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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, $Co_3(\mu_3\text{-}C_nR)(\mu\text{-dppm})(CO)_7$ [R = Bu$^t$, Ph, $C_6H_4I$, $C_6H_4C\equiv CH$, $SiMe_3$, Fc, Au(PPh$_3$)] containing three, five or seven carbons in the chain, has been prepared by elimination of phosphine-gold(I) halides in reactions between $Co_3(\mu_3\text{-CBr})(\mu\text{-dppm})(CO)_7$ and $Au(C\equiv CR)(PPh_3)$ or between $Co_3\{\mu_3\text{-}CC\equiv CAu(PR_3)\}(\mu\text{-dppm})(CO)_7$ (R = Ph, tol) and $IC\equiv CR'$ (R' = SiMe$_3$, Fc). The use of poly-substituted arenes or ferrocenes has enabled preparation of the complexes 1,4-$C_6H_3\{C\equiv C\text{-}\mu_3\text{-}C[Co_3(\mu\text{-dppm})(CO)_7]\}_2X$-5 (X = H, Br), 1,3,5- $C_6H_3\{C\equiv C\text{-}\mu_3\text{-}C[Co_3(\mu\text{-dppm})(CO)_7]\}_3$ and 1,1'-Fc'$\{\{C\equiv C\text{-}\mu_3\text{-}C[Co_3(\mu\text{-dppm})(CO)_7]\}_2$ (Fc' = Fe($\eta$-C$_5$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.[1] Synthetic methods have used synthons derived from alkynes or poly-ynes, in which the substituent-free carbon chains are already present. As a result, the majority of known compounds have even-numbered carbon chains.[2]

The formation of odd-numbered chains is dependent on methods which have an odd-numbered carbon precursor, either being converted to a $C_n$ chain by subsequent reactions, or as a component in an appropriate coupling reaction. Notable examples include $[\{Tp^*(OC)_2M\}=C=C=C=\{M(CO)_2Tp^*\}]^{2+}$ and $\{Tp^*(OC)_2M\}\equiv CC\equiv C\{M'(O)_2Tp^*\}$ (M, M' = Mo, W),[5] $[\{Cp'(OC)_2Mn\}CCC\{Re(NO)(PPh_3)Cp^*\}]^+$[6] and $\{(Bu^tO)_3W\}\equiv CC\equiv C\{Re(NO)(PPh_3)Cp^*\}$.[7] We and others have considered an approach to this type of complex using a precursor in which a carbyne ligand, $\equiv CR$, is attached to a metal centre. Recent examples have used the Group 6 complexes $M(\equiv CR)(CO)_2Tp'$ (R = halogen, $SiMe_3$; M = Mo, W; Tp' = $BH(pz)_3$ (Tp), $BH(dmpz)_3$ (Tp*)][8] or cluster-bonded halocarbynes, such as $M_3(\mu\text{-}CR)(CO)_9$ [$M_3 = Ru_3(\mu\text{-}H)_3$,[9] $Os_3(\mu\text{-}H)_3$,[9] $Co_3$[10]].

The $CCo_3$ trigonal cluster has been known since the late1950s[11] and its extensive chemistry has been reviewed on several occasions.[12-17] Attachment to unsaturated groups such as alkynes and diynes was first described in 1970.[18-20] Common routes to the formation of the carbyne-C(sp) bond include the Cadiot-Chodkiewicz and Sonogashira and related reactions.[19] In some instances, appropriate Grignard or Lewis-acid (AlCl_3)-induced coupling reactions between alkynes and $Co_3(\mu\text{-}CBr)(CO)_9$ have been employed.[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.[19]

Some time ago, we described a modification of this reaction whereby reactions of $Co_3(\mu_3\text{-}CBr)(\mu\text{-}dppm)(CO)_7$ (**1**), chosen because the presence of the edge-bridging diphosphine

ligand prevents break-up of the CCo$_3$ cluster, with phosphine-gold(I) alkynyls resulted in elimination of AuBr(PR$_3$) 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 Co$_3$ cluster and a second metal-containing group,[10] we have also extended these reactions to the synthesis of a range of Co$_3$ clusters containing more conventional groups as described below.

**Results and Discussion**

Reactions of Co$_3$($\mu_3$-CBr)($\mu$-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)(PPh$_3$), or occasionally the P(tol)$_3$ analogue to improve solubility, which has allowed the complexes Co$_3$($\mu_3$-CC≡CR)($\mu$-dppm)(CO)$_7$ to be obtained [R = Bu$^t$ (**2**, 47%), Ph (**3**, 91%), SiMe$_3$ (**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 $\nu$(C≡C) bands at ca 2130 cm$^{-1}$ and medium to strong $\nu$(CO) absorptions between 2061 and 1966 cm$^{-1}$. In addition to common signals at $\delta$ 3.44 and 4.49 and between $\delta$ 6.5 and 8.0 arising from the dppm ligand, the $^1$H NMR spectrum contain other resonances characteristic of the R groups present. Limited solubility restricted the availability of $^{13}$C NMR spectra, but in **2**, signals at $\delta$ 101.14 and 121.95 can be assigned to two carbons of the C$_3$ moiety. That of the carbyne carbon, attached to three cobalt atoms, is broadened by interaction with the $^{59}$Co quadrupole and is not resolved in all spectra.[23,24] The $^{31}$P NMR spectra contain a single resonance at $\delta$ 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 $sp^2$)-I bonds. Thus, the reaction between $Co_3\{\mu_3\text{-CC}\equiv CAu(PPh_3)\}(\mu\text{-dppm})(CO)_7$ (**6**), itself prepared from the $SiMe_3$ derivative **4** and $AuCl(PPh_3)$ in the presence of sodium methoxide, and $1,4\text{-}I_2C_6H_4$ afforded two complexes which were characterised as $Co_3(\mu_3\text{-CC}\equiv CC_6H_4I\text{-}4)(\mu\text{-dppm})(CO)_7$ (**7**) which is green, and orange-brown $\{Co_3(\mu\text{-dppm})(CO)_7\}_2(\mu_3\text{:}\mu_3\text{-CC}\equiv CC_6H_4C\equiv CC)$ (**8**). Similarly, the reaction between $Au(C\equiv CC_6H_4C\equiv CPh)(PPh_3)$ and **1** afforded $Co_3(\mu_3\text{-}CC\equiv CC_6H_4C\equiv CPh)(\mu\text{-dppm})(CO)_7$ (**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 $1,3,5\text{-}\{(Ph_3)AuC\equiv C\}_3C_6H_3$ enabled preparation of the tris-cluster complex $1,3,5\text{-}\{(OC)_7(\mu\text{-dppm})Co_3(\mu_3\text{-CC}\equiv C)\}_3C_6H_3$ (**10**) in 50% yield. This compound has a similar n(CO) spectrum to the complexes described above, while the $^{13}C$ NMR spectrum contains resonances at δ 108.92 and 112.78 from two of the $C_3$ 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 $1,3\text{-}\{(OC)_7(\mu\text{-dppm})Co_3(\mu_3\text{-CC}\equiv C)\}_2C_6H_3Br\text{-}5$ (**11**) from an analogous reaction in which the bromoaryl-diyne $1,3\text{-}\{(Ph_3)AuC\equiv C\}_3C_6H_3Br\text{-}5$ 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 $1,1'\text{-}\{Co_3(\mu\text{-dppm})(CO)_7C\equiv CC\}_2Fc'$ [**12**, $Fc' = Fe(\eta\text{-}C_5H_4\text{-})_2$] in 96% yield from the related reaction between $1,1'\text{-}Fc'\{Au[P(tol)_3]\}_2$ and $Co_3(\mu_3\text{-CBr})(\mu\text{-dppm})(CO)_7$. 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 $C_5H_4$ protons of the ferrocene nucleus, while the ES MS of a solution containing NaOMe contains $[M + Na]^+$ at *m/z* 1793.

Related complexes containing $C_5$ chains, such as $Co_3(\mu_3\text{-CC}{\equiv}CC{\equiv}CR)(\mu\text{-dppm})(CO)_7$ (R = $SiMe_3$, Au(PPh_3), Fc) have been described earlier.[10] Extension to systems containing $C_7$ chains was easily achieved in reactions between $Co_3\{\mu_3\text{-CC}{\equiv}CC{\equiv}CAu(PPh_3)(\mu\text{-dppm})(CO)_7[10]$ and $IC{\equiv}CSiMe_3[25]$ or $IC{\equiv}CFc[26]$ which gave $Co_3\{\mu_3\text{-C(C}{\equiv}C)_3R\}(\mu\text{-dppm})(CO)_7$ [R = $SiMe_3$ (**13**, 54%), Fc (**14**, 87%)] and the further conversion of **13** by treatment with NaOMe and $AuCl(PPh_3)$ gave $Co_3\{\mu_3\text{-C(C}{\equiv}C)_3Au(PPh_3)\}(\mu\text{-dppm})(CO)_7$ (**15**) in 75% yield. The complex $Co_3\{\mu_3\text{-CC}{\equiv}CC{\equiv}CAu(PPh_3)\}(\mu\text{-dppm})(CO)_7$ has been converted to $Co_3(\mu_3\text{-C(C}{\equiv}C)_3Ph\}(\mu\text{-dppm})(CO)_7$ (**16**) in 60% yield by sequential reactions with iodine and $Au(C{\equiv}CPh)(PPh_3)$, without isolation of the presumed intermediate iododiynyl complex $Co_3(\mu_3\text{-CC}{\equiv}CC{\equiv}CI)(\mu\text{-dppm})(CO)_7$.

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 $\nu(C{\equiv}C)$ absorptions are found. In the NMR spectra of **13**, the $SiMe_3$ group gives rise to a singlet at $\delta_H$ 0.26, while for **14**, resonances at $\delta_H$ 4.28, 4.30 and 4.56 and $\delta_C$ 70.35, 69.76 and 72.35 arise from the Cp and $C_5H_4$ 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 $C_7$ 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 $Co_3C$ 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 $Co_3(\mu_3\text{-CC}{\equiv}C\text{-})(\mu\text{-dppm})(CO)_7$ fragment (the molecule of **12** is centrosymmetric), as has been found in several other related

complexes described by us[10,27] and others[28-31] on previous occasions. Atom C(1) is attached to all three metal atoms of the triangular $Co_3$ 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 $Co_3$ 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.[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 $C_7$ 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 $C_n$ chain from the $Co_3$ cluster is evident, while the reverse occurs for the C-C single bonds. The conformations of these two $C_7$ chains can be described as a continuous bend, with total bending at the carbon atoms C(2-7), $\Sigma$, 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.[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$^2$) coated with silica gel (Merck, 0.5 mm thick).

*Instruments*. IR spectra were obtained on a Bruker IFS28 FT-IR spectrometer. Spectra in $CH_2Cl_2$ 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 a Varian 2000 instrument ($^1$H at 300.13 MHz, $^{13}$C at 75.47 MHz, $^{31}$P at 121.503 MHz). Unless otherwise stated, 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 and $^{13}$C NMR spectra and external $H_3PO$ 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.[34] Elemental analyses were by CMAS, Belmont, Vic., Australia.

*Reagents.* $Co_3(\mu_3\text{-}CBr)(\mu\text{-}dppm)(CO)_7$,[27] $AuCl(PR_3)$ (R = Ph; tol made similarly),[35] and $Au(C\equiv CR')(PR_3)$ (R' = Bu$^t$, Ph, SiMe$_3$, Fc) and $\{Au(PR_3)\}_2(\mu\text{-}C\equiv CC_6H_4C\equiv C)$ were obtained as previously described.[36,37]

*Preparation of $Au(C\equiv CC_6H_4C\equiv CPh)(PPh_3)$*

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 $HC\equiv CC_6H_4C\equiv CPh$ (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 $Au(C\equiv CC_6H_4C\equiv CPh)(PPh_3)$ (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 ($CH_2Cl_2$): $\nu(C\equiv C)$ 2114 w cm$^{-1}$. $^1$H NMR: $\delta$ 7.27-7.60 (m, 24H, Ph + $C_6H_4$). $^{31}$P NMR: $\delta$ 42.58s. ES-MS: (positive ion, MeOH + NaOMe, *m/z*): 683, [M + Na]$^+$.

*Preparation of $1,3,5\text{-}\{(Ph_3P)AuC\equiv C\}_3C_6H_3$*

A modified literature method[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 $1,3,5\text{-}(Me_3SiC\equiv C)_3C_6H_3$ (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 $1,3,5\text{-}\{(Ph_3P)AuC\equiv C\}_3C_6H_3$ (181 mg, 87%) as a pale yellow solid. $^1$H NMR: $\delta$ 7.47-7.59 (m, Ph). $^{13}$C NMR: $\delta$ 103.62 (C$\equiv$C), 124.35 (s, $C_{ipso}$ of $C_6H_3$), 18.89-131.44 (m, Ph), 134.20, 134.36 ($C_6H_3$). $^{31}$P NMR: $\delta$ 49.33 (s, PPh$_3$).

*Preparation of carbon-tricobalt complexes*

*$Co_3\{\mu_3\text{-}C(C\equiv C)_nR\}(\mu\text{-}dppm)(CO)_7$, n = 1*

(i)　　R = Bu$^t$ (**2**)

A mixture of Au(C≡CBu$^t$) (64 mg, 0.12 mmol), Co$_3$(μ$_3$-CBr)(μ-dppm)(CO)$_7$ (100 mg, 0.12 mmol), Pd(PPh$_3$)$_4$ (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 CH$_2$Cl$_2$ and separated by preparative t.l.c. (hexane-acetone 5/1). The major brown band ($R_f$ 0.41) contaned Co$_3$(μ$_3$-CC≡CBu$^t$)(μ-dppm)(CO)$_7$ (**2**) (47 mg, 47%) which was isolated as dark brown crystals (CH$_2$Cl$_2$/MeOH). Anal. Found: C, 55.09; H, 3.42. Calcd (C$_{39}$H$_{31}$Co$_3$O$_7$P$_2$): C, 55.06; H, 3.65; $M$, 850. IR (CH$_2$Cl$_2$, cm$^{-1}$): ν(C≡C) 2131vw; ν(CO) 2057s, 2007vs, 1987 (sh), 1966 (sh); (cyclohexane): ν(CO) 2061s, 2015vs, 2011vs, 1997m, 1984w, 1976m, 1960w. $^1$H NMR: δ 1.41 (s, 9H, Bu$^t$), 3.49, 4.41 (2 x s, 2 x 1H, dppm), 6.50-8.50 (m, 20H, Ph). $^{13}$C NMR: δ 30.33 (s, Me), 30.80 (s, C$^4$), 39.94 [t, $J$(CP) 21.8 Hz, PCH$_2$], 101.14 (s, C$^3$), 121.95 (s, C$^2$), 128.12-137.49 (m, Ph), 202.43, 209.83, 231.35 (3 x s, br, CO). $^{31}$P NMR: δ 33.8s. ES-MS (MeOH, $m/z$): 850, M$^+$.

(ii)    R = Ph (**3**)

Method A:  A mixture of Au(C≡CPh)(PPh$_3$) (66 mg, 0.12 mmol), Co$_3$(μ$_3$-CBr)(μ-dppm)(CO)$_7$ (100 mg, 0.12 mmol), Pd(PPh$_3$)$_4$ (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 CH$_2$Cl$_2$ and purified by preparative t.l.c. (acetone-hexane 3/7). The major brown-green band ($R_f$ 0.69) contained Co$_3$(μ$_3$-CC≡CPh)(μ-dppm)(CO)$_7$ (**3**) (93.2 mg, 91%) as dark green crystals (CH$_2$Cl$_2$ / MeOH). Anal. Found: C, 54.73; H, 2.75. Calcd (C$_{41}$H$_{27}$Co$_3$O$_7$P$_2$.0.5CH$_2$Cl$_2$): C, 54.57; H, 3.28; $M$, 870. IR (CH$_2$Cl$_2$, cm$^{-1}$): ν(C≡C) 2116vw; ν(CO) 2058s, 2009vs, 1989 (sh), 1969 (sh), 1948 (sh). $^1$H NMR: δ 3.44, 4.49 (2 x s, 2 x 1H, dppm), 5.30 (s, CH$_2$Cl$_2$), 7.14-7.59 (m, 25H, Ph). $^{31}$P 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)(PPh$_3$) was used under the same conditions, **3** was obtained in 55% yield.

(iii)       R = SiMe$_3$ (**4**)

Method A:  Pd(PPh$_3$)$_4$ (6 mg, 0.005 mmol) and CuI (1 mg, 0.005 mmol) were added to a solution of Co$_3$($\mu_3$-CBr)($\mu$-dppm)(CO)$_7$ (84.9 mg, 0.1 mmol) and Au(C≡CSiMe$_3$)(PPh$_3$) (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 silioca gel column using the same solvent mixture as eluent.  A major brown-green fraction was collected and after evaporation gave Co$_3$($\mu_3$-CC≡CSiMe$_3$)($\mu$-dppm)(CO)$_7$ (**4**) (75 mg, 86%) as dark green crystals (hexane).  Anal. Calcd (C$_{38}$H$_{31}$Co$_3$O$_7$P$_2$Si): C, 52.68;  H, 3.61;  *M*, 866.  Found:  C, 52.64;  H, 3.62.  IR (CH$_2$Cl$_2$, cm$^{-1}$):  ν(C≡C) 2138vw;  ν(CO) 2065s, 2048s, 2010vs, 1990 (sh).  $^1$H NMR:  δ 0.32 (s, 9H, SiMe$_3$), 3.49, 4.54 (2 x m, 2 x 1H, CH$_2$), 7.13-7.58 (m, 20H, Ph).  $^{13}$C NMR: δ 0.10 (s, SiMe$_3$), 39.52 [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].  $^{31}$P 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 Co$_3$($\mu_3$-CBr)($\mu$-dppm)(CO)$_7$ (200 mg, 0.24 mmol) and HC≡CSiMe$_3$ (48 mg, 0.5 mmol) in thf (10 ml) was treated with CuI (2 mg, 0.012 mmol) and Pd(PPh$_3$)$_4$ (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 Co$_3$($\mu_3$-CC≡CSiMe$_3$)($\mu$-dppm)(CO)$_7$ (**4**) (157 mg, 75%).  A minor product formed on some occasions was identified as {Co$_3$($\mu$-dppm)(CO)$_7$}$_2$($\mu_3$:$\mu_3$-C$_6$).[10a]

(iv)    R = Fc (**5**)

Thf (10 ml) was added to a solid mixture of Au(C≡CFc)(PPh$_3$) (100 mg, 0.15 mmol), Co$_3$($\mu_3$-CBr)($\mu$-dppm)(CO)$_7$ (127 mg, 0.15 mmol), Pd(PPh$_3$)$_4$ (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 CH$_2$Cl$_2$ and purified by preparative t.l.c. (acetone-hexane 1/4).  One brown band developed (*R*$_f$ 0.43) and contained Co$_3$($\mu_3$-CC≡CFc)($\mu$-dppm)(CO)$_7$ (**5**) (134 mg, 91%) as very dark red crystals (CH$_2$Cl$_2$ / MeOH). Anal.  Found:  C, 55.19;  H, 3.20. Calcd (C$_{45}$H$_{31}$Co$_3$FeO$_7$P$_2$):  C, 55.22;  H, 3.17;  *M*, 978.  IR (CH$_2$Cl$_2$, cm$^{-1}$):  ν(C≡C)

2123vw; ν(CO) 2057s, 2007vs, 1988 (sh), 1965 (sh), 1948 (sh). $^1$H 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, $C_5H_4$), 7.12-7.59 (m, 20H, Ph). $^{13}$C NMR: δ 40.49 [t, $J$(CP) 21.4 Hz, dppm], 69.84 (s, Cp), 69.14, 70.45 (2 x s, $C_a$, $C_b$, $C_5H_4$), 67.99 ($C_{ipso}$, $C_5H_4$), 107.95, 111.77 (2 x s, chain carbons), 128.24-145.06 (m, Ph), 202.44, 212.58, 226.21 [s (br), CO]. $^{31}$P NMR: δ 33.71 (s, dppm). ES-MS (positive ion mode, MeOH, $m/z$): 978, M$^+$; 950, [M – CO]$^+$; (negative ion, MeOH, $m/z$): 977, [M - H]$^+$.

(v)      R = Au(PPh$_3$) (**6**)

A solution containing **4** (100 mg, 0.12 mmol) and AuCl(PPh$_3$) (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 (CH$_2$Cl$_2$ / MeOH) gave Co$_3$\{μ$_3$-CC≡CAu(PPh$_3$)\}(μ-dppm)(CO)$_7$ (**6**) (130 mg, 90%) as dark red crystals. Anal. Found: C, 50.65; H, 3.02. Calcd (C$_{53}$H$_{37}$AuCo$_3$O$_7$P$_3$): C, 50.80; H, 2.95; $M$, 1252. IR (CH$_2$Cl$_2$, cm$^{-1}$): ν(C≡C) 2137vw; ν(CO) 2053s, 2005vs, 1983 (sh), 1961 (sh); (cyclohexane): ν(CO) 2061s, 2015vs, 2011vs, 1997m, 1984w, 1976m, 1960w. $^1$H NMR: δ 3.24, 5.04 (2 x s, 2 x 1H, dppm), 7.15-7.59(m, 35H, Ph). $^{31}$P NMR: δ 32.53 [s (br), dppm], 43.5 [s (br), PPh$_3$]. ES-MS (positive ion, MeOH, $m/z$): 1253, [M + H]$^+$; (MeOH + NaOMe, $m/z$): 1275, [M + Na]$^+$

(vi)      R = C$_6$H$_4$C≡CPh (**9**)

A mixture of Au(C≡CC$_6$H$_4$C≡CPh-4) (90 mg, 0.14 mmol), Co$_3$(μ$_3$-CBr)(μ-dppm)(CO)$_7$ (116 mg, 0.14 mmol), Pd(PPh$_3$)$_4$ (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 CH$_2$Cl$_2$ and separated by preparative t.l.c. (hexane-acetone 10/1). The major brown band ($R_f$ 0.56) contaned Co$_3$(μ$_3$-CC≡CC$_6$H$_4$C≡CPh)(μ-dppm)(CO)$_7$ (**9**) (51 mg, 39%) which was isolated as dark brown crystals (CH$_2$Cl$_2$/MeOH). Anal. Found: C, 60.61; H, 3.17. Calcd (C$_{49}$H$_{31}$Co$_3$O$_7$P$_2$): C, 60.62; H, 3.19; $M$, 970. IR (CH$_2$Cl$_2$, cm$^{-1}$): ν(C≡C) 2115vw, 2100 vw; ν(CO) 2059s, 2011vs, 1993 (sh), 1967 (sh). $^1$H NMR: δ 3.40, 4.43 (2 x s, 2 x 1H, dppm), 7.18-7.52 (m, 29H, Ph + C$_6$H$_4$). $^{13}$C NMR: δ 41.27 [t,

*J*(CP) 22.5 Hz, PCH$_2$], 89.70, 91.10 (2 x s, C≡CC$_6$H$_4$C≡C), 110.37 (s, C$^3$), 114.19 (s, C$^2$),

121.80-135.96 (m, Ph), 202.15, 210.05, 221.73 (3 x s, br, CO).  $^{31}$P NMR: δ 34.3s.  ES-

MS (positive ion, MeOH + NaOMe, *m/z*):  993, [M + Na]$^+$;  (negative ion, MeOH +

NaOMe, *m/z*): 969, [M - H]$^-$.


Preparation of {Co$_3$(μ-dppm)(CO)$_7$}$_2$(μ$_3$:μ$_3$-CC≡CC$_6$H$_4$C≡CC) (**8**)

(a)   A solution containing Co$_3${μ$_3$-CC≡CAu(PPh$_3$)}(μ-dppm)(CO)$_7$ (50 mg, 0.04 mmol),

1,4-I$_2$C$_6$H$_4$ (6.4 mg, 0.02 mmol), Pd(PPh$_3$)$_4$ (5 mg, 0.004 mmol) and CuI (1 mg, 0.006

mmol) in thf (3 ml) was stirred at r.t. for 6 h.  After removal of solvent, the residue was

extracted with CH$_2$Cl$_2$ and separated by preparative t.l.c. (acetone-hexane 3/7) into two

fractions.  Band 1 (*R*$_f$ 0.50, green) contained Co$_3$(μ$_3$-CC≡CC$_6$H$_4$I-4)(μ-dppm)(CO)$_7$ (**7**)

(12.2 mg, 61%), obtained as very dark green crystals (CH$_2$Cl$_2$ / MeOH). Anal.  Found:  C,

49.65;  H, 2.31.  Calcd (C$_{41}$H$_{26}$Co$_3$IO$_7$P$_2$):  C, 49.40;  H, 2.61;  *M*, 996.  IR (CH$_2$Cl$_2$, cm$^{-1}$):

ν(C≡C) 2117vw;  ν(CO) 2060s, 2010vs, 1980 (sh), 1967 (sh), 1949 (sh).  $^1$H NMR:  δ

3.40, 4.37 (2 x s, 2 x 1H, dppm),  7.05-7.69 (m, 24H, Ph + C$_6$H$_4$).  $^{31}$P NMR: δ 34.32 [s

(br), dppm].  ES-MS (positive ion, MeOH + NaOMe, *m/z*):  1019, [M + Na]$^+$;  (negative

ion, MeOH, *m/z*):  995, [M – H]$^-$;  968, [M – H – CO]$^-$. The second orange-brown band

(*R*$_f$ 0.45) contained {Co$_3$(μ-dppm)(CO)$_7$}$_2$(μ$_3$:μ$_3$-CC≡CC$_6$H$_4$C≡CC) (**8**) (3.6 mg, 11%).

Anal.  Calcd (C$_{76}$H$_{48}$Co$_6$O$_{14}$P$_4$):  C, 54.87;  H, 2.89;  *M*, 1662.  Found:  C, 54.92;  H, 2.75.

IR (CH$_2$Cl$_2$, cm$^{-1}$):  2063s, 2016s, 1984m, 1905m.  $^1$H NMR:  δ  3.42, 4.44 (2 x m, 2 x 2H,

CH$_2$), 7.18-7.50 (m, 44H, Ph + C$_6$H$_4$).  $^{31}$P NMR: δ  35.07 (s, dppm).  ES MS (positive

ion, MeOH + NaOMe, *m/z*):  1685, [M + Na]$^+$;  (negative ion, MeOH + NaOMe, *m/z*):

1661, [M - H]$^-$.


(b)  A  mixture  of  1,4-{AuPPh$_3$(C≡C)}$_2$C$_6$H$_4$  (30  mg,  0.03  mmol),  Co$_3$(μ$_3$-CBr)(μ-

dppm)(CO)$_7$ (98 mg, 0.06 mmol), Pd(PPh$_3$)$_4$ (15 mg, 0.013 mmol) and CuI (5 mg, 0.026

mmol) was stirred in 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-{Co$_3$C(C≡C)(μ-dppm)(CO)$_7$}$_2$C$_6$H$_4$ as an orange band (*R*$_f$ 0.68) (20.3

mg, 41%). Anal. Calcd (C$_{76}$H$_{48}$P$_4$Co$_6$O$_{14}$):  C, 54.87;  H, 2.89.  Found:  C, 54.92;  H, 2.75.  IR

(CH$_2$Cl$_2$, cm$^{-1}$):  ν(C≡C) 2114 w, ν(CO) 2059 s, 2010 vs 1993 sh(m), 1969 sh(w).  $^{31}$P

NMR (CDCl$_3$): $\delta$ 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-{(Ph$_3$P)AuC$\equiv$C}$_3$C$_6$H$_3$ with Co$_3$($\mu_3$-CBr)($\mu$-dppm)(CO)$_7$

(a)      A solution of 1,3,5-{(Ph$_3$P)AuC$\equiv$C}$_3$C$_6$H$_3$ (59.7 mg, 0.039 mmol) and Co$_3$($\mu_3$-CBr)($\mu$-dppm)(CO)$_7$ (100 mg, 0.118 mmol) in thf (10 ml) was treated with Pd(PPh$_3$)$_4$ (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 CH$_2$Cl$_2$ extract of the residue was purified by preparative t/l/c/ (acetone-hexane, 3/7).  The major brown band ($R_f$ 0.40) contained 1,3,5-{Co($\mu$-dppm)(CO)$_7$}$_3$C$_6$H$_3$ (**10**) (48.8 mg, 50%), obtained as dark red crystals (CHCl$_3$ / MeOH).  Anal.  Found:  C, 54.80;  H, 2.83.  Calcd (C$_{111}$H$_{69}$Co$_9$O$_{21}$P$_6$):  C, 54.28; H, 2.83;  *M*, 2454.  IR (CH$_2$Cl$_2$, cm$^{-1}$):  $\nu$(CC) 2115w;  $\nu$(CO) 2059s, 2010vs, 1990 (sh), 1969 (sh), 1953 (sh).  $^1$H NMR:  $\delta$  3.46, 4.43 (2 x m, 2 x 3H, CH$_2$), 7.17-7.58 (m, 63H, Ph + C$_6$H$_3$).  $^{13}$C NMR:  $\delta$  40.81 [s (br), CH$_2$], 108.92, 112.76 (2 x s, 2 x C of C$_3$ chain), 126.54-132.17 (m, Ph + C$_6$H$_3$), 202.24 [s (br), CO].  $^{31}$P NMR:  $\delta$  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-{(Ph$_3$P)AuC$\equiv$C}$_3$C$_6$H$_3$ containing a significant amount of 1,3-{(Ph$_3$P)AuC$\equiv$C}$_2$C$_6$H$_3$Br-5, a similar reaction with Co$_3$($\mu_3$-CBr)($\mu$-dppm)(CO)$_7$ (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 ($R_f$ 0.47) which contained 1,3-{Co($\mu$-dppm)(CO)$_7$}$_2$C$_6$H$_3$Br-5 (**11**) (10.8 mg), obtained as brown-red crystals (CH$_2$Cl$_2$ / MeOH). Anal.  Found:  C, 52.34;  H, 2.61.  Calcd (C$_{76}$H$_{47}$Co$_6$O$_{14}$P$_4$):  C, 52.38;  H, 2.69;  *M*, 1741. IR (CH$_2$Cl$_2$, cm$^{-1}$):  $\nu$(CC) 2114w;  $\nu$(CO) 2057s, 2009vs, 1988 (sh), 1970 (sh), 1951 (sh). $^1$H NMR:  $\delta$  3.40, 4.41 (2 x m, 2 x 2H, CH$_2$), 6.95-7.51 (m, 43H, Ph + C$_6$H$_3$).  $^{31}$P NMR:  $\delta$ 35.21 [s (br), dppm].  ES MS (positive ion, MeOH + NaOMe, *m/z*):  1764, [M + Na]$^+$; (negative ion, MeOH + NaOMe, *m/z*):  1741, M$^-$.

{Co$_3$($\mu$-dppm)(CO)$_7$}($\mu_3$;$\mu_3$-CC$\equiv$CFc'C$\equiv$CC) (**12**)

A solution containing 1,1'-Fc'{C≡CAu[P(tol)$_3$]}$_2$ (26 mg, 0.02 mmol), Co$_3$($\mu_3$-CBr)($\mu$-dppm)(CO)$_7$ (36 mg, 0.04 mmol), Pd(PPh$_3$)$_4$ (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 CH$_2$Cl$_2$ and purified by preparative t.l.c. (acetone-hexane 3/7) to give one major band ($R_f$ 0.34), from which {Co$_3$($\mu$-dppm)(CO)$_7$}($\mu_3$:$\mu_3$-CC≡CFc'C≡CC) (**12**) (35.7 mg, 96%) was isolated as very dark red crystals (CH$_2$Cl$_2$ / MeOH). Anal. Found: C, 54.26; H, 2.96. Calcd (C$_{80}$H$_{52}$Co$_6$FeO$_{14}$P$_4$): C, 54.23; H, 2.94; $M$, 1770. IR (CH$_2$Cl$_2$, cm$^{-1}$): ν(C≡C) 2122vw; ν(CO) 2057s, 2008vs, 1989 (sh), 1977 (sh), 1964 (sh). $^1$H NMR: δ 3.43, 4.44 (2 x s, 2 x 1H, dppm), 4.40, 4.53 (2 x m, 2 x 4H, C$_5$H$_4$), 7.11-7.52 (m, 40H, Ph). $^{31}$P 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]$^-$.

*Co$_3$\{$\mu_3$-C(C≡C)$_n$R\}($\mu$-dppm)(CO)$_7$, n = 3*

    (i)    R = SiMe$_3$ (**13**)

A mixture of Co$_3$\{$\mu_3$-C(C≡CC≡CAu(PPh$_3$)\}($\mu$-dppm)(CO)$_7$ (280 mg, 0.219 mmol), IC≡CSiMe$_3$ (85 mg, 0.379 mmol), Pd(PPh$_3$)$_4$ (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 CH$_2$Cl$_2$ extract of the residue developed two bands. Band 1 ($R_f$ 0.55, brown) contained Co$_3$\{$\mu_3$-C(C≡C)$_3$SiMe$_3$\}($\mu$-dppm)(CO)$_7$ (**13**) (108 mg, 54%), obtained a brown-black crystals from CH$_2$Cl$_2$ / MeOH. Anal. Found: C, 55.20; H, 3.48. Calcd (C$_{42}$H$_{31}$Co$_3$O$_7$P$_2$Si): C, 55.16; H, 3.42; $M$, 914. IR (CH$_2$Cl$_2$, cm$^{-1}$): ν(C≡C) 2134vw; ν(CO) 2062s, 2018vs, 1974 (sh). $^1$H NMR: δ 0.26 (s, 9H, SiMe$_3$), 3.41, 4.24 (2 x s, 2 x 1H, dppm), 7.20-7.41 (m, 20H, Ph). $^{31}$P NMR: δ 34.64 (s, dppm). ES-MS (positive ion, MeOH + NaOMe, $m/z$): 937, [M + Na]$^+$; 915, [M + H]$^+$; 865, [M + H + Na – SiMe$_3$]$^+$; (negative ion, MeOH + NaOMe, $m/z$): 913, [M – H]$^-$; 841, [M – SiMe$_3$]$^-$; 814, [M + H – CO – SiMe$_3$]$^-$. Band 2 ($R_f$ 0.38, red-brown) contained {Co$_3$($\mu$-dppm)(CO)$_7$}$_2$($\mu_3$:$\mu_3$-C$_{10}$), identified by comparison with an authentic sample.[10a]

    (ii)    R = Fc (**14**)

A mixture of Co$_3$\{$\mu_3$-CC≡CC≡CAu(PPh$_3$)\}$\mu$-dppm)(CO)$_7$} (60 mg, 0.05 mmol), FcC≡CI (15.3 mg, 0.05 mmol), Pd(PPh$_3$)$_4$ (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 FcC≡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)$_3$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)$_7$}$_2$(μ$_3$:μ$_3$-C$_{10}$) (0.6 mg, 1%), identified by comparison with an authentic sample.[10a]

    (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)$_3$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)$_3$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 $Co_3\{\mu_3\text{-}CC\equiv CC\equiv CAu(PPh_3)\}\mu\text{-dppm})(CO)_7\}$ (50 mg, 0.04 mmol) and $Pd(PPh_3)_4$(00 mg, 00 mmol) in thf (5 ml) was added to a mixture of iodine (10 mg, 0.04 mmol) and CuI (00 mg, 00 mmol) in thf (5 ml) at –78°C, and the mixture was stirred for 1 h. After this time, a soluton of $Au(C\equiv CPh)(PPh_3)$ (20 mg, 0.04 mmol) in thf (5 ml) was added dropwise and the mixture was stirred for a further 1 h at –78°C. After allowing to warm to r.t., the filtered soluton was evaporated and the residue was extracted into $CH_2Cl_2$ and purified by preparative t.l.c. (acetone-hexane 3/7). The brown band (Rf 0.76) contained $Co_3\{\mu_3\text{-}C(C\equiv C)_3Ph\}(\mu\text{-dppm})(CO)_7$ (**16**) (21 mg, 60%), obtained as black needles ($CH_2Cl_2$ / MeOH). Anal. Found: C, 58.98; H, 2.87. Calcd ($C_{45}H_{27}Co_3O_7P_2$): C, 58.82; H, 2.94%; M, 918. IR ($CH_2Cl_2$, cm$^{-1}$): $\nu(C\equiv C)$ 2190w, 2171vw; $\nu(CO)$ 2065s, 2040m, 2014m, 1973 (sh), 1955 (sh) cm$^{-1}$. $^1$H NMR: $\delta$ 3.30, 4.15 (2 x m, 2 x 1H, dppm), 7.09-7.47 (m, 25H, Ph). $^{31}$P NMR: $\delta$ 34.63 (s, dppm). ES-MS (positive ion, MeOH + NaOMe, $m/z$): 941, $[M + Na]^+$; (negative ion, MeOH, $m/z$): 918, M$^-$; 917, $[M – H]^-$; 890, $[M – CO]^-$.


*Structure determinations*

Full spheres of 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. All data were measured using monochromatic Mo-$K$a radiation, $\lambda = 0.71073$ Å. Anisotropic displacement parameter forms were refined for the non-hydrogen atoms, $(x, y, z, U_{iso})_h$ being refined. Conventional residuals $R$, $R_w$ on |$F$| are quoted [weights: $(\sigma^2(F) + 0.000n_wF^2)^{-1}$]. Neutral atom complex scattering factors were used; computation used the XTAL 3.7 program system.[39] 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**. $(x, y, z, U_{iso})_H$ 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).

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