

Alkynyl and poly-ynyl derivatives of carbon-tricobalt clusters

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Abstract

A series of alkynyl-tricobalt carbonyl clusters, $\text{Co}_3(\mu_3\text{-C}_n\text{R})(\mu\text{-dppm})(\text{CO})_7$ [$\text{R} = \text{Bu}^t, \text{Ph}, \text{C}_6\text{H}_4\text{I}, \text{C}_6\text{H}_4\text{C}\equiv\text{CPh}, \text{SiMe}_3, \text{Fc}, \text{Au}(\text{PPh}_3)$] containing three, five or seven carbons in the chain, have been prepared by elimination of phosphine–gold(I) halides in reactions between $\text{Co}_3(\mu_3\text{-CBr})(\mu\text{-dppm})(\text{CO})_7$ and $\text{Au}(\text{C}\equiv\text{CR})(\text{PPh}_3)$ or between $\text{Co}_3\{\mu_3\text{-CC}\equiv\text{CAu}(\text{PR}_3)\}(\mu\text{-dppm})(\text{CO})_7$ ($\text{R} = \text{Ph}, \text{tol}$) and $\text{IC}\equiv\text{CR}'$ ($\text{R}' = \text{SiMe}_3, \text{Fc}$). The use of poly-substituted arenes or ferrocenes has enabled preparation of the complexes $1,4\text{-}\{(\text{OC})_7(\mu\text{-dppm})\text{-Co}_3(\mu_3\text{-CC}\equiv\text{C})\}_2\text{C}_6\text{H}_3\text{X-5}$ ($\text{X} = \text{H}, \text{Br}$), $1,3,5\text{-}\{(\text{OC})_7(\mu\text{-dppm})\text{Co}_3(\mu_3\text{-CC}\equiv\text{C})\}_3\text{C}_6\text{H}_3$ and $1,1'\text{-}\{(\text{OC})_7(\mu\text{-dppm})\text{Co}_3(\mu_3\text{-CC}\equiv\text{C})\}_2\text{Fc}'$ [$\text{Fc}' = \text{Fe}(\eta\text{-C}_5\text{H}_4)_2$]. The X-ray determined molecular structures of 12 of the complexes are reported.

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Keywords: Carbon-tricobalt cluster; Alkyne; Poly-yne; X-ray structure; Gold

1. 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 [2–4].

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 $[\{\text{Tp}^*(\text{OC})_2\text{M}\}=\text{C}=\text{C}=\text{C}=\{\text{M}(\text{CO})_2\text{Tp}^*\}]^{2+}$ and $\{\text{Tp}^*(\text{OC})_2\text{M}\}\equiv\text{CC}\equiv\text{C}\{\text{M}'(\text{O})_2\text{Tp}^*\}$ ($\text{M}, \text{M}' = \text{Mo}, \text{W}$) [5], $[\{\text{Cp}'(\text{OC})_2\text{Mn}\}\text{-CCC}\{\text{Re}(\text{NO})(\text{PPh}_3)\text{Cp}^*\}]^+$ [6] and $\{(\text{Bu}^t\text{O})_3\text{W}\}\equiv\text{CC}\equiv\text{C}\{\text{Re}(\text{NO})(\text{PPh}_3)\text{Cp}^*\}$ [7]. We and others have considered an approach to this type of complex using a precursor in which a carbyne ligand, $\equiv\text{CR}$, is attached to a metal centre. Recent examples have used the Group 6 complexes $\text{M}(\equiv\text{CR})(\text{CO})_2\text{Tp}'$ [$\text{R} = \text{halogen}, \text{SiMe}_3$; $\text{M} = \text{Mo}, \text{W}$; $\text{Tp}' = \text{BH}(\text{pz})_3$ (Tp), $\text{BH}(\text{dmpz})_3$ (Tp^*)] [8] or cluster-bonded halocarbynes, such as $\text{M}_3(\mu\text{-CR})(\text{CO})_9$ ($\text{M}_3 = \text{Ru}_3(\mu\text{-H})_3$ [9], $\text{Os}_3(\mu\text{-H})_3$ [9], Co_3 [10]).

The trigonal prismatic CCo_3 cluster has been known since the late 1950s [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

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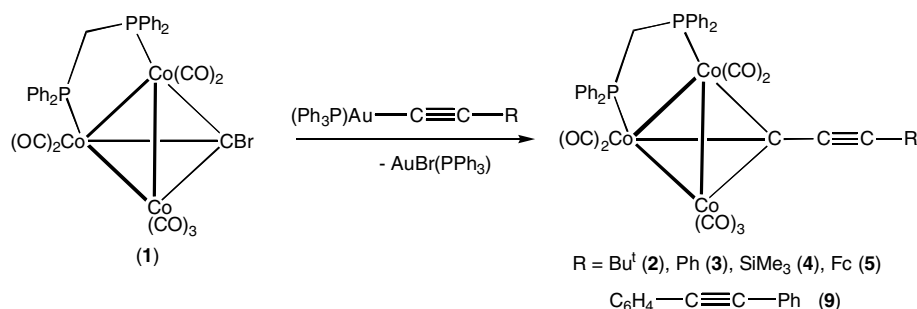
formation of the carbyne–C(sp) bond include the Cadiot–Chodkiewicz, Sonogashira and related reactions [19]. In some instances, appropriate Grignard or Lewis-acid (AlCl_3)-induced coupling reactions between alkynes and $\text{Co}_3(\mu_3\text{-CBr})(\text{CO})_9$ have been employed. It was early noted 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 whereby reactions of $\text{Co}_3(\mu_3\text{-CBr})(\mu\text{-dppm})(\text{CO})_7$ (**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 $\text{AuBr}(\text{PR}_3)$ 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 condi-

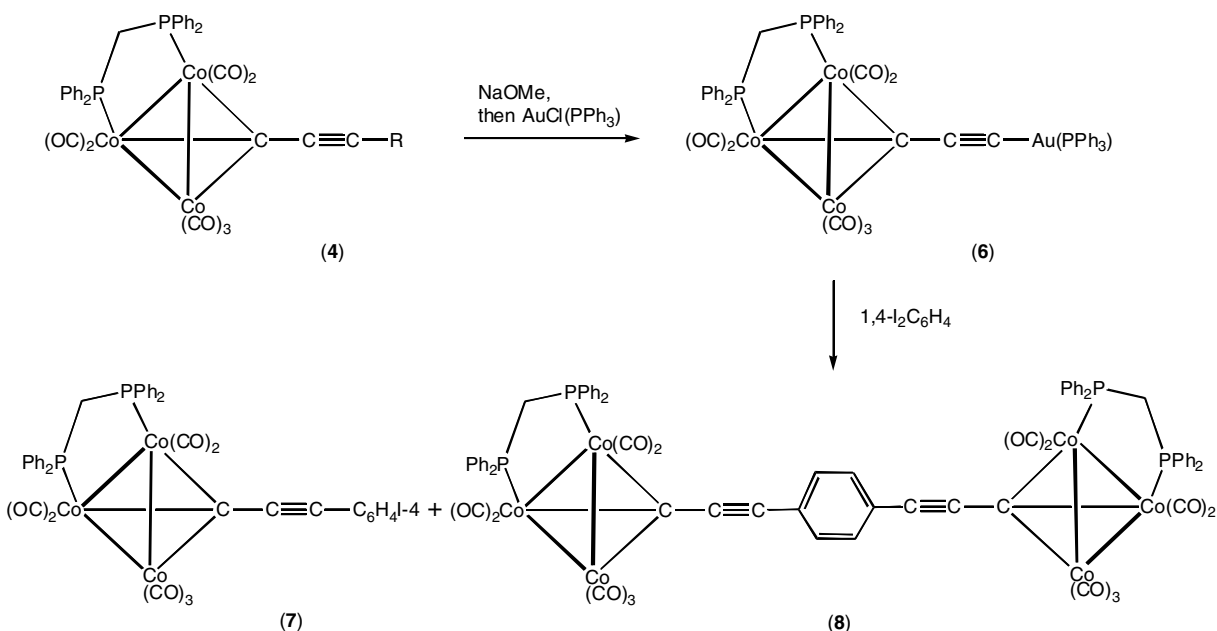
tions of the reaction, in which no base is required, would prevent the formation of unwanted by-products. While our first accounts concentrated on the formation of carbon chains end-capped by the Co_3 cluster and a second metal-containing group [10], we have also extended these reactions to the synthesis of a range of Co_3 clusters containing more conventional groups as described below.

2. Results and discussion

Reactions of $\text{Co}_3(\mu_3\text{-CBr})(\mu\text{-dppm})(\text{CO})_7$ (**1**) [22] with phosphine–gold(I) alkynyls proceed readily in solvents such as thf under mild conditions (r.t., hours) (Scheme 1). 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 $\text{Au}(\text{C}\equiv\text{CR})(\text{PPh}_3)$, or occasionally the $\text{P}(\text{tol})_3$ analogue to improve solubility, which



Scheme 1.

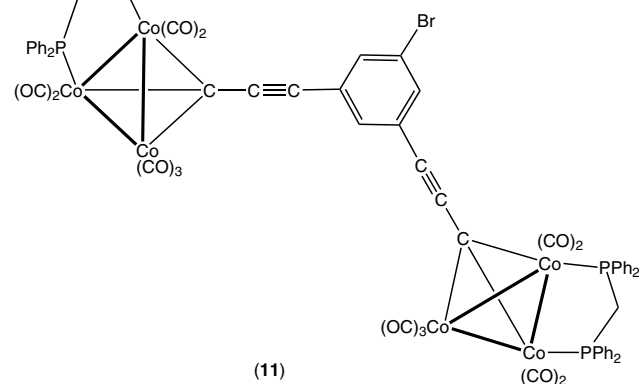
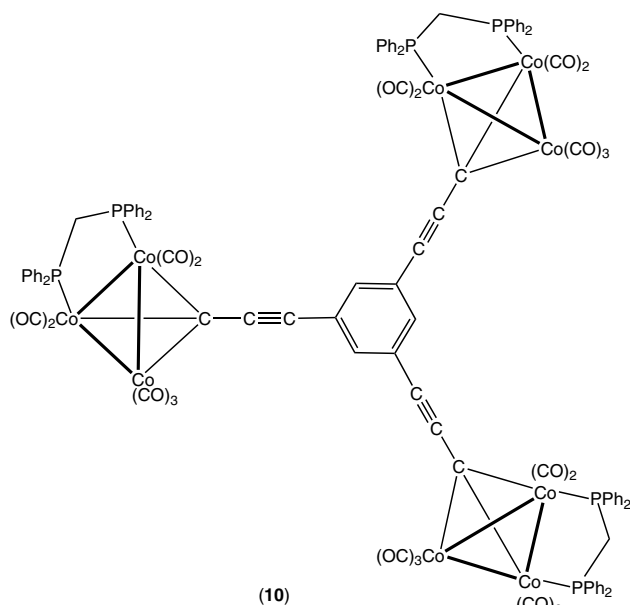


Scheme 2.

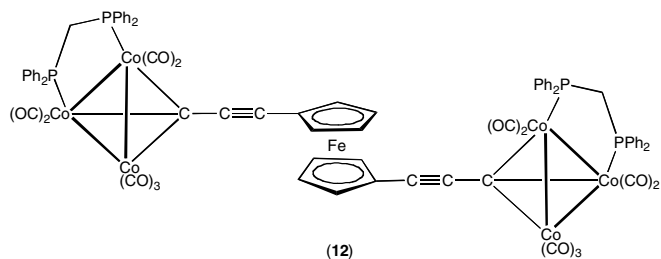
has allowed the complexes $\text{Co}_3(\mu_3\text{-CC}\equiv\text{CR})\text{-}(\mu\text{-dppm})(\text{CO})_7$ to be obtained [$\text{R} = \text{Bu}'$ (**2**, 47%), Ph (**3**, 91%), SiMe_3 (**4**, 86%), Fc (**5**, 91%)]. The co-product $\text{AuBr}(\text{PR}'_3)$ ($\text{R}' = \text{Ph}$, tol) can be easily recovered and recycled. The IR spectra of these complexes contain weak $\nu(\text{C}\equiv\text{C})$ bands at ca. 2130 cm^{-1} and medium to strong $\nu(\text{CO})$ absorptions between 2061 and 1966 cm^{-1} . In addition to common signals at δ 3.44 and 4.49 and between δ 6.5 and 8.0 arising from the dppm ligand, the ^1H NMR spectra contain other resonances characteristic of the R groups present. Limited solubility restricted the availability of ^{13}C NMR spectra, but in **2**, signals at δ 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 δ 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 12 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 $\text{C}(\text{sp}$ or $\text{sp}^2)\text{-I}$ bonds. Thus, the reaction between $\text{Co}_3\{\mu_3\text{-CC}\equiv\text{CAu}(\text{PPh}_3)\}(\mu\text{-dppm})(\text{CO})_7$ (**6**), itself prepared from the SiMe_3 derivative **4** and $\text{AuCl}(\text{PPh}_3)$ in the presence of sodium methoxide, and 1,4- $\text{I}_2\text{C}_6\text{H}_4$ afforded two complexes which were characterised as $\text{Co}_3(\mu_3\text{-CC}\equiv\text{CC}_6\text{H}_4\text{I-4})(\mu\text{-dppm})(\text{CO})_7$ (**7**) which is green, and orange-brown 1,4- $\{(\text{OC})_7(\mu\text{-dppm})\text{Co}_3(\mu_3\text{-CC}\equiv\text{C})\}_2\text{C}_6\text{H}_4$ (**8**) (Scheme 2). Similarly, the reaction between $\text{Au}(\text{C}\equiv\text{CC}_6\text{H}_4\text{C}\equiv\text{CPh})(\text{PPh}_3)$ and **1** afforded $\text{Co}_3(\mu_3\text{-CC}\equiv\text{CC}_6\text{H}_4\text{C}\equiv\text{CPh})(\mu\text{-dppm})(\text{CO})_7$ (**9**). These complexes were readily separated by preparative t.l.c. and identified by elemental analysis and from 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- $\{(\text{Ph}_3\text{P})\text{AuC}\equiv\text{C}\}_3\text{-C}_6\text{H}_3$ enabled preparation of the tris-cluster complex 1,3,5- $\{(\text{OC})_7(\mu\text{-dppm})\text{Co}_3(\mu_3\text{-CC}\equiv\text{C})\}_3\text{C}_6\text{H}_3$ (**10**) in 50% yield. This compound has a similar $\nu(\text{CO})$ spectrum to the complexes described above, while the ^{13}C NMR spectrum contains resonances at δ 108.92 and 112.76 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- $\{(\text{OC})_7(\mu\text{-dppm})\text{Co}_3(\mu_3\text{-CC}\equiv\text{C})\}_2\text{C}_6\text{H}_3\text{Br-5}$ (**11**) from an analogous reaction in which the bromoaryl-diyne 1,3- $\{(\text{Ph}_3\text{P})\text{AuC}\equiv\text{C}\}_2\text{C}_6\text{H}_3\text{Br-5}$ was inadvertently used. Its spectroscopic properties were similar to those found for **9**, with the exception of the negative ion ES MS, in which the peak at a m/z 1741 corresponds to $[\text{M}-\text{H}]^-$.



In addition to **8**, which contains two Co_3 clusters end-capping the organic ligand, we have prepared 1,1'- $\{(\text{OC})_7(\mu\text{-dppm})\text{Co}_3(\mu_3\text{-CC}\equiv\text{C})\}_2\text{Fc}'$ [**12**, $\text{Fc}' = \text{Fe}(\eta\text{-C}_5\text{H}_4\text{-})_2$] in 96% yield from the related reaction between 1,1'- $\text{Fc}'\{\text{C}\equiv\text{CAu}[\text{P}(\text{tol})_3]\}_2$ and $\text{Co}_3(\mu_3\text{-CBr})(\mu\text{-dppm})(\text{CO})_7$. This dark red complex has an IR $\nu(\text{CO})$ spectrum similar to those of the other complexes described above, together with a $\nu(\text{C}\equiv\text{C})$ band at 2122 cm^{-1} . The ^1H NMR spectrum has two multiplets at δ 4.40 and 4.53 (4H each) assigned to the C_5H_4 protons of the ferrocene nucleus, while the ES MS of a solution containing NaOMe has $[\text{M}+\text{Na}]^+$ at m/z 1793.



Related complexes with C_5 chains, such as $Co_3(\mu_3-CC\equiv C\equiv CR)(\mu-dppm)(CO)_7$ [$R = SiMe_3$, $Au(PPh_3)$, Fc] have been described earlier [10]. Extension to systems containing C_7 chains was easily achieved in reactions between $Co_3\{\mu_3-CC\equiv C\equiv CAu(PPh_3)\}(\mu-dppm)(CO)_7$ [10] and $IC\equiv CSiMe_3$ [25] or $IC\equiv CFc$ [26] which gave $Co_3\{\mu_3-C(C\equiv C)_3R\}(\mu-dppm)(CO)_7$ [$R = SiMe_3$ (**13**, 54%), Fc (**14**, 87%)] and the further conversion of **13** by treatment with $NaOMe$ and $AuCl(PPh_3)$ gave $Co_3\{\mu_3-C(C\equiv C)_3-Au(PPh_3)\}(\mu-dppm)(CO)_7$ (**15**) in 75% yield (Scheme 3). The complex $Co_3\{\mu_3-CC\equiv C\equiv CAu(PPh_3)\}(\mu-dppm)(CO)_7$ has been converted to $Co_3\{\mu_3-C(C\equiv C)_3Ph\}(\mu-dppm)(CO)_7$ (**16**) in 60% yield by sequential reactions with iodine and $Au(C\equiv CPh)(PPh_3)$, without isolation of the presumed intermediate iododiyne complex $Co_3(\mu_3-CC\equiv C\equiv CI)(\mu-dppm)(CO)_7$.

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 δ_H 0.26, while for **14**, resonances at δ_H 4.28, 4.30 and 4.56 and δ_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 δ 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 δ 57 and 99 are assigned to five of the seven chain carbons, the Co_3C atom again not being observed.

3. 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

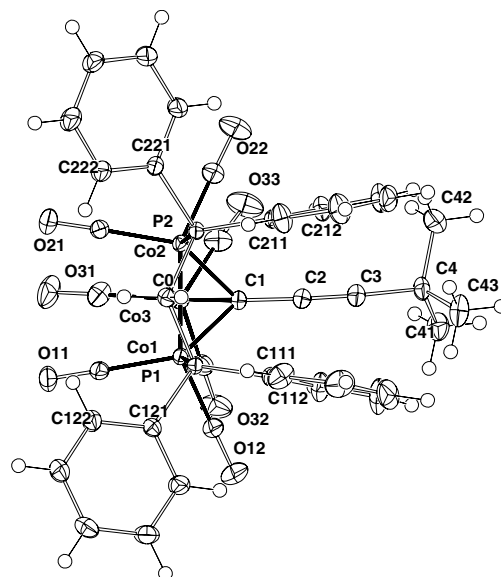
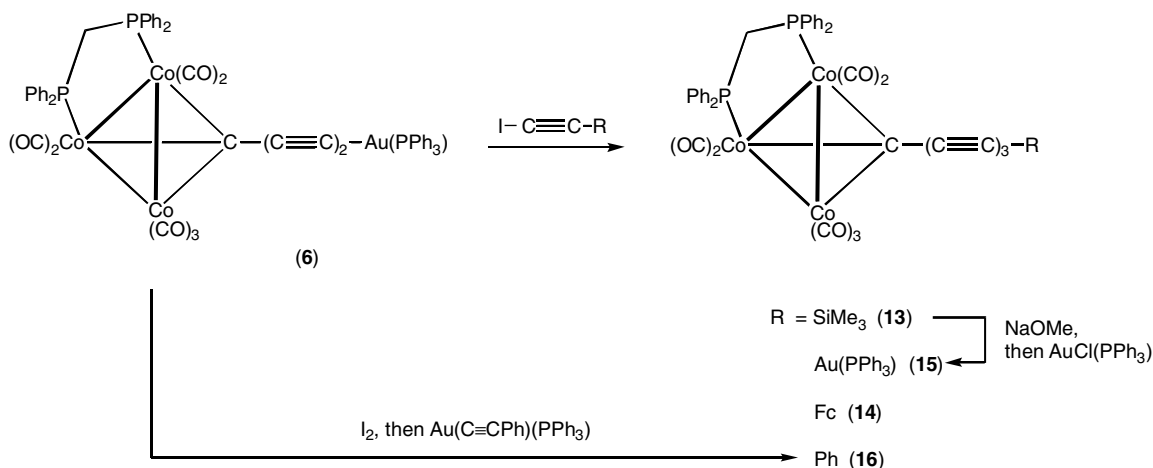


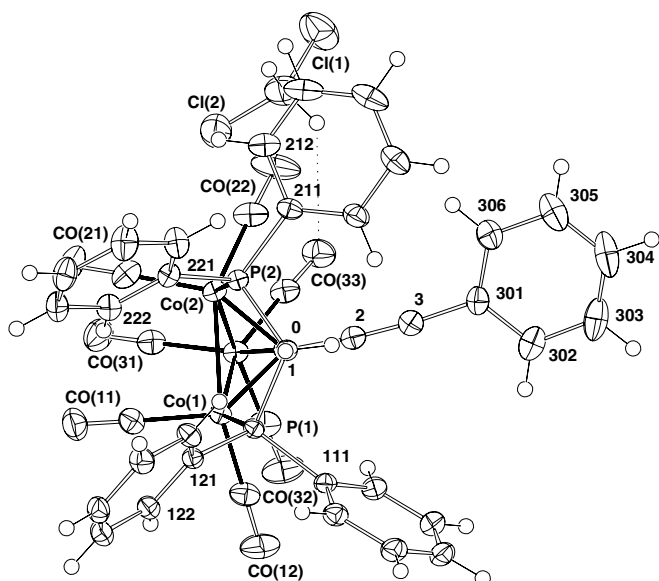
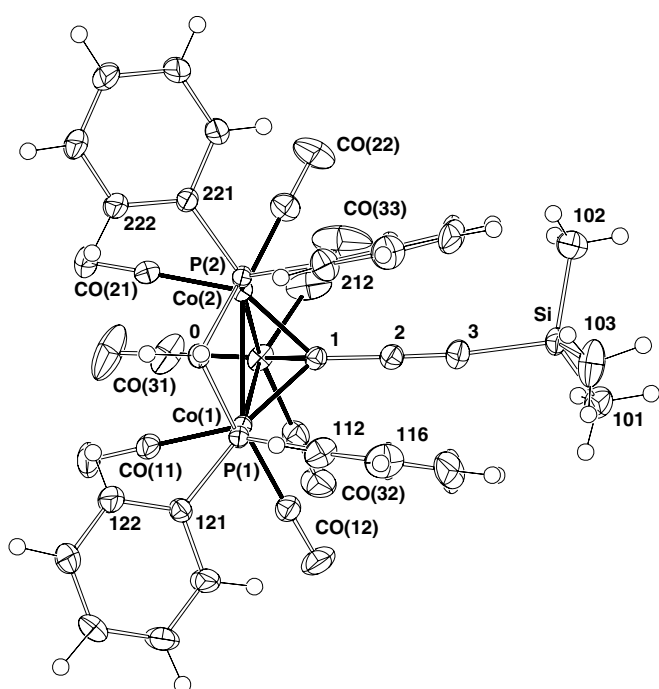
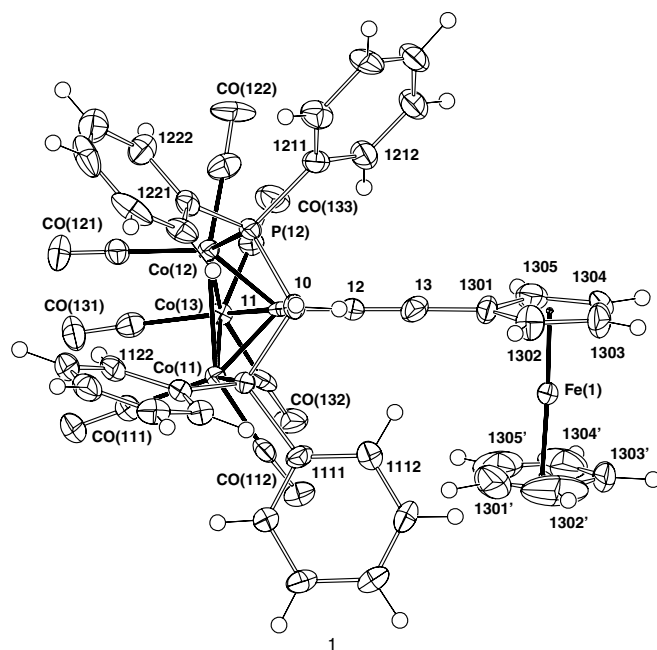
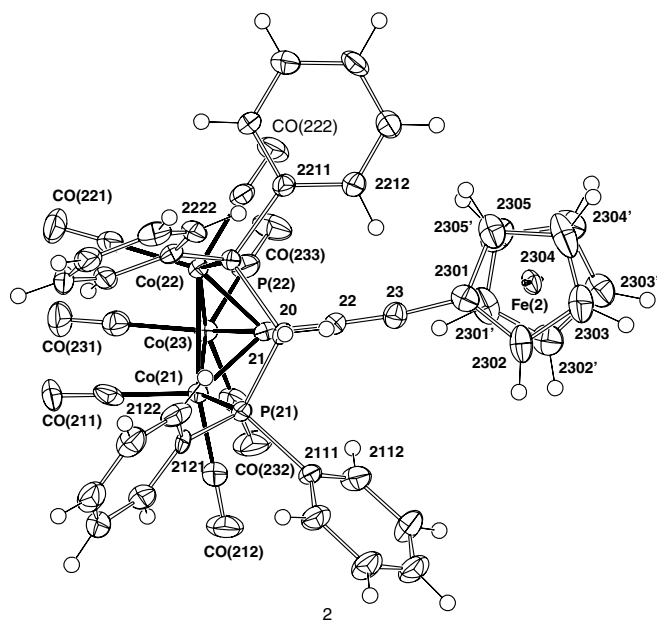
Fig. 1. Plot of a molecule of $Co_3(\mu_3-CC\equiv CBu^t)(\mu-dppm)(CO)_7$ (**2**).

common structural feature the $Co_3(\mu_3-CC\equiv C)(\mu-dppm)(CO)_7$ 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, all distances are identical (2.48 Å), with ranges for

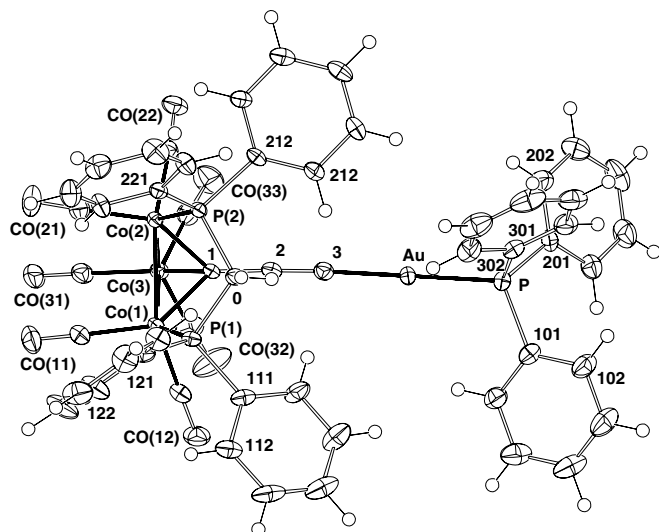
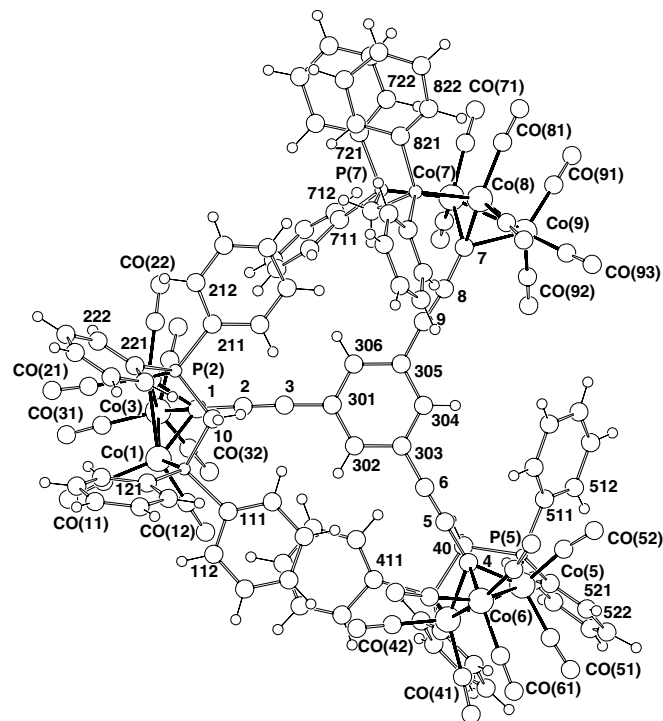
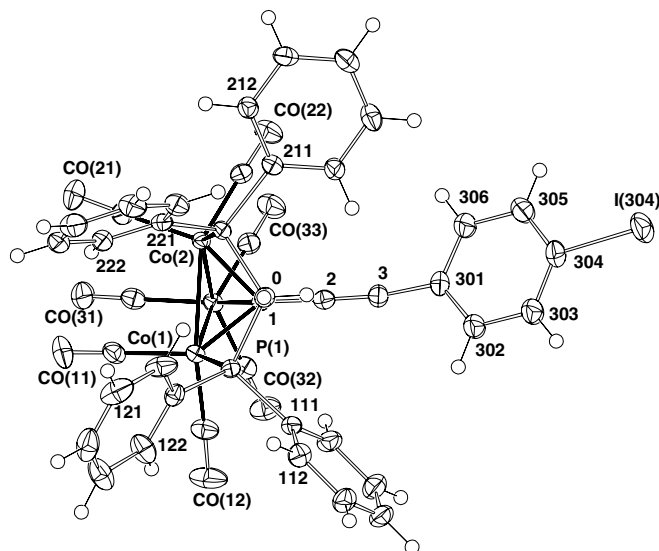
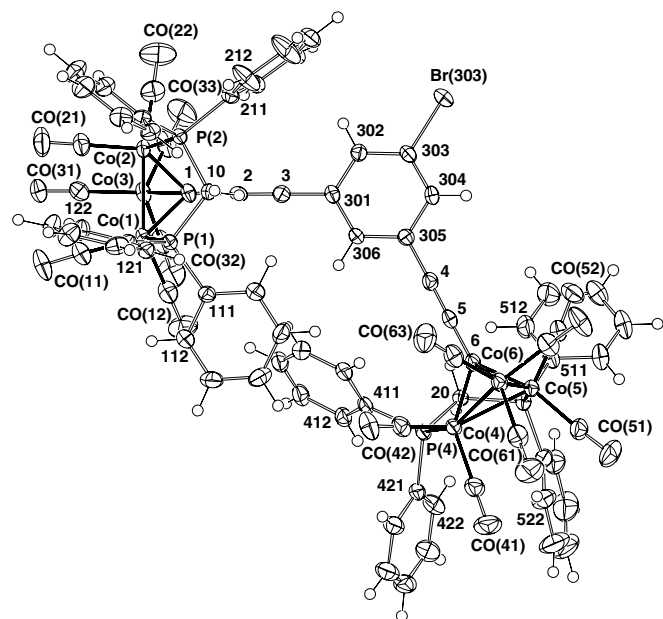
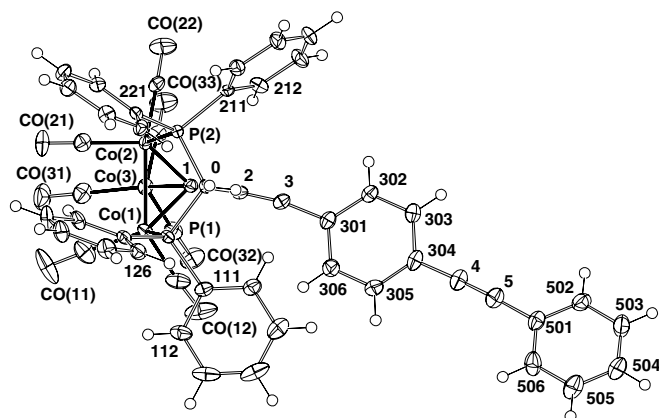


Scheme 3.

Fig. 2. Plot of a molecule of $\text{Co}_3(\mu_3\text{-CC}\equiv\text{CPh})(\mu\text{-dppm})(\text{CO})_7$ (**3**).Fig. 3. Plot of a molecule of $\text{Co}_3(\mu_3\text{-CC}\equiv\text{CSiMe}_3)(\mu\text{-dppm})(\text{CO})_7$ (**4**).Fig. 4. Plots of molecules **1** and **2** of $\text{Co}_3(\mu_3\text{-CC}\equiv\text{CFe})(\mu\text{-dppm})(\text{CO})_7$ (**5**).

Co(1)–Co(2) of between 2.4624 and 2.5144 Å and for Co(1,2)–Co(3) of 2.4651 and 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 and 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

Fig. 5. Plot of a molecule of $\text{Co}_3\{\mu_3\text{-CC}\equiv\text{CAu(PPh}_3)\}(\mu\text{-dppm})(\text{CO})_7$ (**6**).Fig. 8. Plot of a molecule of $1,3,5\text{-C}_6\text{H}_3\{\text{C}\equiv\text{C-}\mu_3\text{-C}[\text{Co}_3(\mu\text{-dppm})(\text{CO})_7]\}_3$ (**10**).Fig. 6. Plot of a molecule of $\text{Co}_3(\mu_3\text{-CC}\equiv\text{CC}_6\text{H}_4\text{I-4})(\mu\text{-dppm})(\text{CO})_7$ (**7**).Fig. 9. Plot of a molecule of $1,3,5\text{-C}_6\text{H}_3\text{Br}\{\text{C}\equiv\text{C-}\mu_3\text{-C}[\text{Co}_3(\mu\text{-dppm})(\text{CO})_7]\}_2$ (**11**).Fig. 7. Plot of a molecule of $\text{Co}_3(\mu_3\text{-CC}\equiv\text{CC}_6\text{H}_4\text{C}\equiv\text{CPh-4})(\mu\text{-dppm})(\text{CO})_7$ (**9**).

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), Σ , being 19.4° (for **11**) and 23.6° (for **12**). Others have commented previously about the facile bending of $\text{C}(\text{sp})$ chains, the most probable explanation being found in intermolecular

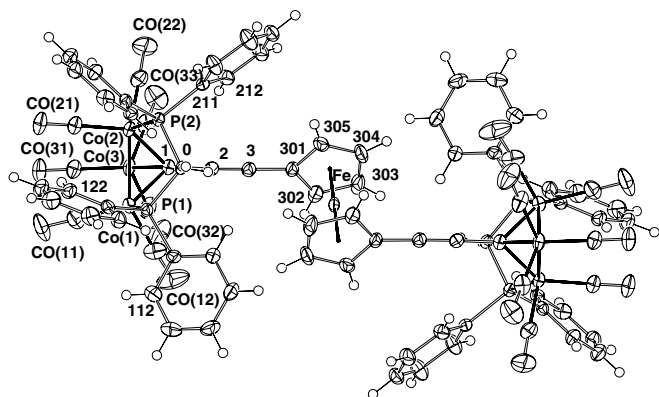


Fig. 10. Plot of a molecule of $1,1'\text{-Fc}'\{\text{C}\equiv\text{C}-\mu_3\text{-C}[\text{Co}_3(\mu\text{-dppm})(\text{CO})_7]\}_2$ (12).

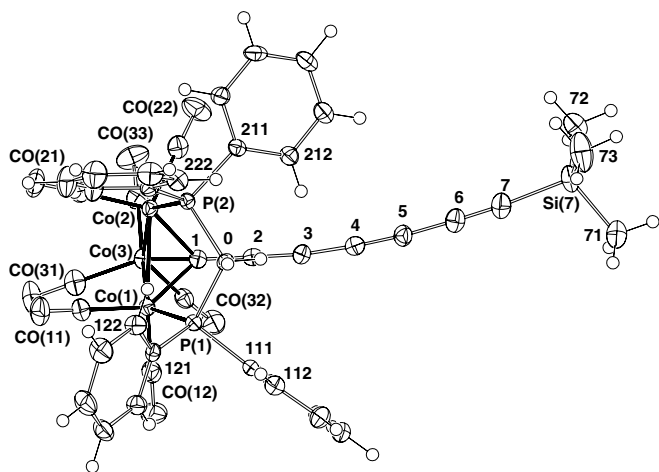


Fig. 11. Plot of a molecule of $\text{Co}_3\{\mu_3\text{-C}(\text{C}\equiv\text{C})_3\text{SiMe}_3\}(\mu\text{-dppm})(\text{CO})_7$ (13).

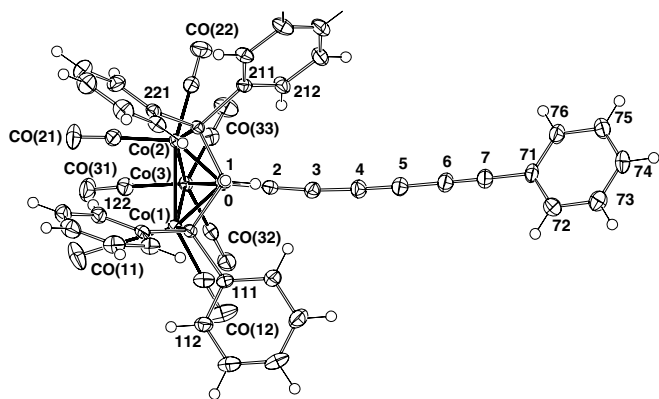


Fig. 12. Plot of a molecule of $\text{Co}_3\{\mu_3\text{-C}(\text{C}\equiv\text{C})_3\text{Ph}\}(\mu\text{-dppm})(\text{CO})_7$ (16).

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.

4. Experimental

4.1. General

All reactions were carried out under dry nitrogen, although normally no special precautions to exclude air were taken during subsequent work-up. Common solvents were dried, distilled under argon and degassed before use. Separations were carried out by preparative thin-layer chromatography on glass plates (20 × 20 cm²) coated with silica gel (Merck, 0.5 mm thick).

4.2. Instruments

IR spectra were obtained on a Bruker IFS28 FT-IR spectrometer. Spectra in CH₂Cl₂ 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, ¹³C at 75.47 MHz, ³¹P at 121.503 MHz). Unless otherwise stated, samples were dissolved in CDCl₃ contained in 5 mm sample tubes. Chemical shifts are given in ppm relative to internal tetramethylsilane for ¹H and ¹³C NMR spectra and external H₃PO₄ for ³¹P 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.

4.3. Reagents

Co₃(μ₃-CBr)(μ-dppm)(CO)₇ [27], IC≡CFc [26], AuCl(PR₃) (R = Ph; tol made similarly) [35], and Au(C≡CR') (PR₃) (R' = Bu^t, Ph, SiMe₃, Fc) and {Au(PR₃)₂(μ-C≡CC₆H₄C≡C)} were obtained as previously described [36,37].

4.4. Preparation of Au(C≡CC₆H₄C≡CPh)(PPh₃)

Sodium (30 mg, 1.3 mg atom) was added to a solution of AuCl(PPh₃) (91 mg, 0.184 mmol) in MeOH (28 ml). After hydrogen evolution had ceased, a solution of HC≡CC₆H₄C≡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 with benzene. Concentration of the extract to 3 ml and diffusion

Table 1
Selected bond parameters for some alkynyl-Co₃C complexes

Bond	2	3	4	5 ^a
<i>Distances (Å)</i>				
Co(1)–Co(2)	2.5103(6)	2.4794(4)	2.4924(6)	2.465, 2.460(1)
Co(1)–Co(3)	2.5085(4)	2.4867(5)	2.4719(5)	2.468, 2.485(1)
Co(2)–Co(3)	2.4989(4)	2.4831(4)	2.4651(4)	2.484, 2.486(1)
Co(1)–P(1)	2.2154(5)	2.1938(6)	2.1896(6)	2.177, 2.195(2)
Co(2)–P(2)	2.2118(4)	2.2018(6)	2.1842(6)	2.189, 2.191(2)
P(1)–C(0)	1.862(1)	1.832(2)	1.836(2)	1.842, 1.839(7)
P(2)–C(0)	1.858(2)	1.830(2)	1.832(2)	1.843, 1.843(7)
Co(1)–C(1)	1.918(2)	1.896(2)	1.895(2)	1.910, 1.903(6)
Co(2)–C(1)	1.928(1)	1.906(2)	1.898(2)	1.895, 1.911(6)
Co(3)–C(1)	1.978(1)	1.932(2)	1.943(2)	1.914, 1.940(8)
C(1)–C(2)	1.422(2)	1.403(3)	1.403(3)	1.409, 1.384(10)
C(2)–C(3)	1.225(2)	1.209(3)	1.217(3)	1.206, 1.205(10)
C(3)–X [X]	1.494(2) [C(4)]	1.433(3) [C(301)]	1.824(2) [Si]	1.405, 1.433(10) [C(301)]
<i>Angles (°)</i>				
Co(3)–Co(1)–P(1)	153.68(2)	146.77(2)	154.05(2)	148.49, 147.14(6)
Co(3)–Co(2)–P(2)	155.67(1)	147.3(2)	155.00(2)	147.26, 147.88(6)
P(1)–C(0)–P(2)	106.83(7)	110.5(1)	107.3(1)	108.2, 108.9(4)
Co(1)–C(1)–C(2)	137.0(1)	139.2(2)	136.2(2)	130.6, 137.8(5)
Co(2)–C(1)–C(2)	134.1(1)	126.0(2)	134.2(1)	137.0, 126.4(4)
Co(3)–C(1)–C(2)	122.9(1)	128.3(2)	123.1(1)	126.5, 130.6(5)
C(1)–C(2)–C(3)	176.7(2)	175.8(2)	177.9(2)	179.8, 177.1(7)
C(2)–C(3)–X [X]	177.3(2) [C(4)]	175.9(2) [C(301)]	174.7(2) [Si]	178.8, 174.1(8) [C(301)]
Bond	6 ^b	7 ^b	9 ^c	10 ^d
<i>Distances (Å)</i>				
Co(1)–Co(2)	2.4628(7)	2.4760(5)	2.4870(7)	2.467, 2.463, 2.484(5)
Co(1)–Co(3)	2.4743(8)	2.4804(7)	2.4802(7)	2.486, 2.469, 2.475(5)
Co(2)–Co(3)	2.4982(7)	2.4884(8)	2.4801(7)	2.505, 2.489, 2.480(5)
Co(1)–P(1)	2.192(1)	2.194(1)	2.203(1)	2.190, 2.194, 2.200(9)
Co(2)–P(2)	2.202(1)	2.203(1)	2.200(1)	2.193, 2.205, 2.207(9)
P(1)–C(0)	1.825(3)	1.839(3)	1.824(3)	1.84, 1.83, 1.80(3)
P(2)–C(0)	1.836(6)	1.849(3)	1.831(4)	1.87, 1.84, 1.84(3)
Co(1)–C(1)	1.907(3)	1.907(3)	1.927(4)	1.96, 1.95, 1.93(2)
Co(2)–C(1)	1.910(4)	1.921(3)	1.888(4)	1.88, 1.86, 1.92(3)
Co(3)–C(1)	1.928(4)	1.934(3)	1.935(4)	1.96, 1.92, 1.98(4)
C(1)–C(2)	1.401(5)	1.394(4)	1.394(5)	1.38, 1.41, 1.39(5)
C(2)–C(3)	1.213(6)	1.214(5)	1.213(5)	1.24, 1.20, 1.17(5)
C(3)–X [X]	1.983(4) [Au]	1.436(5) [C(301)]	1.434(5) [C(301)]	1.44, 1.42, 1.43(5) [C(30n)]
<i>Angles (°)</i>				
Co(3)–Co(1)–P(1)	148.08(3)	145.62(3)	149.82(3)	147.1, 146.2, 146.9(2)
Co(3)–Co(2)–P(2)	143.48(4)	147.66(3)	148.42(3)	146.5, 147.4, 149.5(3)
P(1)–C(0)–P(2)	110.4(2)	110.3(2)	109.2(2)	107, 108, 110(2)
Co(1)–C(1)–C(2)	133.4(3)	136.1(2)	124.2(3)	129, 127, 130(2)
Co(2)–C(1)–C(2)	133.5(2)	127.8(2)	138.8(3)	140, 139, 139(2)
Co(3)–C(1)–C(2)	128.0(3)	131.0(2)	130.9(3)	126, 128, 128(2)
C(1)–C(2)–C(3)	177.3(4)	175.1(5)	174.3(4)	177, 178, 173(3)
C(2)–C(3)–X [X]	171.3(3) [Au]	171.4(4) [C(301)]	167.9(4)	178, 179, 175(3)
Bond	11 ^e	12	13 ^f	16 ^g
<i>Distances (Å)</i>				
Co(1)–Co(2)	2.4789, 2.5144(7)	2.4788(6)	2.4624(6)	2.4853(5)
Co(1)–Co(3)	2.4760, 2.4779(7)	2.4738(6)	2.4612(6)	2.4922(5)
Co(2)–Co(3)	2.4654, 2.4728(7)	2.4695(6)	2.4853(7)	2.4855(5)
Co(1)–P(1)	2.192, 2.211(1)	2.1923(9)	2.179(1)	2.2023(7)
Co(2)–P(2)	2.189, 2.186(1)	2.1915(9)	2.210(1)	2.2136(7)
P(1)–C(0)	1.826, 1.836(3)	1.830(3)	1.832(3)	1.830(2)
P(2)–C(0)	1.839, 1.829(3)	1.838(3)	1.842(4)	1.839(2)
Co(1)–C(1)	1.903, 1.893(3)	1.905(3)	1.903(4)	1.911(2)
Co(2)–C(1)	1.900, 1.895(3)	1.895(3)	1.903(4)	1.905(2)
Co(3)–C(1)	1.923, 1.951(4)	1.930(3)	1.942(4)	1.937(2)
C(1)–C(2)	1.405, 1.405(5)	1.402(4)	1.381(6)	1.385(3)

(continued on next page)

Table 1 (continued)

Bond	11 ^c	12	13 ^f	16 ^g
C(2)–C(3)	1.210, 1.201(5)	1.209(4)	1.224(7)	1.230(3)
C(3)–X	1.431, 1.440(5) [C(301, 305)]	1.419(4) [C(301)]	1.343(7) [C(4)]	1.355(4) [C(4)]
<i>Angles (°)</i>				
Co(3)–Co(1)–P(1)	147.28, 149.83(4)	149.97(3)	146.44(4)	147.47(2)
Co(3)–Co(2)–P(2)	146.61, 152.08(3)	147.49(3)	148.25(4)	149.24(2)
P(1)–C(0)–P(2)	108.8, 110.9(2)	108.1(1)	111.8(2)	109.1(1)
Co(1)–C(1)–C(2)	130.6, 134.7(3)	131.2(2)	136.5(3)	129.1(2)
Co(2)–C(1)–C(2)	132.7, 133.1(3)	135.2(2)	130.0(3)	137.2(2)
Co(3)–C(1)–C(2)	131.3, 125.2(3)	128.1(2)	129.0(3)	127.7(2)
C(1)–C(2)–C(3)	176.5, 178.9(4)	178.2(3)	178.0(4)	177.6(3)
C(2)–C(3)–X	179.3, 178.1(4) [C(301, 305)]	175.8(3) [C(301)]	173.0(4) [C(4)]	174.1(3) [C(4)]

^a For **5**: Values for two independent molecules.

^b For **6**: Au–P 2.271(1) Å, C(3)–Au–P 175.4(1)°.

^c For **7**: C(304)–I 2.105(3) Å.

^d For **9**: C(304)–C(4) 1.431(6), C(4)–C(5) 1.203(6), C(5)–C(501) 1.420(6) Å; C(304)–C(4)–C(5) 177.6(5), C(4)–C(5)–C(501) 177.4(5)°. For **10**: Second and third entries are for second and third clusters involving Co(4–6), P(4,5), C(303, 4–6) and Co(7–9), P(7,8), C(305, 7–9).

^e For **11**: Second entries are values for second cluster involving Co(4–6), P(4,5), C(305, 4–6). C(303)–Br 1.895(3) Å.

^f For **13**: C(4)–C(5) 1.226(7), C(5)–C(6) 1.358(7), C(6)–C(7) 1.209(7), C(7)–Si 1.845(6) Å; C(3)–C(4)–C(5) 175.5(4), C(4)–C(5)–C(6) 175.7(4), C(5)–C(6)–C(7) 178.3(4), C(6)–C(7)–Si 175.9(4)°.

^g For **16**: C(4)–C(5) 1.217(4), C(5)–C(6) 1.366(4), C(6)–C(7) 1.203(4), C(7)–C(71) 1.437(4) Å; C(3)–C(4)–C(5) 177.6(3), C(4)–C(5)–C(6) 176.1(3), C(5)–C(6)–C(7) 176.8(3), C(6)–C(7)–C(71) 178.4(3)°.

of heptane (3 ml) into the concentrated solution gave light yellow microcrystalline $\text{Au}(\text{C}\equiv\text{CC}_6\text{H}_4\text{C}\equiv\text{CPh})(\text{PPh}_3)$ (99.5 mg, 83%), which was washed with hexane and dried. Anal. Calc. for $\text{C}_{34}\text{H}_{24}\text{AuP}$ (Mw = 660): C, 61.82; H, 3.64. Found: C, 61.62; H, 3.57%. IR (CH_2Cl_2): $\nu(\text{C}\equiv\text{C})$ 2114w cm^{-1} . ^1H NMR: δ 7.27–7.60 (m, 24H, Ph + C_6H_4). ^{31}P NMR: δ 42.6 (s, PPh_3). ES-MS: (positive ion, MeOH + NaOMe, m/z): 683, $[\text{M}+\text{Na}]^+$.

4.5. Preparation of 1,3,5- $\{(\text{Ph}_3\text{P})\text{AuC}\equiv\text{C}\}_3\text{C}_6\text{H}_3$

A modified literature method [38] was used. NaOMe (excess) in MeOH (4 ml) was added to a solution of $\text{AuCl}(\text{PPh}_3)$ (202.7 mg, 0.41 mmol) and 1,3,5- $(\text{Me}_3\text{SiC}\equiv\text{C})_3\text{C}_6\text{H}_3$ (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 sintered filter with MeOH (5 ml) and washed with more MeOH and hexane, and dried in air to give 1,3,5- $\{(\text{Ph}_3\text{P})\text{AuC}\equiv\text{C}\}_3\text{C}_6\text{H}_3$ (181 mg, 87%) as a pale yellow solid. ^1H NMR: δ 7.47–7.59 (m, Ph). ^{13}C NMR: δ 103.62 ($\text{C}\equiv\text{C}$), 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: δ 49.3 (s, PPh_3).

4.6. Preparation of carbon-tricobalt complexes

4.6.1. $\text{Co}_3(\mu_3\text{-CC}\equiv\text{CR})(\mu\text{-dppm})(\text{CO})_7$

4.6.1.1. $R = \text{Bu}^t$ (**2**). A mixture of $\text{Au}(\text{C}\equiv\text{CBu}^t)(\text{PPh}_3)$ (64 mg, 0.12 mmol), $\text{Co}_3(\mu_3\text{-CBr})(\mu\text{-dppm})(\text{CO})_7$ (100 mg, 0.12 mmol), $\text{Pd}(\text{PPh}_3)_4$ (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_2Cl_2 and separated by preparative t.l.c. (hexane–acetone 5/1). The major brown band (R_f 0.41) contained $\text{Co}_3(\mu_3\text{-CC}\equiv\text{CBu}^t)(\mu\text{-dppm})(\text{CO})_7$ (**2**) (47 mg, 47%) which was isolated as dark brown crystals ($\text{CH}_2\text{Cl}_2/\text{MeOH}$). Anal. Calc. for $\text{C}_{39}\text{H}_{31}\text{Co}_3\text{O}_7\text{P}_2$ (MW = 850): C, 55.06; H, 3.65. Found: C, 55.09; H, 3.42%. IR (CH_2Cl_2 , cm^{-1}): $\nu(\text{C}\equiv\text{C})$ 2131vw; $\nu(\text{CO})$ 2057s, 2007vs, 1987 (sh), 1966 (sh); (cyclohexane): $\nu(\text{CO})$ 2061s, 2015vs, 2011vs, 1997m, 1984w, 1976m, 1960w. ^1H NMR: δ 1.41 (s, 9H, Bu^t), 3.49, 4.41 (2 × s, 2 × 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, $J(\text{CP})$ 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 × s, br, CO). ^{31}P NMR: δ 33.8 (s, dppm). ES-MS (MeOH, m/z): 850, M^+ .

4.6.1.2. $R = \text{Ph}$ (**3**). Method A: A mixture of $\text{Au}(\text{C}\equiv\text{CPh})(\text{PPh}_3)$ (66 mg, 0.12 mmol), $\text{Co}_3(\mu_3\text{-CBr})(\mu\text{-dppm})(\text{CO})_7$ (100 mg, 0.12 mmol), $\text{Pd}(\text{PPh}_3)_4$ (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_2Cl_2 and purified by preparative t.l.c. (acetone–hexane 3/7). The major brown-green band (R_f 0.69) contained $\text{Co}_3(\mu_3\text{-CC}\equiv\text{CPh})(\mu\text{-dppm})(\text{CO})_7$ (**3**) (93.2 mg, 91%) as dark green crystals ($\text{CH}_2\text{Cl}_2/\text{MeOH}$). Anal. Calc. for $\text{C}_{41}\text{H}_{27}\text{Co}_3\text{O}_7\text{P}_2 \cdot 0.5\text{CH}_2\text{Cl}_2$ (MW = 870): C, 54.57; H, 3.28. Found: C, 54.73; H, 2.75%. IR (CH_2Cl_2 , cm^{-1}): $\nu(\text{C}\equiv\text{C})$ 2116vw; $\nu(\text{CO})$ 2058s, 2009vs, 1989 (sh), 1969 (sh), 1948 (sh). ^1H NMR: δ 3.44, 4.49 (2 × s, 2 × 1H, dppm), 5.30 (s, CH_2Cl_2), 7.14–7.59 (m, 25H, Ph). ^{31}P NMR: δ 34.2 [s (br), dppm]. ES-MS (positive ion, MeOH + NaOMe, m/z): 893, $[\text{M}+\text{Na}]^+$; (negative ion, MeOH, m/z): 869, $[\text{M}-\text{H}]^-$.

Method B: When $\text{Ag}(\text{C}\equiv\text{CPh})(\text{PPh}_3)$ was used under the same conditions, **3** was obtained in 55% yield.

4.6.1.3. $R = \text{SiMe}_3$ (**4**). Method A: $\text{Pd}(\text{PPh}_3)_4$ (6 mg, 0.005 mmol) and CuI (1 mg, 0.005 mmol) were added to a solution of $\text{Co}_3(\mu_3\text{-CBr})(\mu\text{-dppm})(\text{CO})_7$ (84.9 mg, 0.1 mmol) and $\text{Au}(\text{C}\equiv\text{CSiMe}_3)(\text{PPh}_3)$ (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 silica gel column using the same solvent mixture as eluent. A major brown-green fraction was collected and after evaporation gave $\text{Co}_3(\mu_3\text{-CC}\equiv\text{CSiMe}_3)(\mu\text{-dppm})(\text{CO})_7$ (**4**) (75 mg, 86%) as dark green crystals (hexane). Anal. Calc. for $\text{C}_{38}\text{H}_{31}\text{Co}_3\text{O}_7\text{P}_2\text{Si}$ (MW = 866): C, 52.68; H, 3.61. Found: C, 52.64; H, 3.62. IR (CH_2Cl_2 , cm^{-1}): $\nu(\text{C}\equiv\text{C})$ 2138vw; $\nu(\text{CO})$ 2065s, 2048s, 2010vs, 1990 (sh). ^1H NMR: δ 0.32 (s, 9H, SiMe_3), 3.49, 4.54 (2 \times m, 2 \times 1H, CH_2), 7.13–7.58 (m, 20H, Ph). ^{13}C NMR: δ 0.10 (s, SiMe_3), 39.52 [t, $J(\text{CP})$ 25.4 Hz, dppm], 116.70, 126.19 (2 \times s, carbon chain), 128.22–137.28 (m, Ph), 202.13, 210.08, 225.14 [s (br), CO]. ^{31}P NMR: δ 33.3 [s (br), dppm]. ES-MS (positive ion, $\text{MeOH} + \text{NaOMe}$, m/z): 889, $[\text{M} + \text{Na}]^+$; (negative ion, $\text{MeOH} + \text{NaOMe}$, m/z), 865, $[\text{M} - \text{H}]^-$.

Method B: A solution of $\text{Co}_3(\mu_3\text{-CBr})(\mu\text{-dppm})(\text{CO})_7$ (200 mg, 0.24 mmol) and $\text{HC}\equiv\text{CSiMe}_3$ (48 mg, 0.5 mmol) in thf (10 ml) was treated with CuI (2 mg, 0.012 mmol) and $\text{Pd}(\text{PPh}_3)_4$ (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 $\text{Co}_3(\mu_3\text{-CC}\equiv\text{CSiMe}_3)(\mu\text{-dppm})(\text{CO})_7$ (**4**) (157 mg, 75%). A minor product formed on some occasions was identified as $\{\text{Co}_3(\mu\text{-dppm})(\text{CO})_7\}_2(\mu_3\text{-}\mu_3\text{-C}_6)$ [**10a**].

4.6.1.4. $R = \text{Fc}$ (**5**). Thf (10 ml) was added to a solid mixture of $\text{Au}(\text{C}\equiv\text{CFc})(\text{PPh}_3)$ (100 mg, 0.15 mmol), $\text{Co}_3(\mu_3\text{-CBr})(\mu\text{-dppm})(\text{CO})_7$ (127 mg, 0.15 mmol), $\text{Pd}(\text{PPh}_3)_4$ (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_2Cl_2 and purified by preparative t.l.c. (acetone–hexane 1/4). One brown band developed (R_f 0.43) and contained $\text{Co}_3(\mu_3\text{-CC}\equiv\text{CFc})(\mu\text{-dppm})(\text{CO})_7$ (**5**) (134 mg, 91%) as very dark red crystals ($\text{CH}_2\text{Cl}_2/\text{MeOH}$). X-ray quality crystals were obtained as the mono- CHCl_3 solvate from $\text{CHCl}_3/\text{hexane}$. Anal. Calc. for $\text{C}_{45}\text{H}_{31}\text{Co}_3\text{FeO}_7\text{P}_2$ (MW = 978): C, 55.22; H, 3.17. Found: C, 55.19; H, 3.20%. IR (CH_2Cl_2 , cm^{-1}): $\nu(\text{C}\equiv\text{C})$ 2123vw; $\nu(\text{CO})$ 2057s, 2007vs, 1988 (sh), 1965 (sh), 1948 (sh). ^1H NMR: δ 3.40, 4.41 (2 \times s, 2 \times 1H, dppm), 4.20 (s, 5H, Cp), 4.33, 4.48 (2 \times m, 2 \times 2H, C_5H_4), 7.12–7.59 (m, 20H, Ph). ^{13}C NMR: δ 40.49 [t, $J(\text{CP})$ 21.4 Hz, dppm], 69.84 (s, Cp), 69.14, 70.45 (2 \times s, C_a , C_b , C_5H_4), 67.99 (C_{ipso} , C_5H_4), 107.95, 111.77 (2 \times s, chain carbons), 128.24–145.06 (m, Ph), 202.44, 212.58, 226.21 [s (br), CO]. ^{31}P NMR: δ 33.7 (s, dppm). ES-MS (positive ion mode, MeOH , m/z): 978, M^+ ; 950, $[\text{M} - \text{CO}]^+$; (negative ion, MeOH , m/z): 977, $[\text{M} - \text{H}]^-$.

4.6.1.5. $R = \text{Au}(\text{PPh}_3)$ (**6**). A solution containing **4** (100 mg, 0.12 mmol) and $\text{AuCl}(\text{PPh}_3)$ (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 sintered filter, washed with MeOH and hexane and dried. Crystallisation ($\text{CH}_2\text{Cl}_2/\text{MeOH}$) gave $\text{Co}_3\{\mu_3\text{-CC}\equiv\text{CAu}(\text{PPh}_3)\}(\mu\text{-dppm})(\text{CO})_7$ (**6**) (130 mg, 90%) as dark red crystals. Anal. Calc. for $\text{C}_{53}\text{H}_{37}\text{AuCo}_3\text{O}_7\text{P}_3$ (MW = 1252): C, 50.80; H, 2.95. Found: C, 50.65; H, 3.02%. IR (CH_2Cl_2 , cm^{-1}): $\nu(\text{C}\equiv\text{C})$ 2137vw; $\nu(\text{CO})$ 2053s, 2005vs, 1983 (sh), 1961 (sh); (cyclohexane): $\nu(\text{CO})$ 2061s, 2015vs, 2011vs, 1997m, 1984w, 1976m, 1960w. ^1H NMR: δ 3.24, 5.04 (2 \times s, 2 \times 1H, dppm), 7.15–7.59(m, 35H, Ph). ^{31}P NMR: δ 32.5 [s (br), dppm], 43.5 [s (br), PPh_3]. ES-MS (positive ion, MeOH , m/z): 1253, $[\text{M} + \text{H}]^+$; ($\text{MeOH} + \text{NaOMe}$, m/z): 1275, $[\text{M} + \text{Na}]^-$.

4.6.1.6. $R = \text{C}_6\text{H}_4\text{I}$ (**7**). A solution containing $\text{Co}_3\{\mu_3\text{-CC}\equiv\text{CAu}(\text{PPh}_3)\}(\mu\text{-dppm})(\text{CO})_7$ (50 mg, 0.04 mmol), $1,4\text{-I}_2\text{C}_6\text{H}_4$ (6.4 mg, 0.02 mmol), $\text{Pd}(\text{PPh}_3)_4$ (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_2Cl_2 and separated by preparative t.l.c. (acetone–hexane 3/7) into two fractions. Band 1 (R_f 0.50, green) contained $\text{Co}_3(\mu_3\text{-CC}\equiv\text{CC}_6\text{H}_4\text{I-4})(\mu\text{-dppm})(\text{CO})_7$ (**7**) (12.2 mg, 61%), obtained as very dark green crystals ($\text{CH}_2\text{Cl}_2/\text{MeOH}$). Anal. Calc. for $\text{C}_{41}\text{H}_{26}\text{Co}_3\text{IO}_7\text{P}_2$ (MW = 996): C, 49.40; H, 2.61. Found: C, 49.65; H, 2.31%. IR (CH_2Cl_2 , cm^{-1}): $\nu(\text{C}\equiv\text{C})$ 2117vw; $\nu(\text{CO})$ 2060s, 2010vs, 1980 (sh), 1967 (sh), 1949 (sh). ^1H NMR: δ 3.40, 4.37 (2 \times s, 2 \times 1H, dppm), 7.05–7.69 (m, 24H, Ph + C_6H_4). ^{31}P NMR: δ 34.3 [s (br), dppm]. ES-MS (positive ion, $\text{MeOH} + \text{NaOMe}$, m/z): 1019, $[\text{M} + \text{Na}]^+$; (negative ion, MeOH , m/z): 995, $[\text{M} - \text{H}]^-$; 967, $[\text{M} - \text{H} - \text{CO}]^-$. The second orange-brown band (R_f 0.45) contained $1,4\text{-}\{(\text{OC})_7(\mu\text{-dppm})\text{Co}_3(\mu_3\text{-CC}\equiv\text{C})\}_2\text{C}_6\text{H}_4$ (**8**) (3.6 mg, 11%), identified by comparison with a sample prepared as described below.

4.6.1.7. $R = \text{C}_6\text{H}_4\text{C}\equiv\text{CPh}$ (**9**). A mixture of $\text{Au}(\text{C}\equiv\text{C-C}_6\text{H}_4\text{C}\equiv\text{CPh-4})(\text{PPh}_3)$ (90 mg, 0.14 mmol), $\text{Co}_3(\mu_3\text{-CBr})(\mu\text{-dppm})(\text{CO})_7$ (116 mg, 0.14 mmol), $\text{Pd}(\text{PPh}_3)_4$ (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_2Cl_2 and separated by preparative t.l.c. (hexane–acetone 10/1). The major brown band (R_f 0.56) contained $\text{Co}_3(\mu_3\text{-CC}\equiv\text{CC}_6\text{H}_4\text{C}\equiv\text{CPh})(\mu\text{-dppm})(\text{CO})_7$ (**9**) (51 mg, 39%) which was isolated as dark brown crystals ($\text{CH}_2\text{Cl}_2/\text{MeOH}$). Anal. Calc. for $\text{C}_{49}\text{H}_{31}\text{Co}_3\text{O}_7\text{P}_2$ (MW = 970): C, 60.62; H, 3.19. Found: C, 60.61; H, 3.17%. IR (CH_2Cl_2 , cm^{-1}): $\nu(\text{C}\equiv\text{C})$ 2115vw, 2100vw; $\nu(\text{CO})$ 2059s, 2011vs, 1993 (sh), 1967 (sh). ^1H NMR: δ 3.40, 4.43 (2 \times s, 2 \times 1H, dppm), 7.18–7.52 (m, 29H, Ph + C_6H_4). ^{13}C NMR: δ 41.27 [t, $J(\text{CP})$ 22.5 Hz, PCH_2], 89.70, 91.10 (2 \times s, $\text{C}\equiv\text{CC}_6\text{H}_4\text{C}\equiv\text{C}$), 110.37 (s, C^3), 114.19

(s, C²), 121.80–135.96 (m, Ph), 202.15, 210.05, 221.73 (3 × s, br, CO). ³¹P NMR: δ 34.3 (s, dppm). ES-MS (positive ion, MeOH + NaOMe, *m/z*): 993, [M+Na]⁺; (negative ion, MeOH + NaOMe, *m/z*): 969, [M–H][–].

4.7. Preparation of 1,4-{(OC)₇(μ-dppm)Co₃}₂{(μ₃-CC≡C)}₂C₆H₄ (**8**)

A mixture of 1,4-{Au(PPh₃)(C≡C)}₂C₆H₄ (30 mg, 0.03 mmol), Co₃(μ₃-CBr)(μ-dppm)(CO)₇ (98 mg, 0.06 mmol), Pd(PPh₃)₄ (15 mg, 0.013 mmol) and CuI (5 mg, 0.026 mmol) was stirred in thf (20 ml) at r.t. for 1 h. 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-{(OC)₇(μ-dppm)Co₃}₂-(μ₃-CC≡C)}₂C₆H₄ (**8**) as an orange band (*R_f* 0.68) (20.3 mg, 41%). Anal. Calc. for C₇₆H₄₈P₄Co₆O₁₄ (MW = 1662): C, 54.87; H, 2.89. Found: C, 54.92; H, 2.75%. IR (CH₂Cl₂, cm⁻¹): ν(C≡C) 2114w, ν(CO) 2059s, 2010vs, 1993sh(m), 1969sh(w). ¹H NMR: δ 3.42, 4.44 (2 × m, 2 × 2H, CH₂), 7.18–7.50 (m, 44H, Ph + C₆H₄). ³¹P NMR (CDCl₃): δ 37.0 (s, br, 4P, dppm). ES MS (positive ion, MeOH + NaOMe, *m/z*): 1685 [M+Na]⁺; (negative ion, MeOH, *m/z*): 1661, [M–H][–].

4.8. Reaction of 1,3,5-{(Ph₃P)AuC≡C}₃C₆H₃ with Co₃(μ₃-CBr)(μ-dppm)(CO)₇

(a) A solution of 1,3,5-{(Ph₃P)AuC≡C}₃C₆H₃ (59.7 mg, 0.039 mmol) and Co₃(μ₃-CBr)(μ-dppm)(CO)₇ (100 mg, 0.118 mmol) in thf (10 ml) was treated with Pd(PPh₃)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, a CH₂Cl₂ 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-{(OC)₇(μ-dppm)Co₃(μ₃-CC≡C)}₃C₆H₃ (**10**) (48.8 mg, 50%), obtained as dark red crystals (CHCl₃/MeOH). CHCl₃-solvated crystals were obtained for the X-ray study. Anal. Calc. for C₁₁₁H₆₉Co₉O₂₁P₆ (MW = 2454): C, 54.28; H, 2.83. Found: C, 54.80; H, 2.83%. IR (CH₂Cl₂, cm⁻¹): ν(C≡C) 2115w; ν(CO) 2059s, 2010vs, 1990 (sh), 1969 (sh), 1953 (sh). ¹H NMR: δ 3.46, 4.43 (2 × m, 2 × 3H, CH₂), 7.17–7.58 (m, 63H, Ph + C₆H₃). ¹³C NMR: δ 40.81 [s (br), CH₂], 108.92, 112.76 (2 × s, 2 × C of C₃ chain), 126.54–132.17 (m, Ph + C₆H₃), 202.24 [s (br), CO]. ³¹P NMR: δ 35.0 [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-{(Ph₃P)AuC≡C}₃C₆H₃ containing a significant amount of 1,3-{(Ph₃P)AuC≡C}₂C₆H₃Br-5, a similar reaction with Co₃(μ₃-CBr)(μ-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-{(OC)₇(μ-dppm)Co₃(μ₃-CC≡C)}₂C₆H₃Br-5 (**11**) (10.8 mg), obtained as brown-red crystals (CH₂Cl₂/MeOH). Crystals of a CH₂Cl₂-solvate for the X-ray study were obtained by recrystallisation from the same solvent mixture. Anal. Calc. for C₇₆H₄₇BrCo₆O₁₄P₄ (MW = 1742): C, 52.38; H, 2.69. Found: C, 52.34; H, 2.61%. IR (CH₂Cl₂, cm⁻¹): ν(C≡C) 2114w; ν(CO) 2057s, 2009vs, 1988 (sh), 1970 (sh), 1951 (sh). ¹H NMR: δ 3.40, 4.41 (2 × m, 2 × 2H, CH₂), 6.95–7.51 (m, 43H, Ph + C₆H₃). ³¹P NMR: δ 35.2 [s (br), dppm]. ES MS (positive ion, MeOH + NaOMe, *m/z*): 1765, [M+Na]⁺; (negative ion, MeOH + NaOMe, *m/z*): 1741, [M–H][–].

4.9. 1,1'-{(OC)₇(μ-dppm)Co₃(μ₃-CC≡C)}₂Fe' (**12**)

A solution containing 1,1'-Fc' {C≡CAu[P(tol)₃]}₂ (26 mg, 0.02 mmol), Co₃(μ₃-CBr)(μ-dppm)(CO)₇ (36 mg, 0.04 mmol), Pd(PPh₃)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 CH₂Cl₂ and purified by preparative t.l.c. (acetone–hexane 3/7) to give one major band (*R_f* 0.34), from which 1,1'-{(OC)₇(μ-dppm)Co₃(μ₃-CC≡C)}₂Fe' (**12**) (35.7 mg, 96%) was isolated as very dark red crystals (CH₂Cl₂/MeOH). Anal. Calc. for C₈₀H₅₂Co₆FeO₁₄P₄ (MW = 1770): C, 54.23; H, 2.94. Found: C, 54.26; H, 2.96%. IR (CH₂Cl₂, cm⁻¹): ν(C≡C) 2122vw; ν(CO) 2057s, 2008vs, 1989 (sh), 1977 (sh), 1964 (sh). ¹H NMR: δ 3.43, 4.44 (2 × s, 2 × 1H, dppm), 4.40, 4.53 (2 × m, 2 × 4H, C₅H₄), 7.11–7.52 (m, 40H, Ph). ³¹P NMR: δ 33.7 [s (br), dppm]. ES-MS (positive ion, MeOH + NaOMe, *m/z*): 1793, [M+Na]⁺; (negative ion, MeOH, *m/z*): 1769, [M–H][–].

4.10. Co₃{μ₃-C(C≡C)₃R}(μ-dppm)(CO)₇

4.10.1. R = SiMe₃ (**13**)

A mixture of Co₃{(μ₃-CC≡CC≡)CAu(PPh₃)}(μ-dppm)(CO)₇ (280 mg, 0.219 mmol), IC≡CSiMe₃ (85 mg, 0.379 mmol), Pd(PPh₃)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 CH₂Cl₂ extract of the residue developed two bands. Band 1 (*R_f* 0.55, brown) contained Co₃{μ₃-C(C≡C)₃-SiMe₃}(μ-dppm)(CO)₇ (**13**) (108 mg, 54%), obtained a brown-black crystals from CH₂Cl₂/MeOH. Anal. Calc. for C₄₂H₃₁Co₃O₇P₂Si (MW = 914): C, 55.16; H, 3.42. Found: C, 55.20; H, 3.48%. IR (CH₂Cl₂, cm⁻¹): ν(C≡C) 2134vw; ν(CO) 2062s, 2018vs, 1974 (sh). ¹H NMR: δ 0.26 (s, 9H, SiMe₃), 3.41, 4.24 (2 × s, 2 × 1H, dppm), 7.20–7.41 (m, 20H, Ph). ³¹P NMR: δ 34.6 (s, dppm). ES-MS (positive ion, MeOH + NaOMe, *m/z*): 937, [M+Na]⁺; 915, [M+H]⁺; 865, [M+H+Na–SiMe₃]⁺; (negative ion, MeOH + NaOMe, *m/z*): 913, [M–H][–]; 841, [M–SiMe₃][–];

Table 2
Crystal data and refinement details

Complex	2	3 · CH ₂ Cl ₂	4	5 · CHCl ₃
Formula	C ₃₉ H ₃₁ Co ₃ O ₇ P ₂	C ₄₁ H ₂₇ Co ₃ O ₇ P ₂ · CH ₂ Cl ₂	C ₃₈ H ₃₁ Co ₃ O ₇ P ₂ Si	C ₄₅ H ₃₁ Co ₃ FeO ₇ P ₂ · CHCl ₃
Molecular weight	850.42	955.34	866.49	1097.71
Crystal system	Triclinic	Monoclinic	Triclinic	Triclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>a</i> (Å)	11.551(2)	15.819(1)	11.497(2)	13.388(2)
<i>b</i> (Å)	11.951(2)	11.869(1)	11.847(2)	15.437(2)
<i>c</i> (Å)	14.206(3)	22.280(2)	14.230(3)	23.798(4)
α (°)	86.870(5)		86.192(4)	103.256(3)
β (°)	77.758(5)	103.505(2)	77.441(4)	91.655(3)
γ (°)	87.216(5)		86.772(4)	111.921(3)
<i>V</i> (Å ³)	1912	4067	1886	4405
ρ_c (g cm ⁻³)	1.47 ₇	1.56 ₀	1.52 ₆	1.65 ₅
<i>Z</i>	2	4	2	4
2 θ_{max} (°)	75	70	65	50
μ (Mo K α) (mm ⁻¹)	1.42	1.47	1.47	1.74
<i>T</i> _{min/max}	0.87	0.88	0.85	0.69
Crystal dimensions (mm)	0.46 × 0.25 × 0.20	0.38 × 0.32 × 0.25	0.43 × 0.35 × 0.28	0.25 × 0.20 × 0.10
<i>N</i> _{tot}	36 883	72 089	38 998	60 143
<i>N</i> (<i>R</i> _{int})	18 952 (0.028)	17 984 (0.053)	13 305 (0.034)	14 912 (0.085)
<i>N</i> ₀	14 566	11 543	10 511	11 005
<i>R</i>	0.037	0.044	0.038	0.065
<i>R</i> _w (<i>n</i> _w)	0.048 (8)	0.049 (6)	0.045 (5)	0.132 (40)
	6	7	9	10 · 2CHCl ₃
Formula	C ₅₃ H ₃₇ AuCo ₃ O ₇ P ₃	C ₄₁ H ₂₆ Co ₃ IO ₇ P ₂	C ₄₉ H ₃₁ Co ₃ O ₇ P ₂	C ₁₁₁ H ₆₉ Co ₉ O ₂₁ P ₆ · 2CHCl ₃
Molecular weight	1252.56	996.30	970.53	2693.75
Crystal system	Triclinic	Triclinic	Orthorhombic	Triclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>Pbca</i>	<i>P</i> $\bar{1}$
<i>a</i> (Å)	13.687(2)	10.550(1)	12.214(2)	17.615(5)
<i>b</i> (Å)	13.764(2)	11.467(1)	22.689(3)	18.507(5)
<i>c</i> (Å)	14.039(2)	18.061(2)	30.421(4)	19.930(6)
α (°)	89.615(4)	73.721(2)		68.971(5)
β (°)	78.234(4)	81.711(2)		74.113(5)
γ (°)	69.498(4)	66.440(2)		71.475(5)
<i>V</i> (Å ³)	2419	1921	8431	5656
ρ_c (g cm ⁻³)	1.71 ₉	1.72 ₂	1.52 ₉	1.58 ₂
<i>Z</i>	2	2	8	2
2 θ_{max} (°)	66.5	65	52	45
μ (Mo K α) (mm ⁻¹)	4.2	2.22	1.30	1.58
<i>T</i> _{min/max}	0.68	0.61	0.84	0.79
Crystal dimensions (mm)	0.28 × 0.23 × 0.16	0.52 × 0.20 × 0.15	0.85 × 0.05 × 0.04	0.33 × 0.28 × 0.05
<i>N</i> _{tot}	39 993	30 132	69 472	41 488
<i>N</i> (<i>R</i> _{int})	18 377 (0.053)	13 651 (0.043)	8090 (0.074)	14 868 (0.12)
<i>N</i> ₀	13 474	9372	6420	8601
<i>R</i>	0.041	0.046	0.047	0.16
<i>R</i> _w (<i>n</i> _w)	0.044 (4)	0.051 (6)	0.059 (15)	0.26 (328)
	11 · CH ₂ Cl ₂	12	13	16
Formula	C ₇₆ H ₄₇ Co ₆ O ₁₄ P ₄ · CH ₂ Cl ₂	C ₈₀ H ₅₂ Co ₆ FeO ₁₄ P ₄	C ₄₂ H ₃₁ Co ₃ O ₇ P ₂ Si	C ₄₅ H ₂₇ Co ₃ O ₇ P ₂
Molecular weight	1826.53	1770.62	914.54	918.45
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> (Å)	17.054(3)	11.294(1)	18.271(2)	10.044(1)
<i>b</i> (Å)	20.202(3)	19.911(2)	12.644(1)	25.238(2)
<i>c</i> (Å)	21.897(3)	17.047(2)	19.171(2)	16.303(2)
α (°)				
β (°)	100.459(2)	102.174(2)	114.498(2)	94.785(2)
γ (°)				
<i>V</i> (Å ³)	7419	3747	4030	4118
ρ_c (g cm ⁻³)	1.63 ₅	1.58 ₁	1.50 ₇	1.48 ₁
<i>Z</i>	4	2	4	4
2 θ_{max} (°)	58	58	58	65
μ (Mo K α) (mm ⁻¹)	2.07	1.63	1.38	1.32

(continued on next page)

Table 2 (continued)

	11 · CH ₂ Cl ₂	12	13	16
<i>T</i> _{min/max}	0.79	0.88	0.77	0.86
Crystal dimensions (mm)	0.28 × 0.15 × 0.08	0.32 × 0.15 × 0.13	0.56 × 0.41 × 0.12	0.20 × 0.12 × 0.10
<i>N</i> _{tot}	71 451	21 820	57 543	72 405
<i>N</i> (<i>R</i> _{int})	18 439 (0.045)	9750 (0.031)	10 606 (0.075)	17 960 (0.060)
<i>N</i> ₀	13 097	7363	7553	10 430
<i>R</i>	0.045	0.044	0.048	0.046
<i>R</i> _w (<i>n</i> _w)	0.053 (1.5)	0.054 (10)	0.098 (3000)	0.062 (20)

814, [M+H–CO–SiMe₃][−]. Band 2 (*R*_f 0.38, red-brown) contained {Co₃(μ-dppm)(CO)₇}₂(μ₃-C₁₀), identified by comparison with an authentic sample [10a].

4.10.2. *R* = Fc (14)

A mixture of Co₃{μ₃-CC≡CC≡CAu(PPh₃)}(μ-dppm)(CO)₇ (60 mg, 0.05 mmol), FcC≡CI (15.3 mg, 0.05 mmol), Pd(PPh₃)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 [26]. The major product was contained in the second brown-orange band (*R*_f 0.26), which gave Co₃{(μ₃-CC≡C)₃-Fc}(μ-dppm)(CO)₇ (14) (40.8 mg, 87.4%) as very thin red plates (CH₂Cl₂/hexane). Anal. Calc. for C₄₉H₃₁Co₃FeO₇P₂ (MW = 1026): C, 57.31; H, 3.02. Found: C, 56.74; H, 2.57%. IR (CH₂Cl₂, cm^{−1}): ν(C≡C) 2168w, 2100vw; ν(CO) 2063s, 2013vs, 1973 (sh), 1958 (sh) cm^{−1}. ¹H NMR: δ 3.40, 4.25 (2 × m, 2 × 1H, CH₂), 4.28 (s, 5H, Cp), 4.30, 4.56 (2 × m, 2 × 2H, C₅H₄), 7.15–7.69 (m, 20H, Ph). ¹³C NMR: δ 42.75 [t, *J*(CP) 18.3, CH₂P], 70.35 (s, Cp), 69.76, 72.35 (2 × m, C₅H₄), 63.38, 65.66, 72.73, 80.95, 85.99, 97.13, 99.03 (C_{ipso} of C₅H₄ + six C of C₇ chain), 201.43, 209.79, 212.4 (3 × s, CO). ³¹P NMR: δ 33.8 (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*): 1025, [M–H][−]. The third band (*R*_f 0.15, brown-orange) contained {Co₃(μ-dppm)(CO)₇}₂(μ₃-C₁₀) (0.6 mg, 1%), identified by comparison with an authentic sample [10a].

4.10.3. *R* = Au(PPh₃) (15)

NaOMe [from 10 mg Na in MeOH (10 ml)] was added to a solution of Co₃{μ₃-C(C≡C)₃SiMe₃}(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(PPh₃) (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 × 2 ml) affording Co₃{μ₃-C(C≡C)₃Au(PPh₃)}(μ-dppm)(CO)₇ (15) (90 mg, 75%) as a brown powder. Anal. Calc. for C₅₇H₃₇AuCo₃O₇P₃ (MW = 1300): C, 52.64; H, 2.87. Found: C, 52.59; H, 2.83%. IR (CH₂Cl₂, cm^{−1}): ν(C≡C) 2117vw; ν(CO) 2060s, 2012vs, 1974 (sh). ¹H NMR: δ 3.40, 4.34 (2 × s, 2 × 1H, dppm), 7.18–7.56 (m,

35H, Ph). ¹³C NMR: δ 42.63 (m, CH₂), 57.49, 82.83, 88.79, 95.20, 98.81 (5 × s, carbon chain), 128.38–131.86 (m, Ph), 134.20–134.52 (m, Ph), 201.52 (br, CO). ³¹P NMR: δ 34.7 [s (br), dppm]. ES-MS (positive ion, MeOH + NaOMe, *m/z*): 1323, [M+Na]⁺.

4.10.4. *R* = Ph (16)

A solution containing Co₃{μ₃-CC≡CC≡CAu(PPh₃)}(μ-dppm)(CO)₇ (50 mg, 0.04 mmol) and Pd(PPh₃)₄ (3 mg, 0.0025 mmol) in thf (5 ml) was added to a mixture of iodine (10 mg, 0.04 mmol) and CuI (1 mg, 0.005 mmol) in thf (5 ml) at −78 °C, and the mixture was stirred for 1 h. After this time, a solution of Au(C≡CPh)(PPh₃) (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 solution was evaporated and the residue was extracted into CH₂Cl₂ and purified by preparative t.l.c. (acetone–hexane 3/7). The brown band (*R*_f 0.76) contained Co₃{(μ₃-CC≡C)₃Ph}(μ-dppm)(CO)₇ (16) (21 mg, 60%), obtained as black needles (CH₂Cl₂/MeOH). Anal. Calc. for C₄₅H₂₇Co₃O₇P₂ (MW = 918): C, 58.82; H, 2.94. Found: C, 58.98; H, 2.87%. IR (CH₂Cl₂, cm^{−1}): ν(C≡C) 2190w, 2171vw; ν(CO) 2065s, 2040m, 2014m, 1973 (sh), 1955 (sh) cm^{−1}. ¹H NMR: δ 3.30, 4.15 (2 × m, 2 × 1H, dppm), 7.09–7.47 (m, 25H, Ph). ³¹P NMR: δ 34.6 (s, dppm). ES-MS (positive ion, MeOH + NaOMe, *m/z*): 941, [M+Na]⁺; (negative ion, MeOH, *m/z*): 917, [M–H][−]; 889, [M–H–CO][−].

4.11. 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*₀ with *F* > 4σ(*F*) being used in the full matrix least squares refinements. All data were measured using monochromatic Mo Kα radiation, λ = 0.71073 Å. Anisotropic displacement parameter forms were refined for the non-hydrogen atoms, (*x*, *y*, *z*, *U*_{iso})_H being included, constrained at estimates. Conventional residuals *R*, *R*_w on |*F*| are quoted [weights: (σ²(*F*) + 0.000*n*_w*F*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. Refinement on F^2 .

11. The dichloromethane of solvation was modelled as disordered over two sets of sites, occupancies 0.694(5) and complement.

13. Refinement on F^2 .

5. Supplementary material

Full details of the structure determinations (except structure factors) have been deposited with the Cambridge Crystallographic Data Centre as CCDC 284347–284358. 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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References

- [1] J.L. Bredas, R.R. Chance (Eds.), *Conjugated Polymeric Materials: Opportunities in Electronics, Optoelectronics and Molecular Electronics*, Kluwer, Dordrecht, 1990.
- [2] F. Paul, C. Lapinte, in: M. Gielen, R. Willem, B. Wrackmeyer (Eds.), *Unusual Structures and Physical Properties in Organometallic Chemistry*, Wiley, New York, 2002, p. 220.
- [3] F. Paul, C. Lapinte, *Coord. Chem. Rev.* 178–180 (1978) 431.
- [4] M.I. Bruce, P.J. Low, *Adv. Organomet. Chem.* 50 (2004) 179.
- [5] B.E. Woodworth, J.L. Templeton, *J. Am. Chem. Soc.* 118 (1996) 7418.
- [6] (a) W. Weng, J.A. Ramsden, A.M. Arif, J.A. Gladysz, *J. Am. Chem. Soc.* 115 (1993) 3824;
(b) T. Bartik, W. Weng, J.A. Ramsden, S. Szafert, S.B. Falloon, A.M. Arif, J.A. Gladysz, *J. Am. Chem. Soc.* 120 (1998) 11071;
(c) W. Weng, T. Bartik, J.A. Gladysz, *Angew. Chem.* 106 (1994) 2272; *Angew. Chem., Int. Ed. Engl.* 33 (1994) 2199.
- [7] R. Dembinski, S. Szafert, P. Haquette, T. Lis, J.A. Gladysz, *Organometallics* 18 (1999) 5438.
- [8] (a) R.D. Dewhurst, A.F. Hill, M.K. Smith, *Angew. Chem. Int. Ed.* 43 (2004) 476;
(b) R.D. Dewhurst, A.F. Hill, A.C. Willis, *Organometallics* 23 (2004) 1646;
(c) R.D. Dewhurst, A.F. Hill, A.C. Willis, *Organometallics* 23 (2004) 5903;
(d) R.D. Dewhurst, A.F. Hill, A.C. Willis, *Chem. Commun.* (2004) 2826.
- [9] M.I. Bruce, P.A. Humphrey, G. Melino, B.W. Skelton, A.H. White, N.N. Zaitseva, *Inorg. Chim. Acta* 358 (2005) 1453.
- [10] (a) M.I. Bruce, M.E. Smith, N.N. Zaitseva, B.W. Skelton, A.H. White, *J. Organomet. Chem.* 670 (2003) 170;
(b) M.I. Bruce, B.W. Skelton, A.H. White, N.N. Zaitseva, *J. Organomet. Chem.* 683 (2003) 398.
- [11] R. Markby, I. Wender, R.A. Friedel, F.A. Cotton, H.W. Sternberg, *J. Am. Chem. Soc.* 80 (1958) 6529.
- [12] G. Palyi, F. Piacenti, L. Marko, *Inorg. Chim. Acta Rev.* 4 (1970) 109.
- [13] B.R. Penfold, B.H. Robinson, *Acc. Chem. Res.* 6 (1973) 73.
- [14] D. Seyferth, *Adv. Organomet. Chem.* 14 (1976) 97.
- [15] G. Schmid, *Angew. Chem.* 90 (1978) 417; *Angew. Chem., Int. Ed. Engl.* 17 (1978) 392.
- [16] R.D.W. Kemmitt, in: G. Wilkinson, F.G.A. Stone, E.W. Abel (Eds.), *Comprehensive Organometallic Chemistry*, vol. 5, Pergamon, Oxford, 1982, p. 162 (Chapter 34.3.9).
- [17] C.E. Barnes, in: E.W. Abel, F.G.A. Stone, G. Wilkinson (Eds.), *Comprehensive Organometallic Chemistry II*, vol. 8, Pergamon, Oxford, 1995, p. 423 (Chapter 4.3.1.2).
- [18] (a) R.J. Dellaca, B.R. Penfold, B.H. Robinson, W.T. Robinson, J.L. Spencer, *Inorg. Chem.* 9 (1970) 2204;
(b) R.J. Dellaca, B.R. Penfold, *Inorg. Chem.* 10 (1971) 1269.
- [19] G.H. Worth, B.R. Robinson, J. Simpson, *Organometallics* 11 (1992) 501.
- [20] D. Seyferth, R.J. Spohn, M.R. Churchill, K. Gold, F.J. Scholer, *Organomet. Chem.* 23 (1970) 237.
- [21] A.B. Antonova, M.I. Bruce, B.G. Ellis, M. Gaudio, P.A. Humphrey, M. Jevric, G. Melino, B.K. Nicholson, G.J. Perkins, B.W. Skelton, B. Stapleton, A.H. White, N.N. Zaitseva, *Chem. Commun.* (2004) 960.
- [22] (a) A.J. Downard, B.H. Robinson, J. Simpson, *Organometallics* 5 (1986) 1122;
(b) A.J. Downard, B.H. Robinson, J. Simpson, *Organometallics* 5 (1986) 1132;
(c) A.J. Downard, B.H. Robinson, J. Simpson, *Organometallics* 5 (1986) 1140.
- [23] S. Aime, L. Milone, M. Valle, *Inorg. Chim. Acta* 18 (1976) 9.
- [24] P. Yuan, M.G. Richmond, M. Schwarz, *Inorg. Chem.* 30 (1990) 679.
- [25] J. Hlavaty, L. Kavan, M. Sticha, *J. Chem. Soc., Perkin Trans. 1* (2002) 705.
- [26] M.I. Bruce, B.W. Skelton, M.E. Smith, A.H. White, *Aust. J. Chem.* 52 (1999) 431.
- [27] M.I. Bruce, K.A. Kramarczuk, G.J. Perkins, B.W. Skelton, A.H. White, N.N. Zaitseva, *J. Cluster Sci.* 15 (2004) 119.
- [28] G. Balavoine, J. Collin, J.-J. Bonnet, G. Lavigne, *J. Organomet. Chem.* 280 (1985) 429.
- [29] A.J. Downard, B.H. Robinson, J. Simpson, *J. Organomet. Chem.* 447 (1993) 281.
- [30] D.N. Duffy, M.M. Kassis, A.D. Rae, *Acta Crystallogr., Sect. C* 47 (1991) 2054.
- [31] F.-E. Hong, Y.-L. Huang, Y.-C. Cheng, K.-M. Chu, *Appl. Organomet. Chem.* 17 (2003) 458.
- [32] D. Seyferth, C.S. Eschbach, M.O. Nestle, *J. Organomet. Chem.* 97 (1975) C11.
- [33] S. Szafert, J.A. Gladysz, *Chem. Rev.* 103 (2003) 4175.
- [34] W. Henderson, J.S. McIndoe, B.K. Nicholson, P.J. Dyson, *J. Chem. Soc., Dalton Trans.* (1998) 519.
- [35] M.I. Bruce, B.K. Nicholson, O. bin Shawkataly, *Inorg. Synth.* 26 (1989) 325.
- [36] R.J. Cross, M.F. Davidson, *J. Chem. Soc., Dalton Trans.* (1986) 411.
- [37] M.I. Bruce, E. Horn, J.G. Matison, M.R. Snow, *Aust. J. Chem.* 37 (1984) 1163.
- [38] I.R. Whittall, M.G. Humphrey, S. Houbrechts, J. Maes, A. Persoons, S. Schmid, D.C.R. Hockless, *J. Organomet. Chem.* 544 (1997) 277.
- [39] S.R. Hall, D.J. du Boulay, R. Olthof-Hazekamp (Eds.), *The XTAL 3.7 System*, University of Western Australia, 2000.