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Syntheses and molecular structures of some compounds containing many-atom chains end-capped by tricobalt carbonyl clusters

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ABSTRACT

Several complexes containing Co_3 carbonyl clusters end-capping carbon chains of various lengths are described. Pd(0)/Cu(I)-catalysed reactions between $\{Co_3\{\mu_3\text{-}C(C{\equiv}C)_2Au(PPh_3)\}(\mu\text{-dppm})(CO)_7$ and $I(C{\equiv}C)_2SiMe_3$ or $FcC{\equiv}CI$ gave $\{Co_3\{\mu_3\text{-}C(C{\equiv}C)_xR\}(\mu\text{-dppm})(CO)_7$ [$x = 4$, R = $SiMe_3$ **3**; $x = 3$, R = Fc **8**]; treatment of **3** with NaOMe and $AuCl(PPh_3)$ gave **4** [$x = 4$, R = $Au(PPh_3)$]. Related preparations of $Co_3\{\mu_3\text{-}C(C{\equiv}C)_2[Ru(PP)Cp']\}(\mu\text{-dppm})_n(CO)_{9-2n}$ [PP = $(PPh_3)_2$, Cp' = Cp, $n = 1$, **5**; PP = dppe, Cp' = Cp^*, $n = 1$, **6**; 0, **7**] are also described. Syntheses of bis-cluster complexes $\{Co_3(\mu\text{-dppm})(CO)_7\}_2(\mu\text{-}C_x)$ ($x = 14$, **12**; 16, **9**; 18, **11**; 26, **10**) – the latter being the longest cluster-capped C_x chains so far described – and the mercury-bridged compounds $Hg\{(C{\equiv}C)_xC[Co_3(\mu\text{-dppm})(CO)_7]\}_2$ ($x = 1$, **13**; 2, **14**) are reported. The molecular structures of **7**, **12**, **13** and **14**, as well as of $Co_3(\mu_3\text{-}CC{\equiv}CSiMe_3)(\mu\text{-dppm})(CO)_6(PPh_3)$ (**15**) and $Co_3\{\mu_3\text{-}CC(O)OEt\}(\mu\text{-dppm})(CO)_7$ (**16**), are reported.

1. Introduction

Molecules containing chains of C(sp) atoms are of contemporary interest as models for molecular wires, as well as for their potential as sources of highly unsaturated derivatives [1]. Although the redox properties of complexes containing such chains end-capped by mononuclear and binuclear metal–ligand fragments have received the most attention, an important sub-group consists of those compounds containing the carbon chain capped by metal cluster moieties. Predominant among these is the tricobalt carbonyl cluster by virtue of its tendency to interact in μ_3 mode with the terminal carbon atom. Much of the chemistry of tricobalt–carbon clusters $Co_3(\mu_3\text{-}CR)(CO)_9$ with a large variety of substituents R, which have been known since the 1960s, has been summarised in several reviews [2].

While the majority of complexes in which redox centres are connected by chains of carbon (or other) atoms have eight or fewer atoms in the chain, there is an increasing number of reports describing compounds with longer chains. Thus, Gladysz's pioneering studies of rhenium- and platinum-containing systems has so far culminated in the complexes $\{Re(NO)(PPh_3)Cp^*\}_2(\mu\text{-}C_{20})$ [3] and $\{trans\text{-}Pt(C_6F_5)[P(tol)_3]_2\}_2(\mu\text{-}C_{28})$ [4], elegant synthetic strategies being developed to access the longer chains. Others have described complexes containing C_{12} chains linking $Fe(CO)_2Cp^*$ [5], *trans*-$RuCl(dppe)_2$ [6] and $Ru_2(ap)_4$ (ap = 2-anilinopyridinate) [7] fragments. A variety of other end-groups have been linked via reactions involving a phosphine–gold(I) halide elimination reaction, which has some relation to the well-known Sonogashira reaction. A preliminary report describing the compounds $\{Ru(dppe)Cp^*\}_2(\mu\text{-}C_{14})$ and $\{Co_3(\mu\text{-dppm})(CO)_7\}_2(\mu\text{-}C_{16})$ has been published [8].

In the course of our work on molecules of this type, we have prepared and characterised (including XRD structures) several unusual examples, together with relevant intermediates and side-products. These results are collected in this paper, which describes the complexes $Co_3\{\mu_3\text{-}C(C{\equiv}C)_2[Ru(PP)Cp']\}(\mu\text{-dppm})_n(CO)_{9-2n}$ [$n = 0$, 1, PP = dppe, Cp' = Cp^*; $n = 1$, PP = $(PPh_3)_2$, Cp' = Cp], containing C_5 chains end-capped by different metal centres, and $Co_3\{\mu_3\text{-}C(C{\equiv}C)_3Fc\}(\mu\text{-dppm})(CO)_7$ in which the redox centres are separated by seven carbon atoms. The complexes $\{Co_3(\mu\text{-dppm})(CO)_7\}_2(\mu\text{-}C_x)$ ($x = 14$, 16, 18, 26) contain the longest C_x chains end-capped by Co_3 clusters yet described. We have also utilised coupling of carbon chains through mercury atoms, the well-established linear geometry of the Hg(II) atom providing a facile means of doubling the chain length of the precursors by incorporation of the heteroatom in the centre. The compounds $Hg\{(C{\equiv}C)_xC[Co_3(\mu\text{-dppm})(CO)_7]\}_2$ ($x = 1$, 2) were made in this way. In addition, details of the preparations of the related materials, $Co_3\{\mu_3\text{-}C(C{\equiv}C)_xR\}(\mu\text{-dppm})(CO)_7$ [$x = 2$, 4, R = $SiMe_3$; $x = 4$,

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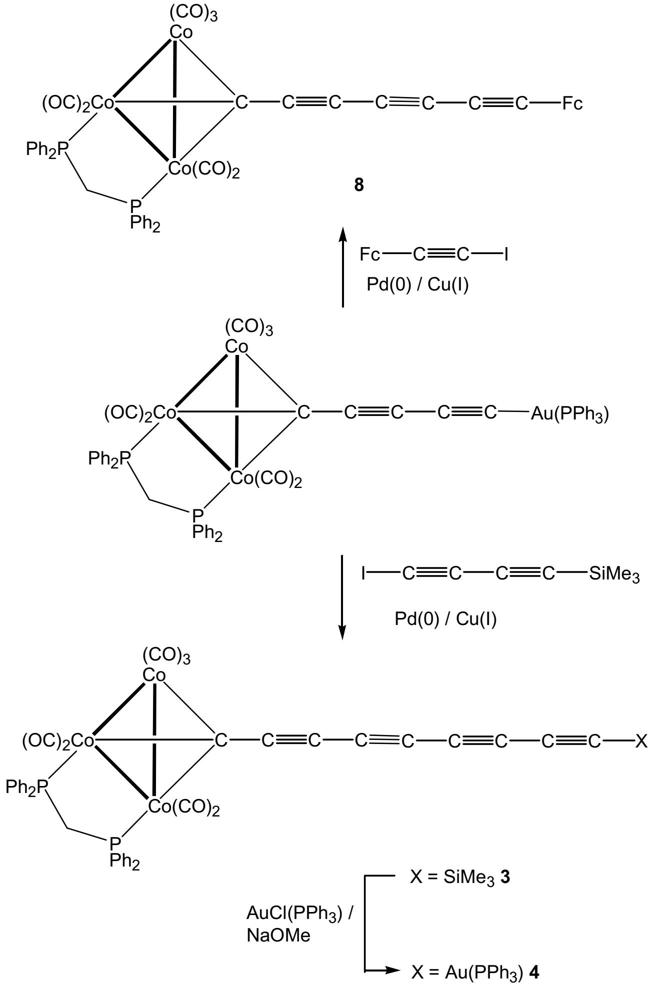
R = Au(PPh$_3$)] and the molecular structures of the by-products Co$_3$(μ_3-CR)(μ-dppm)(CO)$_6$(L) (R = CC≡CSiMe$_3$, L = PPh$_3$; R = CO$_2$Et, L = CO) are given.

2. Results and discussion

We have found that useful precursors for complexes containing extended carbon chains are the monometallic complexes in which the other end of the chain bears a SiMe$_3$ group. Complexes Co$_3${μ_3-C(C≡C)$_x$SiMe$_3$}(μ-dppm)(CO)$_7$ (x = 1, **1**; 2, **2**) have been previously reported, having been obtained by reactions between Co$_3$(μ_3-CBr)(μ-dppm)(CO)$_7$ and Au{(C≡C)$_x$SiMe$_3$}(PR$_3$) (R = Ph or tol) [9]. These are examples of the Pd(0)/Cu(I)-catalysed phosphine–gold(I) elimination reaction between alkynyl-gold(I) complexes and C(sp or sp^2)–X (X = Br, I) groups described earlier as a general base-free route to many transition metal complexes containing alkynyl and poly-ynyl groups [8]. Preparation of the Au(PPh$_3$) precursors is readily achieved by reaction of the corresponding SiMe$_3$ derivatives with AuCl(PPh$_3$) in the presence of NaOMe.

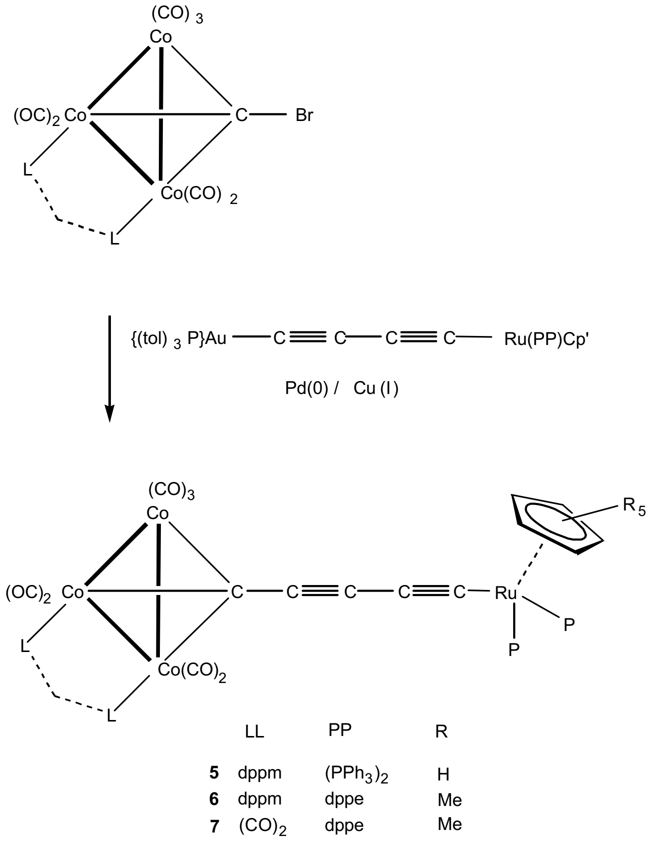
In seeking to extend the carbon chain lengths in these compounds, we have now prepared dark brown-red {Co$_3${μ_3-C(C≡C)$_4$SiMe$_3$}(μ-dppm)(CO)$_7$ (**3**) in 68% yield from the Pd(0)/Cu(I)-catalysed reaction between {Co$_3${μ_3-C(C≡C)$_2$Au(PPh$_3$)}(μ-dppm)(CO)$_7$ [8b] and IC≡CC≡CSiMe$_3$ [10]. Conversion to the Au(PPh$_3$) derivative as described above gave brown {Co$_3${μ_3-C(C≡C)$_4$Au(PPh$_3$)}(μ-dppm)(CO)$_7$ (**4**) in 76% yield (Scheme 1).



Scheme 1.

The complexes were characterised by microanalyses and from their spectroscopic properties, including weak ν(C≡C) bands between 2113 and 2156 cm^{-1} and terminal ν(CO) band patterns between 2067 and 1972 cm^{-1}. In their NMR spectra, the SiMe$_3$ group resonates at δ_H 0.30, δ_C −0.27, with the two dppm CH$_2$ proton multiplets centred at δ_H 3.45, 4.30; the CH$_2$ carbon gives a triplet at δ_C 43.8. In the ^{13}C NMR spectrum of **3** eight singlets between δ_C 63.59 and 98.76 arise from eight of the nine carbon chain nuclei, that attached to the Co$_3$ cluster being broadened past visibility by the ^{59}Co quadrupole [11,12]. Resonances in the ^{31}P NMR spectra at δ_P ca. 34 and 41 are assigned to dppm and PPh$_3$ (if present). The electrospray mass spectra (ES-MS) contain ions [M−SiMe$_3$]$^-$ or M$^+$, respectively.

We have used Pd(0)/Cu(I)-catalysed coupling reactions [8] between Co$_3$(μ_3-CBr)(μ-dppm)(CO)$_7$ and Ru{C≡CC≡CAu[P(tol)$_3$]}(PP)Cp′ to prepare Co$_3${μ_3-C(C≡C)$_2$[Ru(PP)Cp′]}(μ-dppm)(CO)$_7$ [PP = (PPh$_3$)$_2$, Cp′ = Cp **5**; PP = dppe, Cp′ = Cp* **6**] in 77% and 69% yields, respectively (Scheme 2). The related complex Co$_3${μ_3-C(C≡C)$_2$[Ru(dppe)Cp*]}(CO)$_9$ (**7**) was obtained similarly in 40% yield. These compounds formed orange to brown crystals, which were identified by microanalyses and spectroscopy. The IR spectra contain weak ν(C≡C) bands at ca 2107 or 2124 cm^{-1} and terminal ν(CO) bands between 2063 and 1952 cm^{-1} for **5** and **6**, these bands moving to higher energy for **7** [ν(CC) 2124, ν(CO) 2094–1976 cm^{-1}]. In the NMR spectra, resonances for Ru–Cp′ [δ_H 4.45, δ_C 87.18 (Cp in **5**), δ_H 1.59 [1.59], δ_C 10.13, 93.64 [10.38, 94.93] (Cp* in **6** [**7**])], CH$_2$ from dppm and dppe (δ_H 1.92, 2.24, δ_C 29.94) and Ph groups (δ_H 7.03–7.67, δ_C 130.21–138.40) are present. The Co–CO groups give rise to resonances at δ_C ca 201, while three or four carbon chain resonances are found as singlets between δ_C 86.0 and 138.35. As found earlier, the resonance of the carbon at-



Scheme 2.

tached to the Co_3 cluster is not obvious, probably because of broadening by the ^{59}Co quadrupole. The ^{31}P NMR spectra variously contain resonances at δ_P ca. 33.5 (dppm), 49.4 (PPh_3) and 79.45 (dppe). In the ES-MS, either M^+, $[M+Na]^+$ or $[M+OMe]^-$ are present in spectra obtained from solutions in MeOH containing NaOMe.

The deep red C_7 complex $Co_3\{\mu_3\text{-}C(C\equiv C)_3Fc\}(\mu\text{-dppm})(CO)_7$ (**8**) could be obtained from the Pd(0)/Cu(I)-catalysed reaction between FcC$\equiv$CI [13] and $Co_3\{\mu_3\text{-}C(C\equiv C)_2Au(PPh_3)\}(\mu\text{-dppm})(CO)_7$, carried out in thf (Scheme 1). Spectroscopic properties of **8** include weak $\nu(C\equiv C)$ bands at 2168 and 2100 cm^{-1} and terminal ν(CO) absorptions between 2063 and 1958 cm^{-1}. In the NMR spectra, resonances at δ_H 4.28, δ_C 70.35 (FeCp), δ_H 4.30, 4.56, δ_C 69.76, 72.35 [Fe(C_5H_4)], δ_H 3.40, 4.25, δ_C 42.75 (PCH_2) and δ_H 7.15–7.69 (Ph) are accompanied by signals between δ_C 63.38 and 99.03 (C_{ipso} and six of seven carbon chain nuclei). The expected $[M+H]^+$ or $[M-H]^-$ ion clusters are present in the positive and negative ion ES-MS of **8**.

In seeking to prepare long, symmetrical Co_3 cluster-capped carbon chains, we have applied the coupling reactions used so successfully above and elsewhere [8] to Co_3 clusters containing Au(PPh_3)-capped chains and diiodopoly-ynes (Scheme 3). In this way, the Pd(0)/Cu(I)-catalysed reactions between $Co_3\{\mu_3\text{-}C(C\equiv C)_2Au(PPh_3)\}(\mu\text{-dppm})(CO)_7$ and $I(C\equiv C)_3I$ [10,14] afforded dark red $\{Co_3(\mu\text{-dppm})(CO)_7\}_2(\mu\text{-}C_{16})$ (**9**) in 86% yield. This complex was characterised by a single-crystal XRD structure determination (see below), its spectroscopic properties being similar to other complexes containing this Co_3 cluster described above. Only three very weak $\nu(C\equiv C)$ bands, between 2171 and 2127 cm^{-1}, are present in the IR spectrum. In the ^{13}C NMR spectrum, seven singlets between δ_C 64.36 and 99.83 arise from 14 of the C_{16} chain carbons, the CCo_3 nucleus being broadened by the ^{59}Co quadrupole. In the positive ion ES-MS, $[M+Na]^+$ appears at *m/z* 1729, while $[M-H]^-$ (*m/z* 1705) is present in the negative ion spectrum. The latter also contained $[Co_3(C_8)(dppm)-H]^-$ as a strong fragment ion at *m/z* 852.

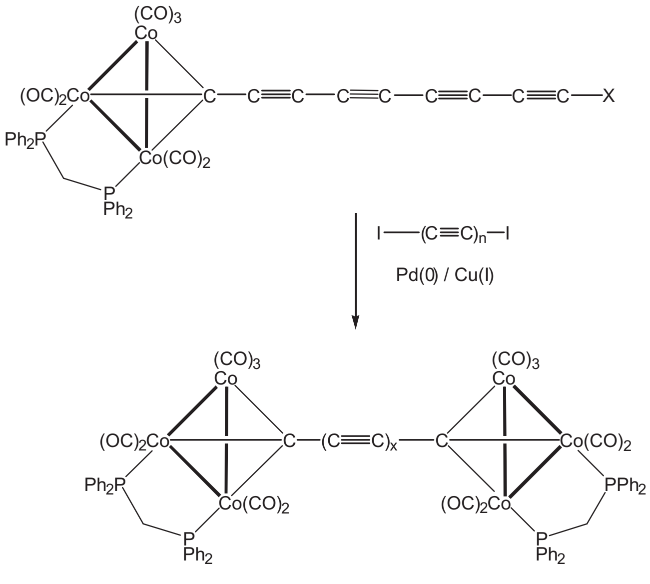
From the analogous reaction between $Co_3\{\mu_3\text{-}C(C\equiv C)_4Au(PPh_3)\}(\mu\text{-dppm})(CO)_7$ (**4**) and $I(C\equiv C)_4I$ [10,14], we obtained two products which were easily separated by preparative tlc. The faster moving was found to be the expected coupling product $\{Co_3(\mu\text{-dppm})(CO)_7\}_2(\mu\text{-}C_{26})$ (**10**), obtained as dark purple crystals, which unfortunately proved to be unsuitable for an XRD structure determination. Characterisation rests upon the ES-MS, which contains $[M+Na]^+$ and $[M+OMe]^-$ at *m/z* 1849 and 1857, respectively. The IR spectrum contains two very weak $\nu(C\equiv C)$ bands at 2168 and 2129 cm^{-1}, while the ^{1}H and ^{31}P NMR spectra show resonances for dppm at δ_H 3.50, 4.24 (CH_2) and 7.31–7.62 (Ph) and δ_P 34.0. Lack of solubility and a tendency to decompose in solution have precluded our obtaining a ^{13}C NMR spectrum.

The second product is dark red $\{Co_3(\mu\text{-dppm})(CO)_7\}_2(\mu\text{-}C_{18})$ (**11**), apparently formed by oxidative coupling of the gold-containing precursor **4**. In this case, microanalytical and ES-MS data ($[M+Na]^+$ and $[M-H]^-$ at *m/z* 1753 and 1729, respectively) support the formulation. The IR spectrum contains two $\nu(C\equiv C)$ and five terminal ν(CO) bands, while the dppm ligand gives resonances at δ_H 3.46, 4.24 (CH_2), 7.27–7.71 (Ph) and δ_P 34.1.

On one occasion, we isolated a small amount of crystalline material from the reaction between **4** and $Ru_3(\mu\text{-}H)_3(\mu_3\text{-}CBr)(CO)_9$ which, on the basis of the low-precision XRD structural determination reported here and an ES-MS (M^+ at *m/z* 1682), was identified as $\{Co_3(\mu\text{-dppm})(CO)_7\}_2(\mu\text{-}C_{14})$ (**12**). However, we did not obtain enough for microanalysis nor for any further characterisation.

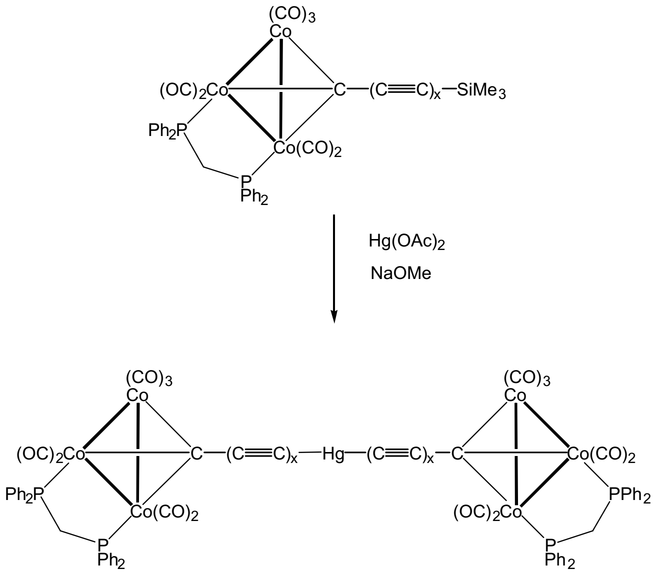
It occurred to us that a further facile route to complexes containing many-atom chains is the coupling reaction between Au^- or Hg and terminal alkynes. We and others have already reported on the reactions of [ppn][Au(acac)$_2$] with $H(C\equiv C)_xR$ to give [ppn][Au$\{(C\equiv C)_xR\}_2$] [15,16], while similar linking of alkynyl groups by attachment to the isoelectronic Hg(II) centre is also well established [17]. In the present study, cobalt clusters containing carbon chains linked through a mercury atom have been made by treatment of 2 equiv. of the $SiMe_3$ derivative with Hg(OAc)$_2$ in the presence of an excess of NaOMe at r.t. Reactions were monitored by spot tlc and were usually complete within 2 h. Work-up by preparative tlc then afforded the pure complexes. In this way, we have prepared $Hg\{(C\equiv C)_xC[Co_3(\mu\text{-dppm})(CO)_7]\}_2$ (*x* = 1, **13**; 2, **14**) in 13 and 74% yields, respectively, from $Co_3\{\mu_3\text{-}C(C\equiv C)_xSiMe_3\}(\mu\text{-dppm})(CO)_7$ (Scheme 4).

The IR spectra of **13** and **14** contain ν(CO) bands between 2060 and 1948 cm^{-1} and weak absorptions assigned to $\nu(C\equiv C)$ between 2135 and 2112 cm^{-1}. Not surprisingly, the ^{1}H NMR spectra are similar for both complexes: the dppm ligand gives multiplet reso-



9 x = 8 (n = 3); **10** x = 13 (n = 4); **11** x = 9; **12** x = 7

Scheme 3.



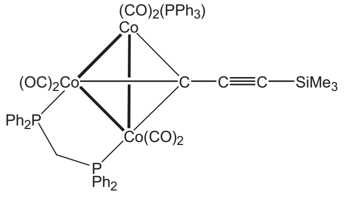
x = 1 **13**; 2 **14**

Scheme 4.

nances between δ 3.66 and 4.60, while the Ph protons give multiplets between δ 7.18 and 7.56. Broad resonances for the dppm ligands are found at δ_P 34.6 and 35.0 in the ^{31}P NMR spectra. Positive and negative ion ES-MS contain $[M+Na]^+$ and $[M-H]^-$, respectively, when NaOMe is present.

During work-up, products of homo-coupling of the initial $SiMe_3$ derivatives, i.e., $\{Co_3(\mu\text{-dppm})(CO)_7\}_2(\mu\text{-}C_{2x+2})$ ($x = 3, 4$) were also isolated [9]. Although both **13** and **14** are stable in air in the solid form, they have a tendency to lose mercury to give the same homo-coupled products, so that it is unclear at what stage the mercury-free products form. Elimination of mercury becomes easier as the chain length increases and is found especially when solutions in chlorinated solvents are left to stand for some time (hours) and also upon heating. Heating **14** in refluxing thf for 1 h gave the C_{10} derivative [9] in 27% yield. Similar extrusion of the heteroatom occurs easily with *cis*-$Pt\{C_5Co_3(\mu\text{-dppm})(CO)_7\}_2(PEt_3)_2$, but not with the *trans* isomer [18].

The complex $Co_3(\mu_3\text{-}CC{\equiv}CSiMe_3)(\mu\text{-dppm})(CO)_6(PPh_3)$ **15** was obtained serendipitously from a reaction between $Co_3(\mu_3\text{-}CC{\equiv}CSiMe_3)(\mu\text{-dppm})(CO)_7$ and RuCl(dppe)Cp* containing PPh_3 (^{31}P NMR detection) and was initially characterised by the XRD structure determination (below). Its spectroscopic properties include ν(C≡C) at 2111, terminal ν(CO) bands between 2044 and 1937 cm^{-1}, and characteristic resonances for $SiMe_3$ (δ_H −0.025) and dppm (δ_H 3.29, 4.50). In the ^{31}P NMR spectrum, signals at δ_P 34.5 and 49.5 (ratio 2/1) were assigned to the dppm and PPh_3 ligands, respectively. The ES-MS contained $[M+Na]^+$ and $[M-nCO]^+$ ($n = 0, 1$) at *m/z* 1123, 1100 and 1072, and $[M-H]^-$ at *m/z* 1099.



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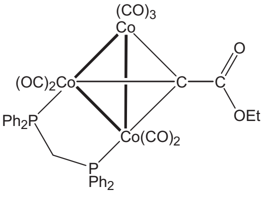

16

Attempted replacement of Br by azide in the reaction of $Co_3(\mu_3\text{-}CBr)(\mu\text{-dppm})(CO)_7$ with NaN_3 in EtOH gave instead deep green $Co_3\{\mu_3\text{-}CC(O)OEt\}(\mu\text{-dppm})(CO)_7$ (**16**), initially identified by the XRD structure determination reported below. The spectroscopic properties were in accord with the solid-state structure, with terminal ν(CO) bands between 2069 and 1964, and ν(ester CO) at 1649 cm^{-1}. The NMR spectra contained resonances for the Et group (δ_H 0.93, 4.19) and dppm ligand (δ_P 35.1).

These complexes are further examples of Co_3 clusters supporting carbon chains of various lengths attached by a μ^3–η^1 interaction with their terminal carbon atoms. The other end-groups in the present selection are Fc, Ru(dppe)Cp* or $SiMe_3$, while for **13** and **14**, we have used an Hg atom to link two C_x chains to give approximately linear 7- and 11-atom sequences. The reactions used to prepare these complexes are conventional: coupling of alkynyl-gold phosphine complexes with iodoalkynes or the bromocarbyne Co_3 cluster, desilylation (NaOMe) of $Co_3\{\mu_3\text{-}C(C{\equiv}C)_xSiMe_3\}(\mu\text{-dppm})(CO)_7$ in the presence of $Hg(OAc)_2$, or substitution of CO by PPh_3. The formation of the μ_3-$C(CO_2Et)$ complex likely occurs with NaN_3 acting as a base and allowing addition of OEt^- to an intermediate ketenylidene complex.

Cyclic voltammetric studies of **13** and **14** show only one reversible reduction process at $E^1 = -1.11$ and -1.09 V, respectively. This suggests that the presence of the mercury atom blocks electronic communication along the chain, since analogous tricobalt clusters containing C_x chains show two reduction processes, consistent with some electronic interaction between the two terminal clusters [19]. For the mercury complexes, irreversible oxidation waves are also found at $E^2 = +0.94$ and $+0.89$ V, respectively.

3. Molecular structures

Figs. 1–6 are projections of single molecules of **7** and **12**–**16**, selected structural parameters being collected in Table 1. With the exception of **7**, the common feature is the $Co_3(\mu_3\text{-}C)(\mu\text{-dppm})$ carbonyl cluster, for which the Co–Co [2.445(4)–2.497(1) Å], Co–P [2.154(6)–2.2155(6) Å] and Co(1,2)–C [1.881(1)–1.924(2) Å] and longer Co(3)–C separations [1.92(2)–1.943(7) Å] are similar to those found in many other related structures [8,18,20–24]. The dppm ligand takes up the chair conformation in all molecules, again being similar to most previously described systems.

Of most interest in the present context are the carbon chains, which show the usual short-long alternation of C–C bonds, although the actual distances suggest that there is a small degree of delocalisation along the chain. For example, in the two Hg-bridged complexes, the separations are 1.220(8), 1.397(7) Å (for **13**) and 1.245(11), 1.364(10), 1.231(10), 1.383(10) Å (**14**); the Hg–C bonds are 1.973(5) and 1.985(6) Å, respectively, values which may be compared with those found in $Hg(C{\equiv}CR)_2$ [2.00(2) Å (R = Ph, $SiMe_3$) [26], 1.994(9) Å (R = $C{\equiv}CC(NMe_2){=}\{W(CO)_5\}$) [27]], for example. The chains are not strictly linear, with angles at individual carbon atoms ranging between 172.7(5)° and 178.4(8)°. In **7**, the C–C separations from C(5) (attached to Ru) are 1.236(4), 1.350(4), 1.231(4) and 1.367(4) Å, with angles at the carbon atoms between 174.0(3)° and 178.4(3)°. Total bending at the C atoms amounts to 9.3° (for **13**) and 6.1° (**14**); the molecules are centrosymmetric, so that the C–Hg–C angles are necessarily 180°. This contrasts with the situation found for $\{[Cp^*(dppe)Ru]C{\equiv}CC{\equiv}C\}_2Hg$, where the C–Hg–C angle is 166.5(3)°, likely the result of steric interactions within the crystal [28].

Recent structural analyses of conjugated poly-ynes have concluded that experimental limits for C≡C triple and C–C single bond lengths for C(sp) atoms are between 1.208 and 1.216 Å and 1.351 and 1.366 Å, respectively [29]. Computational studies have given lengths of 1.225 and 1.361 Å [30], while in HC≡CH and HC≡CC≡CH, the experimental (microwave) C≡C separations are 1.2033(1) [31] and 1.20964(14) Å [32], respectively, with the C(sp)–C(sp) single bond separation in the diyne being 1.37081(2) Å. In general, the C≡C and C–C bonds tend to become longer and shorter, respectively, as the C_x chains lengthen, with reasonable limits being ca. 1.25 and 1.33 Å for these two bonds [29].

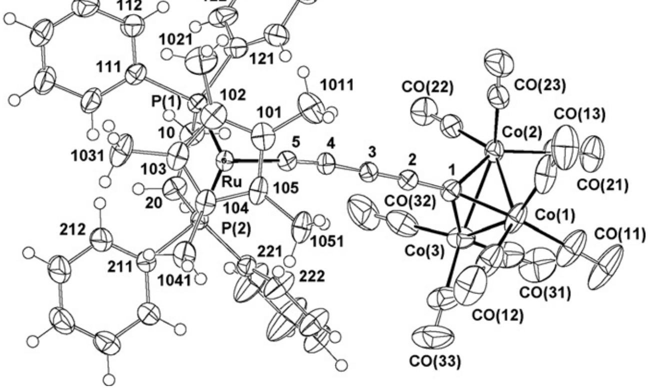

Fig. 1. Projection of a molecule of $\{Co_3(CO)_9\}\{\mu_3\text{-}C(C{\equiv}C)_2\}\{Ru(dppe)Cp^*\}$ (**7**).

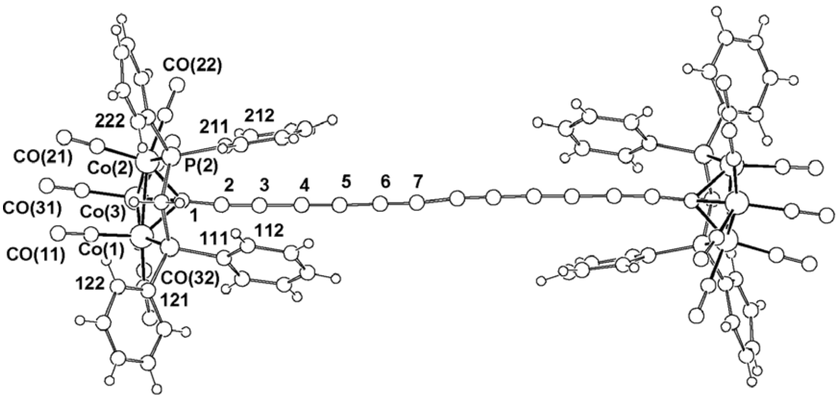

Fig. 2. Projection of a molecule of $\{Co_3(\mu\text{-dppm})(CO)_7\}_2(\mu\text{-}C_{14})$ (**12**).

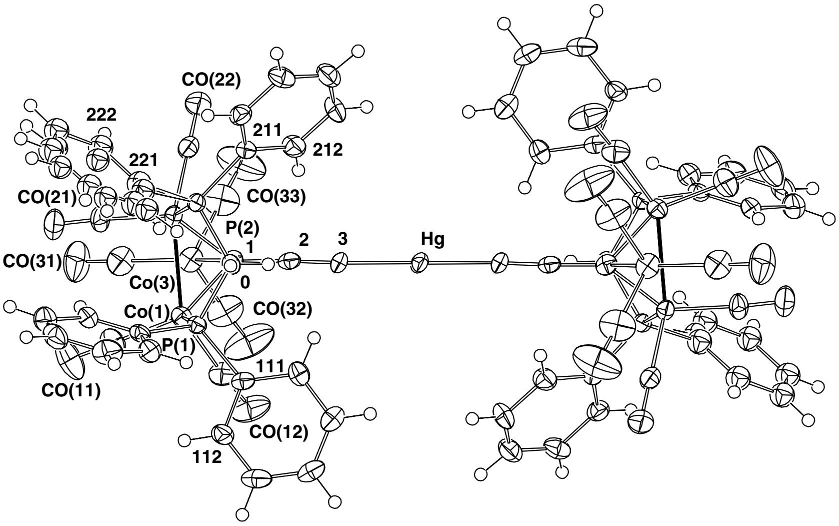

Fig. 3. Projection of a molecule of $Hg\{C{\equiv}CC[Co_3(\mu\text{-dppm})(CO)_7]\}_2$ (**13**).

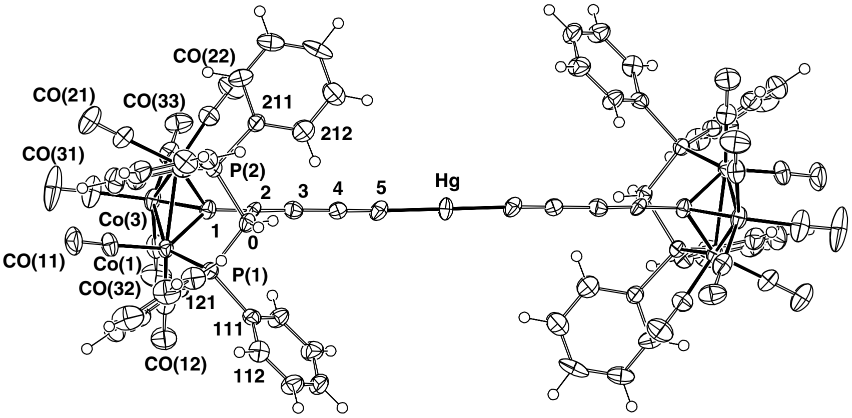

Fig. 4. Projection of a molecule of $Hg\{(C{\equiv}C)_2C[Co_3(\mu\text{-dppm})(CO)_7]\}_2$ (**14**).

Table 2 summarises the various data pertaining to these bonds as found in the complexes described above and related compounds reported elsewhere. Interestingly, both the C$\equiv$C and C(sp)–C(sp) separations are at the longer ends of the ranges cited above, suggesting that any lengthening of the C$\equiv$C triple bond may not be the result of conjugation (delocalisation). There is a slight but inconsistent trend towards the inner C$\equiv$C triple bonds being shorter than those towards the metal end-cap, paralleling the trend observed for other poly-ynes surveyed. Of further interest is the observation that the C$\equiv$C triple bonds in carbon chains which have both ends capped by metal centres involved in triply-bonding C$\equiv$M interactions appear to be somewhat shorter (av. 1.205 Å) than those in the other complexes considered here (av. 1.224 Å). The separation between the carbon atom attached

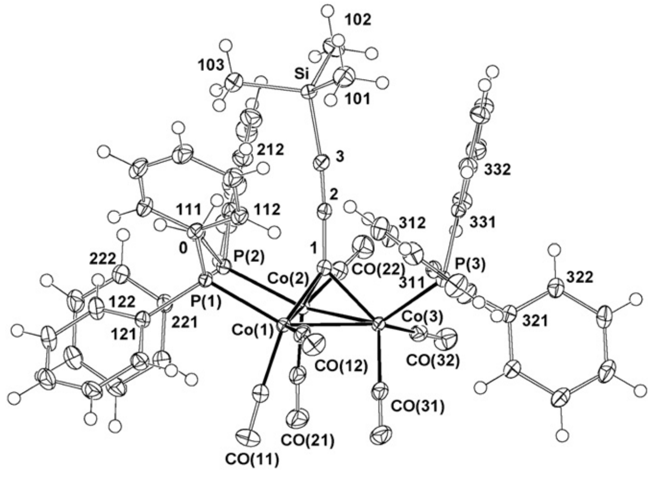

Fig. 5. Projection of a molecule of $Co_3(\mu_3\text{-}CC{\equiv}CSiMe_3)(\mu\text{-dppm})(CO)_6(PPh_3)$ (**15**).

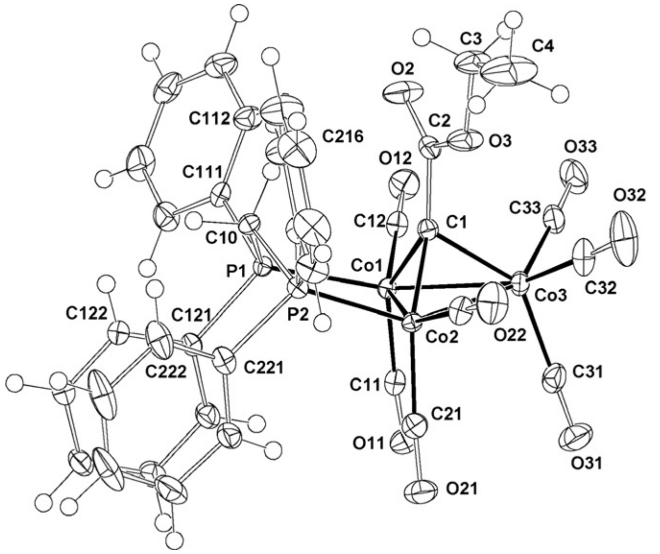

Fig. 6. Projection of a molecule of $Co_3\{\mu_3\text{-}CC(O)OEt\}(\mu\text{-dppm})(CO)_7$ (**16**).

to the Co_3 cluster (formally sp hybridised) and the next atom in the chain ranges from 1.30(3) (in **12**) to 1.397(3) Å (in **15**), the extremes in the more precise determination reflecting the relativities in strong electron-donating and -withdrawing powers, respectively, of the other end-capping groups. Angles at the poly-yne carbons range between 169.8(3)° and 179.5(9)°, with no consistent trends found. The usual conclusion that distortions along the C_x chains are due to "crystal packing effects" allied with intrinsically low bending force constants is not contradicted here.

4. Conclusions

In this account, we have described several complexes containing carbon chains end-capped by $Co_3(\mu\text{-dppm})(CO)_7$ clusters, with other metal-containing fragments at the other end. Included in these are two compounds in which a mercury atom bridges two cluster-terminated chains. Consideration of available structural data confirms the major conclusions of earlier surveys [30,33], highlighting an apparent tendency for the C≡C triple bond lengths in these complexes to be at the longer end of the range found, with shorter bonds occurring when the terminal poly-yne carbons are involved in carbynic interactions with either an M_3 cluster or an $M(CO)_2Tp$ group.

5. Experimental

5.1. 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 nitrogen and degassed before use. Separations were carried out by preparative thin-layer chromatography on glass plates ($20 \times 20\ cm^2$) coated with silica gel (Merck, 0.5 mm thick).

5.2. Instruments

IR spectra were obtained using 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 (^1H 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 ^1H and ^{13}C NMR spectra and external H_3PO_4 for ^{31}P NMR spectra. Electrospray mass spectra (ES-MS) were obtained from samples dissolved in MeOH containing NaOMe as an aid to ionisation [34]. Solutions were injected into a Fisons VG Platform II spectrometer via a 10 ml injection loop. Nitrogen was used as the drying and nebulising gas. Peaks listed are the most intense of the isotopic clusters. Electrochemical samples (1 mM) were dissolved in CH_2Cl_2 containing 0.5 M $[NBu_4]BF_4$ as the supporting electrolyte. Cyclic voltammograms were recorded using a PAR model 263 apparatus, with a saturated calomel electrode. A 1 mm path-length cell was used with a Pt-mesh working electrode, Pt wire counter and pseudo-reference electrodes. Ferrocene was used as internal calibrant ($FeCp_2/[FeCp_2]^+$ = +0.46 V). Elemental analyses were by CMAS, Belmont, Vic., Australia.

5.3. Reagents

The compounds FcC≡CI [13], $Co_3(\mu_3\text{-CBr})(\mu\text{-dppm})(CO)_7$ [25b], $Co_3\{\mu_3\text{-}C(C{\equiv}C)Au(PPh_3)\}(\mu\text{-dppm})(CO)_7$ (x = 1, 2) [25a] and $Co_3\{\mu_3\text{-}C(C{\equiv}C)_xSiMe_3\}(\mu\text{-dppm})(CO)_7$ (x = 1, 2) [9], IC≡CC≡CSiMe$_3$ and $I(C{\equiv}C)_xI$ (x = 3, 4) [10,14] were prepared by the cited methods.

5.3.1. $Co_3\{\mu_3\text{-}C(C{\equiv}C)_4SiMe_3\}(\mu\text{-dppm})(CO)_7$ (3)

A solution containing $Co_3\{\mu_3\text{-}C(C{\equiv}C)_2Au(PPh_3)\}(\mu\text{-dppm})(CO)_7$ (200 mg, 0.156 mmol) and IC≡CC≡CSiMe$_3$ (38.7 mg, 0.156 mmol) in thf (7 ml) was treated with CuI (2 mg, 0.0078 mmol) and $Pd(PPh_3)_4$ (9 mg, 0.0078 mmol) and stirred at r.t. for 1 h. After removal of solvent and extraction of the residue with acetone–hexane (3/7), chromatography on silica gel using the same solvent gave two bands. Band 1 (brown) contained $Co_3\{\mu_3\text{-}C(C{\equiv}C)_4SiMe_3\}(\mu\text{-dppm})(CO)_7$ (**3**) (100 mg, 68%), isolated as small very dark brown-red crystals. Anal. Calc. for $C_{44}H_{31}Co_3O_7P_2Si$: C, 55.01; H, 3.31. Found: C, 54.98; H, 3.31%. *M*, 938. IR (cyclohexane, cm^{-1}): ν(C≡C) 2156vw, 2141vw, 2113vw; ν(CO) 2067s, 2047 m, 2024 (sh), 2019vs, 2007 (sh), 1991w, 1982w. ^1H NMR: δ 0.30 (s, 9H, SiMe$_3$), 3.47, 4.30 (2 × m, 2H, CH$_2$), 7.26–7.56 (m, 20H, Ph). ^{13}C NMR: δ −0.27 (s, SiMe$_3$), 43.82 [t, J(CP) = 35 Hz, CH$_2$], 63.59, 64.34, 70.60, 80.90, 89.38, 91.56, 96.34, 98.76 (8 × s, C$_9$ carbons), 128.78–135.01 (m, Ph), 201,42 [s (br), CO]. ^{31}P NMR: δ 34.2 [s (br), dppm]. ES-MS (positive ion, MeOH+NaOMe, *m/z*): 889,

Table 1
Selected bond distances (Å) and angles (°)

Complex	**7**	**12**	**13**	**14**	**15**	**16**
Bond distances (Å)						
Co(1)—Co(2)	2.4776(7)	2.449(4)	2.486(1)	2.482(1)	2.4946(3)	2.4834(3)
Co(1)—Co(3)	2.4853(9)	2.445(4)	2.497(1)	2.467(1)	2.4860(3)	2.4722(3)
Co(2)—Co(3)	2.4647(8)	2.448(4)	2.479(1)	2.484(1)	2.4789(4)	2.4885(3)
Co(1)—P(1)		2.154(6)	2.199(2)	2.196(2)	2.2155(6)	2.2036(4)
Co(2)—P(2)		2.180(6)	2.201(2)	2.201(2)	2.1974(6)	2.2052(4)
Co(1)—C(1)	1.925(3)	1.96(2)	1.898(5)	1.898(7)	1.924(2)	1.887(1)
Co(2)—C(1)	1.919(3)	1.92(2)	1.898(5)	1.921(7)	1.922(2)	1.881(1)
Co(3)—C(1)	1.931(3)	1.92(2)	1.931(5)	1.943(7)	1.922(2)	1.925(1)
C(1)—C(2)	1.367(4)	1.30(3)	1.397(7)	1.38(1)	1.397(3)	1.470(2)
C(2)—C(3)	1.231(4)	1.25(3)	1.220(8)	1.23(1)	1.224(3)	1.208(2) [O(2)]
C(3)—X	1.350(4) [C(4)]	1.38(2)	1.973(5) [Hg]	1.36(1) [C(4)]	1.830(2) [Si]	1.498(3) [C(4)]
C(4)—C(5)	1.236(4)	1.24(2)		1.25(1)		
Co(1)—CO	1.819, 1.800, 1.792(5)	1.75(3), 1.73(2)	1.815, 1.794(7)	1.801, 1.783(8)	1.793, 1.781(2)	1.780, 1.784(2)
Co(2)—CO	1.829, 1.796, 1.794(6)	1.75(2), 1.73(2)	1.799, 1.778(6)	1.820, 1.786(8)	1.804, 1.783(2)	1.793, 1.790(2)
Co(3)—CO	1.823, 1.799, 1.782(4)	1.80(2), 1.74(2), 1.74(2)	1.813, 1.796, 1.812(7)	1.807, 1.797, 1.776(9)	1.782, 1.762(2)	1.816, 1.788, 1.795(2)
Bond angles (°)						
Co(1)—C(1)—C(2)	133.0(2)	130(2)	129.7(4)	138.4(6)	130.5(1)	137.9(1)
Co(2)—C(1)—C(2)	133.8(2)	134(2)	138.1(4)	129.5(5)	129.3(1)	132.0(1)
Co(3)—C(1)—C(2)	129.4(3)	136(2)	125.2(4)	127.2(5)	135.1(1)	121.8(1)
C(1)—C(2)—C(3)	177.6(3)	174(2)	178.0(6)	177.8(7)	176.1(2)	
C(2)—C(3)—X	178.4(3) [C(4)]	171(2) [C(4)]	172.7(5) [Hg]	178.4(8) [C(4)]	173.0(2) [Si]	
C(3)—C(4)—C(5)	174.0(3)	175(2)		177.7(8)		

For **7**: For the Ru(dppe)Cp* fragment: Ru—P(1,2) 2.2666, 2.2752(9), Ru—C(cp) 2.238–2.275(3) [av. 2.259(15)], Ru—C(5) 1.955(3) Å; P(1)—Ru—P(2) 84.84(3)°, P(1,2)—Ru—C(5) 84.61°, 83.28(9)°.
For **12**: C(5)—C(6) 1.32(3), C(6)—C(7) 1.18(3), C(7)—C(7′) 1.33(4) Å; C(4)—C(5)—C(6) 176(2)°, C(5)—C(6)—C(7) 178(2)°, C(6)—C(7)—C(7′) 175(3)°.
For **13**: C(3)—Hg—C(3′) 180°.
For **14**: Hg–C(5) 1.985(6) Å; C(4)—C(5)—Hg 175.4(6)°, C(5)—Hg—C(5′) 180°.
For **15**: Co(3)—P(3) 2.2221(6), Si—C(101,102,103) 1.864, 1.862, 1.864(2) Å.
For **16**: C(2)—O(3) 1.345(2), O(3)—C(3) 1.447(2) Å.

[M+H+Na−SiMe$_3$]$^+$; (negative ion): 865, [M−SiMe$_3$]$^-$; 837, [M−SiMe$_3$−CO]$^-$. Band 2 contained {Co$_3$(μ-dppm)(CO)$_7$}$_2$(μ-C$_{10}$) (30 mg, 23%), identified by comparison with an authentic sample [9].

5.3.2. *Co$_3${μ$_3$-C(C≡C)$_4$Au(PPh$_3$)}(μ-dppm)(CO)$_7$ (**4**)*

NaOMe [from Na (5.5 mg) in MeOH (1 ml)] was added to a solution of Co$_3${μ$_3$-C(C≡C)$_4$SiMe$_3$}(μ-dppm)(CO)$_7$ (78 mg, 0.08 mmol) in thf/MeOH (3/5, 8 ml). After stirring at r.t. for 30 min, AuCl(PPh$_3$) (41 mg, 0.08 mmol) was added. After stirring a further 2 h, solvent was removed and the residue was suspended in MeOH (5 ml). The insoluble brown solid was transferred to a sinter, washed with cold MeOH and extracted with a minimum of benzene. Addition of hexane to the filtrate gave Co$_3${μ$_3$-C(C≡C)$_4$Au(PPh$_3$)}(μ-dppm)(CO)$_7$ (**4**) (84 mg, 76%) as a brown powder. Anal. Calc. for $C_{59}H_{37}AuCo_3O_7P_3$: C, 53.47; H, 2.80. Found: C, 53.41; H, 2.74%. *M*, 1324. IR (CH$_2$Cl$_2$, cm^{-1}): *ν*(C≡C) 2140w (br); *ν*(CO) 2063 s, 2015vs, 1984 (sh), 1972 (sh). ^{1}H NMR: *δ* 3.45, 4.30 (2 × m, 2 H, CH$_2$), 7.25–7.54 (m, 35 H, Ph). ^{31}P NMR: *δ* 33.9 [s (br), 2P, dppm], 41.2 [s (br), 1P, PPh$_3$]. ES-MS (positive ion, MeOH, *m/z*): 1325, [M+H]$^+$; 1324, M$^+$; 1296, [M−CO]$^+$; (MeOH+NaOMe): 1347, [M+Na]$^+$.

5.3.3. *{Cp(Ph$_3$P)$_2$Ru}C≡CC≡CC{Co$_3$(μ-dppm)(CO)$_7$} (**5**)*

A mixture of Ru{(C≡C)$_2$Au[P(tol)$_3$]}(PPh$_3$)$_2$Cp* (71 mg, 0.06 mmol), Co$_3$(μ$_3$-CBr)(μ-dppm)(CO)$_7$ (51 mg, 0.06 mmol), Pd(PPh$_3$)$_4$ (7 mg, 0.006 mmol) and CuI (1 mg, 0.005 mmol) in thf (10 ml) was stirred at r.t. for 2 h to give a brown solution. Separation by preparative tlc (acetone–hexane 3/7) afforded a major brown band (R_f = 0.38) from which {Cp(Ph$_3$P)$_2$Ru}C≡CC≡CC{Co$_3$(μ-dppm)(CO)$_7$} (**5**) (69.4 mg, 77%) was isolated as dark red crystals (PhMe/MeOH). Anal. Calc. for $C_{78}H_{57}Co_3O_7P_4Ru$: C, 62.11; H, 3.78. Found: C, 62.12; H, 3.73%. *M*, 1508. IR (cyclohexane, cm^{-1}): *ν*(C≡C) 2108vw; *ν*(CO) 2063w, 2046 m, 2005 (sh), 2004vs, 1985 (sh), 1976 (sh), 1968w, 1952vw. ^{1}H NMR: *δ* 3.38, 4.61 (2 × m, 2H, CH$_2$), 4.45 (s, 5H, Cp), 6.94–7.51 (m, 50H, Ph). ^{13}C NMR: *δ* 39.61 [s (br), dppm], 86.01, 100.79, 108.07, 138.35 (C$_4$ chain), 87.18 (s, Cp), 127.40–133.75 (m, Ph), 203.12 [s (br), CO]. ^{31}P NMR: *δ* 33.6 (s, 2P, dppm), 49.4 (s, 2P, PPh$_3$). ES-MS (positive ion, MeOH+NaOMe, *m/z*): 1531, [M+Na]$^+$; (negative ion, MeOH+NaOMe): 1507, [M−H]$^-$.

5.3.4. *{Cp*(dppe)Ru}C≡CC≡CC{Co$_3$(μ-dppm)(CO)$_7$} (**6**)*

A mixture of Ru{(C≡C)$_2$Au[P(tol)$_3$]}(dppe)Cp* (50 mg, 0.05 mmol), Co$_3$(μ$_3$-CBr)(μ-dppm)(CO)$_7$ (45 mg, 0.05 mmol), Pd(PPh$_3$)$_4$ (4 mg, 0.003 mmol) and CuI (1 mg, 0.005 mmol) in thf (7 ml) was stirred at r.t. for 1 h. Separation by preparative tlc (acetone–hexane 3/7) afforded a major brown band (R_f = 0.44) from which {Cp*(dppe)Ru}C≡CC≡CC{Co$_3$(μ-dppm)(CO)$_7$} (**6**) (52.7 mg, 69.5%) was isolated as dark red crystals (PhMe/MeOH). Anal. Calc. for $C_{73}H_{61}Co_3O_7P_4Ru$: C, 60.38; H, 4.23. Found: C, 60.25; H, 4.17%. *M*, 1452. IR (cyclohexane, cm^{-1}): *ν*(C≡C) 2107vw; *ν*(CO) 2062w, 2044 m, 2009 s, 2003vs, 1989 (sh), 1976vw, 1968vw, 1952vw. ^{1}H NMR: *δ* 1.59 (s, 15H, Cp*), 2.03, 2.69 (2 × m, 2 × 2H, dppe), 3.21, 4.52 (2 × m, 2 × 1H, dppm), 7.03–7.70 (m, 40H, Ph). ^{13}C NMR: *δ* 10.13 (s, C$_5$*Me*$_5$), 29.69 [s (br), dppe], 38.38 (s, dppm), 86.08, 96.09, 109.60, 137.61 (C$_4$ chain), 93.64 (s, *C*$_5$Me$_5$), 127.42–133.38 (m, Ph), 202.83, 203.35, 210.32 (CO). ^{31}P NMR: *δ* 33.5 (s, 2P, dppm), 79.45 (s, 2P, dppe). ES-MS (positive ion, MeOH, *m/z*): 1452, M$^+$; 1424, 1396 [M−*n*CO]$^+$ (*n* = 1, 2); (negative ion, MeOH+NaOMe): 1452, M$^-$.

5.3.5. *{Cp*(dppe)Ru}C≡CC≡CC{Co$_3$(CO)$_9$} (**7**)*

A solution of Ru{C≡CC≡CAu(PPh$_3$)}(dppe)Cp* (150 mg, 0.13 mmol) and Co$_3$(μ$_3$-CBr)(CO)$_9$ (67.7 mg, 0.13 mmol) in thf (10 ml) was treated with Pd(PPh$_3$)$_4$ (8.1 mg, 0.007 mmol) and CuI (2 mg, 0.1 mmol). After stirring at r.t. for 30 min, spot tlc showed the absence of starting material. Removal of thf under reduced pressure and purification of a CH$_2$Cl$_2$ extract of the

Table 2
Bond lengths and angles along C_x ($x \geqslant 5$) chains attached to $Co_3(\mu\text{-dppm})(CO)_7$ end-groups

Entry	Complex[a]	$\equiv C^1-C^2\equiv$ $\equiv C^1-C^2\equiv C^3-$	$-C^2\equiv C^3-$ $-C^2\equiv C^3-C^4\equiv$	$\equiv C^3-C^4\equiv$ $\equiv C^3-C^4\equiv C^5-$	$-C^4\equiv C^5-$ $-C^4\equiv C^5-C^6\equiv$	$\equiv C^5-C^6\equiv$ $\equiv C^5-C^6\equiv C^7-$	$-C^6\equiv C^7-$ $-C^6\equiv C^7-C^8\equiv$	$\equiv C^7-C^8\equiv$ $\equiv C^7-C^8\equiv C^9-$	Reference
1	$[Co_3]C_5Fc$	1.385(2)	1.227(2)	1.364(2)	1.215(2)				[c]
		176.6(2)	176.7(2)	177.6(2)	177.0(2)				
2	$[Co_3]C_5[W]$	1.377(5)	1.219(5)	1.367(6)	1.216(6)				[24a]
		178.8(5)	178.5(4)	178.4(4)	177.0(4)				
3	$[Co'_3]C_5[Ru^*]$ **7**	1.367(4)	1.231(4)	1.350(4)	1.236(4)				This work
		177.6(3)	178.4(3)	174.0(3)	176.6(3)				
4	$\{[Co_3]C_5\}_2[Pt]$	1.42(1)	1.21(1)	1.37(1)	1.19(1)				[18]
		177.8(8)	179.5(9)	173.5(8)	177.8(8)				
5	$[Co_3]C_5[Au]$	1.383(10)	1.23(1)	1.36(1)	1.22(1)				[24a]
		178.8(8)	176.7(8)	177.2(8)	177.6(6)				
6	$\{[Co_3]C_5\}_2Hg$ (**14**)	1.383(10)	1.23(1)	1.36(1)	1.25(1)				This work
		177.8(7)	178.4(8)	177.7(8)	175.4(6)				
7	$[Co_3]C_5R[Co_3]$	1.380(3)	1.226(3)	1.345(3)	1.219(4)				[9]
		179.3(3)	177.5(3)	178.2(3)	169.8(3)				
8	$[Co_3]C_7Ph$	1.385(3)	1.230(3)	1.355(4)	1.217(4)	1.366(4)	1.203(4)		[8b]
		177.6(3)	174.1(3)	177.6(3)	176.1(3)	176.9(3)	178.4(3)		
9	$[Co_3]C_7SiMe_3$	1.381(6)	1.224(7)	1.343(7)	1.226(7)	1.357(7)	1.208(7)		[8b]
		178.0(4)	173.0(4)	175.5(4)	175.7(4)	178.3(4)	175.9(4)		
10	$[Co_3]C_7[Ru^*]$	1.398(7)	1.225(7)	1.350(7)	1.232(7)	1.348(7)	1.241(6)		[d]
		177.7(5)	177.6(5)	177.6(5)	177.8(5)	176.8(5)	176.9(4)		
11	$[Co_3]C_7[Ru]$	1.393(7)	1.226(7)	1.356(7)	1.220(7)	1.350(7)	1.228(7)		[d]
		178.3(8)	178.9(8)	175.8(8)	174.4(9)	173.1(9)	171.6(7)		
	Ranges for entries 1–11 (averages)	1.367–1.42 (1.388)	1.213–1.231 (1.225)	1.341–1.365 (1.353)	1.214–1.236 (1.226)	1.348–1.366 (1.355)	1.203–1.241 (1.220)		
		176.1–179.3 (177.8)	172.7–179.5 (176.0)	174.0–178.2 (176.8)	169.8–177.8 (175.4)	173.1–178.3 (176.2)	171.6–178.4 (175.7)		
12	$[Co_3]C_6[Mo]$	1.371(6)	1.231(6)	1.332(6)	1.246(6)	1.355(6)			[24f]
		178.7(7)	179.9(6)	177.8(6)	176.7(6)				
13	$[Co_3]C_6[Ru_3]$	1.43(3)	1.15(3)	1.39(3)	1.19(3)	1.46(3)			[24c]
		177(3)	180(2)	168(2)	174(3)				
14	$[Co_3]C_6[Os_3]$	1.41(3)	1.17(2)	1.40(2)	1.14(3)	1.44(3)			[24c]
		177(2)	174(2)	175(2)	172(2)				
15	$[Co_3]_2C_6$[b]	1.377(3)	1.225(3)	1.346(3)					[9]
		175.6(2)	177.9(2)						
16	$[Co_3]_2C_{10}$[b]	1.376(2)	1.226(3)	1.345(3)	1.221(3)	1.347(3)			[9]
		176.1(2)	173.3(2)	176.8(2)	178.4(2)				
17	$[Co_3]_2C_{14}$[b] (**12**)	1.30(3)	1.25(3)	1.38(3)	1.24(3)	1.32(3)	1.18(3)	1.33(4)	This work
		174(2)	171(2)	175(2)	176(2)	178(2)	175(3)		
18	$[Co_3]_2C_{16}$[b] (**9**)	1.371(6)	1.221(8)	1.335(8)	1.228(8)	1.339(8)	1.221(8)	1.342(9)	[8a]
		176.4(5)	169.7(6)	176.2(6)	178.8(6)	178.4(6)	178.6(6)	179.5(7)	
	Ranges for entries 12–16, 18 (averages)	1.371–1.440 (1.391)	1.147–1.230 (1.203)	1.333–1.398 (1.357)	1.145–1.246 (1.206)	1.339–1.463 (1.388)			
		175.6–178.4 (176.7)	169.7–179.8 (177.4)	167.4–177.6 (174.5)	171.6–178.8 (176.0)				

[a] $[Co_3] = Co_3(\mu\text{-dppm})(CO)_7$; $[Co'_3] = Co_3(CO)_9$; $R = C[{=}C(CN)_2]C[{=}C(CN)_2]C$; $[W] = W(CO)_3Cp$; $[Ru^*] = Ru(dppe)Cp^*$; $[Pt] = \mathit{trans}\text{-}Pt(PPh_3)_2$; $[Au] = Au\{P(tol)_3\}$; $[Ru] = Ru(dppe)Cp$; $[Mo] = Mo(CO)_2Tp$; $[Ru_3] = Ru_3(\mu\text{-}H)_3(CO)_9$; $[Os_3] = Os_3(\mu\text{-}H)_3(CO)_9$.

[b] Centrosymmetric; $-C(8)\equiv C(9)-$ 1.211(9)Å.

[c] M.I. Bruce, M. Gaudio, B.W. Skelton, A.H. White, unpublished work.

[d] M.I. Bruce, C.R. Parker, B.W. Skelton, A.H. White, unpublished work.

residue by preparative tlc (acetone–hexane, 1/4) gave a major brown band ($R_f = 0.41$) containing $\{Cp^*(dppe)Ru\}C{\equiv}CC{\equiv}CC\{Co_3(CO)_9\}$ (**7**) (58.7 mg, 40%), obtained as dark brown crystals from hexane. Anal. Calc. for $C_{50}H_{39}Co_3O_9P_2Ru$: C, 53.45; H, 3.50. Found: C, 53.51; H, 3.55%. *M*, 1124. IR (CH_2Cl_2, cm^{-1}): $\nu(C{\equiv}C)$ 2124vw; $\nu(CO)$ 2094w, 2044vs, 2026s, 2013 (sh), 1976m (br). ^1H NMR (C_6D_6): δ 1.42 (s, br, 15H, Cp^*), 1.92, 2.24 (2 × m, 4H, dppe), 7.03–7.67 (m, 20H, Ph). ^{13}C NMR (C_6D_6): δ 10.38 (s, $C_5\mathit{Me}_5$), 29.94 (s, CH_2), 94.93 (s, C_5Me_5), 87.49, 98.91, 114.67 (3 × s, carbon chain), 130.21–138.40 (m, Ph), 201.45 (s br, CO). ^{31}P NMR (C_6D_6): δ 79.5 (s, dppe). ES-MS (positive ion, MeOH/NaOMe, *m/z*): 1147, $[M+Na]^+$; 1124, M^+; 1096, $[M-CO]^+$; (negative ion mode, MeOH/NaOMe, *m/z*): 1155, $[M+OMe]^-$; 1096, $[M-CO]^-$.

5.3.6. $Co_3\{\mu_3\text{-}C(C{\equiv}C)_3Fc\}(\mu\text{-dppm})(CO)_7$ (8)

A mixture of $Co_3\{\mu_3\text{-}C(C{\equiv}C)_2Au(PPh_3)\}(\mu\text{-dppm})(CO)_7$ (60 mg, 0.05 mmol), $FcC{\equiv}CI$ (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, after which time tlc showed no starting materials to be present. Evaporation of solvent, dissolution of the residue in CH_2Cl_2 and separation on silica plates (acetone–hexane 1/4) gave two fractions. The major product was isolated from a brown-orange band ($R_f = 0.26$) to give $Co_3\{\mu_3\text{-}C(C{\equiv}C)_3Fc\}(\mu\text{-dppm})(CO)_7$ (**8**) (40.8 mg, 87%) as very thin red plates. Anal. Calc. for $C_{49}H_{31}Co_3FeO_7P_2$: C, 57.31; H, 3.02. Found: C, 56.74; H, 2.57%. *M*, 1026. IR (CH_2Cl_2, cm^{-1}): $\nu(C{\equiv}C)$ 2168w, 2100vw; $\nu(CO)$ 2063s, 2013vs, 1973 (sh), 1958 (sh). ^1H NMR: δ 3.40, 4.25 (2 × m, 2H, CH_2), 4.28 (s, 5H, FeCp), 4.30, 4.56 (2 × m, 4H, CH_2), 7.15–7.69 (m, 20H, Ph). ^{31}P NMR: δ 33.8 (s, dppm). ^{13}C NMR: δ 42.75 [t, *J*(CP) 18.3 Hz, dppm], 70.35 (FeCp), 69.76, 72.35 ($Fe-C_5H_4$), 63.38, 65.66, 72.73, 80.95, 85.99, 97.13, 99.03 (C_{ipso} and C_6 of carbon chain), 201.43, 209.79, 212.4 (Co–CO), 128.45–134.77 (m, Ph). ES-MS (positive ion mode, MeOH, *m/z*): 1027, $[M+H]^+$; 1026, M^+; 998, $[M-CO]^+$; (MeOH+NaOMe): 1049, $[M+Na]^+$; (negative ion mode, MeOH+NaOMe): 1025, $[M-H]^-$.

5.4. Syntheses of $\{Co_3(\mu\text{-}dppm)(CO)_7\}_2(\mu\text{-}C_y)$

(a) $y = 16$, **9**: A mixture of $Co_3\{\mu_3\text{-}C(C{\equiv}C)_2Au(PPh_3)\}(\mu\text{-}dppm)(CO)_7$ (153.1 mg, 0.12 mmol), $I(C{\equiv}C)_3I$ (20 mg, 0.06 mmol), $Pd(PPh_3)_4$ (7 mg, 0.006 mmol) and CuI (1 mg, 0.006 mmol) in thf (7 ml) was stirred at r.t., the solution rapidly turning dark red. After 1 h, solvent was removed and the residue taken up in CH_2Cl_2. Separation by preparative tlc (acetone–hexane, 3/7) gave one dark red-purple band ($R_f = 0.38$) containing $\{Co_3(\mu\text{-}dppm)(CO)_7\}_2(\mu\text{-}C_{16})$ (**9**) (90.9 mg, 86%), obtained as very dark red crystals (CH_2Cl_2/MeOH). Anal. Calc. for $C_{80}H_{44}Co_6O_{14}P_4$: C, 56.27; H, 2.58. Found: C, 56.38; H, 2.60%. *M*, 1706. IR (CH_2Cl_2, cm^{-1}): $\nu(C{\equiv}C)$ 2172w, 2157vw, 2127vw; $\nu(CO)$ 2065s, 2020vs, 2008 (sh), 1990 (sh), 1986m (br), 1960 (sh). ^1H NMR: δ 3.46, 4.25 ($2 \times$ m, $2 \times$ 2H, CH_2), 6.97–7.58 (m, 40H, Ph). ^{13}C NMR: δ 44.51 [s (br), dppm], 64.36, 66.66, 6828, 70.22, 81.45, 95.98, 99.83 ($7 \times$ s, C_{14} chain), 124.21–136.43 (m, Ph), 201.06 [s (br), CO]. ^{31}P NMR: δ 33.9 [s (br), dppm]. ES-MS (positive ion, MeOH+NaOMe, *m/z*): 1729, $[M+Na]^+$; (negative ion, MeOH); 1705, $[M-H]^-$; 852, $[Co_3(C_8)(dppm)-H]^-$. Some $\{Co_3(\mu\text{-}dppm)(CO)_7\}_2(\mu\text{-}C_{10})$ [9] (3 mg) is formed as a by-product.

(b) $y = 26$, **10**; 18, **11**: A mixture of $Co_3\{\mu_3\text{-}C(C{\equiv}C)_4Au(PPh_3)\}(\mu\text{-}dppm)(CO)_7$ (70 mg, 0.05 mmol) and $I(C{\equiv}C)_4I$ (10 mg, 0.025 mmol) in thf (7 ml) was treated with $Pd(PPh_3)_4$ (2 mg) and CuI (2 mg). After stirring at r.t. for 1 h, the solution was brown-red and spot tlc showed the absence of starting material. Separation by preparative tlc (acetone–hexane 3/7) gave two major bands and a black base-line. The faster moving purple band ($R_f = 0.31$) contained $\{Co_3(\mu\text{-}dppm)(CO)_7\}_2(\mu\text{-}C_{26})$ (**10**) (20.3 mg, 39%) as very dark microcrystals. IR (CH_2Cl_2, cm^{-1}): $\nu(C{\equiv}C)$ 2168vw, 2129vw; $\nu(CO)$ 2094w, 2065s, 2019vs, 1978 (sh), 1928 (sh). ^1H NMR: δ 3.50, 4.24 ($2 \times$ m, $2 \times$ 2H, CH_2), 7.31–7.62 (m, 40H, Ph). ^{31}P NMR: δ 34.0 [s (br), dppm]. ES-MS (positive ion, MeOH+NaOMe, *m/z*): 1849, $[M+Na]^+$; (negative ion, MeOH+NaOMe, *m/z*): 1857, $[M+OMe]^-$; 1825, $[M-H]^-$ (calc. *M*, 1826). This complex partly decomposes on plates and in solution, and a satisfactory elemental analysis could not be obtained. The second dark red band ($R_f = 0.29$) gave $\{Co_3(\mu\text{-}dppm)(CO)_7\}_2(\mu\text{-}C_{18})$ **11** (5.3 mg, 13%) as a dark red powder. Anal. Calc. for $C_{82}H_{44}Co_6O_{14}P_4$: C, 56.88; H, 2.54. Found: C, 56.81; H, 2.60%. *M*, 1730. IR (CH_2Cl_2, cm^{-1}): $\nu(C{\equiv}C)$ 2154vw, 2123vw; $\nu(CO)$ 2094w, 2065m, 2020vs, 1967m (br), 1927 (sh). ^1H NMR: δ 3.46, 4.24 ($2 \times$ m, $2 \times$ 2H, CH_2), 7.27–7.71 (m, 40H, Ph). ^{31}P NMR: δ 34.1 [s (br), dppm]. ES-MS (positive ion, MeOH+NaOMe, *m/z*): 1753, $[M+Na]^+$; (negative ion, MeOH+NaOMe, *m/z*): 1729, $[M-H]^-$.

5.5. Syntheses of $Hg\{(C{\equiv}C)_xC[Co_3(\mu\text{-}dppm)(CO)_7]\}_2$ ($x = 1$, **13**; 2, **14**)

5.5.1. $Hg\{C{\equiv}CC[Co_3(\mu\text{-}dppm)(CO)_7]\}_2$ (**13**)

A solution of $Co_3(\mu_3\text{-}CC{\equiv}CSiMe_3)(\mu\text{-}dppm)(CO)_7$ (50 mg, 0.058 mmol) and $Hg(OAc)_2$ (9.2 mg, 0.029 mmol) in a mixture of thf and MeOH (1/1, 6 ml) was treated with NaOMe (excess) in MeOH (1 ml), and the mixture was stirred at r.t. for 2 h. Removal of solvent under reduced pressure and separation of a CH_2Cl_2 extract of the residue by preparative tlc (silica, acetone–hexane 3/7) afforded two bands. The red band ($R_f = 0.53$) contained $\{Co_3(\mu\text{-}dppm)(CO)_7\}_2(\mu\text{-}C_{10})$ (2.5 mg, 5.5%), identified by comparison with an authentic sample [9]. The brown band ($R_f = 0.47$) contained $Hg\{C{\equiv}CC[Co_3(\mu\text{-}dppm)(CO)_7]\}_2$ (**13**) (6.9 mg, 13%) obtained as dark brown crystals (CH_2Cl_2/MeOH). Anal. Calc. for $C_{70}H_{44}Co_6HgO_{14}P_4$: C, 47.03; H, 2.46. Found: C, 46.92; H, 2.42%. *M*, 1786. IR (CH_2Cl_2, cm^{-1}): $\nu(C{\equiv}C)$ 2124vw; $\nu(CO)$ 2060s, 2005vs (br), 1985 (sh), 1968 (sh), 1948 (sh). ^1H NMR: δ 3.47, 4.53 ($2 \times$ m, 4H, CH_2), 7.22–7.53 (m, 40H, Ph). ^{31}P NMR: δ 34.8 (s, br, dppm). ES-MS (positive ion mode, MeOH+NaOMe, *m/z*): 1811, $[M+Na]^+$; (negative ion mode, MeOH + NaOMe, *m/z*): 1787, $[M-H]^-$.

5.5.2. $Hg\{(C{\equiv}C)_2C[Co_3(\mu\text{-}dppm)(CO)_7]\}_2$ (**14**)

A solution of $Co_3\{\mu_3\text{-}C(C{\equiv}C)_2SiMe_3\}(\mu\text{-}dppm)(CO)_7$ (50 mg, 0.056 mmol) and $Hg(OAc)_2$ (9 mg, 0.028 mmol) in a mixture of thf and MeOH (1/3, 4 ml) was treated with NaOMe (excess) in MeOH (1 ml), and the mixture was stirred at r.t. for 1 h. Removal of solvent under reduced pressure and separation of a CH_2Cl_2 extract of the residue by preparative tlc (silica, acetone–hexane 3/7) afforded two bands. The red band ($R_f = 0.50$) contained $\{Co_3(\mu\text{-}dppm)(CO)_7\}_2(\mu\text{-}C_{10})$ (1.5 mg, 3%), identified by comparison with an authentic sample [9]. The brown band ($R_f = 0.48$) contained $Hg\{(C{\equiv}C)_2C[Co_3(\mu\text{-}dppm)(CO)_7]\}_2$ (**14**) (38.1 mg, 74%) obtained as dark brown crystals (CH_2Cl_2/MeOH). Anal. Calc. for $C_{74}H_{44}Co_6HgO_{14}P_4$: C, 48.42; H, 2.40. Found: C, 48.30; H, 2.47%. *M*, 1834. IR (CH_2Cl_2, cm^{-1}): $\nu(C{\equiv}C)$ 2112w (br); $\nu(CO)$ 2061s, 2014vs, 1995 (sh), 1971 (sh). ^1H NMR: δ 3.45, 4.29 (2 x m, 4H, CH_2), 7.18–7.52 (m, 40H, Ph). ^{13}C NMR: δ 42.76 [t, *J*(CP) 22 Hz, dppm], 92.33, 96.16 (s, carbon chain), 128.57–135.28 (m, Ph), 201.67, 209.91, 214.93 ($3 \times$ s, br, Co-CO). ^{31}P NMR: δ 34.6 (s, br, dppm). ES-MS (positive ion mode, MeOH+NaOMe, *m/z*): 1859, $[M+Na]^+$; (negative ion mode, MeOH+NaOMe, *m/z*): 1835, $[M-H]^-$.

5.5.3. Thermolysis of $Hg\{C(C{\equiv}C)_2[Co_3(\mu\text{-}dppm)(CO)_7]\}_2$ (**14**)

A solution containing $Hg\{C(C{\equiv}C)_2[Co_3(\mu\text{-}dppm)(CO)_7]\}_2$ (20 mg, 0.011 mmol) in thf (5 ml) was heated at reflux point for 1 h. The usual work-up afforded $\{Co_3(\mu\text{-}dppm)(CO)_7\}_2(\mu\text{-}C_{10})$ [9] (5 mg, 27%). This reaction is accompanied by a considerable amount of decomposition.

5.5.4. $Co_3(\mu_3\text{-}CC{\equiv}CSiMe_3)(\mu\text{-}dppm)(CO)_6(PPh_3)$ (**15**)

This complex was isolated from the products of the reaction between $Co_3(\mu_3\text{-}CC{\equiv}CSiMe_3)(\mu\text{-}dppm)(CO)_7$ (100 mg, 0.115 mmol), $RuCl(dppe)Cp^*$ (77.3 mg, 0.115 mmol) and KF (6.5 mg, 0.113 mmol), which were heated in a refluxing mixture of thf/MeOH (1/5, 12 ml) for 5 h. After removal of solvents, preparative tlc of a CH_2Cl_2 extract (acetone–hexane. 3/7) afforded a major green-brown band ($R_f = 0.44$) containing $Co_3(\mu_3\text{-}CC{\equiv}CSiMe_3)(\mu\text{-}dppm)(CO)_6(PPh_3)$ (**15**) (45.1 mg, 35%), which gave dark red crystals from CH_2Cl_2/MeOH. Anal. Calc. for $C_{55}H_{46}Co_3O_6P_3Si$: C, 60.01; H, 4.21. Found: C, 60.19; H, 4.92%. *M*, 1100. IR (CH_2Cl_2, cm^{-1}): $\nu(C{\equiv}C)$ 2111vw; $\nu(CO)$ 2044w, 2024vs, 1992vs, 1971 m (br), 1937 (sh). ^1H NMR: δ −0.025 (s, 9H, $SiMe_3$), 3.29, 4.50 ($2 \times$ m, 4H, CH_2), 6.93–7.55 (m, 35H, Ph). ^{31}P NMR: δ 34.5 (s (br, 2P, dppm), 49.5 (s br, 1P, PPh_3). ES-MS (positive ion, MeOH+NaOMe, *m/z*): 1123, $[M+Na]^+$; 1100, M^+; 1072, $[M-CO]^+$; (negative ion, MeOH+NaOMe, *m/z*): 1099, $[M-H]^-$. The source of the PPh_3 is likely an impurity in the starting Ru complex, subsequently confirmed by a ^{31}P NMR spectrum of the latter.

5.5.5. $Co_3\{\mu_3\text{-}CC(O)OEt\}(\mu\text{-}dppm)(CO)_7$ (**16**)

A suspension of $Co_3(\mu_3\text{-}CBr)(\mu\text{-}dppm)(CO)_7$ (75 mg, 0.09 mmol) and NaN_3 (35 mg, 0.54 mmol) in degassed EtOH (7 ml) was heated at reflux point until tlc showed the absence of starting complex (2 h). The filtered solution as evaporated and a CH_2Cl_2 extract was purified by preparative tlc (CH_2Cl_2/hexane 1/1). The major dark green band (R_f 0.44) contained $Co_3\{\mu_3\text{-}CC(O)OEt\}(\mu\text{-}dppm)(CO)_7$ (**16**) (30.7 mg, 41%), obtained as dark green crystals (pentane). Anal. Calc. for $C_{36}H_{27}Co_3O_9P_2$: C, 51.31; H, 3.21. Found: C 51.64; H, 3.23%. *M*, 842. IR (cyclohexane, cm^{-1}): $\nu(CO)$ 2069s, 2026vs, 2004m, 1991w, 1980w, 1964w; ν(ester CO) 1649w (br). ^1H NMR: δ 0.93 [s (br), 3H, $CH_2\mathit{Me}$], 3.50, 4.62 ($2 \times$ m, 2H, CH_2), 4.19 [s (br), 2H, $\mathit{CH_2}Me$], 7.13–7.51 (m, 20H, Ph). ^{31}P NMR: δ 35.1 [s (br), dppm].

5.6. Structure determinations

Full spheres of diffraction data were measured using CCD area-detector instruments. N_{tot} reflections were merged to *N* unique

Table 3
Crystal data and refinement details

Complex	**7**	**12**	**13**	**14**	**15**	**16**
Formula	$C_{50}H_{39}Co_3O_9P_2Ru$	$C_{78}H_{44}Co_6O_{14}P_4$	$C_{70}H_{44}Co_6HgO_{14}P_4$	$C_{74}H_{44}Co_6HgO_{14}P_4 \cdot 2CH_2Cl_2$	$C_{55}H_{46}Co_3O_6P_3Si$	$C_{36}H_{27}Co_3O_9P_2$
MW	1123.67	1682.68	1787.19	2005.10	1100.77	842.31
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/n$	$P2_1/c$	$P2_1/n$	$P\bar{1}$	$P2_1/n$
a (Å)	17.378(3)	8.951(7)	10.0415(9)	10.100(2)	12.009(1)	12.3198(3)
b (Å)	14.299(2)	20.213(10)	22.681(2)	17.675(3)	12.131(1)	25.563(1)
c (Å)	19.338(3)	18.90(1)	15.480(1)	21.151(4)	18.836(2)	12.8938(7)
α (°)					90.832(2)	
β (°)	98.744(4)	93.73(2)	91.649(2)	93.681(3)	96.323(2)	95.054(3)
γ (°)					112.721(2)	
V (Å^3)	4749	3412	3524	3768	2511	3570
ρ_c (g cm^{-3})	1.57_1	1.63_7	1.68_4	1.76_7	1.45_6	1.56_7
Z	*4*	*2*	*2*	*2*	*2*	*4*
$2\theta_{max}$ (°)	66	45	55	53	65	68
μ(Mo Kα) (mm^{-1})	1.46	1.59	3.7	3.6	1.15	1.52
$T_{min/max}$	0.79	0.53	0.79	0.79	0.85	0.86
Crystal dimensions (mm^3)	0.48 × 0.25 × 0.10	0.48 × 0.09 × 0.03	0.18 × 0.07 × 0.06	0.15 × 0.05 × 0.03	0.55 × 0.25 × 0.10	0.34 × 0.19 × 0.14
N_{tot}	72241	26214	48251	34197	39527	63697
N (R_{int})	17835 (0.036)	4304 (0.19)	8081 (0.046)	7697 (0.072)	17953 (0.028)	14341 (0.031)
N_o	12862	2476	7036	5501	14280	9832
R	0.050	0.116	0.052	0.051	0.035	0.031
R_w (n_w/a)	0.097 (18)	0.23 (25)	0.098 (42)	0.107 (53)	0.073 (0.6)	0.083 ($wR2$) (0.047)
T (K)	150	150	170	170	150	100

(R_{int} cited) after "empirical"/multiscan absorption correction (proprietary software), N_o with $F > 4\sigma(F)$ being considered "observed". All data were measured using monochromatic Mo Kα radiation, $\lambda = 0.7107_3$ Å. In the full-matrix least squares refinements on F^2 anisotropic displacement parameter forms were refined for the non-hydrogen atoms, $(x, y, z, U_{iso})_H$ being included following a riding model. Neutral atom complex scattering factors were used; computation used the XTAL 3.7 [35] [weights: $(\sigma^2(F^2) + n_wF^2)^{-1}$] and SHELXL 97 [36] [weights: $(\sigma^2(F^2) + (aP)^2)^{-1}$ $(P = (F_o^2 + 2F_c^2)/3)$] program systems. Pertinent results are given in the figures (which show non-hydrogen atoms with 50% probability amplitude displacement envelopes and hydrogen atoms with arbitrary radii of 0.1 Å, as well as numbering schemes) and in Tables 1 and 3.

Variata. **12**: Weak and limited data supported meaningful anisotropic displacement parameter refinement for Co, P only.

Compound **13**: Phenyl ring 22 was modelled as disordered over two sets of sites, occupancies set at 0.5 after trial refinement.

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Appendix A. Supplementary material

CCDC 656417, 656418, 656419, 656420, 656422, 668738 contain the supplementary crystallographic data for **7**, **13**, **14**, **15**, **16** and **12**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2008.06.007.

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