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Alkynyl and poly-ynyl derivatives of carbon-tricobalt clusters

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Summary
A series of alkynyl-tricobalt carbonyl clusters, $\text{Co}_3(\mu_3-C_n\text{R})(\mu$-dpmm)(CO)$_7$ ($\text{R} = \text{Bu}^t, \text{Ph}$, $\text{C}_2\text{H}_4\text{I}, \text{C}_2\text{H}_4\text{C}=\text{CH}, \text{SiMe}_3, \text{Fc}, \text{Au}($P$\text{Ph}_3)$] containing three, five or seven carbons in the chain, has been prepared by elimination of phosphine-gold(I) halides in reactions between $\text{Co}_3(\mu_3-C\text{Br})(\mu$-dpmm)(CO)$_7$ and $\text{Au}(\text{C}=\text{CR})(\text{PPh}_3)$ or between $\text{Co}_3(\mu_3$-CC=CAu($\text{PR}_3$))($\mu$-dpmm)(CO)$_7$ ($\text{R} = \text{Ph}, \text{tol}$) and $\text{I}[\text{C}=\text{CR}’$ ($\text{R}’ = \text{SiMe}_3, \text{Fc}$). The use of poly-substituted arenes or ferrocenes has enabled preparation of the complexes $\text{1,4-C}_6\text{H}_3\{\text{C}=\mu_3-C[\text{Co}_3(\mu$-dpmm)(CO)$_7]\}_2\text{X}^{-5}$ ($\text{X} = \text{H}, \text{Br}$), $\text{1,3,5-C}_6\text{H}_3\{\text{C}=\mu_3-C[\text{Co}_3(\mu$-dpmm)(CO)$_7]\}_3$ and $\text{1,1’-Fc}’\{\text{C}=\mu_3-C[\text{Co}_3(\mu$-dpmm)(CO)$_7]\}_2$ ($\text{Fc}’ = \text{Fe(η-C}_5\text{H}_4-)_2$). The X-ray determined molecular structures of twelve of the complexes are reported.
Introduction

Current interest in metal complexes containing metal-ligand centres end-capping carbon chains derives in part from their potential as models for molecular wires or as components of molecular-scale electronic devices and memories and for their non-linear optical properties.\textsuperscript{1} Synthetic methods have used synthons derived from alkynes or polyynes, in which the substituent-free carbon chains are already present. As a result, the majority of known compounds have even-numbered carbon chains.\textsuperscript{2}

The formation of odd-numbered chains is dependent on methods which have an odd-numbered carbon precursor, either being converted to a C\textsubscript{n} chain by subsequent reactions, or as a component in an appropriate coupling reaction. Notable examples include

\[
\{[\text{Tp}*(\text{OC})\text{M}]=\text{C}=\text{C}=\text{C}=[\text{M}(\text{CO})\text{Tp}^*]\}\textsuperscript{2+}\text{ and }\{[\text{Tp}*(\text{OC})\text{M}]\equiv\text{C}=\text{C}=\text{C}=[\text{M}’(\text{O})\text{Tp}^*]\}(\text{M, M’ = Mo, W})^5
\]

\[
\{[\text{Cp}’(\text{OC})\text{Mn}]\text{CCC}\{\text{Re(NO)(PPh}_3\text{)}\text{Cp}^*\}\}\textsuperscript{16}\text{ and }\{[\text{Bu’O})\text{W}]\equiv\text{C}=\text{C}\{\text{Re(NO)(PPh}_3\text{)}\text{Cp}^*\}\textsuperscript{7}\text{.}
\]

We and others have considered an approach to this type of complex using a precursor in which a carbyne ligand, ≡CR, is attached to a metal centre. Recent examples have used the Group 6 complexes M(≡CR)(CO)\textsubscript{2}Tp’ (R = halogen, SiMe\textsubscript{3}; M = Mo, W; Tp’ = BH(pz), (Tp), BH(dmpz), (Tp*))\textsuperscript{8} or cluster-bonded halocarbynes, such as M\textsubscript{3}(μ-CR)(CO)\textsubscript{9} [M\textsubscript{3} = Ru\textsubscript{3}(μ-H),\textsuperscript{9} Os\textsubscript{3}(μ-H),\textsuperscript{9} Co\textsubscript{3}\textsuperscript{10}].

The CCo\textsubscript{3} trigonal cluster has been known since the late1950s\textsuperscript{11} and its extensive chemistry has been reviewed on several occasions.\textsuperscript{12-17} Attachment to unsaturated groups such as alkynes and diynes was first described in 1970.\textsuperscript{18-20} Common routes to the formation of the carbyne-C(sp) bond include the Cadiot-Chodkiewicz and Sonogashira and related reactions.\textsuperscript{19} In some instances, appropriate Grignard or Lewis-acid (AlCl\textsubscript{3})-induced coupling reactions between alkynes and Co\textsubscript{3}(μ-CBr)(CO)\textsubscript{3} have been employed.\textsuperscript{10c} It was early noted that with metal complexes the amine solvent commonly used often resulted in competing degradation of the cluster and conversion to other unwanted cluster products.\textsuperscript{19}

Some time ago, we described a modification of this reaction whereby reactions of Co\textsubscript{3}(μ-\text{CBr})(μ-dppm)(CO)\textsubscript{3} (1), chosen because the presence of the edge-bridging diphosphine...
ligand prevents break-up of the CCo₃ cluster, with phosphine-gold(I) alkynyls resulted in elimination of AuBr(PR₃) and formation of the C-C bonded product in high yields.²¹ We had reasoned that the presence of the dppm ligand, bridging one of the Co-Co edges, would serve to prevent cluster degradation, while the mild conditions of the reaction, in which no base is required, would prevent the formation of unwanted by-products. While our first accounts concentrated on the formation of carbon chains end-capped by the Co₃ cluster and a second metal-containing group,¹⁰ we have also extended these reactions to the synthesis of a range of Co₃ clusters containing more conventional groups as described below.

**Results and Discussion**

Reactions of Co₃(µ₃-CBr)(µ-dppm)(CO)₇ (1)²² with phosphine-gold(I) alkynyls proceed readily in solvents such as thf under mild conditions (r.t., hours). Conventional work-up involving chromatography on silica gel affords the alkynyl-tricobaltcarbon clusters in high yield as dark coloured crystals. To exemplify this reaction, we have used Au(C≡CR)(PPh₃), or occasionally the P(tol)₃ analogue to improve solubility, which has allowed the complexes Co₃(µ₃-CC≡CR)(µ-dppm)(CO)₇ to be obtained [R = Bu² (2, 47%), Ph (3, 91%), SiMe₃ (4, 86%), Fc (5, 91%)]. The co-product AuBr(PR’₃) (R’ = Ph, tol) can be easily recovered and recycled. The IR spectra of these complexes contain weak ν(C≡C) bands at ca 2130 cm⁻¹ and medium to strong ν(CO) absorptions between 2061 and 1966 cm⁻¹. In addition to common signals at δ 3.44 and 4.49 and between δ 6.5 and 8.0 arising from the dppm ligand, the ¹H NMR spectrum contain other resonances characteristic of the R groups present. Limited solubility restricted the availability of ¹³C NMR spectra, but in 2, signals at δ 101.14 and 121.95 can be assigned to two carbons of the C₃ moiety. That of the carbyne carbon, attached to three cobalt atoms, is broadened by interaction with the ⁵⁹Co quadrupole and is not resolved in all spectra.²³,²⁴ The ³¹P NMR spectra contain a single resonance at δ ca 35. The formulations of these complexes are confirmed by elemental analyses and by their electrospray mass spectra (ES MS), which usually contain molecular ions or appropriate adduct ions. As described further below, the molecular structures of twelve of the complexes have been determined by single-crystal X-ray diffraction studies.
The elimination reaction also proceeds between phosphine-gold(I) derivatives of the alkynyl-tricobalt cluster and appropriate C(sp or sp²)-I bonds. Thus, the reaction between Co₃{µ₃-CC≡CAu(PPh₃)}(µ-dppm)(CO), (6), itself prepared from the SiMe₃ derivative 4 and AuCl(PPh₃) in the presence of sodium methoxide, and 1,4-I₂C₆H₄ afforded two complexes which were characterised as Co₃{µ₃-CC≡CC₆H₄-I-4}(µ-dppm)(CO), (7) which is green, and orange-brown {Co₃(µ-dppm)(CO),}µ₃{µ₃-CC≡CC₆H₄C≡CC} (8).

Similarly, the reaction between Au(C≡CC₆H₄C≡CPh)(PPh₃) and 1 afforded Co₃{µ₃-CC≡CC₆H₄C≡CPh}(µ-dppm)(CO), (9). These complexes were readily separated by preparative t.l.c. and identified by elemental analysis and their ES MS. The other spectroscopic properties were similar to those found for the related phenyl complex.²²a

Extension of the reaction to 1,3,5-{(Ph₃)AuC≡C}₃C₆H₄ enabled preparation of the tris-cluster complex 1,3,5-{(OC)(µ-dppm)Co₃(µ₃-CC≡C)}₃C₆H₄ (10) in 50% yield. This compound has a similar n(CO) spectrum to the complexes described above, while the ¹³C NMR spectrum contains resonances at δ 108.92 and 112.78 from two of the C₃ chain carbons. Further characterisation results from the ES MS which contains a molecular ion at m/z 2454, and by an X-ray structural determination (see below). On one occasion, we isolated and crystallographically characterised the bis-cluster 1,3-{(OC)(µ-dppm)Co₃(µ₃-CC≡C)}₂C₆H₄Br-5 (11) from an analogous reaction in which the bromoaryl-diyne 1,3-{(Ph₃)AuC≡C}₃C₆H₄Br-5 was inadvertently used. Its spectroscopic properties were similar to those found for 9, with the exception of the negative ion ES MS, which a molecular anion was found at m/z 1741.

In addition to the binuclear complex 8, we have prepared 1,1’-{Co₃(µ-dppm)(CO),C≡CC}₂Fc’ [12, Fc’ = Fe(η-C₅H₅)₂] in 96% yield from the related reaction between 1,1’-Fc’{Au[P(tol)₃]}₂ and Co₃(µ₃-CBr)(µ-dppm)(CO),. This dark red complex has an IR ν(CO) spectrum similar to those of the other complexes described above, together with ν(CC) at 2122 cm⁻¹. The ¹H NMR spectrum has two 4H multiplets at δ
4.40 and 4.53 assigned to the C,H, protons of the ferrocene nucleus, while the ES MS of a solution containing NaOMe contains [M + Na]$^+$ at m/z 1793.

Related complexes containing C, chains, such as $\text{Co}_3(\mu_3-\text{CC}=\text{CC}=\text{CR})(\mu$-dppm)(CO), (R = SiMe, Au(PPh), Fc) have been described earlier. Extension to systems containing C, chains was easily achieved in reactions between $\text{Co}_3(\mu_3-\text{CC}=\text{CC}=$CAu(PPh)$_3(\mu$-dppm)(CO)$_7$ and $\text{IC}=$C$\text{SiMe}_3$ or $\text{IC}=$C$\text{Fc}$ which gave $\text{Co}_3(\mu_3-$C(C=C),R)(\mu$-dppm)(CO)$_7$, [R = SiMe, (13, 54%), Fc (14, 87%)] and the further conversion of 13 by treatment with NaOMe and AuCl(PPh)$_3$ gave $\text{Co}_3(\mu_3-$C(C=C),Au(PPh)$_3(\mu$-dppm)(CO)$_7$, (15) in 75% yield. The complex $\text{Co}_3(\mu_3-$C(C=C)Ph)(\mu$-dppm)(CO)$_7$, has been converted to $\text{Co}_3(\mu_3-$C(C=C),Ph)(\mu$-dppm)(CO)$_7$ (16) in 60% yield by sequential reactions with iodine and Au(C=CPh)(PPh)$_3$, without isolation of the presumed intermediate iododiynyl complex $\text{Co}_3(\mu_3-$CC=CC=Cl)(\mu$-dppm)(CO)$_7$.

Complexes 13-16 were initially characterised by elemental microanalyses and from their ES MS. Other spectroscopic properties were also in agreement with the proposed structures. These complexes have similar IR spectra to their shorter chain analogues, although for 14 and 16, two v(C=C) absorptions are found. In the NMR spectra of 13, the SiMe$_3$ group gives rise to a singlet at $\delta$ 0.26, while for 14, resonances at $\delta$ 4.28, 4.30 and 4.56 and $\delta$ 70.35, 69.76 and 72.35 arise from the Cp and C,H, rings of the Fc group. We assign seven resonances found between $\delta$ 63.38 and 99.03 in the $^{13}$C NMR spectrum to six of the C, carbons and the ipso carbons of the Ph groups. In the $^{13}$C NMR spectra of 14 and 15, resonances between $\delta$ 57 and 99 are assigned to five of the seven chain carbons, the Co,C atom again not being observed.

**Structural studies**

The molecular structures of 12 of the complexes described above have been determined by single-crystal X-ray diffraction studies. Figs. 1-12 contain plots of single molecules of each complex, that of 5 showing the two different conformers found in the unit cell. All contain as a common structural feature the $\text{Co}_3(\mu_3-$CC=CC$>$(\mu$-$dppm)(CO)$_7$, fragment (the molecule of 12 is centrosymmetric), as has been found in several other related
complexes described by us\textsuperscript{10,27} and others\textsuperscript{28-31} on previous occasions. Atom C(1) is attached to all three metal atoms of the triangular Co\textsubscript{3} cluster, of which one edge [Co(1)-Co(2)] is bridged by the dppm ligand. In all cases except 2 and 4 (which are isomorphous), the methylene bridge of the dppm ligand lies 'endo' to the pendant alkyne group, whereas it is 'exo' in the two exceptions. Nevertheless, the ranges encompassed by the various bond distances and angles extend over many standard deviations (see Table 1), although it is not evident that any particular structural or electronic feature can account for the differences.

In some instances, the dppm-bridged Co(1)-Co(2) bond is significantly different from the other two Co-Co separations, although when averaged over the present examples, both distances are identical (2.481 Å), with ranges for Co(1)-Co(2) of between 2.4624-2.5144 Å and for Co(1,2)-Co(3) of 2.4651-2.5085 Å. The Co-P bonds to the dppm ligand average 2.197 Å (range 2.177-2.2154 Å). Only in the interactions of the Co\textsubscript{3} cluster with the capping C(1) atom are differences found, with Co(1,2)-C(1) averaging 1.905 Å (range 1.888-1.928 Å) and Co(3)-C(1) averaging 1.937 Å (range 1.914-1.978 Å), resulting from the increased electron density at Co(1,2) and increased back-bonding into the corresponding Co-C Mos.\textsuperscript{32}

The carbon chains show the expected alternation of C-C bond lengths, with C(1)-C(2) ranging between 1.381-1.422 Å (av. 1.399 Å) and C(2)-C(3) being shorter at 1.213 Å (av.), range 1.201-1.230 Å, consistent with its being a C≡C triple bond. As expected, angles at C(1,2) are close to linear, averaging 177.2° (range 174.3-179.8°) and 174.7 (range 167.9-179.3°), respectively. In triyne complexes 11 and 12, separations further along the C\textsubscript{n} chain are consistent with this formulation, with C(4)-C(5) and C(6)-C(7) triple bonds [1.217, 1.203(4) Å in 11, 1.226, 1.209(7) in 12] and C(3)-C(4) and C(5)-C(6) single bonds [1.355, 1.366(4) Å in 11, 1.343, 1.358(7) in 12]. In these two examples, a trend for shorter C≡C triple bonds further along the C\textsubscript{n} chain from the Co\textsubscript{3} cluster is evident, while the reverse occurs for the C-C single bonds. The conformations of these two C\textsubscript{n} chains can be described as a continuous bend, with total bending at the carbon atoms C(2-7), Σ, being 19.4 (for 11) and 23.6° (for 12). Others have commented previously about the facile bending of C(sp) chains, the most probable explanation being
found in intermolecular interactions within the cell and the facile bending modes of C(sp) chains.\textsuperscript{33}

Other features of the structures are consistent with the groups found at the other end of the carbon chain, with C(3)-X distances [X = Au 1.983(4), C(301) of aromatic groups 1.405-1.440(5), Si 1.845(6) Å]. Despite pseudo-symmetry in their disposition in the cell, the two independent molecules of 5 have different conformations of the Fc group, with the Fe-mid-ring vectors being approximately parallel and perpendicular to the Co(1)-Co(2) vector, no doubt imposed by packing requirements of the Ph and Fc groups therein.

**Experimental**

**General.** All reactions were carried out under dry nitrogen, although normally no special precautions to exclude air were taken during subsequent work-up. Common solvents were dried, distilled under argon and degassed before use. Separations were carried out by preparative thin-layer chromatography on glass plates (20 x 20 cm\textsuperscript{2}) coated with silica gel (Merck, 0.5 mm thick).

**Instruments.** IR spectra were obtained on a Bruker IFS28 FT-IR spectrometer. Spectra in CH\textsubscript{2}Cl\textsubscript{2} were obtained using a 0.5 mm path-length solution cell with NaCl windows. Nujol mull spectra were obtained from samples mounted between NaCl discs. NMR spectra were recorded on a Varian 2000 instrument (\textsuperscript{1}H at 300.13 MHz, \textsuperscript{13}C at 75.47 MHz, \textsuperscript{31}P at 121.503 MHz). Unless otherwise stated, samples were dissolved in CDCl\textsubscript{3} contained in 5 mm sample tubes. Chemical shifts are given in ppm relative to internal tetramethylsilane for \textsuperscript{1}H and \textsuperscript{13}C NMR spectra and external H\textsubscript{3}PO for \textsuperscript{31}P NMR spectra. Electrospray mass spectra (ES MS) were obtained from samples dissolved in MeOH unless otherwise indicated. Solutions were injected into a Varian Platform II spectrometer via a 10 ml injection loop. Nitrogen was used as the drying and nebulising gas. Chemical aids to ionisation were used.\textsuperscript{34} Elemental analyses were by CMAS, Belmont, Vic., Australia.
Reagents. Co$_3$(μ$_3$-CBr)(μ-dppm)(CO)$_7$,\textsuperscript{27} AuCl(PR$_3$) (R = Ph; tol made similarly),\textsuperscript{35} and Au(C≡CR')(PR$_3$) (R' = Bu, Ph, SiMe$_3$, Fc) and {Au(PR$_3$)$_2$(μ-C≡CC$_6$H$_4$C≡C)} were obtained as previously described.\textsuperscript{36,37}

**Preparation of Au(C≡CC$_6$H$_4$C≡CPh)(PPh$_3$)**

Sodium (30 mg) was added to a solution of AuCl(PPh$_3$) (91 mg, 0.184 mmol) in MeOH (28 ml). After hydrogen evolution had ceased, a solution of HC≡CC$_6$H$_4$C≡CPh (37 mg, 0.183 mmol) in MeOH (2 ml) was added dropwise. After stirring at r.t. for 12 h, solvent was removed and the residue was extracted into benzene. Concentration of the extract to 3 ml and diffusion of hexanes (3 ml) into the concentrated solution gave light yellow microcrystalline Au(C≡CC$_6$H$_4$C≡CPh)(PPh$_3$) (99.5 mg, 83%), which was washed with hexane and dried. Anal. Found: C, 61.62; H, 3.57. Calcd (C$_{34}$H$_{24}$AuP): C, 61.82; H, 3.64; M, 660. IR (CH$_2$Cl$_2$): ν(C≡C) 2114 w cm$^{-1}$. $^1$H NMR: δ 7.27-7.60 (m, 24H, Ph + C$_6$H$_4$). $^{31}$P NMR: δ 42.58 s. ES-MS: (positive ion, MeOH + NaOMe, m/z): 683, [M + Na]$^+$. 

**Preparation of 1,3,5-{(Ph$_3$P)AuC≡C}$_3$C$_6$H$_3$**

A modified literature method\textsuperscript{38} was used. NaOMe (excess) in MeOH (4 ml) was added to a solution of AuCl(PPh$_3$) (202.7 mg, 0.41 mmol) and 1,3,5-(Me$_3$SiC≡C)$_3$C$_6$H$_3$ (50 mg, 0.137 mmol) in thf / MeOH (30 ml / 8 ml) at 0°C (ice-bath) and the mixture was allowed to warm to r.t. After stirring overnight, a white precipitate had separated from the pale yellow solution. Solvent was removed and the solid remaining was transferred to a sinter with MeOH (5 ml) and washed with more MeOH and hexane, and dried in air to give 1,3,5-{(Ph$_3$P)AuC≡C}$_3$C$_6$H$_3$ (181 mg, 87%) as a pale yellow solid. $^1$H NMR: δ 7.47-7.59 (m, Ph). $^{13}$C NMR: δ 103.62 (C≡C), 124.35 (s, C$_{qeq}$ of C$_6$H$_3$), 18.89-131.44 (m, Ph), 134.20, 134.36 (C$_6$H$_3$). $^{31}$P NMR: δ 49.33 (s, PPh$_3$).

**Preparation of carbon-tricobalt complexes**

Co$_3$(μ$_3$-C(C≡C)R)(μ-dppm)(CO)$_n$, $n = 1$

(i) R = Bu$^1$ (2)
A mixture of Au(C≡CBu′) (64 mg, 0.12 mmol), Co₃(μ₃-CBr)(μ-dppm)(CO), (100 mg, 0.12 mmol), Pd(PPh₃)₄ (6.2 mg, 0.006 mmol) and CuI (1 mg, 0.005 mmol) in thf (7 ml) was stirred at r.t. for 2 h. After removal of solvent, the residue was extracted with CH₂Cl₂ and separated by preparative t.l.c. (hexane-acetone 5/1). The major brown band (R, 0.41) contained Co₃(μ₃-CC≡CBu′)(μ-dppm)(CO), (2) (47 mg, 47%) which was isolated as dark brown crystals (CH₂Cl₂/MeOH). Anal. Found: C, 55.09; H, 3.42. Calcd (C₃₉H₃₁Co₃O₇P₂): C, 55.06; H, 3.65; M, 850. IR (CH₂Cl₂, cm⁻¹): ν(C≡C) 2131vw; ν(CO) 2057s, 2007vs, 1987 (sh), 1966 (sh); (cyclohexane): ν(CO) 2061s, 2015vs, 2011vs, 1977m, 1964w, 1957w. ¹H NMR: 3.49, 4.41 (2 x s, 2 x 1H, dppm), 6.50-8.50 (m, 20H, Ph). ¹³C NMR: δ 30.33 (s, Me), 39.94 [t, J(CP) 21.8 Hz, PCH₂], 101.14 (s, C⁴), 121.95 (s, C⁵), 128.12-137.49 (m, Ph), 202.43, 209.83, 231.35 (3 x s, br, CO). ³¹P NMR: δ 33.8s. ES-MS (MeOH, m/z): 850, M⁺.

(iii) R = Ph (3)
Method A: A mixture of Au(C≡Ph)(PPh₃) (66 mg, 0.12 mmol), Co₃(μ₃-CBr)(μ-dppm)(CO), (100 mg, 0.12 mmol), Pd(PPh₃)₄ (7 mg, 0.006 mmol) and CuI (2 mg, 0.012 mmol) in thf (7 ml) was stirred at r.t. for 1 h. After removal of solvent, the residue was taken up in CH₂Cl₂ and purified by preparative t.l.c. (acetone-hexane 3/7). The major brown-green band (R, 0.69) contained Co₃(μ₃-CC≡CPh)(μ-dppm)(CO), (3) (93.2 mg, 91%) as dark green crystals (CH₂Cl₂/MeOH). Anal. Found: C, 54.73; H, 2.75. Calcd (C₄₁H₂₇Co₃O₇P₂.0.5CH₂Cl₂): C, 54.57; H, 3.28; M, 870. IR (CH₂Cl₂, cm⁻¹): ν(C≡C) 2116vw; ν(CO) 2058s, 2009vs, 1989 (sh), 1969 (sh), 1948 (sh). ¹H NMR: δ 3.44, 4.49 (2 x s, 2 x 1H, dppm), 5.30 (s, CH₂Cl₂), 7.14-7.59 (m, 25H, Ph). ³¹P NMR: δ 34.19 [s (br), dppm]. ES-MS (positive ion, MeOH + NaOMe, m/z): 893, [M + Na]+; (negative ion, MeOH, m/z): 869, [M - H]+.

Method B: When Ag(C≡CPh)(PPh₃) was used under the same conditions, 3 was obtained in 55% yield.

(iii) R = SiMe₃ (4)
Method A: Pd(PPh₃)₄ (6 mg, 0.005 mmol) and CuI (1 mg, 0.005 mmol) were added to a solution of Co₃(µ₃-CBr)(µ-dppm)(CO)₃ (84.9 mg, 0.1 mmol) and Au(C≡CSiMe₃)(PPh₃) (55.6 mg, 0.1 mmol) in thf (5 ml) and the mixture was stirred at r.t. for 2 h. After removal of solvent under reduced pressure, the residue was dissolved in acetone-hexane (3/7) and run through a silica gel column using the same solvent mixture as eluent. A major brown-green fraction was collected and after evaporation gave Co₃(µ₃-C≡CSiMe₃)(µ-dppm)(CO)₇ (4) (75 mg, 86%) as dark green crystals (hexane). Anal. Calcd (C₃₈H₃₁Co₃O₇P₂Si): C, 52.68; H, 3.61; M, 866. Found: C, 52.64; H, 3.62. IR (CH₂Cl₂, cm⁻¹): ν(C≡C) 2138vw; ν(CO) 2065s, 2048s, 2010vs, 1990 (sh). ¹H NMR: δ 0.32 (s, 9H, SiMe₃), 3.49, 4.54 (2 x m, 2 x 1H, CH₂), 7.13-7.58 (m, 20H, Ph). ¹³C NMR: δ 0.10 (s, SiMe₃), 3.95 [t, J(CP) 25.4 Hz, dppm], 116.70, 126.19 (2 x s, carbon chain), 1228.22-137.28 (m, Ph), 202.13, 210.08, 225.14 [s (br), CO]. ³¹P NMR: δ 33.32 [s (br), dppm]. ES-MS (positive ion, MeOH + NaOMe, m/z): 889, [M + Na]⁺; (negative ion, MeOH + NaOMe, m/z), 865, [M – H].

Method B: A solution of Co₃(µ₃-CBr)(µ-dppm)(CO)₇ (200 mg, 0.24 mmol) and HCC≡CSiMe₃ (48 mg, 0.5 mmol) in thf (10 ml) was treated with CuI (2 mg, 0.012 mmol) and Pd(PPh₃)₄ (14 mg, 0.012 mmol), followed by addition of dbu (several drops). After stirring at r.t. for 2 h, work-up as above gave Co₃(µ₃-C≡CSiMe₃)(µ-dppm)(CO)₇ (4) (157 mg, 75%). A minor product formed on some occasions was identified as {Co₃(µ-dppm)(CO)₇}₂(µ-µ₃:µ₃-C₆).₁₀a

(iv) R = Fc (5)
Thf (10 ml) was added to a solid mixture of Au(C≡CFc)(PPh₃) (100 mg, 0.15 mmol), Co₃(µ₃-CBr)(µ-dppm)(CO)₇ (127 mg, 0.15 mmol), Pd(PPh₃)₄ (17 mg, 0.015 mmol) and CuI (3 mg, 0.015 mmol) and the reaction was stirred at r.t. for 1 h., after which spot t.l.c. showed the absence of starting materials. After evaporation of thf, the residue was extracted with CH₂Cl₂ and purified by preparative t.l.c. (acetone-hexane 1/4). One brown band developed (Rₖ 0.43) and contained Co₃(µ₃-C≡CFc)(µ-dppm)(CO)₇ (5) (134 mg, 91%) as very dark red crystals (CH₂Cl₂ / MeOH). Anal. Found: C, 55.19; H, 3.20. Calcd (C₄₅H₃₁Co₃FeO₇P₂): C, 55.22; H, 3.17; M, 978. IR (CH₂Cl₂, cm⁻¹): ν(C≡C)
2123vw; ν(CO) 2057s, 2007vs, 1988 (sh), 1965 (sh), 1948 (sh). ¹H NMR: δ 3.40, 4.41 (2 x s, 2 x 1H, dppm), 4.20 (s, 5H, Cp), 4.33, 4.48 (2 x m, 2 x 2H, C₅H₄), 7.12-7.59 (m, 20H, Ph). ¹³C NMR: δ 40.49 [t, J(13C) 21.4 Hz, dppm], 69.84 (s, Cp), 69.14, 70.45 (2 x s, C₅, C₆, C₇C₈), 67.99 (13C ipso, C₅H₄), 107.95, 111.77 (2 x s, chain carbons), 128.24-145.06 (m, Ph), 202.44, 212.58, 226.21 [s (br), CO]. ³¹P NMR: δ 33.71 (s, dppm). ES-MS (positive ion mode, MeOH, m/z): 978, [M + H]+; 950, [M – CO]+; (negative ion, MeOH, m/z): 977, [M - H]+.

(v)  R = Au(PPh₃) (6)
A solution containing 4 (100 mg, 0.12 mmol) and AuCl(PPh₃) (57 mg, 0.12 mmol) in thf / MeOH (4/1, 5 ml) was treated with NaOMe (from Na (6 mg) in MeOH (1 ml)] and the mixture was stirred at r.t. for 3 h. After removal of solvent under vacuum, the brown residue was transferred to a sinter, washed with MeOH and hexane and dried. Crystallisation (CH₂Cl₂ / MeOH) gave Co₃[µ₃-CC≡CAu(PPh₃)](µ-dppm)(CO), (6) (130 mg, 90%) as dark red crystals. Anal. Found: C, 50.65; H, 3.02. Calcd
(C₅₃H₃₇AuCo₃O₇P₃): C, 50.80; H, 2.95; M, 1252. IR (CH₂Cl₂, cm⁻¹): ν(C≡C) 2137vw; ν(CO) 2053s, 2005vs, 1983 (sh), 1961 (sh); (cyclohexane) ν(CO) 2061s, 2015vs, 2011vs, 1997m, 1984w, 1976m, 1960w. ¹H NMR: δ 3.24, 5.04 (2 x s, 2 x 1H, dppm), 7.15-7.59 (m, 35H, Ph). ³¹P NMR: δ 32.53 [s (br), dppm], 43.5 [s (br), PPh₃]. ES-MS (positive ion, MeOH, m/z): 1253, [M + H]+; (MeOH + NaOMe, m/z): 1275, [M + Na]+

(vi)  R = C₆H₄C≡CPh (9)
A mixture of Au(C≡CC₆H₄C≡CPh-4) (90 mg, 0.14 mmol), Co₃(µ₃-CBr)(µ-dppm)(CO), (116 mg, 0.14 mmol), Pd(PPh₃)₄ (7.2 mg, 0.006 mmol) and CuI (1.3 mg, 0.006 mmol) in thf (10 ml) was stirred at r.t. for 2.5 h. After removal of solvent, the residue was extracted with CH₂Cl₂ and separated by preparative t.l.c. (hexane-acetone 10/1). The major brown band (Rᵣ 0.56) contained Co₃(µ₃-CC≡CC₆H₄C≡CPh)(µ-dppm)(CO), (9) (51 mg, 39%) which was isolated as dark brown crystals (CH₂Cl₂/MeOH). Anal. Found: C, 60.61; H, 3.17. Calcd (C₄₉H₂₆Co₃O₇P₂): C, 60.62; H, 3.19; M, 970. IR (CH₂Cl₂, cm⁻¹): ν(C≡C) 2115vw, 2100 vw; ν(CO) 2059s, 2011vs, 1993 (sh), 1967 (sh). ¹H NMR: δ 3.40, 4.43 (2 x s, 2 x 1H, dppm), 7.18-7.52 (m, 29H, Ph + C₆H₄). ¹³C NMR: δ 41.27 [t,
J(\text{CP}) 22.5 \text{ Hz}, \text{PCH}_3, 89.70, 91.10 (2 \times s, \text{C} \equiv \text{CC}_6\text{H}_4\text{C} \equiv \text{C}), 110.37 (s, \text{C}^2), 114.19 (s, \text{C}^3), 121.80\text{-}135.96 (m, \text{Ph}), 202.15, 210.05, 221.73 (3 \times s, \text{br}, \text{CO}). \quad ^{31}\text{P} \text{NMR: } \delta 34.3 \text{s. ES-MS (positive ion, MeOH + NaOMe, } m/z): 993, [\text{M} + \text{Na}]^+; \quad \text{(negative ion, MeOH + NaOMe, } m/z): 969, [\text{M} - \text{H}]^-.\n
\text{Preparation of } \{\text{Co}_3(\mu\text{-dppm})(\text{CO})_7\}_2(\mu_2: \mu_3\text{-CC} \equiv \text{CC}_6\text{H}_4\text{C} \equiv \text{CC})(8)\n
(a) A solution containing \text{Co}_3(\mu_3\text{-CC} \equiv \text{CAu(PPh}_3)_2(\mu\text{-dppm})(\text{CO})_7 (50 mg, 0.04 mmol), 1,4-I\text{C}_6\text{H}_4 (6.4 mg, 0.02 mmol), \text{Pd(PPh}_3)_4 (5 mg, 0.004 mmol) and CuI (1 mg, 0.006 mmol) in \text{thf} (3 ml) was stirred at r.t. for 6 h. After removal of solvent, the residue was extracted with CH\text{Cl}_2 and separated by preparative t.l.c. (acetone-hexane 3/7) into two fractions. Band 1 \((R_f 0.50, \text{green})\) contained \text{Co}_3(\mu_3\text{-CC} \equiv \text{C} \equiv \text{C}_6\text{H}_4\text{I}-4)(\mu\text{-dppm})(\text{CO})_7 (7) (12.2 mg, 61\%), obtained as very dark green crystals (CH\text{Cl}_2 / \text{MeOH}). \quad \text{Anal. Found: C, 49.65; H, 2.31. Calcd (C}_{41}\text{H}_{26}\text{Co}_3\text{I}_7\text{P}_2): C, 49.40; H, 2.61; M, 996. IR (CH\text{Cl}_2, \text{cm}^{-1}): \nu(\text{C} \equiv \text{C}) 2117 \text{vw}; \nu(\text{CO}) 2060 \text{s, 2010 vs, 1980 (sh), 1967 (sh)}, 1949 (sh). \quad ^1\text{H NMR: } \delta 3.40, 4.37 (2 \times s, 2 \times 1\text{H}, \text{dppm}), 7.05\text{-}7.69 (m, 24\text{H, Ph + C}_6\text{H}_4). \quad ^{31}\text{P NMR: } \delta 34.32 \text{[s (br), dppm]. ES-MS (positive ion, MeOH + NaOMe, } m/z): 1019, [\text{M} + \text{Na}]^+; \quad \text{(negative ion, MeOH, } m/z): 995, [\text{M} - \text{H}]^+; 968, [\text{M} - \text{H} - \text{CO}]. \quad \text{The second orange-brown band} \quad (R_f 0.45) \text{ contained } \{\text{Co}_3(\mu\text{-dppm})(\text{CO})_7\}_2(\mu_2: \mu_3\text{-CC} \equiv \text{CC}_6\text{H}_4\text{C} \equiv \text{CC})(8) \quad (3.6 \text{ mg, 11}%). \quad \text{Anal. Calcd (C}_{76}\text{H}_{48}\text{P}_4\text{Co}_6\text{O}_{14}: C, 54.87; H, 2.89; M, 1662. Found: C, 54.92; H, 2.75. IR (CH\text{Cl}_2, \text{cm}^{-1}): 2063 \text{s, 2016 vs, 1984 m, 1905 m.} \quad ^1\text{H NMR: } \delta 3.42, 4.44 (2 \times m, 2 \times 2\text{H, CH}_2), 7.18\text{-}7.50 (m, 44\text{H, Ph + C}_6\text{H}_4). \quad ^{31}\text{P NMR: } \delta 35.07 \text{ (s, dppm). ES MS (positive} \quad \text{ion, MeOH + NaOMe, } m/z): 1685, [\text{M} + \text{Na}]^+; \quad \text{(negative ion, MeOH + NaOMe, } m/z): 1661, [\text{M} - \text{H}].\n
(b) A mixture of 1,4-{\text{AuPPh}_3(C \equiv \text{C})}_2\text{C}_6\text{H}_4 (30 mg, 0.03 mmol), \text{Co}_3(\mu_3\text{-CBr})(\mu\text{-dppm})(\text{CO})_7 (98 mg, 0.06 mmol), \text{Pd(PPh}_3)_4 (15 mg, 0.013 mmol) and CuI (5 mg, 0.026 mmol) was stirred in \text{thf} (20 ml) at r.t. for 1h. The solvent was then removed and the resulting dark purple residue purified by preparative t.l.c. eluting with acetone / hexane (2:3) to obtain 1,4-{\text{Co}_3C(C \equiv \text{C})(\mu\text{-dppm})(\text{CO})_7}_2\text{C}_6\text{H}_4 as an orange band} \quad (R_f 0.68) \quad (20.3 \text{ mg, 41}%). \quad \text{Anal. Calcd (C}_{76}\text{H}_{48}\text{P}_4\text{Co}_6\text{O}_{14}: C, 54.87; H, 2.89. Found: C, 54.92; H, 2.75. IR (CH\text{Cl}_2, \text{cm}^{-1}): \nu(\text{C} \equiv \text{C}) 2114 \text{ w, } \nu(\text{CO}) 2059 \text{ s, 2010 vs 1993 sh(m), 1969 sh(w)}. \quad ^{31}\text{P}
NMR (CDCl₃): δ 37.01 (s(br), 4P, dppm). ES MS (positive ion, MeOH + NaOMe, m/z): 1685 [M + Na⁺]; (negative ion, MeOH, m/z): 1661, [M - H].

Reaction of 1,3,5-{(Ph₃P)AuC≡C}₃C₆H₃ with Co₃(µ₃-CBr)(µ⁻dppm)(CO),
(a) A solution of 1,3,5-{(Ph₃P)AuC≡C}₃C₆H₃ (59.7 mg, 0.039 mmol) and Co₃(µ₃-
CBr)(µ⁻dppm)(CO), (100 mg, 0.118 mmol) in thf (10 ml) was treated with Pd(PPh₃), (4.5
mg, 0.0035 mmol) and CuI (1 mg, 0.005 mmol) and the mixture was stirred at r.t. for 4 h.
After removal of solvent under vacuum and a CH₂Cl₂ extract of the residue was purified
by preparative t/l/c/ (acetone-hexane, 3/7). The major brown band (R, 0.40) contained
1,3,5-{(Co(µ⁻dppm)(CO),)₃C₆H₃ (10) (48.8 mg, 50%), obtained as dark red crystals
(CHCl₃ / MeOH). Anal. Found: C, 54.80; H, 2.83. Calcd (C₁₁₁H₆₉Co₉O₂₁P₆): C, 54.28;
H, 2.83; M, 2454. IR (CH₂Cl₂, cm⁻¹): v(CC) 2115w; v(CO) 2059s, 2010vs, 1990 (sh),
1969 (sh), 1953 (sh). ¹H NMR: δ 3.46, 4.43 (2 x m, 2 x 3H, CH₂), 7.17 -7.58 (m, 63H,
Ph + C₆H₃). ¹³C NMR: δ 40.81 [s (br), CH₂], 108.92, 112.76 (2 x s, 2 x C of C₃ chain),
126.54-132.17 (m, Ph + C₆H₃), 202.24 [s (br), CO]. ³¹P NMR: δ 34.95 [s (br), dppm].
ES MS (positive ion, MeOH, m/z): 2454, M⁺; (MeOH + NaOMe, m/z): 2477, [M +
Na⁺].

(b) From a sample of 1,3,5-{(Ph₃P)AuC≡C}₃C₆H₃ containing a significant amount of
1,3-{(Ph₃P)AuC≡C}₃C₆H₃Br-5, a similar reaction with Co₃(µ₃-CBr)(µ⁻dppm)(CO), (33
mg, 0.039 mmol) was carried out with the addition of a few drops of dbu. After 2 h at
r.t., work-up as above afforded a green-brown band (R, 0.47) which contained 1,3-{(Co(µ-
dppm)(CO),)₃C₆H₃Br-5 (11) (10.8 mg), obtained as brown-red crystals (CH₂Cl₂ / MeOH).
Anal. Found: C, 52.34; H, 2.61. Calcd (C₇₆H₄₉Co₉O₁₄P₄): C, 52.38; H, 2.69; M, 1741.
IR (CH₂Cl₂, cm⁻¹): v(CC) 2114w; v(CO) 2057s, 2009vs, 1988 (sh), 1970 (sh), 1951 (sh).
¹H NMR: δ 3.40, 4.41 (2 x m, 2 x 2H, CH₂), 6.95-7.51 (m, 43H, Ph + C₆H₃). ³¹P NMR: δ
35.21 [s (br), dppm]. ES MS (positive ion, MeOH + NaOMe, m/z): 1764, [M + Na⁺];
(negative ion, MeOH + NaOMe, m/z): 1741, M.

{Co₃(µ⁻dppm)(CO),}(µ₃;µ₃-CC≡CFc’C≡CC) (12)
A solution containing 1,1’-Fc’{C≡CAu[P(tol)]}₂ (26 mg, 0.02 mmol), Co₃(μ₃-CBr)(μ-dppm)(CO), (36 mg, 0.04 mmol), Pd(PPh₃), (1 mg, 0.001 mmol) and CuI (1 mg, 0.005 mmol) in THF (5 ml) was stirred at r.t. for 2 h. After removal of solvent, the residue was extracted with CH₂Cl₂ and purified by preparative t.l.c. (acetone-hexane 3/7) to give one major band (R, 0.34), from which {Co₃(μ₃-dppm)(CO)}₃(μ₃:μ₃-CC≡CFc’≡C≡C) (12) (35.7 mg, 96%) was isolated as very dark red crystals (CH₂Cl₂ / MeOH). Anal. Found: C, 54.26; H, 2.96. Calcd (C₈₀H₅₂Co₆FeO₁₄P₄): C, 54.23; H, 2.94; M, 1770. IR (CH₂Cl₂, cm⁻¹): ν(C≡C) 2122vw; ν(CO) 2057s, 2008vs, 1989 (sh), 1977 (sh), 1964 (sh). ¹H NMR: δ 3.43, 4.44 (2 x s, 2 x 1H, dppm), 4.40, 4.53 (2 x m, 2 x 4H, C₅H₄), 7.11 - 7.52 (m, 40H, Ph). ³¹P NMR: δ 33.68 [s (br), dppm]. ES-MS (positive ion, MeOH + NaOMe, m/z): 1793, [M + Na]⁺; (negative ion, MeOH, m/z): 1769, [M – H].

Co₃{μ₃-C(C≡C)ₙR}(μ-dppm)(CO), n = 3
(i) R = SiMe₃ (13)
A mixture of Co₃{μ₃-C(C≡C≡CAu(PPh₃))}(μ-dppm)(CO), (280 mg, 0.219 mmol), IC≡CSiMe₃ (85 mg, 0.379 mmol), Pd(PPh₃), (13 mg, 0.01 mmol) and CuI (2 mg, 0.01 mmol) in THF (10 ml) was stirred at r.t. for 2 h. After removal of solvent, preparative t.l.c. (acetone-hexane 1/2) of a CH₂Cl₂ extract of the residue developed two bands. Band 1 (R, 0.55, brown) contained Co₃{μ₃-C(C≡C≡SiMe₃)}(μ-dppm)(CO), (13) (108 mg, 54%), obtained a brown-black crystals from CH₂Cl₂ / MeOH. Anal. Found: C, 55.20; H, 3.48. Calcd (C₄₂H₃₁Co₃O₇P₂Si): C, 55.16; H, 3.42; M, 914. IR (CH₂Cl₂, cm⁻¹): ν(C≡C) 2134vw; ν(CO) 2062s, 2018vs, 1974 (sh). ¹H NMR: δ 0.26 (s, 9H, SiMe₃), 3.41, 4.24 (2 x s, 2 x 1H, dppm), 7.20 - 7.41 (m, 20H, Ph). ³¹P NMR: δ 34.64 (s, dppm). ES-MS (positive ion, MeOH + NaOMe, m/z): 937, [M + Na]⁺; 915, [M + H]⁺; 865, [M + H + Na – SiMe₃]⁺; (negative ion, MeOH + NaOMe, m/z): 913, [M – H]; 841, [M – SiMe₃]; 814, [M + H – CO – SiMe₃]. Band 2 (R, 0.38, red-brown) contained {Co₃(μ-dppm)(CO)}₂{μ₃:μ₃-C₉}, identified by comparison with an authentic sample.¹⁰a

(ii) R = Fc (14)
A mixture of Co₃{μ₃-CC≡CC≡CAu(PPh₃)}(μ-dppm)(CO), (60 mg, 0.05 mmol), FeC≡CI (15.3 mg, 0.05 mmol), Pd(PPh₃), (3 mg, 0.0025 mmol) and CuI (1 mg, 0.005 mmol) in
thf (7 ml) was stirred at r.t. for 30 min. Evaporation and purification of the residue by preparative t.l.c. (acetone/hexane 1/4) gave three bands. The fastest moving ($R_f$ 0.93) contained FeC≡CC≡CFc (2 mg, 5%), identified by comparison with an authentic sample. The major product was contained in the second brown-orange band ($R_f$ 0.26), which gave Co$_3$[μ$_3$-C(C≡C)Fc](μ-dppm)(CO)$_7$ (14) (40.8 mg, 87.4%) as very thin red plates (CH$_2$Cl$_2$ / hexane). Anal. Found: C, 56.74; H, 2.57. Calcd (C$_{49}$H$_{31}$Co$_3$FeO$_7$P$_2$): C, 57.31; H, 3.02%; M, 1026. IR (CH$_2$Cl$_2$, cm$^{-1}$): ν(C≡C) 2168w, 2100vw; ν(CO) 2063s, 2013vs, 1973 (sh), 1958 (sh) cm$^{-1}$. $^1$H NMR: δ 3.40, 4.25 (2 x m, 2 x 1H, CH$_2$), 4.28 (s, 5H, Cp), 4.30, 4.56 (2 x m, 2 x 2H, C$_5$H$_4$), 7.15-7.69 (m, 20H, Ph). $^{13}$C NMR: δ 42.75 [t, J(Cp) 18.3, CH$_2$P], 70.35 (s, Cp), 69.76, 72.35 (2 x m, C$_5$H$_4$), 63.38, 65.66, 72.73, 80.95, 85.99, 97.13, 99.03 (C$_{ipso}$ + six C of C$_7$ chain), 201.43, 209.79, 212.4 (3 x s, CO). $^{31}$P NMR: δ 33.78 (s, dppm). ES-MS (positive ion, MeOH, $m/z$): 1027, [M + H]$^+$; 1026, [M]$^+$; 998, [M - CO]$^+$. (positive ion, MeOH + NaOMe, $m/z$): 1049, [M + Na]$^+$; (negative ion, MeOH + NaOMe, $m/z$): 1026 + 1025, overlapping [M]$^+$ + [M - H]$^+$. The third band ($R_f$ 0.15, brown-orange) contained [Co$_3$(μ-dppm)(CO)$_7$_][μ$_3$;μ$_2$-C$_{10}$] (0.6 mg, 1%), identified by comparison with an authentic sample.

(iii) R = Au(PPh$_3$) (15)
NaOMe [from 10 mg Na in MeOH (10 ml)] was added to a solution of Co$_3$[μ$_3$-C(C≡C)SiMe$_3$](μ-dppm)(CO)$_7$ (84 mg, 0.092 mmol) in thf / MeOH (1/1, 10 ml), and after stirring for 10 min at r.t., AuCl(PPh$_3$) (46 mg, 0.093 mmol) was added. A brown precipitate separated and after stirring at r.t. for 1 h, the precipitate was collected and washed with MeOH (2 x 2 ml) affording Co$_3$[μ$_3$-C(C≡C)Au(PPh$_3$)](μ-dppm)(CO)$_7$ (15) (90 mg, 75%) as a brown powder. Anal. Found: C, 52.59; H, 2.83. Calcd (C$_{57}$H$_{37}$AuCo$_3$O$_7$P$_3$): C, 52.64; H, 2.87; M, 1300. IR (CH$_2$Cl$_2$, cm$^{-1}$): ν(C≡C) 2117vw; ν(CO) 2060s, 2012vs, 1974 (sh). $^1$H NMR: δ 3.40, 4.34 (2 x s, 2 x 1H, dppm), 7.18-7.56 (m, 35H, Ph). $^{13}$C NMR: δ 42.63 (m, CH$_2$), 57.49, 82.83, 88.79, 95.20, 98.81 (5 x s, carbon chain), 128.38-131.86 (m, Ph), 134.20-134.52 (m, Ph), 201.52 (br, CO). $^{31}$P NMR: δ 34.69 [s (br), dppm]. ES-MS (positive ion, MeOH + NaOMe, $m/z$): 1323, [M + Na]$^+$. 

(iv) R = Ph (16)
A solution containing \(\text{Co}_3\{\mu_3-\text{CC}≡\text{CC}=\text{CAu(PPh}_3\}}\{\mu\text{-dppm})\text{(CO)}_7\} (50 \text{ mg, 0.04 mmol})\) and \(\text{Pd(PPh}_3\}_4 (00 \text{ mg, 00 mmol})\) in \(\text{thf (5 ml)}\) was added to a mixture of iodine (10 mg, 0.04 mmol) and \(\text{CuI (00 mg, 00 mmol)}\) in \(\text{thf (5 ml)}\) at \(-78^\circ\text{C}\), and the mixture was stirred for 1 h. After this time, a solution of \(\text{Au(C≡CPh)(PPh}_3\} (20 \text{ mg, 0.04 mmol})\) in \(\text{thf (5 ml)}\) was added dropwise and the mixture was stirred for a further 1 h at \(-78^\circ\text{C}\). After allowing to warm to r.t., the filtered solution was evaporated and the residue was extracted into \(\text{CH}_2\text{Cl}_2\) and purified by preparative t.l.c. (acetone-hexane 3/7). The brown band (Rf 0.76) contained \(\text{Co}_3\{\mu_3-\text{C(C≡C)Ph}\}(\mu\text{-dppm})(\text{CO})_7\) (16) (21 mg, 60%), obtained as black needles (\(\text{CH}_2\text{Cl}_2 / \text{MeOH}\)). Anal. Found: C, 58.98; H, 2.87. Calcd (\(\text{C}_{45}\text{H}_{27}\text{Co}_3\text{O}_7\text{P}_2\)): C, 58.82; H, 2.94%; M, 918. IR (\(\text{CH}_2\text{Cl}_2, \text{cm}^{-1}\)): \(\nu(\text{C≡C}) 2190\text{w}, 2171\text{vw}\); \(\nu(\text{CO}) 2065\text{s}, 2040\text{m}, 2014\text{m}, 1973\) (sh), 1955 (sh) cm\(^{-1}\). \(\text{^1H NMR:}\) \(\delta 3.30, 4.15 (2 \times \text{m}, 2 \times 1\text{H}, \text{dppm})\), \(7.09 - 7.47 \text{ (m, 25H, Ph)}\). \(\text{^31P NMR:}\) \(\delta 34.63 \text{ (s, dppm)}\). ES-MS (positive ion, \(\text{MeOH + NaOMe, m/z}\)): 941, [\(\text{M + Na}\)]\(^+\); (negative ion, \(\text{MeOH, m/z}\)): 918, M; 917, [\(\text{M – H}\)]; 890, [\(\text{M – CO}\)]

Structure determinations

Full spheres of diffraction data were measured at ca 153 K using a Bruker AXS CCD area-detector instrument. \(N_{\text{in}}\) reflections were merged to \(N\) unique \(R_{\text{int}}\) cited after “empirical” / multiscan absorption correction (proprietary software), \(N_0\) with \(F > 4\sigma(F)\) being used in the full matrix least squares refinements. All data were measured using monochromatic Mo-K\(_a\) radiation, \(\lambda = 0.71073 \text{ Å}\). Anisotropic displacement parameter forms were refined for the non-hydrogen atoms, \((x, y, z, U_{\text{iso}})_h\), being refined. Conventional residuals \(R, R_{\text{w}}\) on \(|F|\) are quoted [weights: \((\sigma^2(F) + 0.000n_F^2)\)^{-1}]. Neutral atom complex scattering factors were used; computation used the XTAL 3.7 program system. Pertinent results are given in the figures (which show non-hydrogen atoms with 50% probability amplitude displacement ellipsoids and hydrogen atoms with arbitrary radii of 0.1 Å) and in Tables 1 and 2.

Variata. 4. \((x, y, z, U_{\text{iso}})_h\) were refined throughout; it is isomorphous with 2 and was refined in the same cell and coordinate setting.
5. The iron atoms of both molecules were modelled as disordered over pairs of sites, occupancies refining in concert to 0.888(3) and complement. Fe ... Fe are 0.88(1) and 0.86(1) Å; minor components of the associated Cp ligands were not located.

10. Weak and limited data resulted in a determination of inferior precision.

11. The dichloromethane of solvation was modelled as disordered over two sets of sites, occupancies 0.694(5) and complement.

Supplementary material
Full details of the structure determinations (except structure factors) have been deposited with the Cambridge Crystallographic Data Centre as CCDC #. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: + 44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements
We thank the ARC for support of this work.

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