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FULL PAPER

Reactions of a ditungsten-capped tetrayne with cobalt carbonyls: molecular structures of {W(CO)$_3$Cp}$_2${μ-C$_8$[Co$_2$(μ-dppm)$_m$-(CO)$_{6-2m}$]$_n$} (m = 0, 1; n = 1, 2)

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The carbon-rich complex {W(CO)$_3$Cp}$_2$(μ-C$_8$) reacts with Co$_2$(μ-dppm)$_m$(CO)$_{8-2m}$ (m = 0, 1) to give several complexes formed by addition of Co$_2$(μ-dppm)$_m$(CO)$_{6-2m}$ moieties to one or two C≡C triple bonds. X-Ray structure determinations on {W(CO)$_3$Cp}$_2${μ-C$_8$[Co$_2$(μ-dppm)$_m$(CO)$_{6-2m}$]$_n$} [m = 0, n = 1, 2; m = 1, n = 1, 2 (two isomers)] confirm the presence of the C$_8$ chain linking the two W(CO)$_3$Cp groups.

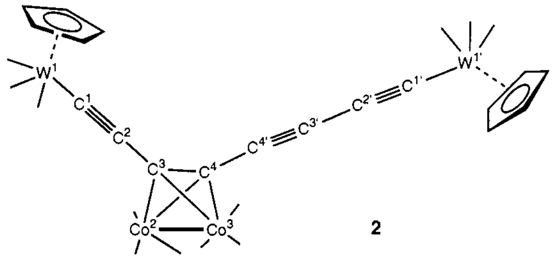
Introduction

There is much current interest in molecules containing carbon chains capped by transition metal–ligand groups.[1] These materials have potential utility as quasi-one dimensional conductors,[2] poly-yne systems allowing electronic interactions over relatively long distances through π-delocalisation.[3–5] Unsaturated carbon chains with up to 20 carbon atoms have been used to link redox-active metal centres.[6–8] While π-bonding of ML$_n$ groups to complexes of this type is thought to reduce communication along the chain,[9,10] recent studies of diyne complexes of cobalt have suggested that both through-bond and through-space interactions may occur.[11]

Three groups have described compounds containing C$_8$ chains bridging two W(CO)$_3$Cp,[12] Re(NO)(PPh$_3$)Cp*,[13] or Fe(dppe)Cp* groups.[14] However, complexes of this type have proved difficult to characterise crystallographically, as crystals of suitable size and quality have not been obtained. The use of Co$_2$(CO)$_6$ and Co$_2$(μ-dppm)(CO)$_4$ as protecting groups for C≡C triple bonds is well-established as these groups can be easily displaced to regenerate the parent alkyne.[15] Consequently, the preparation of similar derivatives of metal complexes containing carbon chains would provide independent evidence for the existence of these chains, although distortions in the C$_n$ geometry as a result of complexation do not give any useful structural information about the uncomplexed polyalkynes. In the limit, it is possible to envisage a novel form of carbon consisting of C$_n$ chains which might be stabilised by formation of the dicobalt derivatives. Indeed, just such a material is considered to form the black insoluble polymer obtained from {Co$_2$(CO)$_6$}$_2$(μ,μ-Me$_3$SiC$_2$C$_2$SiMe$_3$) on standing in methanol.[16] In this paper we describe several complexes which we have prepared from the recently described C$_8$ complex {W(CO)$_3$Cp}$_2$-(μ-C$_8$) **1**[12] and the dicobalt carbonyl complexes.

Results and discussion

Reactions between **1** and Co$_2$(CO)$_8$ were carried out at room temperature in thf. The black reaction products were purified by preparative TLC, initial separation into two black fractions occurring. Subsequent crystallisation afforded X-ray quality crystals of mono- and di-adducts, which were shown by the X-ray structural studies to have Co$_2$(CO)$_6$ groups attached to the C(3)–C(4) (**2**) and C(3)–C(4), C(3′)–C(4′) triple bonds (**3**), respectively. Numbering the C≡C triple bonds along the chain from one tungsten allows these complexes to be formulated as {W(CO)$_3$Cp}$_2${μ-C$_8$[Co$_2$(CO)$_6$]-2} **2** and {W(CO)$_3$Cp}$_2${μ-C$_8$-[Co$_2$(CO)$_6$]$_2$-2,3} **3**, respectively. The IR ν(CO) spectra contained only terminal ν(CO) bands between 2096 and 1951 cm^{-1}. The ^{1}H NMR spectra contained singlet resonances for the Cp protons at δ 5.64 and 5.67 (**2**) and at δ 5.59 (**3**).



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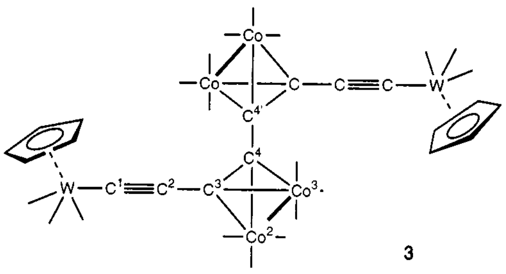

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Similar reactions between **1** and Co$_2$(μ-dppm)(CO)$_6$ afforded a mono-adduct {W(CO)$_3$Cp}$_2${μ-C$_8$[Co$_2$(μ-dppm)(CO)$_4$]} **4** and two isomeric products, again characterised by single crystal X-ray studies as the bis-adducts, containing Co$_2$(μ-dppm)(CO)$_4$ groups attached to the C(1)–C(2) and C(1′)–C(2′) or to the C(3)–C(4) and C(3′)–C(4′) triple bonds, respectively, namely {W(CO)$_3$Cp}$_2${μ-C$_8$[Co$_2$(μ-dppm)(CO)$_4$]$_2$-1,4} **5** and {W(CO)$_3$-Cp}$_2${μ-C$_8$[Co$_2$(μ-dppm)(CO)$_4$]$_2$-2,3} **6**. Complexes **5** and **6** have essentially indistinguishable IR spectra (Table 1) with terminal ν(CO) bands between 2038 and 1933 cm^{-1}, at lower energies than those in **2** and **3**; those for **4** are found some 3–10 cm^{-1} higher. The ^{1}H NMR spectra contained singlet resonances for the Cp protons at δ 5.56 and 5.81, respectively, while the CH$_2$ protons of the dppm ligands occurred at δ 3.19 and 3.91 (**5**) and at δ 3.30 and 3.82 (**6**).

Molecular structures of 2–6

Representations of the five molecular structures are given in

Table 1 IR ν(CO) spectra

Complex	ν(CO)/cm^{-1}
1	2043s, 1959vs
7	2101m, 2082s, 2062vs, 2037s, 2028s (sh), 1984w (br)
2	2090w, 2057s, 2038s, 2031m (sh), 1967vs, 1955s
3	2096w, 2079s, 2057vs, 2038s, 2025s, 1965s, 1951s
8	2029m, 2002vs, 1968s
4	2047w, 2038m, 2010m, 1995s, 1967s, 1955s, 1943m
5	2037m, 2030m, 2004s, 1992vs, 1960m, 1942m, 1933m
6	2038m, 2034m, 2011vs, 1996m, 1972s (br), 1960s (br), 1940m (sh)

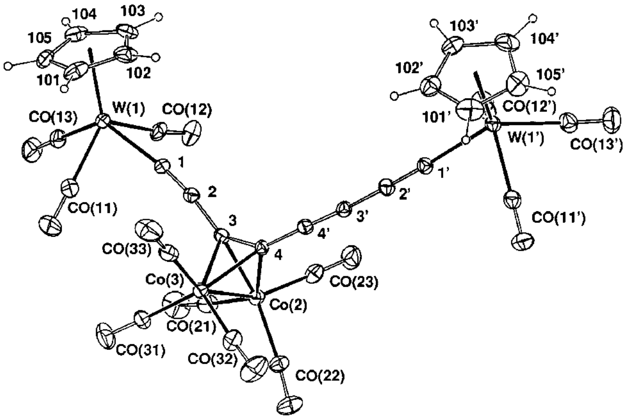
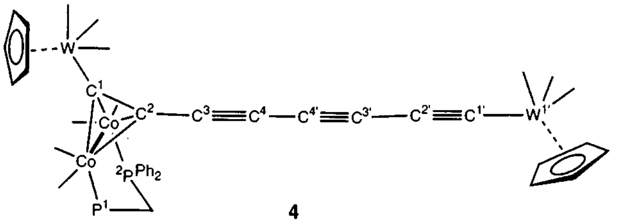


Fig. 1 Projection of $\{W(CO)_3Cp\}_2\{\mu\text{-}C_8[Co_2(CO)_6]\}$ **2**. For this and subsequent figures, 20% thermal ellipsoids are shown for the non-hydrogen atoms, hydrogen atoms having arbitrary radii of 0.1 Å.



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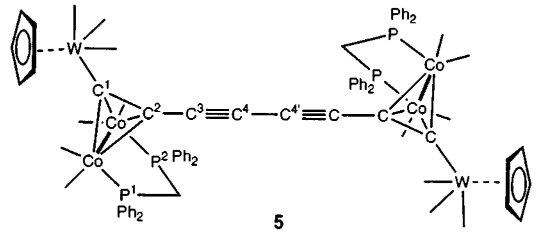
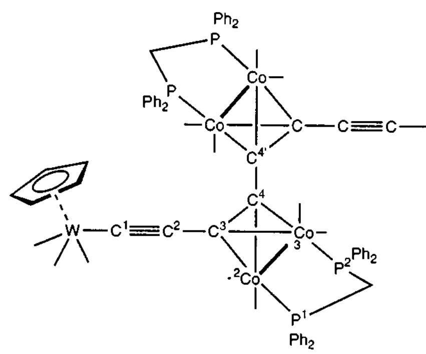


5



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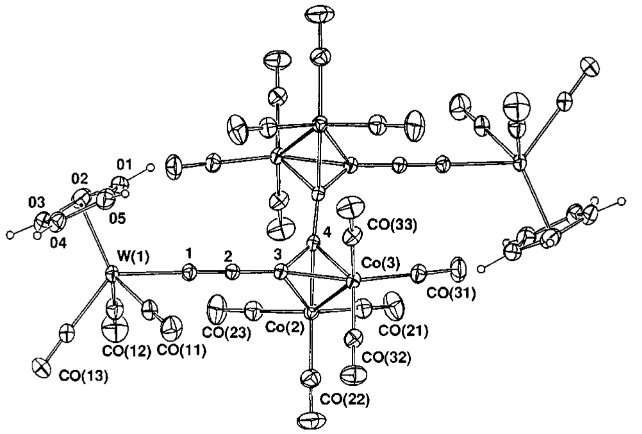

Fig. 2 Projection of $\{W(CO)_3Cp\}_2\{\mu\text{-}C_8[Co_2(CO)_6]_2\}$ **3**.

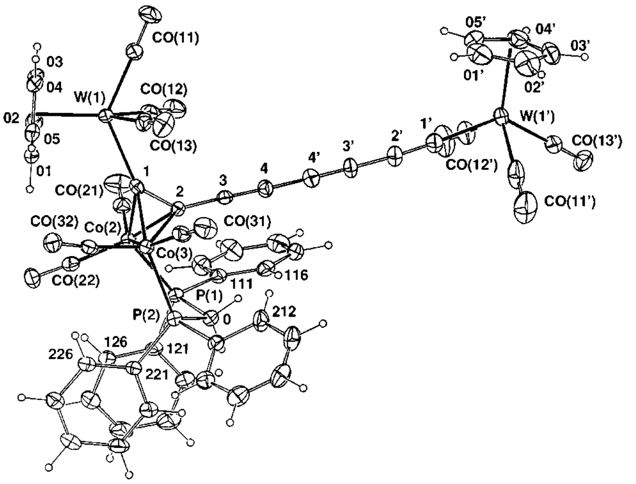

Fig. 3 Projection of $\{W(CO)_3Cp\}_2\{\mu\text{-}C_8[Co_2(\mu\text{-dppm})(CO)_4]\}$ **4**.

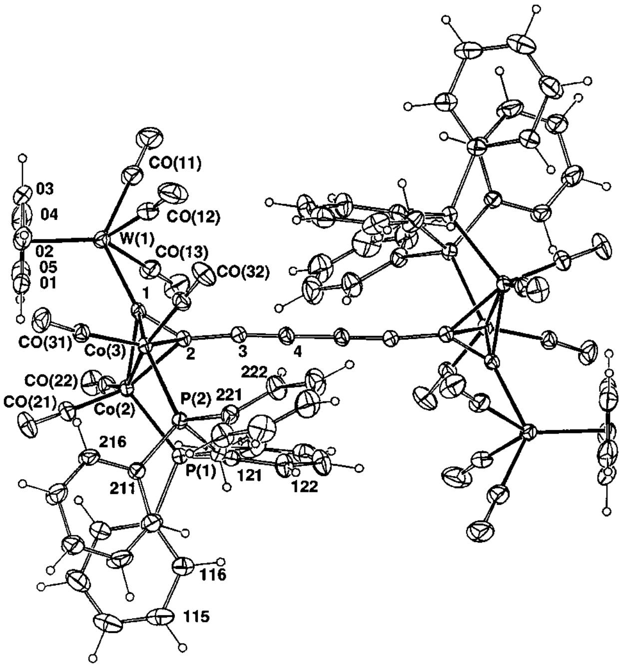

Fig. 4 Projection of $\{W(CO)_3Cp\}_2\{\mu\text{-}C_8[Co_2(\mu\text{-dppm})(CO)_4]_2\}$ (1,4-isomer) **5**.

Fig. 1–5, while significant structural parameters are summarised in Table 2. Molecules of **3**, **5** and **6** are centrosymmetric. Comparison of the $W(CO)_3Cp$ groups with that found in $W(C{\equiv}CC{\equiv}CSiMe_3)(CO)_3Cp$[12] show no significant differences to result from the coordination of the dicobalt fragments to the C≡C triple bonds. Thus the W–C(Cp) distances all fall in the range 2.27–2.37(1) Å, with the W–CO distances being between 1.929(8) and 2.02(1) Å.

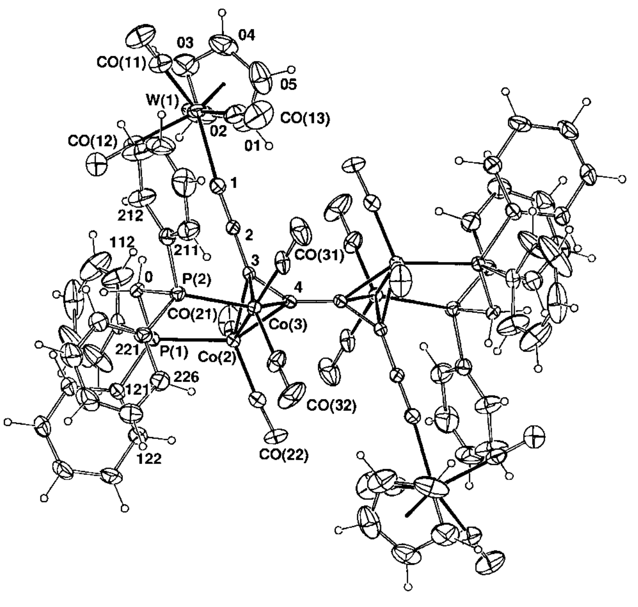

Fig. 5 Projection of $\{W(CO)_3Cp\}_2\{\mu\text{-}C_8[Co_2(\mu\text{-dppm})(CO)_4]_2\}$ (2,3-isomer) **6**.

The C_2Co_2 tetrahedra are similar to those found in many other related complexes, with Co–Co separations of 2.4595(8)–2.480(1) Å, Co–C distances of between 1.951(8) and 2.023(5) Å, and C-C bonds now between 1.33(1) and 1.358(6) Å. The uncoordinated $C\equiv C$ triple bond lengths are between 1.20(1) and 1.214(5) Å. These data may be compared with the other similarly characterised pair of derivatives, $\{Co_2(CO)_6\}_2(\mu,\mu\text{-}PhC_2C_2Ph)$ **7**[17] and $\{Co_2(\mu\text{-dppm})(CO)_4\}_2(\mu,\mu\text{-}PhC_2C_2Ph)$ **8**,[18] in which the Co–Co and Co–C distances are between 2.438 and 2.469(4) Å, and between 1.94 and 1.98(1) Å, respectively. The separation of the centre-points of the two Co–Co bonds in **3** and **6** are both 4.373 Å, very similar to the values of 4.43 and 4.36 Å found for **7** and **8**.

As expected, significant distortions of the C_8 chains from linearity occur in these complexes. The bend-back angles of the coordinated $C\equiv C$ triple bonds range from 33.8 to 38.2(5)°. Comparison of **2** and **4**, in which the Co_2 units are attached to the C(3)–C(4) and C(1)–C(2) bonds, respectively, shows that the total bending is greater in the latter (79.3 *vs.* 70.3°), suggesting that steric pressure from the bulky $W(CO)_3Cp$ group may play a role here.

As a result of the symmetry of the bis-adducts, the C_8 chains describe transoid or S-shaped conformations, with the W–C(1) vectors being approximately orthogonal to the central C(4)–C(4′) vectors (range 82.6–92.6°). Although the dppm ligands are much larger than the CO groups which they replace, comparison of the bending of the C_8 chains shows essentially no difference, with angles at C(3) and C(4) in **3** and **6** summing to 276.8° and 276.1°, respectively. In **3** and **6**, the W–C(1)–C(2)–C(3) sequences are approximately linear, with angles at C(1) and C(2) being 176.9(4) and 175.7(5)° (for **3**) and 174.5(4) and 176.1(4)° (for **6**). The central sequence in **5** has angles at C(3) and C(4) of 170.9(4) and 179.3(4)°, respectively.

Closer structural comparisons can be made between **5** and the centrosymmetric molecule $Me_3SiC_2\{Co_2(\mu\text{-dppm})(CO)_4\}(C\equiv C)_2C_2\{Co_2(\mu\text{-dppm})(CO)_4\}SiMe_3$ **9**,[19] the only other tetrayne–dicobalt complex to have been structurally characterised. The C–C bond lengths are 1.343(11), 1.386(9), 1.210(10) and 1.372(14) Å for the bonds between atoms C(1)–C(2)–C(3)–C(4)–C(4′), all closely similar to those found in **5**. In **9**, angles at atoms C(1–4) are 147.0(7), 144.4(9), 171.1(11) and 178.8(3)°, respectively, resulting in the two Si–C(1,1′) vectors forming angles of 68.6° with the central C(4)–C(4′) bond. Again, this suggests that the bulk of the substituent at C(1) has an effect on the bend-back angle, in additon to any electronic influence of the dicobalt fragment.

In the case of **6**, in spite the bulk of the $Co_2(\mu\text{-dppm})(CO)_4$ moiety, the angles subtended by the CO and diynyl groups at the W atoms are not significantly different from those in **5**. As expected, the W–C(1) distance in the latter has lengthened to 2.213(4) Å compared with 2.123(6) Å in **6**, consistent with rehybridisation of this carbon towards sp^2.

The structural results enable a rationalisation of the ^1H NMR data to be obtained. Coordination of a Co_2 group to the inner $C\equiv C$ triple bonds results in the Cp signal being at lower field than the resonance observed for the complex in which the outer $C\equiv C$ triple bond is coordinated. For **1**, the Cp resonance is at δ 5.67; in the case of the mono-adduct **2**, two Cp signals separated by 0.03 ppm are found. The presence of the dppm ligands results in a shift of *ca.* 0.3 ppm to low field.

Small amounts of other products were also present in the reaction mixtures, as evidenced by several other bands developing on the TLC plate. However, we have not been able to characterise these compounds. Their IR ν(CO) spectra contained bands at significantly lower energies, suggesting that mono-adducts were present, while their ^1H NMR spectra contained multiple Cp resonances, perhaps indicating that there were up to three other, unsymmetrical isomers of the mono-adducts.

Finally, the $Co_2(CO)_6$ groups may be removed from the complexed diyndiyl complexes by treatment with ammonium cerium(IV) nitrate in acetone, a method which has been used for more conventional alkyne–$Co_2(CO)_6$ complexes.[15] Thus, treatment of **2** with $[NH_4]_2[Ce(NO_3)_6]$ in acetone resulted in lightening of the colour to orange; conventional work-up afforded **1** in 50% yield.

Conclusions

We have shown that it is possible to prepare and characterise derivatives of the C_8 complex **1** containing dicobalt carbonyl groups attached to one or two $C\equiv C$ triple bonds; in contrast to the parent complex, crystalline samples of four of these complexes were readily obtained, for which single crystal X-ray studies showed that apparent preferential coordination to the inner $C\equiv C$ triple bonds occurred with $Co_2(CO)_8$. However, with $Co_2(\mu\text{-dppm})(CO)_6$, two isomeric complexes containing two dicobalt units attached to the two outer (**5**) or the two inner $C\equiv C$ triple bonds (**6**) were obtained. It is of interest that we have been able to isolate derivatives containing $Co_2(CO)_6$ moieties attached only to the 'inner' $C\equiv C$ triple bonds, whereas with the $Co_2(\mu\text{-dppm})(CO)_4$-substituted complexes the 'outer' $C\equiv C$ triple bonds can also coordinate. The dicobalt carbonyl moiety may be removed by oxidation with cerium(IV).

Experimental

General reaction conditions

Reactions were carried out under an atmosphere of nitrogen, but no special precautions were taken to exclude oxygen during work-up.

Instrumentation

IR: Perkin-Elmer 1700X FT IR. NMR: Bruker CXP300 or ACP300 (^1H NMR at 300.13 MHz, ^{13}C NMR at 75.47 MHz). ES MS: Finnegan LCQ: solutions were directly infused into the instrument. Chemical aids to ionisation were used as required.[20]

Reagents

Complex **1**[12] and $Co_2(\mu\text{-dppm})(CO)_6$[21] were prepared by the literature methods; $Co_2(CO)_8$ (Strem) was used as received.

Reaction of $\{W(CO)_3Cp\}_2(\mu\text{-}C_8)$ with $Co_2(CO)_8$

A mixture of $\{W(CO)_3Cp\}_2(\mu\text{-}C_8)$ (100 mg, 0.13 mmol) and

Table 2 Selected bond lengths (Å) and angles (°)

	2[a]	**3**	**4**	**5**	**6**
W–CO	1.99–2.02(1)	1.992–2.006(6)	1.96–2.02(1)	1.955–1.997(5)	1.929–2.002(8)
(av.)	1.998	1.998	1.977	1.977	1.972
W–C(Cp)	2.27–2.37(1)	2.302–2.351(7)	2.293(8)–2.370(9)	2.307–2.368(6)	2.28–2.35(1)
(av.)	2.33	2.329	2.327	2.337	2.31
W–C(1)	2.143(8) [2.118(8)]	2.127(4)	2.216(7), 2.108(9)	2.213(4)	2.123(6)
Co(2)–Co(3)	2.461(1)	2.4794(9)	2.476(1)	2.4595(8)	2.480(1)
Co–CO	1.802–1.838(9)	1.794–1.825(6)	1.765(9)–1.79(1)	1.752–1.787(4)	1.750–1.783(7)
(av.)	1.821	1.812	1.774	1.773	1.767
Co(2)–P(1)			2.243(3)	2.221(1)	2.219(1)
Co(3)–P(2)			2.232(2)	2.244(1)	2.232(1)
Co(2)–C(1/3)	1.951(8)	1.995(4)	2.019(7)	1.996(4)	1.975(5)
Co(2)–C(2/4)	1.987(7)	1.964(4)	1.954(7)	1.969(4)	1.955(5)
Co(3)–C(1/3)	1.978(7)	1.978(5)	2.023(5)	2.022(3)	1.964(6)
Co(3)–C(2/4)	1.963(7)	1.970(5)	1.961(6)	1.983(3)	1.973(5)
P(1)–C(0)			1.827(8)	1.830(4)	1.821(5)
P(2)–C(0)			1.834(9)	1.842(4)	1.834(5)
C(1)–C(2)	1.19(1), 1.23(1)	1.213(5)	1.36(1), 1.22(1)	1.353(5)	1.219(8)
C(2)–C(3)	1.43(1), 1.36(1)	1.398(5)	1.40(1), 1.36(1)	1.398(5)	1.395(8)
C(3)–C(4)	1.33(1), 1.21(1)	1.353(5)	1.20(1), 1.20(1)	1.214(5)	1.358(6)
C(4)–C(4′)	1.40(1)	1.425(6)	1.37(1)	1.372(5)	1.424(6)
C(11)–W–C(12)	111.8(4) [107.5(4)]	113.0(3)	76.0(4), 109.7(4)	78.2(2)	78.9(3)
C(11)–W–C(13)	77.4(4) [79.6(4)]	78.6(2)	77.1(3), 77.6(4)	76.7(2)	78.0(3)
C(12)–W–C(13)	79.4(4) [76.6(4)]	77.8(2)	106.9(4), 79.9(4)	105.7(2)	110.7(3)
C(1)–W–C(11)	72.5(4) [75.6(3)]	75.2(2)	132.1(4), 75.4(4)	132.8(2)	131.7(3)
C(1)–W–C(12)	76.5(3) [73.6(3)]	73.4(2)	73.2(3), 74.3(4)	76.0(2)	77.0(2)
C(1)–W–C(13)	130.5(3) [132.8(4)]	128.8(2)	77.9(3), 133.2(3)	73.3(2)	72.5(3)
C(21)–Co(2)–C(22)	105.3(4)	102.3(2)	101.8(4)	99.6(2)	103.9(3)
C(21)–Co(2)–C(23)	103.8(4)	103.6(2)			
C(22)–Co(2)–C(23)	98.3(4)	97.6(3)			
C(31)–Co(3)–C(32)	108.6(4)	105.2(2)	99.7(4)	97.7(2)	101.6(3)
C(31)–Co(3)–C(33)	98.6(4)	102.2(2)			
C(32)–Co(3)–C(33)	98.3(4)	99.0(2)			
Co(2)–C(4)–C(4′)	131.5(46)	134.2(3)			134.1(3)
Co(3)–C(3)–C(2)	131.3(6)	137.4(3)			132.7(4)
W–C(1)–C(2)	173.4(7)	176.9(4)	141.9(4)	143.7(3)	174.5(4)
C(1)–C(2)–C(3)	171.6(8)	175.7(5)	138.8(5)	143.5(4)	176.1(4)
C(2)–C(3)–C(4)	146.2(8)	142.7(5)	177.6(8)	170.9(4)	142.2(5)
C(3)–C(4)–C(4′)	143.5(7)	133.6(5)	178.1(8)	179.3(4)	141.8(6)
Co(2)–P(1)–C(0)			107.7(3)	108.5(1)	108.6(2)
P(1)–C(0)–P(2)			108.7(5)	110.5(2)	109.3(2)
C(0)–P(2)–Co(3)			108.8(2)	110.2(1)	108.9(2)
P(1)–Co(2)–C(21)			97.6(3)	104.4(2)	95.9(2)
P(1)–Co(2)–C(22)			107.8(3)	103.7(2)	112.2(2)
P(2)–Co(3)–C(31)			96.0(3)	112.1(2)	97.2(2)
P(2)–Co(3)–C(32)			112.9(2)	96.5(2)	109.8(2)

[a] This molecule has no crystallographic centre of symmetry; second entries correspond to the counterpart atoms in the primed/second 'half' of the molecule.

$Co_2(CO)_8$ (54 mg, 0.16 mmol) in thf (10 mL) was left to stir for 1 h at r.t., then concentrated under reduced pressure. The resulting black residue was extracted with CH_2Cl_2 and purified by TLC (silica gel; hexane–CH_2Cl_2 3 : 2). The top two black bands were removed.

Band 1 (R_f 0.7) contained {W(CO)$_3$Cp}$_2${μ-C≡CC$_2$[Co$_2$(CO)$_6$]C$_2$[Co$_2$(CO)$_6$]C≡C} **3** (10 mg, 6%). Crystals suitable for X-ray study were obtained from CH_2Cl_2–pentane (Found: C, 31.38; H, 0.59. $C_{36}H_{10}Co_4O_{18}W_2\cdot CH_2Cl_2$ calcd.: C, 31.32; H, 0.85%; M, 1334). IR (cyclohexane) ν(CO) 2096w, 2079s, 2057vs, 2038s, 2025s, 1965s, 1951s cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 5.59 (s, Cp).

Band 2 (R_f 0.6) afforded {W(CO)$_3$Cp}$_2${μ-C≡CC$_2$[Co$_2$(CO)$_6$](C≡C)$_2$} **2** (37 mg, 37%). Crystals suitable for X-ray study were obtained from CH_2Cl_2–pentane (Found: C, 34.38; H, 0.96. $C_{30}H_{10}Co_2O_{12}W_2$ calcd.: C, 34.40; H, 1.16%; M, 1048). IR (cyclohexane) ν(CO) 2090w, 2057s, 2038s, 1967vs, 1955s cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 5.64, 5.67 (2s, Cp). ES MS (with NaOMe in MeOH): *m/z* 1071, [M + Na]$^+$.

Reaction of {W(CO)$_3$Cp}$_2$(μ-C$_8$) with Co$_2$(μ-dppm)(CO)$_6$

A stirred mixture of {W(CO)$_3$Cp}$_2$(μ-C$_8$) (56 mg, 0.07 mmol) and Co$_2$(μ-dppm)(CO)$_6$ (100 mg, 0.15 mmol) in benzene (20 mL) was refluxed for 1 h. The mixture was allowed to cool, concentrated under reduced pressure and the resulting black residue extracted with CH_2Cl_2 and purified by TLC (silica gel; hexane–CH_2Cl_2 1 : 1). The top three black bands were removed.

Band 1 (R_f 0.8) afforded {W(CO)$_3$Cp}$_2${μ-C≡CC$_2$[Co$_2$(μ-dppm)(CO)$_4$]C$_2$[Co$_2$(μ-dppm)(CO)$_4$]C≡C} **6** (45 mg, 31%). Crystals suitable for X-ray study were obtained from CH_2Cl_2–pentane (Found: C, 46.13; H, 2.74. $C_{82}H_{54}Co_4O_{14}P_4W_2\cdot 2CH_2Cl_2$ calcd.: C, 46.70; H, 2.71%; M, 1991). IR (cyclohexane) ν(CO) 2026m, 1997s, 1974s, 1958m, 1941m, 1925s, 1912s cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 3.30, 3.82 (2m, 4H, CH_2P_2), 5.81 (s, 10H, Cp), 7.09–7.39 (m, 40H, Ph).

Band 2 (R_f 0.7) contained {W(CO)$_3$Cp}$_2${μ-C$_2$[Co$_2$(μ-dppm)(CO)$_4$](C≡C)$_2$C$_2$[Co$_2$(μ-dppm)(CO)$_4$]} **5** (25 mg, 17%). Crystals suitable for X-ray study were obtained from CH_2Cl_2–benzene–pentane (Found: C, 48.48; H, 2.42. $C_{82}H_{54}Co_4O_{14}P_4W_2$ calcd.: C, 47.77; H, 2.64%; M, 1991. IR (cyclohexane) ν(CO) 2031m, 1991s, 1956s, 1947m, 1937m, 1922s, 1913s cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 3.19, 3.91 (2m, 4H, CH_2P_2), 5.56 (s, 10H, Cp), 6.87–7.58 (m, 40H, Ph).

Band 3 (R_f 0.5) contained {W(CO)$_3$Cp}$_2${μ-C$_2$[Co$_2$(μ-dppm)(CO)$_4$](C≡C)$_3$}·C_6H_6 **4** (10 mg, 7%). Crystals of the hemi-

Table 3 Crystal and refinement data

Compound	**2**	**3**	**4**	**5**	**6**
Formula	$C_{30}H_{10}Co_2O_{12}W_2$	$C_{36}H_{10}Co_4O_{18}W_2 \cdot CH_2Cl_2$	$C_{53}H_{32}Co_2O_{10}P_2W_2 \cdot 0.5C_6H_6$	$C_{82}H_{54}Co_4O_{14}P_4W_2 \cdot 2CH_2Cl_2$	$C_{82}H_{54}Co_4O_{14}P_4W_2 \cdot 2C_6H_6$
M	1048.0	1418.8	1415.4	2160.5	2146.9
Crystal system	Triclinic	Triclinic	Triclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$C2/c$	$P2_1/c$
a/Å	6.9570(8)	9.753(2)	13.656(2)	19.256(2)	18.304(1)
b/Å	12.280(1)	11.498(1)	14.520(2)	14.656(2)	14.0866(8)
c/Å	18.768(2)	12.046(2)	15.450(2)	30.588(4)	18.729(1)
α/°	99.267(2)	108.760(2)	100.616(3)		
β/°	96.708(2)	103.562(2)	103.489(3)	105.234(2)	115.739(1)
γ/°	94.144(2)	111.034(2)	113.166(3)		
V/Å^3	1564.9	1096.3	2605	8321	4350
Z	2	1	2	4	2
D_C/g cm^{-3}	2.224	2.149	1.804	1.724	1.639
F(000)	976	668	1366	4232	2116
Crystal size/mm	0.37 × 0.10 × 0.10	0.55 × 0.35 × 0.12	0.20 × 0.10 × 0.04	0.2 (cuboid)	0.20 × 0.18 × 0.14
T (min, max)	0.53, 0.91	0.47, 0.77	0.65, 0.88	0.76, 0.89	0.582, 0.773
μ cm^{-1}	84	69.0	52	38.0	35.2
N	18066	12368	30621	44221	44160
N_r (R_{int})	7621 (0.048)	5322 (0.025)	12876 (0.029)	10489 (0.023)	10855 (0.045)
N_o	6299	4442	7498	7746	6205
R	0.048	0.026	0.040	0.034	0.040
R_w	0.056	0.032	0.039	0.041	0.041

benzene solvate suitable for the X-ray study were obtained from CH_2Cl_2–benzene–hexane (Found: C, 47.23; H, 2.70; $C_{53}H_{32}Co_2O_{10}P_2W_2 \cdot 0.5C_6H_6$ calcd.: C, 47.52; H, 2.49%). IR (cyclohexane) ν(CO) 2047w, 2038m, 2010m, 1995s, 1967s, 1955s, 1943m cm^{-1}. ^{1}H NMR (CDCl$_3$); δ 3.30, 3.65 (2 × m, 2H, CH_2P), 5.66, 5.78 (2 × s, 10H, Cp), 6.97–7.36 (m, 20H, Ph).

Decomplexation of 2

A mixture of **2** (20 mg, 0.019 mmol) and $[NH_4]_2[Ce(NO_3)_6]$ (35 mg, 0.064 mmol) in acetone (10 ml) was stirred at r.t. for 2 h. The initial black solution became orange over this time. Evaporation, extraction of the residue with CH_2Cl_2 (3 × 50 ml) and washing the extracts with water (2 × 100 ml) and evaporation of the dried ($MgSO_4$) organic phase gave **1** (7 mg, 50%), identified by ^{1}H NMR [δ(CDCl$_3$) 5.63 (Cp); lit.,[12] δ 5.67].

Crystallography

Full spheres of data were measured at *ca.* 300 K to $2\theta_{max} = 58°$ using a Bruker AXS CCD instrument (monochromatic Mo-Kα radiation, λ 0.71073 Å); N data were measured and reduced to N_r independent reflections, N_o with $|F| > 4\sigma(F)$ being considered 'observed' and used in the full matrix least squares refinement after 'absorption correction' (proprietary software SADABS).[22] Anisotropic thermal parameters were refined for the non-hydrogen atoms; $(x, y, z, U_{iso})_H$ were included constrained at estimated values. Conventional residuals R, R' on $|F|$ are quoted, statistical weights derivative of $\sigma^2(I) = \sigma^2(I_{diff}) + 0.0004\sigma^4(I_{diff})$ being used. Computation used the XTAL 3.4 program system[23] implemented by S. R. Hall; neutral atom complex scattering factors were employed. Pertinent results are given in the figures and Table 3.

Special features 3. Difference map residues were modelled in terms of a molecule of dichloromethane, population constrained at unity after trial refinement, but disordered about an inversion centre.

4 Difference map residues were modelled in terms of benzene of solvation, disposed about a crystallographic centre of symmetry, site occupancy set at unity after trial refinement.

5 Difference map residues were modelled in terms of a molecule of dichloromethane disordered over two sets of sites, total occupancy constrained at unity after trial refinement, occupancies of the individual components being x, $1 - x$, with $x = 0.57(1)$.

6 Difference map residues were modelled in terms of benzene of solvation, site occupancy set at unity after trial refinement.

CCDC reference number 186/1311.

See http://www.rsc.org/suppdata/dt/1999/847/ for crystallographic files in .cif format.

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