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Polymetallation of alkenes: Formation of some complexes containing branched chain carbon-rich ligands

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Abstract

Reactions of $\{(Ph_3P)AuC\equiv C\}_2C=C\{C\equiv CAu(PPh_3)\}_2$ (**1b**), with $Co_3(\mu\text{-CBr})(\mu\text{-dppm})_n(CO)_{9-2n}$ ($n = 0, 1$) result in complete or partial elimination of $AuBr(PPh_3)$ to give the complexes $\{(OC)_9Co_3\text{-}\mu_3\text{-CC}\equiv C\}_2C=C\{C\equiv C\text{-}\mu_3\text{-CCo}_3(CO)_9\}_2$ (**3**), $trans\text{-}\{(OC)_7(\mu\text{-dppm})\text{-}Co_3\text{-}\mu_3\text{-CC}\equiv C\}(HC\equiv C)C=C\{C\equiv CAu(PPh_3)\}\{C\equiv C\text{-}\mu_3\text{-CCo}_3(\mu\text{-dppm})(CO)_7\}$ (**4**), $\{(OC)_7(\mu\text{-dppm})Co_3\text{-}\mu_3\text{-CC}\equiv C\}_2C=C(C\equiv CH)\{C\equiv C\text{-}\mu_3\text{-CCo}_3(\mu\text{-dppm})(CO)_7\}$ (**5**) and $\{(OC)_7(\mu\text{-dppm})Co_3\text{-}\mu_3\text{-CC}\equiv C\}_2C=C\{C\equiv CAu(PPh_3)\}\{C\equiv C\text{-}\mu_3\text{-CCo}_3(\mu\text{-dppm})(CO)_7\}$ (**6**), which have been identified by spectroscopic methods and in the cases of **3**, **4** and **5**, by single-crystal X-ray diffraction methods.
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1. Introduction

Continuing attention to compounds containing all-carbon chains end-capped by transition metal fragments stems from their potential as components of molecular scale electronic assemblies as well as from the inherent interest in their chemistry [1]. In addition to a multitude of examples of complexes containing C(sp) chains, generalised as $\{L_nM\}\text{-}(C\equiv C)_x\text{-}\{M'L_m\}$, a growing number of complexes containing two or more metal fragments separated by branched chain carbon-rich ligands has been described. Recent examples include complexes derived from 1,3,5-triethynyl-benzene, $1,3,5\text{-}\{L_nMCC\}_3C_6H_3$ [ML_n = Fe(dppe)Cp* [2], *trans*-PdCl(PEt_3)_2 [3], $1,3\text{-}\{(Et_3P)_2ClPdC\equiv C\}_2\text{-}5\text{-bpy})(O\text{-}C)_3ReC\equiv C\}C_6H_3$ [4], *trans*-PtI(PEt_3)_2 [5], related platinum(II) and gold(I) complexes from $C_6Me_3(C\equiv CH)_3\text{-}$

1,3,5 [6], and 1,2,4,5-$\{trans\text{-}(Et_3P)_2IPtC\equiv C\}_4C_6H_2$ [5]. Further examples of complexes of this type have been employed in the construction of metal-containing dendrimers [5,7,8]. Less common are complexes containing branched chain all-carbon ligands, i.e., those containing only carbon atoms, the first of these being the platinum(II) derivatives of tetra-ethynylethene described by Diederich [9]. Fully metallated complexes of this poly-yne are apparently limited to $\{(Cy_3P)AuC\equiv C\}_2C=C\{C\equiv CAu(PCy_3)\}_2$ (**1a**) obtained from $(Me_3SiC\equiv C)_2C=C(C\equiv CSiMe_3)_2$ [10]. The optical properties of the latter have excited interest, it being shown that the spectra of this and related C_n complexes are influenced by the nature of the carbon bridge, the Au(PR_3) derivatives showing triplet state character for the excited states [10,11].

The recent discovery of a simple high-yielding route to $(Me_3SiC\equiv C)_2C=C(C\equiv CSiMe_3)_2$ by one of us [12] suggested its use as a source of highly metallated poly-alkynylalkenes by conversion to the tetragold derivative

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$\{(Ph_3P)AuC\equiv C\}_2C=C\{C\equiv CAu(PPh_3)\}_2$ (**1b**) and subsequent phosphine-gold(I) halide elimination reactions with suitable transition metal halide precursors [13]. This paper describes the first complexes of this type, obtained from reactions of **1b** with $Co_3(\mu_3\text{-CBr})(\mu\text{-dppm})_n(CO)_{9-2n}$ ($n = 0, 1$).

2. Results and discussion

Complex **1b** was readily obtained in 81% yield from the reaction between $AuCl(PPh_3)$ and $(Me_3SiC\equiv C)_2C=C(C\equiv CSiMe_3)_2$ in the presence of NaOMe as a light yellow precipitate which was collected by filtration. The IR spectrum contained weak absorptions at 2090 and 1585 cm^{-1}, assigned to $v(C\equiv C)$ and $v(C=C)$, respectively, while phenyl resonances at δ_H 7.08–7.62 (Ph) and δ_P 42.8 (PPh$_3$) were found in the NMR spectra.

The Pd(0)/Cu(I)-catalysed reaction between **1b** and four equivalents of $Co_3(\mu_3\text{-CBr})(CO)_9$ was carried out in THF at r.t. (Scheme 1). After 4 h, work-up of the reaction mixture using preparative t.l.c. on silica gel afforded two fractions. The faster moving contained the previously known C$_4$ complex $\{Co_3(CO)_9\}_2(\mu_3:\mu_3\text{-CC}\equiv CC)$ (**2**) [14], here obtained in less than 1% yield and identified from a single-crystal X-ray structure determination. This compound is formed by reductive transformation of the bromomethylidyne cluster precursor, probably with additional incorporation of CO. This reaction is under further investigation and the results will be reported elsewhere.

The major product is contained in a dark blue band which afforded very dark red crystals of $\{(OC)_9Co_3\text{-}\mu_3\text{-}CC\equiv C\}_2C=C\{C\equiv C\text{-}\mu_3\text{-CCo}_3(CO)_9\}_2$ (**3**) in 62% yield, identified by a single-crystal X-ray structural determination (see below). Elemental analysis and spectroscopic properties were also consistent with the solid-state structure, the most convincing being the positive-ion ES MS which contained the molecular cation at m/z 1884. In the IR spectrum, a band at 2142 cm^{-1} is assigned to $v(C\equiv C)$, while $v(CO)$ bands between 2099 and 2039 cm^{-1} are similar in profile to those found for other complexes containing the

Co$_3$(CO)$_9$ fragment. The low solubility of **3** in common solvents together with the long relaxation time of quaternary carbon centres hampered our efforts to obtain a useful ^{13}C NMR spectrum.

Previous studies have shown that related complexes containing dppm sometimes have greater solubility than their unsubstituted carbonyl analogues. The reaction between **1b** and $Co_3(\mu_3\text{-CBr})(\mu\text{-dppm})(CO)_7$ carried out as described for **3** afforded a mixture of three new products, together with a small amount of previously characterised $Co_3(\mu_3\text{-CCO}_2H)(\mu\text{-dppm})(CO)_7$ [15], which were readily separated by preparative t.l.c. (Scheme 2). Magenta-coloured needles of $\{(OC)_7(\mu\text{-dppm})Co_3\text{-}\mu_3\text{-CC}\equiv C\}(HC\equiv C)\text{-}C=C\{C\equiv CAu(PPh_3)\}\{C\equiv C\text{-}\mu_3\text{-CCo}_3(\mu\text{-dppm})(CO)_7\}$ (**4**) were initially identified spectroscopically, with IR bands between 2086 and 1970 cm^{-1} characteristic of the $Co_3(\mu\text{-dppm})(CO)_7$ cluster and weak bands at 2179, 2148 and 2115 cm^{-1} assigned to $v(C\equiv C)$. In the ^{1}H NMR spectrum, the dppm ligands gave multiplets at δ 3.39 and 4.69, while a broad singlet at δ 3.05 was assigned to the $\equiv$CH proton. The ^{31}P NMR spectrum contains two resonances at δ 34.4 and 43.0 in a ratio 4/1, assigned to the dppm and PPh$_3$ ligands, respectively; the former could not be resolved although the two dppm ligands are strictly non-equivalent. The ES MS spectra, obtained from solutions in MeOH containing NaOMe, contain $[M + Na]^+$ at m/z 2142 and M^- at m/z 2119. A subsequent single-crystal X-ray structure determination enabled confirmation of its formulation and showed that the two C$_3$Co$_3$ moieties are mutually *trans*.

The second product was identified from a single-crystal X-ray study as the tri-cluster complex $\{(OC)_7(\mu\text{-dppm})\text{-}Co_3\text{-}\mu_3\text{-CC}\equiv C\}_2C=C(C\equiv CH)\{C\equiv C\text{-}\mu_3\text{-CCo}_3(\mu\text{-dppm})\text{-}(CO)_7\}$ (**5**) (16%). The IR spectrum contains several $v(CO)$ bands between 2103 and 1969 cm^{-1} together with weak $v(C\equiv C)$ bands at 2191 and 2115 cm^{-1}. A singlet at δ 3.28 is assigned to the $\equiv$CH proton, together with two multiplets at δ 3.61 and 4.44 (total intensities 1/6) from the dppm ligands. Only one broad ^{31}P resonance is found at δ 34.0. The ES MS spectra (from solutions in MeOH containing
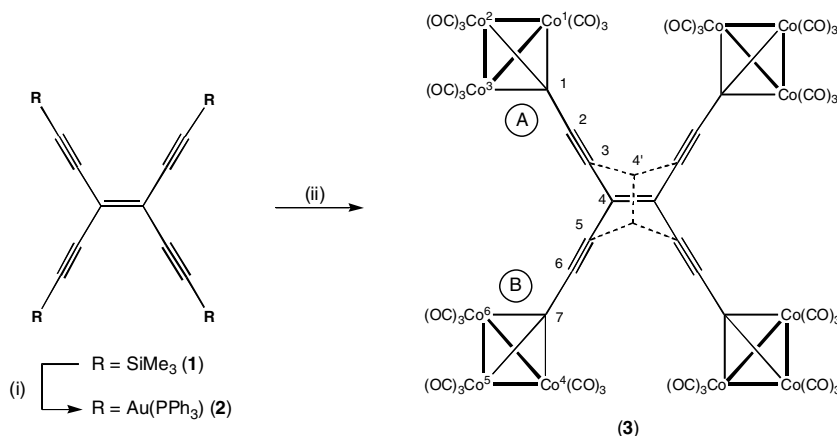
Scheme 1. Reagents: (i) NaOMe/AuCl(PPh$_3$).(ii) Co$_3(\mu_3$-CBr)(CO)$_9$, Pd(PPh$_3$)$_4$/CuCl.
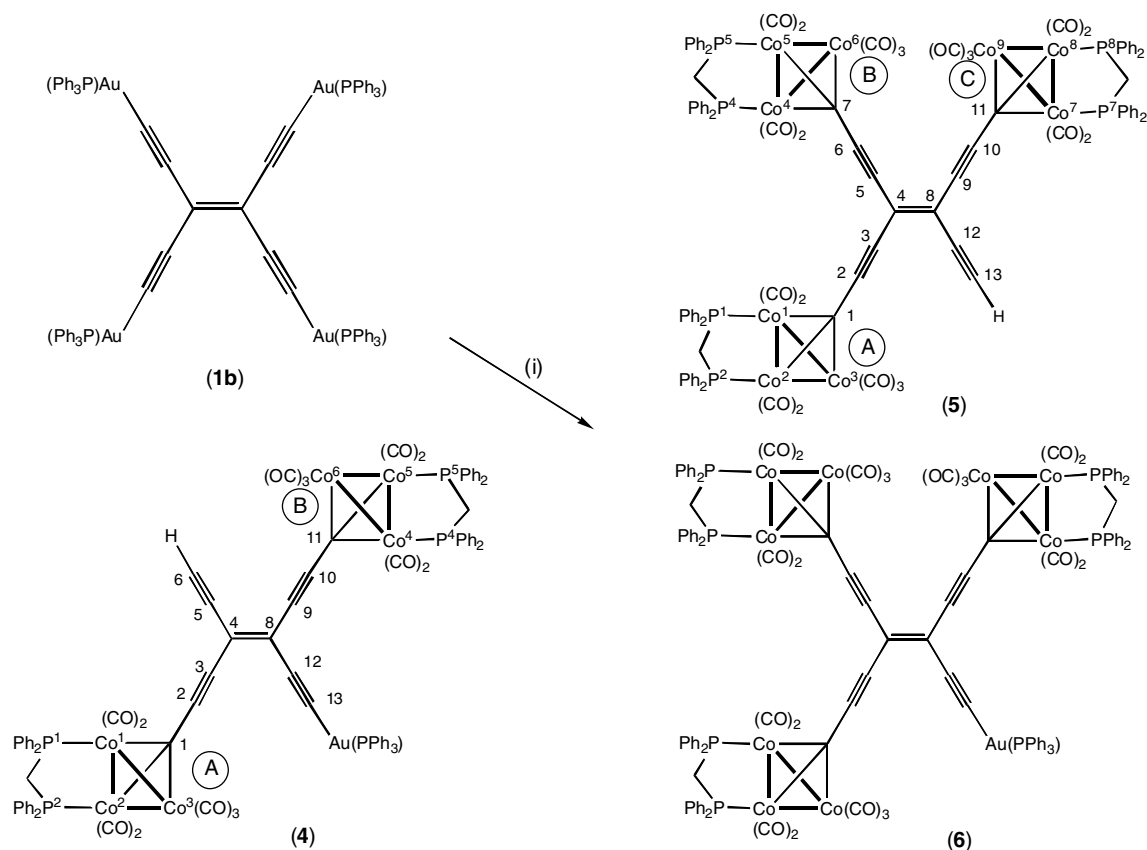
Scheme 2. Reagents: (i) Co$_3$(μ$_3$-CBr)(μ-dppm)(CO)$_7$, Pd(PPh$_3$)$_4$/CuCl.

NaOMe) have as highest mass ions, m/z 2451 and 2427, assigned to $[M + Na]^+$ and $[M - H]^-$, respectively.

Small dark coloured crystals of {(OC)$_7$(μ-dppm)Co$_3$-μ$_3$-CC≡C}$_2$C=C{C≡CAu(PPh$_3$)}{C≡C-μ$_3$-CCo$_3$(μ-dppm)-(CO)$_7$} (6) were isolated in 25% yield. Its structure was established from spectroscopic data, with the usual IR v(CO) bands between 2103 and 1966 cm^{-1} and two weak v(C≡C) absorptions at 2142 and 2117 cm^{-1}. Comparison of the IR v(C≡C) bands of the three complexes 4–6 suggests that the absorptions at ca 2180, 2150 and 2115 cm^{-1} can be assigned to the C≡CH, C≡CAu(PPh$_3$) and C≡CCCo$_3$ moieties, respectively, in these complexes. The ^{1}H NMR spectrum contains Ph resonances between δ 6.69 and 7.89, together with two multiplets at δ 3.75 and 4.47 from the dppm ligands. In the ^{31}P NMR spectrum, two signals at δ 35.0 and 42.75 (ratio 6/1) are assigned to the dppm and PPh$_3$ ligands. Further evidence concerning the formulation of 6 comes from the ES MS spectrum, which contains peaks at m/z 2909 and 2887, assigned to $[M + Na]^+$ and $[M + H]^+$, respectively; some fragmentation by loss of two CO groups is also found.

Several other minor products were also separated by t.l.c., the most interesting being the dark blue fraction having a low R_f, which may be {(OC)$_7$(μ-dppm)Co$_3$-μ$_3$-CC≡C}$_2$C=C{C≡C-μ$_3$-CCo$_3$(μ-dppm)(CO)$_7$}$_2$ (7). However, this could not be confirmed, the complex being totally insoluble after removal from the t.l.c. plate.

2.1. Molecular structures

Single-crystal X-ray diffraction studies enabled the molecular structures of 3, 4 and 5 to be confirmed. Plots of individual molecules of each complex are presented in Figs. 1–3 and selected bond parameters are collected in Table 1. There is some disorder present in 3, whereby the central C=C double bond [atoms C(4)–C(4′)] occupies two orthogonal positions, with other atoms remaining unchanged. Disorder is also present in 4, which involves two of the Co atoms of one Co$_3$ triangle (B), their associated CO groups and one Ph group of the attached dppm ligand, together with two Ph groups of the PPh$_3$ ligand. This disorder was modelled in terms of equal occupancy of two sites. No associated superlattice was found.

All complexes retain the 1,1,2,2-tetraethynylethene nucleus derived from precursor 1b. They vary in the planarity of their conjugated cores: the C$_{14}$ core of 3 and the C$_{13}$ core of 5 are essentially planar ($\chi^2 = 331$ and 377, respectively), but the C$_{12}$ core of 4 has atom deviations of as much as 0.66(1) Å with δ Au 0.138(8) Å ($\chi^2 = 1.4 \times 10^4$). As mentioned above, there are two orthogonal orientations of the central C=C double bond in 3 [angle C(4)–C(4′)/C(4′)–C(4′) 90°], with distances C(4)–C(4) and C(4′)–C(4′) being 1.367(12) and 1.384(11) Å, respectively. There is an inversion centre in the molecule, at the centre of this double bond.

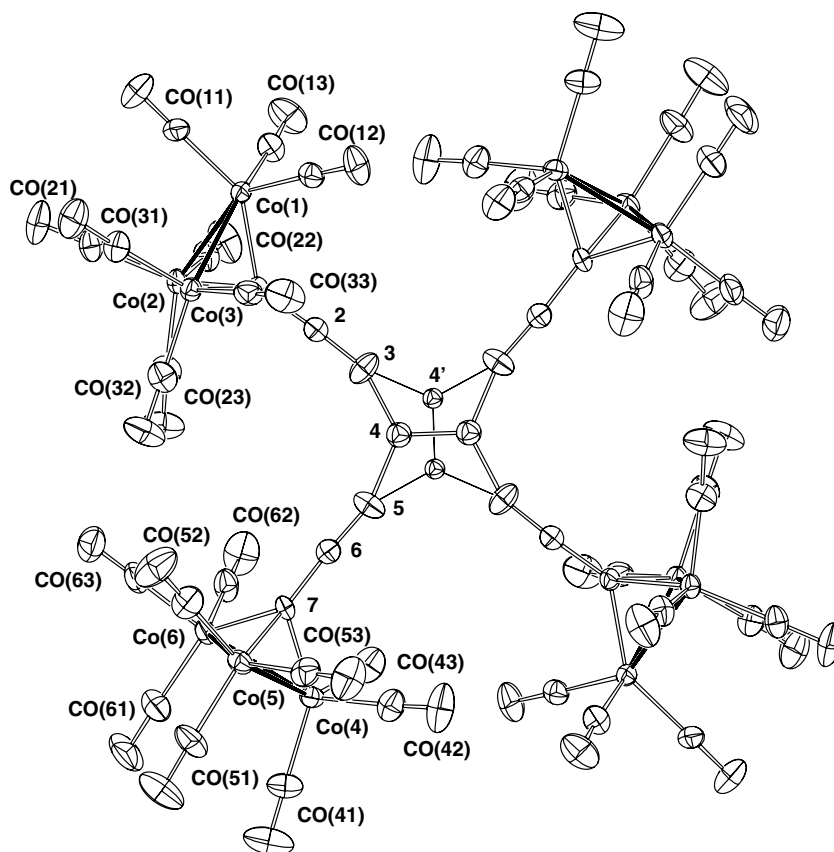Fig. 1. Plot of a molecule of {(OC)₉Co₃-μ₃-CC≡C}₂C=C{C≡C-μ₃-CCo₃(CO)₉}₂ (**3**), showing atom numbering scheme.

Considering the interactions of the Co_3 clusters with the methynyl carbons and the phosphine ligands, scatter is large in many of the parameters (compounded by the disorder in cluster B of **4**) and definable differences/trends are meagre. Thus, in **3**, ⟨Co–Co⟩ is 2.476(8) and ⟨Co–C(methynyl)⟩ 1.913(11) Å; in **4**, in the non-disordered cluster ⟨Co_C–Co_P⟩ is 2.478(10), Co_P-Co_P 2.491(1), Co_C–C 1.933(6), ⟨Co_P–C⟩ 1.894(8), ⟨Co_P–P⟩ 2.21(2) Å, and in **5**, ⟨Co_C–Co_P⟩ is 2.480(5), ⟨Co_P–Co_P⟩ 2.50(2), ⟨Co_C–C⟩ 1.96(1), ⟨Co_P–P⟩ 1.91(2), ⟨Co_P–P⟩ 2.201(3) Å, while the ranges of C–C–Co_C and C–C–Co_P angles overlap [Co_P is cobalt bound to P, Co_C the Co(CO)₃ group].

In **3**, atom C(4) is attached to the two −C≡C−C≡ chains [atoms C(3)–C(2)–C(1) and C(5)–C(6)–C(7), respectively], with separations 1.471(10), 1.210(6), 1.401(6) and 1.494(10), 1.210(6), 1.390(6) Å, respectively, consistent with the sequence −C−C≡C−C≡ as expected. The Co_3 clusters are attached to C(1) and C(7) [Co–C range 1.901(4) to 1.926(4) Å] to form the usual tetrahedral CCo₃ arrangements. Angles at individual carbon atoms vary somewhat from the linear arrangements expected for the C_3 chains [C(1)–C(2)–C(3) 175.7(5), C(5)–C(6)–C(7) 176.1(5) and C(2)–C(3)–C(4) 156.4(6), C(4)–C(5)–C(6) 161.6(6); C(2)–C(3)–C(4') 164.9(5), C(4')–C(5)–C(6) 160.1(6)°] although angles at C(3) and C(6) may reflect the disorder present in that part of the molecule.

The two C_3Co_3 moieties attached to C(4) and C(7) in **4** are *trans* to one another, while the other two substituents on the C=C double bond are −C≡CH [on C(4)] and −C≡CAu(PPh₃) [on C(8)]. The disorder present in the Co_3 cluster attached to C(11) renders the structural parameters of lower precision. Within the carbon chains, the distances are consistent with the ≡C−C≡C− arrangement found in **3** and **5**, although the C(5)–C(6) separation may be somewhat shorter [1.172(11) Å]. Similarly, angles at individual carbon atoms are consistent with those expected for Co_3≡C−C [129.9–134.3(5)°], C(sp) [169.1(7)–179.8(7)°] and C(sp²) atoms [117.7(6)–123.7(6)°]. The Au(PPh₃) fragment is attached to C(13) [Au–C(13) 1.997(7) Å, cf. 1.98(1)–2.02(2) Å in **1a**[10], the atoms C(8)–C(11)–C(13)–Au–P(6) forming an approximately linear array [171.5(6)–178.5(2)°]. Similar degrees of non-linearity at the C(sp) and Au atoms were found in **1a** [range 171(1)–179.1(4)°][10].

For **5**, for which the precision of the determination is lower, the central C=C unit [1.32(2) Å] is attached to three C_3Co_3 and one C_2H substituents, the pattern of C–C separations again confirming the −C≡C−C≡ formulation for the former [separations along the chain from C(4) or C(8): cluster A 1.43(2), 1.21(2), 1.37(2); cluster B 1.49(2), 1.20(2), 1.40(2); cluster C 1.49(2), 1.21(2), 1.39(2) Å] and the ethynyl group C(12)–C(13) [1.17(2) Å]. In the ethynyl group, C(8)–C(12) and C(12)–C(13) are 1.44(2) and 1.17(2) Å, respectively.
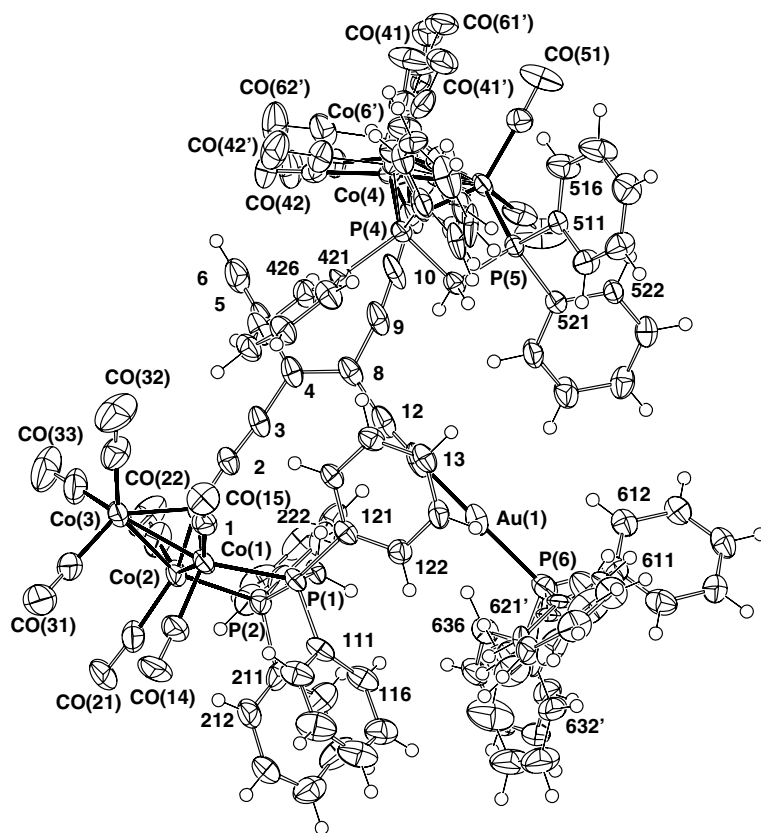
Fig. 2. Plot of a molecule of $\{(OC)_7(\mu\text{-dppm})Co_3\text{-}\mu_3\text{-}CC{\equiv}C\}(HC{\equiv}C)C{=}C\{C{\equiv}CAu(PPh_3)\}\{C{\equiv}C\text{-}\mu_3\text{-}CCo_3(\mu\text{-dppm})(CO)_7\}$ (**4**), showing atom numbering scheme.

In summary, this work has again demonstrated the utility of phosphine-gold(I) derivatives of alkynes in the synthesis of complexes containing transition metal fragments attached to carbon-rich (in this case, all-carbon) ligands. The use of mild solvents in the absence of other bases reduces the degradation of the tricobalt clusters found to occur under usual Sonogashira conditions. In the reaction of the parent $Co_3(CO)_9$ cluster, only one major product is formed, in which all four $Au(PPh_3)$ groups present in **1b** have been replaced by $CCo_3(CO)_9$ clusters. With the more sterically encumbered $Co_3(\mu\text{-dppm})(CO)_7$ cluster, products containing two or three tricobalt clusters were formed. Complexes **4** and **6** have retained one $C{\equiv}CAu(PPh_3)$ group, but in **4** and **5** another $Au(PPh_3)$ group has been replaced by H. Compounds **4**–**6** are all examples of complexes containing large, branched chain all-carbon ligands (C_{12}–C_{14}) bearing between two and four Co_3 clusters which, in the limit, may act as sources of novel materials.

3. Experimental

3.1. 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 (20×20 cm^2) coated with silica gel (Merck, 0.5 mm thick).

3.2. Instruments

IR spectra were obtained on a Bruker IFS28 FT-IR spectrometer. Nujol mull spectra were obtained from samples mounted between NaCl discs. NMR spectra were recorded on a Varian 2000 instrument (^{1}H at 300.13 MHz, ^{31}P at 121.503 MHz). Samples were dissolved in CDCl$_3$ contained in 5 mm sample tubes. Chemical shifts are given in ppm relative to internal tetramethylsilane for ^{1}H spectra and external H_3PO_4 for ^{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 [16]. Elemental analyses were by and CMAS, Belmont, Vic., Australia.

3.3. Reagents

The complexes $Co_3(\mu_3\text{-CBr})(CO)_9$ [15], $Co_3(\mu_3\text{-CBr})(\mu\text{-dppm})(CO)_7$ [15] and $AuCl(PPh_3)$ [17] were prepared as described in the literature.
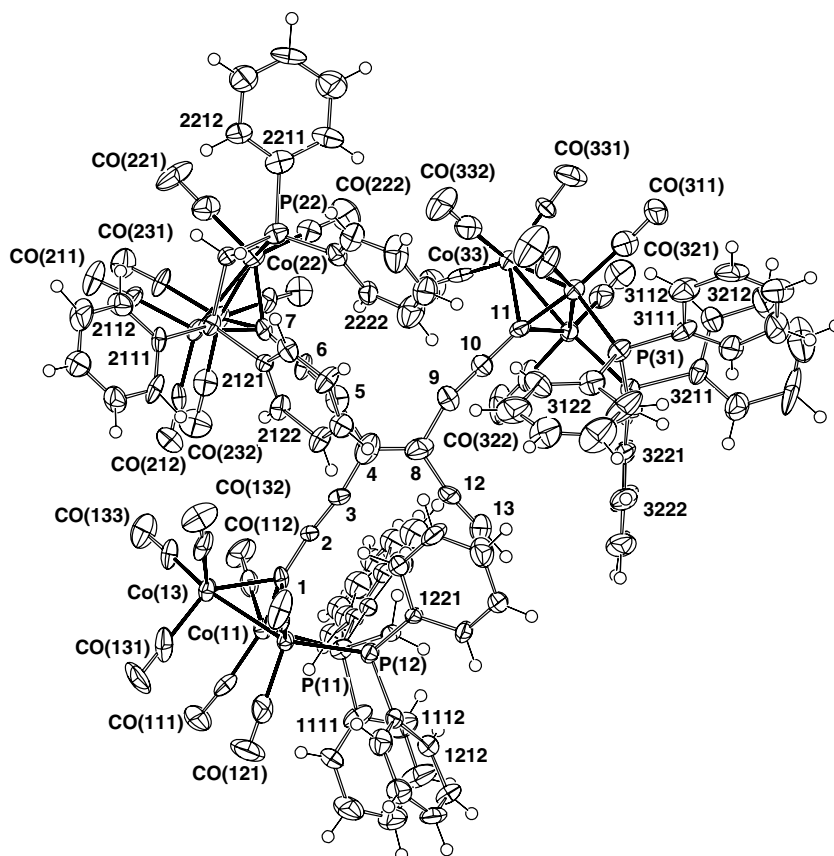
Fig. 3. Plot of a molecule of $\{(OC)_7(\mu\text{-dppm})Co_3\text{-}\mu_3\text{-}CC\equiv C\}_2C=C(C\equiv CH)\{C\equiv C\text{-}\mu_3\text{-}CCo_3(\mu\text{-dppm})(CO)_7\}_2$ (**5**), showing atom numbering scheme.

3.4. Preparation of $\{(Ph_3P)AuCC\}_2C=C\{CCAu(PPh_3)\}_2$ (**1b**)

A solution of NaOMe [from Na (45 mg) in MeOH (3 ml)] was added to a stirred mixture of $(Me_3SiC\equiv C)_2$-$C=C(C\equiv CSiMe_3)_2$ (100 mg, 0.24 mmol) and AuCl(PPh$_3$) (480 mg, 0.97 mmol) in a mixture of THF (25 ml) and MeOH (10 ml) cooled in an ice bath. A yellow precipitate gradually separated. After 30 min at 0 °C, the mixture was warmed to r.t. and stirred for 4 h. The resulting light yellow precipitate was filtered off, washed with cold MeOH and hexane, and dried to give $\{(Ph_3P)AuC\equiv C\}_2C=C$-$\{C\equiv CAu(PPh_3)\}_2$ (**1b**) (385 mg, 81%). Anal. Found: C, 50.28; H, 2.93. Calcd ($C_{82}H_{60}Au_4P_4$): C, 50.31; H, 3.07; *M*, 1956. ^{1}H NMR: δ 7.08–7.62 (m, Ph). ^{31}P NMR: δ 42.8 (s, PPh$_3$).

3.5. Reactions of $\{(Ph_3P)AuCC\}_2C=C\{CCAu(PPh_3)\}_2$ (**1b**)

3.5.1. With $Co_3(\mu_3\text{-}CBr)(CO)_9$

A mixture of $\{(Ph_3P)AuC\equiv C\}_2C=C\{C\equiv CAu(PPh_3)\}_2$ (**1b**) (50 mg, 0.025 mmol) and $Co_3(\mu_3\text{-}CBr)(CO)_9$ (53 mg, 0.1 mmol) in THF (50 ml) was stirred at r.t. for 1 h to dissolve the gold complex. Then Pd(PPh$_3$)$_4$ (11.5 mg, 0.01 mmol) and CuI (2 mg, 0.01 mmol) were added and stirring was continued for 4 h. Removal of THF and pre-

parative t.l.c. (CH$_2$Cl$_2$–hexane 1/2) of a CH$_2$Cl$_2$ extract of the residue afforded two fractions. The top orange band (R_f 0.78) afforded red crystals of $\{Co_3(CO)_9\}_2(\mu_3\text{:}\mu_3\text{-}CC\equiv CC)$ (1.6 mg, <1%), identified by a single-crystal X-ray structural determination [11]. The major product was contained in a dark blue band (R_f 0.69) which afforded very dark red crystals of $\{(OC)_9Co_3\text{-}\mu_3\text{-}CC\equiv C\}_2C=C\{C\equiv C\text{-}\mu_3\text{-}CCo_3(CO)_9\}_2$ (**3**) (30 mg, 62%) from CHCl$_3$. Anal. Found: C, 31.92; H, 0.00. Calcd ($C_{50}Co_{12}O_{36}$): C, 31.88; H, 0.00; *M*, 1884. IR (cm^{-1}): ν(C≡C) 2142vw; ν(CO) 2099 m, 2067vs, 2062 (sh), 2039s. ES MS (positive ion, CH$_2$Cl$_2$/MeOH, *m/z*): 1884, M$^+$.

3.5.2. With $Co_3(\mu_3\text{-}CBr)(\mu\text{-}dppm)(CO)_7$

Pd(PPh$_3$)$_4$ (11.5 mg, 0.01 mmol) and CuI (2 mg, 0.01 mmol) were added to a mixture of $\{(Ph_3P)AuC\equiv C\}_2$-$C=C\{C\equiv CAu(PPh_3)\}_2$ (**1b**) (50 mg, 0.025 mmol) and $Co_3(\mu_3\text{-}CBr)(\mu\text{-}dppm)(CO)_7$ (86.6 mg, 0.1 mmol) in THF (20 ml) and the mixture was left stirring at r.t. overnight. The filtered solution was evaporated and the residue was taken up in CH$_2$Cl$_2$. Preparative t.l.c. (acetone–hexane 3/7) of the extract gave several fractions. A magenta band (R_f 0.41) contained $\{(OC)_7(\mu\text{-}dppm)Co_3\text{-}\mu_3\text{-}CC\equiv C\}$-$(HC\equiv C)C=C\{C\equiv CAu(PPh_3)\}\{C\equiv C\text{-}\mu_3\text{-}CCo_3(\mu\text{-}dppm)\text{-}(CO)_7\}$ (**4**) obtained as needles (4 mg, 7%) from CH$_2$Cl$_2$/MeCN. Anal. Found: C, 53.30; H, 2.91. Calcd ($C_{94}H_{60}Au\text{-}Co_6O_{14}P_5$): C, 53.28; H, 2.85; *M*, 2119. IR (cm^{-1}): ν(C≡C)

Table 1
Selected bond distances (Å) and angles (°) in **3**, **4** and **5**

Bond	3	4	5
Distances (Å)			
C(1)–C(2)	1.401(6)	1.393(8)	1.37(2)
C(2)–C(3)	1.210(6)	1.216(8)	1.21(2)
C(3)–C(4)	1.471(10)	1.414(8)	1.43(2)
C(4)–C(n) [C(n)]	1.367(12) [4]	1.383(8) [8]	1.32(2) [8]
C(4)–C(5)	1.494(10)	1.444(10)	1.49(2)
C(5)–C(6)	1.210(6)	1.172(11)	1.20(2)
C(6)–C(7)	1.390(6)		1.40(2)
C(8)–C(9)		1.418(9)	1.49(2)
C(9)–C(10)		1.204(10)	1.21(2)
C(10)–C(11)		1.394(10)	1.39(2)
C(8)–C(12)		1.427(10)	1.44(2)
C(12)–C(13)		1.208(11)	1.17(2)
Angles (°)			
C(1)–C(2)–C(3)	175.7(5)	174.8(6)	172.9(12)
C(2)–C(3)–C(4)	156.4(6)	171.7(6)	171.1(12)
C(2)–C(3)–C(4′)	164.9(5)		
C(3)–C(4)–C(4′)	115.8(7)		
C(3)–C(4)–C(5)	129.4(6)	117.0(5)	118.4(13)
C(3)–C(4)–C(8)		123.7(6)	120.4(13)
C(n)–C(4)–C(5) [n]	114.8(7) [4]	119.1(5) [8]	121.1(15) [8]
C(4)–C(5)–C(6)	161.6(5)	179.8(7)	165.0(15)
C(5)–C(6)–C(7)	176.1(5)		179.1(14)
C(4)–C(8)–C(9)		117.7(6)	120.4(13)
C(4)–C(8)–C(12)		122.9(5)	122.8(14)
C(8)–C(9)–C(10)		169.1(7)	163.9(14)
C(9)–C(10)–C(11)		175.9(7)	171.5(13)
C(8)–C(12)–C(13)		171.5(6)	170.4(15)

Italicised atoms (in **3** only) are inversion related.
Other data: for **3**: C(3)–C(4′) 1,469(9), C(4′)–C(4′) 1.384(11), C(5)–C(4′) 1.469(9) Å; C(3)–C(4′)–C(4′) 115.3(6), C(3)–C(4′)–C(5) 127.6(6) C(4′)–C(4′)–C(5) 117.1(6)°. For **4**: Au–P(6) 2.276(2), Au–C(13) 1.997(7) Å; C(9)–C(8)–C(12) 119.1(5), C(8)–C(9)–C(10) 169.1(7), C(9)–C(10)–C(11) 175.9(10), C(12)–C(13)–Au 175.4(5), C(13)–Au–P(6) 178.5(2)°.

2179vw, 2148vw, 2115vw; $v(CO)$ 2086 (sh), 2056s, 2009vs, 1990 (sh), 1970 (sh). [1H] NMR: δ 3.05 [s (br), 1H, ≡CH], 3.39, 4.69 (2 × m, 2 × 2H, dppm), 7.11–7.68 (m, 55H, Ph). [31P] NMR: δ 34.4 [s(br), 4P, dppm], 43.0 (s, 1P, PPh$_3$). ES MS (positive ion, MeOH/NaOMe, m/z): 2142, $[M + Na]^+$; (negative ion, MeOH/NaOMe, m/z): 2119, M^-. The second band (blue, R_f 0.39) afforded {(OC)$_7$(μ-dppm)Co$_3$-μ$_3$-CC≡C}$_2$C=C(C≡CH){C≡C-μ$_3$-CCo$_3$(μ-dppm)(CO)$_7$} (**5**) as dark purple-blue crystals (9.9 mg, 16%; from CHCl$_3$/MeOH). Anal. Found: C, 53.87; H, 2.76. Calcd (C$_{109}$H$_{67}$Co$_9$O$_{21}$P$_6$): C, 53.90; H, 2.78; M, 2428. IR (cm^{-1}): $v(C≡C)$ 2191vw, 2115vw; $v(CO)$ 2103vw, 2065 (sh), 2055 m, 2019 (sh), 2008vs, 1992 (sh), 1969w (br). [1H] NMR: δ 3.28 [s (br), 1H, ≡CH], 3.61, 4.44 (2 × m, 2 × 3H, dppm), 6.98-7.78 (m, 60H, Ph). [31P] NMR: δ 34.0 [s(br), dppm]. ES MS (positive ion, MeOH/NaOMe, m/z): 2451, $[M + Na]^+$; (negative ion, MeOH/NaOMe, m/z): 2427, $[M - H]^-$. Band 3 (green, R_f 0.31) contained Co$_3$(μ$_3$-CCO$_2$H)(μ-dppm)(CO)$_7$ (11.8 mg, 00%), identified by comparison with an authentic sample [12]. The blue band (R_f 0.22) afforded small very dark coloured crystals of {(OC)$_7$(μ-dppm)Co$_3$-μ$_3$-CC≡C}$_2$C=C{C≡CAu(PPh$_3$)}-

{C≡C-μ$_3$-CCo$_3$(μ-dppm)(CO)$_7$} (**6**) (18.8 mg, 25%). Anal. Found: C, 52.91; H, 2.61. Calcd (C$_{127}$H$_{81}$AuCo$_9$O$_{21}$P$_7$): C, 52.84; H, 2.80; M, 2886. IR (cm^{-1}): $v(C≡C)$ 2147vw, 2117vw; $v(CO)$ 2103vw, 2065 s, 2059 (sh), 2019 (sh), 2002vs, 1988 (sh), 1966m (br). [1H] NMR: δ 3.75, 4.47 (2 × m, 2 × 3H, dppm), 6.69–7.89 (m, 75H, Ph). [31P] NMR: δ 35.0 [s(br), 8P, dppm], 42.75 (s, 1P, PPh$_3$). ES MS (positive ion, MeOH/NaOMe, m/z): 2909, $[M + Na]^+$; 2887, $[M + H]^+$; 2855, $[M + H - CO]^+$; 2831, $[M + H - 2CO]^+$.

4. Structure determinations

Full spheres of X-ray diffraction data were measured at *ca* 153 K using a Bruker AXS CCD area-detector instrument. N_{tot} reflections were merged to N unique (R_{int} cited) after "empirical"/multiscan absorption correction (proprietary software), N_o with $F > 4\sigma(F)$ being used in the full matrix least squares refinements on F^2. All data were measured using monochromatic Mo Kα radiation, $\lambda = 0.71073$ Å. Anisotropic displacement parameter forms were refined for the non-hydrogen atoms, $(x, y, z, U_{iso})_H$ being constrained at estimates. Conventional residuals R, R_w on F^2 are quoted [weights: $(\sigma^2(F)^2 + n_w F^2)^{-1}$]. Neutral atom complex scattering factors were used; computation used the XTAL 3.7 program system [18]. 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 Table 1.

(**3**) {(OC)$_9$Co$_3$-μ$_3$-CC≡C}$_2$C=C{C≡C-μ$_3$-CCo$_3$(CO)$_9$}$_2$ ≡C$_{50}$Co$_{12}$O$_{36}$, MW = 1883.71. Monoclinic, space group $P2_1/c$, $a = 9.143(2)$ Å, $b = 13.121(3)$ Å, $c = 26.343(6)$ Å, $\beta = 93.053(5)°$, $V = 3156$ Å^3, $Z = 2$. $2\theta_{max} = 58°$. $D_c = 1.982$ g cm^{-3}, $\mu = 3.2$ mm^{-1}, $T_{min/max} = 0.78$. Crystal $0.21 \times 0.20 \times 0.10$ mm. $N_{tot} = 29559$, $N = 7678$ ($R_{int} = 0.044$), $N_o = 5941$, $R = 0.041$, $R_w = 0.089$.

The core of the molecule was modelled as rotationally disordered over two sets of sites 90° apart, i.e., the whole molecule may be regarded as rotationally disordered, site occupancies of the core carbons being set at 0.5 after trial refinement. Refinement was on $|F|$, weights being $(\sigma^2(F) + 0.005F^2)^{-1}$.

(**4**) {(OC)$_7$(μ-dppm)Co$_3$-μ$_3$-CC≡C}(HC≡C)C=C{C≡CAu(PPh$_3$)}{C≡C-μ$_3$-CCo$_3$(μ-dppm)(CO)$_7$}≡C$_{94}$H$_{60}$Au-Co$_6$O$_{14}$P$_5$, MW = 2118.93. Monoclinic, space group $P2_1/c$, $a = 12.664(2)$ Å, $b = 32.908(4)$ Å, $c = 20.927(3)$ Å, $\beta = 93.079(2)°$, $V = 8709$ Å^3, $Z = 4$. $2\theta_{max} = 55°$. $D_c = 1.616$ g cm^{-3}, $\mu = 2.95$ mm^{-1}, $T_{min/max} = 0.70$. Crystal $0.58 \times 0.14 \times 0.10$ mm. $N_{tot} = 106724$, $N = 19995$ ($R_{int} = 0.060$), $N_o = 12919$, $R = 0.044$, $R_w = 0.089$, $n_w = 6.5$.

Two of the Co atoms of one of the Co$_3$ triangles with pendant CO groups and a nearby phenyl group on the associated dppm, together with a phenyl group of the PPh$_3$, were modelled as disordered over pairs of sites, occupancies set at 0.5 after trial refinement. Disordered Co···Co′ separations are 0.609(2), 0.725(2) Å.

(5) $\{(OC)_7(\mu\text{-dppm})Co_3\text{-}\mu_3\text{-CC}{\equiv}C\}_2C{=}C(C{\equiv}CH)\text{-}\{C{\equiv}C\text{-}\mu_3\text{-CCo}_3(\mu\text{-dppm})(CO)_7\}_2 \cdot 0.6CHCl_3 \equiv C_{109}H_{67}\text{-}Co_9O_{21}P_6 \cdot 0.6CHCl_3$, MW = 2500.77. Monoclinic, space group $P2_1/c$, $a = 18.831(4)$ Å, $b = 25.350(6)$ Å, $c = 23.011(5)$ Å, $\beta = 99.456(4)°$, $V = 10835$ Å^3, $Z = 4$. $2\theta_{max} = 50$. $D_c = 1.533$ g cm^{-3}, $\mu = 1.54$ mm^{-1}, $T_{min/max} = 0.75$. Crystal $0.18 \times 0.14 \times 0.07$ mm. $N_{tot} = 80692$, $N = 18627$ ($R_{int} = 0.027$), $N_o = 10577$, $R = 0.087$, $R_w = 0.106$, $n_w = 2.2$.

One of the phenyl rings of the ligand was modelled as disordered over two sets of sites, occupancies set at 0.5 after trial refinement. Solvent residues were modelled in terms of chloroform, occupancy refining to 0.618(7).

Acknowledgements

Appendix A. Supplementary material

Full details of the structure determinations (except structure factors) have been deposited with the Cambridge Crystallographic Data Centre as CCDC 299112–299114. 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. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2006.06.037.

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