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Complexes containing long carbon chains: Synthesis and characterisation of a C_{19} derivative end-capped by W and Co_3

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Dedicated to our friend and colleague Professor Pierre Dixneuf.

Summary

The first example of a complex containing a C_{19} chain, $\{Co_3(\mu\text{-dppm})(CO)_7\}\{\mu_3\text{-}C(C\equiv C)_9\}\{W(CO)_3Cp\}$, has been prepared in 22% yield from the Pd(0) / Cu(I)-catalysed reaction between $I(C\equiv C)_3I$, $W\{C\equiv CC\equiv CAu(PPh_3)\}(CO)_3Cp$ and $Co_3\{\mu_3\text{-}C(C\equiv C)_4Au(PPh_3)\}(\mu\text{-dppm})(CO)_7$. Other products also formed include $\{Co_3(\mu\text{-dppm})(CO)_7\}\{\mu_3\text{-}C(C\equiv C)_6\}\{W(CO)_3Cp\}$ (32%), $\{Co_3(\mu\text{-dppm})(CO)_7\}_2\{\mu_3:\mu_3\text{-}C(C\equiv C)_nC\}$ [n = 8 (6%) and 11 (5%)], containing respectively C_{13}, C_{18} and C_{24} chains, and $\{W(CO)_3Cp\}_2\{\mu\text{-}(C\equiv C)_n\}$ (n = 4, 7) (traces). The syntheses of $Co_3\{\mu_3\text{-}C(C\equiv C)_4R\}(\mu\text{-dppm})(CO)_7$ [R = $SiMe_3$, $Au(PPh_3)$] are also described.

Introduction

There is a continuing interest in complexes containing carbon chains end-capped by transition metal moieties on account of their potential as models for molecular wires,[1] which involves an understanding of ways in which electrons (or holes) might transfer from one end to the other through the carbon atoms of the chain.[2,3] In addition, the synthetic challenges of making such complexes, with either even- or odd-numbered chains, or with different end-caps, provide when successful, interesting and useful additions to chemists' armoury.[4]

We have recently described a new methodology whereby complexes containing long carbon chains end-capped by two metal centres may be obtained by elimination of phosphine-gold(I) halides in reactions between alkynyl- or poly-ynyl-gold(I) phosphine complexes and compounds containing C(sp)-halogen bonds.[5] We have used this approach to generate carbon chain complexes which may have two metal-ligand end-caps, either identical or different,[6-8] and which may have even- or odd-numbers of carbon atoms, according to the nature of the end-caps. We have sought to apply this reaction to the synthesis of specific complexes and this Note describes some novel chemistry found when we targeted complexes containing C_{19} and C_{26} chains, chosen firstly to honour Professor Pierre Dixneuf, whose work in the area of carbon-rich compounds is well-known,[9] and secondly, to test the stability of complexes containing long carbon chains terminated by metal cluster carbonyl fragments. To the best of our knowledge there is no previous example of a C_{19} complex [the longest odd-numbered carbon chains yet described are in $\{Cp(OC)_3W\}(\mu:\mu_3\text{-}C\equiv CC\equiv CC)\{Co_3(\mu\text{-dppm})_n(CO)_{9\text{-}2n}\}$ (n = 0,[10] 1[7]), $\{Cp^*(dppe)Ru\}\{\mu:\mu_3\text{-}(C\equiv C)_xC\}\{Co_3(\mu\text{-dppm})(CO)_7\}$ (x = 2,[10] 4[5]) and $Os_3(\mu\text{-}H)_3\{\mu_3\text{-}C(C\equiv C)_3Fc\}(CO)_7$,[8] which contain C_5, C_7 and C_9 chains, respectively], while the Pt_2-C_{24} complex described by Gladysz and coworkers[11] and obtained in only milligram amounts was only recently surpassed by the same group's Pt_2-C_{28} complex obtained using a novel desilylation-oxidative coupling methodology.[12]

Results and discussion

Our approach has been to use double eliminations which would be possible between appropriate known poly-ynyl-gold(I) complexes, such as $W\{C\equiv CC\equiv CAu(PPh_3)\}(CO)_3Cp$[7] or $Co_3\{\mu_3\text{-}C(C\equiv C)_2Au(PPh_3)\}(\mu\text{-dppm})(CO)_7$[7] and the recently described di-iodo-poly-ynes, $I(C\equiv C)_xI$ (x = 3 or 4).[13,14] Longer carbon chains can be assembled on the cobalt cluster by a combination of related reactions, of which the sequence shown in Scheme 1 allows lengthening by several C_2 units in each step. Use of $I(C\equiv C)_ySiMe_3$ gives products containing

m extra C_2 units, the iodo-poly-ynylsilanes also being readily available.[15] Conversion of the silyl complex to the phosphine-gold(I) derivative is achieved in a one-pot reaction by proto-desilylation with NaOMe followed by addition of AuCl(PPh$_3$), the base being common to both steps of the reaction. Thus, sequential reactions of **1** (x = 2) with IC≡CC≡CSiMe$_3$ to give Co$_3$\{μ_3-C(C≡C)$_4$SiMe$_3$\}(μ-dppm)(CO)$_7$ (**2**, x + y = 4), followed by auration afforded Co$_3$\{μ_3-C(C≡C)$_4$Au(PPh$_3$)\}(μ-dppm)(CO)$_7$ (**3**, x + y = 4). The gold complexes are stable and can be isolated easily in high yield by direct crystallisation, any impurities being removed by prior filtration of the solution through a short column of alumina.

Coupling of two equivalents of Co$_3$\{μ_3-C(C≡C)$_4$Au(PPh$_3$)\}(μ-dppm)(CO)$_7$ (**3**, x + y = 4) with 1,8-di-iodo-octatetrayne[14] afforded the C_{26} derivative \{Co$_3$(μ-dppm)(CO)$_7$\}$_2$\{μ_3:μ_3-C(C≡C)$_{12}$C\} (**4**; Scheme 2) which contains a Co$_3$ cluster capping each end, as a brown-orange powder in 40% yield. This was readily characterised by IR, NMR and ES-mass spectroscopies, together with elemental microanalyses. As yet, no X-ray quality crystals have been obtained, the crystal form following the molecular structure in giving very fine fibres. The composition of the C_{26} complex was established mainly from the ES-MS spectra from solutions in MeOH containing NaOMe, which contained [M + Na]$^+$ and [M + OMe]$^-$ at m/z 1894 and 1857, respectively.

A second product from this reaction is the C_{18} complex \{Co$_3$(μ-dppm)(CO)$_7$\}$_2$\{μ_3:μ_3-C(C≡C)$_8$C\} (**5**), again characterised from its ES MS, with ions at m/z 1753 and 1729, assigned to [M + Na]$^+$ and [M – H]$^-$, respectively. Its formation suggests that an alternative course of the reaction between the alkynyl-gold(I) complex and the di-iodo-poly-yne is that of oxidative homo-coupling, perhaps of radical species derived by initial elimination of the Au(PPh$_3$) group as the iodide. In both **4** and **5**, the IR ν(CO) spectra were characteristic of the Co$_3$(CO)$_7$ cluster fragments, while other spectroscopic and analytical data are consistent with the above formulations.

The above reaction generates even-numbered carbon chains, even though the cobalt cluster precursor contains an odd-numbered chain, because two of the latter are joined by reaction with the α,ω-di-iodopoly-yne. However, encouraged by the above results, we devised a synthesis of a complex containing a C_{19} chain by allowing 1,6-di-iodohexatriyne[14] to react with an equimolar mixture of the two gold-containing precursors W\{C≡CC≡CAu(PPh$_3$)\}(CO)$_3$Cp and **1** (x = 4), i.e., with the objective of carrying out a (C_4 +

$C_6 + C_9) = C_{19}$ synthesis (Scheme 3). In the event, separation of the products of this reaction, which was carried out in thf at -50°C, afforded several compounds, which included both hetero- and homo-coupled products either with or without the C_6 fragment. We have identified the following complexes: [W]-C_{13}-[Co$_3$] (**6**), [W]-C_{19}-[Co$_3$] (**7**), [Co$_3$]-C_{18}-[Co$_3$] (**5**) and [Co$_3$]-C_{24}-[Co$_3$] (**8**) ([W] = W(CO)$_3$Cp, [Co$_3$] = Co$_3$(μ-dppm)(CO)$_7$). Ready separation of the various complexes was achieved by preparative t.l.c. on silica gel. In independent experiments, we have shown that the relatively unstable [W]-C_8-[W] and [W]-C_{14}-[W] complexes are also likely to have been formed, although we have not unequivocally isolated and characterised these species from the mixed reaction.

The complexes have been identified by the usual spectroscopic methods but not so far by X-ray crystal structural studies. In particular, the IR ν(CO) spectra are essentially identical, being composed of either Co$_3$(CO)$_7$ or of superimposed W(CO)$_3$ + Co$_3$(CO)$_7$ patterns. The anticipated ν(CC) absorptions are all very weak and appear as either one or two bands at ca 2100 cm^{-1}. We have been unable to obtain ^{13}C NMR spectra which show resonances of the chain carbon atoms, although we would not expect to find the Co$_3$C signal as a result of broadening by the ^{57}Co quadrupole.[16-18] The presence of appropriate M$^+$, [M + Na]$^+$ and / or [M + OMe]$^-$ ions in the positive and negative ion ES-MS spectra, together with elemental analytical results, confirm the compositions of these materials. Interestingly, complexes with longer carbon chains are more soluble but less stable than analogous compounds containing shorter chains.

In summary, we describe an extension of our approach to form C(sp) chain linking two metal centres, which may be the same or different. The shorter carbon chain complexes **5** and **6** are derived from "oxidative" coupling of two Co$_3$-C$_9$ or of one Co$_3$-C$_9$ with one W-C$_4$ fragments without involvement of the hexatriyne, whereas the longer carbon chains in **7** and **8** have also incorporated one C$_6$ moiety from the di-iodohexatriyne. Although the reactions are complex in the sense that coupling between any two of the components as well as the desired three-component coupling has occurred, it is gratifying that the compounds formed in highest yield are the two hetero-coupled complexes **6** and **7**, again showing that the gold halide-elimination reaction that we have found has wide applicability.

Experimental

General experimental conditions

All reactions were carried out under dry, high purity nitrogen using standard Schlenk techniques. Common solvents were dried, distilled under nitrogen and degassed before use.

Instrumentation

Infrared spectra were obtained on a Bruker IFS28 FT-IR spectrometer. Spectra in CH_2Cl_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 Bruker AM300WB or ACP300 (^1H at 300.13 MHz, ^{13}C at 75.47 MHz, ^{31}P at 121.503 MHz) instruments. Samples were dissolved in $CDCl_3$, unless otherwise stated, contained in 5 mm sample tubes. Chemical shifts are given in ppm relative to internal tetramethylsilane for ^1H and ^{13}C NMR spectra and external H_3PO_4 for ^{31}P NMR spectra. ES mass spectra: VG Platform 2 or Finnigan LCQ. Solutions were directly infused into the instrument. Chemical aids to ionisation were used as required.[19] Elemental analyses were performed at CMAS, Belmont, Australia.

Reagents

The compounds $I(C{\equiv}C)_3I$,[14] $IC{\equiv}CC{\equiv}CSiMe_3$,[15] $W\{C{\equiv}CC{\equiv}CAu(PPh_3)\}(CO)_3Cp$[7] and $Co_3\{\mu_3\text{-}C(C{\equiv}C)_2Au(PPh_3)\}(\mu\text{-dppm})(CO)_7$[7] were made by the cited methods.

Preparation of $Co_3\{\mu_3\text{-}C(C{\equiv}C)_4SiMe_3\}(\mu\text{-dppm})(CO)_7$ (2)

A solution containing $Co_3\{\mu_3\text{-}CC{\equiv}CC{\equiv}CAu(PPh_3)\}(\mu\text{-dppm})(CO)_7$ (200 mg, 0.156 mmol) and $IC{\equiv}CC{\equiv}CSiMe_3$ (38.7 mg, 0.156 mmol) in thf (7 ml) was treated with CuI (2 mg, 0.008 mmol) and $Pd(PPh_4)_4$ (9 mg, 0.008 mmol) and stirred at r.t. for 1 h. After evaporation of solvent in vacuum, the residue was dissolved in acetone-hexane (3/7) and chromatographed on a silica gel column, using the same solvent mixture as eluent. The first brown band gave $Co_3\{\mu_3\text{-}C(C{\equiv}C)_4SiMe_3\}(\mu\text{-dppm})(CO)_7$ (2) (100 mg, 68%) as small dark brown-red crystals. Anal. Found: C, 54.98; H, 3.31. Calcd ($C_{44}H_{31}Co_3O_7P_2Si$): C, 55.01; H, 3.31%; *M*, 938. IR (cyclohexane): $\nu(C{\equiv}C)$ 2156vw, 2141vw, 2113vw; $\nu(CO)$ 2067s, 2047m, 2024s (sh), 2019vs, 2007m (sh), 1991w, 1982w cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.30 (s, 9H, $SiMe_3$), 3.47, 4.30 (2 x m, 2 x 1H, CH_2), 7.26-7.56 (m, 20H, Ph). ^{13}C NMR ($CDCl_3$): δ -0.27 (s, $SiMe_3$), 43.82 [t, *J*(CP) 35 Hz, dppm], 63.59, 64.34, 70.60, 80.90, 89.38, 91.56, 96.34, 98.76 (8 x s, 8 x C of C_9 chain), 128.78-135.01 (m, Ph), 201.42 [s (br), CO]. ^{31}P NMR ($CDCl_3$): δ 34.16 [s (br), dppm]. ES-MS (negative ion, with NaOMe, *m/z*): 865, $[M - SiMe_3]^-$; 837, $[M - SiMe_3 - CO]^-$; (positive ion, with NaOMe, *m/z*): 889, $[M + H + Na - SiMe_3]^=$.

A second band contained $\{Co_3(\mu\text{-}dppm)(CO)_7\}_2\{\mu_3\text{:}\mu_3\text{-}C(C{\equiv}C)_4C\}$ (30 mg, 23%), identified by comparison with an authentic sample.

Preparation of $Co_3\{\mu_3\text{-}C(C{\equiv}C)_4Au(PPh_3)\}(\mu\text{-}dppm)(CO)_7$ (3, x + y = 4)

A solution of $Co_3\{\mu_3\text{-}C(C{\equiv}C)_4SiMe_3\}(\mu\text{-}dppm)(CO)_7$ (78 mg, 0.08 mmol) in thf / MeOH (3/5; 8 ml) was treated with NaOMe [from Na (5.5 mg in MeOH (1 ml)] and the mixture was stirred at r.t. for 30 min. AuCl(PPh$_3$) (41 mg, 0.08 mmol) was then added and the mixture stirred for a further 2 h. Solvents were evaporated in vacuum and the residue was washed with MeOH (5 ml), filtered and washed again with cold MeOH. Addition of hexane to a benzene extract gave $Co_3\{\mu_3\text{-}C(C{\equiv}C)_4Au(PPh_3)\}(\mu\text{-}dppm)(CO)_7$ (**3**, x + y = 4) (83.9 mg, 76%) as a brown powder. Anal. Found: C, 53.41; H, 2.74. Calcd ($C_{59}H_{37}AuCo_3O_7P_3$): C, 53.47; H, 2.80%; *M*, 1324. IR (CH$_2$Cl$_2$): ν(C$\equiv$C) 2140w (br); ν(CO) 2063s, 2015vs, 1984m (sh), 1972m (sh) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 3.45, 4.30 (2 x m, 2 x 1H, CH$_2$), 7.25-7.54 (m, 35H, Ph). ^{31}P NMR (CDCl$_3$): δ 33.89 [s (br), dppm], 41.23 [s (br), PPh$_3$] (ratio 2/1). ES-MS (positive ion, *m/z*): 1325, [M + H]$^+$; 1324, M$^+$; 1296, [M - CO]$^+$; (positive ion, with NaOMe, *m/z*): 1347, [M + Na]$^+$.

Preparation of $\{Co_3(\mu\text{-}dppm)(CO)_7\}_2\{\mu_3\text{:}\mu_3\text{-}C(C{\equiv}C)_nC\}$ [n = 8 (5), 12 (4)]

A solution containing $Co_3\{\mu_3\text{-}C(C{\equiv}C)_4Au(PPh_3)\}(\mu\text{-}dppm)(CO)_7$ (70 mg, 0.05 mmol) and I(C$\equiv$C)$_4$I (10 mg, 0.025 mmol) in thf (7 ml) was treated with Pd(PPh$_3$)$_4$ (2 mg) and CuI (2 mg), and the reaction mixture was stirred at r.t. After 1 h, the solution was brown-red and t.l.c. showed the absence of the starting cobalt complex. Removal of solvent under reduced pressure and separation of a dichloromethane extract of the residue by preparative t.l.c. gave two major bands and a black base-line. The first band (R_f 0.31) contained $\{Co_3(\mu\text{-}dppm)(CO)_7\}_2\{\mu_3\text{:}\mu_3\text{-}C(C{\equiv}C)_{12}C\}$ (**4**) (20.3 mg, 39%), isolated as dark purple microcrystals. IR (CH$_2$Cl$_2$, cm^{-1}): ν(C$\equiv$C) 2168vw, 2129vw; ν(CO) 2094w, 2065s, 2019vs, 1978 (sh), 1928 (sh, br). ^{1}H NMR: δ 3.50, 4.24 (2 x m, 4H, CH$_2$), 7.31-7.62 (m, 40H, Ph). ^{31}P NMR: δ 34.02 [s (br), dppm]. ES MS (MeOH + NaOMe, positive ion, *m/z*): 1894, [M + Na]$^+$; (negative ion): 1857, [M + Na]$^-$; 1753, [M − H]$^-$. A dark red band (R_f 0.29) contained $\{Co_3(\mu\text{-}dppm)(CO)_7\}_2\{\mu_3\text{:}\mu_3\text{-}C(C{\equiv}C)_8C\}$ (**5**) (5.3 mg, 13%), obtained as a dark red powder. Anal. Found: C, 56.81; H, 2.60. Calcd ($C_{82}H_{44}Co_6O_{14}P_4$): C, 56.88; H, 2.54; M, 1730. IR (CH$_2$Cl$_2$, cm^{-1}): ν(C$\equiv$C) 2154vw, 2123vw; ν(CO) 2094w, 2065m, 2020vs, 1967m (br), 1927 (sh). ^{1}H NMR: δ 3.46, 4.24 (2 x m, 4H, CH$_2$), 7.27-7.71 (m, 40H, Ph). ^{31}P NMR: δ

34.09 [s (br), dppm]. ES MS (MeOH + NaOMe, positive ion, m/z): 1753, $[M + Na]^+$; (negative ion) 1729, $[M – H]^-$.

Reaction of I(C≡C)$_6$I, W{C≡CC≡CAu(PPh$_3$)}(CO)$_3$Cp and {Co$_3${μ$_3$-C(C≡C)$_4$Au(PPh$_3$)}(μ-dppm)(CO)$_7$

A mixture of Co$_3${μ$_3$-C(C≡C)$_4$Au(PPh$_3$)}(μ-dppm)(CO)$_7$ (50 mg, 0.038 mmol), W{C≡CC≡CAu(PPh$_3$)}(CO)$_3$Cp (31.7 mg, 0.038 mmol), I(C≡C)$_3$I (12.4 mg, 0.038 mmol), CuI (1 mg, 0.005 mmol) and Pd(PPh$_3$)$_4$ (5 mg, 0.004 mmol) in thf (20 ml) was stirred at -50°C for 30 min, after which it was allowed to warm to r.t., stirring being continued for a further 2 h. The dark red solution was evaporated in vacuum and the residue was dissolved in dichloromethane and the products were separated by preparative t.l.c. (silica gel, dichloromethane / hexane 2/3). Several coloured bands developed:

(a) Band 1 (yellow, R_f 0.79) contained AuI(PPh$_3$) (20.2 mg, identified by comparison with an authentic sample) and other yellow products, which were not investigated further.

Band 2 (purple, R_f 0.63) gave {Co$_3$(μ-dppm)(CO)$_7$}$_2${μ$_3$:μ$_3$-C(C≡C)$_{11}$C} (**8**) as a dark purple solid (3.4 mg, 5%). IR (CH$_2$Cl$_2$, cm^{-1}): ν(CO) ν(C≡C) 2170w, 2122w; ν(CO) 2090w, 2064s, 2017vs, 1976 (sh), 1935s (br). ES-MS (negative ion, with NaOMe, m/z): 1833, $[M + OMe]^-$; 1805, $[M + OMe - CO]^-$; 1801, $[M - H]^-$. This complex is not stable in solution and decomposes on the plates.

Band 3 (dark red, R_f 0.60) afforded {Co$_3$(μ-dppm)(CO)$_7$}$_2${μ$_3$:μ$_3$-C(C≡C)$_8$C} (**5**) (4.1 mg, 6%), identified by comparison with an authentic sample above.

Band 4 (orange, R_f 0.28), contained {Co$_3$(μ-dppm)(CO)$_7$}{μ$_□$□μ-C(C≡C)$_9$}{W(CO)$_3$Cp} (**7**) as a brown solid (11.2 mg, 22%). Anal. Found: C, 53.74; H, 2.13. Calcd (C$_{59}$H$_{27}$Co$_3$O$_{10}$P$_2$W): C, 53.72; H, 2.05%; M, 1318. IR (CH$_2$Cl$_2$, cm^{-1}): ν(C≡C) 2160w, 2119w; ν(CO) 2096vw, 2063s, 2042m, 2016vs, 1987m, 1966m (br), 1912w (br). ^{1}H NMR (C$_6$D$_6$): δ 3.03, 4.02 (2 x m, 2 x 1H, CH$_2$), 4.26 (s, 5H, Cp), 6.73-7.42 (m, 20H, Ph). ^{31}P NMR (C$_6$D$_6$): δ 34.76 [s (br), dppm]. ES-MS (negative ion, with NaOMe, m/z): 1349, $[M + OMe]^-$; 1317, $[M - H]^-$; (positive ion, with NaOMe, m/z): 1341, $[M + Na]^+$.

Band 5 (yellow, R_f 0.23), afforded {Co$_3$(μ-dppm)(CO)$_7$}{μ$_□$□μ-C(C≡C)$_6$}{W(CO)$_3$Cp} (**6**) as a brown powder (15.1 mg, 32%). Anal. Found: C, 50.95; H, 2.09. Calcd (C$_{53}$H$_{27}$Co$_3$O$_{10}$P$_2$W): C, 51.04; H, 2.17%; M, 1246. IR (CH$_2$Cl$_2$, cm^{-1}): ν(C≡C) 2147vw, 2126w; ν(CO) 2080vw, 2062vs, 2041s, 2016vs, 1989m (br), 1962s (br). ^{1}H NMR (C$_6$D$_6$): δ 2.98, 3.92 (2 x m, 2 x 1H, CH$_2$), 4.27 (s, 5H, Cp), 6.75-7.40 (m, 20H, Ph). ^{31}P NMR (C$_6$D$_6$):

δ 34.82 [s (br), dppm]. ES-MS (negative ion, with NaOMe, m/z): 1277, $[M + OMe]^-$; 1245, $[M - H]^-$; (positive ion, with NaOMe, m/z): 1269, $[M + Na]^+$.

Further t.l.c. of the reaction mixture afforded a yellow band (R_f 0.21) which travelled with some decomposition to a brown "tail". IR (CH_2Cl_2, cm^{-1}): $\nu(C\equiv C)$ 2138w, 2115vw; $\nu(CO)$ 2041s, 1989w, 1956vs (br). The t.l.c. behaviour and IR spectrum are consistent with this material being $\{W(CO)_3Cp\}_2(\mu-C_8)$.[20]
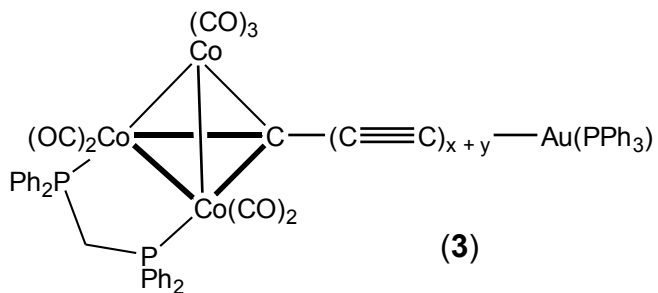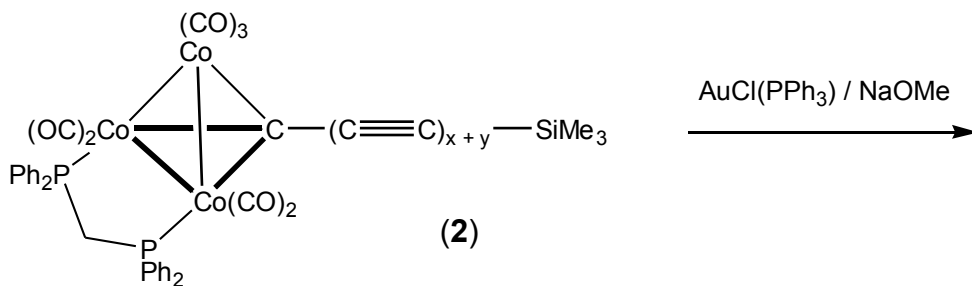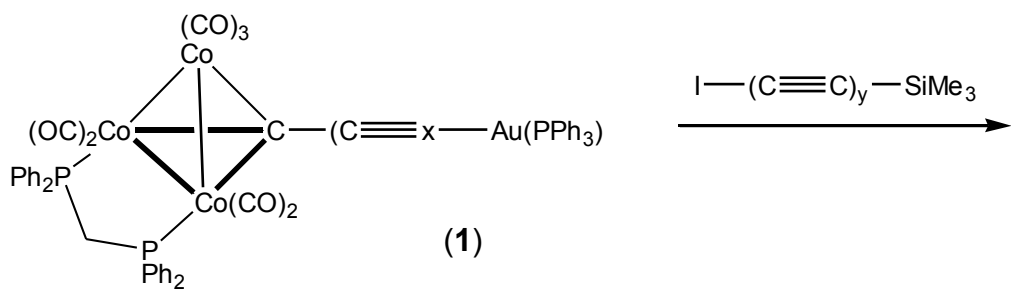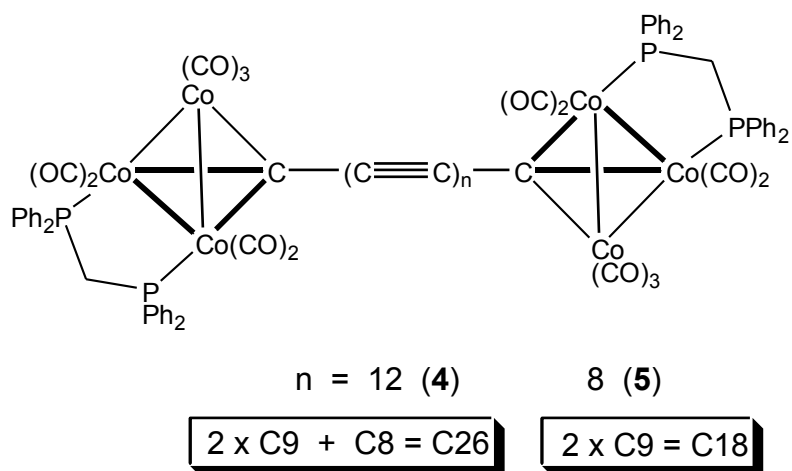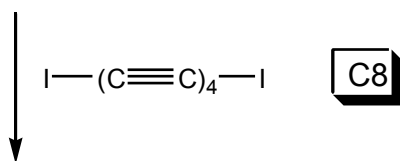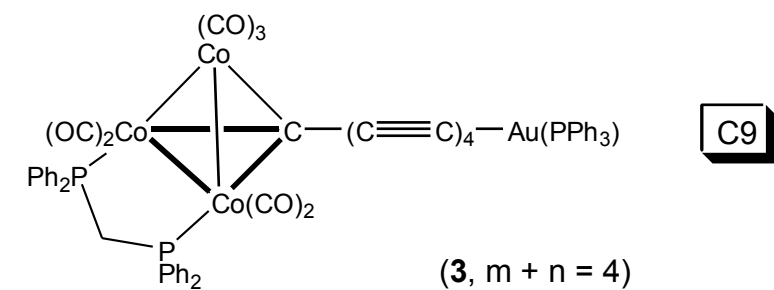
Acknowledgements

References

1. J.L. Brédas, R.R. Chance (eds), *Conjugated Polymeric Materials: Opportunities in Electronics, Optoelectronics and Molecular Electronics*, Kluwer: Dordrecht, 1990.

2. F. Paul, C. Lapinte in M. Gielen, R. Willem, B. Wrackmeyer (eds), *Unusual Structures and Physical Properties in Organometallic Chemistry*, Wiley: New York, 2002, p. 220.

3. F. Paul, C. Lapinte, Coord. *Chem. Rev*., 1978, **178-180**, 431.

4. M.I. Bruce, P.J. Low, *Adv. Organomet. Chem*., 2004, **50**, 179.

5. A.B. Antonova, M.I. Bruce, B.G. Ellis, M. Gaudio, P.A. Humphrey, M. Jevric, G. Melino, B.K. Nicholson, G.J. Perkins, B.W. Skelton, B. Stapleton, A.H. White, N.N. Zaitseva, *Chem. Commun*., 2004, 960.

6. M.I. Bruce, M.E. Smith, N.N. Zaitseva, B.W. Skelton, A.H. White, *J. Organomet. Chem*., 2003, **670**, 170.

7. M.I. Bruce, B.W. Skelton, A.H. White, N.N. Zaitseva, *J. Organomet. Chem*., 2003, **683**, 398.

8. M.I. Bruce, P.A. Humphrey, G. Melino, B.W. Skelton, A.H. White, N.N. Zaitseva, *Inorg. Chim. Acta*, 2005, **358**, 1453.

9. See, for example: (a) D. Touchard, P. Haquette, A. Daridor, L. Toupet, P.H. Dixneuf, *J. Am. Chem. Soc*., 1994, **116**, 11157. (b) D. Peron, A. Romero, P.H. Dixneuf, *Gazz. Chim. Ital*., 1994, **124**, 497. (c) D. Peron, A. Romero, P.H. Dixneuf, *Organometallics*, 1995, **14**, 3319. (d) D. Touchard, N. Pirio, L. Toupet, M. Fettouhi, L. Ouahab, P.H. Dixneuf, *Organometallics*, 1995, **14**, 5263. (e) S. Rigaut, D. Touchard, P.H. Dixneuf, *Coord. Chem Rev*., 2004, **248**, 1585.

10.   M.I. Bruce, K.A. Kramarczuk, N.N. Zaitseva, B.W. Skelton, A.H. White, *J. Organomet. Chem*., 2005, **690**, 1549.

11.   W. Mohr, J. Stahl, F. Hampel, J.A. Gladysz, Chem. Eur. J., 2003, 9, 3324.

12.   Q. Zheng, J.A. Gladysz, *J. Am. Chem. Soc*., 2005, **127**, 10508.

13.   H. Hopf, B. Witulski, in P.J. Stang, F. Diederich (eds), *Modern Acetylene Chemistry*, VCH: Weinheim, 1995, p. 33.

14.   K. Gao, N.S. Goroff, *J. Am. Chem. Soc*., 2000, **122**, 9320.

15.   J. Hlavaty, L. Kavan, M. Sticha, *J. Chem. Soc., Perkin Trans. 1*, 2002, 705.

16.   D. Seyferth, C.S. Eschbach, M.O. Nestle, *J. Organomet. Chem*., 1975, **97**, C11.

17.   S. Aime, L. Milone, M. Valle, *Inorg. Chim. Acta*, 1976, **18**, 9.

18.   P. Yuan, M.G. Richmond, M. Schwarz, *Inorg. Chem*., 1990, **32**, 679.

19.   W. Henderson, J.S. McIndoe, B.K. Nicholson, P.J. Dyson, *J. Chem. Soc., Dalton Trans*., 1998, 519.

20.   M.I. Bruce, M. Ke, P.J. Low, B.W. Skelton, A.H. White, *Organometallics*, 1998, **17**, 3539.

SCHEME 1

$$\mathbf{(1)} \quad \xrightarrow{\text{I}-(\text{C}\!\equiv\!\text{C})_y-\text{SiMe}_3}$$

$$\mathbf{(2)} \quad \xrightarrow{\text{AuCl(PPh}_3\text{)} \text{ / NaOMe}}$$

$$\mathbf{(3)}$$

For structure (1):

(CO)₃Co — (OC)₂Co — C — Co(CO)₂ cluster with Ph₂P–CH₂–PPh₂ bridging ligand;

$C-(C\!\equiv\!C)_x-\text{Au(PPh}_3)$

For structure (2):

$C-(C\!\equiv\!C)_{x+y}-\text{SiMe}_3$

For structure (3):

$C-(C\!\equiv\!C)_{x+y}-\text{Au(PPh}_3)$

SCHEME 2

(CO)₃
Co

(OC)₂Co———C—(C≡C)₄—Au(PPh₃)

Ph₂P

Co(CO)₂

P
Ph₂

(3, m + n = 4)

I—(C≡C)₄—I   C8

(CO)₃
Co

(OC)₂Co———C—(C≡C)ₙ—C

Ph₂P

Co(CO)₂

Ph₂
P

(OC)₂Co

PPh₂

Co(CO)₂

Co
(CO)₃

P
Ph₂

n = 12 **(4)**   8 **(5)**

2 x C9 + C8 = C26   2 x C9 = C18

SCHEME 3

Co(CO)$_3$ / (OC)$_2$Co / Ph$_2$P / P Ph$_2$ / Co(CO)$_2$ / C—(C≡C)$_4$—Au(PPh$_3$)

(4, m + n = 4)

hetero-coupling

(Ph$_3$P)Au—(C≡C)$_2$—W(CO)$_3$Cp

I—(C≡C)$_3$—I

(CO)$_3$ / Co / (OC)$_2$Co / Ph$_2$P / P Ph$_2$ / Co(CO)$_2$ / C—(C≡C)$_n$—W(CO)$_3$Cp

n = 6 (**6**)

C9 + C4 = C13

n = 9 (**7**)

C9 + C6 + C4 = C19

homo-coupling

I—(C≡C)$_3$—I

homo-coupling

(CO)$_3$ / Co / (OC)$_2$Co / Ph$_2$P / P Ph$_2$ / Co(CO)$_2$ / C—(C≡C)$_n$—C

n = 8 (**5**)

2 x C9 = C18

Ph$_2$ / P / PPh$_2$ / (OC)$_2$Co / Co(CO)$_2$ / Co / (CO)$_3$

n = 11 (**8**)

2 x C9 + C6 = C18

Cp(OC)$_3$W—(C≡C)$_4$—W(CO)$_3$Cp

2 x C4 = C8