO})_{15}$ 

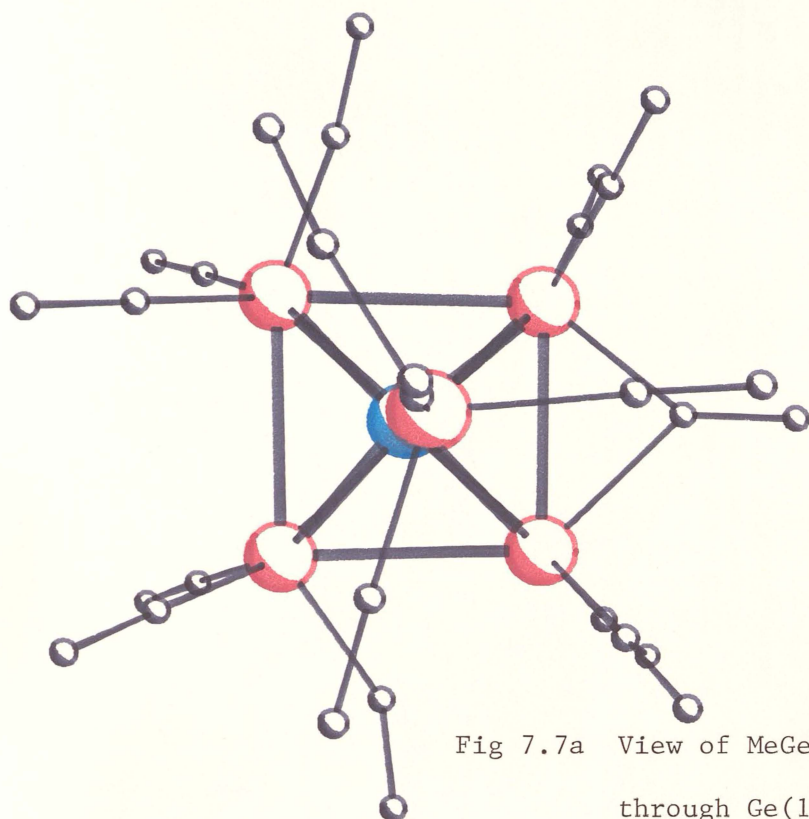


Fig 7.7a View of $\text{MeGe}_2\text{Co}_5(\text{CO})_{15}$
through Ge(1), Ge(2) and Co(5)

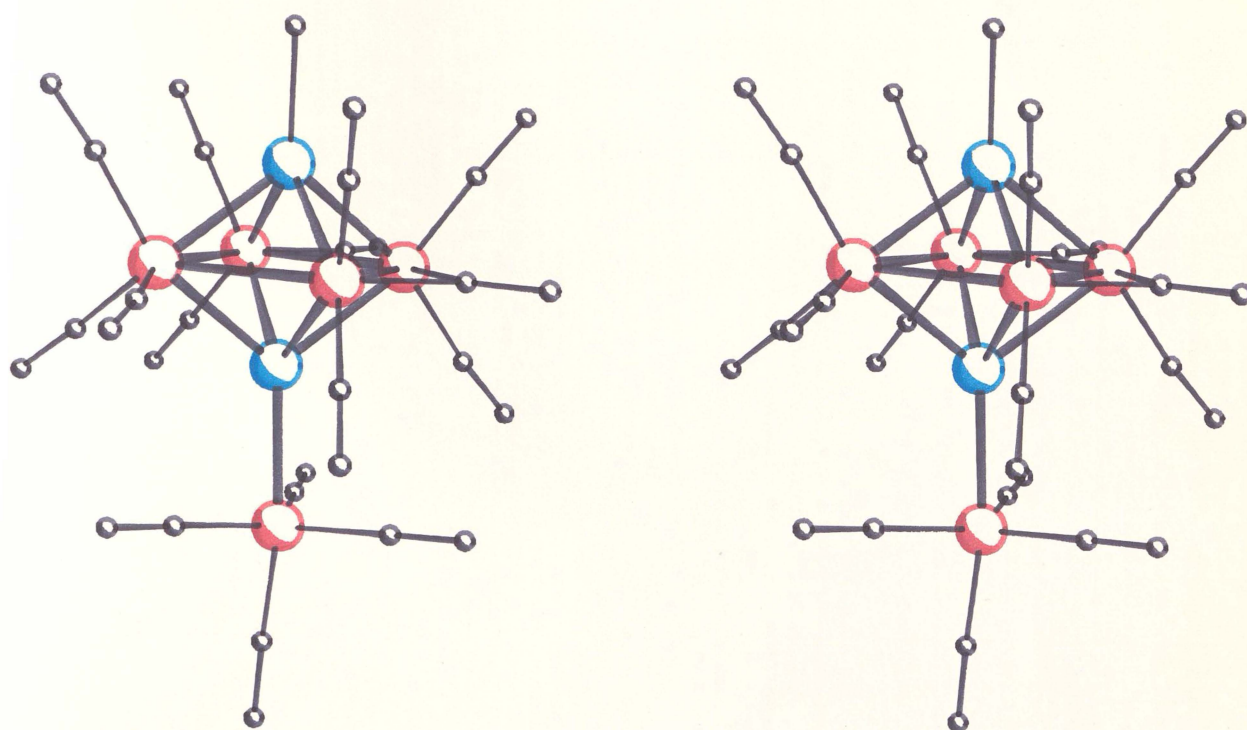


Fig 7.7b Stereo View of $\text{MeGe}_2\text{Co}_5(\text{CO})_{15}$

positional parameters are presented in Appendix 5, while the structure factors are retained by the University of Waikato.

Table 7.9 Bond Lengths (Å) for $\text{MeGe}_2\text{Co}_5(\text{CO})_{15}$

Ge(1) ---Ge(2)	2.957(3)	Co(3) ---Cb(2)	2.26(2)
Ge(1) ---Co(1)	2.422(4)	Co(4) ---C(41)	1.77(3)
Ge(1) ---Co(2)	2.411(4)	Co(4) ---C(42)	1.79(3)
Ge(1) ---Co(3)	2.425(4)	Co(4) ---Cb(2)	1.82(2)
Ge(1) ---Co(4)	2.423(4)	Co(5) ---C(51)	1.78(3)
Ge(1) ---Co(5)	2.403(4)	Co(5) ---C(52)	1.81(2)
Ge(2) ---Co(1)	2.400(4)	Co(5) ---C(53)	1.76(2)
Ge(2) ---Co(2)	2.377(4)	Co(5) ---C(54)	1.79(3)
Ge(2) ---Co(3)	2.409(4)	C(11) ---O(11)	1.21(3)
Ge(2) ---Co(4)	2.397(4)	C(12) ---O(12)	1.13(3)
Ge(2) ---Cm(1)	1.97(2)	C(21) ---O(21)	1.18(3)
Co(1) ---Co(2)	2.739(4)	C(22) ---O(22)	1.17(3)
Co(1) ---Co(4)	2.745(4)	C(31) ---O(31)	1.16(2)
Co(1) ---C(11)	1.71(3)	C(32) ---O(32)	1.16(3)
Co(1) ---C(12)	1.79(3)	C(41) ---O(41)	1.17(3)
Co(1) ---Cb(3)	1.77(3)	C(42) ---O(42)	1.18(3)
Co(2) ---Co(3)	2.610(4)	C(51) ---O(51)	1.16(3)
Co(2) ---C(21)	1.79(3)	C(52) ---O(52)	1.13(2)
Co(2) ---C(22)	1.76(2)	C(53) ---O(53)	1.16(3)
Co(2) ---Cb(1)	1.86(2)	C(54) ---O(54)	1.18(3)
Co(3) ---Co(4)	2.654(4)	Cb(1) ---Ob(1)	1.17(2)
Co(3) ---C(31)	1.82(2)	Cb(2) ---Ob(2)	1.13(2)
Co(3) ---C(32)	1.77(3)	Cb(3) ---Ob(3)	1.16(3)
Co(3) ---Cb(1)	2.04(2)		

Table 7.10 Bond Angles (°) of $\text{MeGe}_2\text{Co}_5(\text{CO})_{15}$

Ge(2)-Ge(1)-Co(1)	51.8(1)	Ge(2)-Co(1)-C(11)	141.4(9)
Ge(2)-Ge(1)-Co(2)	51.4(1)	Ge(2)-Co(1)-C(12)	82.5(8)
Ge(2)-Ge(1)-Co(3)	52.0(1)	Ge(2)-Co(1)-Cb(3)	115.3(8)
Ge(2)-Ge(1)-Co(4)	51.8(1)	Co(2)-Co(1)-Co(4)	87.2(1)
Ge(2)-Ge(1)-Co(5)	174.7(2)	Co(2)-Co(1)-C(11)	140.0(9)

Table 7.10 *cont'd...*

Co(1)-Ge(1)-Co(2)	69.1(1)	Co(2)-Co(1)-C(12)	119.3(8)
Co(1)-Ge(1)-Co(3)	103.9(1)	Co(2)-Co(1)-Cb(3)	71.1(8)
Co(1)-Ge(1)-Co(4)	69.0(1)	Co(4)-Co(1)-C(11)	87.1(9)
Co(1)-Ge(1)-Co(5)	130.8(2)	Co(4)-Co(1)-C(12)	102.2(8)
Co(2)-Ge(1)-Co(3)	65.3(1)	Co(4)-Co(1)-Cb(3)	155.8(8)
Co(2)-Ge(1)-Co(4)	103.0(1)	C(11)-Co(1)-C(12)	100(1)
Co(2)-Ge(1)-Co(5)	124.0(2)	C(11)-Co(1)-Cb(3)	102(1)
Co(3)-Ge(1)-Co(4)	66.4(1)	C(12)-Co(1)-Cb(3)	97(1)
Co(3)-Ge(1)-Co(5)	125.0(2)	Ge(1)-Co(2)-Ge(2)	76.3(1)
Co(4)-Ge(1)-Co(5)	132.5(2)	Ge(1)-Co(2)-Co(1)	55.7(1)
Ge(1)-Ge(2)-Co(1)	52.5(1)	Ge(1)-Co(2)-Co(3)	57.6(1)
Ge(1)-Ge(2)-Co(2)	52.4(1)	Ge(1)-Co(2)-C(21)	92.7(8)
Ge(1)-Ge(2)-Co(3)	52.5(1)	Ge(1)-Co(2)-C(22)	159.2(8)
Ge(1)-Ge(2)-Co(4)	52.6(1)	Ge(1)-Co(2)-Cb(1)	96.6(7)
Ge(1)-Ge(2)-Cm(1)	177.7(7)	Ge(2)-Co(2)-Co(1)	55.4(1)
Co(1)-Ge(2)-Co(2)	70.0(1)	Ge(2)-Co(2)-Co(3)	57.5(1)
Co(1)-Ge(2)-Co(3)	105.0(1)	Ge(2)-Co(2)-C(21)	163.1(8)
Co(1)-Ge(2)-Co(4)	69.8(1)	Ge(2)-Co(2)-C(22)	86.9(8)
Co(1)-Ge(2)-Cm(1)	125.9(7)	Ge(2)-Co(2)-Cb(1)	95.7(7)
Co(2)-Ge(2)-Co(3)	66.1(1)	Co(1)-Co(2)-Co(3)	91.0(1)
Co(2)-Ge(2)-Co(4)	104.8(1)	Co(1)-Co(2)-C(21)	107.8(8)
Co(2)-Ge(2)-Cm(1)	126.1(8)	Co(1)-Co(2)-C(22)	104.6(8)
Co(3)-Ge(2)-Co(4)	67.0(1)	Co(1)-Co(2)-Cb(1)	141.8(6)
Co(3)-Ge(2)-Cm(1)	129.0(7)	Co(3)-Co(2)-C(21)	126.9(8)
Co(4)-Ge(2)-Cm(1)	129.1(8)	Co(3)-Co(2)-C(22)	122.6(8)
Ge(1)-Co(1)-Ge(2)	75.6(1)	Co(3)-Co(2)-Cb(1)	50.8(6)
Ge(1)-Co(1)-Co(2)	55.3(1)	C(21)-Co(2)-C(22)	100(1)
Ge(1)-Co(1)-Co(4)	55.5(1)	C(21)-Co(2)-Cb(1)	98(1)
Ge(1)-Co(1)-C(11)	89.7(9)	C(22)-Co(2)-Cb(1)	97(1)
Ge(1)-Co(1)-C(12)	155.2(8)	Ge(1)-Co(3)-Ge(2)	75.4(1)
Ge(1)-Co(1)-Cb(3)	101.9(8)	Ge(1)-Co(3)-Co(2)	57.1(1)
Ge(2)-Co(1)-Co(2)	54.6(1)	Ge(1)-Co(3)-Co(4)	56.8(1)
Ge(2)-Co(1)-Co(4)	55.0(1)	Ge(1)-Co(3)-C(31)	89.2(7)
Ge(1)-Co(3)-C(32)	166.3(8)	Co(1)-Co(4)-C(42)	100.1(8)
Ge(1)-Co(3)-Cb(1)	91.7(6)	Co(1)-Co(4)-Cb(2)	146.9(7)
Ge(1)-Co(3)-Cb(2)	88.7(6)	Co(3)-Co(4)-C(41)	130.4(8)
Ge(2)-Co(3)-Co(2)	56.4(1)	Co(3)-Co(4)-C(42)	123.9(8)

Table 7.10 *cont'd...*

Ge(2)-Co(3)-Co(4)	56.3(1)	Co(3)-Co(4)-Cb(2)	57.0(6)
Ge(2)-Co(3)-C(31)	164.6(7)	C(41)-Co(4)-C(42)	100(1)
Ge(2)-Co(3)-C(32)	91.0(8)	C(41)-Co(4)-Cb(2)	98(1)
Ge(2)-Co(3)-Cb(1)	90.4(6)	C(42)-Co(4)-Cb(2)	99(1)
Ge(2)-Co(3)-Cb(2)	88.6(6)	Ge(1)-Co(5)-C(51)	83.3(9)
Co(2)-Co(3)-Co(4)	91.9(1)	Ge(1)-Co(5)-C(52)	89.5(7)
Co(2)-Co(3)-C(31)	116.5(7)	Ge(1)-Co(5)-C(53)	83.5(8)
Co(2)-Co(3)-C(32)	117.0(8)	Ge(1)-Co(5)-C(54)	171(1)
Co(2)-Co(3)-Cb(1)	45.2(6)	C(51)-Co(5)-C(52)	115(1)
Co(2)-Co(3)-Cb(2)	134.4(5)	C(51)-Co(5)-C(53)	130(1)
Co(4)-Co(3)-C(31)	113.6(7)	C(51)-Co(5)-C(54)	90(1)
Co(4)-Co(3)-C(32)	113.9(8)	C(52)-Co(5)-C(53)	111(1)
Co(4)-Co(3)-Cb(1)	137.0(6)	C(52)-Co(5)-C(54)	98(1)
Co(4)-Co(3)-Cb(2)	42.5(5)	C(53)-Co(5)-C(54)	95(1)
C(31)-Co(3)-C(32)	104.2(9)	Co(1)-C(11)-O(11)	177(2)
C(31)-Co(3)-Cb(1)	91.9(9)	Co(1)-C(12)-O(12)	174(2)
C(31)-Co(3)-Cb(2)	89.2(9)	Co(2)-C(21)-O(21)	178(2)
C(32)-Co(3)-Cb(1)	90(1)	Co(2)-C(22)-O(22)	178(2)
C(32)-Co(3)-Cb(2)	88(1)	Co(3)-C(31)-O(31)	173(2)
Cb(1)-Co(3)-Cb(2)	178.9(9)	Co(3)-C(32)-O(32)	175(2)
Ge(1)-Co(4)-Ge(2)	75.7(1)	Co(4)-C(41)-O(41)	176(2)
Ge(1)-Co(4)-Co(1)	55.5(1)	Co(4)-C(42)-O(42)	177(2)
Ge(1)-Co(4)-Co(3)	56.8(1)	Co(5)-C(51)-O(51)	173(3)
Ge(1)-Co(4)-C(41)	93.1(8)	Co(5)-C(52)-O(52)	178(2)
Ge(1)-Co(4)-C(42)	154.7(8)	Co(5)-C(53)-O(53)	178(2)
Ge(1)-Co(4)-Cb(2)	100.1(7)	Co(5)-C(54)-O(54)	177(3)
Ge(2)-Co(4)-Co(1)	55.1(1)	Co(2)-Cb(1)-Co(3)	84.0(9)
Ge(2)-Co(4)-Co(3)	56.7(1)	Co(2)-Cb(1)-Ob(1)	142(2)
Ge(2)-Co(4)-C(41)	159.7(8)	Co(3)-Cb(1)-Ob(1)	133(2)
Ge(2)-Co(4)-C(42)	84.8(8)	Co(3)-Cb(2)-Co(4)	80.5(7)
Ge(2)-Co(4)-Cb(2)	100.5(7)	Co(3)-Cb(2)-Ob(2)	127(2)
Co(1)-Co(4)-Co(3)	89.9(1)	Co(4)-Cb(2)-Ob(2)	152(2)
Co(1)-Co(4)-C(41)	104.5(8)	Co(1)-Cb(3)-Ob(3)	172(2)

Table 7.10 *cont'd...*

Dihedral angle

Ob(1)-Cb(1)-Co(2)-Co(3) to Co(2)-Co(3)-Ge(2)	132.8(3)
Ob(1)-Cb(1)-Co(2)-Co(3) to Co(2)-Co(3)-Ge(1)	133.1(3)
Co(1)-Co(2)-Co(3)-Co(4) to Ob(1)-Cb(1)-Co(2)-Co(3)	0.6(3)
Co(1)-Co(2)-Co(3)-Co(4) to Co(2)-Co(3)-Ge(2)	133.4(1)
Co(1)-Co(2)-Co(3)-Co(4) to Co(2)-Co(3)-Ge(1)	132.6(1)
Co(1)-Co(2)-Co(3)-Co(4) to Co(2)-Co(1)-Ge(1)	131.2(1)
Co(1)-Co(2)-Co(3)-Co(4) to Co(2)-Co(1)-Ge(2)	131.8(1)
Co(1)-Co(2)-Co(3)-Co(4) to Co(1)-Co(4)-Ge(2)	47.9(1)
Co(1)-Co(2)-Co(3)-Co(4) to Co(1)-Co(4)-Ge(1)	48.6(1)
Co(1)-Co(2)-Co(3)-Co(4) to Co(3)-Co(4)-Ge(2)	133.3(1)
Co(1)-Co(2)-Co(3)-Co(4) to Co(3)-Co(4)-Ge(1)	133.4(1)

The structure is intermediate between those of $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ [84] and $\text{Ge}_2\text{Co}_6(\text{CO})_{19}$ [27].

The metallic core of $\text{MeGe}_2\text{Co}_5(\text{CO})_{15}$ consists of two Ge atoms each quadruply bridging a distorted square planar array of four Co atoms. One Ge atom is further bonded to a $\text{Co}(\text{CO})_4$ unit and the other to a Me. Of the eleven CO groups, eight are completely terminal (two on each Co), one fully bridging and two semi-bridging across opposite Co-Co bonds.

Co-Co bonds : the length of the Co-Co bond is directly related to the degree of bridging across it, as shown in Fig 7.8. The shortest Co-Co bond is the one with a fully bridging CO across it (Co(2)-Co(3), 2.610(4)Å), and the longest (Co(1)-Co(4), 2.745(4)Å) is the one without any bridging CO. Co(1)-Co(2) (2.739(4)Å) and Co(3)-Co(4) (2.654(4)Å) each with a semi-bridging CO are of intermediate bond length.

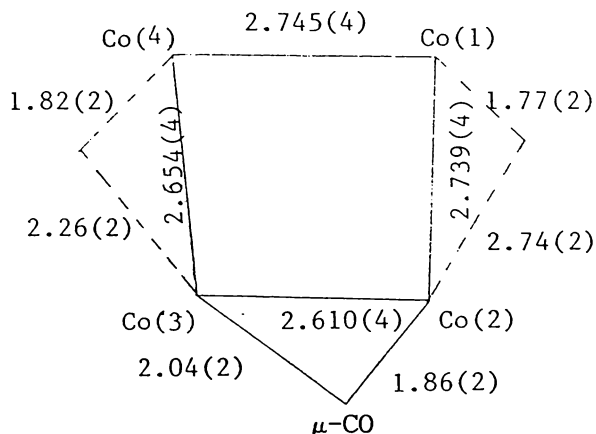


Fig 7.8 Co-Co bond lengths and the degree of bridging across them

Ge-Co bonds : the bond lengths of the Ge atoms to the cobalt atoms in the metallic Co₄ core are not equal. The Ge-Co bond length ranges from 2.411(4)Å to 2.425(4)Å on the half carrying the apical Co(CO)₄ group and from 2.377(4)Å to 2.409(4)Å on the Ge-Me half. The average Ge-Co bond length on the Co(CO)₄ half (2.420(4)Å) is significantly longer (> 4 e.s.d) than the Me half (2.396(4)Å). This is possibly due to the steric demand of the bulky Co(CO)₄ group which forces the Ge further from the Co₄ plane.

The Ge-Co(5) (apical) bond length (2.403(4)Å) is shorter than the the average Ge-Co bond distance of 2.420(4)Å for the half carrying the Co(CO)₄ group, but longer than those in the Me half (2.396(4)Å)). It is very similar to that in Ge₂Co₆(CO)₁₉ (2.405(4)Å) [27]. The Ge-Co(5) (apical) bond is significantly longer than those in GeCo₄(CO)₁₃ (2.349(1)Å) [88]. This is possibly due to the different type of bonding, the Ge-Co bonds are five co-ordinated in MeGe₂Co₅(CO)₁₅ and four coordinated in GeCo₄(CO)₁₃.

Co-CO bonds :

a) in the central $\text{Co}_4(\text{CO})_{11}$ unit : the eight terminal CO's are normal and in expected positions with an average Co-C distance of 1.80(3)Å and C-O distance of 1.17(3)Å. Unlike $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ and $\text{Ge}_2\text{Co}_6(\text{CO})_{19}$, the fully bridging CO in $\text{MeGe}_2\text{Co}_5(\text{CO})_{15}$ is asymmetric: Co-C distances of 2.04(2)Å and 1.86(2)Å with a C-O distance of 1.17(2)Å. The dihedral angle between the Co_4 plane to the $\text{Ob}(1)\text{-Cb}(1)\text{-Co}(2)\text{-Co}(3)$ is $0.6(3)^\circ$, indicating that the $\mu\text{-CO}$ is virtually planar. One of the semi-bridging CO's is almost terminal (Co-C of 2.738Å and 1.77(3)Å) and the other has Co-C distances of 2.26(2)Å and 1.82(2)Å which are as expected for such types of bond (compare 2.53(1)Å and 1.92(1)Å in $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$, 2.39(4) and 1.70(4) in $\text{Ge}_2\text{Co}_6(\text{CO})_{19}$).

b) in the apical $\text{Co}(\text{CO})_4$ unit :

The apical Co-C bonds average 1.78(3)Å and C-O distance of 1.16(3)Å. Like those in $\text{Ge}_2\text{Co}_6(\text{CO})_{19}$, three of them are equatorial and one axial as is normal for $\text{Co}(\text{CO})_4$ group [88].

The equatorial CO's in the apical $\text{Co}(\text{CO})_4$ group are bent towards Ge_1 . This is also found in $\text{Ge}_2\text{Co}_6(\text{CO})_{19}$.

Ge-C bond : the Ge-C distance of 1.97(2)Å appears normal for a germanium-aliphatic carbon bond (compare Ge-CH₃ in Me_4Ge of 1.95Å [11], and an average of 1.98(4)Å in Me_3GeCN [151]). It is also comparable to those of $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ (av 1.95(1)Å) and those in $\text{Me}_3\text{Ge}_3\text{Co}_5(\text{CO})_{15}$ (av 1.93(1)Å).

A detailed comparison of $\text{MeGe}_2\text{Co}_5(\text{CO})_{15}$ with other such *clos*o-clusters is referred to in Section 9.3 in Chapter Nine.

7.5 Discussion :

The reaction of $(\text{MeGeH})\text{GeCo}_4(\text{CO})_{13}$ with $\text{Co}_2(\text{CO})_8$ showed that, depending on the conditions of the experiment, either $\text{MeGe}_2\text{Co}_5(\text{CO})_{17}$ or $\text{MeGe}_2\text{Co}_5(\text{CO})_{15}$ or both were formed. Though only two runs were carried out, it was quite clear that at low temperature (-4°C) without the removal of the incondensable gas, $\text{MeGe}_2\text{Co}_5(\text{CO})_{17}$ was formed. Room temperature reaction with the removal of incondensable gas resulted in the formation of the decarbonylated product, $\text{MeGe}_2\text{Co}_5(\text{CO})_{15}$. Similar results were obtained in the reaction of $(\text{PhGeH})\text{GeCo}_4(\text{CO})_{13}$ with $\text{Co}_2(\text{CO})_8$. The decarbonylation reaction of $\text{MeGe}_2\text{Co}_5(\text{CO})_{17}$ at 55°C has been studied previously [82]. Two mole equivalents of CO were evolved, giving $\text{MeGe}_2\text{Co}_5(\text{CO})_{15}$ as the sole product.

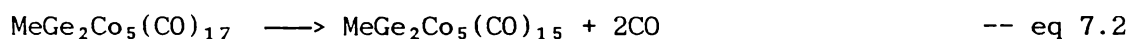
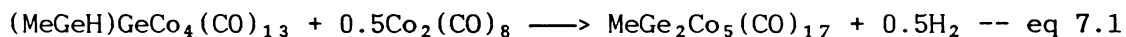
The amount of incondensable gas could not be accounted for by the yield of $\text{MeGe}_2\text{Co}_5(\text{CO})_{15}$ in Run 1. Not including incondensable gases evolved due to the decarbonylation of $\text{GeCo}_4(\text{CO})_{14}$ to $\text{GeCo}_4(\text{CO})_{13}$ and $\text{Co}_2(\text{CO})_8$ to $\text{Co}_4(\text{CO})_{12}$, plus those due to decomposition, at least 0.23 mmol of gas ($2\text{CO} + 0.5\text{H}_2$ per mole $\text{MeGe}_2\text{Co}_5(\text{CO})_{15}$ formed) would be required to produce 0.08g (0.092 mmol) of $\text{MeGe}_2\text{Co}_5(\text{CO})_{15}$, but only 0.11 mmol was measured. It was possible that the unaccounted CO was removed by vacuum when the hexane soluble fraction was pumped on the Schlenk line to remove any unreacted $\text{Co}_2(\text{CO})_8$. This fraction in hexane produced further $\text{MeGe}_2\text{Co}_5(\text{CO})_{15}$ when cooled in the freezer, however, no $\text{MeGe}_2\text{Co}_5(\text{CO})_{15}$ was noted in the solution before pumping.

No H_2 was measured in any of the gas samples in Run 1 of the $(\text{MeGeH})\text{GeCo}_4(\text{CO})_{13}$ reaction. No H_2 was measured in the initial stage of the $(\text{PhGeH})\text{GeCo}_4(\text{CO})_{13}$ reaction, while ~18% of the expected H_2 was measured on the last gas determination. Though the volatile fraction from the $(\text{MeGeH})\text{GeCo}_4(\text{CO})_{13}$ and $\text{Co}_2(\text{CO})_8$ reaction were not examined, those from the $(\text{PhGeH})\text{GeCo}_4(\text{CO})_{13}$ reaction showed that a small amount

of $\text{HCo}(\text{CO})_4$ was present. Due to the small scale in which the reaction was carried out and the unstable nature of the $\text{HCo}(\text{CO})_4$, this recovery of $\text{HCo}(\text{CO})_4$ could not be made quantitative. The low H_2 measured in the $(\text{RGeH})\text{GeCo}_4(\text{CO})_{13}$ with $\text{Co}_2(\text{CO})_8$ reaction seems to indicate that H_2 released from reaction was in the form of $\text{HCo}(\text{CO})_4$. The small amount of H_2 measured in the $(\text{PhGeH})\text{GeCo}_4(\text{CO})_{13}$ reaction may be due to the slow conversion of $\text{HCo}(\text{CO})_4$ to H_2 and $\text{Co}_2(\text{CO})_8$ [143]. The latter further decarbonylated to give $\text{Co}_4(\text{CO})_{12}$ under the continuous removal of gas. In the $(\text{PhGeH})\text{GeCo}_4(\text{CO})_{13}$ reaction with $\text{Co}_2(\text{CO})_8$, slightly more than two mole equivalent of CO was measured, no doubt the excess due to the decarbonylation of $\text{Co}_2(\text{CO})_8$ (excess $\text{Co}_2(\text{CO})_8$ was used).

Unlike the $(\text{MeGeH})\text{GeCo}_4(\text{CO})_{13}$ reaction, no phenyl equivalent of $\text{MeGe}_2\text{Co}_5(\text{CO})_{17}$ type compound was observed in the $(\text{PhGeH})\text{GeCo}_4(\text{CO})_{13}$ reaction. This could be due to the phenyl group which is more bulky than the methyl group, thus favouring a closed structure.

The overall reactions are therefore :



A brief discussion of the condensation of the extended chain cluster to the *clos*o- hexanuclear compound with $\text{RR}'\text{Ge}_2\text{Co}_4(\text{CO})$ type skeleton is given in Section 7.10.

$\text{MeGe}_2\text{Co}_5(\text{CO})_{15}$ and $\text{MeGe}_2\text{Co}_5(\text{CO})_{17}$ were also synthesised by L.McLeod [82] via the reaction of MeGe_2H_5 with $\text{Co}_2(\text{CO})_8$. The products were accompanied by $\text{GeCo}_4(\text{CO})_{13}$, $\text{GeCo}_4(\text{CO})_{14}$, $\text{MeGeCo}_3(\text{CO})_{11}$ and $\text{Co}_4(\text{CO})_{12}$. $\text{MeGe}_2\text{Co}_5(\text{CO})_{17}$ has also been synthesised by the replacement of Cl in $(\text{MeGeCl})\text{GeCo}_4(\text{CO})_{13}$ by $\text{Co}(\text{CO})_4^-$ (see Chapter Six). The latter synthesis is a quicker and cleaner reaction as $(\text{MeGeCl})\text{GeCo}_4(\text{CO})_{13}$ can be easily prepared and purified and the ensuing reaction with $\text{Co}(\text{CO})_4^-$ is almost instantaneous.

7.6 Reaction of $(RGeH)_2GeCo_4(CO)_{12}$ with $Co_2(CO)_8$, R = Me, Et

7.6.1 Reaction of $(EtGeH)_2GeCo_4(CO)_{12}$ with $Co_2(CO)_8$

7.6.1.1 Experimental :

$(EtGeH)_2GeCo_4(CO)_{12}$ (0.09g, 0.11 mmol) was reacted with $Co_2(CO)_8$ (0.044g, 0.13 mmol) in hexane (3ml) in an open tube reaction as in Section 7.2, Run 1.

7.6.1.2 Observations and workup :

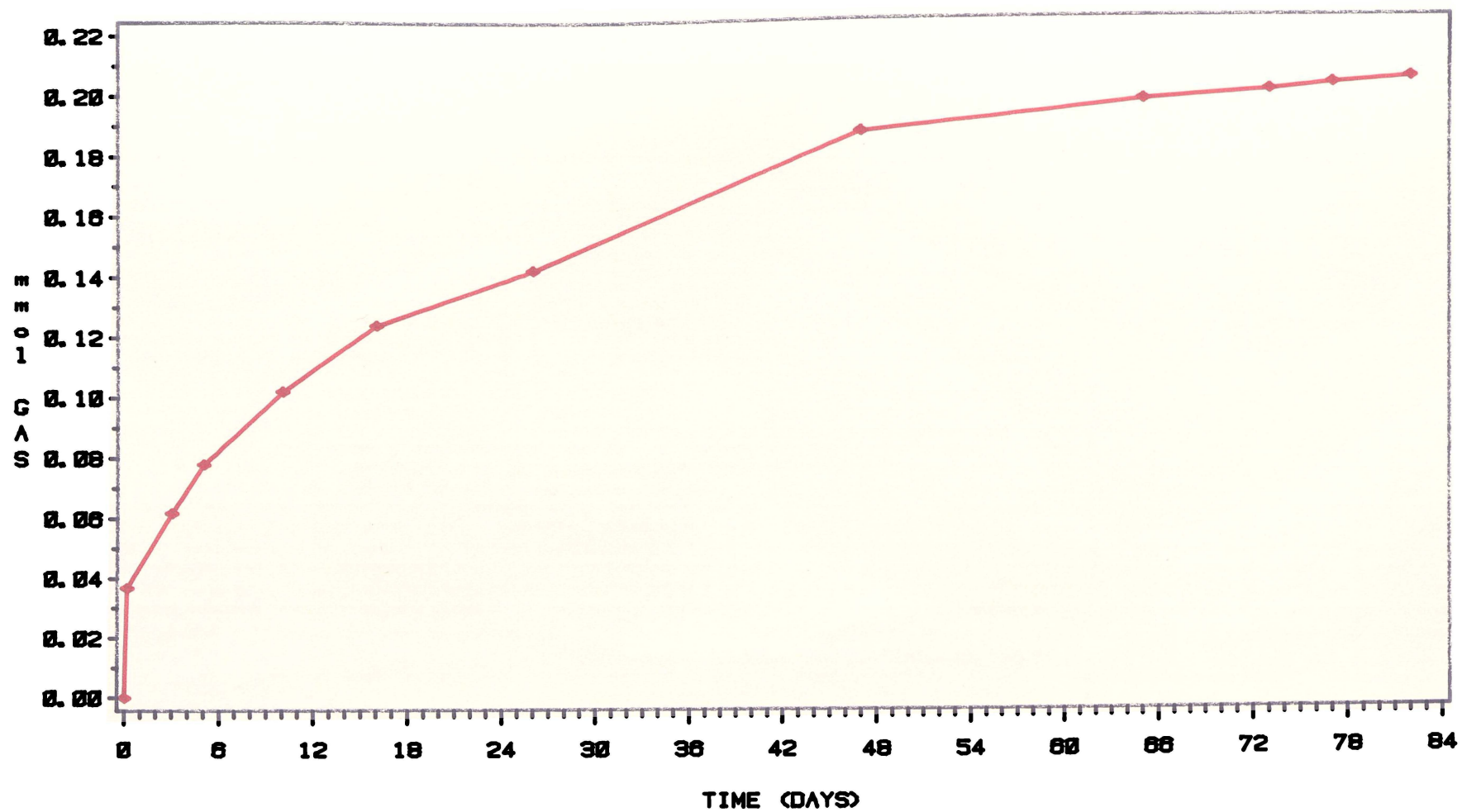
Gas bubbles were observed as soon as the reactants were warmed to room temperature. An orange coloured solid settled to the bottom of the reaction tube. The incondensable gas curve showed a smooth release of gas in the initial period followed by a slowing down period after the 47th day (Fig 7.9). The incondensable gas results are given in Table 7.11.

Table 7.11 Incondensable gas evolution of the reaction of $(EtGeH)_2GeCo_4(CO)_{12}$ with $Co_2(CO)_8$

Days	mmol of gas	Total mmol gas
0.17 (4 hr)	0.037	0.037
3	0.025	0.062
5	0.016	0.078
10	0.024	0.102
16	0.022	0.124
26	0.018	0.142
47	0.045	0.187
65	0.010	0.197
73	0.003	0.200
77	0.002	0.202
82	0.002	0.204

An infrared spectrum (Table 7.12) of the reaction mixture run on the 26th day showed bands assignable to $Co_4(CO)_{12}$, $Co_2(CO)_8$, a new

Figure 7.9
Incondensable Gas Evolution Of The Reaction
Of $(EtGeH)_2GeCo_4(CO)_{12} + Co_2(CO)_8$



TOTAL GAS = -----

compound later characterised as $\text{Et}_2\text{Ge}_3\text{Co}_6(\text{CO})_{17}$ (section 7.7), and another new compound which may be $\text{Et}_2\text{Ge}_3\text{Co}_6(\text{CO})_{20}$ (assignment made by comparison with the infrared spectrum of $\text{Me}_2\text{Ge}_3\text{Co}_6(\text{CO})_{20}$, Chapter Six).

Table 7.12 Infrared spectrum of reaction mixture on day 26 (hexane)

Bands	Int	Possible assignments
2089	w	$\text{Et}_2\text{Ge}_3\text{Co}_6(\text{CO})_{17}$
2077	w sh	$\text{Et}_2\text{Ge}_3\text{Co}_6(\text{CO})_{20}?$
2069	m sh	$\text{Co}_2(\text{CO})_8$ [142]
2062	s	$\text{Et}_2\text{Ge}_3\text{Co}_6(\text{CO})_{17} + \text{Co}_4(\text{CO})_{12}?$ [142]
2053	ms	$\text{Et}_2\text{Ge}_3\text{Co}_6(\text{CO})_{17} + \text{Co}_4(\text{CO})_{12}?$
2040	vs	$\text{Co}_2(\text{CO})_8$
2034	ms sh	$\text{Et}_2\text{Ge}_3\text{Co}_6(\text{CO})_{17}$
2025	m sh	$\text{Co}_2(\text{CO})_8$
2018	ms	$\text{Et}_2\text{Ge}_3\text{Co}_6(\text{CO})_{17} + \text{Et}_2\text{Ge}_3\text{Co}_6(\text{CO})_{20}?$
1983	w	$\text{Et}_2\text{Ge}_3\text{Co}_6(\text{CO})_{17}$
1863	w	$\text{Co}_2(\text{CO})_8$
1855	w	$\text{Co}_2(\text{CO})_8$
1840	w	$\text{Et}_2\text{Ge}_3\text{Co}_6(\text{CO})_{17}$

The reaction was terminated after 82 days when the evolution of gas slowed down. An infrared spectrum of the volatile fraction showed a trace of $\text{HCo}(\text{CO})_4$. The involatile products of the reaction were pumped for a day to sublime away any unreacted $\text{Co}_2(\text{CO})_8$. Extraction of the residue gave two fractions, a dark brown hexane soluble fraction and a brownish red CH_2Cl_2 soluble fraction.

The CH_2Cl_2 fraction was concentrated, topped with hexane and left in the freezer. After a few days, dark long crystals (block shaped) of $\text{Et}_2\text{Ge}_3\text{Co}_6(\text{CO})_{17}$ were produced.

The same crystals ($\text{Et}_2\text{Ge}_3\text{Co}_6(\text{CO})_{17}$) were obtained from the hexane fraction on cooling. The supernatant solution from this was to give a second crop of crystals. Further recrystallisation produced square plates of $\text{Co}_4(\text{CO})_{12}$ (identified by infrared spectrum) and more crystals of $\text{Et}_2\text{Ge}_3\text{Co}_6(\text{CO})_{17}$. However, there was no indication of $\text{Et}_2\text{Ge}_3\text{Co}_6(\text{CO})_{20}$.

Yield :

Weight of $\text{Et}_2\text{Ge}_3\text{Co}_6(\text{CO})_{17}$ (from CH_2Cl_2 fraction) $\approx 0.07\text{g}$

$\approx 0.063 \text{ mmol} \approx 58\%$

Weight of $\text{Et}_2\text{Ge}_3\text{Co}_6(\text{CO})_{17}$ (from hexane fraction) $\approx 0.02\text{g}$

$\approx 0.018 \text{ mmol} \approx 17\%$

Weight of $\text{Co}_4(\text{CO})_{12} + \text{Et}_2\text{Ge}_3\text{Co}_6(\text{CO})_{17} \approx 0.02\text{g}$

7.6.2 Reaction of $(\text{MeGeH})_2\text{GeCo}_4(\text{CO})_{12}$ with $\text{Co}_2(\text{CO})_8$

7.6.2.1 Experimental :

$(\text{MeGeH})_2\text{GeCo}_4(\text{CO})_{12}$ (0.25g, 0.3 mmol) was reacted with $\text{Co}_2(\text{CO})_8$ (0.131g, 0.38 mmol) in hexane (5ml) in a 25ml open tube, as in Section 7.2, Run 1. The reaction was followed by the evolution of incondensable gases, Table 7.13.

7.6.2.2 Observations workup and discussion :

Table 7.13 Incondensable gas evolution of the reaction of $(\text{MeGeH})_2\text{GeCo}_4(\text{CO})_{12}$ with $\text{Co}_2(\text{CO})_8$

Days	mmol of gas	Total mmol of gas
6	0.236 (5% H_2)	0.236
8	0.042	0.278
15	0.073 (91% H_2)	0.351

The first incondensable gas measurement showed an unexpectedly high gas evolution compared to that of the $(\text{EtGeH})_2\text{GeCo}_4(\text{CO})_{12}$ reaction. The infrared spectrum (Table 7.14) of a sample of the reaction mixture on the 15th day showed that no $(\text{MeGeH})_2\text{Co}_4(\text{CO})_{12}$ was left, but a new product, characterised as $\text{Me}_2\text{Ge}_3\text{Co}_6(\text{CO})_{20}$ (in Chapter Six), $\text{Co}_2(\text{CO})_8$ and $\text{Co}_4(\text{CO})_{12}$ were present.

Table 7.14 Infrared spectrum of the reaction of $(\text{MeGeH})_2\text{GeCo}_4(\text{CO})_{12}$ with $\text{Co}_2(\text{CO})_8$ on the 15th day

Bands	Int	$\text{Me}_2\text{Ge}_3\text{Co}_6(\text{CO})_{20}$	$\text{Co}_4(\text{CO})_{12}$
2091	m	2090 ms	
2072	mw	2072 mw	
2062	s		2063 s
2056	vs br	2058 ms	2054 s
2043	vvs	2043 vs	
2016	vs	2018 s	
1864	w		2065 mw

As no bands due to $(\text{MeGeH})_2\text{GeCo}_4(\text{CO})_{12}$ remained, the reaction was stopped. On working up, two fractions were obtained : a hexane soluble fraction and a CH_2Cl_2 fraction. The hexane solution contained $\text{Co}_4(\text{CO})_{12}$ and $\text{Me}_2\text{Ge}_3\text{Co}_6(\text{CO})_{20}$. The CH_2Cl_2 fraction had infrared spectrum bands very similar to those of $\text{Et}_2\text{Ge}_3\text{Co}_6(\text{CO})_{17}$: 2089(mw), 2062(s), 2053(s), 2039(vs), 2016(m), 1837(w). Therefore, this product is assigned the formula $\text{Me}_2\text{Ge}_3\text{Co}_6(\text{CO})_{17}$.

Yield :

Weight of $\text{Co}_4(\text{CO})_{12}$ crystals = 0.03g

Weight of $\text{Me}_2\text{Ge}_3\text{Co}_6(\text{CO})_{17} \approx 0.1\text{g} \approx 0.093 \text{ mmol} \approx 30\%$

Weight of $\text{Me}_2\text{Ge}_3\text{Co}_6(\text{CO})_{20}$ (contaminated with $\text{Co}_4(\text{CO})_{12}$) $\approx 0.2\text{g} \approx 57\%$

7.7 Characterisation of $\text{Et}_2\text{Ge}_3\text{Co}_6(\text{CO})_{17}$ and $\text{Me}_2\text{Ge}_3\text{Co}_6(\text{CO})_{17}$

$\text{Et}_2\text{Ge}_3\text{Co}_6(\text{CO})_{17}$ was characterised by a full X-ray crystal structure. The $\text{Me}_2\text{Ge}_3\text{Co}_6(\text{CO})_{17}$ was characterised based on the similarity of the infrared spectrum to that of the ethyl analogue.

7.7.1 Infrared spectra :

Based on a symmetry of C_s , a total of 17 bands are predicted ($9A' + 8A''$) for $\text{R}_2\text{Ge}_3\text{Co}_6(\text{CO})_{17}$. Between seven to nine bands were observed in the solution infrared spectra, the number of bands depending on the solvent. The solid infrared spectrum was not as well resolved as the solution spectra, showing a total of fourteen bands. The details of the infrared spectra are given in Table 7.15 and Figs 7.10 to 7.13. Discussion on the infrared spectra of $\text{R}_2\text{Ge}_3\text{Co}_6(\text{CO})_{17}$ and $(\text{RM}')_2\text{Co}_4(\text{CO})_{11}$ type compounds is given in Chapter Nine.

Table 7.15 Infrared spectra of $\text{R}_2\text{Ge}_3\text{Co}_6(\text{CO})_{17}$

$\text{Me}_2\text{Ge}_3\text{Co}_6(\text{CO})_{17}$ (CH_2Cl_2)	$\text{Et}_2\text{Ge}_3\text{Co}_6(\text{CO})_{17}$ (hexane)	$\text{Et}_2\text{Ge}_3\text{Co}_6(\text{CO})_{17}$ (CH_2Cl_2)	$\text{Et}_2\text{Ge}_3\text{Co}_6(\text{CO})_{17}$ (CsI)
			2115 vw ?
2089 mw	2091 w	2092 mw	2095 mw
2062 s	2062 vs	2063 vs	2067 ms, sh
			2060 ms
2053 s	2053 s	2052 s	2053 ms, sh
			2046 m
2039 vs	2038 vs		
	2034 s	2034 vs	2033 ms, sh
	2022 mw		2027 ms
2016 m	2017 m	2017 s br	2016 s, sh
			2013 s
			2008 s, sh
			2001 ms, sh
			1993 m
	1980 mw sh	1988 m	
1837 w	1840 w	1827 w br	1826 mw

Fig 7.10 IR spcetrum of $\text{Me}_2\text{Ge}_3\text{Co}_6(\text{CO})_{17}$ (in CH_2Cl_2)

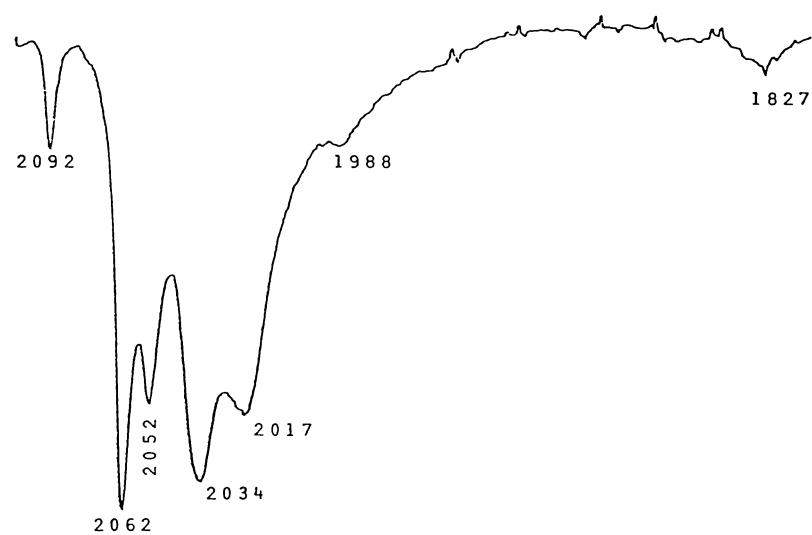


Fig 7.11 Solution IR of $\text{Et}_2\text{Ge}_3\text{Co}_6(\text{CO})_{17}$
(in CH_2Cl_2)

Fig 7.12 Solution IR spectrum of $\text{Et}_2\text{Ge}_3\text{Co}_6(\text{CO})_{17}$ (hexane)

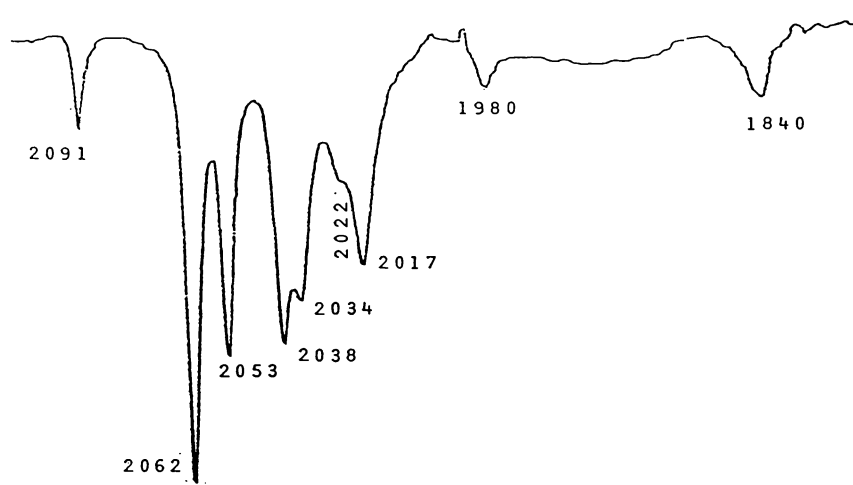
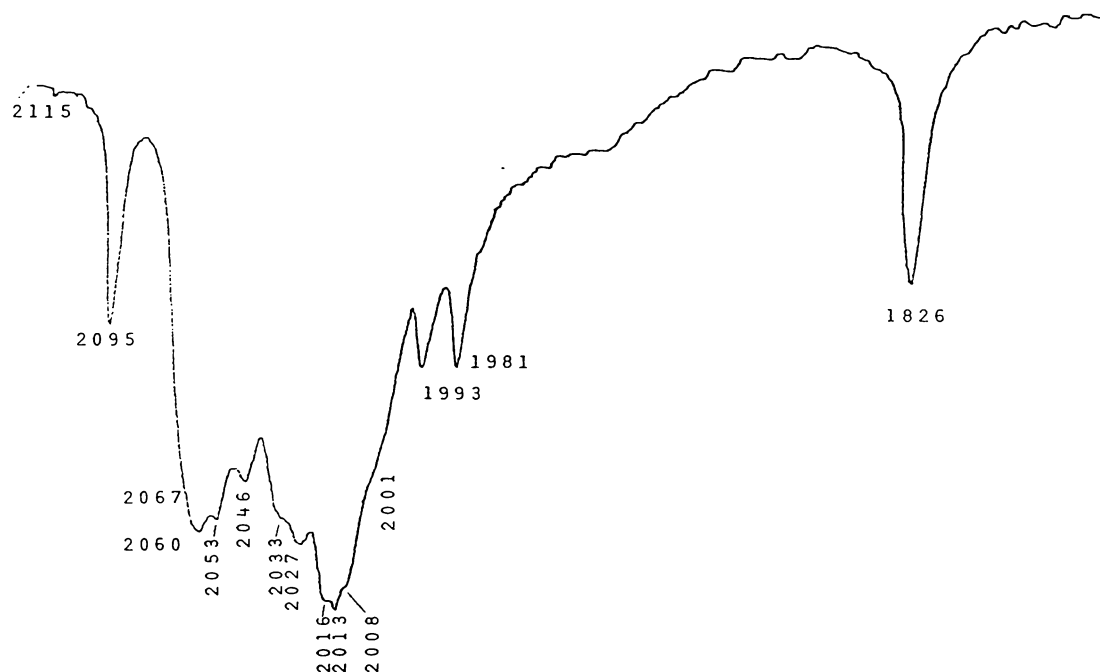


Fig 7.13 Solid IR spectrum of $\text{Et}_2\text{Ge}_3\text{Co}_6(\text{CO})_{17}$ (CsI disc)



7.7.2 Mass spectrum :

The molecular weight of $\text{Et}_2\text{Ge}_3\text{Co}_6(\text{CO})_{17}$ is 1106 which is beyond the capability of the mass spectrometer. The highest envelope in Table 7.16 was 1039-1050 which is that of $[\text{P-2CO}]^+$. A $[\text{P-nCO}]^+$ series was observed. The five envelopes between m/e 842-731 have m/e about 5-10 units higher than expected. Except for the envelope 810-816 which is tentatively assigned as that of $[\text{P-10CO-Me}]^+$, each envelope was about 28 m/e units apart and were assigned as $[\text{P-nCO}]^+$.

A total loss of 17 CO's was followed by the loss of the two ethyl groups. A distinct Ge_3 type pattern was observed in almost all the envelopes. The mass spectrum is detailed in Table 7.16.

Table 7.16 Mass spectrum of $\text{Et}_2\text{Ge}_3\text{Co}_6(\text{CO})_{17}$

m/e	Int	Possible assignments
1038-1050	ms	$[\text{P-2CO}]^+$
988-990	w	$[\text{P-4CO}]^+$
962-966	w	$[\text{P-5CO}]^+$
932-940	mw	$[\text{P-6CO}]^+$
903-915	ms	$[\text{P-7CO}]^+$
882-890	vs	$[\text{P-8CO}]^+$
857-863	s	$[\text{P-9CO}]^+$
830-842	mw	$[\text{P-10CO}]^+$
810-816	ms	$[\text{P-10CO-Me}]^{+?}$
782-792	ms	$[\text{P-11CO}]^+$
758-765	ms	$[\text{P-12CO}]^+$
731-740	m	$[\text{P-13CO}]^+$

Table 7.16 *cont'd...*

705-712	m	[P-14CO] ⁺
677-686	mw	[P-15CO] ⁺
648-660	mw	[P-16CO] ⁺
619-630	mw	[P-17CO] ⁺
591-601	mw	[P-17CO-Et] ⁺
565-576	ms	[P-17CO-2Et] ⁺ , [P-16CO-Et-Co] ⁺
538-540	vw	[P-17CO-Et-Co] ⁺
508-515	m	[P-17CO-2Et-Co] ⁺

7.7.3 NMR spectrum :

¹H NMR : The ¹H NMR spectrum showed a distinct triplet (CH₃) and quartet (CH₂) of relative intensity of 3 : 2 respectively. This confirms the presence of the ethyl group.

¹³C NMR : The ¹³CO NMR signals of Et₂Ge₃Co₆(CO)₁₇ are given in Table 7.17. Though the spectrum were not as well resolved as those of Me₃Ge₃Co₅(CO)₁₄ in Section 3.5.3 (Chapter Three), the spectrum indicated that at least three ¹³CO environments were present in the molecule at low temperature. The δ 202.8 ppm singlet may be assigned to the four terminal CO's on Co(1) and Co(2) plus the two semi-bridging CO's; the shoulder at δ 202.2 ppm to the four terminal CO's on Co(3) and Co(4); and the δ 199.0 ppm singlet to the seven CO's on μ-GeCo₂(CO)₇ unit. No differentiation of the bridging CO from the

terminal CO's in the $\mu\text{-GeCo}_2(\text{CO})_7$ unit is observed. This indicated that the seven CO's on the $\mu\text{-GeCo}_2(\text{CO})_7$ unit were exchanging rapidly even at -50°C .

When the temperature was brought up to room temperature, the two singlets broadened, and the shoulder on the δ 202.8 ppm singlet disappeared.

The ^{13}C signal of the ethyl carbons could not be obtained despite the use of various conditions such as the use of different relaxation times and different temperature settings. This could be due to the unusual coordination number of the two apical Ge atoms. The effect of the five coordinated Ge atom on the alkyl proton is a low field shift as discussed in Section 9.2. The alkyl ^{13}C signals may experience a similar effect, therefore not appearing in the expected position of about δ 20 ppm.

Table 7.17 NMR data of $\text{Et}_2\text{Ge}_3\text{Co}_6(\text{CO})_{17}$

^1H NMR :	δ 1.96 ppm triplet (3x)
	δ 3.29 ppm quartet (2x)
^{13}CO NMR :	singlet at δ 202.8 ppm with a shoulder at δ 202.2 ppm
(-50°C)	singlet at δ 199.0 ppm
	relative intensity of signals = 202.8 : 202.2 : 199.0
	~ 1.5 : 1 : 1.5
(27°C)	singlet at δ 202.7 ppm and broad singlet at δ 199.2 ppm
	of relative intensity of approximately 2 : 1

7.8 Crystal structure of $\text{Et}_2\text{Ge}_3\text{Co}_6(\text{CO})_{17}$

7.8.1 Experimental :

A pure concentrated CH_2Cl_2 solution (topped with a small amount of hexane) of $\text{Et}_2\text{Ge}_3\text{Co}_6(\text{CO})_{17}$ was placed in the freezer overnight. Dark rectangular rod shaped crystals of $\text{Et}_2\text{Ge}_3\text{Co}_6(\text{CO})_{17}$ were obtained. A crystal of dimension $0.3 \times 0.3 \times 1$ mm was mounted with Araldite on a glass fibre for preliminary investigation.

7.8.2 Preliminary precession studies and data collection

Preliminary precession photographs using Ni filtered $\text{Cu-K}\alpha$ X-radiation indicated the crystal to be triclinic. As $Z = 2$, the space group was assumed as $P\bar{1}$ which was confirmed by the successful solution of the structure.

The refined lattice parameters and intensity data were collected at the University of Auckland using an Enraf Nonius CAD 4 diffractometer. The cell parameters were calculated using $\text{Mo-K}\alpha$ X-rays from 25 high angle reflections. The crystal data is given in Table 7.18.

Table 7.18 Crystal data of $\text{Et}_2\text{Ge}_3\text{Co}_6(\text{CO})_{17}$

Formula $\text{C}_{21}\text{H}_{10}\text{O}_{17}\text{Ge}_3\text{Co}_6$
Mr = 1105.2
Triclinic, space group $P\bar{1}$
$A = 10.617(1)\text{\AA}$, $B = 16.895(3)\text{\AA}$, $C = 9.822(4)\text{\AA}$,
$\alpha = 104.22(2)^\circ$, $\beta = 94.40(2)^\circ$, $\gamma = 102.03(1)^\circ$
Unit cell volume = $1672.438\text{\AA}^3$
Density = 2.147g/cm^3
$Z = 2$
$F_{000} = 1060$, $\mu(\text{MoK}\alpha) = 55$, $T = 292\text{K}$

A total of 5052 reflexions in the range of $1^\circ \leq \theta \leq 28^\circ$ were collected, which corresponded to 4395 unique reflexions. 3398 reflections had $F^2 > 3\sigma(F^2)$ and these were used for all calculations. The data were corrected for Lorentz and polarisation effects and for linear absorption using an empirical method.

7.8.3 Solution and refinement :

The metal atoms were located using the TREF routine of SHELXS86. The coordinates of the heavy metal atoms were used in SHELX76 program and subsequent refinement and difference maps located all 17 CO's and the four ethyl carbons. In the final cycles of full-matrix least-squares refinement, all atoms were assigned anisotropic temperature factors, with the hydrogens placed in calculated positions using the AFIX routine of SHELX76. The final refinement converged with $R = 0.0252$, $R_w = 0.0263$ where $w = (\sigma^2 F + 0.0004 F^2)^{-1}$.

A final difference map shows no residual electron density more than $0.83 \text{ e}\text{\AA}^{-3}$, and no parameter shifted by more than 0.009 times its standard deviation in the final cycle.

7.8.4 Discussion of the Structure :

Full diagrams of $\text{Et}_2\text{Ge}_3\text{Co}_6(\text{CO})_{17}$ are shown in Figs 7.14 to 7.15. Its bond lengths and bond angles are in Tables 7.19 and 7.20. The final positional parameters are presented in Appendix 6, while the structure factors are retained by the University of Waikato.

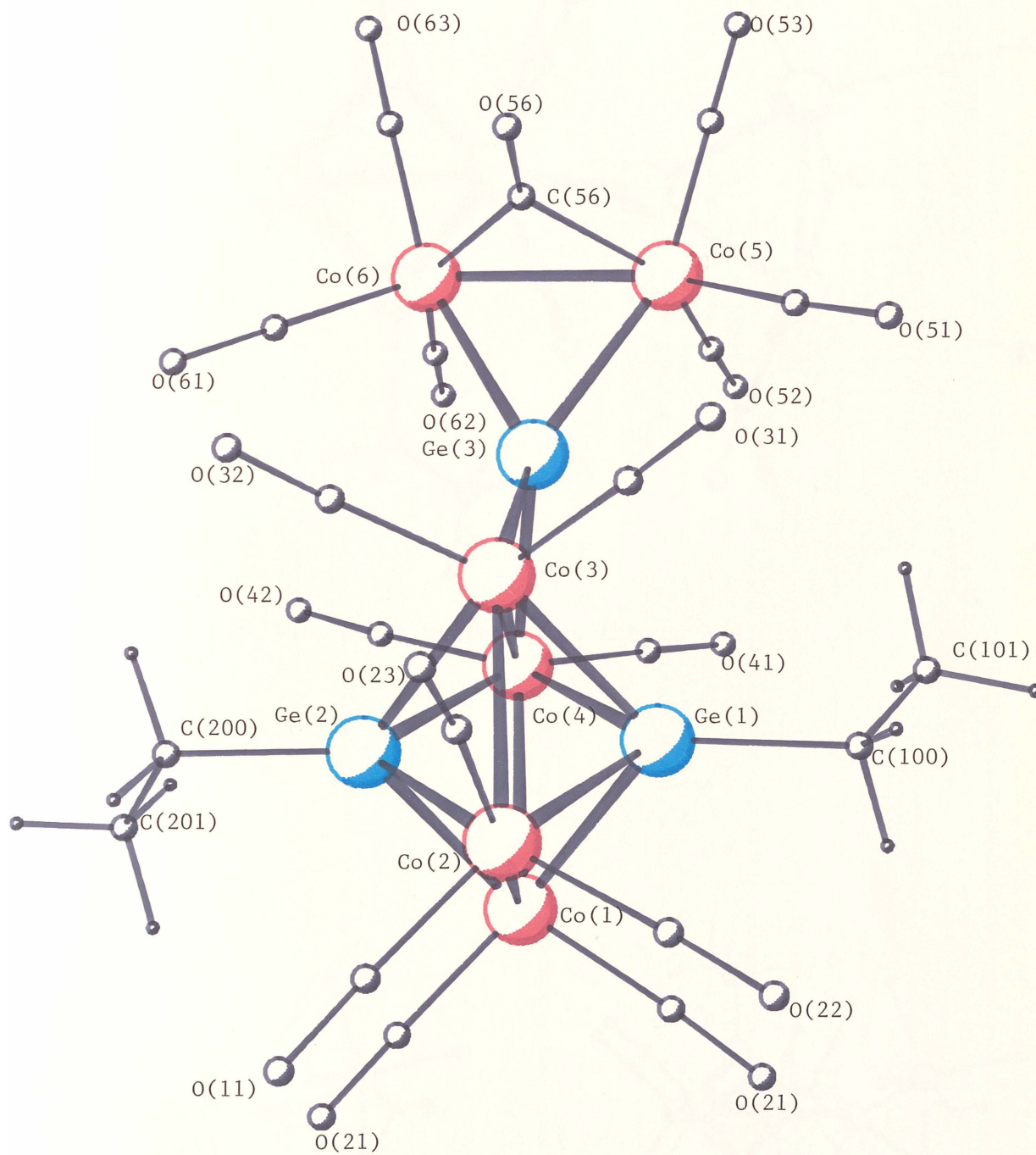


Fig 7.14 Crystal structure of $\text{Et}_2\text{Ge}_3\text{Co}_6(\text{CO})_{17}$

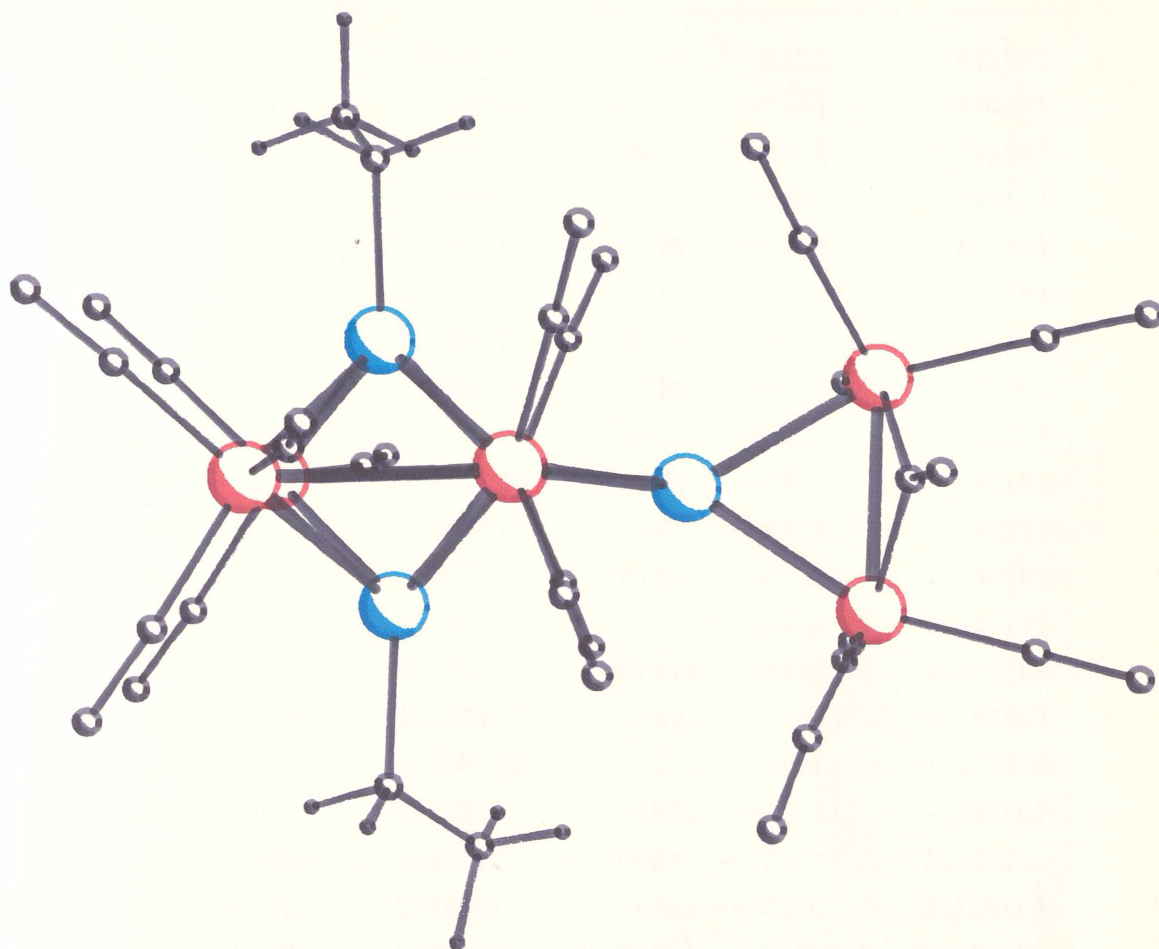


Fig 7.15a View of $\text{Et}_2\text{Ge}_3\text{Co}_6(\text{CO})_{17}$ through Co(1) and Co(2)

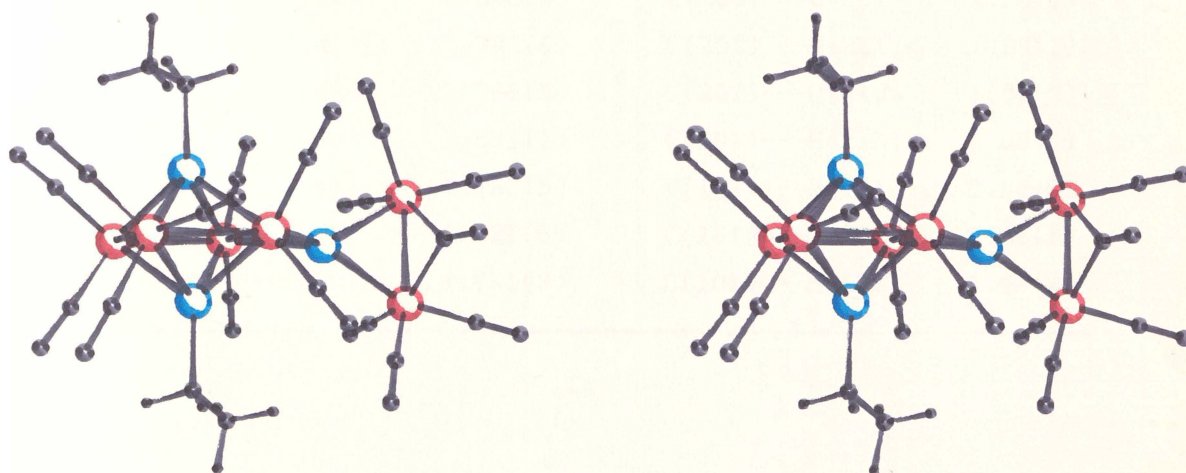


Fig 7.15b Stereo view of $\text{Et}_2\text{Ge}_3\text{Co}_6(\text{CO})_{17}$

Table 7.19 Bond Lengths (Å) for $\text{Et}_2\text{Ge}_3\text{Co}_6(\text{CO})_{17}$

Ge(1) ---Ge(2)	2.890(1)	Co(5) ---C(56)	1.962(6)
Ge(1) ---Co(2)	2.422(1)	Co(6) ---C(56)	1.915(4)
Ge(1) ---Co(1)	2.413(1)	Co(6) ---C(61)	1.781(6)
Ge(1) ---Co(3)	2.360(1)	Co(6) ---C(62)	1.833(5)
Ge(1) ---Co(4)	2.390(1)	Co(6) ---C(63)	1.819(6)
Ge(1) ---C(100)	1.962(6)	C(11) ---O(11)	1.138(8)
Ge(2) ---Co(2)	2.400(1)	C(12) ---O(12)	1.12(1)
Ge(2) ---Co(1)	2.379(1)	C(14) ---O(14)	1.137(6)
Ge(2) ---Co(3)	2.373(1)	C(21) ---O(21)	1.123(7)
Ge(2) ---Co(4)	2.415(1)	C(22) ---O(22)	1.133(7)
Ge(2) ---C(200)	1.964(5)	C(23) ---O(23)	1.143(7)
Co(2) ---Co(1)	2.715(1)	C(31) ---O(31)	1.130(6)
Co(2) ---Co(3)	2.703(1)	C(32) ---O(32)	1.127(7)
Co(2) ---C(11)	1.783(6)	C(41) ---O(41)	1.139(8)
Co(2) ---C(22)	1.802(5)	C(42) ---O(42)	1.137(6)
Co(2) ---C(23)	1.765(6)	C(51) ---O(51)	1.114(7)
Ge(3) ---Co(3)	2.315(1)	C(52) ---O(52)	1.127(8)
Ge(3) ---Co(4)	2.317(1)	C(53) ---O(53)	1.12(1)
Ge(3) ---Co(5)	2.383(1)	C(56) ---O(56)	1.165(6)
Ge(3) ---Co(6)	2.384(1)	C(61) ---O(61)	1.131(7)
Co(1) ---Co(4)	2.657(1)	C(62) ---O(62)	1.118(6)
Co(1) ---C(12)	1.788(7)	C(63) ---O(63)	1.125(8)
Co(1) ---C(14)	1.789(5)	C(100)---H(121)	1.08(1)
Co(1) ---C(21)	1.805(6)	C(100)---H(122)	1.080(8)
Co(3) ---Co(4)	2.722(1)	C(100)---C(101)	1.28(1)
Co(3) ---C(31)	1.784(5)	C(200)---H(221)	1.08(1)
Co(3) ---C(32)	1.796(6)	C(200)---H(222)	1.080(9)
Co(4) ---C(14)	2.345(6)	C(200)---C(201)	1.50(1)
Co(4) ---C(41)	1.781(6)	C(201)---H(211)	1.08(1)
Co(4) ---C(42)	1.796(5)	C(201)---H(212)	1.08(2)
Co(5) ---Co(6)	2.531(1)	C(201)---H(213)	1.08(1)
Co(5) ---C(51)	1.765(5)	C(101)---H(111)	1.08(2)
Co(5) ---C(52)	1.822(6)	C(101)---H(112)	1.08(3)
Co(5) ---C(53)	1.781(9)	C(101)---H(113)	1.08(2)

Table 7.20 Bond Angles (°) for $\text{Et}_2\text{Ge}_3\text{Co}_6(\text{CO})_{17}$

Ge(2)-Ge(1)-Co(2)	52.80(0)	Co(3)-Ge(3)-Co(4)	72.00(0)
Ge(2)-Ge(1)-Co(3)	52.60(0)	Co(3)-Ge(3)-Co(6)	131.20(0)
Ge(2)-Ge(1)-Co(4)	53.40(0)	Co(3)-Ge(3)-Co(5)	132.30(0)
Ge(2)-Ge(1)-Co(1)	52.40(0)	Co(4)-Ge(3)-Co(6)	129.90(0)
Ge(2)-Ge(1)-C(100)	175.6(2)	Co(4)-Ge(3)-Co(5)	139.30(0)
Co(2)-Ge(1)-Co(3)	68.80(0)	Co(5)-Ge(3)-Co(6)	64.10(0)
Co(2)-Ge(1)-Co(4)	106.20(0)	Ge(1)-Co(1)-Ge(2)	74.20(0)
Co(2)-Ge(1)-Co(1)	68.30(0)	Ge(1)-Co(1)-Co(2)	56.00(0)
Co(2)-Ge(1)-C(100)	124.0(2)	Ge(1)-Co(1)-Co(4)	56.00(0)
Co(1)-Ge(1)-Co(3)	104.90(0)	Ge(1)-Co(1)-C(12)	155.7(2)
Co(1)-Ge(1)-Co(4)	67.20(0)	Ge(1)-Co(1)-C(14)	105.0(2)
Co(1)-Ge(1)-C(100)	124.5(2)	Ge(1)-Co(1)-C(21)	84.3(2)
Co(3)-Ge(1)-Co(4)	69.90(0)	Ge(2)-Co(1)-Co(2)	55.70(0)
Co(3)-Ge(1)-C(100)	130.4(2)	Ge(2)-Co(1)-Co(4)	57.00(0)
Co(4)-Ge(1)-C(100)	129.5(2)	Ge(2)-Co(1)-C(12)	92.5(2)
Ge(1)-Ge(2)-Co(2)	53.50(0)	Ge(2)-Co(1)-C(14)	100.5(2)
Ge(1)-Ge(2)-Co(3)	52.20(0)	Ge(2)-Co(1)-C(21)	152.0(1)
Ge(1)-Ge(2)-Co(4)	52.60(0)	Co(2)-Co(1)-Co(4)	91.50(0)
Ge(1)-Ge(2)-Co(1)	53.40(0)	Co(2)-Co(1)-C(12)	99.7(2)
Ge(1)-Ge(2)-C(200)	178.6(2)	Co(2)-Co(1)-C(14)	151.1(2)
Co(2)-Ge(2)-Co(3)	69.00(0)	Co(2)-Co(1)-C(21)	97.4(1)
Co(2)-Ge(2)-Co(4)	106.10(0)	Co(4)-Co(1)-C(12)	132.6(2)
Co(2)-Ge(2)-Co(1)	69.20(0)	Co(4)-Co(1)-C(14)	59.9(2)
Co(2)-Ge(2)-C(200)	127.5(2)	Co(4)-Co(1)-C(21)	123.6(2)
Co(1)-Ge(2)-Co(3)	105.60(0)	C(12)-Co(1)-C(14)	97.2(3)
Co(1)-Ge(2)-Co(4)	67.30(0)	C(12)-Co(1)-C(21)	100.5(3)
Co(1)-Ge(2)-C(200)	127.6(2)	C(14)-Co(1)-C(21)	102.3(3)
Co(3)-Ge(2)-Co(4)	69.30(0)	Ge(1)-Co(3)-Ge(2)	75.30(0)
Co(3)-Ge(2)-C(200)	126.8(2)	Ge(1)-Co(3)-Co(2)	56.70(0)
Co(4)-Ge(2)-C(200)	126.4(2)	Ge(1)-Co(3)-Ge(3)	92.00(0)
Ge(1)-Co(2)-Ge(2)	73.60(0)	Ge(1)-Co(3)-Co(4)	55.60(0)
Ge(1)-Co(2)-Co(3)	54.50(0)	Ge(1)-Co(3)-C(31)	93.2(2)
Ge(1)-Co(2)-Co(1)	55.70(0)	Ge(1)-Co(3)-C(32)	159.7(2)
Ge(1)-Co(2)-C(11)	146.1(2)	Ge(2)-Co(3)-Co(2)	56.00(0)
Ge(1)-Co(2)-C(22)	83.5(2)	Ge(2)-Co(3)-Ge(3)	101.40(0)
Ge(1)-Co(2)-C(23)	114.1(2)	Ge(2)-Co(3)-Co(4)	56.10(0)
Ge(2)-Co(2)-Co(3)	55.00(0)	Ge(2)-Co(3)-C(31)	161.5(2)

Table 7.20 *cont'd...*

Ge(2)-Co(2)-Co(1)	55.00(0)	Ge(2)-Co(3)-C(32)	86.3(2)
Ge(2)-Co(2)-C(11)	88.7(2)	Co(2)-Co(3)-Ge(3)	143.50(0)
Ge(2)-Co(2)-C(22)	152.1(2)	Co(2)-Co(3)-Co(4)	90.40(0)
Ge(2)-Co(2)-C(23)	103.5(2)	Co(2)-Co(3)-C(31)	105.6(2)
Co(1)-Co(2)-Co(3)	88.60(0)	Co(2)-Co(3)-C(32)	105.8(2)
Co(1)-Co(2)-C(11)	90.5(2)	Ge(3)-Co(3)-Co(4)	54.00(0)
Co(1)-Co(2)-C(22)	98.8(2)	Ge(3)-Co(3)-C(31)	93.3(2)
Co(1)-Co(2)-C(23)	156.9(2)	Ge(3)-Co(3)-C(32)	100.1(2)
Co(3)-Co(2)-C(11)	135.0(2)	Co(4)-Co(3)-C(31)	128.6(2)
Co(3)-Co(2)-C(22)	122.3(2)	Co(4)-Co(3)-C(32)	120.1(1)
Co(3)-Co(2)-C(23)	70.2(2)	C(31)-Co(3)-C(32)	102.2(2)
C(11)-Co(2)-C(22)	102.3(3)	Ge(1)-Co(4)-Ge(2)	73.90(0)
C(11)-Co(2)-C(23)	97.9(3)	Ge(1)-Co(4)-Ge(3)	91.20(0)
C(22)-Co(2)-C(23)	100.4(2)	Ge(1)-Co(4)-Co(3)	54.50(0)
Ge(1)-Co(4)-Co(1)	56.80(0)	C(56)-Co(6)-C(62)	146.5(2)
Ge(1)-Co(4)-C(14)	90.2(1)	C(56)-Co(6)-C(63)	88.8(2)
Ge(1)-Co(4)-C(41)	92.5(2)	C(61)-Co(6)-C(62)	106.0(2)
Ge(1)-Co(4)-C(42)	159.8(2)	C(61)-Co(6)-C(63)	103.8(3)
Ge(2)-Co(4)-Ge(3)	100.10(0)	C(62)-Co(6)-C(63)	97.1(2)
Ge(2)-Co(4)-Co(3)	54.60(0)	Co(2)-C(11)-O(11)	177.6(6)
Ge(2)-Co(4)-Co(1)	55.70(0)	Co(1)-C(12)-O(12)	177.0(6)
Ge(2)-Co(4)-C(14)	85.3(1)	Co(1)-C(14)-Co(4)	78.7(2)
Ge(2)-Co(4)-C(41)	161.8(2)	Co(1)-C(14)-O(14)	160.0(6)
Ge(2)-Co(4)-C(42)	85.9(2)	Co(4)-C(14)-O(14)	121.2(5)
Ge(3)-Co(4)-Co(3)	54.00(0)	Co(1)-C(21)-O(21)	176.9(6)
Ge(3)-Co(4)-Co(1)	142.60(0)	Co(2)-C(22)-O(22)	177.6(6)
Ge(3)-Co(4)-C(14)	174.6(1)	Co(2)-C(23)-O(23)	171.1(5)
Ge(3)-Co(4)-C(41)	92.2(2)	Co(3)-C(31)-O(31)	175.5(5)
Ge(3)-Co(4)-C(42)	92.4(2)	Co(3)-C(32)-O(32)	174.6(4)
Co(1)-Co(4)-Co(3)	89.40(0)	Co(4)-C(41)-O(41)	176.5(4)
Co(1)-Co(4)-C(14)	41.3(1)	Co(4)-C(42)-O(42)	177.1(5)
Co(1)-Co(4)-C(41)	106.8(2)	Co(5)-C(51)-O(51)	173.8(6)
Co(1)-Co(4)-C(42)	111.4(2)	Co(5)-C(52)-O(52)	177.2(7)
Co(3)-Co(4)-C(14)	130.6(1)	Co(5)-C(53)-O(53)	178.5(7)
Co(3)-Co(4)-C(41)	126.8(1)	Co(5)-C(56)-Co(6)	81.5(2)
Co(3)-Co(4)-C(42)	113.3(2)	Co(5)-C(56)-O(56)	137.3(4)
C(14)-Co(4)-C(41)	82.5(2)	Co(6)-C(56)-O(56)	141.2(5)
C(14)-Co(4)-C(42)	88.0(2)	Co(6)-C(61)-O(61)	175.8(4)

Table 7.20 *cont'd...*

C(41)-Co(4)-C(42)	107.1(2)	Co(6)-C(62)-O(62)	178.1(5)
Ge(3)-Co(5)-Co(6)	57.90(0)	Co(6)-C(63)-O(63)	177.5(4)
Ge(3)-Co(5)-C(51)	95.1(2)	Ge(1)-C(100)-H(121)	106.3(5)
Ge(3)-Co(5)-C(52)	92.9(2)	Ge(1)-C(100)-H(122)	106.3(6)
Ge(3)-Co(5)-C(53)	160.5(3)	Ge(1)-C(100)-C(101)	121.8(7)
Ge(3)-Co(5)-C(56)	75.4(2)	H(121)-C(100)-H(122)	109.5(8)
Co(6)-Co(5)-C(51)	142.4(2)	H(121)-C(100)-C(101)	105(1)
Co(6)-Co(5)-C(52)	99.3(2)	H(122)-C(100)-C(101)	107.7(8)
Co(6)-Co(5)-C(53)	103.2(3)	Ge(2)-C(200)-H(221)	107.8(5)
Co(6)-Co(5)-C(56)	48.4(1)	Ge(2)-C(200)-H(222)	108.0(5)
C(51)-Co(5)-C(52)	108.5(3)	Ge(2)-C(200)-C(201)	115.3(5)
C(51)-Co(5)-C(53)	98.9(3)	H(221)-C(200)-H(222)	109.5(8)
C(51)-Co(5)-C(56)	103.0(3)	H(221)-C(200)-C(201)	108.1(7)
C(52)-Co(5)-C(53)	95.5(3)	H(222)-C(200)-C(201)	107.9(6)
C(52)-Co(5)-C(56)	147.2(2)	C(200)-C(201)-H(211)	109(1)
C(53)-Co(5)-C(56)	88.2(3)	C(200)-C(201)-H(212)	109.7(8)
Ge(3)-Co(6)-Co(5)	57.90(0)	C(200)-C(201)-H(213)	109.5(9)
Ge(3)-Co(6)-C(56)	76.1(2)	H(211)-C(201)-H(212)	109(1)
Ge(3)-Co(6)-C(61)	89.1(2)	H(211)-C(201)-H(213)	109(1)
Ge(3)-Co(6)-C(62)	90.7(2)	H(212)-C(201)-H(213)	109(1)
Ge(3)-Co(6)-C(63)	162.3(2)	C(100)-C(101)-H(111)	109(1)
Co(5)-Co(6)-C(56)	50.0(2)	C(100)-C(101)-H(112)	108(1)
Co(5)-Co(6)-C(61)	140.2(2)	C(100)-C(101)-H(113)	111(1)
Co(5)-Co(6)-C(62)	96.8(2)	H(111)-C(101)-H(112)	109(2)
Co(5)-Co(6)-C(63)	105.2(2)	H(111)-C(101)-H(113)	109(2)
C(56)-Co(6)-C(61)	104.5(2)	H(112)-C(101)-H(113)	109(2)

Dihedral Angles

Co(1)-Co(2)-Co(3)-Co(4) to Ge(3)-Co(3)-Co(4)	171.44(1)
Co(1)-Co(2)-Co(3)-Co(4) to Ge(1)-Co(1)-Co(2)	130.60(0)
Co(1)-Co(2)-Co(3)-Co(4) to Ge(1)-Co(2)-Co(3)	132.73(0)
Co(1)-Co(2)-Co(3)-Co(4) to Ge(1)-Co(3)-Co(4)	131.91(1)
Co(1)-Co(2)-Co(3)-Co(4) to Ge(1)-Co(1)-Co(4)	133.61(0)
Co(1)-Co(2)-Co(3)-Co(4) to Ge(2)-Co(1)-Co(2)	132.87(1)
Co(1)-Co(2)-Co(3)-Co(4) to Ge(2)-Co(2)-Co(3)	132.88(0)
Co(1)-Co(2)-Co(3)-Co(4) to Ge(2)-Co(3)-Co(4)	132.95(0)
Co(1)-Co(2)-Co(3)-Co(4) to Ge(2)-Co(1)-Co(4)	133.76(0)
Ge(3)-Co(3)-Co(4) to Ge(3)-Co(5)-Co(6)	85.51(1)
Ge(3)-Co(5)-Co(6) to Co(5)-Co(6)-C(56)-O(56)	99.32(0)

As shown in the diagrams, the molecule has a basic structure similar to that of $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$, but with the $\mu\text{-CO}$ replaced by a bridging $\text{GeCo}_2(\text{CO})_7$ group. The two apical Ge's ($\text{Ge}(1)$ and $\text{Ge}(2)$) are each quadruply bridged to a distorted square planar array of four cobalt atoms. Of the ten CO's on the Ge_2Co_4 core eight are completely terminal and two are semi-bridging. One of the seven CO's on the bridging $\text{GeCo}_2(\text{CO})_7$ group is fully bridging. The structure can be considered as a combination of $\text{Ge}[\text{Co}_2(\text{CO})_7]_2$ (2a) and $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ (1a).

Co-Co bonds in the Ge_2Co_4 core :

Like $\text{Me}_3\text{Ge}_3\text{Co}_5(\text{CO})_{14}$ discussed in Chapter Three, the Co-Co bond bridged by the $\mu\text{-Ge}$ is the longest bond, and the two shortest are those involving the semi-bridging CO's, while the non-bridged is intermediate (Fig 7.16). This is consistent with the shortening of M-M bonds bridged by a CO group [117,125] while those bridged by a metal atom are generally lengthened [156].

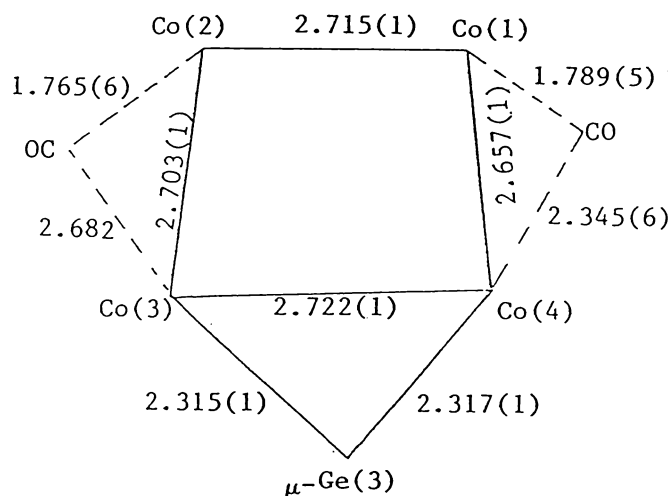


Fig 7.16 Co-Co bond lengths in the Co_4 plane of $\text{Et}_2\text{Ge}_3\text{Co}_6(\text{CO})_{17}$

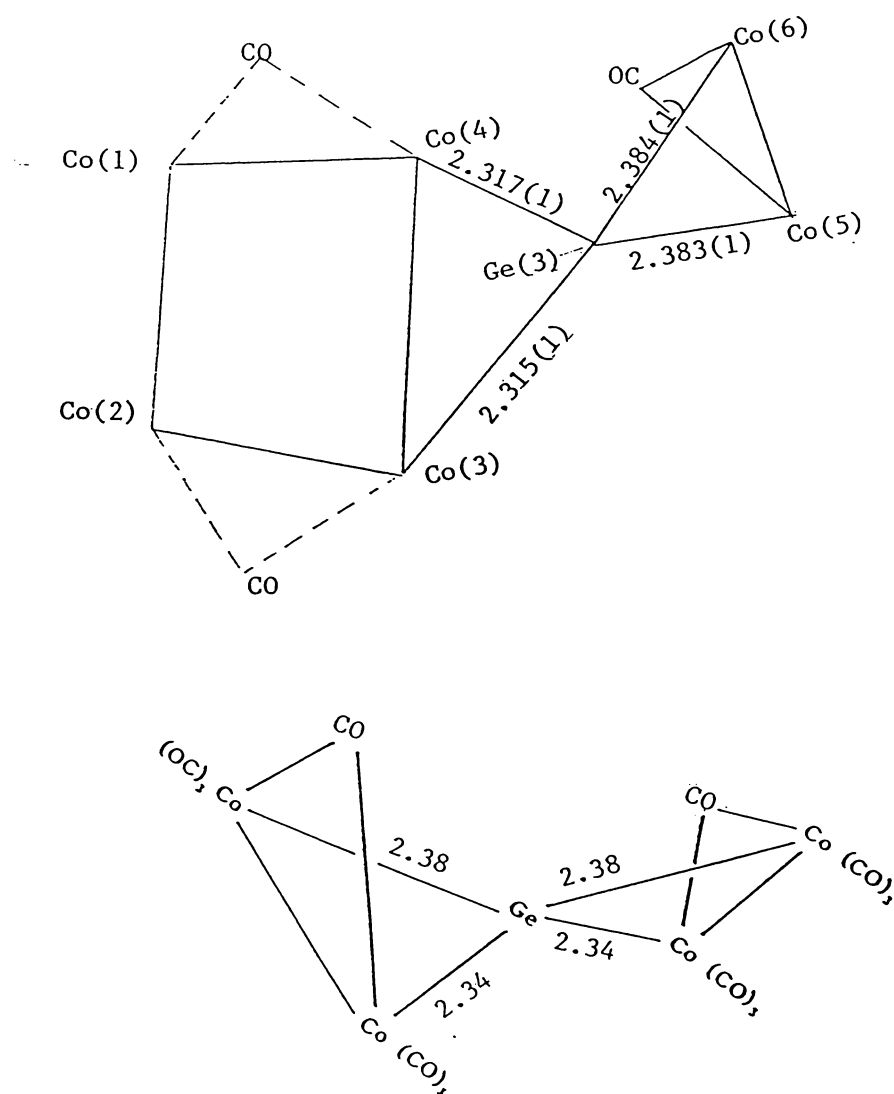


Fig 7.17 Comparison of Ge-Co bond lengths in $\text{Et}_2\text{Ge}_3\text{Co}_6(\text{CO})_{17}$ and $\text{GeCo}_4(\text{CO})_{14}$

Ge-Co bonds :

The Ge-Co distances on both sides of the Co_4 plane are only very slightly different (2.401(1) and 2.392(1)Å). But, no difference is expected from the structure. The bridging by the third Ge atom is symmetric (2.315(1)Å, 2.317(1)Å). The Ge(3) to Co distances are shown in Fig 7.17. The Ge-Co distances on the $\text{Co}_2(\text{CO})_7$ side (Ge(3)-Co(5), Ge(3)-Co(6)) are longer than to the two Co's on the Ge_2Co_4 core (Ge(3)-Co(3), Ge(3)-Co(4)). This is unlike that in $\text{GeCo}_4(\text{CO})_{14}$ as shown in Fig 7.17. The Ge(3)-Co(3) and Ge(3)-Co(4) distances (2.315(1)Å) are exceptionally short and comparable to that in $\text{Cl}_3\text{GeCo}(\text{CO})_4$ (2.310(7)Å) [50] where the short Ge-Co distance is due to the electron withdrawing forces of the three Cl groups (see Chapter Six). This short Ge-Co distance is possibly due to the need of bridging the long Co(3)-Co(4) distance while maintaining a large Co(3)-Ge-Co(4) angle of 72° to alleviate strain in the bonds.

Co-CO bonds :

The terminal Co-C and C-O bond lengths in $\text{Et}_2\text{Ge}_3\text{Co}_6(\text{CO})_{17}$ average 1.795Å and 1.127Å respectively, which are typical for these compounds (see Table 9.6). Like $\text{Me}_3\text{Ge}_3\text{Co}_5(\text{CO})_{14}$ and $\text{Me}_2\text{GeCo}_5(\text{CO})_{15}$, one of the semi-bridging CO's is almost terminal (1.765(6)Å, 2.682Å). The bridging CO in the bridging $\text{GeCo}_2(\text{CO})_7$ unit has an average Co-C distance of 1.935(5)Å, C-O distance of 1.165(6)Å. This is very similar to those in $\text{GeCo}_4(\text{CO})_{14}$ (average Co-C of 1.93(2)Å and C-O of 1.16(2)Å).

Dihedral angles :

The bridging $\text{GeCo}_2(\text{CO})_7$ unit is slightly off-plane from the Co_4 core as indicated by the dihedral angle of 8.5° (between Co_4 plane and

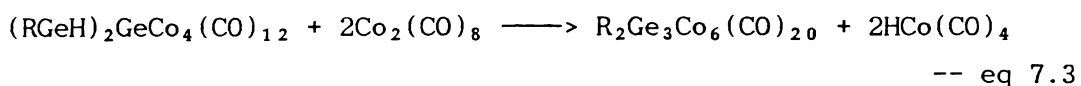
Ge(3)-Co(3)-Co(4)). The dihedral angle between the μ -CO-Co(5)-Co(6) plane and the Ge(3)-Co(5)-Co(6) plane is 99.32° which is very similar to that in $\text{SiCo}_4(\text{CO})_{14}$ (99.08°) [78], but smaller than that of $\text{GeCo}_4(\text{CO})_{14}$ (about 107°) [80]. The dihedral angle between the two GeCo_2 triangles (Ge(3)-Co(5)-Co(6) and Ge(3)-Co(3)-Co(4)) is $85.51(1)^\circ$ and is quite similar to that in $\text{GeCo}_4(\text{CO})_{14}$ ($\sim 84^\circ$). In comparison, the two SiCo_2 triangles in $\text{SiCo}_4(\text{CO})_{14}$ are twisted from the mutually perpendicular orientation to 80.92° .

C-C distances :

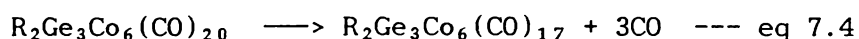
It is worth mentioning here that one of the C-C distances in the ethyl groups appears unusually short for a σ carbon-carbon bond ($1.28(1)\text{\AA}$). This is probably an artifact due to the ethyl group being partly disordered, as indicated by high temperature factors for the carbon atoms.

7.9 Discussion :

The reaction of $(\text{MeGeH})_2\text{GeCo}_4(\text{CO})_{12}$ with $\text{Co}_2(\text{CO})_8$ showed a rapid initial gas evolution consisting mainly of CO. The presence of $\text{HCo}(\text{CO})_4$ in the volatile fraction indicated that some of the hydrogen evolved (equation 7.3) had probably reacted with $\text{Co}_2(\text{CO})_8$ to form $\text{HCo}(\text{CO})_4$ [143]. Both $\text{Me}_2\text{Ge}_3\text{Co}_6(\text{CO})_{20}$ and $\text{Me}_2\text{Ge}_3\text{Co}_6(\text{CO})_{17}$ were formed.



Further decarbonylation can then take place as in equation 7.4 :



The amount of CO evolved (assuming the second gas reading consisted of mainly CO) is consistent with the yield of $\text{Me}_2\text{Ge}_3\text{Co}_6(\text{CO})_{17}$.

The reaction of $(\text{EtGeH})_2\text{GeCo}_4(\text{CO})_{12}$ with $\text{Co}_2(\text{CO})_8$ produced only $\text{Et}_2\text{Ge}_3\text{Co}_6(\text{CO})_{17}$. The incondensable gas evolved was however only half of that expected to produce $\text{Et}_2\text{Ge}_3\text{Co}_6(\text{CO})_{17}$. Some of the H_2 may be trapped in the form of $\text{HCo}(\text{CO})_4$ in the volatile fraction of the product mixture. Some of the unaccounted CO could have been removed by vacuum pumping on the Schlenk line.

An infrared spectrum (Table 7.12) taken of the hexane solution on the 26th day of the reaction (7.6.1) showed the presence of mainly $\text{Et}_2\text{Ge}_3\text{Co}_6(\text{CO})_{17}$ and $\text{Co}_2(\text{CO})_8$, with a weak shoulder at 2077 cm^{-1} assignable to $\text{Et}_2\text{Ge}_3\text{Co}_6(\text{CO})_{20}$. It seems that an anomaly between the product formed and the gas evolved does in fact exist. One explanation could be that the reaction actually started as soon as the reactants were put together at the Schlenk line. The initial gas evolved could have been removed by vacuum pumping aimed at removing unwanted gas at the very beginning of the reaction.

Comparison of the two reactions seems to indicate that $\text{Et}_2\text{Ge}_3\text{Co}_6(\text{CO})_{20}$ has a higher tendency to close down than its Me analogue into the *closo*- cluster $\text{Et}_2\text{Ge}_3\text{Co}_6(\text{CO})_{17}$ (equation 7.4). The ethyl groups could be sterically more demanding than the methyl groups, thus forcing the molecule to assume the *closo*- structure.

7.10 The condensation of extended chain clusters to *closo*-hexanuclear clusters of the type $(\text{RR}'\text{M}')_2\text{Co}_4(\text{CO})_{10}(\mu\text{-X})$ for $\text{X} = \text{CO}$ or $\text{GeCo}_2(\text{CO})_7$

The first of such reactions was illustrated by the closing down of $\text{Ge}_2\text{Co}_6(\text{CO})_{20}$ (3) to (1c) by Foster [18,27]. A similar type of condensation reaction could be envisaged for the formation of

$\text{MeGe}_2\text{Co}_5(\text{CO})_{17}$ to $\text{MeGe}_2\text{Co}_5(\text{CO})_{15}$. In Fig 7.18, the cobalt atom labelled Co(1) is close enough to Co(5) such that when the Co(1) to Co(2) bond breaks, a bond between Co(1) and Co(5) could be formed easily. This initiates the Co-Co and Ge-Co bond formation. This mechanism is of course only a simplification, showing only the rearrangement of the metals and not the carbonyls. The arrows in the figures only represent the breaking and forming of bonds and not the transfer of electron pairs.

The mechanism for the formation of $\text{Et}_2\text{Ge}_3\text{Co}_6(\text{CO})_{17}$ (11) from $\text{Et}_2\text{Ge}_3\text{Co}_6(\text{CO})_{20}$ (Fig 7.19) cannot be explained in a similar way to Fig 7.18. No proposal may be made at the moment as this mechanism has not been studied. However, it is reasonable to speculate that Ge(1) and Ge(2) end up as the apical Ge atoms while Ge(3) is squeezed out to form the bridging Ge atom as ethyl transfer is unlikely. From the model of $\text{Et}_2\text{Ge}_3\text{Co}_6(\text{CO})_{20}$, Co(5) is close to Co(1) while Co(6) is close to Co(4). The breaking of Co(1)-Co(2) and Co(3)-Co(4) bonds may result in the formation of Co(5)-Co(1) and Co(6)-Co(4) bonds. The central Ge atom, Ge(3) becomes the edge bridging atom, forming a GeCo_2 triangle with Co(2) and Co(3). The bridging CO in the $\mu\text{-GeCo}_2(\text{CO})_7$ unit indicates complex rearrangement of CO's in the cluster formation.

The condensation reactions observed in $\text{Ge}_2\text{Co}_6(\text{CO})_{20}$, $\text{MeGe}_2\text{Co}_5(\text{CO})_{17}$ and $\text{Et}_2\text{Ge}_3\text{Co}_6(\text{CO})_{20}$ may be extended to more complex molecules such as $\text{Ge}_3\text{Co}_8(\text{CO})_{26}$ (4) and a hypothetical compound such as $\text{R}_2\text{Ge}_4\text{Co}_8(\text{CO})_{32}$ (R = organic group, a preparative route to this compound would be the reaction of RGeH_3 with $\text{Ge}_2\text{Co}_6(\text{CO})_{20}$, followed by a reaction of the product with $\text{Co}_2(\text{CO})_8$). From $\text{Ge}_3\text{Co}_8(\text{CO})_{26}$, a *closo*-cluster of structure parallels to $\text{Et}_2\text{Ge}_3\text{Co}_6(\text{CO})_{17}$ (11) could be formed, but with the Et groups replaced by $\text{Co}(\text{CO})_4$ units.

$R_2Ge_4Co_8(CO)_{32}$ similarly should produce a *closo*- cluster but containing an attached extended chain as proposed in Fig 7.20.

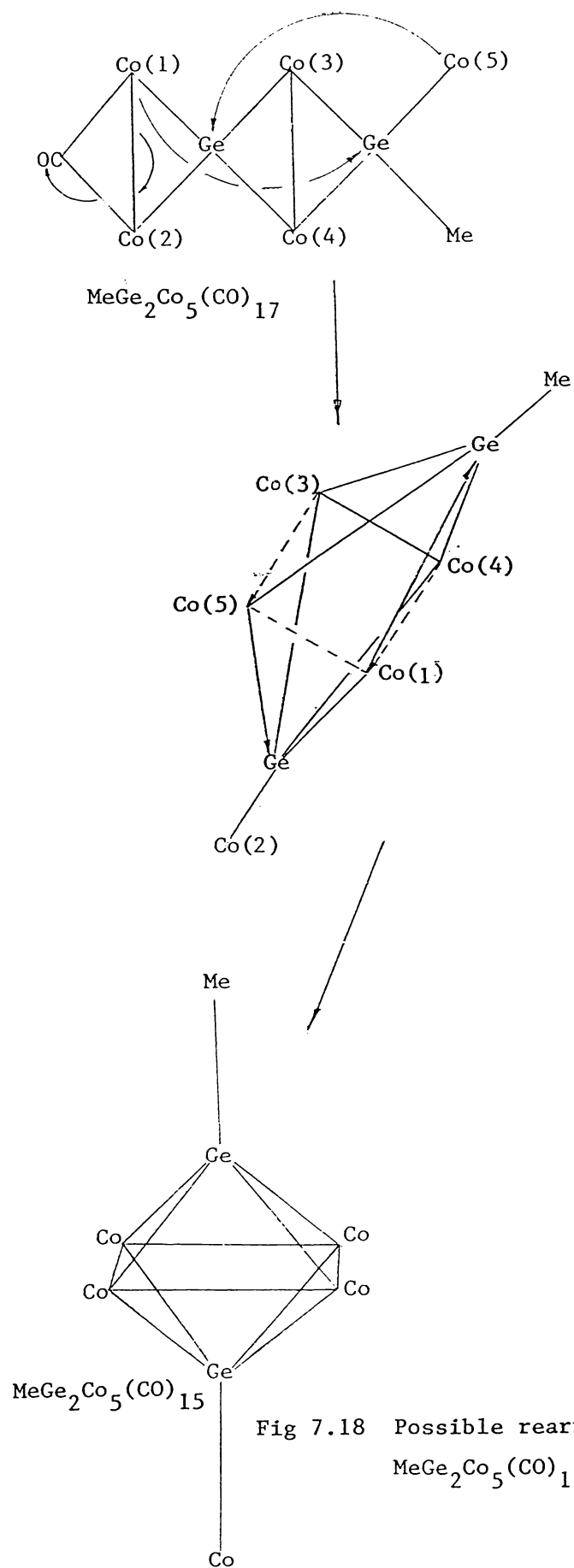


Fig 7.18 Possible rearrangement of $MeGe_2Co_5(CO)_{17}$ to $MeGe_2Co_5(CO)_{15}$

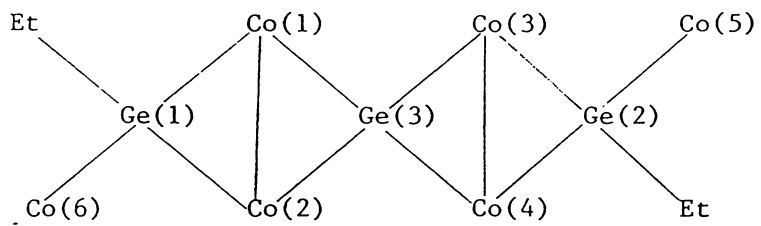


Fig 7.19 $\text{Et}_2\text{Ge}_3\text{Co}_6(\text{CO})_{20}$

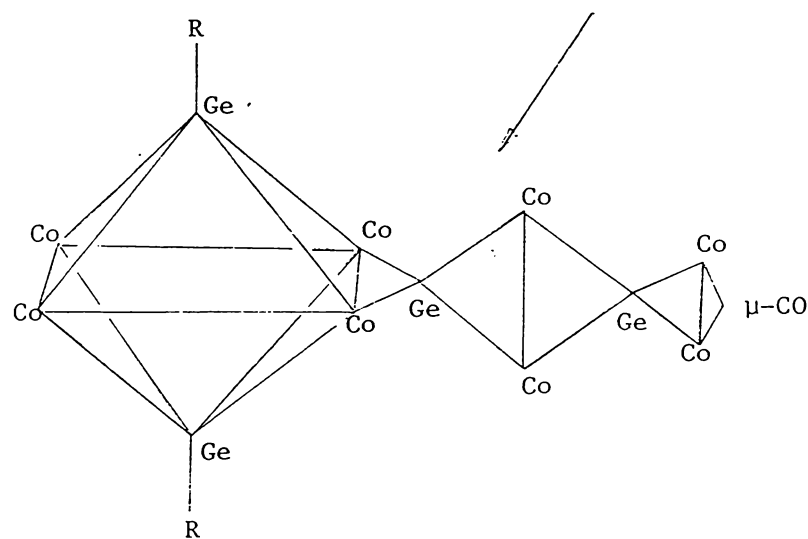
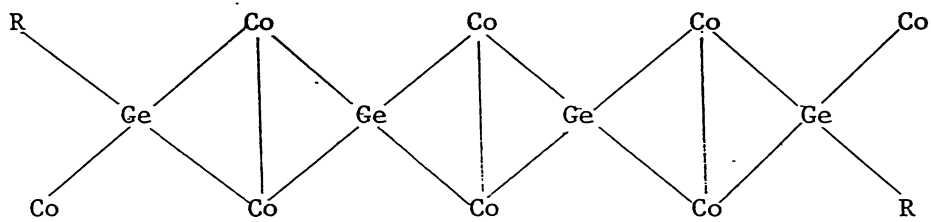


Fig 7.20 Speculated product from the condensation of $R_2Ge_4Co_8(CO)_{32}$

CHAPTER EIGHT

The Reaction of $\text{SiCo}_4(\text{CO})_{14}$ with $\text{R}_x\text{M}'\text{H}_{4-x}$

where $\text{M}' = \text{Ge, Si}$, $\text{R} = \text{Me and Et}$, and $x = 1 \text{ and } 2$

The reactions of $\text{GeCo}_4(\text{CO})_{14}$ (**2a**) with germyl hydrides have produced some interesting compounds, however no equivalent reactions of $\text{SiCo}_4(\text{CO})_{14}$ have yet been observed. This Chapter describes the reaction of $\text{SiCo}_4(\text{CO})_{14}$ (**2b**) with germyl hydrides and silyl hydrides $\text{R}_x\text{M}'\text{H}_{4-x}$ where $\text{M}' = \text{Ge, Si}$, $\text{R} = \text{Me and Et}$, and $x = 1 \text{ and } 2$.

8.1 Reaction of RGeH_3 with $\text{SiCo}_4(\text{CO})_{14}$

8.1.1 Experimental :

Run 1 ($\text{EtGeH}_3 : \text{SiCo}_4(\text{CO})_{14} = 2 : 1$)

$\text{SiCo}_4(\text{CO})_{14}$ (0.1891g, 0.288mmol) and hexane (10 ml) were loaded into a nitrogen flushed ampoule at the Schlenk line. The ampoule was transferred to the vacuum line where it was degassed and cooled by liquid nitrogen. EtGeH_3 (0.576mmol) was condensed in and the ampoule sealed. This was left to react (at room temperature) for two months under constant shaking (wrapped with Al foil) and then left to react in the dark for another five months.

8.1.2 Observations and workup :

The reaction mixture, initially deep red, went slightly purple after two weeks. The purple colour slowly subsided and a reddish brown

solution was obtained before the ampoule was opened. 0.42mmol of total incondensable gases were measured, of which 37% was H_2 and 63% CO.

The volatile fraction was collected and its infrared spectrum showed some $EtGeH_3$ remained, but could not be quantified because of the difficulty of removing the relatively small amount of $EtGeH_3$ from the solvent.

Incondensable gas measurements indicated that approximately 0.104 mmol (18%) of the 0.576 mmol $EtGeH_3$ was consumed, and the presence of $EtGeH_3$ in the volatiles showed that some remained unreacted.

The involatile material was separated into two fractions : a brownish orange hexane soluble fraction and a dark red solid.

The red solid dissolved in CH_2Cl_2 to form a red solution. This was characterised as $EtGeSiCo_5(CO)_{15}$ (Fig 8.6 and 8.7) by X-ray crystallography and spectroscopic means. A full characterisation is given in Section 8.1.3.

The infrared spectrum of the hexane soluble fraction showed a mixture of products, but no $SiCo_4(CO)_{14}$ was left. The infrared spectrum and the tentative assignment is given in Table 8.1. The assignments are based on the infrared spectra of the known methyl analogues of $EtGeCo_3(CO)_{11}$, $Et_2Ge_2Co_4(CO)_{14}$ and $(EtGe)_2Co_4(CO)_{11}$. A small amount of $SiCo_4(CO)_{13}$ was indicated, and this may have accounted for the purple colour observed at the initial stage of the reaction.

Hexane was removed from the solution. The dark brown solid was extracted several times each with 1-2 ml of hexane. $Et_2Ge_2Co_4(CO)_{14}$, $EtGeCo_3(CO)_{11}$ and $SiCo_3(CO)_{13}$ were removed after three hexane extracts. The next few extracts consisted of $(EtGe)_2Co_4(CO)_{11}$ contaminated with a small amount of $EtGeSiCo_5(CO)_{15}$. A few crystals of $(EtGe)_2Co_4(CO)_{11}$ were isolated by recrystallisation. Its identification is based on the infrared spectrum (Table 8.2, Fig 8.1)

which is almost the same as that of $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$. The solubility of $(\text{EtGe})_2\text{Co}_4(\text{CO})_{11}$ and the colour (red in hexane and CH_2Cl_2) also support the assignment.

Table 8.1 Hexane soluble fraction of Runs 1 and 2

Bands/int	Possible assignments	I	II	III	IV
2102vw sh	$\text{EtGeCo}_3(\text{CO})_{11}$ + $\text{EtGeSiCo}_5(\text{CO})_{15}$	2105m			
2099vw	$\text{Et}_2\text{Ge}_2\text{Co}_4(\text{CO})_{14}$		2097w		
2092w	$\text{SiCo}_3(\text{CO})_{13}$?				2087s
2083m	$\text{Et}_2\text{Ge}_2\text{Co}_4(\text{CO})_{14}$		2087s		
2079mw	$\text{EtGeCo}_3(\text{CO})_{11}$	2082vs			
2072mw	$\text{EtGeSiCo}_5(\text{CO})_{15}$				
2062mw sh	$\text{Et}_2\text{Ge}_2\text{Co}_4(\text{CO})_{14}$		2067mw		
2057mw sh	$(\text{EtGe})_2\text{Co}_4(\text{CO})_{11}$			2060m sh	
2052m	$\text{EtGeCo}_3(\text{CO})_{11}$	2056s			
2048m sh	$\text{SiCo}_4(\text{CO})_{13}$?				2047w sh
2040s	$\text{Et}_2\text{Ge}_2\text{Co}_4(\text{CO})_{14}$ + $\text{EtGeSiCo}_5(\text{CO})_{15}$	2046sh	2039ms		
2033s	$(\text{EtGe})_2\text{Co}_4(\text{CO})_{11}$ + $\text{SiCo}_4(\text{CO})_{13}$?		2034vs	2031vs	2031vs
2029s sh	$\text{EtGeCo}_3(\text{CO})_{11}$ + $\text{Et}_2\text{Ge}_2\text{Co}_4(\text{CO})_{14}$	2030s	2029ms		
2020s br	$\text{Et}_2\text{Ge}_2\text{Co}_4(\text{CO})_{14}$		2017vs		
2013s	$(\text{EtGe})_2\text{Co}_4(\text{CO})_{11}$?	2020m	2016ms	2011ms sh	
2005ms	$\text{EtGeCo}_3(\text{CO})_{11}$ + $(\text{EtGe})_2\text{Co}_4(\text{CO})_{14}$	2007m	2002mw	2005m sh	
1845w	$\text{EtGeCo}_3(\text{CO})_{11}$ + $(\text{EtGe})_2\text{Co}_4(\text{CO})_{11}$?	1850m		1850w, br	
1835vw sh	$\text{EtGeCo}_3(\text{CO})_{11}$	1838w			

I = $\text{MeGeCo}_3(\text{CO})_{11}$ [20,71], II = $\text{Me}_2\text{Ge}_2\text{Co}_4(\text{CO})_{14}$ [76],

III = $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ [84], IV = $\text{SiCo}_4(\text{CO})_{13}$ [22]

Fig 8.1 Infrared spectrum of $(\text{EtGe})_2\text{Co}_4(\text{CO})_{11}$

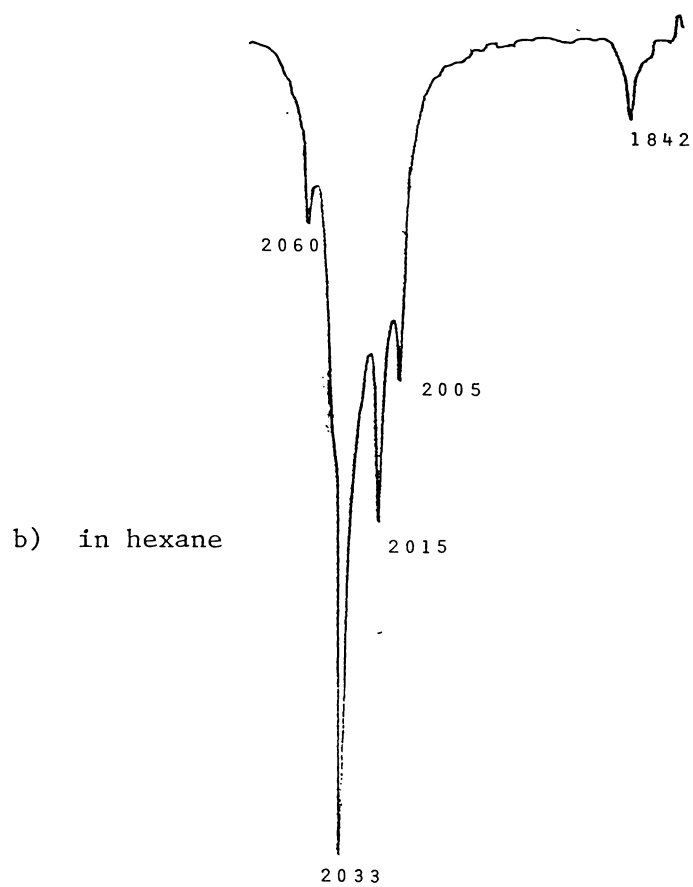
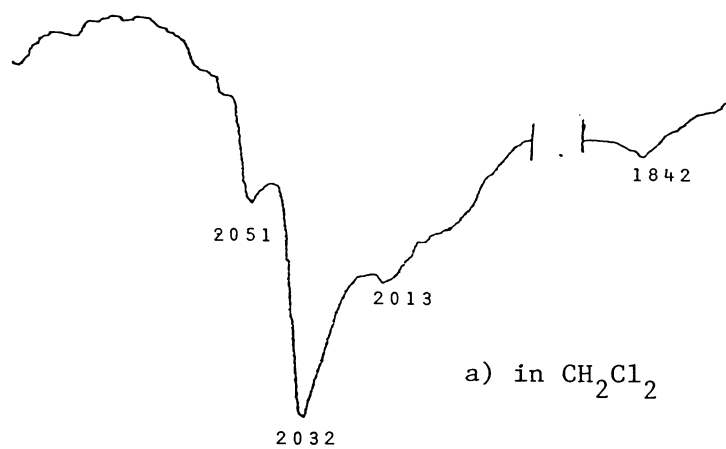


Table 8.2 Infrared spectrum of $(\text{EtGe})_2\text{Co}_4(\text{CO})_{11}$ compared
to $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$

$(\text{EtGe})_2\text{Co}_4(\text{CO})_{11}$			$(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ (see Chapter Four)		
Bands /Intensity			Bands /Intensity		
2051	mw sh	CH_2Cl_2	2031	s	
2032	s		2010	m sh	
2013	m		1841-1833	w br	
1842	vw				
2060	mw	Hexane	2063	vw sh	
2033	vs		2034	vs	
2015	ms		2016	ms	
2005	m		2006	m	
1842	w		1843	w br	

The very small amount of solid left after the extraction of the $(\text{EtGe})_2\text{Co}_4(\text{CO})_{11}$ and $\text{EtGeSiCo}_5(\text{CO})_{15}$ fraction has an infrared spectrum (Table 8.3, Fig 8.2) suggests formulation as an $\text{R}_2\text{Ge}_3\text{Co}_6(\text{CO})_{17}$ (**II**) type compound possibly $\text{Et}_2\text{Ge}_2\text{SiCo}_6(\text{CO})_{17}$:

Table 8.3 Infrared spectrum of $\text{R}_2\text{Ge}_3\text{Co}_6(\text{CO})_{17}$ type compound
Bands Int $\text{EtGeSiCo}_5(\text{CO})_{15}$ " $\text{Et}_2\text{Ge}_2\text{SiCo}_6(\text{CO})_{17}$ " $\text{Et}_2\text{Ge}_3\text{Co}_6(\text{CO})_{17}$

2104 w	2105w		
2090 w		2091w	2091w
2073 w	2073w		
2062 m		2062vs	2062vs
2053 m		2053s	2053s
2038 vs	2039vs	2038vs	2038vs
2032 s sh		2034s	2034s
2023 m		2022mw	2011mw
2016 mw	2016mw	2017m	2017m
2004 w	2004w		
1840 w br		1840w	1840w

Note : the infrared bands of $\text{EtGeSiCo}_5(\text{CO})_{15}$ are indicated by #
those of " $\text{Et}_2\text{Ge}_2\text{SiCo}_6(\text{CO})_{17}$ " are indicated by * in Fig 8.2.

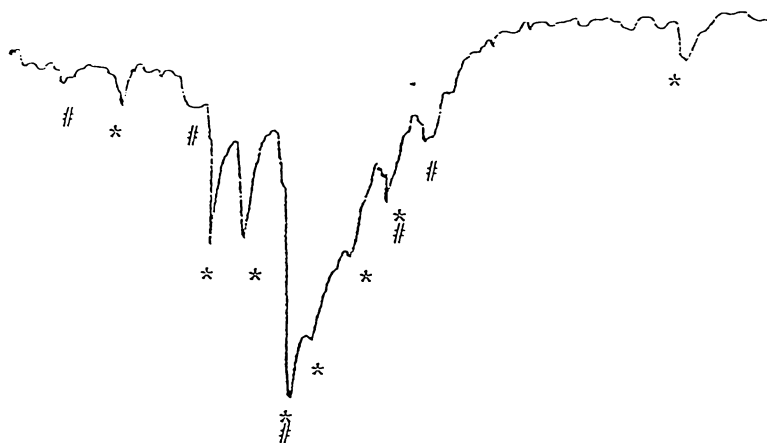


Fig 8.2 IR spectrum of "Et₂Ge₂SiCo₆(CO)₁₇"

Unfortunately, this last fraction was available in such small quantity that it was not possible to confirm the composition of this compound by other means. This spectrum could also be assigned as a mixture of Co₄(CO)₁₂, EtGeSiCo₅(CO)₁₅ and (EtGe)₂Co₄(CO)₁₁, but this was ruled out as Co₄(CO)₁₂ would be removed by the first few washings of hexane and there were no Co₄(CO)₁₂ bands in the spectrum.

Other runs :

Two other runs were completed, The experimental procedures were as in Run 1. Details of these runs are given in Table 8.4.

Table 8.4 Experimental details of Runs 2 and 3 (at 20°C)

	Run 2	Run 3
SiCo ₄ (CO) ₁₄ (g)	0.0954	0.0972
SiCo ₄ (CO) ₁₄ (mmol)	0.146	0.162
RGeH ₃ (mmol)	0.291	0.532
Ratio SiCo ₄ (CO) ₁₄ : RGeH ₃	1 : 2	1 : 3.3
RGeH ₃	EtGeH ₃	MeGeH ₃
Ampoule size (ml)	50	15
Solvent (hexane, ml)	10	5
Reaction time (months)	8	8
Shaking (months)	4	4

Run 2 (EtGeH_3 : $\text{SiCo}_4(\text{CO})_{14}$ = 2 : 1)

Like Run 1, the colour of the reaction turned to a slight purplish red two weeks into the reaction. After 4 months of shaking the colour had changed to a red brown colour. Just before the ampoule was opened, an orange red powder was observed to settle on to the side of the ampoule. The reaction was worked up as in Run 1.

The total amount of incondensable gas measured was 0.358 mmol, of which 26% consisted of H_2 , and 74% CO . The H_2 corresponded to 0.062 mmol of EtGeH_3 which was 21% of the EtGeH_3 input (0.291 mmol), therefore the reaction ratio was ~ 2.5 : 1 for $\text{SiCo}_4(\text{CO})_{14}$: EtGeH_3 . This was consistent with the presence of EtGeH_3 (not measured) observed in the infrared spectrum of the volatile fraction of the reaction.

The infrared spectrum (Table 8.5) of the hexane soluble fraction showed that a mixture of compounds similar to those in Table 8.1, Run 1 were obtained. Hexane was removed from the hexane fraction. A mixture of $\text{EtGeSiCo}_5(\text{CO})_{15}$ and $(\text{EtGe})_2\text{Co}_4(\text{CO})_{11}$ was obtained after extracting with ~ 4 ml of pentane/hexane. The latter seemed to be of lower concentration than the former and was estimated to be $\sim 0.002\text{g}$ (seemed to be less than in Run 1). Unlike Run 1, no indication of the " $\text{Et}_2\text{Ge}_2\text{SiCo}_6(\text{CO})_{17}$ " compound was observed.

The CH_2Cl_2 fraction consisted of entirely $\text{EtGeSiCo}_5(\text{CO})_{15}$.

The amount of EtGeH_3 used in the formation of $\text{EtGeSiCo}_5(\text{CO})_{15}$ and $(\text{EtGe})_2\text{Co}_4(\text{CO})_{11}$ was approximately 0.027 mmol.

Yield :

$\text{EtGeSiCo}_5(\text{CO})_{15}$ = 0.020g = 0.023 mmol = 16% yield

$(\text{EtGe})_2\text{Co}_4(\text{CO})_{11}$ $\approx$ 0.008g $\approx$ 0.011 mmol $\approx$ 8% yield

Hexane soluble mixture = 0.072g

* consisted of $\text{Et}_2\text{Ge}_2\text{Co}_4(\text{CO})_{14}$, $\text{EtGeCo}_3(\text{CO})_{11}$, $(\text{EtGe})_2\text{Co}_4(\text{CO})_{11}$ and possibly a very small amount of $\text{Co}_4(\text{CO})_{14}$ and $\text{SiCo}_4(\text{CO})_{13}$ in decreasing order.

Table 8.5 Infrared spectrum of the hexane soluble fraction of Run 2

Bands/int	Possible assignments
2110vw	$\text{EtGeCo}_3(\text{CO})_{11}?$
2100w	$\text{EtGeCo}_3(\text{CO})_{11} + \text{EtGeSiCo}_5(\text{CO})_{15}$
2090w sh	$\text{SiCo}_3(\text{CO})_{13}?$
2084m	$\text{Et}_2\text{Ge}_2\text{Co}_4(\text{CO})_{14}$
2078m	$\text{EtGeCo}_3(\text{CO})_{11}$
2070mw	$\text{EtGeSiCo}_5(\text{CO})_{15}$
2057mw sh	$(\text{EtGe})_2\text{Co}_4(\text{CO})_{11}$
2052m sh	$\text{EtGeCo}_3(\text{CO})_{11} + \text{Co}_4(\text{CO})_{12}?$
2039vs	$\text{Et}_2\text{Ge}_2\text{Co}_4(\text{CO})_{14} + \text{EtGeSiCo}_5(\text{CO})_{15}$
2032s sh	$(\text{EtGe})_2\text{Co}_4(\text{CO})_{11} + \text{SiCo}_4(\text{CO})_{13}?$
2017s sh	$\text{EtGeCo}_3(\text{CO})_{11} + \text{Et}_2\text{Ge}_2\text{Co}_4(\text{CO})_{14}$
2022s	$\text{Et}_2\text{Ge}_2\text{Co}_4(\text{CO})_{14}$
2012s	$(\text{EtGe})_2\text{Co}_4(\text{CO})_{11}?$
2005ms sh	$\text{EtGeCo}_3(\text{CO})_{11} + (\text{EtGe})_2\text{Co}_4(\text{CO})_{14}$
1993w sh	$\text{SiCo}_4(\text{CO})_{13}?$
1863w	$\text{Co}_4(\text{CO})_{12}?$
1846w br	$\text{EtGeCo}_3(\text{CO})_{11} + (\text{EtGe})_2\text{Co}_4(\text{CO})_{11}?$
1837w	$\text{EtGeCo}_3(\text{CO})_{11}$

Run 3 ($\text{MeGeH}_3 : \text{SiCo}_4(\text{CO})_{14} = 3.3 : 1$)

Like Runs 1 and 2, the colour of the reaction mixture changed from deep red to a purple red and then to a brown red after eight months of reaction. More orange red powder was observed to settle to the bottom of the ampoule.

Total incondensable gas = 0.377mmol, %H₂ = 23%, %Co = 77%

If the incondensable gas measurements were correct, only 0.058mmol (10.9% of the 0.532mmol) of MeGeH₃ was consumed. Therefore the SiCo₄(CO)₁₄ : MeGeH₃ reaction ratio is ~2.8 : 1. The volatile fraction showed the presence of MeGeH₃, but again this was difficult to measure due to the small amount.

The involatile solid consisted of a dark brown hexane soluble fraction and a reddish hexane insoluble/CH₂Cl₂ soluble fraction.

CH₂Cl₂ soluble fraction :

Unlike Runs 1 and 2, the CH₂Cl₂ fraction consisted of a mixture of compounds, the infrared spectrum and possible assignment is given in Table 8.6.

Table 8.6 Infrared spectrum of CH₂Cl₂ fraction

Bands	Int	Assignment (in CH ₂ Cl ₂)	
		MeGeSiCo ₅ (CO) ₁₅	Me ₃ Ge ₃ Co ₅ (CO) ₁₄
2105	w	2105mw	
2092	vw		2092mw
2073	w sh	2073mw	
2065	mw		2062ms
2036	vs	2036vs	
2017	s		2016vs
2015	s, sh	2015m	2010ms, sh
1850	w, br	1850w, br	

The solvent (CH₂Cl₂) was removed, and the solid was washed several times with 1-2 ml of pentane/hexane each time. Almost pure Me₃Ge₃Co₅(CO)₁₄ was extracted in the washings. Pure MeGeSiCo₅(CO)₁₅ remained behind (IR spectrum in Table 8.6).

Hexane fraction :

The infrared spectrum of the hexane soluble fraction was very poorly resolved in the 2040-2000 cm^{-1} region, the infrared spectrum and its possible assignment is given in Table 8.7.

Table 8.7 Infrared spectrum of the hexane soluble fraction of Run 3

Bands Int	P o s s i b l e a s s i g n m e n t s				
	1	2	3	4	5
2105 w					
2100 w	2102w	2097 w	2105 mw		
2090 w					2092 mw
2087 ms sh		2087 s			
2079 s	2079s				
2071 ms			2073 mw		
2065 ms sh		(2067 mw)			
2062 ms sh				2063 s	2062 ms
2052 s	2053s			2054 s	
2040 s sh		2039 s			
2036 s sh			2036 vs		
2028 vs sh	2029s	2029 s			
2022 vs sh	2020/5				2023 ms
2017 vs sh		2017 vs	2015 m		2016 vs
2001 mw sh			2002 mw	2000 m sh	(2010 ms sh)
1995 w		(1989)			1994 w
1865 vvw				1865w	
1848 w	1847 w		1850 w		
1837 w	1835 w				
1 = $\text{MeGeCo}_3(\text{CO})_{11}$ (7a), 2 = $\text{Me}_2\text{Ge}_2\text{Co}_4(\text{CO})_{14}$ (6), 3 = $\text{MeGeSiCo}_5(\text{CO})_{15}$ (1j), 4 = $\text{Co}_4(\text{CO})_{12}$, 5 = $\text{Me}_3\text{Ge}_3\text{Co}_5(\text{CO})_{14}$ (10a)					

Dark brown crystals of $\text{Me}_3\text{Ge}_3\text{Co}_5(\text{CO})_{14}$ and $\text{MeGeCo}_3(\text{CO})_{11}$ and a small amount of $\text{MeGeSiCo}_5(\text{CO})_{15}$ were obtained after a series of extractions and recrystallisations.

No $\text{SiCo}_4(\text{CO})_{13}$ was observed in both the CH_2Cl_2 and hexane fractions. This is consistent with the disappearance of the purple colour as the reaction progressed.

Approximate yield :

$\text{MeGeSiCo}_5(\text{CO})_{15} \approx 0.018\text{g} \approx 0.023 \text{ mmol} \approx 16\%$

$\text{Me}_3\text{Ge}_3\text{Co}_5(\text{CO})_{14} \approx 0.006\text{g} \approx 0.006 \text{ mmol} \approx 4\%$

Hexane mixture $\approx 0.073\text{g}$

* consisted of $\text{Me}_2\text{Ge}_2\text{Co}_4(\text{CO})_{14}$, $\text{MeGeCo}_3(\text{CO})_{11}$, $\text{Me}_3\text{Ge}_3\text{Co}_5(\text{CO})_{14}$, $\text{MeGeSiCo}_5(\text{CO})_{15}$ and possibly $\text{Co}_4(\text{CO})_{12}$ in decreasing order.

8.1.3 Characterisation of Products

Characterisation of $\text{EtGeSiCo}_5(\text{CO})_{15}$ and $\text{MeGeSiCo}_5(\text{CO})_{15}$

Infrared spectrum :

The infrared spectra of $\text{EtGeSiCo}_5(\text{CO})_{15}$ and $\text{MeGeSiCo}_5(\text{CO})_{15}$ are given in Table 8.8 and Figs 8.3 and 8.4. The infrared spectrum of $\text{RGeSiCo}_5(\text{CO})_{15}$ ($\text{R} = \text{Me}$ and Et) is very similar to that of $\text{MeGe}_2\text{Co}_5(\text{CO})_{15}$ (**1g**) (listed below for comparison). Of the fifteen (including one bridging carbonyl band) predicted bands, only six were observed. The solid state infrared spectrum of $\text{EtGeSiCo}_5(\text{CO})_{15}$ (Table 8.8 and Fig 8.5) showed considerably more detail : 13 out of the 15 predicted bands were observed.

A comparison and discussion of the infrared spectrum of $\text{RGeSiCo}_5(\text{CO})_{15}$ with all *closo*- type clusters is presented in Section 9.1 in Chapter Nine.

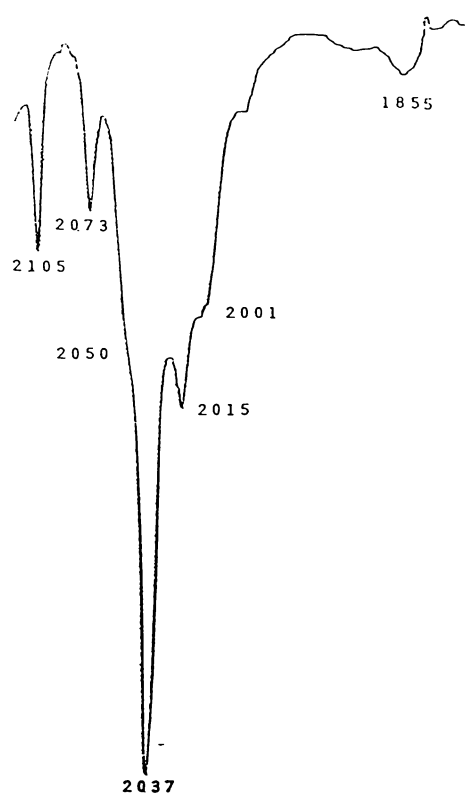


Fig 8.3 IR spectrum of $\text{EtGeSiCo}_5(\text{CO})_{15}$ in CH_2Cl_2

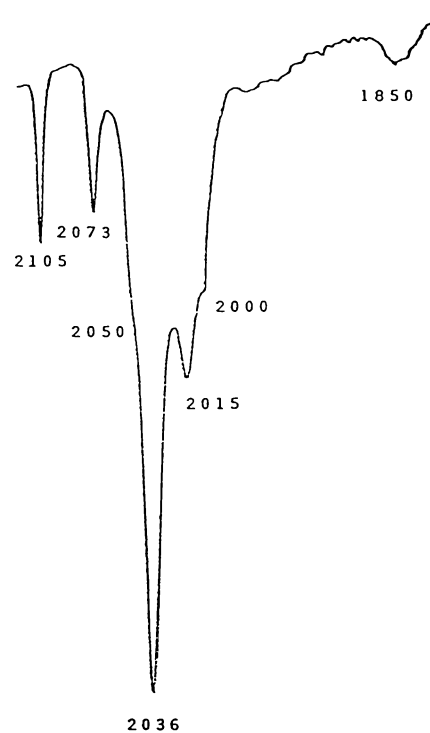


Fig 8.4 IR spectrum of $\text{MeGeSiCo}_5(\text{CO})_{15}$ in CH_2Cl_2

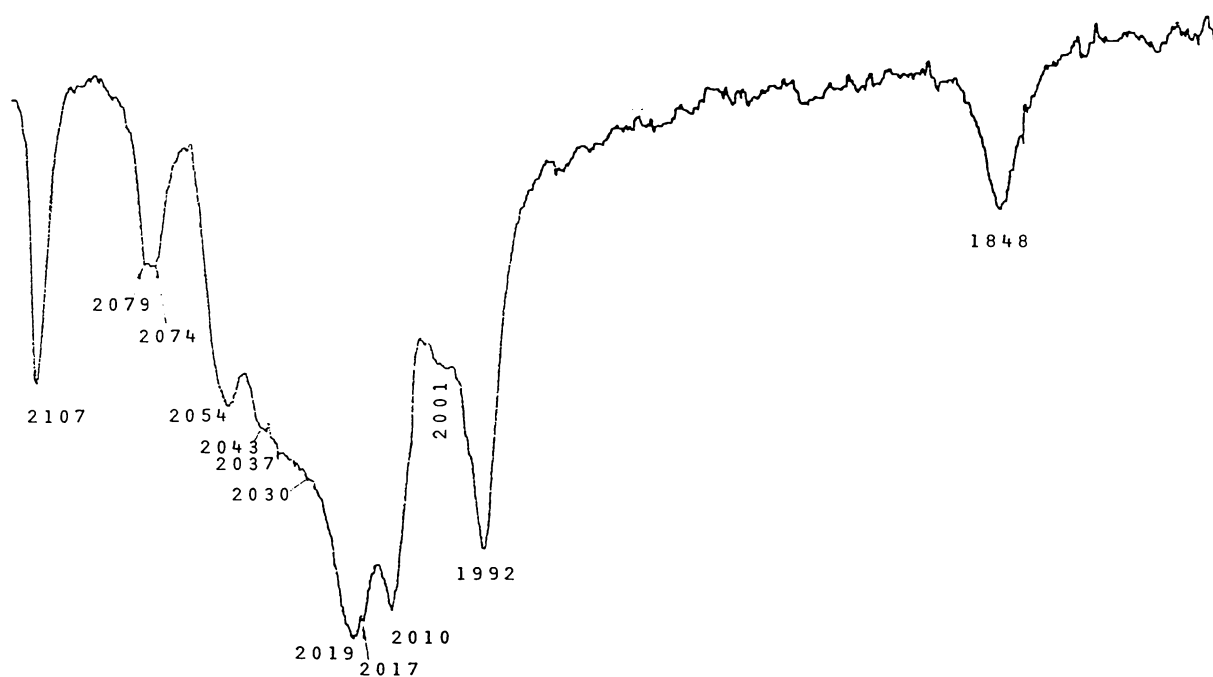


Fig 8.5 Solid phase IR spectrum of $\text{EtGeSiCo}_5(\text{CO})_{15}$ (CsI disc)

Table 8.8 infrared spectra of $\text{EtGeSiCo}_5(\text{CO})_{15}$ and $\text{MeGeSiCo}_5(\text{CO})_{15}$

$\text{EtGeSiCo}_5(\text{CO})_{15}$			$\text{MeGeSiCo}_5(\text{CO})_{15}$		$\text{MeGe}_2\text{Co}_5(\text{CO})_{15}$
Hexane	CH_2Cl_2	CsI	Hexane	CH_2Cl_2	CH_2Cl_2
2105mw	2105mw	2106m 2077mw	2105mw	2105mw	2106m
2072m	2073mw	2073mw 2054m	2073mw	2073mw	2067m
2050m sh	2050m sh	2052m 2043-1m sh	2050m sh	2050 m sh	2050m sh
2039vs	2037vs	2037m 2029ms sh 2018vs	2039vs	2036vs	2037vs
2014ms	2014ms	2016vs sh 2009vs	2015m	2015m	2013ms
2001m s	2001m sh	2001m sh 2000m sh 1991ms	2001m sh	2000m sh	2000m sh
1858w	1855w	1852mw	1858w	1850w	1841w

Mass spectrum :

The mass spectra of $\text{EtGeSiCo}_5(\text{CO})_{15}$ and $\text{MeGeSiCo}_5(\text{CO})_{15}$ are given in Tables 8.9 and 8.10. Neither compound showed a parent ion. The spectra were poor especially for the higher masses. As the mass spectrometer is known to be only reliable at low mass number (about 700 m/e and below), the higher envelopes were only tentatively assigned as $[\text{P}-n\text{CO}]^+$, but $[\text{P}-n\text{CO}+0]^+$ is also a possibility due to the well known high affinity of Si for oxygen. Except for the highest envelopes, both the mass spectra were very similar with $[\text{P}-n\text{CO}]^+$ as the predominate envelopes. The envelopes of m/e lower than 426 could be assigned to either $[\text{P}-15\text{CO}-\text{Et}-n\text{Co}]^+$ (n=0 to 3) or $[\text{P}-15\text{CO}-\text{Si}-n\text{Co}]^+$.

The occurrence of only one weak envelope of $[\text{P-15CO-Si}]^+$ in the mass spectrum of $\text{MeGeSiCo}_5(\text{CO})_{15}$ indicated that those envelopes in $\text{EtGeSiCo}_5(\text{CO})_{15}$ were likely to be due to those of $[\text{P-15CO-Et-nCo}]^+$.

Table 8.9 Mass spectrum of $\text{EtGeSiCo}_5(\text{CO})_{15}$

m/e	int	Possible assignments
775-783	ms	$[\text{P-3CO}+0]^+?$ or $[\text{P-2CO}]^+?$
750-760	w	$[\text{P-4CO}+0]^+?$
702-708	ms	$[\text{P-5CO}]^+$
678-682	vs	$[\text{P-6CO}]^+$
648-653	ms	$[\text{P-7CO}]^+$
622-627	m	$[\text{P-8CO}]^+$
591-596	mw	$[\text{P-9CO}]^+$
562-565	mw	$[\text{P-10CO}]^+$
533-538	mw	$[\text{P-11CO}]^+$
505-510	mw	$[\text{P-12CO}]^+$
478-482	mw	$[\text{P-13CO}]^+$
448-452	mw	$[\text{P-14CO}]^+$
422-426	mw	$[\text{P-15CO}]^+$
393-400	m	$[\text{P-15CO-Et}]^+$ or $[\text{P-15CO-Si}]^+$
383-400	m	$[\text{P-15CO-Et-Co}]^+$ or $[\text{P-15CO-Si-Co}]^+$
275-282	mw	$[\text{P-15CO-Et-2Co}]^+$ or $[\text{P-15CO-Si-2Co}]^+$
215-221	w	$[\text{P-15CO-Et-3Co}]^+$ or $[\text{P-15CO-Si-3Co}]^+$

Table 8.10 Mass spectrum of $\text{MeGeSiCo}_5(\text{CO})_{15}$

m/e	int	Possible assignments
790	vvw	$[\text{P-CO}]^+?$ or $[\text{P-2CO}+0]^+$
762-770	vvw	$[\text{P-2CO}]^+$
740-750	vw	$[\text{P-3CO}]^+$
715-720	vvw	$[\text{P-4CO}]^+$
689-696	mw	$[\text{P-5CO}]^+$
664-666	vs	$[\text{P-6CO}]^+$

Table 8.10 *cont'd...*

634-640 ms	[P-7CO] ⁺
608-612 mw	[P-8CO] ⁺
578-582 ms	[P-9CO] ⁺
548-552 mw	[P-10CO] ⁺
519-528 mw	[P-11CO] ⁺
490-498 mw	[P-12CO] ⁺
461-470 mw	[P-13CO] ⁺
438-441 mw	[P-14CO] ⁺
406-412 s	[P-15CO] ⁺
393-397 vvw	[P-15CO-Me] ⁺
379-381 vvw	[P-15CO-Si] ⁺
348-353 m	[P-15CO-Co] ⁺
332-340 w	[P-15CO-Me-Co] ⁺
289-294 w	[P-15CO-2Co] ⁺
272-280 mw	[P-15CO-Me-2Co] ⁺
230-235 vvw	[P-15CO-3Co] ⁺
217-220 w	[P-15CO-Me-3Co] ⁺

Electron probe analysis :

Two crystals of EtGeSiCo₅(CO)₁₅ were used in this analysis. The average Co : Ge : Si ratio is 5 : 1 : 1.09 which is very close to the expected value of 5 : 1 : 1.

*NMR spectrum :*Table 8.11 ¹H NMR in CDCl₃ at probe temperature of 27°C :

Compounds	Chemical shift (δ ppm)
MeGeSiCo ₅ (CO) ₁₅	2.42 (s)
EtGeSiCo ₅ (CO) ₁₅	2.00 (t, 3x), 3.45 (q, 2x)

The ^1H NMR spectra of $\text{MeGeSiCo}_5(\text{CO})_{15}$ (Table 8.11) showed a singlet at δ 2.42 ppm, and for $\text{EtGeSiCo}_5(\text{CO})_{15}$, a triplet at δ 2.00 ppm and a quartet at δ 3.45 ppm. The intensity ratio of t : q = 3 : 2 is as expected. A discussion of the chemical shifts of $(\text{RM}')_2\text{Co}_4(\text{CO})_{10}(\mu\text{-X})$ type compounds is found in Section 9.2, Chapter Nine.

8.1.4 Crystal structure of $\text{EtGeSiCo}_5(\text{CO})_{15}$

Experimental :

A pure CH_2Cl_2 solution of $\text{EtGeSiCo}_5(\text{CO})_{15}$ was concentrated, topped with hexane and placed in a freezer overnight. Dark red hexagonal needles were obtained. A crystal of approximate dimensions 0.1 x 0.1 x 0.3 mm was mounted with Araldite on a glass fibre for preliminary investigation.

Preliminary studies and Data collection :

Preliminary precession photography using Ni filtered $\text{Cu-K}\alpha$ X-radiation indicated the crystal to be in a primitive monoclinic space group. Inspection of the data set showed systematic absences consistent with space group $\text{P}2_1/\text{c}$, with $Z = 4$. The intensity data and refined lattice parameters were collected at the University of Auckland using an Enraf Nonius CAD4 diffractometer. The cell parameters were calculated using Zr-filtered $\text{Mo-K}\alpha$ X-rays from 25 high angle reflections. The crystal data is given in Table 8.12.

Table 8.12 Crystal data of $\text{EtGeSiCo}_5(\text{CO})_{15}$:

 Formula : $\text{C}_{17}\text{H}_5\text{O}_{15}\text{SiGeCo}_5$

Mr : 844.6

Monoclinic, space group = $\text{P2}_1/\text{c}$ $a = 9.443(3)\text{\AA}$, $b = 14.707(2)\text{\AA}$, $c = 18.748(2)\text{\AA}$ $\beta = 93.54(1)^\circ$ Volume = $2598.896(4)\text{\AA}^3$ $D_{\text{calc}} = 2.16 \text{ g/cm}^3$ $Z = 4$ $F(000) = 1632$, $\mu(\text{MoK}\alpha) = 42\text{cm}^{-1}$, $T = 292\text{K}$

A total of 5083 reflexions in the range of $1^\circ \leq \theta \leq 30^\circ$ were collected. This corresponded to 3920 unique reflexions of which 2851 had $F^2 > 2\sigma F^2$ and were used for all calculations. The data were corrected for Lorentz and Polarisation effects, linear absorption and for decomposition effects.

Solution and Refinement :

The seven metal atoms were located using the TREF Routine of SHELXS86. These coordinates were used in the SHELX76 program. All 15 unique CO's and the two ethyl carbons were located in the subsequent difference maps. In the final cycles of least squares refinement, the hydrogens were included in calculated positions and all non-hydrogen atoms were assigned anisotropic temperature factors. The refinement converged with $R = 0.0315$, $R_w = 0.0345$ where $w = 0.7303/(\sigma^2(F) + 0.0001076F^2)$. No non-hydrogen parameter shifted by more than 0.517 times its standard deviation and a final difference map showed no residual electron density greater than $0.48\text{e}\text{\AA}^{-3}$.

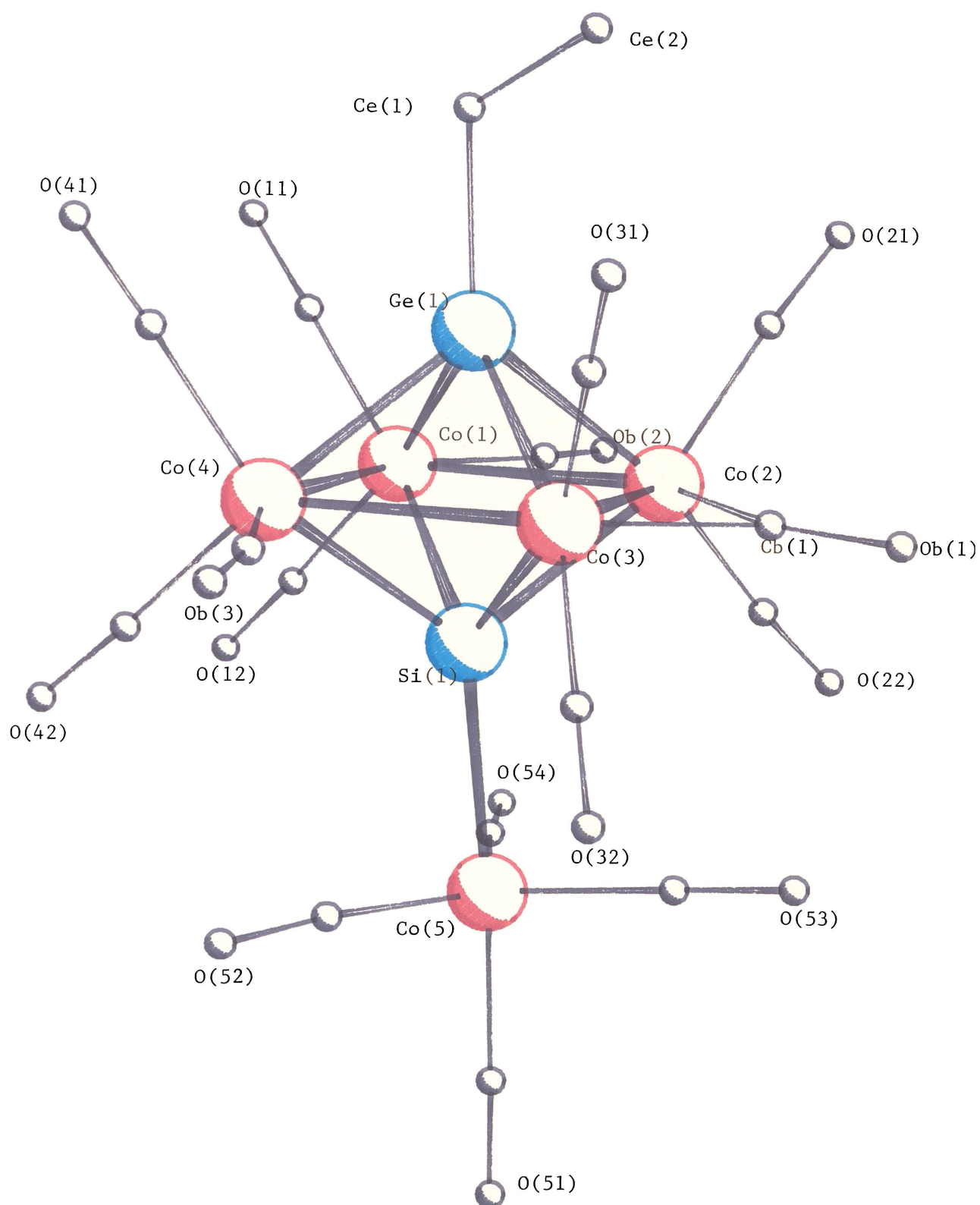


Fig 8.6 Crystal structure of $\text{EtGeSiCo}_5(\text{CO})_{15}$

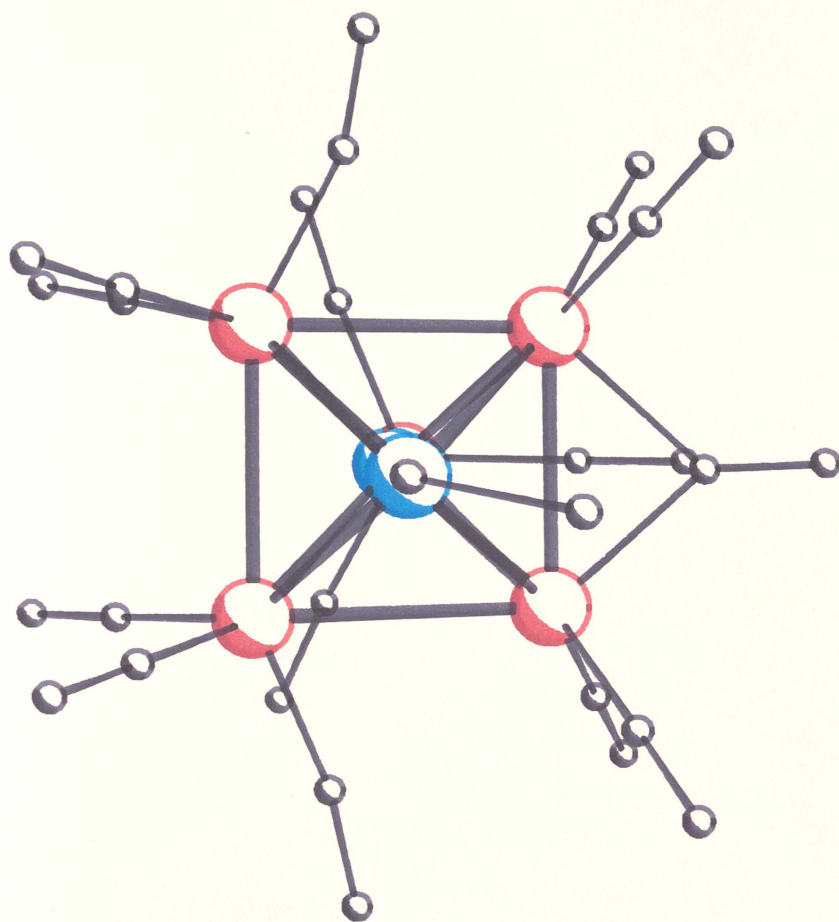


Fig 8.7a View of $\text{EtGeSiCo}_5(\text{CO})_{15}$ through Ge(1), Si(1) and Co(5)

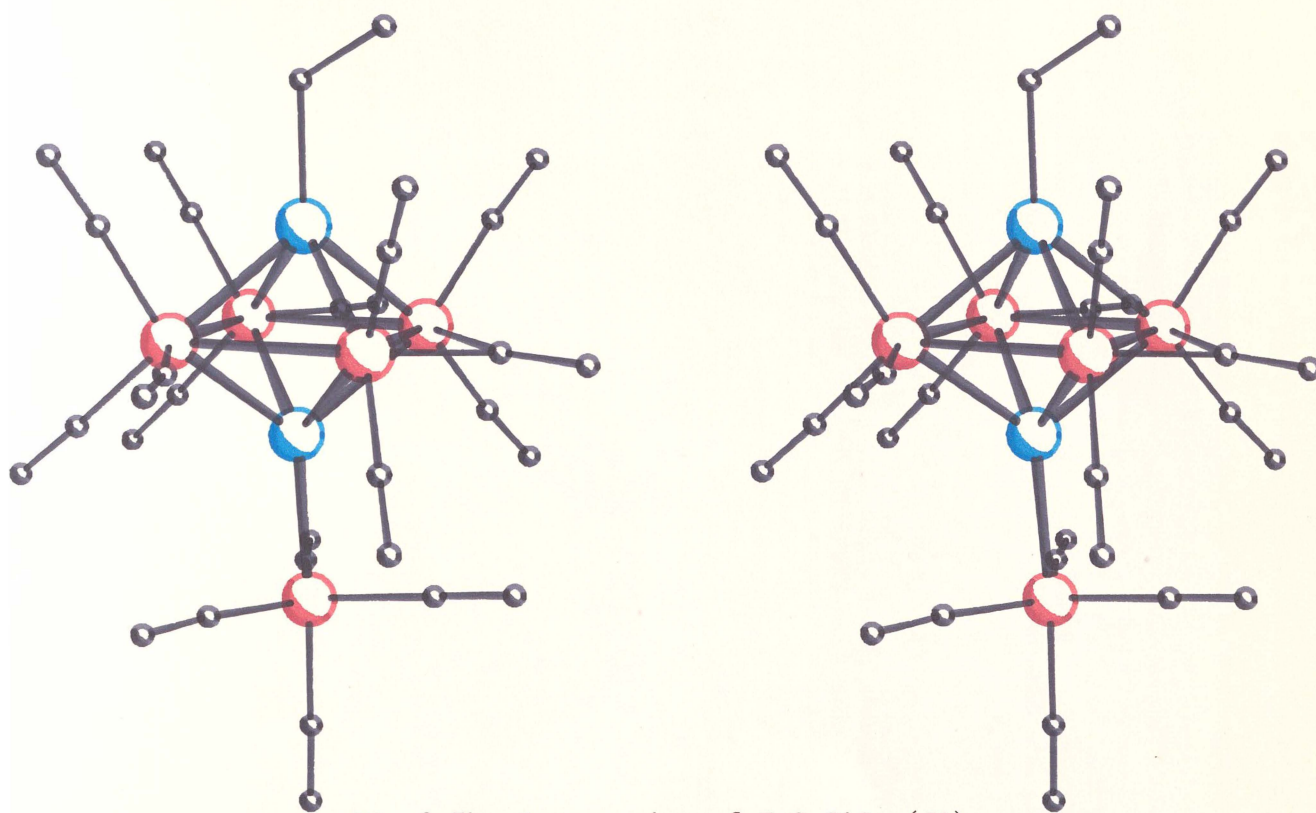


Fig 8.7b Stereo view of $\text{EtGeSiCo}_5(\text{CO})_{15}$

Discussion of the Structure :

Diagrams of the full molecule are given in Fig 8.6 and 8.7, tables of bond lengths are given in Table 8.13, bond angles are in Table 8.14 and the final positional parameters are given in Appendix 7. The structure factors are retained by the University of Waikato.

Table 8.13 Bond Lengths (Å) of EtGeSiCo₅(CO)₁₅

Ge(1) ---Co(1)	2.394(1)	Co(4) ---C(41)	1.804(7)
Ge(1) ---Co(2)	2.374(1)	Co(4) ---C(42)	1.802(8)
Ge(1) ---Co(3)	2.368(1)	Co(4) ---Cb(3)	1.77(1)
Ge(1) ---Co(4)	2.396(1)	Co(5) ---C(51)	1.826(7)
Ge(1) ---Ce(1)	1.965(6)	Co(5) ---C(52)	1.769(8)
Si(1) ---Co(1)	2.345(2)	Co(5) ---C(53)	1.814(8)
Si(1) ---Co(2)	2.345(2)	Co(5) ---C(54)	1.810(8)
Si(1) ---Co(3)	2.331(2)	C(11) ---O(11)	1.138(8)
Si(1) ---Co(4)	2.357(2)	C(12) ---O(12)	1.141(7)
Si(1) ---Co(5)	2.357(2)	C(21) ---O(21)	1.118(7)
Co(1) ---Co(2)	2.668(1)	C(22) ---O(22)	1.132(7)
Co(1) ---Co(4)	2.697(1)	C(31) ---O(31)	1.124(8)
Co(1) ---C(11)	1.799(7)	C(32) ---O(32)	1.135(8)
Co(1) ---C(12)	1.785(7)	C(41) ---O(41)	1.142(8)
Co(1) ---Cb(2)	1.787(8)	C(42) ---O(42)	1.125(8)
Co(2) ---Co(3)	2.581(1)	C(51) ---O(51)	1.099(8)
Co(2) ---C(21)	1.819(7)	C(52) ---O(52)	1.156(9)
Co(2) ---C(22)	1.790(7)	C(53) ---O(53)	1.124(8)
Co(2) ---Cb(1)	1.959(6)	C(54) ---O(54)	1.126(8)
Co(2) ---Cb(2)	2.440(7)	Cb(1) ---Ob(1)	1.156(7)
Co(3) ---Co(4)	2.696(1)	Cb(2) ---Ob(2)	1.131(8)
Co(3) ---C(31)	1.809(8)	Cb(3) ---Ob(3)	1.13(1)
Co(3) ---C(32)	1.796(8)	Ce(1) ---Ce(2)	1.47(1)
Co(3) ---Cb(1)	1.904(7)		

Table 8.14 Bond Angles (°) of EtGeSiCo₅(CO)₁₅

Co(1)-Ge(1)-Co(2)	68.00(0)	Co(4)-Co(1)-C(12)	98.6(2)
Co(1)-Ge(1)-Co(3)	103.90(0)	Co(4)-Co(1)-Cb(2)	152.1(2)
Co(1)-Ge(1)-Co(4)	68.50(0)	C(11)-Co(1)-C(12)	98.7(3)
Co(1)-Ge(1)-Ce(1)	124.1(3)	C(11)-Co(1)-Cb(2)	99.4(3)
Co(2)-Ge(1)-Co(3)	65.90(0)	C(12)-Co(1)-Cb(2)	99.7(3)
Co(2)-Ge(1)-Co(4)	104.60(0)	Ge(1)-Co(2)-Si(1)	74.60(0)
Co(2)-Ge(1)-Ce(1)	128.7(2)	Ge(1)-Co(2)-Co(1)	56.30(0)
Co(3)-Ge(1)-Co(4)	68.90(0)	Ge(1)-Co(2)-Co(3)	56.90(0)
Co(3)-Ge(1)-Ce(1)	132.0(3)	Ge(1)-Co(2)-C(21)	88.9(2)
Co(4)-Ge(1)-Ce(1)	126.6(2)	Ge(1)-Co(2)-C(22)	166.8(2)
Co(1)-Si(1)-Co(2)	69.3(1)	Ge(1)-Co(2)-Cb(1)	94.3(2)
Co(1)-Si(1)-Co(3)	106.7(1)	Ge(1)-Co(2)-Cb(2)	87.5(2)
Co(1)-Si(1)-Co(4)	70.0(1)	Si(1)-Co(2)-Co(1)	55.30(0)
Co(1)-Si(1)-Co(5)	130.1(1)	Si(1)-Co(2)-Co(3)	56.20(0)
Co(2)-Si(1)-Co(3)	67.00(0)	Si(1)-Co(2)-C(21)	162.8(2)
Co(2)-Si(1)-Co(4)	106.7(1)	Si(1)-Co(2)-C(22)	94.6(2)
Co(2)-Si(1)-Co(5)	122.4(1)	Si(1)-Co(2)-Cb(1)	91.0(2)
Co(3)-Si(1)-Co(4)	70.2(1)	Si(1)-Co(2)-Cb(2)	85.7(2)
Co(3)-Si(1)-Co(5)	122.8(1)	Co(1)-Co(2)-Co(3)	91.20(0)
Co(4)-Si(1)-Co(5)	130.5(1)	Co(1)-Co(2)-C(21)	111.3(2)
Ge(1)-Co(1)-Si(1)	74.30(0)	Co(1)-Co(2)-C(22)	111.3(2)
Ge(1)-Co(1)-Co(2)	55.60(0)	Co(1)-Co(2)-Cb(1)	138.2(2)
Ge(1)-Co(1)-Co(4)	55.80(0)	Co(1)-Co(2)-Cb(2)	40.7(2)
Ge(1)-Co(1)-C(11)	85.5(2)	Co(3)-Co(2)-C(21)	118.6(2)
Ge(1)-Co(1)-C(12)	154.4(2)	Co(3)-Co(2)-C(22)	123.4(2)
Ge(1)-Co(1)-Cb(2)	104.6(2)	Co(3)-Co(2)-Cb(1)	47.2(2)
Si(1)-Co(1)-Co(2)	55.30(0)	Co(3)-Co(2)-Cb(2)	131.8(2)
Si(1)-Co(1)-Co(4)	55.20(0)	C(21)-Co(2)-C(22)	100.9(3)
Si(1)-Co(1)-C(11)	152.8(3)	C(21)-Co(2)-Cb(1)	95.3(3)
Si(1)-Co(1)-C(12)	92.4(2)	C(21)-Co(2)-Cb(2)	88.6(2)
Si(1)-Co(1)-Cb(2)	103.2(2)	C(22)-Co(2)-Cb(1)	93.6(3)
Co(2)-Co(1)-Co(4)	89.40(0)	C(22)-Co(2)-Cb(2)	84.0(3)
Co(2)-Co(1)-C(11)	125.9(2)	Cb(1)-Co(2)-Cb(2)	175.7(2)
Co(2)-Co(1)-C(12)	133.1(2)	Ge(1)-Co(3)-Si(1)	75.00(0)
Co(2)-Co(1)-Cb(2)	62.8(2)	Ge(1)-Co(3)-Co(2)	57.20(0)
Co(4)-Co(1)-C(11)	98.3(2)	Ge(1)-Co(3)-Co(4)	56.00(0)
Ge(1)-Co(3)-C(31)	89.3(2)	Co(3)-Co(4)-Cb(3)	68.9(3)

Table 8.14 *cont'd...*

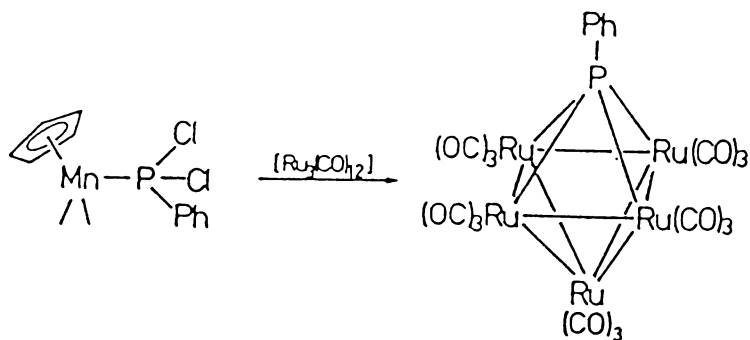
Ge(1)-Co(3)-C(32)	163.6(2)	C(41)-Co(4)-C(42)	100.5(3)
Ge(1)-Co(3)-Cb(1)	96.0(2)	C(41)-Co(4)-Cb(3)	98.8(4)
Si(1)-Co(3)-Co(2)	56.80(0)	C(42)-Co(4)-Cb(3)	100.5(4)
Si(1)-Co(3)-Co(4)	55.40(0)	Si(1)-Co(5)-C(51)	176.6(3)
Si(1)-Co(3)-C(31)	161.7(2)	Si(1)-Co(5)-C(52)	84.9(2)
Si(1)-Co(3)-C(32)	92.6(2)	Si(1)-Co(5)-C(53)	88.0(2)
Si(1)-Co(3)-Cb(1)	92.8(2)	Si(1)-Co(5)-C(54)	85.4(2)
Co(2)-Co(3)-Co(4)	91.30(0)	C(51)-Co(5)-C(52)	92.3(3)
Co(2)-Co(3)-C(31)	122.1(3)	C(51)-Co(5)-C(53)	95.0(3)
Co(2)-Co(3)-C(32)	124.8(2)	C(51)-Co(5)-C(54)	94.9(3)
Co(2)-Co(3)-Cb(1)	49.0(2)	C(52)-Co(5)-C(53)	116.8(3)
Co(4)-Co(3)-C(31)	108.0(2)	C(52)-Co(5)-C(54)	128.7(3)
Co(4)-Co(3)-C(32)	108.1(2)	C(53)-Co(5)-C(54)	113.1(3)
Co(4)-Co(3)-Cb(1)	140.1(2)	Co(1)-C(11)-O(11)	177.3(7)
C(31)-Co(3)-C(32)	100.7(3)	Co(1)-C(12)-O(12)	177.2(6)
C(31)-Co(3)-Cb(1)	98.3(3)	Co(2)-C(21)-O(21)	175.0(6)
C(32)-Co(3)-Cb(1)	95.4(3)	Co(2)-C(22)-O(22)	175.1(6)
Ge(1)-Co(4)-Si(1)	74.00(0)	Co(3)-C(31)-O(31)	176.0(7)
Ge(1)-Co(4)-Co(1)	55.70(0)	Co(3)-C(32)-O(32)	176.4(6)
Ge(1)-Co(4)-Co(3)	55.00(0)	Co(4)-C(41)-O(41)	177.6(6)
Ge(1)-Co(4)-C(41)	81.9(2)	Co(4)-C(42)-O(42)	177.0(8)
Ge(1)-Co(4)-C(42)	148.2(3)	Co(5)-C(51)-O(51)	177.6(8)
Ge(1)-Co(4)-Cb(3)	110.5(3)	Co(5)-C(52)-O(52)	174.9(7)
Si(1)-Co(4)-Co(1)	54.80(0)	Co(5)-C(53)-O(53)	179.0(6)
Si(1)-Co(4)-Co(3)	54.40(0)	Co(5)-C(54)-O(54)	174.8(7)
Si(1)-Co(4)-C(41)	150.7(2)	Co(2)-Cb(1)-Co(3)	83.8(2)
Si(1)-Co(4)-C(42)	91.7(2)	Co(2)-Cb(1)-Ob(1)	135.5(6)
Si(1)-Co(4)-Cb(3)	105.1(3)	Co(3)-Cb(1)-Ob(1)	140.7(6)
Co(1)-Co(4)-Co(3)	88.10(0)	Co(1)-Cb(2)-Co(2)	76.5(3)
Co(1)-Co(4)-C(41)	97.8(2)	Co(1)-Cb(2)-Ob(2)	162.1(6)
Co(1)-Co(4)-C(42)	92.7(3)	Co(2)-Cb(2)-Ob(2)	121.3(5)
Co(1)-Co(4)-Cb(3)	156.5(3)	Co(4)-Cb(3)-Ob(3)	169.6(8)
Co(3)-Co(4)-C(41)	122.4(2)	Ge(1)-Ce(1)-Ce(2)	115.5(6)
Co(3)-Co(4)-C(42)	136.6(2)		

Table 8.14 *cont'd...*

Dihedral angles (°)

Co(1)-Co(2)-Co(3)-Co(4) to Ob(1)-Cb(1)-Co(2)-Co(3)	4.42(9)
Co(1)-Co(2)-Co(3)-Co(4) to Ge(1)-Co(1)-Co(2)	132.23(2)
Co(1)-Co(2)-Co(3)-Co(4) to Ge(1)-Co(3)-Co(2)	132.65(2)
Co(1)-Co(2)-Co(3)-Co(4) to Ge(1)-Co(3)-Co(4)	131.85(3)
Co(1)-Co(2)-Co(3)-Co(4) to Ge(1)-Co(1)-Co(4)	132.36(3)
Co(1)-Co(2)-Co(3)-Co(4) to Si(1)-Co(1)-Co(2)	133.51(4)
Co(1)-Co(2)-Co(3)-Co(4) to Si(1)-Co(1)-Co(2)	134.17(4)
Co(1)-Co(2)-Co(3)-Co(4) to Si(1)-Co(1)-Co(2)	133.14(3)
Co(1)-Co(2)-Co(3)-Co(4) to Si(1)-Co(1)-Co(2)	133.40(4)
Ob(1)-Cb(1)-Co(2) to Si(1)-Co(2)-Co(3)	129.75(9)
Ob(1)-Cb(1)-Co(2) to Ge(1)-Co(2)-Co(3)	137.06(9)

$\text{EtGeSiCo}_5(\text{CO})_{15}$ can be considered as an ethyl analogue of $\text{MeGe}_2\text{Co}_5(\text{CO})_{15}$ except that the apical $\text{Co}(\text{CO})_4$ group is attached to a Si atom instead of to a Ge atom (compare Fig 8.6 and Fig 7.6). No *clos*o-hexanuclear cluster with different $\mu_4\text{-E}$ groups on both ends is known to date. However, a cluster with a EM_5 skeleton, $(\mu_4\text{-PhP})\text{Ru}_4(\text{CO})_{12}(\mu_4\text{-Ru}(\text{CO})_3)$ (Fig 8.8) has been reported [100,159]. The 5th transition metal atom, Ru acts as the second capping group. $\text{EtGeSiCo}_5(\text{CO})_{15}$ is the first Group IVB-Co cluster to incorporate both Si and Ge (both E atoms) within the structure.

Fig 8.8 $(\mu_4\text{-PhP})\text{Ru}_4(\text{CO})_{12}(\mu_4\text{-Ru}(\text{CO})_3)$

The metallic $\text{Co}_4(\text{CO})_{11}$ core is very similar to that of $\text{MeGe}_2\text{Co}_5(\text{CO})_{15}$ and consists of a distorted square planar array of cobalts, quadruply bridged by a Ge on one side and a Si on the other end. The Si---Ge distance (2.862Å) is the average of the Si---Si distance in $\text{Si}_2\text{Co}_6(\text{CO})_{19}$ (1d) (2.817Å) and that of the Ge---Ge distance in $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ (2.926Å). It is less than the sum of the Van der Waals radii of Si and Ge (~4.2Å), but significantly longer than would be expected for a Si-Ge bond (Si-Ge = 2.357Å in H_3SiGeH_3 [153], Si-Si = 2.32Å in Si_2H_6 [154], Ge-Ge = 2.41Å in Ge_2H_6 [155]). This short M'---M' distance is common in all such types of compounds (see Table 9.6).

M'-Co bonds :

The presence of Si and Ge resulted in a significant difference (17x e.s.d) in the M'-Co bond on either sides of the Co_4 plane. The average Ge-Co distance (2.383(1)Å) is slightly shorter than that of $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ (2.390(2)Å) while the average Si-Co bond length (2.345(2)Å) is slightly longer than that of $\text{Si}_2\text{Co}_6(\text{CO})_{19}$ (2.337(2)Å). A shortening of Ge-Co bond compensated by a lengthening in the Si-Co bond seems to have occurred. The two M' atoms seem to be inclined towards the cobalts containing the fully bridging CO. This is more fully discussed in Section 9.3. The Si- $\text{Co}_{(\text{apical})}$ bond (2.357(2)Å) is again slightly longer than the corresponding bond in $\text{Si}_2\text{Co}_6(\text{CO})_{19}$ (2.347(2)Å).

Co-Co bonds of the Co_4 plane :

Like $\text{MeGe}_2\text{Co}_5(\text{CO})_{15}$, the Co-Co bond length of the central square Co_4 plane is directly related to the degree of bridging (see Fig 8.9). The higher the degree of bridging, the shorter the bond. Therefore the

shortest Co-Co bond is the one that is fully bridged ($2.581(1)\text{\AA}$), the longest is the one without any bridging CO ($2.697(1)\text{\AA}$) and the one carrying the semi-bridging CO has intermediate bond length ($2.668(1)\text{\AA}$). The other Co-Co bond (Co(3)-Co(4)) carrying the second semi-bridging CO is longer than expected ($2.696(1)\text{\AA}$) essentially the same as for the non bridging Co-Co bond. This is due to the presence of the CO which is involved in only a small degree of bridging (Co(4)-C(3B) = $1.773\text{\AA}$ and Co(3)-C(3B) = $2.639\text{\AA}$).

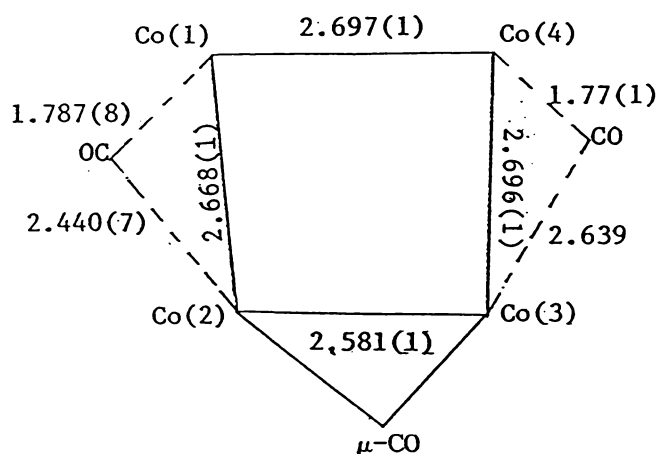


Fig 8.9 Co-Co bonds in $\text{EtGeSiCo}_5(\text{CO})_{15}$

Co-CO bonds :

Like $\text{MeGe}_2\text{Co}_5(\text{CO})_{15}$, the fully bridging CO is asymmetrically bonded to the two Co atoms (Co(2) and Co(3)). It is slightly off the Co_4 plane ($4.42(9)^\circ$) and is inclined towards the Si atom ($\text{Si}-\mu\text{-CO} = 3.081\text{\AA}$, $\text{Ge}-\mu\text{-CO} = 3.189\text{\AA}$, dihedral angle between $\text{Ob}(1)\text{-Cb}(1)\text{-Co}(2)$ and $\text{Si}(1)\text{-Co}(2)\text{-Co}(3) = 129.75(9)^\circ$ and that between $\text{Ob}(1)\text{-Cb}(1)\text{-Co}(2)$ and $\text{Ge}(1)\text{-Co}(2)\text{-Co}(3) = 137.06(9)^\circ$). The Co-C and C-O distances of the terminal CO's (including those on the apical $\text{Co}(\text{CO})_4$) are within the ranges found in this type of compounds (see Table 9.6). The Co-C bonds

on the Ge side average 1.805(7)Å while those on the Si side average (1.793(7)Å).

Ge-C and C-C distances (of the ethyl group) :

The Ge-C distances of 1.965Å appear to be in the range for normal carbon σ bonds (Ge-C in EtGeH₃ = 1.95Å [11], but the C-C distance of the ethyl group (1.47(1)Å) is slightly shorter than that in C₂H₆ (1.53Å) [157]).

Positioning of the terminal CO's :

The Ge-Co-C angles ranged from 81.9 to 89.3° while the Si-Co-C angles from 91.7 to 92.4°. This is expected as the terminal CO's are in closer proximity to those on the apical SiCo(CO)₄ group because of the shorter Si-Co bonds. The wider Si-Co-C angles reduce steric interactions between the two groups of CO's.

As for MeGe₂Co₅(CO)₁₅, Si₂Co₆(CO)₁₉ and Ge₂Co₆(CO)₁₉, the equatorial CO's in the apical SiCo(CO)₄ group are displaced towards the Si atom.

8.1.5 Discussion :

Of the reaction :

The reaction of RGeH₃ with GeCo₄(CO)₁₄ (R = Me, Et and Ph), discussed in Chapter Five produced either (RGeH)GeCo₄(CO)₁₃ and/or (RGeH)₂GeCo₄(CO)₁₂ depending on the reaction conditions. The reaction of RGeH₃ with SiCo₄(CO)₁₄ however did not produce analogous results. A number of products were formed, among them RGeSiCo₅(CO)₁₅ (*1j,1k*), RGeCo₃(CO)₁₁ (*7*), R₂Ge₂Co₄(CO)₁₄ (*6*), (RGe)₂Co₄(CO)₁₁ (*1l*) and possibly Co₄(CO)₁₂ and SiCo₄(CO)₁₃. A trace amount of a "Et₂Ge₂SiCo₆(CO)₁₇" like compound (*11*) was observed in Run 1 while a

small amount of $\text{Me}_3\text{Ge}_3\text{Co}_5(\text{CO})_{14}$ (*10a*) was isolated in Run 3. $\text{RGeSiCo}_5(\text{CO})_{15}$ was the only product that could be isolated easily due to its lower solubility in hexane.

The following data are obtained from the incondensable gas measurement :

Total mmole gas	$\text{SiCo}_4(\text{CO})_{14} : \text{EtGeH}_3$	mmole CO	$\text{CO}/\text{SiCo}_4(\text{CO})_{14}$
0.42	2.8 : 1	0.265	0.92/1
0.358	2.5 : 1	0.265	1.82/1
0.377	2.8 : 1	0.290	1.79/1

The actual $\text{SiCo}_4(\text{CO})_{14} : \text{EtGeH}_3$ reactant ratio was consistently about 2.5 : 1. But the moles of CO evolved per mole $\text{SiCo}_4(\text{CO})_{14}$ in Run 1 was only half that of the other two runs. The lower $\text{CO}/\text{SiCo}_4(\text{CO})_{14}$ evolution in Run 1 may be due to the shorter reaction time (five months) compared to the other two runs (eight months) and the larger quantity of reactants used, therefore higher gas build-up. As at least six products were formed and most of them inseparable, it was difficult to analyse the above data more quantitatively. Of these products, $\text{EtGeSiCo}_5(\text{CO})_{15}$ was characterised by spectroscopic and crystallographic means. The rest were characterised by infrared spectra only.

The reaction of $\text{SiCo}_4(\text{CO})_{14}$ with RGeH_3 is indeed very different from that the corresponding reaction of $\text{GeCo}_4(\text{CO})_{14}$. This may be explained in terms of the crystal structures of the two molecules [78,16]. In $\text{SiCo}_4(\text{CO})_{14}$, the smaller Si atom resulted in an increase of terminal O---O interactions. To minimise these interactions, the SiCo_2 triangles were therefore twisted to a dihedral angle of 80.92°

(compare $\sim 84^\circ$ in $\text{GeCo}_4(\text{CO})_{14}$). The relative sizes of the Si and Ge atoms also account for the smaller $\text{SiCo(1)Co(2)/Co(1)Co(2)C(B1)}$ dihedral angle of 99.08° compare with the germanium analogue of 107° . The crystal structures of the two compounds indicate that $\text{SiCo}_4(\text{CO})_{14}$ is more strained of the two molecules. Therefore, an attack on the Co-Co bond by Ge-H in $\text{SiCo}_4(\text{CO})_{14}$ may lead to the breaking up of bonds forming smaller $\text{Co}(\text{CO})_4$ fragments such as $\text{HCo}(\text{CO})_4$, $\text{Co}_2(\text{CO})_8$ or $\text{Co}_4(\text{CO})_{12}$. It was difficult to detect the presence of $\text{HCo}(\text{CO})_4$ formed in the volatiles because of its low stability. Its strong infrared bands fall in the same positions as the RGeH_3 bands. Mass balance of all three runs did not indicate any appreciable loss of cobalt as $\text{HCo}(\text{CO})_4$. No $\text{Co}_2(\text{CO})_8$ was observed in all three runs, but a very small amount of $\text{Co}_4(\text{CO})_{12}$ was formed in Runs 2 and 3 (see Tables 8.5 and 8.7). This however does not rule out the possibility of the existence of $\text{Co}_2(\text{CO})_8$ as it could have decarbonylated into $\text{Co}_4(\text{CO})_{12}$, or reacted further as soon as it was formed.

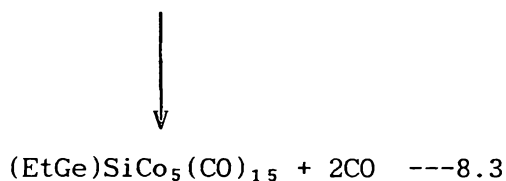
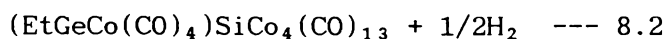
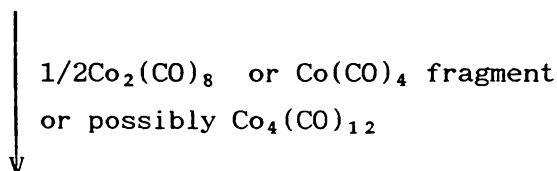
The colour of the reaction at the initial stage was purple. This suggested that $\text{SiCo}_4(\text{CO})_{14}$ might have decarbonylated to $\text{SiCo}_4(\text{CO})_{13}$, therefore the reaction was left to continue until obvious changes were observed. This colour faded with time and a red brown was observed after four months. It is unclear if $\text{SiCo}_4(\text{CO})_{13}$ then reacted with RGeH_3 to form some of the products and $\text{HCo}(\text{CO})_4$.

The paragraphs that follow are an attempt to explain the formation of the products obtained based on the weak bonds in the strained molecule of $\text{SiCo}_4(\text{CO})_{14}$. However, studies have also shown that there is a general tendency for $\text{R}_3\text{M}'$ groups bonded to transition metals to be displaced in the series :



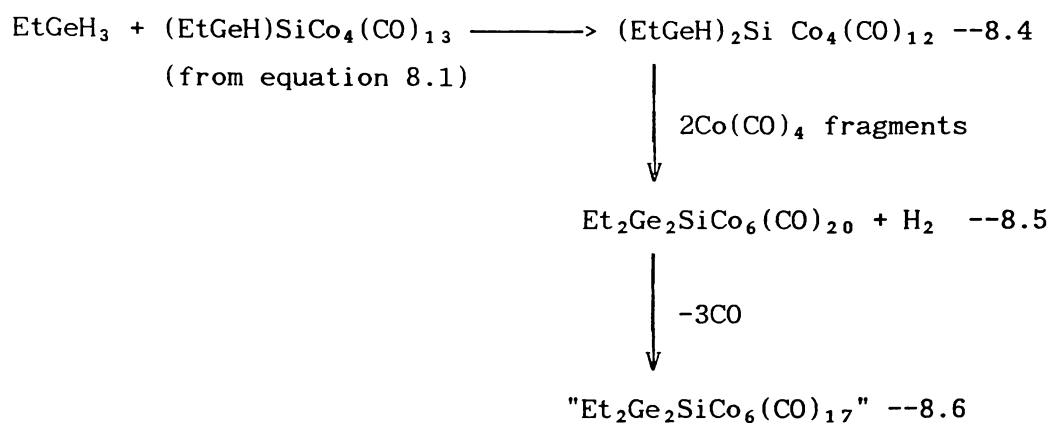
In one study, Me_3SnH gave 75% $[(\text{Me}_3\text{Sn})_2\text{Ru}(\text{CO})_4]$ when reacted with $[(\text{Me}_3\text{Ge})_2\text{Ru}(\text{CO})_4]$ [6,158]. Therefore, there is a possibility that some of the products formed in the RGeH_3 and $\text{SiCo}_4(\text{CO})_{14}$ reaction may have been formed by the replacement of Si by Ge.

The mechanism of the formation of $\text{RGeSiCo}_5(\text{CO})_{15}$ has not been studied, but a possible pathway is proposed in equations 8.1 to 8.3. The formation of $(\text{EtGe})\text{SiCo}_5(\text{CO})_{15}$ (or $[(\text{EtGe})\text{Co}_4(\text{CO})_{11}\{\text{SiCo}(\text{CO})_4\}]$) required that $\text{SiCo}_4(\text{CO})_{14}$ to stay intact at least in the initial stage of the reaction (equation 8.1) forming $(\text{RGeH})\text{SiCo}_4(\text{CO})_{13}$ (not detected among the products). The formation of $\text{RGeSiCo}_5(\text{CO})_{15}$ from $(\text{RGeH})\text{SiCo}_4(\text{CO})_{13}$ was probably analogous to the formation of $\text{MeGe}_2\text{Co}_5(\text{CO})_{15}$ from the reaction of $(\text{MeGeH})\text{GeCo}_4(\text{CO})_{13}$ with $\text{Co}_2(\text{CO})_8$ (in Chapter Seven).



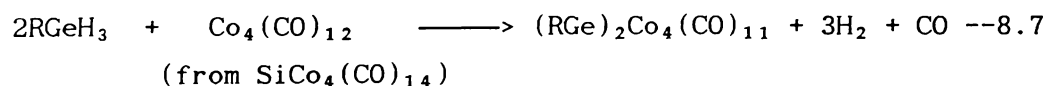
However, the observation of a purple colour at the initial stage of the reaction may indicate that $\text{SiCo}_4(\text{CO})_{14}$ in equation 8.1 may actually be its decarbonylated product, $\text{SiCo}_4(\text{CO})_{13}$. Reaction of $\text{SiCo}_4(\text{CO})_{13}$ with RGeH_3 would explain for its disappearance as reaction proceeded. This of course is only speculative and a more definite proof is required.

It is quite interesting to note that " $\text{Et}_2\text{Ge}_2\text{SiCo}_6(\text{CO})_{17}$ " compound similar to Ge was being observed in the infrared spectrum of one of the washings of the hexane soluble fraction (appeared after $\text{EtGeCo}_3(\text{CO})_{11}$, $\text{Et}_2\text{Ge}_2\text{Co}_4(\text{CO})_{14}$, and $(\text{EtGe})_2\text{Co}_4(\text{CO})_{11}$ were being removed). As it was formed in only trace amount, its presence could have been obscured by the other products in Runs 2 and 3. It is more likely that " $\text{Et}_2\text{Ge}_2\text{SiCo}_6(\text{CO})_{17}$ " was formed by a reaction analogous to that postulated for the formation of $\text{Et}_2\text{Ge}_3\text{Co}_6(\text{CO})_{17}$ in Chapter Seven:

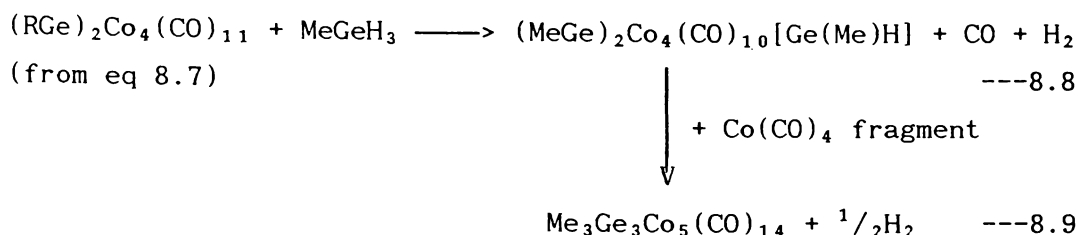


The formation of $\text{RGeCo}_3(\text{CO})_{11}$ and $\text{R}_2\text{Ge}_2\text{Co}_4(\text{CO})_{14}$ in this reaction may be very similar to that described in Chapter Three in the reaction of MeGeH_3 with $\text{Co}_2(\text{CO})_8$ and need not be repeated here.

$(\text{EtGe})_2\text{Co}_4(\text{CO})_{11}$ (observed in Runs 1 and 2) could be formed via the reaction of RGeH_3 with $\text{Co}_4(\text{CO})_{12}$ (breakdown product of $\text{SiCo}_4(\text{CO})_{14}$), by a similar reaction as described in Chapter Four (equation 8.7).



The isolation of $\text{Me}_3\text{Ge}_3\text{Co}_5(\text{CO})_{14}$ instead of $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ from Run 3 was surprising. This could be due to the higher ratio of MeGeH_3 to $\text{SiCo}_4(\text{CO})_{14}$ in Run 3 (3.3 : 1) than Runs 1 and 2 (2 : 1). Proposed reaction equations :



The synthesis and characterisation of $\text{Me}_3\text{Ge}_3\text{Co}_5(\text{CO})_{14}$ (**10a**) was discussed in Chapter Three. It was formed by the heating of $\text{Me}_2\text{Ge}_2\text{Co}_4(\text{CO})_{14}$ [76] and $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$. If equations 8.8 and 8.9 were true, then this would present yet another route to its synthesis.

The low yield of $\text{RGeSiCo}_5(\text{CO})_{15}$ from all the runs is possibly due to the breakdown of $\text{SiCo}_4(\text{CO})_{14}$ to form some cobalt carbonyl compound, $\text{Co}_2(\text{CO})_8$ or more likely $\text{Co}_4(\text{CO})_{12}$ as the reaction proceeded. Therefore the reactions leading to all other products took place after equation 8.1.

The formation of $\text{RGeSiCo}_5(\text{CO})_{15}$ ($\text{R} = \text{Et}, \text{Me}$), though in low yield has indicated that similar compounds of different R groups (such as Ph, *t*-Bu) could be synthesised by the reaction of RGeH_3 with $\text{SiCo}_4(\text{CO})_{14}$. A particularly useful $\text{RGeSiCo}_5(\text{CO})_{15}$ type compound would be one in which $\text{R} = \text{X} = \text{halogen}$. This could be made from XGeH_3 with $\text{SiCo}_4(\text{CO})_{14}$. The replacement of X by transition metal anion such as $\text{Co}(\text{CO})_4^-$, $\text{MnCo}(\text{CO})_5^-$ and $\text{Fe}(\text{CO})_4^{2-}$ could result in a quite interesting new series of clusters.

8.2 The Reaction of MeSiH_3 with $\text{SiCo}_4(\text{CO})_{14}$

8.2.1 Experimental :

$\text{SiCo}_4(\text{CO})_{14}$ (0.1656g, 0.253mmol) and MeSiH_3 (1.09 mmol) together with hexane (10ml) were sealed in a 50 ml ampoule. The reaction was allow to proceed at room temperature for about 4 months, and then left in the oil bath at 30°C for about 6 months.

8.2.2 Observations and workup :

The reddish brown colour of the starting material changed to a purple colour one day after the reactants were sealed. Ten months later the colour of the solution was a dark 'dirty' purple. The ampoule was opened and 0.323mmol of total incondensable gases were measured, of which 36% was H_2 and 64% CO.

The volatiles were removed and an infrared spectrum showed the presence of $MeSiH_3$ and hexane. No further separation was possible. The involatile components washed with hexane to give two fractions, a hexane soluble fraction (dirty purple) and a hexane insoluble, CH_2Cl_2 soluble fraction.

Hexane soluble fraction

The infrared spectrum (Table 8.15) showed a mixture of compounds : $SiCo_4(CO)_{13}$, $MeSiH_2Co(CO)_4$, $Co_2(CO)_8$ and some unreacted $SiCo_4(CO)_{14}$ (in decreasing order) could be noted. As the solubilities of all components were virtually the same, no separation was possible.

Table 8.15 Infrared spectrum of the hexane soluble fraction

Bands	Intensity	Possible assignments
2105	vw	$MeSiH_2Co(CO)_4$ [4,31]
2084	m	$SiCo_4(CO)_{13}$ [21,77]
2063	mw	$SiCo_4(CO)_{14}$ [77] + $Co_2(CO)_8$ + $Co_4(CO)_{12}$? [142]
2044	vs	$MeSiH_2Co(CO)_4$ + $SiCo_4(CO)_{13}$ + $SiCo_4(CO)_{14}$ + $Co_2(CO)_8$
2037	mw sh	$SiCo_4(CO)_{14}$
2028	mw sh	$SiCo_4(CO)_{13}$ + $SiCo_4(CO)_{14}$
2021	mw sh	$MeSiH_2Co(CO)_4$ + $SiCo_4(CO)_{14}$
2005	vw sh	$SiCo_4(CO)_{13}$ + $SiCo_4(CO)_{14}$
1863	vw	$Co_2(CO)_8$ + $Co_4(CO)_{12}$?
1853	vvw	$Co_2(CO)_8$
1842	vvw	$SiCo_4(CO)_{14}$

CH₂Cl₂ fraction

The CH₂Cl₂ fraction formed a red solution in CH₂Cl₂. This was characterised as MeSi₂Co₅(CO)₁₅ (*1m*) by comparing its infrared spectrum, mass spectrum and X-Ray precession photographs to those of MeGe₂Co₅(CO)₁₅. Its characterisation is given in Section 8.3.3. The proposed structure is given in Fig 8.10.

Yield :

SiCo₄(CO)₁₃ + all hexane soluble fraction = 0.12g

MeSi₂Co₅(CO)₁₅ = 0.06g = 0.076 mmol = 30%

The yield of MeSi₂Co₅(CO)₁₅ would account for 0.114mmol of H₂ evolved. The amount of H₂ calculated from the incondensable measurement is 0.116 mmol. This leaves only 0.002mmol of H₂ to be attributed to the formation of MeSiH₂Co(CO)₄ (i.e. 0.004mmol of MeSiH₂Co(CO)₄ was formed) assuming the H₂ value to be correct. This seems to be a reasonable estimate.

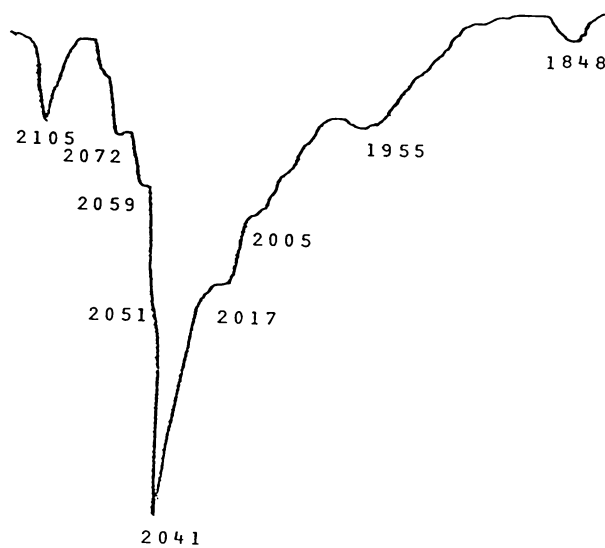
8.2.3 Characterisation of MeSi₂Co₅(CO)₁₅*Infrared spectrum :*

The infrared pattern of MeSi₂Co₅(CO)₁₅ (Table 8.16, Fig 8.10) is very similar to those of MeGe₂Co₅(CO)₁₅, RGeSiCo₅(CO)₁₅ and SiCo₂Co₆(CO)₁₉. Nine infrared bands of MeSi₂Co₅(CO)₁₅ were observed out of the fifteen predicted based on a C_s symmetry. A full discussion on the infrared spectrum of MeSi₂Co₅(CO)₁₅ and clusters with the Co₄(CO)₁₁ core is presented in Section 9.1.

Table 8.16 Infrared spectrum of $\text{MeSi}_2\text{Co}_5(\text{CO})_{15}$ compared to those of $\text{MeGe}_2\text{Co}_5(\text{CO})_{15}$ and $\text{Si}_2\text{Co}_6(\text{CO})_{19}$

$\text{MeSi}_2\text{Co}_5(\text{CO})_{15}$ $\text{CH}_2\text{Cl}_2/\text{hexane}$	$\text{MeGe}_2\text{Co}_5(\text{CO})_{15}$ [82] CH_2Cl_2	$\text{Si}_2\text{Co}_6(\text{CO})_{19}$ [93] CH_2Cl_2
2106 w	2106 m	2101 s
2072 w	2067 m	2074 w
2059 mw sh		
2051 m sh	2050 m sh	2053s sh
2041 vs	2037 vs	2041 vs
2017 m sh	2013 s	2019 m
2005w sh	2004 ms sh	2004 m
1955 w sh	1965 w sh	
1848 vw br	1843 vw br	1850 w, br

Fig 8.10 Infrared spectrum of $\text{MeSi}_2\text{Co}_5(\text{CO})_{15}$ in hexane/ CH_2Cl_2



Mass spectrum of $\text{MeSi}_2\text{Co}_5(\text{CO})_{15}$:

The mass spectrum of $\text{MeSi}_2\text{Co}_5(\text{CO})_{15}$ is presented in Table 8.17. The parent ion at m/e 786 was not observed. The highest m/e envelope (688-692) corresponded to either $[\text{P-Me-nCO}]^+$ or $[\text{P-Si-Me-(n-1)CO}]^+$. As CO and Si are of equal mass value, it is difficult to assign the ions unambiguously. The observation of a medium weak envelope at 315-325 and the knowledge of the reasonable strong Si-Me bond suggested that $[\text{P-Si-Me-nCO}]^+$ was most probable. A similar situation was encountered in the mass spectrum of $(\text{MeSi})_2\text{Co}_4(\text{CO})_{11}$. However, $[\text{P-Me-nCO}]^+$ may also be assigned as $[\text{P-(n-1)CO}+0]^+$. This possibility was discussed in the mass spectra of $\text{EtGeSiCo}_5(\text{CO})_{11}$ and $\text{MeGeSiCo}_5(\text{CO})_{11}$.

Table 8.17 Mass spectrum of $\text{MeSi}_2\text{Co}_5(\text{CO})_{15}$

m/e	Int	Possible assignments
688-692	mw	$[\text{P-Me-3CO}]^+$ or $[\text{P-Si-Me-2CO}]^+$
658-664	m	$[\text{P-Me-4CO}]^+$ or $[\text{P-Si-Me-3CO}]^+$
631-639	m	$[\text{P-Me-5CO}]^+$ or $[\text{P-Si-Me-4CO}]^+$
603-609	m	$[\text{P-Me-6CO}]^+$ or $[\text{P-Si-Me-5CO}]^+$
571-572	vs	$[\text{P-Me-7CO}]^+$ or $[\text{P-Si-Me-6CO}]^+$
543-553	vs	$[\text{P-Me-8CO}]^+$ or $[\text{P-Si-Me-7CO}]^+$
518-527	m	$[\text{P-Me-9CO}]^+$ or $[\text{P-Si-Me-8CO}]^+$
507-512	vvw	$[\text{P-10CO}]^+$
485-501	m	$[\text{P-Me-10CO}]^+$ or $[\text{P-Si-Me-9CO}]^+$
475-485	w	$[\text{P-11CO}]^+$
462-472	m	$[\text{P-Me-11CO}]^+$ or $[\text{P-Si-Me-10CO}]^+$
448-456	w	$[\text{P-12CO}]^+$
435-442	m	$[\text{P-Me-12CO}]^+$ or $[\text{P-Si-Me-11CO}]^+$
422-430	w	$[\text{P-13CO}]^+$
405-413	ms	$[\text{P-Me-13CO}]^+$ or $[\text{P-Si-Me-12CO}]^+$
385-400	s	$[\text{P-14CO}]^+$
375-385	m	$[\text{P-Me-14CO}]^+$ or $[\text{P-Si-Me-13CO}]^+$
355-367	vw	$[\text{P-15CO}]^+$
345-351	vw	$[\text{P-Me-15CO}]^+$ or $[\text{P-Si-Me-14CO}]^+$

Table 8.17 *cont'd*

329-337	mw	$[P-14CO-Co]^+ ?$
315-325	mw	$[P-Si-Me-15CO]^+$
301-310	mw	$[P-15CO-Co]^+ ?$ or $[P-14CO-Co-Si]^+ ?$
286-296	mw	$[P-Co-Me-15CO]^+ ?$

NMR spectrum :

The 1H NMR showed a singlet at δ 2.44 ppm which is in the region of $(RM')_2Co_4(CO)_{11}$ type compounds (*1*) for R = alkyl, aryl groups and $Co(CO)_4$. The low field methyl signal indicates a Me group attached to a five coordinated M' as discussed in Section 9.2.

X-Ray crystallographic preliminary studies

Preliminary precession photographs of a crystal of $MeSi_2Co_5(CO)_{15}$ showed that the crystal is isomorphous with that of $MeGe_2Co_5(CO)_{15}$. The germanium analogue has been fully characterised by crystal structure analysis as described in Chapter Seven therefore a full study of $Me_2SiCo_5(CO)_{15}$ was not undertaken. Approximate unit cell dimensions ($MeGe_2Co_5(CO)_{15}$'s in bracket) : $a = 13\text{\AA}$ (12.852), $b = 14.5\text{\AA}$ (14.528), $c = 27.5\text{\AA}$ (26.566) and $\beta = 90.5^\circ$ (90.32), Molecular weight = 786.03 (875.2), $D_{calc} = 2.16$ (2.34) g/cm^3 . The calculated density (using 786.03 as the molecular weight) is in the correct region for such type of Si cluster, compare $EtGeSiCo_5(CO)_{15}$ of 2.16 g/cm^3 and $Si_2Co_6(CO)_{19}$ of 2.17 g/cm^3 [93].

8.2.4 Discussion :

The reaction of $MeSiH_3$ with $SiCo_4(CO)_{14}$ was not analogous to that of $MeGeH_3$ and $GeCo_4(CO)_{14}$ (Chapter Five) as no $(MeSiH)SiCo_4(CO)_{13}$ was obtained. However, the formation of the new product $MeSi_2Co_5(CO)_{15}$ (*1m*) seems to suggest that $(MeSiH)SiCo_4(CO)_{13}$ could have existed as an

transient intermediate or a very unstable product. A possible reaction scheme parallels those of equations 8.1 to 8.3. The breaking down of $\text{SiCo}_4(\text{CO})_{14}$ into simpler species like $\text{Co}_2(\text{CO})_8$ or possibly $\text{Co}_4(\text{CO})_{12}$ is supported by the presence of these two species in the products.

A very small amount of $\text{SiCo}_4(\text{CO})_{14}$ was recovered though almost all of the starting material had decarbonylated to $\text{SiCo}_4(\text{CO})_{13}$. This was unlike the RGeH_3 with $\text{SiCo}_4(\text{CO})_{14}$ reaction where all the latter (and possibly $\text{SiCo}_4(\text{CO})_{13}$) was totally consumed forming products including $\text{RGeCo}_3(\text{CO})_{11}$, $\text{R}_2\text{Ge}_2\text{Co}_4(\text{CO})_{14}$, $\text{RGeSiCo}_4(\text{CO})_{15}$, $(\text{RGe})_2\text{Co}_4(\text{CO})_{11}$ and even $\text{Me}_3\text{Ge}_3\text{Co}_5(\text{CO})_{14}$ in the MeGeH_3 reaction (only a small amount of $\text{GeCo}_4(\text{CO})_{13}$ was observed). The recovery of a substantial amount of $\text{SiCo}_4(\text{CO})_{14}$ in the form of $\text{SiCo}_4(\text{CO})_{13}$ again demonstrates the lower reactivity of MeSiH_3 toward $\text{M}'\text{Co}_4(\text{CO})_{14}$ in comparison to MeGeH_3 . In Chapter Six, no reaction was obtained between MeSiH_3 with $\text{GeCo}_4(\text{CO})_{14}$ while substitution of the bridging CO's was achieved by MeGeH_3 .

As $\text{Co}_2(\text{CO})_8$ was observed in the product mixture, the product $\text{MeSiH}_2\text{Co}(\text{CO})_4$ was not unexpected. It can be formed by the reaction of MeSiH_3 with $\text{Co}_2(\text{CO})_8$ with the higher substituted species being formed only with forced conditions [4,51].

An interesting observation in this reaction is the absence of $(\text{MeSi})_2\text{Co}_4(\text{CO})_{11}$. This is easily formed by the reaction of MeSiH_3 with $\text{Co}_4(\text{CO})_{12}$ in Chapter Four. Its absence may indicate that the tentatively assigned $\text{Co}_4(\text{CO})_{12}$ in Table 8.16 is most probably not produced in the reaction.

8.3 The Reaction of Me_2GeH_2 with $\text{SiCo}_4(\text{CO})_{14}$

8.3.1 Experimental :

$\text{SiCo}_4(\text{CO})_{14}$ (0.4442g, 0.678mmol) and Me_2GeH_2 (4.25mmoles, 6.3x that of $\text{SiCo}_4(\text{CO})_{14}$) together with 10 ml of hexane were sealed in a 50 ml ampoule and left to react in the dark for 1.5 months at room temperature. It was then shaken for 4 months.

8.3.1 Results :

The colour of the solution changed from a red/brown to a dark purple colour about two months into the reaction. The ampoule was opened and the 0.57mmol of total incondensable gas was measured and of this, 77% was H_2 and 23% CO.

The volatiles of the reaction were not examined. The involatile products were all soluble in hexane. An infrared spectrum indicated the presence of $\text{Me}_2\text{GeCo}_2(\text{CO})_7$, $\text{Me}_2\text{GeCo}_2(\text{CO})_8$, $(\text{Me}_2\text{Ge})_2\text{Co}_2(\text{CO})_6$ [17,18,61,Section 4.5] and $\text{SiCo}_4(\text{CO})_{13}$. The infrared spectrum of the first hexane extract is shown in Table 8.18. The products could not be separated, but an estimate from the infrared spectra is that the three Ge-Co products were of equal proportion (no estimate could be placed for $\text{SiCo}_4(\text{CO})_{13}$).

A very small amount of black deposit and some fine transparent particles were observed at the bottom of the flask after extraction with hexane and CH_2Cl_2 .

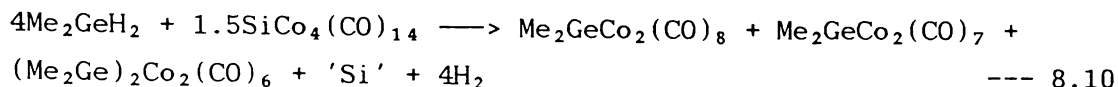
Table 8.18 Infrared spectrum of hexane washing of the reaction of Me_2GeH_2 with $\text{SiCo}_4(\text{CO})_{14}$

Bands	Intensity	$\text{Me}_2\text{GeCo}_2(\text{CO})_8$	$\text{Me}_2\text{GeCo}_2(\text{CO})_7$	$(\text{Me}_2\text{Ge})_2\text{Co}_2(\text{CO})_6$
2088	m		2088 s	
2080	w	2081 vs		
2065	mw			2066 s
2060	mw sh			
2050	s		2048 vs	2048 vs
2039	m sh			
2027	vvs	2027 vs	2026 vs	2028 vs
2007	vs	2006 vs	2008 vs	
2000-1998	vs	1996 m	1998 sh w	
1994	s sh			1990 vs
1980	mw			1981 m
1841	m		1841 m-s	

8.3.3 Discussion :

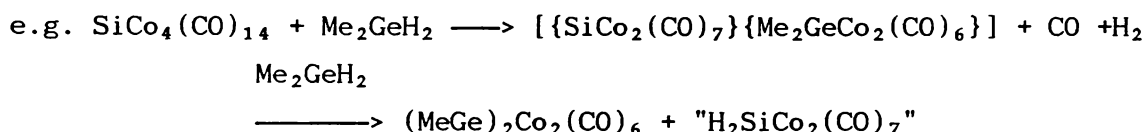
The reaction of Me_2GeH_2 with $\text{GeCo}_4(\text{CO})_{14}$ in Chapter Six produced $(\text{Me}_2\text{Ge})_n\text{GeCo}_4(\text{CO})_{14-n}$ ($n = 1$ or 2). The reaction of Me_2GeH_2 with $\text{SiCo}_4(\text{CO})_{14}$ did not produce the analogous silicon products. Instead smaller molecules $\text{Me}_2\text{GeCo}_2(\text{CO})_8$, $\text{Me}_2\text{GeCo}_2(\text{CO})_7$ and $(\text{Me}_2\text{Ge})_2\text{Co}_2(\text{CO})_6$ were formed. These products indicated a breakdown of $\text{SiCo}_4(\text{CO})_{14}$ as in the reactions of EtGeH_3 with $\text{SiCo}_4(\text{CO})_{14}$ and MeSiH_3 with $\text{SiCo}_4(\text{CO})_{14}$. Unlike the latter two reactions, no $\text{Co}_2(\text{CO})_8$ or $\text{Co}_4(\text{CO})_{12}$ was observed in the product mixture. Because of the absence of the two cobalt carbonyls, Me_2GeH_2 could have reacted with $\text{SiCo}_4(\text{CO})_{14}$ to form intermediates like $'(\text{Me}_2\text{Ge})\text{SiCo}_4(\text{CO})_{13}'$ and $'(\text{Me}_2\text{Ge})_2\text{SiCo}_4(\text{CO})_{12}'$ analogues of $\text{GeCo}_4(\text{CO})_{14}$ reaction with Me_2GeH_2 in Chapter Five. The Si part of the intermediates then cleaves and breaks down to give $\text{Co}(\text{CO})_4$ fragments and CO to form the three products observed. The reaction of

Me_2GeH_2 with $\text{SiCo}_4(\text{CO})_{14}$ may be represented by the following simple equation which ignores any formation of intermediates :



The fate of the silicon, 'Si' was not known. It is not certain if it constitutes part of the black insoluble solid (polymeric $\text{Si}[\text{OCCo}(\text{CO})_x]_n$?) and some fine transparent particles left after extraction with hexane and CH_2Cl_2 .

Alternatively, a replacement reaction (mentioned in Section 8.1.5) is also possible :



The products $\text{Me}_2\text{GeCo}_2(\text{CO})_8$, $\text{Me}_2\text{GeCo}_2(\text{CO})_7$ and $(\text{Me}_2\text{Ge})_2\text{Co}_2(\text{CO})_6$ were similar to those obtained in the reaction of excess Me_2GeH_2 with $\text{Co}_2(\text{CO})_8$ [18]. Studies by Foster [18] had shown that a 1:1 reactant ratio produced $\text{Me}_2\text{GeCo}_2(\text{CO})_8$ and $\text{Me}_2\text{GeCo}_2(\text{CO})_7$. It was also found that decreasing the Me_2GeH_2 concentration produced only $\text{Me}_2\text{GeCo}_2(\text{CO})_7$ while increasing the Me_2GeH_2 ratio produced the three products $\text{Me}_2\text{GeCo}_2(\text{CO})_8$, $\text{Me}_2\text{GeCo}_2(\text{CO})_7$ and $(\text{MeGe})_2\text{Co}_2(\text{CO})_6$.

8.4 The Reaction of Me_2SiH_2 with $\text{SiCo}_4(\text{CO})_{14}$

8.4.1 Experimental :

$\text{SiCo}_4(\text{CO})_{14}$ (0.2795g, 0.426mmol) and Me_2SiH_2 (1.8mmol, 4 mole equivalent) together with 10 ml of hexane was sealed in a 50 ml ampoule. This was left to react for 11 months in the dark. Working up procedures were as in 8.1.1, Run 1.

8.4.2 Results :

The reaction mixture turned purple after a few days and remained so even after 11 months. The total incondensable gas produced was 1.63 mmoles, with a composition of 99% H_2 and 1% CO . The infrared spectrum of the hexane extracts (Table 8.19) indicated the following products in decreasing order : $\text{Me}_2\text{SiHCo}(\text{CO})_4$, $\text{Me}_2[\text{Co}(\text{CO})_4]\text{SiOCCo}_3(\text{CO})_9$, $\text{Co}_4(\text{CO})_{12}$ and $\text{Co}_2(\text{CO})_8$.

Table 8.19 Hexane extracts of the reaction of Me_2SiH_2 with $\text{SiCo}_4(\text{CO})_{14}$

Bands (cm^{-1})	Intensity	Possible assignments
2092	mw	$\text{Me}_2\text{SiHCo}(\text{CO})_4$
2083	w	?
2070	mw	$\text{Co}_2(\text{CO})_8$
2061	m	$\text{Co}_4(\text{CO})_{12}$
2053	m	$\text{Co}_4(\text{CO})_{12}$
2048	m sh	$\text{Me}_2[\text{Co}(\text{CO})_4]\text{SiOCCo}_3(\text{CO})_9$
2040	m	$\text{Me}_2\text{SiCo}_4(\text{CO})_{14}$
2032	ms sh	$\text{Me}_2[\text{Co}(\text{CO})_4]\text{SiOCCo}_3(\text{CO})_9$
2028	s	$\text{Me}_2\text{SiCo}_4(\text{CO})_{14} + \text{Me}_2\text{SiHCo}(\text{CO})_4$
2020	m sh	$\text{Co}_2(\text{CO})_8$
2012	m	$\text{Me}_2\text{SiCo}_4(\text{CO})_{14}$, $\text{Me}_2[\text{Co}(\text{CO})_4]\text{SiOCCo}_3(\text{CO})_9$
1992	vs	$\text{Me}_2\text{SiHCo}(\text{CO})_4$
1865	mw	$\text{Co}_4(\text{CO})_{12} + \text{Co}_2(\text{CO})_8$
1856	w sh	$\text{Co}_2(\text{CO})_8$

Infrared spectra of subsequent washings were very similar except that the intensity of the bands of $\text{Me}_2[\text{Co}(\text{CO})_4]\text{SiOCCo}_3(\text{CO})_9$ and $\text{Co}_4(\text{CO})_{12}$ were stronger. These products could not be separated due to similar solubility so yields could not be measured.

8.4.3 Discussion :

The reaction products of Me_2SiH_2 and $\text{SiCo}_4(\text{CO})_{14}$ are very similar to those of the reaction of Me_2SiH_2 with $\text{Co}_2(\text{CO})_8$ [18] and those of Me_2SiH_2 and $\text{Co}_4(\text{CO})_{12}$ in Chapter Four. From the intensity of the infrared spectrum, the major product was $\text{Me}_2\text{SiHCo}(\text{CO})_4$. The major product in the Me_2SiH_2 plus $\text{Co}_4(\text{CO})_{12}$ reaction was $\text{Me}_2[\text{Co}(\text{CO})_4]\text{SiOCCo}_3(\text{CO})_9$, followed by $\text{Me}_2\text{SiHCo}(\text{CO})_4$. Studies by [18] had shown that $\text{Me}_2[\text{Co}(\text{CO})_4]\text{SiOCCo}_3(\text{CO})_9$ was obtained only in reaction when the CO in the Me_2SiH_2 with $\text{Co}_2(\text{CO})_8$ reaction was removed. This may indicate that the CO atmosphere in the $\text{Co}_4(\text{CO})_{12}$ reaction was lower than the $\text{SiCo}_4(\text{CO})_{14}$ reaction. The formation of $\text{Me}_2[\text{Co}(\text{CO})_4]\text{SiOCCo}_3(\text{CO})_9$ and $\text{Co}_2(\text{CO})_8$ required the consumption of CO and this was consistent with the low CO composition measured in the incondensable gas.

The products obtained again indicated ~~that~~ $\text{SiCo}_4(\text{CO})_{14}$ did not stay intact throughout the reaction as in Sections 8.1, 8.2 and 8.3. Thus, there is a clear difference between $\text{SiCo}_4(\text{CO})_{14}$ and $\text{GeCo}_4(\text{CO})_{14}$ in these reactions, the silicon examples acting as a source of $\text{Co}(\text{CO})_n$ groups by the cleavage of the Si-Co bonds, while the germanium example remains largely intact and reacts by addition of reagents subsequently. This may be due to the strain in $\text{SiCo}_4(\text{CO})_{14}$ as discussed in Section 8.1.5. Table 8.20 summaries the products from the reaction of $\text{M}'\text{Co}_4(\text{CO})_{14}$ with $\text{R}_n\text{M}'\text{H}_{4-n}$ ($n = 1$ or 2).

Table 8.20 Products from the reaction of $M'Co_4(CO)_{14}$ with $R_nM'H_{4-n}$ ($n = 1$ or 2)

	$SiCo_4(CO)_{14}$	$GeCo_4(CO)_{14}$
MeSiH ₃	MeSiH ₂ Co(CO) ₄ , SiCo ₄ (CO) ₁₃ , Co ₂ (CO) ₈ , MeSi ₂ Co ₅ (CO) ₁₅ (Section 8.2)	GeCo ₄ (CO) ₁₃ (Section 5.8)
MeGeH ₃	Me ₂ Ge ₂ Co ₄ (CO) ₁₄ , MeGeCo ₃ (CO) ₁₁ (MeGe) ₂ Co ₄ (CO) ₁₁ , Co ₄ (CO) ₁₂ , SiCo ₄ (CO) ₁₃ , Me ₃ Ge ₃ Co ₅ (CO) ₁₄ , MeGeSiCo ₅ (CO) ₁₅ (Section 8.1)	(MeGeH)GeCo ₄ (CO) ₁₃ (MeGeH) ₂ GeCo ₄ (CO) ₁₂ (Section 5.2)
EtGeH ₃	Et ₂ Ge ₂ Co ₄ (CO) ₁₄ , EtGeCo ₃ (CO) ₁₁ , (EtGe) ₂ Co ₄ (CO) ₁₁ , Co ₄ (CO) ₁₂ , SiCo ₄ (CO) ₁₃ , "Et ₂ Ge ₂ SiCo ₆ (CO) ₁₇ ", EtGeSiCo ₅ (CO) ₁₅ (Section 8.1)	(EtGeH)GeCo ₄ (CO) ₁₃ (EtGeH) ₂ GeCo ₄ (CO) ₁₂ (Section 5.3)
Me ₂ SiH ₂	Me ₂ SiHCo(CO) ₄ , Co ₄ (CO) ₁₂ Co ₂ (CO) ₈ , Me ₂ [Co(CO) ₄]SiOCCo ₃ (CO) ₉ , (Section 8.4)	GeCo ₄ (CO) ₁₃ (Section 6.14.2)
Me ₂ GeH ₂	(MeGe) ₂ Co ₂ (CO) ₆ , Me ₂ GeCo ₂ (CO) ₇ , Me ₂ GeCo ₂ (CO) ₈ , SiCo ₄ (CO) ₁₃ (Section 8.3)	(Me ₂ Ge)GeCo ₄ (CO) ₁₃ (Me ₂ Ge)GeCo ₄ (CO) ₁₂ (Section 6.2)

CHAPTER NINE

A discussion of the *closo*-cluster compounds of formula $(RM')_2Co_4(CO)_{10}(\mu-X)$: their Infrared, NMR Spectra and Crystal Structures, $M' = Si, Ge$, $R =$ alkyl, aryl or $Co(CO)_4$, $X = CO, GeCo_2(CO)_7$ or $Ge(Me)Co(CO)_4$

This Chapter attempts to summarise the infrared and NMR spectra of *closo*-cluster compounds of formula $(RM')_2Co_4(CO)_{10}(\mu-X)$ in terms of the known crystal structures of some of the compounds.

9.1 Infrared spectra

The solution infrared spectra of $(RM')_2Co_4(CO)_{10}(\mu-X)$ were simple and showed less infrared bands than predicted. The solid infrared spectra were more detailed in most compounds, and were useful in assigning the bands.

By assuming a local symmetry of C_{2v} for the $Co_4(CO)_{11}$ unit for all the compounds (*1a-j*) listed in Tables 9.1 and 9.2, eight infrared active terminal stretches are predicted ($3A_1 + 3B_1 + 2B_2$) plus a bridging CO stretch (A_1). Comparison of the infrared spectra of all such compounds indicates that the following vibrations are characteristic of the central $Co_4(CO)_{11}$ group (cm^{-1}) : ~2035 (strongest band), ~2015 (m), ~2000 (m, sh) and a weak bridging carbonyl band at ~1840 cm^{-1} . The silicon compounds show a slight shift to the higher wavenumber (average shift of about 5 cm^{-1}) as expected.

The solid state infrared spectra were considerably more detailed with the 2035 and 2015 bands split into two or more components and often accompanied by a phase shift. Therefore, bands (cm^{-1}) at 2040,

2037, 2029, 2015, 2012 and 2001 were observed for the $\text{Co}_4(\text{CO})_{11}$ core of $\text{MeGe}_2\text{Co}_5(\text{CO})_{15}$ with the strongest band at 2029. The presence of a weak band at 2083 in the solid state infrared spectrum of $(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$ may indicate that the $\sim 2070\text{--}2075$ band common in all other $\text{Co}_4(\text{CO})_{11}$ compounds is actually part of the central $\text{Co}_4(\text{CO})_{11}$ vibrations, but weak when RM' ($\text{R} = \text{Me}, \text{Et}, \text{M}' = \text{Si}, \text{Ge}$) is present. $\text{Et}_2\text{Ge}_3\text{Co}_6(\text{CO})_{17}$ (11) and $\text{Me}_3\text{Si}_3\text{Co}_5(\text{CO})_{14}$ (10b) both have a central $\text{Co}_4(\text{CO})_{10}(\mu\text{-X})$ unit. It possesses all the terminal carbonyl bands characteristic of the $\text{Co}_4(\text{CO})_{11}$ unit, but the intensity and positions of the bands were different. The infrared spectrum of $\text{Me}_3\text{Ge}_3\text{Co}_5(\text{CO})_{14}$ however has little resemblance to that of $\text{M}'_2\text{Co}_4(\text{CO})_{11}$ type compounds.

The infrared bands of apical $\text{Co}(\text{CO})_4$ groups can be recognised by comparing the infrared spectra of compounds with these groups (1c,d,g,h,j,k,m) to those of $(\text{RM}')_2\text{Co}_4(\text{CO})_{11}$, $\text{R} = \text{alkyl or aryl groups}$, (1a,b,e,f,l). Three additional bands are expected when the Me group is replaced by a $\text{Co}(\text{CO})_4$ group by assuming a C_{3v} local symmetry in the terminal $\text{Co}(\text{CO})_4$ group ($2\text{A}_1 + \text{E}$). These bands are at $\sim 2100\text{--}2120$ (A_1) and ~ 2050 (A_1) and possibly at $2000\text{--}2020$ (E) [13,30,31]. In $\text{Me}_3\text{Ge}_3\text{Co}_5(\text{CO})_{14}$, the $\text{Co}(\text{CO})_4$ group is in a different environment from those in Table 9.2 i.e. $(\text{RM}')\text{Co}_4(\text{CO})_{11}(\text{M}'\text{Co}(\text{CO})_4)$ type compounds. The $\text{Co}(\text{CO})_4$ group is part of the bridging unit and bonded to a four- rather than five-coordinated germanium. Only the medium weak bands at 2092 (2097 in solid infrared) and possibly 2062 could be assigned to the $\text{Co}(\text{CO})_4$ vibrations. Only seven out of a total of fourteen predicted infrared bands for the whole molecule were observed. Overlapping of bands may have occurred and it is difficult to assign the positions of all the bands.

The solid infrared spectrum of $\text{Et}_2\text{Ge}_3\text{Co}_6(\text{CO})_{17}$ showed a total of fourteen of the predicted seventeen bands (C_s symmetry). Since the

basic $\text{Co}_4(\text{CO})_{10}$ core terminal vibrations were not altered much by the presence of the $\mu\text{-GeCo}_2(\text{CO})_7$ group, the carbonyl infrared spectrum of $\text{Et}_2\text{Ge}_3\text{Co}_6(\text{CO})_{17}$ (Table 9.3) could be approximately regarded as one in which a $\text{Co}_2(\text{CO})_7$ spectrum was superimposed on a $\text{Co}_4(\text{CO})_{11}$ spectrum. The bands at (cm^{-1}) 2095, 2055, 2016, 2013, 2008 and 1825 may be attributed to the carbonyl bands of the $\text{Co}_2(\text{CO})_7$ unit. Those that belong to the $\text{Co}_4(\text{CO})_{10}$ core are likely to be (cm^{-1}) 2067, 2060, 2046, 2033, 2027, 2001, 1993, 1988 (compared to 2058?, 2043, 2001, 1992 and 1963 in the solid infrared spectrum of $\text{Me}_3\text{Ge}_3\text{Co}_5(\text{CO})_{14}$).

In conclusion, the infrared bands due to the $\text{Co}_4(\text{CO})_{11}$ core and the apical $\text{Co}(\text{CO})_4$ units could be assigned by comparing the infrared spectra of the $(\text{RM}')_2\text{Co}_4(\text{CO})_{11}$ with $\text{R} = \text{alkyl or aryl groups only}$, (*1a,b,e,f,l*) (Table 9.1) with those in which one or both $\text{R} = \text{Co}(\text{CO})_4$ units, (*1c,d,g,h,j,k,m*) (Table 9.2). The infrared spectrum of $\text{Et}_2\text{Ge}_3\text{Co}_6(\text{CO})_{17}$ (*11*) can be interpreted as one in which bands of $\text{Co}_2(\text{CO})_7$ are superimposed on that of a $\text{Co}_4(\text{CO})_{11}$ spectrum, even though it contains a $\text{Co}_4(\text{CO})_{10}$ core. The infrared spectrum of $\text{Me}_3\text{Ge}_3\text{Co}_5(\text{CO})_{14}$ (*10a*), however is very different from that of $\text{Et}_2\text{Ge}_3\text{Co}_6(\text{CO})_{17}$ and the $\text{Co}_4(\text{CO})_{11}$ containing compounds.

Keys to Tables 9.1 to 9.3: c = CH_2Cl_2 , h = hexane, hc = hexane/ CH_2Cl_2 , cy = cyclohexane, CsI = CsI disc, KBr disc = K, n = nujol mull

Table 9.1 Compounds of formula $(RM')_2Co_4(CO)_{11}$

RM' = MeGe		EtGe	<i>t</i> -BuGe	PhGe	MeSi
h [76]	CsI	h	cy [91]	cy [91]	hc [144]
2083w					
2063vw sh		2060mw	2061sh	2069	2061w sh
		2040s sh			2048m sh
2034vs		2033vs	2037vs	2032	2039vs
2016m	2024vs	2015ms		2018	2022ms
2005mw sh	2000s sh	2005m	2008m	2006	2009mw
	1995s		1996m		
	1963w sh				
1843w br	1827m	1842w	1849?, br	1858	1855w

Table 9.2 Compounds of formula $(RM')Co_4(CO)_{11}(M''Co(CO)_4)$

$Si_2Co_6(CO)_{19}$	$Ge_2Co_6(CO)_{19}$		$MeGeSiCo_5(CO)_{15}$	$EtGeSiCo_5(CO)_{15}$	
c [93]	c [81]	n	c	c	CsI
2101w	2100s	2102s	2105mw	2105w	2106m
		2090sh			
2074w	2065w sh	2079m	2073mw	2072mw	2077mw
					2073mw
		2056sh	2053s sh		2054m
2050s	2049s	2051m sh	2051sh	2050m sh	2052m
			2041vs		2043-1m sh
	2037vs	2036sh	2036vs	2037vs	2037m
		2027vvs			2029ms sh
2019m		2018vs			2108vs
	2014m		2015m	2014ms	2016vs sh
					2009vs
2004m	2003m	2004vs	2000m sh	2001m sh	2001m sh
	1990w sh	1995vs			2000m sh
		1991sh			1991ms
		1964sh,w			
1850w br	1844w br	1847ms	1850w	1855w	1852mw

Table 9.2 cont'd

$\text{MeGe}_2\text{Co}_5(\text{CO})_{15}$		$\text{EtGe}_2\text{Co}_5(\text{CO})_{15}$	$\text{PhGeCo}_5(\text{CO})_{15}$		$\text{MeSi}_2\text{Co}_5(\text{CO})_{15}$
c	n [82]	c [82]	hc	CsI	c
2106w	2106m 2090sh	2105 m	2105mw	2106m	2106w
2067m	2072m	2069m	2061mw	2076mw	2072w 2059mw sh
2050m sh	2051sh 2040sh	2050sh	2050m sh	2054m sh 2041/39s sh	2051m sh 2041vs
2037vvs	2037sh 2029vs	2037vs 2022sh	2038 vvs	2032s sh 2029vs	
2013s	2015ms 2012sh	2004sh	2015m 2005m sh	2016s 2008s	2017m sh 2005w sh
2004ms sh		2001s			2000s
	1994sh 1991sh			1995s sh	1995w sh
1965w sh		1966sh		1969w sh	1970w sh
1850w	1854m	1845w br	1845vw br	1853mw	1848vw br

Table 9.3 Compounds of formula $(RM')_2Co_4(CO)_{10}(\mu-X)$

$Me_3Ge_3Co_5(CO)_{14}$		$Me_3Si_3Co_5(CO)_{14}$	$Et_2Ge_3Co_6(CO)_{17}$	
hc	K	c	h	CsI
	2120vw?			2115vw?
2092mw	2097mw	2102w	2091w	2095mw
				2067ms sh
2062ms	2058ms	2076mw	2062vs	2060ms
		2051m	2053s	2053ms sh
	2043w			2046m
			2038vs	
			2034s	2033ms sh
2023mw		2033vs	2022mw	2027ms
2016vs		2025vs br	2017m	2016s sh
				2013s
				2008s sh
2010ms sh	2001 vs sh	2018m sh		2001ms sh
1994w	1992vs	2005mw		1993m
1980w	1963m	1994w		1988m
		1966w	1840w	1825mw

9.2 NMR spectra :

The NMR study of $(RM')_2Co_4(CO)_{10}(\mu-X)$ type compounds is a relatively new area as only one such study has been reported [91]. The 1H NMR resonance of $(PhGe)_2Co_4(CO)_{11}$ (δ 7.94 ppm) and $(t-BuGe)_2Co_4(CO)_{11}$ (δ 1.80 ppm) were studied. The chemical shift of the $(PhGe)_2Co_4(CO)_{11}$ compares fairly closely to those of $PhGeCo_5(CO)_{15}$ (δ 7.71 ppm, δ 8.42 ppm in Table 9.4) and the signal was better resolved in this study. The alkyl proton signals of all the $(RM')_2Co_4(CO)_{10}(\mu-X)$ type compounds were observed to be shifted to the low field side -- in the region of δ 2.5 ppm for Me protons, δ 2.0 ppm for Me on the Et group and 3.5 ppm for the CH_2 protons. The methyl protons of four coordinated Ge or Si compounds are in the region of δ 0.8 to 1.5 ppm (see Chapter Three, Five and Six, also [17,20,61,75,86,87,91,105]). The low field shift is most likely caused by the M' which is now five coordinated. The Me protons on the ethyl group which are three bonds away from the M' showed a smaller low field shift compare to those on the Me group directly attached to the five coordinated Ge which are two bonds away from the M' atom. This would also explain the smaller low field shift reported for $(t-BuGe)_2Co_4(CO)_{11}$. The Me group in this case is three bonds away from the Ge, i.e. in the similar situation as the Me group on the Et group. However, the 1H chemical shift of the protons on $t-BuGeCo_3(CO)_{11}$ is δ 1.18 ppm in $CDCl_3$ [105] indicating a low field shift associated with the increase in coordination number of the Ge atom in $(t-BuGe)_2Co_4(CO)_{11}$ did take place. Similarly, the phenyl protons closer to the Ge atom in $PhGe_2Co_5(CO)_{15}$ showed a larger low field shift (8.24 ppm) compared to the those further away (7.71ppm).

The ^{13}CO NMR of the CO groups of $(RM')_2Co_4(CO)_{10}(\mu-X)$ has never been reported. They are in the region of δ 200 ppm for those in the

Co_4 central core and δ 196 ppm for those on the apical $\text{M}'\text{Co}(\text{CO})_4$ and bridging $\text{GeCo}(\text{CO})_4$ and δ 199 ppm for bridging $\text{GeCo}_2(\text{CO})_7$ unit (Table 9.5).

The observation of only one CO environment in $(\text{RM}')_2\text{Co}_4(\text{CO})_{11}$ type compounds indicates that the terminal and bridging CO's in the central Co_4 core are rapidly exchanging even at -50°C . Studies by Richmond and Kochi [129] with $(\text{PPh})_2\text{Co}_4(\text{CO})_8(\mu\text{-CO})_2$ showed a broad singlet at δ 208 ppm at 0°C . However, at -100°C , two singlets were observed : δ 238 ppm (1x) and δ 204 ppm (4x). The first peak was assigned to the ^{13}C O signal of the two bridging CO's while the former to the eight terminal CO's. The temperature of -50°C used in this work is obviously not low enough to differentiate the terminal and bridging CO's.

However, the presence of a bridging Ge group in $\text{Me}_3\text{Ge}_3\text{Co}_5(\text{CO})_{14}$ (10a) and $\text{Et}_2\text{Ge}_3\text{Co}_6(\text{CO})_{17}$ (11) acts as a barrier to the rapid exchange of CO's in the central Co_4 core. Up to three different CO environments in the central Co_4 core were observed for $\text{Me}_3\text{Ge}_3\text{Co}_5(\text{CO})_{14}$ (see Section 3.5.3 for details) and up to two were observed for $\text{Et}_2\text{Ge}_3\text{Co}_6(\text{CO})_{17}$ (Section 7.7.3 for details). However, the bridging CO on the bridging $\text{GeCo}_2(\text{CO})_7$ unit in $\text{Et}_2\text{Ge}_3\text{Co}_6(\text{CO})_{17}$ was not differentiated from the six terminal CO's.

The ^{13}C O NMR chemical shifts were not as greatly affected by the coordination of the M' atom as the ^1H NMR. The ^{13}C O signals of $(\text{RM}')_2\text{Co}_4(\text{CO})_{10}(\mu\text{-X})$ were in the same region as those of $(\text{RR}'\text{Ge})\text{GeCo}_4(\text{CO})_{13}$ (5) and $\text{M}'\text{Co}_4(\text{CO})_{14}$ (2) (see Chapters Five, Six and Appendix 2).

Table 9.4 ^1H NMR of $(\text{RM}')_2\text{Co}_4(\text{CO})_{10}(\mu\text{-X})$ at probe temperature = 27°C

Compounds	^1H signals
$(\text{PhGe})_2\text{Co}_4(\text{CO})_{11}$	7.94 (m) [91]
$(t\text{-BuGe})_2\text{Co}_4(\text{CO})_{11}$	1.80 (s) [91]
$(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$	2.75
$(\text{MeSi})_2\text{Co}_4(\text{CO})_{11}$	2.37
$\text{MeGe}_2\text{Co}_5(\text{CO})_{15}$	2.77
$\text{PhGeCo}_2(\text{CO})_{15}$	7.71 (m, 3x), 8.24 (m, 2x)
$\text{MeSiCo}_5(\text{CO})_{15}$	2.44
$\text{EtGeSiCo}_5(\text{CO})_{15}$	2.00 (t, 3x), 3.45 (q, 2x)
$\text{Me}_3\text{Ge}_3\text{Co}_5(\text{CO})_{14}$	1.97 (1x), 2.47 (1x), 2.56 (1x)
$\text{Et}_2\text{Ge}_3\text{Co}_6(\text{CO})_{17}$	1.96 (t, 3x), 3.29 (q, 2x)

All peaks are singlets unless stated, solvent = CDCl_3

Table 9.5 ^{13}C NMR of $(\text{RM}')_2\text{Co}_4(\text{CO})_{10}(\mu\text{-X})$

Compounds	Temp $^\circ\text{C}$	^{13}C NMR
$(\text{MeGe})_2\text{Co}_4(\text{CO})_{11}$	27	203.2 (br)
	-50	202.6 (br)
$(\text{MeSi})_2\text{Co}_4(\text{CO})_{11}$	-50	202.6 (br)
$\text{Ge}_2\text{Co}_6(\text{CO})_{19}$	-50	202.9 (3x, br), 195.6 (2x, br)
$\text{MeGe}_2\text{Co}_5(\text{CO})_{15}$	0	203.2 (3x, br), 195.3 (1x, br)
	-5	203.1 (3x, br), 195.7 (1x, br)
	-50	202.6 (3x, br), 195.9 (1x)
$\text{Me}_3\text{Ge}_3\text{Co}_5(\text{CO})_{14}$	27	201.9 (broad peak), 197.0 (s)
	-50	203.4, 200.5, 199.6, 196.8 (see Fig 3.7a)
$\text{Et}_2\text{Ge}_3\text{Co}_6(\text{CO})_{17}$	27	202.7 (2x) 199.2 (1x, br)
	-50	202.8, 202.2, 199.0 (see Table 7.17)

All signals are singlets unless stated, solvent = CDCl_3

9.3 Crystal structures

Tables 9.1 to 9.3 above show all the $(RM')_2Co_4(CO)_{11}$ type compounds and their derivatives known to date. Table 9.6 gives the summary of bond lengths and bond angles of the crystal structures of some of these compounds.

The $M'---M'$ non-bonded distances in these clusters, are much less than twice the Van der Waals radius of M' involved and about 20% longer than the $M'-M'$ bond (about 2.35Å for Si and 2.44Å for Ge). The Si---Ge non-bonded distance of 2.862Å is also about 20% longer than that of the average Si and Ge bonded distance (2.357(4)Å for H_3SiGeH_3 [59,153]). The Ge---Ge non-bonded distances are shorter in $Et_2Ge_3Co_5(CO)_{17}$ and $Me_3Ge_3Co_5(CO)_{14}$ compared to those with $Co_4(CO)_{11}$ core : only about 18% longer than the Ge-Ge bonded distances. Theoretical analysis on the hypothetical $(HP)_2Fe_4(CO)_{12}$ cluster has shown the short P---P non-bonding distance can be attributed to the small energy gap between the bonding molecular orbitals and the first anti-bonding orbital as shown in Fig 1.36 [122]. This anti-bonding orbital becomes approximately non-bonding, allowing the extra set of skeletal electrons to be accommodated (7 skeletal pairs are predicted by PSEP theory, but most possess 8 -- see Chapter One). Dahl et al [117,125], have suggested that the close E---E (E = P,S) distance in the analogous phosphorus and sulphur cluster is due mainly to the constraints imposed upon the heteroatoms by the cobalt-E bond, lengths and angles.

One of the interesting features in the bonding of M' to the Co_4 core is the slightly shorter $M'-Co$ bonds on the Co atoms containing the fully bridging carbonyls or bridging M' (note also the very slightly larger dihedral angle between $M'-Co_b-Co_b$ plane and Co_4 plane compared to that between $M'-Co_n-Co_n$ and Co_4 plane in Table 9.6). This

is true for all the clusters in the table, but for $\text{MeGe}_2\text{Co}_5(\text{CO})_{15}$ and $\text{Et}_2\text{Ge}_3\text{Co}_5(\text{CO})_{17}$ this is not as pronounced. The observed inequality in the $\text{M}'\text{-Co}$ bonds may be related to the difference in electron counts in the two sets of Co's : the Co's containing the bridging CO (labelled Co_b , see Fig 9.1) have 17.5 electrons each while the other two Co's (labelled Co_n) contain 18.5 electrons each. This uneven distribution can be compensated by the formation of a semi-bridging CO across Co_b and Co_n . In this way, electrons are donated from the electron rich Co_n to Co_b . This is observed in all the clusters. The shorter (so stronger) $\text{Co}_n\text{-CO}$ semi-bridging bond is consistent with the higher electron count on Co_n . Another way of compensating this uneven electron distribution is by the M' moving towards Co_b , thus acting as a stronger electron donor to both the Co_b and a weaker electron donor to Co_n 's. The shorter $\text{M}'\text{-Co}_b$ distances observed in most of the clusters are probably the result of the second type of electron distribution.

It is also interesting to note that the shorter of the two $\text{M}'\text{-Co}_b$ bonds occurs on the side where the semi-bridging CO is almost terminal on Co_n (Fig 9.1). This Co_n is therefore still holding most of the extra electrons (i.e. 18.5 electrons on Co_n). The electron compensation is probably the result of M' moving towards Co_b , therefore shorter $\text{M}'\text{-Co}_b$ bond on this side of the molecule.

If however, the electron compensation discussed above did not completely even out the electron density, the extra residual electron density in the two Co_n 's may result in a stronger $\text{Co}_n\text{-Co}_n$ bond i.e. shorter bond. This effect could not be assessed in this study.

The $\text{M}'\text{-Co}_{\text{apical}}$ bond averages 2.405Å for $\text{M}' = \text{Ge}$ and 2.35Å for Si which are normal for such type of bond.

The Co_4 cores of all the clusters are distorted. The unequal Co-Co bonds can be related to the type and degree of bridging. The shortest

Co-Co bond is (except for $\text{Ge}_2\text{Co}_6(\text{CO})_{19}$ and $\text{Si}_2\text{Co}_6(\text{CO})_{19}$) the one carrying a fully bridging CO ($\text{Co}_b\text{-Co}_b$), the longest being the one without any bridging CO ($\text{Co}_n\text{-Co}_n$), while those carrying the semi-bridging CO's are of intermediate bond length (Fig 7.8 and Fig 8.9). This is consistent with the shortening of M-M bonds with CO bridging across them [117,125]. This however is not true for the isomorphous $\text{Ge}_2\text{Co}_6(\text{CO})_{19}$ and $\text{Si}_2\text{Co}_6(\text{CO})_{19}$, which is likely to be due to packing effects. In $\text{Me}_3\text{Ge}_3\text{Co}_5(\text{CO})_{14}$ and $\text{Et}_2\text{Ge}_3\text{Co}_5(\text{CO})_{17}$ (Section 3.5.4 and Fig 7.16) the longest Co-Co bond is the one fully bridged by the Ge atom while the shortest are the two containing the semi-bridging carbonyls. The replacement of the $\mu\text{-CO}$ by a M' results in the lengthening of the bond, presumably to accommodate the bigger Ge atom [156].

The fully bridging CO in $(\text{MeM}')_2\text{Co}_4(\text{CO})_{11}$ is planar and symmetric, as required by their mirror symmetry while those on $\text{M}'_2\text{Co}_6(\text{CO})_{19}$ were planar but slightly asymmetrical. The $\mu\text{-CO}$ in $\text{EtGeSiCo}_5(\text{CO})_{15}$ is asymmetric and non-planar (dihedral angle between $\mu\text{-CO-Co(2)-Co(3)}$ to Co_4 plane is $4.42(9)^\circ$), but the Co-C-O angles were about 135° which is very similar to those in $(\text{MeM}')_2\text{Co}_4(\text{CO})_{11}$ and $\text{M}'_2\text{Co}_6(\text{CO})_{19}$. Unlike the $\mu\text{-CO}$ in $\text{EtGeSiCo}_5(\text{CO})_{15}$, the asymmetric $\mu\text{-CO}$ in $\text{MeGe}_2\text{Co}_5(\text{CO})_{15}$ is virtually planar (dihedral angle between $\mu\text{-CO-Co(2)-Co(3)}$ to Co_4 plane is $179.4(3)^\circ$). In both $\text{Me}_3\text{Ge}_3\text{Co}_5(\text{CO})_{14}$ and $\text{Et}_2\text{Ge}_3\text{Co}_5(\text{CO})_{17}$, the $\mu\text{-Ge}$ units are non-planar (dihedral angles between $\mu\text{-GeCo}_2$ to Co_4 plane are 175.17° and 171.4° respectively).

The bridging Ge-Co bond lengths were unusually short : $\text{Ge(3)-Co(2)} = 2.339\text{\AA}$ in $\text{Me}_3\text{Ge}_3\text{Co}_5(\text{CO})_{14}$ and $\text{Ge(3)-Co(3)} = \text{Ge(3)-Co(4)} = 2.315\text{\AA}$ in $\text{Et}_2\text{Ge}_3\text{Co}_6(\text{CO})_{17}$. The Co-Ge-Co angles are $\sim 72^\circ$ in both molecules, comparable to that in $\text{Me}_2\text{Ge}_2\text{Co}_4(\text{CO})_{14}$ (69.5°), but larger than those in $\text{GeCo}_4(\text{CO})_{14}$ (66°) and $\text{PhGeCo}_3(\text{CO})_{11}$ (64.6°). The short bridging Ge-

Co bonds and the large Co-Ge-Co may be due to the long Co-Co bonds across which the Ge atom bridges.

The Ge-Co and Co-Co bonds in the bridging units of both $\text{Me}_3\text{Ge}_3\text{Co}_5(\text{CO})_{14}$ and $\text{Et}_2\text{Ge}_3\text{Co}_6(\text{CO})_{17}$ are comparable to those in $\text{MeGeCo}_3(\text{CO})_{11}$, $\text{Me}_2\text{Ge}_2\text{Co}_4(\text{CO})_{14}$ and $\text{GeCo}_4(\text{CO})_{14}$:

		I	II	III
Ge(3)-Co(3) in $\text{Me}_3\text{Ge}_3\text{Co}_5(\text{CO})_{14}$	= 2.440Å	2.421Å	2.455Å	-
Ge(3)-Co(5) (av) in $\text{Et}_2\text{Ge}_3\text{Co}_6(\text{CO})_{17}$	= 2.385Å	2.376Å	2.397Å	2.36Å
Co(5)-Co(6) in $\text{Et}_2\text{Ge}_3\text{Co}_6(\text{CO})_{17}$	= 2.531Å	2.582Å	2.733Å	2.56Å

I = $\text{MeGeCo}_3(\text{CO})_{11}$, II = $\text{Me}_2\text{Ge}_2\text{Co}_4(\text{CO})_{14}$, III = $\text{GeCo}_4(\text{CO})_{14}$

The Co-C and C-O bond lengths of the terminal CO's in all the clusters average 1.79Å and 1.15Å respectively which is normal for cobalt carbonyl compounds. The Ge to alkyl carbon average bond distance is 1.96Å which compares well to those in MeGeH_3 and EtGeH_3 (1.95Å each) [11]. The C-C distance in the ethyl group of $\text{EtGeSiCo}_5(\text{CO})_{15}$ is about 1.473Å which is slightly shorter than that in C_2H_6 (1.53Å) [157]. The corresponding C-C distances in $\text{Et}_2\text{Ge}_3\text{Co}_6(\text{CO})_{17}$ are 1.502Å and 1.278Å. The latter C-C bond is unrealistically short (compare carbon double bond of 1.34Å in C_2H_4), and is probably an artifact arising from disorder for the ethyl group.

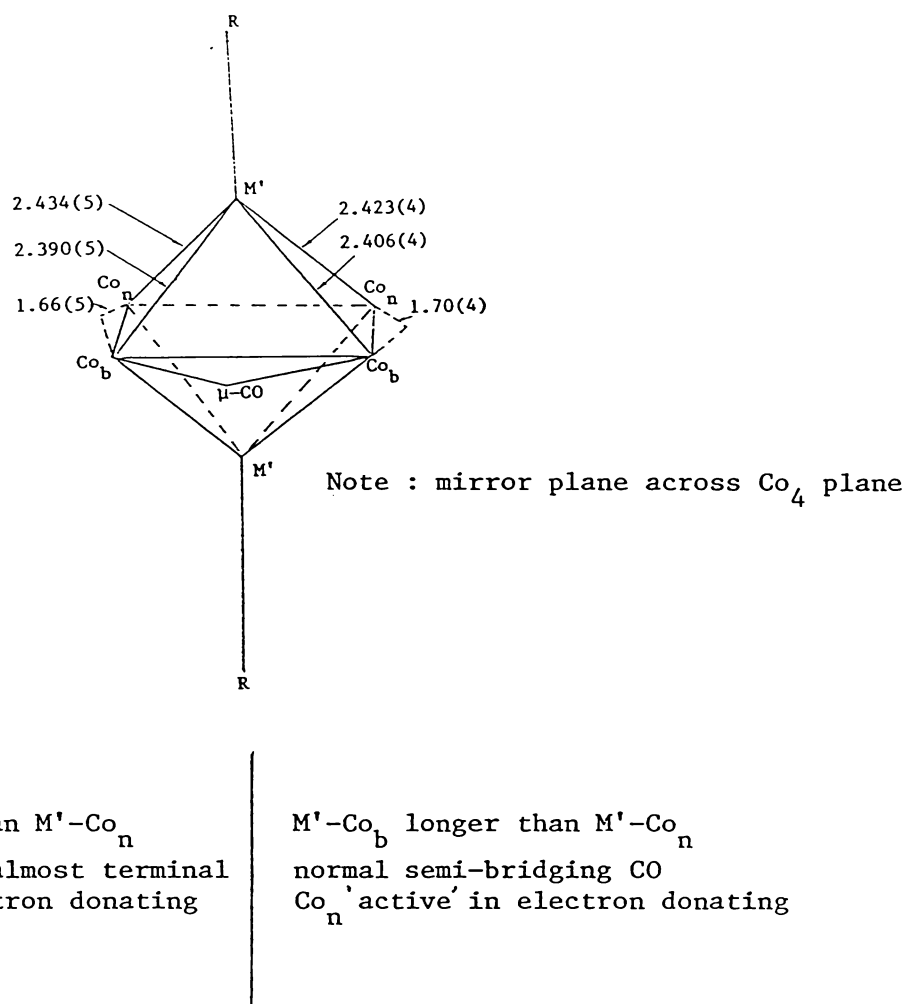


Fig 9.1 $M'-Co$ bond distances in $(RM')_2Co_4(CO)_{11}$
with $R = Co(CO)_4$ and $M' = Ge$ [27] as an example

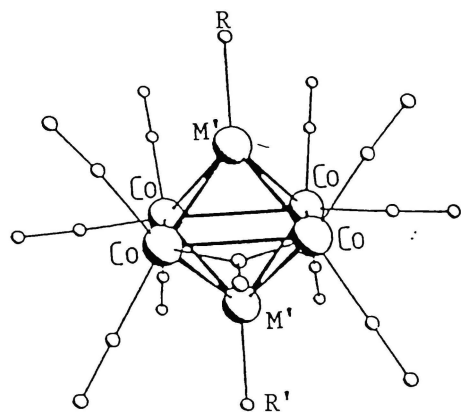
Table 9.6 Crystal structure data of $(RM')_2Co_4(CO)_{10}(\mu-X)$ type compounds

Compounds	$(MeGe)_2Co_4(CO)_{11}$ [84]	$(MeSi)_2Co_4(CO)_{11}$ [144]	$Ge_2Co_6(CO)_{19}$ [18,27]	$Si_2Co_6(CO)_{19}$ [93]	$MeGe_2Co_5(CO)_{15}$ (1g)	$EtGeSiCo_5(CO)_{15}$ (1k)	$Me_3Ge_3Co_5(CO)_{14}$ (10a)	$Et_2Ge_3Co_6(CO)_{17}$ (11)
Space group	C2/m	C2/m	Cmca	Cmca	C2/c	P2 ₁ /c	C2/m	P ₁
M'---M' (Å)	2.926	2.728	2.995	2.817	2.957	2.862	2.882	2.890
M'-Co (Å) :								
M'-Co _n	2.392	2.317	2.429	2.356	2.405	2.373	2.404	2.404
M'-Co _b	2.383	2.302	2.398	2.319	2.396	2.355	2.392	2.385
Co ₄ core (Å) :								
Co _n -Co _n	2.721	2.690	2.694	2.653	2.745	2.697	2.772	2.715
a b	a = 2.6932	2.651	2.672	2.696	a = 2.739	2.668	2.673	2.657
Co _b -Co _b	2.5802	2.548	2.605	2.569	2.610	2.581	2.734	2.722
	b = 2.6932	2.651	2.736	2.623	b = 2.654	2.696	2.673	2.703
Terminal CO (Å) :								
Co-C (av)	1.801	1.805	1.733	1.810	1.797	1.799	1.791	1.791
C-O	1.132	1.136	1.20	1.132	1.169	1.132	1.142	1.131
μCO :	sym/planar	sym/planar	planar	planar	asym	asym/non-planar		
Co-C (av, Å)	1.922	1.912	1.949	1.971	1.862,2.035	1.959,1.904		
C-O (Å)	1.1921	1.163	1.07	1.211	1.174	1.156		
Co-C-O (°)	137.6	138.2	136.4	133.2	133.5	135.5		
Semi-μCO (Å) :								
Co-C : side a	1.771,2.531	1.789,2.510	1.704,2.394	1.771,2.63	1.774,2.738	1.787,2.440	1.776,2.480	1.765,2.682
side b			1.665,2.614	1.781,2.291	1.818,2.257	1.773,2.639		1.789,2.345
C-O (av)	1.132	1.148	1.224	1.201	1.142	1.131	1.148	1.138
Apical Co(CO) ₄ : --		--						
M'-Co (Å)			2.405	2.347	2.403	2.357	2.440	---
Co-C (av, Å)			1.765	1.800	1.784	1.805	1.812	
C-O (av, Å)			1.183	1.136	1.16	1.112	1.123	
M'-C (av, Å)	1.951	1.864			1.969	1.965	1.931	1.963
C-C (Å)						1.473		1.502,1.278

Table 9.6 Crystal structure data of $(RM')_2Co_4(CO)_{10}(\mu-X)$ type compounds *cont'd...*

Compounds	$(MeGe)_2Co_4(CO)_{11}$ [84]	$(MeSi)_2Co_4(CO)_{11}$ [144]	$Ge_2Co_6(CO)_{19}$ [18,27]	$Si_2Co_6(CO)_{19}$ [93]	$MeGe_2Co_5(CO)_{15}$ (1g)	$EtGeSiCo_5(CO)_{15}$ (1k)	$Me_3Ge_3Co_5(CO)_{14}$ (10a)	$Et_2Ge_3Co_6(CO)_{17}$ (11)
μGe unit :	--	--	--	--	--	--	sym	sym
Ge- Co_b (Å)							2.339	2.315
Co_b -Ge- Co_b (°)							71.5	72
Ge-C (Å)							1.949	--
Ge-Co (Å)							see above	2.385
Co-C (av Å)							"	1.800
C-O (Å)							"	1.122
Co-Co (Å)							--	2.531
μCO :							--	
Co-C (Å)								1.915, 1.962
C-O (Å)								1.165
Dihedral angles								
$M'Co_nCo_n$ to Co_4					131.2(1)	133.41(3)	133.36	133.23(1)
$M'Co_bCo_b$ to Co_4					133.0(1)	132.88(4)	132.32	132.03(1)

Appendix 1



(1) $(RM')(R'M')Co_4(CO)_{11}$

$(RM') = (R'M')$

$(RM')(R'M') =$

$a = MeGe$

$g = MeGe, (CO)_4CoGe$

$b = MeSi$

$h = EtGe, (CO)_4CoGe$

$c = (CO)_4CoGe$

$i = (CO)_4Mn, (CO)_4Co$

$d = (CO)_4CoSi$

$j = MeGe, (CO)_4CoSi$

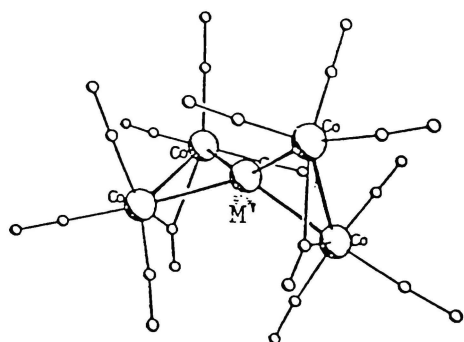
$e = PhGe$

$k = EtGe, (CO)_4CoSi$

$f = t-BuGe$

$m = MeSi, (CO)_4CoSi,$

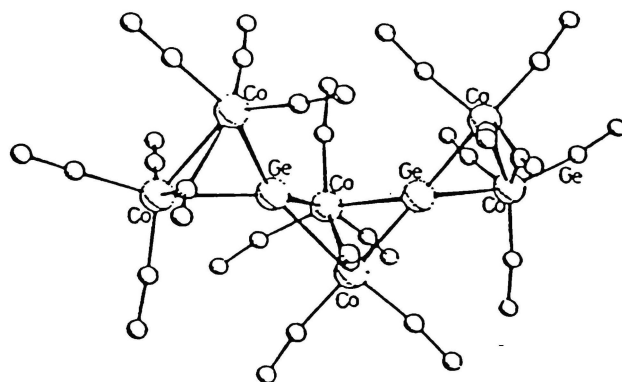
$l = EtGe$



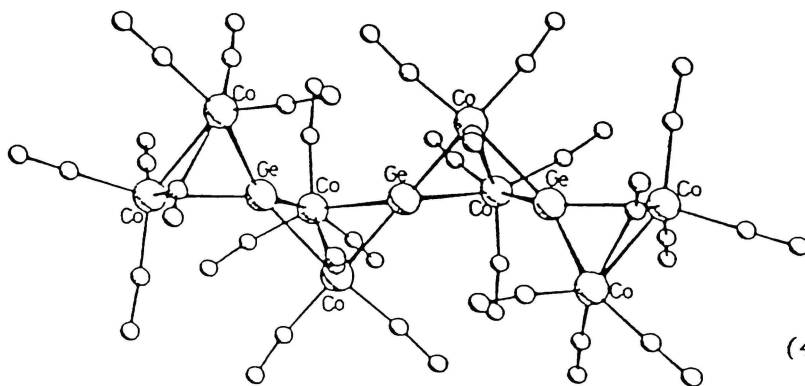
(2) $M'Co_4(CO)_{14}$

$a M' = Ge$

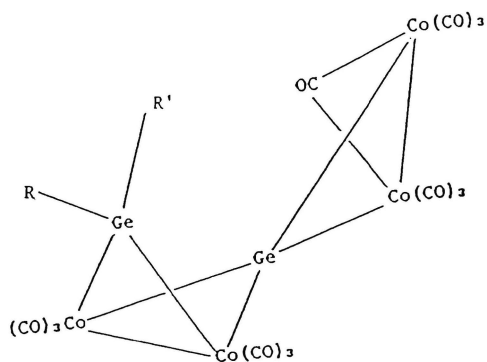
$b M' = Si$



(3) $Ge_2Co_6(CO)_{20}$



(4) $Ge_3Co_8(CO)_{26}$



(5) $(RR'Ge)GeCo_4(CO)_{13}$

$(RR') =$

$a = Me_2$

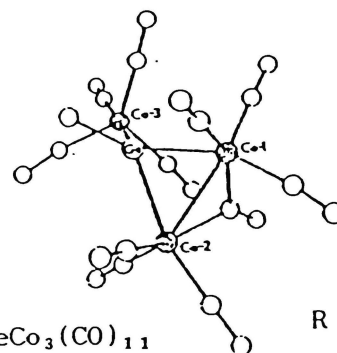
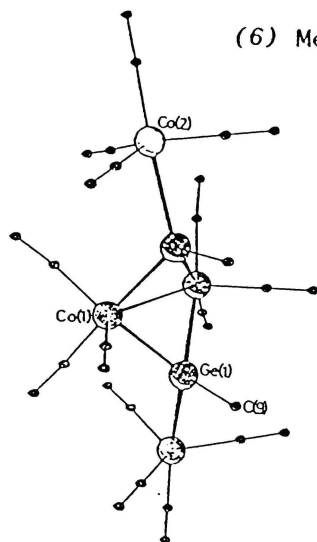
$b = MeH$

$c = Me[Co(CO)_4]$

$d = EtH$

$e = PhH$

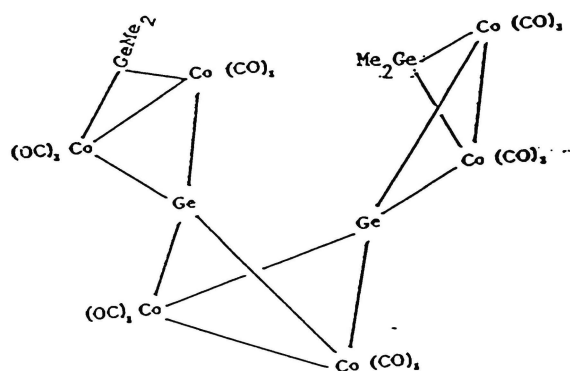
$f = MeCl$

(6) $\text{Me}_2\text{Ge}_2\text{Co}_4(\text{CO})_{14}$ (7) $\text{RGeCo}_3(\text{CO})_{11}$

R =

a = Me

b = Ph

(8) $(\text{Me}_2\text{Ge})_2\text{Ge}_2\text{Co}_6(\text{CO})_{18}$ (9) $(\text{RR}'\text{Ge})_2\text{GeCo}_4(\text{CO})_{12}$ (RR') =a = Me_2

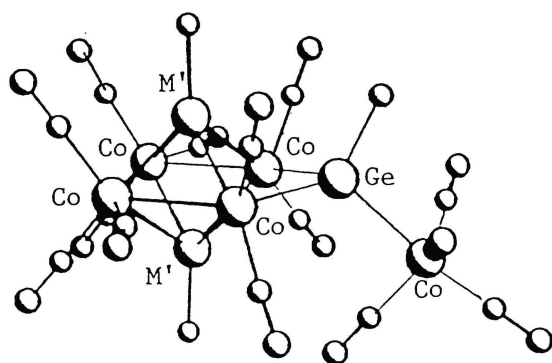
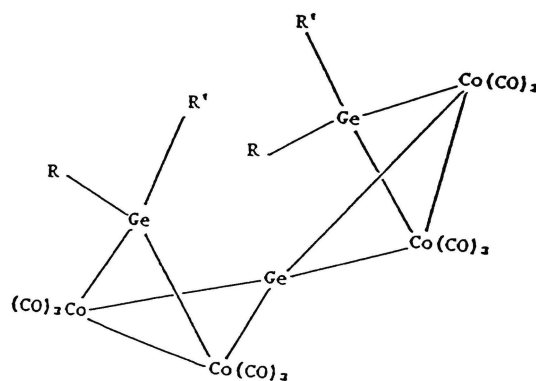
b = MeH

c = EtH

d = PhH

e = EtH, PhH

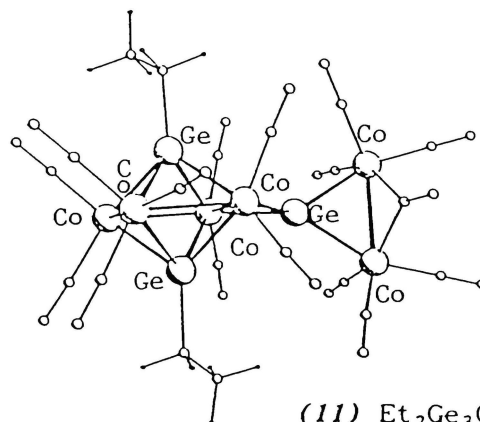
f = MeCl

g = $\text{Me}[\text{Co}(\text{CO})_4]$ h = $\text{Et}[\text{Co}(\text{CO})_4]$ (10) $\text{Me}_3\text{M}'_3\text{Co}_5(\text{CO})_{14}$

M' =

a = Ge

b = Si

(11) $\text{Et}_2\text{Ge}_3\text{Co}_6(\text{CO})_{17}$

Appendix 2

Preliminary studies on the ^{13}C NMR spectra of $\text{SiCo}_4(\text{CO})_{14}$, $\text{GeCo}_4(\text{CO})_{14}$, $\text{Ge}_2\text{Co}_6(\text{CO})_{20}$ and $\text{Ge}_3\text{Co}_8(\text{CO})_{26}$

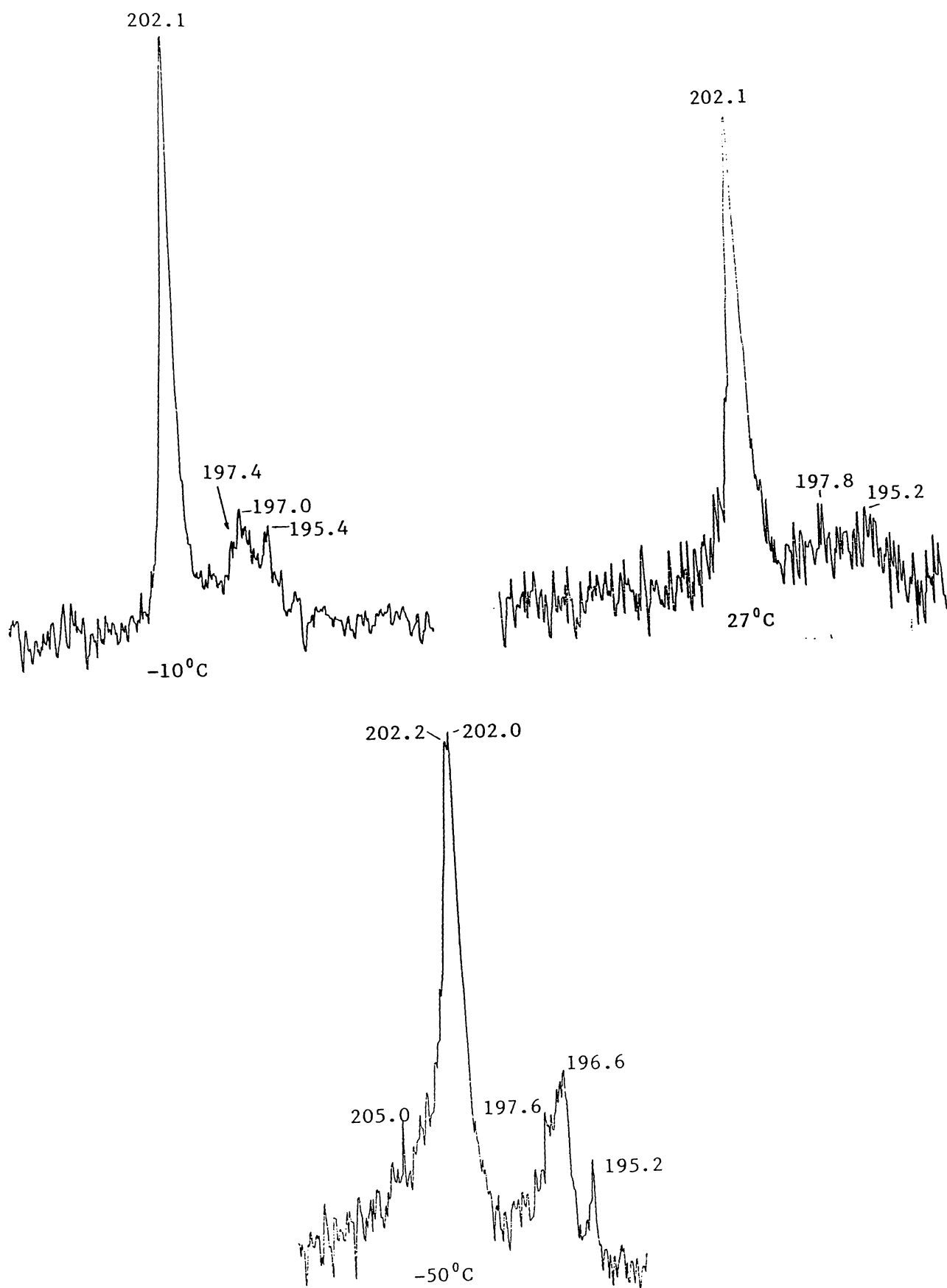
Compounds	Temp ($^{\circ}\text{C}$)	Chemical shifts (δ ppm)
$\text{SiCo}_4(\text{CO})_{14}$	27	201.9
	-8	201.9
	-30	201.9
	-50	201.9
$\text{GeCo}_4(\text{CO})_{14}$	0	201.4
	-20	201.4
	-40	201.4
	-50	201.4
$\text{Ge}_2\text{Co}_6(\text{CO})_{20}$ see Fig A.1. Heating of $\text{Ge}_2\text{Co}_6(\text{CO})_{20}$ (Fig A.4)		
$\text{Ge}_3\text{Co}_8(\text{CO})_{26}$ see Fig A.2.		

Heating of $\text{SiCo}_4(\text{CO})_{14}$ at 30°C for 0.5 hour produced a single at δ 201.9 ppm with a shoulder at δ 200.9 ppm and a small singlet at δ 193.4 ppm : shoulder at δ 200.9 ppm and singlet at δ 193.4 ppm belong to the chemical shift of $\text{SiCo}_4(\text{CO})_{13}$ (spectrum ran at -50°C).

Heating of $\text{GeCo}_4(\text{CO})_{14}$ at 31°C (Fig A.3)

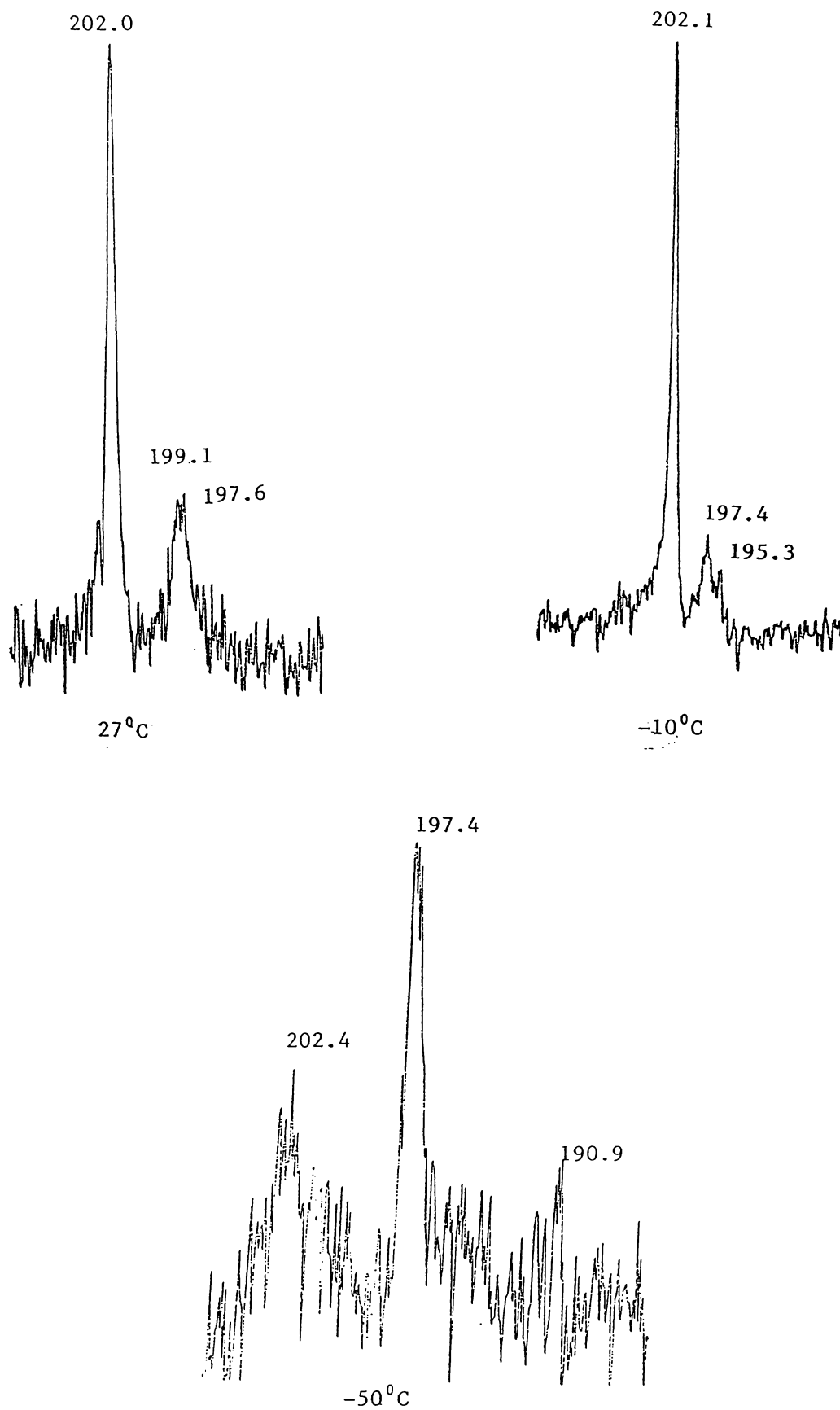
Time	Ratio of 201.4 : 200.9 : 193.5
5 hr	0.72 : 0.20 : 0.08
11.5	0.68 : 0.23 : 0.09
21	0.62 : 0.27 : 0.11
43	0.53 : 0.34 : 0.13
67	0.42 : 0.42 : 0.16

Like, $\text{SiCo}_4(\text{CO})_{14}$, heating of $\text{GeCo}_4(\text{CO})_{14}$ results in the formation of $\text{GeCo}_4(\text{CO})_{13}$ with peaks at δ 200.9 ppm and δ 193.5 ppm.



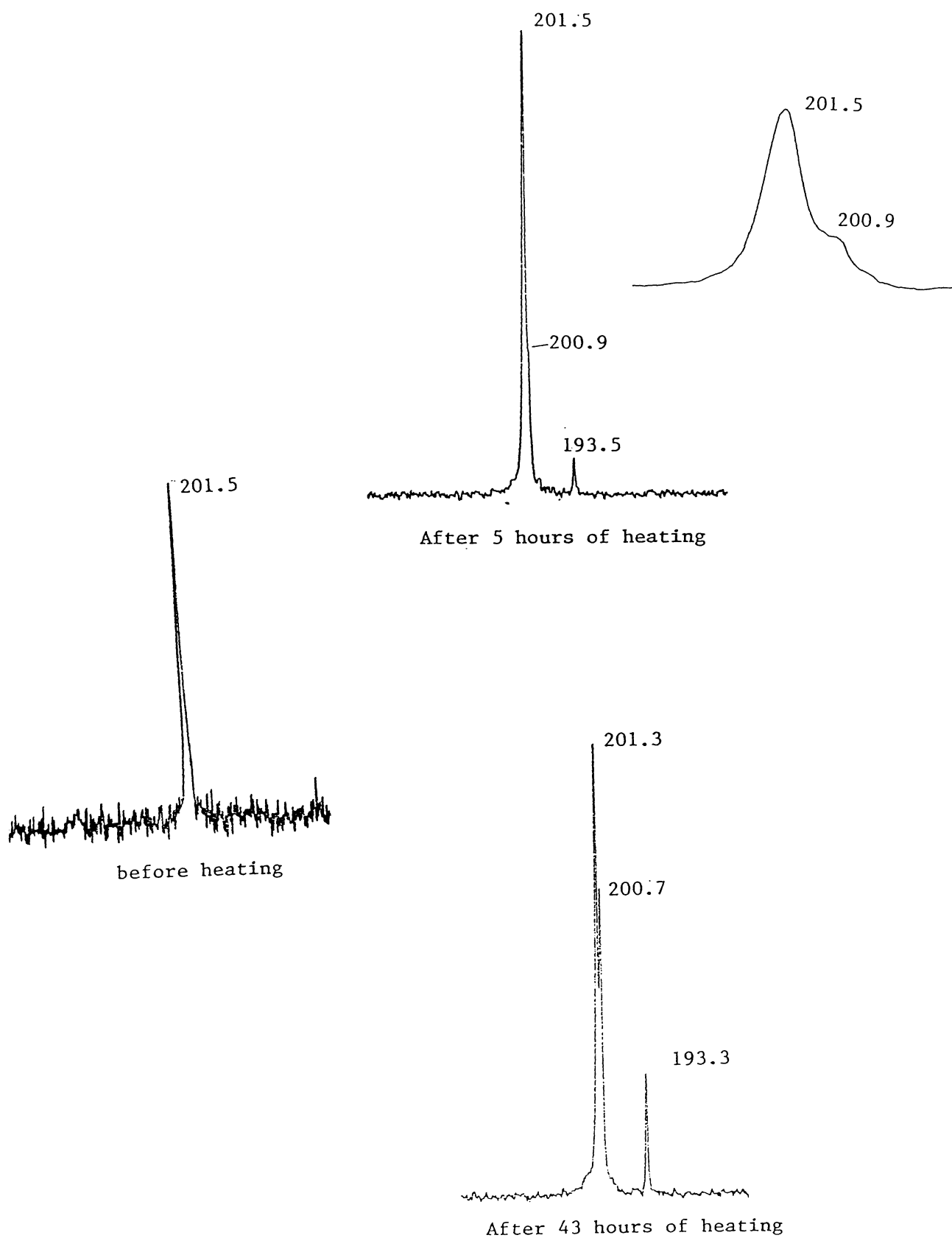
^{13}C NMR spectra of $\text{Ge}_2\text{Co}_6(\text{CO})_{20}$ (3) at different temperatures

Fig A.1



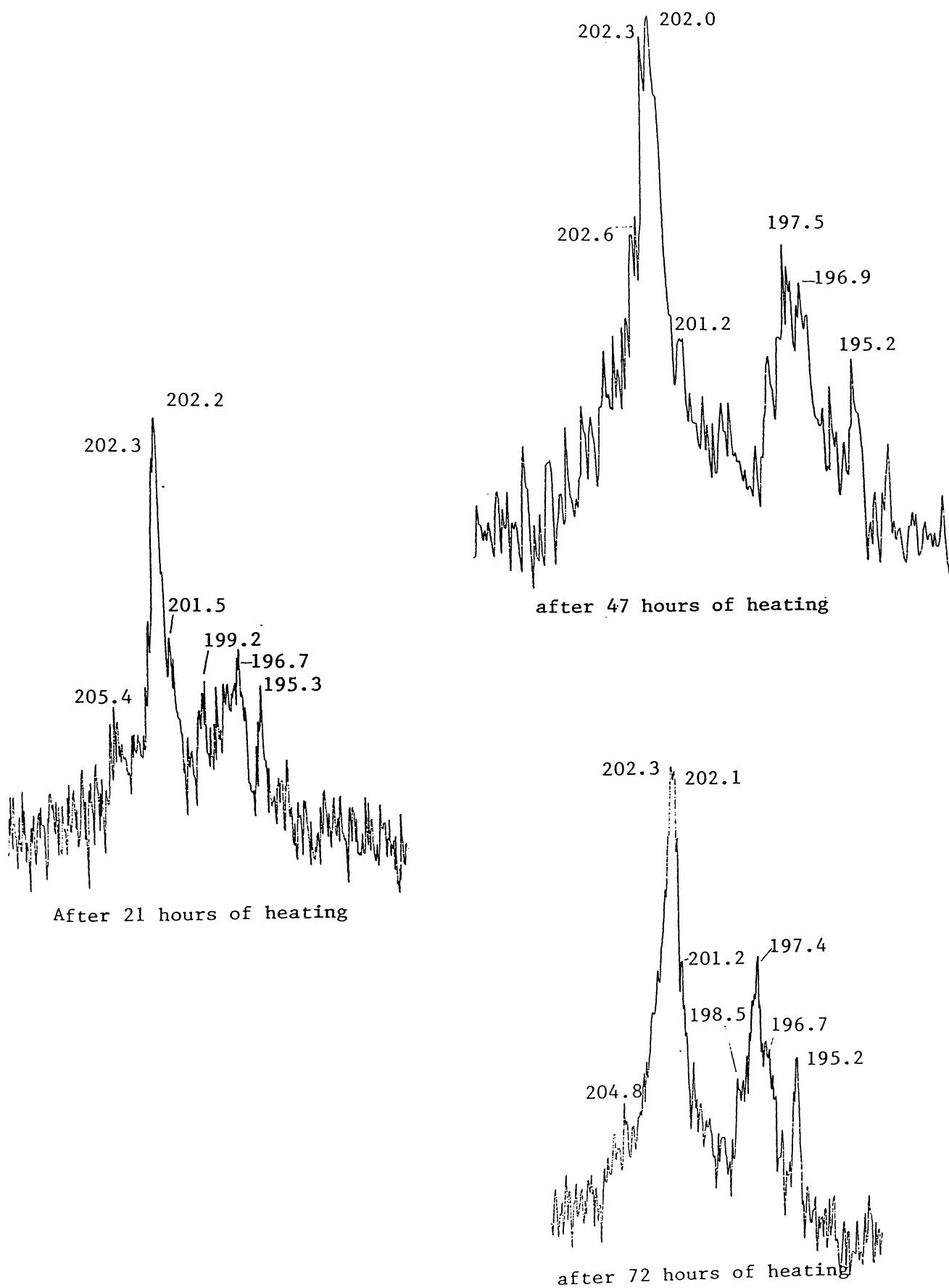
^{13}C NMR spectra of $\text{Ge}_3\text{Co}_8(\text{CO})_{26}$ (4) at various temperatures

Fig A.2



The heating of ^{13}C enriched $\text{GeCo}_4(\text{CO})_{14}$ at 30°C in CDCl_3
 probe temperature = -50°C

Fig A.3



The heating of $\text{Ge}_2\text{Co}_6(\text{CO})_{20}$ at 30°C in CDCl_3 , probe temperature = -50°C

Fig A.4

Appendix 3

Final positional and equivalent thermal parameters
of $\text{Me}_3\text{Ge}_3\text{Co}_5(\text{CO})_{14}$

ATOM	X/A	Y/B	Z/C	Ueq
Ge(1)	0.8396(1)	0.0000(0)	0.3365(1)	0.037
Ge(2)	0.6203(1)	0.0000(0)	0.2757(1)	0.040
Ge(3)	0.8435(1)	0.0000(0)	0.1568(1)	0.038
Co(1)	0.6918(1)	0.1106(1)	0.3727(1)	0.044
Co(2)	0.7682(1)	0.1111(1)	0.2423(1)	0.038
Co(3)	0.7773(2)	0.0000(0)	0.0323(1)	0.074
C(11)	0.772(1)	0.126(1)	0.4546(6)	0.062
O(11)	0.8234(8)	0.1394(8)	0.5056(5)	0.109
C(12)	0.7112(9)	0.241(1)	0.3343(6)	0.056
O(12)	0.7156(7)	0.3324(7)	0.3240(5)	0.083
C(13)	0.5548(9)	0.128(1)	0.3976(6)	0.068
O(13)	0.4690(7)	0.143(1)	0.4144(5)	0.109
C(21)	0.893(1)	0.183(1)	0.2494(6)	0.055
O(21)	0.9725(7)	0.2318(7)	0.2557(5)	0.090
C(22)	0.6815(8)	0.186(1)	0.1801(6)	0.059
O(22)	0.6337(8)	0.2372(9)	0.1400(5)	0.107
C(31)	0.637(2)	0.000(0)	0.0587(9)	0.082
O(31)	0.551(1)	0.000(0)	0.0752(7)	0.121
C(32)	0.844(1)	-0.132(2)	0.0346(8)	0.099
O(32)	0.887(1)	-0.210(1)	0.0358(7)	0.138
C(33)	0.744(2)	0.000(0)	-0.061(1)	0.137
O(33)	0.724(1)	0.000(0)	-0.1209(8)	0.213
C(111)	0.985(1)	0.000(0)	0.3793(9)	0.062
C(222)	1.001(1)	0.000(0)	0.1537(8)	0.058
C(333)	0.470(1)	0.000(0)	0.2409(8)	0.058

Final positional and thermal parameters of calculated
hydrogen atoms

ATOM	X/A	Y/B	Z/C	U11
H(11)	1.042(1)	-0.037(0)	0.3447(9)	0.100
H(12)	0.994(1)	-0.036(0)	0.4315(9)	0.100
H(13)	1.002(1)	0.085(0)	0.3835(9)	0.100
H(21)	1.026(1)	-0.065(0)	0.1197(8)	0.100
H(22)	1.037(1)	-0.011(0)	0.2067(8)	0.100
H(23)	1.028(1)	0.076(0)	0.1328(8)	0.100
H(31)	0.418(1)	0.000(0)	0.2853(8)	0.100
H(32)	0.455(1)	-0.071(0)	0.2089(8)	0.100
H(33)	0.455(1)	0.071(0)	0.2089(8)	0.100

Thermal parameters

ATOM	U11	U22	U33	U23	U13	U12
Ge(1)	0.0339(9)	0.040(1)	0.0352(9)	0.0000(0)	-0.0051(7)	0.0000(0)
Ge(2)	0.0313(9)	0.055(1)	0.0339(9)	0.0000(0)	-0.0028(7)	0.0000(0)
Ge(3)	0.0373(9)	0.046(1)	0.0316(9)	0.0000(0)	0.0013(7)	0.0000(0)
Co(1)	0.0468(8)	0.052(1)	0.0341(8)	-0.0060(8)	0.0006(6)	0.0068(8)
Co(2)	0.0399(8)	0.0370(9)	0.0371(8)	0.0037(7)	0.0019(6)	0.0041(7)
Co(3)	0.053(2)	0.137(3)	0.032(1)	0.000(0)	0.000(1)	0.000(0)
C(11)	0.083(8)	0.061(9)	0.041(7)	-0.023(7)	-0.004(6)	0.002(7)
O(11)	0.151(9)	0.107(9)	0.064(6)	-0.044(6)	-0.050(6)	0.038(7)
C(12)	0.066(8)	0.053(8)	0.048(7)	-0.005(6)	-0.008(6)	0.011(7)
O(12)	0.108(7)	0.049(6)	0.095(7)	-0.007(5)	0.024(6)	0.020(5)
C(13)	0.056(7)	0.09(1)	0.056(8)	0.001(7)	0.012(6)	0.011(8)
O(13)	0.062(6)	0.18(1)	0.086(7)	-0.002(7)	0.025(5)	0.024(7)
C(21)	0.072(8)	0.046(8)	0.047(7)	-0.004(6)	0.007(6)	-0.002(7)
O(21)	0.084(6)	0.074(7)	0.114(8)	-0.011(6)	0.021(6)	-0.048(6)
C(22)	0.053(7)	0.078(9)	0.046(7)	0.023(7)	0.015(6)	0.032(7)
O(22)	0.120(8)	0.129(9)	0.073(6)	0.036(7)	0.002(6)	0.070(8)
C(31)	0.07(1)	0.14(2)	0.03(1)	0.00(0)	0.00(1)	0.00(0)
O(31)	0.058(8)	0.25(2)	0.059(9)	0.000(0)	0.023(7)	0.000(0)
C(32)	0.07(1)	0.17(2)	0.06(1)	-0.07(1)	0.014(8)	0.01(1)
O(32)	0.11(1)	0.16(1)	0.14(1)	-0.08(1)	0.001(8)	0.027(9)
C(33)	0.06(1)	0.31(4)	0.04(1)	0.00(0)	0.01(1)	0.00(0)
O(33)	0.09(1)	0.49(4)	0.05(1)	0.00(0)	-0.004(9)	0.000(0)
C(111)	0.05(1)	0.08(1)	0.06(1)	0.00(0)	-0.022(9)	0.000(0)
C(222)	0.06(1)	0.06(1)	0.06(1)	0.00(0)	0.014(9)	0.000(0)
C(333)	0.043(9)	0.06(1)	0.07(1)	0.00(0)	0.003(8)	0.000(0)

Appendix 4

Final positional and equivalent thermal parameters
of $\text{MeGeCo}_3(\text{CO})_{11}$

ATOM	X/A	Y/B	Z/C	Ueq
Ge(1)	0.0851(2)	0.7306(2)	0.7213(1)	0.035
Co(1)	0.3001(2)	0.7946(2)	0.6276(1)	0.035
Co(2)	0.3620(2)	0.5845(2)	0.7753(1)	0.036
Co(3)	-0.1437(2)	0.9352(2)	0.8278(2)	0.040
C(11)	0.493(2)	0.802(2)	0.564(1)	0.040
O(11)	-0.611(1)	1.193(2)	0.4765(8)	0.058
C(12)	0.280(2)	0.664(2)	0.530(1)	0.047
O(12)	0.274(1)	0.585(2)	0.4656(9)	0.059
C(13)	0.155(2)	1.006(2)	0.617(1)	0.042
O(13)	0.063(1)	1.146(2)	0.607(1)	0.067
C(21)	0.590(2)	0.478(2)	0.777(1)	0.044
O(21)	0.732(1)	0.408(2)	0.776(1)	0.065
C(22)	0.336(2)	0.400(2)	0.736(1)	0.051
O(22)	0.325(2)	0.277(1)	0.716(1)	0.077
C(23)	0.291(2)	0.622(2)	0.906(1)	0.049
O(23)	0.250(2)	0.644(2)	0.9896(9)	0.067
Cb(1)	0.392(2)	0.798(2)	0.754(1)	0.049
Ob(1)	0.443(1)	0.881(1)	0.7951(9)	0.056
C(31)	-0.003(2)	1.023(2)	0.862(1)	0.049
O(31)	0.085(1)	1.089(2)	0.886(1)	0.074
C(32)	-0.139(2)	0.751(2)	0.891(1)	0.053
O(32)	-0.139(2)	0.633(2)	0.931(1)	0.087
C(33)	-0.230(2)	1.000(2)	0.710(1)	0.046
O(33)	-0.290(1)	1.050(2)	0.6379(9)	0.062
O(34)	-0.455(1)	1.153(2)	0.947(1)	0.074
C(34)	-0.334(2)	1.071(2)	0.903(1)	0.052
Cm(1)	-0.017(2)	0.599(2)	0.649(2)	0.064

Final positional and thermal parameters of
calculated hydrogen atoms of $\text{MeGeCo}_3(\text{CO})_{11}$

ATOM	X/A	Y/B	Z/C	U11
H(1)	-0.082(2)	0.554(2)	0.708(2)	0.060
H(2)	0.086(2)	0.492(2)	0.612(2)	0.100
H(3)	-0.105(2)	0.669(2)	0.595(2)	0.120

Thermal parameters of $\text{MeGeCo}_3(\text{CO})_{11}$

ATOM	U11	U22	U33	U23	U13	U12
Ge(1)	0.0261(8)	0.0389(9)	0.041(1)	0.0012(7)	-0.0091(6)	-0.0128(6)
Co(1)	0.027(1)	0.038(1)	0.039(1)	0.0045(9)	-0.0088(8)	-0.0113(8)
Co(2)	0.030(1)	0.037(1)	0.040(1)	0.0055(9)	-0.0112(8)	-0.0108(8)
Co(3)	0.028(1)	0.045(1)	0.044(1)	0.0020(9)	-0.0063(8)	-0.0114(9)
C(11)	0.048(9)	0.045(9)	0.024(8)	0.009(7)	-0.016(7)	-0.012(7)
O(11)	0.042(6)	0.088(9)	0.050(7)	-0.002(6)	0.007(5)	-0.033(6)
C(12)	0.028(8)	0.05(1)	0.06(1)	0.019(9)	0.009(7)	-0.010(7)
O(12)	0.064(7)	0.063(8)	0.050(7)	-0.016(6)	-0.019(6)	-0.020(6)
C(13)	0.039(8)	0.06(1)	0.037(9)	0.010(7)	-0.010(7)	-0.025(8)
O(13)	0.044(7)	0.060(8)	0.09(1)	0.011(7)	-0.005(6)	-0.016(6)
C(21)	0.028(9)	0.06(1)	0.039(9)	0.016(7)	-0.009(6)	-0.013(7)
O(21)	0.037(7)	0.071(8)	0.08(1)	0.017(7)	-0.013(6)	-0.014(6)
C(22)	0.034(8)	0.05(1)	0.06(1)	0.004(9)	-0.020(7)	-0.008(7)
O(22)	0.078(8)	0.040(7)	0.11(1)	-0.003(7)	-0.041(7)	-0.019(6)
C(23)	0.035(8)	0.06(1)	0.05(1)	0.001(9)	-0.001(7)	-0.020(7)
O(23)	0.077(8)	0.092(9)	0.039(8)	0.007(7)	-0.004(6)	-0.042(7)
Cb(1)	0.029(8)	0.05(1)	0.06(1)	0.006(9)	-0.015(7)	-0.011(7)
Ob(1)	0.056(7)	0.064(7)	0.062(8)	0.000(6)	-0.020(6)	-0.034(6)
C(31)	0.039(8)	0.047(9)	0.05(1)	0.008(8)	0.003(7)	-0.013(7)
O(31)	0.051(7)	0.084(9)	0.09(1)	-0.039(8)	0.004(6)	-0.034(7)
C(32)	0.05(1)	0.06(1)	0.05(1)	0.009(9)	-0.001(7)	-0.016(8)
O(32)	0.080(9)	0.08(1)	0.10(1)	0.030(9)	-0.008(7)	-0.037(7)
C(33)	0.033(8)	0.039(9)	0.06(1)	-0.012(8)	-0.007(8)	-0.003(7)
O(33)	0.054(7)	0.073(8)	0.052(8)	0.011(7)	-0.019(6)	-0.015(6)
O(34)	0.039(7)	0.089(9)	0.08(1)	-0.007(7)	0.012(6)	-0.010(6)
C(34)	0.041(9)	0.07(1)	0.05(1)	0.004(9)	-0.010(8)	-0.024(8)
Cm(1)	0.045(9)	0.08(1)	0.08(1)	-0.02(1)	-0.012(9)	-0.037(9)

Appendix 5

Final positional and equivalent thermal parameters
of $\text{MeGe}_2\text{Co}_5(\text{CO})_{15}$

ATOM	X/A	Y/B	Z/C	Ueq/U11
Ge(1)	-0.0025(2)	0.2963(2)	0.1229(1)	0.019
Ge(2)	-0.0035(2)	0.0928(2)	0.1237(1)	0.020
Co(1)	-0.0629(2)	0.1944(2)	0.1885(1)	0.023
Co(2)	-0.1327(2)	0.1929(2)	0.0915(1)	0.021
Co(3)	0.0560(2)	0.1926(2)	0.0576(1)	0.022
Co(4)	0.1332(2)	0.1929(2)	0.1498(1)	0.022
Co(5)	-0.0112(3)	0.4609(2)	0.1154(1)	0.026
C(11)	-0.018(2)	0.270(2)	0.233(1)	0.047(8)
O(11)	0.016(1)	0.320(1)	0.2649(7)	0.059(5)
C(12)	-0.065(2)	0.090(2)	0.2244(9)	0.037(7)
O(12)	-0.064(1)	0.028(1)	0.2502(7)	0.059(6)
C(21)	-0.226(2)	0.283(2)	0.0852(9)	0.033(7)
O(21)	-0.288(1)	0.341(1)	0.0816(6)	0.040(5)
C(22)	-0.214(2)	0.096(2)	0.0882(9)	0.029(6)
O(22)	-0.269(1)	0.032(1)	0.0871(6)	0.038(5)
C(31)	0.095(2)	0.292(2)	0.0204(8)	0.020(6)
O(31)	0.125(1)	0.348(1)	-0.0062(6)	0.043(5)
C(32)	0.094(2)	0.097(2)	0.0210(9)	0.030(7)
O(32)	0.113(1)	0.034(1)	-0.0045(6)	0.033(4)
C(41)	0.199(2)	0.280(2)	0.183(1)	0.037(7)
O(41)	0.246(2)	0.335(1)	0.2057(7)	0.063(6)
C(42)	0.184(2)	0.093(2)	0.1802(9)	0.032(7)
O(42)	0.221(1)	0.028(1)	0.1998(6)	0.046(5)
C(51)	-0.094(2)	0.451(2)	0.168(1)	0.048(8)
O(51)	-0.157(2)	0.444(1)	0.1993(7)	0.064(6)
C(52)	-0.073(2)	0.448(2)	0.0546(8)	0.023(6)
O(52)	-0.108(1)	0.440(1)	0.0160(6)	0.043(5)
C(53)	0.124(2)	0.452(2)	0.1112(9)	0.036(7)
O(53)	0.213(1)	0.447(1)	0.1074(7)	0.052(5)
C(54)	-0.015(2)	0.584(2)	0.120(1)	0.055(8)
O(54)	-0.020(2)	0.665(1)	0.1209(8)	0.068(6)
Cb(1)	-0.086(2)	0.190(2)	0.0255(8)	0.024(5)

Appendix 5 *cont'd...*

Ob(1)	-0.115(1)	0.191(1)	-0.0163(6)	0.037(4)
Cb(2)	0.213(2)	0.192(2)	0.0938(8)	0.022(5)
Ob(2)	0.291(1)	0.192(1)	0.0743(6)	0.036(4)
Cb(3)	-0.197(2)	0.217(2)	0.1885(9)	0.041(7)
Ob(3)	-0.284(2)	0.235(1)	0.1939(8)	0.068(6)
Cm(1)	-0.010(2)	-0.043(1)	0.1252(9)	0.026(6)

Thermal parameters of $\text{MeGe}_2\text{Co}_5(\text{CO})_{15}$

ATOM	U11	U22	U33	U23	U13	U12
Ge(1)	0.023(1)	0.013(1)	0.021(1)	0.000(2)	0.003(1)	0.000(2)
Ge(2)	0.026(2)	0.013(1)	0.020(2)	0.002(2)	0.001(1)	-0.001(2)
Co(1)	0.028(2)	0.024(2)	0.017(2)	-0.006(2)	0.005(1)	-0.001(2)
Co(2)	0.023(2)	0.016(2)	0.025(2)	-0.001(2)	-0.002(1)	-0.002(2)
Co(3)	0.032(2)	0.016(2)	0.017(2)	0.001(2)	0.006(1)	0.004(2)
Co(4)	0.024(2)	0.022(2)	0.020(2)	0.001(2)	-0.002(1)	-0.006(2)
Co(5)	0.033(2)	0.014(2)	0.031(2)	-0.002(2)	0.001(2)	-0.001(2)
C(11)	0.047(8)					
O(11)	0.059(5)					
C(12)	0.037(7)					
O(12)	0.059(6)					
C(21)	0.033(7)					
O(21)	0.040(5)					
C(22)	0.029(6)					
O(22)	0.038(5)					
C(31)	0.020(6)					
O(31)	0.043(5)					
C(32)	0.030(7)					
O(32)	0.033(4)					
C(41)	0.037(7)					
O(41)	0.063(6)					
C(42)	0.032(7)					
O(42)	0.046(5)					
C(51)	0.048(8)					
O(51)	0.064(6)					
C(52)	0.023(6)					
O(52)	0.043(5)					

Appendix 5 *cont'd...*

C(53) 0.036(7)

O(53) 0.052(5)

C(54) 0.055(8)

O(54) 0.068(6)

Cb(1) 0.024(5)

Ob(1) 0.037(4)

Cb(2) 0.022(5)

Ob(2) 0.036(4)

Cb(3) 0.041(7)

Ob(3) 0.068(6)

Cm(1) 0.026(6)

Appendix 6

Final positional and equivalent thermal parameters
of $\text{Et}_2\text{Ge}_2\text{Co}_6(\text{CO})_{17}$

ATOM	X/A	Y/B	Z/C	Ueq
Ge(2)	0.(0)9	0.(0)5	0.(0)6	0.039
Ge(1)	0.(0)2	0.(0)6	0.3278(1)	0.041
Co(2)	0.8475(1)	0.0621(0)	0.2656(1)	0.042
Ge(3)	0.7231(0)	0.2941(0)	0.1446(0)	0.040
Co(3)	0.7799(1)	0.1667(0)	0.1198(1)	0.040
Co(4)	0.8125(1)	0.2907(0)	0.3652(1)	0.039
Co(6)	0.7737(1)	0.3988(0)	0.0199(1)	0.046
Co(1)	0.8807(1)	0.1879(0)	0.5076(1)	0.044
Co(5)	0.5419(1)	0.3318(0)	0.0406(1)	0.049
C(11)	0.9965(5)	0.0387(3)	0.3198(6)	0.057
O(11)	1.0894(4)	0.0224(3)	0.3576(6)	0.088
C(12)	1.0343(7)	0.1816(4)	0.5868(7)	0.070
O(12)	1.1291(6)	0.1790(4)	0.6421(7)	0.116
C(14)	0.8897(5)	0.2951(3)	0.5978(6)	0.058
O(14)	0.9100(4)	0.3557(2)	0.6864(4)	0.073
C(21)	0.7723(6)	0.1315(3)	0.6030(5)	0.057
O(21)	0.7093(5)	0.0950(2)	0.6641(5)	0.080
C(22)	0.7286(5)	-0.0161(3)	0.3129(6)	0.058
O(22)	0.6573(4)	-0.0663(2)	0.3443(6)	0.086
C(23)	0.8370(5)	0.0161(3)	0.0819(6)	0.055
O(23)	0.8371(5)	-0.0214(2)	-0.0320(5)	0.078
C(31)	0.6327(5)	0.1087(3)	0.0076(6)	0.057
O(31)	0.5442(4)	0.0691(3)	-0.0689(5)	0.084
C(32)	0.8937(5)	0.1740(3)	-0.0053(5)	0.057
O(32)	0.9600(5)	0.1724(3)	-0.0898(5)	0.091
C(41)	0.6882(5)	0.3315(3)	0.4496(6)	0.059
O(41)	0.6136(5)	0.3607(3)	0.5084(5)	0.107
C(42)	0.9452(5)	0.3785(3)	0.3760(5)	0.051
O(42)	1.0261(4)	0.4351(2)	0.3788(5)	0.073
C(51)	0.4334(6)	0.2334(3)	0.0173(8)	0.073

Appendix 6 *cont'd...*

O(51)	0.3563(5)	0.1750(3)	0.0031(8)	0.132
C(52)	0.5235(6)	0.4018(4)	0.2076(7)	0.069
O(52)	0.5112(6)	0.4474(3)	0.3080(6)	0.105
C(53)	0.4482(8)	0.3744(5)	-0.0686(8)	0.081
O(53)	0.3886(8)	0.3995(5)	-0.1394(9)	0.142
C(56)	0.6486(5)	0.3094(3)	-0.1124(6)	0.051
O(56)	0.6360(4)	0.2644(2)	-0.2259(4)	0.070
C(61)	0.9254(5)	0.3717(3)	-0.0045(6)	0.057
O(61)	1.0253(4)	0.3593(3)	-0.0152(5)	0.083
C(62)	0.8033(5)	0.4821(3)	0.1864(6)	0.059
O(62)	0.8179(4)	0.5326(2)	0.2880(5)	0.081
C(63)	0.7602(6)	0.4649(3)	-0.0989(6)	0.061
O(63)	0.7490(5)	0.5034(3)	-0.1757(5)	0.095
C(100)	0.5152(5)	0.1050(4)	0.3575(9)	0.081
C(200)	1.1460(5)	0.2443(4)	0.2710(7)	0.073
C(201)	1.2320(7)	0.3019(5)	0.401(1)	0.127
C(101)	0.4290(8)	0.1478(8)	0.358(2)	0.260

Final positional and thermal parameters of calculated
hydrogen atoms of Et₂Ge₂Co₆(CO)₁₇

ATOM	X/A	Y/B	Z/C	U11
H(121)	0.5213(5)	0.0933(4)	0.4608(9)	0.270
H(122)	0.4793(5)	0.0462(4)	0.2771(9)	0.210
H(221)	1.1472(5)	0.2773(4)	0.1897(7)	0.100
H(222)	1.1860(5)	0.1901(4)	0.2364(7)	0.180
H(211)	1.3293(7)	0.3200(5)	0.376(1)	0.230
H(212)	1.2338(7)	0.2700(5)	0.484(1)	0.340
H(213)	1.1951(7)	0.3573(5)	0.437(1)	0.150
H(111)	0.3384(8)	0.1120(8)	0.377(2)	0.180
H(112)	0.4164(8)	0.1597(8)	0.255(2)	0.130
H(113)	0.4584(8)	0.2068(8)	0.439(2)	0.070

Thermal parameters of $\text{Et}_2\text{Ge}_2\text{Co}_6(\text{CO})_{17}$

ATOM	U11	U22	U33	U23	U13	U12
Ge(2)	0.0356(2)	0.0459(2)	0.0385(3)	0.0132(2)	0.0093(2)	0.0114(2)
Ge(1)	0.0349(2)	0.0466(2)	0.0432(3)	0.0147(2)	0.0093(2)	0.0113(2)
Co(2)	0.0442(3)	0.0426(3)	0.0449(3)	0.0177(3)	0.0103(3)	0.0160(3)
Ge(3)	0.0461(3)	0.0374(2)	0.0376(3)	0.0129(2)	0.0036(2)	0.0122(2)
Co(3)	0.0485(3)	0.0387(3)	0.0328(3)	0.0097(2)	0.0037(3)	0.0129(3)
Co(4)	0.0412(3)	0.0411(3)	0.0343(3)	0.0086(2)	0.0054(3)	0.0125(2)
Co(6)	0.0530(4)	0.0399(3)	0.0449(4)	0.0167(3)	0.0028(3)	0.0066(3)
Co(1)	0.0472(3)	0.0561(4)	0.0346(3)	0.0175(3)	0.0075(3)	0.0176(3)
Co(5)	0.0468(4)	0.0480(3)	0.0567(4)	0.0203(3)	0.0035(3)	0.0163(3)
C(11)	0.058(3)	0.056(3)	0.066(3)	0.021(3)	0.016(3)	0.026(2)
O(11)	0.074(3)	0.092(3)	0.111(4)	0.035(3)	0.008(3)	0.044(2)
C(12)	0.067(4)	0.106(5)	0.051(3)	0.029(3)	0.003(4)	0.042(3)
O(12)	0.086(4)	0.182(6)	0.097(4)	0.049(4)	-0.003(4)	0.064(4)
C(14)	0.057(3)	0.066(3)	0.049(3)	0.015(3)	0.013(3)	0.009(3)
O(14)	0.096(3)	0.068(2)	0.043(2)	0.002(2)	0.006(2)	0.010(2)
C(21)	0.074(3)	0.063(3)	0.041(3)	0.020(2)	0.014(3)	0.018(3)
O(21)	0.102(3)	0.081(3)	0.070(3)	0.040(2)	0.035(3)	0.021(2)
C(22)	0.068(3)	0.053(3)	0.060(3)	0.022(3)	0.014(3)	0.019(2)
O(22)	0.085(3)	0.072(2)	0.114(4)	0.052(3)	0.029(3)	0.012(2)
C(23)	0.059(3)	0.050(3)	0.060(3)	0.017(3)	0.015(3)	0.012(2)
O(23)	0.108(3)	0.059(2)	0.061(3)	0.004(2)	0.022(3)	0.017(2)
C(31)	0.068(3)	0.050(3)	0.050(3)	0.009(2)	-0.003(3)	0.018(2)
O(31)	0.085(3)	0.069(3)	0.077(3)	0.002(2)	-0.030(3)	0.006(2)
C(32)	0.076(4)	0.056(3)	0.041(3)	0.015(2)	0.011(3)	0.018(3)
O(32)	0.113(4)	0.105(3)	0.057(2)	0.018(2)	0.045(3)	0.025(3)
C(41)	0.062(3)	0.074(3)	0.046(3)	0.013(3)	0.008(3)	0.032(3)
O(41)	0.113(4)	0.157(4)	0.081(3)	0.025(3)	0.038(3)	0.095(4)
C(42)	0.059(3)	0.049(3)	0.044(3)	0.009(2)	0.003(3)	0.016(2)
O(42)	0.068(2)	0.053(2)	0.084(3)	0.011(2)	0.005(2)	-0.005(2)
C(51)	0.060(3)	0.059(3)	0.102(5)	0.022(3)	0.019(4)	0.012(3)
O(51)	0.091(4)	0.078(3)	0.212(7)	0.025(4)	0.062(5)	-0.008(3)
C(52)	0.068(3)	0.069(3)	0.076(4)	0.019(3)	0.014(3)	0.027(3)
O(52)	0.129(4)	0.111(4)	0.087(3)	0.015(3)	0.033(4)	0.062(3)
C(53)	0.087(4)	0.098(5)	0.078(4)	0.042(4)	-0.004(4)	0.052(4)
O(53)	0.150(5)	0.173(6)	0.141(6)	0.071(5)	-0.001(5)	0.096(5)
C(56)	0.057(3)	0.048(3)	0.051(3)	0.019(3)	0.001(3)	0.011(2)

Appendix 6 *cont'd...*

O(56)	0.079(3)	0.067(2)	0.051(2)	0.004(2)	0.001(2)	0.008(2)
C(61)	0.061(3)	0.055(3)	0.054(3)	0.019(2)	0.010(3)	0.008(2)
O(61)	0.054(2)	0.095(3)	0.107(3)	0.037(3)	0.017(3)	0.022(2)
C(62)	0.066(3)	0.049(3)	0.063(3)	0.018(3)	0.000(3)	0.011(2)
O(62)	0.094(3)	0.064(2)	0.069(3)	-0.008(2)	-0.007(3)	0.018(2)
C(63)	0.071(3)	0.047(3)	0.063(3)	0.023(3)	0.000(3)	0.005(3)
O(63)	0.119(4)	0.083(3)	0.091(3)	0.054(3)	-0.011(3)	0.009(3)
C(100)	0.044(3)	0.077(4)	0.129(6)	0.032(4)	0.033(4)	0.016(3)
C(200)	0.044(3)	0.093(4)	0.080(4)	0.025(4)	0.020(3)	0.008(3)
C(201)	0.050(4)	0.125(6)	0.18(1)	-0.004(7)	0.018(6)	0.007(4)
C(101)	0.072(6)	0.27(2)	0.59(3)	0.32(2)	0.14(1)	0.089(8)

Appendix 7

Final positional and equivalent thermal parameters
of EtGeSiCo₅(CO)₁₅

ATOM	X/A	Y/B	Z/C	Ueq
Ge(1)	0.7503(1)	0.3905(0)	0.1356(0)	0.038
Si(1)	0.7436(2)	0.1965(1)	0.1239(1)	0.033
Co(1)	0.5559(1)	0.2905(1)	0.1542(0)	0.038
Co(2)	0.6875(1)	0.3018(1)	0.0326(0)	0.036
Co(3)	0.9325(1)	0.2921(1)	0.1012(0)	0.039
Co(4)	0.8106(1)	0.2812(1)	0.2273(0)	0.043
Co(5)	0.7485(1)	0.0385(1)	0.1031(0)	0.041
C(11)	0.4830(8)	0.3842(5)	0.2014(4)	0.062
O(11)	0.4319(7)	0.4418(4)	0.2312(4)	0.099
C(12)	0.4695(7)	0.1996(5)	0.1972(4)	0.053
O(12)	0.4125(7)	0.1440(4)	0.2268(3)	0.093
C(21)	0.6403(7)	0.4060(5)	-0.0155(3)	0.042
O(21)	0.6086(6)	0.4663(3)	-0.0491(3)	0.067
C(22)	0.6226(7)	0.2181(4)	-0.0305(4)	0.046
O(22)	0.5793(6)	0.1700(4)	-0.0737(3)	0.068
C(31)	1.0547(8)	0.3869(6)	0.1060(4)	0.060
O(31)	1.1369(6)	0.4422(4)	0.1092(4)	0.101
C(32)	1.0538(8)	0.1986(5)	0.0961(4)	0.055
O(32)	1.1362(6)	0.1426(4)	0.0937(3)	0.084
C(41)	0.7903(8)	0.3788(5)	0.2839(4)	0.058
O(41)	0.7766(8)	0.4386(4)	0.3218(3)	0.096
C(42)	0.7531(9)	0.1919(5)	0.2845(4)	0.060
O(42)	0.7127(8)	0.1386(4)	0.3213(3)	0.098
C(51)	0.7525(9)	-0.0849(5)	0.0927(4)	0.067
O(51)	0.7586(7)	-0.1593(4)	0.0881(4)	0.107
C(52)	0.8544(8)	0.0339(5)	0.1842(4)	0.059
O(52)	0.9305(7)	0.0268(4)	0.2346(3)	0.098
C(53)	0.8394(7)	0.0620(4)	0.0227(4)	0.049
O(53)	0.8942(6)	0.0760(4)	-0.0277(3)	0.068
C(54)	0.5575(8)	0.0475(4)	0.0900(4)	0.054
O(54)	0.4398(6)	0.0520(4)	0.0766(3)	0.080

Appendix 6 *cont'd...*

Cb(1)	0.8816(7)	0.2962(4)	0.0014(3)	0.047
Ob(1)	0.9325(5)	0.2938(4)	-0.0530(3)	0.071
Cb(2)	0.4469(8)	0.2966(4)	0.0729(4)	0.051
Ob(2)	0.3512(5)	0.2977(4)	0.0335(3)	0.070
Cb(3)	0.997(1)	0.2684(7)	0.2390(5)	0.079
Ob(3)	1.1130(7)	0.2603(7)	0.2571(4)	0.126
Ce(1)	0.7426(9)	0.5232(4)	0.1471(4)	0.069
Ce(2)	0.828(2)	0.5760(6)	0.0987(6)	0.119

Thermal parameters of EtGeSiCo₅(CO)₁₅

ATOM	U11	U22	U33	U23	U13	U12
Ge(1)	0.0449(4)	0.0322(3)	0.0388(4)	-0.0036(3)	0.0081(3)	-0.0028(3)
Si(1)	0.0353(8)	0.0310(8)	0.0319(8)	-0.0007(7)	0.0041(7)	-0.0002(7)
Co(1)	0.0382(5)	0.0371(5)	0.0408(5)	-0.0018(4)	0.0135(4)	-0.0005(4)
Co(2)	0.0420(5)	0.0332(4)	0.0323(4)	0.0004(3)	0.0021(4)	0.0022(4)
Co(3)	0.0337(4)	0.0410(5)	0.0438(5)	-0.0029(4)	0.0068(4)	-0.0029(4)
Co(4)	0.0544(5)	0.0448(5)	0.0307(5)	-0.0031(4)	0.0016(4)	-0.0045(4)
Co(5)	0.0443(5)	0.0323(4)	0.0458(5)	-0.0009(4)	0.0005(4)	0.0021(4)
C(11)	0.063(5)	0.063(5)	0.062(5)	-0.016(4)	0.022(4)	0.002(4)
O(11)	0.096(5)	0.096(5)	0.107(5)	-0.046(4)	0.037(4)	0.020(4)
C(12)	0.052(4)	0.055(4)	0.056(4)	0.010(4)	0.022(4)	0.002(4)
O(12)	0.098(5)	0.081(4)	0.105(5)	0.029(4)	0.041(4)	-0.018(4)
C(21)	0.035(4)	0.048(4)	0.044(4)	0.003(3)	0.010(3)	0.001(3)
O(21)	0.087(4)	0.055(3)	0.059(3)	0.020(3)	0.015(3)	0.018(3)
C(22)	0.045(4)	0.046(4)	0.045(4)	-0.003(3)	0.003(3)	0.004(3)
O(22)	0.073(4)	0.068(3)	0.061(3)	-0.026(3)	-0.014(3)	-0.005(3)
C(31)	0.053(5)	0.065(5)	0.065(5)	-0.017(4)	0.016(4)	-0.004(4)
O(31)	0.068(4)	0.092(5)	0.146(6)	-0.037(4)	0.034(4)	-0.048(4)
C(32)	0.043(4)	0.059(5)	0.063(5)	0.001(4)	-0.003(3)	-0.004(4)
O(32)	0.052(3)	0.078(4)	0.120(5)	-0.009(4)	0.000(3)	0.013(3)
C(41)	0.073(5)	0.059(5)	0.042(4)	-0.005(4)	0.004(3)	-0.010(4)
O(41)	0.162(7)	0.075(4)	0.051(3)	-0.028(3)	0.012(4)	-0.003(4)
C(42)	0.086(6)	0.062(5)	0.031(4)	-0.004(4)	0.000(4)	-0.006(4)
O(42)	0.162(7)	0.084(4)	0.049(3)	0.019(3)	0.010(4)	-0.031(4)
C(51)	0.083(6)	0.037(4)	0.080(6)	-0.002(4)	-0.015(4)	0.000(4)

Appendix 7 *cont'd...*

O(51)	0.130(6)	0.034(3)	0.152(7)	-0.013(4)	-0.026(5)	0.006(3)
C(52)	0.067(5)	0.048(4)	0.063(5)	-0.002(4)	0.004(4)	0.010(4)
O(52)	0.122(5)	0.093(5)	0.073(4)	-0.003(3)	-0.045(4)	0.036(4)
C(53)	0.049(4)	0.041(4)	0.057(4)	-0.009(3)	0.000(3)	0.012(3)
O(53)	0.076(4)	0.077(4)	0.054(3)	-0.006(3)	0.023(3)	0.014(3)
C(54)	0.062(5)	0.035(4)	0.065(5)	-0.008(3)	0.003(4)	0.001(4)
O(54)	0.046(3)	0.072(4)	0.120(5)	-0.023(3)	-0.004(3)	-0.004(3)
Cb(1)	0.050(4)	0.047(4)	0.044(4)	0.002(3)	0.012(3)	0.001(3)
Ob(1)	0.065(3)	0.102(5)	0.049(3)	0.003(3)	0.027(3)	0.001(3)
Cb(2)	0.052(4)	0.048(4)	0.054(4)	-0.009(3)	0.008(4)	0.002(3)
Ob(2)	0.047(3)	0.098(5)	0.064(4)	-0.002(3)	-0.004(3)	0.003(3)
Cb(3)	0.060(5)	0.111(7)	0.066(6)	-0.017(5)	0.001(5)	0.010(5)
Ob(3)	0.060(4)	0.231(9)	0.083(5)	-0.013(5)	-0.023(4)	0.007(5)
Ce(1)	0.104(7)	0.028(3)	0.077(5)	-0.008(3)	0.025(5)	-0.002(4)
Ce(2)	0.19(1)					

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