Preparation and molecular structures of some complexes containing C5 chains

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Abstract

Complexes containing a Co_3 cluster linked to $SiMe_3$, $Au(PPh_3)$, $W(CO)_3Cp$ and Fc groups by a C_5 chain have been prepared by elimination of $AuBr(PR_3)$ (R = Ph, tol) in the reactions between $Co_3(\mu_3\text{-}CBr)(\mu\text{-}dppm)(CO)_7$ and $\{(R_3P)Au\}C\equiv CC\equiv CX$ [X = $SiMe_3$, $W(CO)_3Cp$] or $\{(OC)_7(\mu\text{-}dppm)Co_3\}CC\equiv C\{Au(PPh_3)\}$ and $FcC\equiv CI$ (X = Fc). Subsequent auro-desilylation of the $SiMe_3$ compound affords $\{(OC)_7(\mu\text{-}dppm)Co_3\}\equiv CC\equiv CC\equiv C\{Au[P(tol)_3]\}$. Single-crystal X-ray structures of the $W(CO)_3Cp$, $Au\{P(tol)_3\}$ and Fc complexes are reported. The C_5 chain shows little departure from a formal $\equiv C\text{-}C\equiv C\text{-}C\equiv C\text{-}$ fragment.
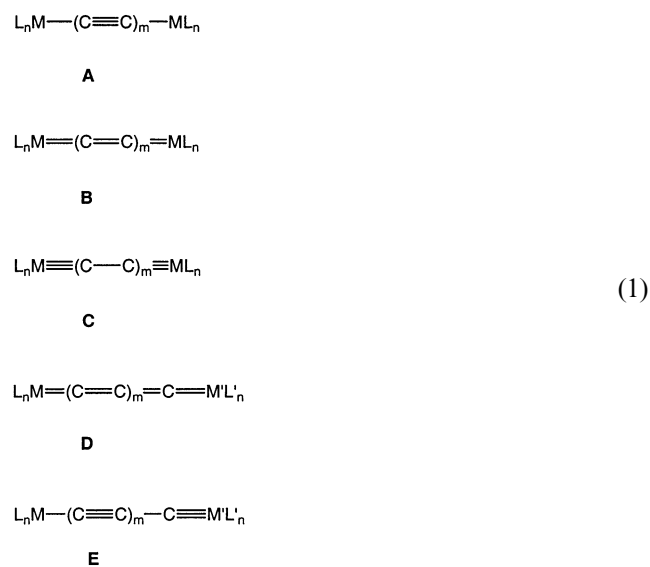© 2003 Elsevier B.V. All rights reserved.

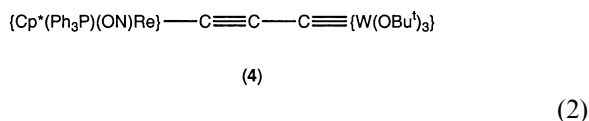*Keywords:* Carbon chains; Tricobaltcarbon cluster; Phosphine–gold(I) complexes
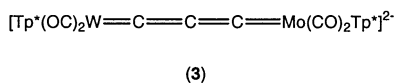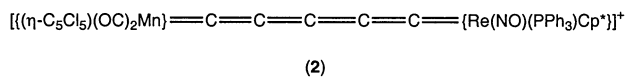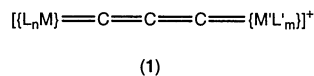
1. Introduction

While there has been much interest in the development of syntheses for, and studies of, complexes containing two metal centres linked by an even-number of carbon atoms, corresponding studies of compounds with odd-numbered carbon chains are limited [1]. Two factors contribute to this inequality: the synthetic approaches used, which have generally employed mono- or poly-yndiyl reagents, and the particular bonding requirements associated with the odd-numbered chain. In the case of the even-numbered chain, attachment to a metal centre may be via formal M–C single, M=C double or M≡C triple bonds (**A**, **B**, **C**; Chart 1), although easy access to all of these derivatives is achieved by using ethyndiyl or butadiynyl or poly-yndiyl reagents, such as Li_2C_2, $C_2(MgBr)_2$ or $C_2(SiMe_3)_2$, Li_2C_4 or $SiMe_3(C\equiv C)_nSiMe_3$ (n = 2, 3, ...). Metal complexes may adopt the bonding modes formally corresponding to structures **A**, **B** or **C**, interconversion among these being possible by redox processes, for example.

L_nM——$(C\equiv C)_m$——ML_n

A

L_nM==$(C\equiv C)_m$==ML_n

B

L_nM≡≡$(C$——$C)_m$≡≡ML_n

C

(1)

L_nM==$(C\equiv C)_m$==C==$M'L'_n$

D

L_nM——$(C\equiv C)_m$——C≡≡≡$M'L'_n$

E

$$[\{L_nM\}\!\!=\!\!\!=\!\!C\!\!=\!\!\!=\!\!C\!\!=\!\!\!=\!\!C\!\!=\!\!\!=\!\!\{M'L'_m\}]^+$$

(1)

$$[\{(\eta\text{-}C_5Cl_5)(OC)_2Mn\}\!\!=\!\!\!=\!\!C\!\!=\!\!\!=\!\!C\!\!=\!\!\!=\!\!C\!\!=\!\!\!=\!\!C\!\!=\!\!\!=\!\!C\!\!=\!\!\!=\!\!\{Re(NO)(PPh_3)Cp^*\}]^+$$

(2)

$$[Tp^*(OC)_2W\!\!=\!\!\!=\!\!C\!\!=\!\!\!=\!\!C\!\!=\!\!\!=\!\!C\!\!=\!\!\!=\!\!Mo(CO)_2Tp^*]^{2-}$$

(3)

$$\{Cp^*(Ph_3P)(ON)Re\}\!\!-\!\!\!-\!\!C\!\!\equiv\!\!C\!\!-\!\!\!-\!\!C\!\!\equiv\!\!\{W(OBu^t)_3\}$$

(4)

$$(2)$$

In the case of odd-numbered chains containing mononuclear end-caps, where representations **D** and **E** can be written, at least one metal must be attached via an M–C multiple bond. To our knowledge, there is only one account describing reactions involving metal carbene intermediates, in the synthesis of $[\{Cp'(OC)_2Mn\}C_n\{Re(NO)(PPh_3)Cp^*\}]^+$ [$n = 3$ (**1**), 5 (**2**; type **D**] from $Mn(CO)_3(\eta\text{-}C_5Cl_5)$ and $Li(C\equiv C)_mRe(NO)(PPh_3)Cp^*$ ($m = 1, 2$), followed by $[OMe_3]BF_4$; treatment with BF_3 eliminated the OMe group [2,3]. Another example is the dianion $[Tp^*(OC)_2Mo=C=C=C=W(CO)_2Tp^*]^{2-}$ (**3**; $Tp^* = [HB(dpmz)_3]$), prepared by modification of an $Mo\equiv CCH_2C\equiv W$ fragment [4]. Most complexes have structures of type **E**, in which one metal atom is attached via a conventional M–C σ bond, whereas the other is involved in a carbynic interaction with the other terminal carbon atom, such as found in $\{(Bu^tO)_3W\}\equiv CC\equiv C\{Re(NO)(PPh_3)Cp^*\}$ (**4**) [5].

An alternative approach to this type of complex is to use a tri-nuclear metal centre, such as that found in the well-known $Co_3(\mu_3\text{-}CX)(CO)_9$ complexes [6]. Here the metal cluster interacts with the terminal carbon to form a trigonal pyramidal $C\equiv M_3$ array, the remaining bond on carbon being available to attach a poly-yne chain capped by a metal centre. Approaches to this type of complex have been reported earlier, e.g. by Robinson, Simpson and their group, who were able to couple terminal alkynes with the halocarbyne complexes $Co_3(\mu_3\text{-}CX)(CO)_9$ using the usual Pd/Cu(I) catalysed reactions carried out in amine-containing solvents [7]. Yields were generally only moderate and on several occasions, amidocarbyne complexes were isolated and characterised.

In our attempts to extend these reactions to alkynes capped by other transition metal groups, we encoun-

tered similar problems and, while having some success with relatively unreactive end-caps, such as $W(CO)_3Cp$, this did not prove to be a general approach. Consequently, we have sought alternative reactions to achieve our goal. This paper is a preliminary account of novel (phosphine)gold(I) halide-elimination reactions which we have found to proceed in high yield without any complicating side reactions.

2. Results and discussion

The reaction was discovered fortuitously when attempting to couple $Au(C\equiv CC\equiv CH)(PPh_3)$ to $Co_3(\mu_3\text{-}CBr)(\mu\text{-}dppm)(CO)_7$ (the dppm complex was being used to reduce cluster breakdown during these reactions) using the normal Pd(0)/Cu(I) catalysed reaction in $NHEt_2$/THF. Among the products we found the complex $\{Co_3(\mu\text{-}dppm)(CO)_7\}_2(\mu_3{:}\mu_3\text{-}CC\equiv CC\equiv CC)$ [8]. The source of this compound was traced to the presence of some $\{Au(PPh_3)\}_2(\mu\text{-}C\equiv CC\equiv C)$ in the supposed butadiynylgold precursor. Use of a pure sample of $\{Au(PPh_3)\}_2(\mu\text{-}C\equiv CC\equiv C)$ afforded the C_6 cluster in high yield, as earlier described [8].

The $Au(PR_3)$ derivatives of alkynyl–metal complexes are readily prepared [9] and we have studied the reactions of several of these with the bromocarbyne cluster. Here we describe the syntheses of three complexes containing a C_5 chain under mild conditions and in high yield. Later accounts will demonstrate the utility of this reaction which can be used with a wide variety of gold-alkynyl derivatives in conjunction with compounds containing halogen–C(sp) and –C(sp^2) bonds.

The reaction between $\{Cp(OC)_3W\}C\equiv CC\equiv C\{Au(PPh_3)\}$ [10] and $Co_3(\mu_3\text{-}CBr)(\mu\text{-}dppm)(CO)_7$ [11] was carried out at room temperature in THF containing catalytic amounts of $Pd(PPh_3)_4$ and CuI. The resulting complex was isolated by preparative t.l.c. as the only product and was identified as $\{Cp(OC)_3W\}C\equiv CC\equiv CC\{Co_3(\mu\text{-}dppm)(CO)_7\}$ (**5**; Scheme 1) from a single-crystal X-ray structural study. Its spectral properties were consistent with the solid-state structure, with the $\nu(CO)$ pattern between 2058 and 1955 cm^{-1} approximating to a superposition of the $W(CO)_3Cp$ and $Co_3(\mu\text{-}dppm)(CO)_7$ precursors. A weak $\nu(C\equiv C)$ band is found at 2117 cm^{-1}. The NMR spectra contained resonances from the Cp and dppm ligands (^{1}H), CO, Cp and dppm ligands (^{13}C) and the dppm ligand (^{31}P). In particular, the ^{13}C-NMR spectrum also contained three signals at δ 53.48, 96.01 and 114.03 which we assign to three of the alkynyl carbons of the C_5 chain. The fifth carbon, capping the Co_3 cluster, is seldom observed in the ^{13}C-NMR spectra of similar complexes, probably because it is broadened by the quadrupole moment of the ^{57}Co nuclei. The electrospray mass spectrum (ESMS; positive

Scheme 1.
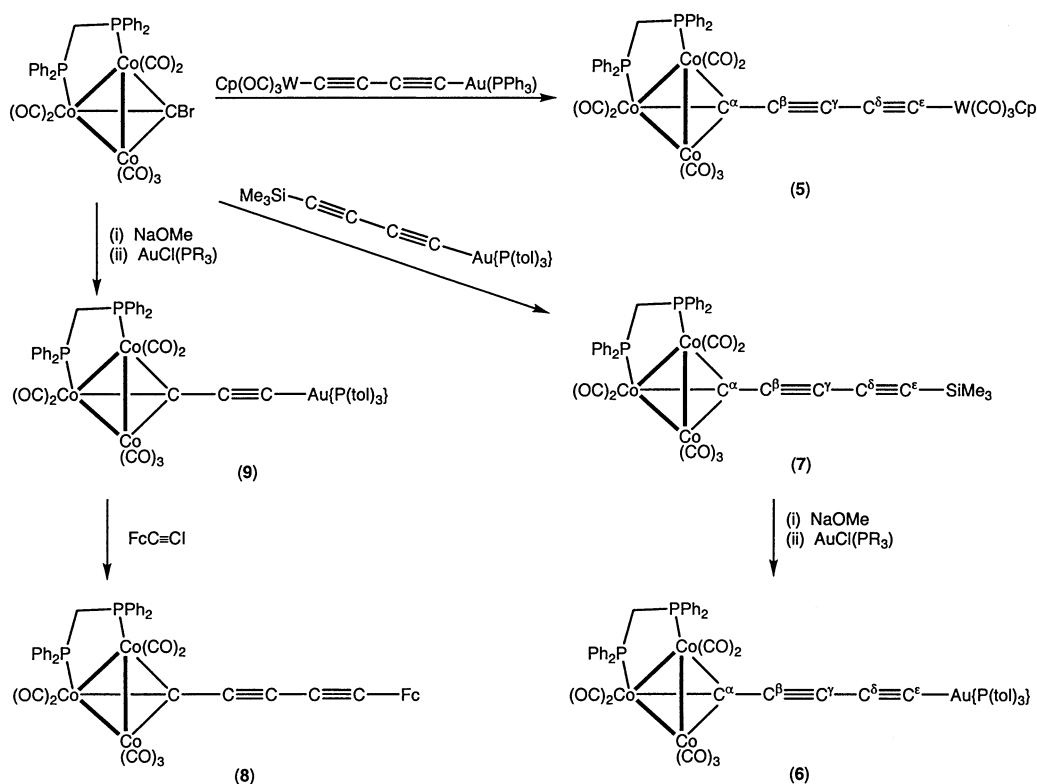
ion with added NaOMe) contains $[M+Na]^+$ at m/z 1173.

A molecule of **5** is portrayed in Fig. 1 and significant bond parameters are collected in Table 1. The end-caps comprise conventional $Co_3(\mu\text{-dppm})(CO)_7$ and $W(CO)_3Cp$ groups, whose geometrical parameters are similar to those found in a number of earlier determina-

tions. Of most interest in the context of this work is the five-carbon chain C(1–5). Atom C(1) is attached to the three Co atoms [Co–C(1) 1.910–1.940(4) Å], distances which are unaffected by the dppm ligand when compared to $Co_3(CO)_9$ complexes. Some asymmetry results from the electron-donating properties of the dppm, leading to shorter Co–Co distances involving the
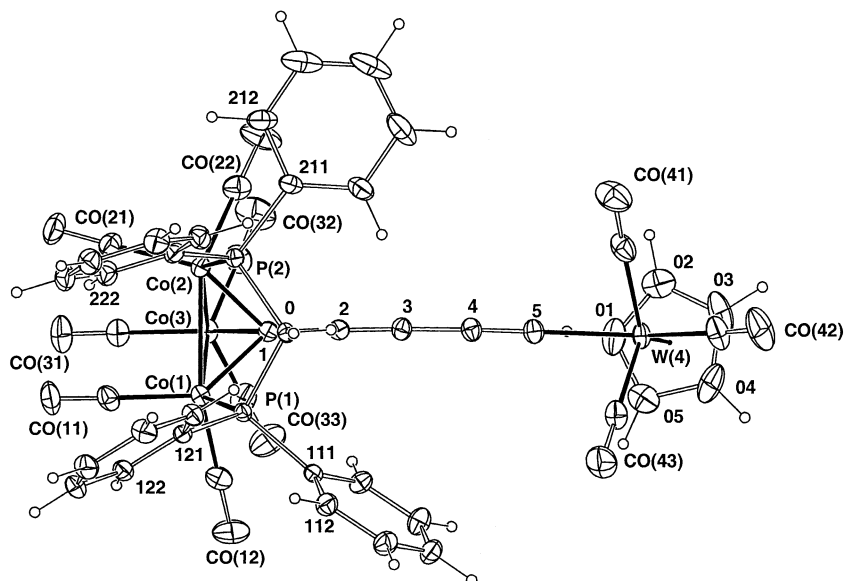

Fig. 1. Plot of a molecule of $\{Cp(OC)_3W\}C\equiv CC\equiv CC\{Co_3(\mu\text{-dppm})(CO)_7\}$ (**5**).

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

Compound	5	6	8
Bond distances			
Co(1)–Co(2)	2.4790(8)	2.496(2)	2.4823(4)
Co(1)–Co(3)	2.4934(8)	2.484(2)	2.4859(4)
Co(2)–Co(3)	2.4874(8)	2.464(2)	2.4882(3)
Co(1)–P(1)	2.217(1)	2.203(2)	2.1931(5)
Co(2)–P(2)	2.201(1)	2.193(2)	2.2093(5)
Co(1)–C(1)	1.910(4)	1.912(7)	1.906(2)
Co(2)–C(1)	1.912(4)	1.901(7)	1.911(2)
Co(3)–C(1)	1.940(4)	1.956(7)	1.948(2)
C(1)–C(2)	1.377(5)	1.383(10)	1.385(2)
C(2)–C(3)	1.219(5)	1.229(10)	1.227(2)
C(3)–C(4)	1.367(6)	1.358(10)	1.364(2)
C(4)–C(5)	1.216(6)	1.216(10)	1.215(2)
C(5)–X [a]	2.119(4)	1.996(7)	1.422(3)
P(1)–C(0)	1.832(4)	1.835(7)	1.840(2)
P(2)–C(0)	1.823(4)	1.829(7)	1.842(2)
Bond angles			
Co(1)–C(1)–C(2)	135.2(4)	131.6(6)	133.2(2)
Co(2)–C(1)–C(2)	132.4(3)	136.5(6)	133.9(1)
Co(3)–C(1)–C(2)	126.9(3)	126.8(6)	127.7(1)
C(1)–C(2)–C(3)	178.8(5)	178.8(8)	176.6(2)
C(2)–C(3)–C(4)	178.5(4)	176.7(8)	176.7(2)
C(3)–C(4)–C(5)	178.4(4)	177.2(8)	177.6(2)
C(4)–C(5)–X [a]	177.0(4)	177.6(6)	177.0(2)
P(1)–C(0)–P(2)	109.7(2)	111.5(3)	110.13(8)

[a] X is W, Au, C(501) in **5**, **6**, **8**, respectively. In **5**, W–C(cp) range between 2.268 and 2.340(5) ($<>2.31_6$ Å); in **6**, Au–P is 2.284(2) Å, C(5)–Au–P 178.6(2)°; in **8**, Fe–C(cp) range between 2.042 and 2.054(3) ($<>2.04_9$ Å).

cobalts bonded to the dppm [Co(1)–Co(2) 2.4790(8), Co(1,2)–Co(3) 2.4934, 2.4874(8) Å]. In general, the carbon chain is bent away from the dppm ligand Ph groups, e.g. angle Co(3)–C(1)–C(2) is ca. 5–10° less than Co(1,2)–C(1)–C(2). The carbon chain has C(1)–C(5) separations (1.377, 1.219, 1.367, 1.216(6) Å) consistent with the $Co_3\equiv C-C\equiv C-C\equiv C$ formulation, with angles at individual carbons being in the quite short range 177.0–178.8(4)°. The W–C(5) separation (2.119(4) Å) is similar to that found in W(C≡CC≡CH)(CO)$_3$Cp (2.148(4) Å) [12].

The reaction is a simple elimination of AuBr(PPh$_3$), which has been detected by t.l.c. examination of the other products of these reactions. Both Pd(0) and Cu(I) are required for the reaction to proceed, comparative systems omitting these reagents either failing to react (with no Pd or Cu) or taking much longer (hours) (with Pd alone).

A multi-step sequence was used to prepare {[(tol)$_3$P]Au}C≡CC≡CC{Co$_3$(μ-dppm)(CO)$_7$} (**6**), involving two successive (phosphine)gold halide-elimination reactions, both proceeding with good yield. The reaction between Au(C≡CC≡CSiMe$_3$){P(tol)$_3$} and

Co$_3$(μ$_3$-CBr)(μ-dppm)(CO)$_7$ gave a 73% yield of Co$_3$(μ$_3$-CC≡CC≡CSiMe$_3$)(μ-dppm)(CO)$_7$ (**7**) after 1 h. This complex was readily characterised from its spectroscopic properties, including ν(C≡C) at 2113 cm^{-1} and the four atoms of the C$_5$ chain not connected to cobalt at δ 90.62, 97.11, 98.58 and 103.45, assigned to C(2–5), respectively. Again, we did not observe any resonance for the cluster-bonded carbon.

Proto-desilylation of **7** with NaOMe, followed by addition of AuCl{P(tol)$_3$}, afforded the desired {[(tol)$_3$P]Au}C≡CC≡CC{Co$_3$(μ-dppm)(CO)$_7$} (**6**) in 68% yield. The spectroscopic properties of this complex differ little from the silylated precursor, only the low energy but broad ν(CO) bands showing more than a 2–3 cm^{-1} shift. Four out of the five carbons of the chain were found between δ 67.92 and 100.31, this time as somewhat broadened singlets.

Fig. 2 is a plot of a molecule of **6**, selected bond parameters being collected in Table 1. The geometries of the end-caps are very similar to previously determined examples and will not be commented on further. Attachment of the C$_5$ chain is similar to that found in **5** above, including the small asymmetry in the C(1)–Co$_3$ bonds induced by the dppm ligand. The C–C separations are in close agreement with those in **5**, while the Au–C(5) bond is 1.996(7) Å [cf. 1.97, 2.02(2) Å in Au(C≡CPh)(PPh$_3$) [13]]. The chain is essentially linear, angles at individual carbons being within the range 176.7–178.8(8)°.

A third example of the application of our reaction is to the synthesis of Co$_3$(μ$_3$-CC≡CC≡CFc)(μ-dppm)(CO)$_7$ (**8**). Here we chose to couple the gold complex {(Ph$_3$P)Au}C≡CC≡CC{Co$_3$(μ-dppm)(CO)$_7$} (**9**), prepared in a manner similar to that described above for **6**, via the I–C(sp) bond in FcC≡CI, a reaction which was complete after 1 h to give the desired complex **8** in 87% yield. Spectroscopic properties were in agreement with the proposed structure, originally confirmed by the M$^+$ ion found at m/z 1002 in the ESMS. Weak ν(C≡C) bands are present in the IR spectrum at 2157 and 2140 cm^{-1}, while resonances at δ_H 4.33, 4.36 and 4.59 and δ_C 70.25, 69.46 and 71.63 arise from the Cp and C$_5$H$_4$ rings of the Fc group. We assign the five resonances in the ^{13}C-NMR spectrum between δ 65.45 and 100.57 to four of the C$_5$ carbons and the *ipso* carbons of the C$_5$H$_4$ group. The single crystal X-ray determination confirmed the molecular structure and a molecule of **8** is depicted in Fig. 3. The arrangement of the Co$_3$C core differs only in detail from those in **5** and **6**, while there are no unexpected features in the ferrocenyl group. The five-atom carbon chain has C–C separations 1.385, 1.227, 1.364, 1.215 and 1.422(3) Å in accord with the diynyl-carbyne formulation depicted in **8**. Angles at individual carbons range between 176.6 and 177.6(2)° except Co–C(1)–C(2) (127.7–133.9(2))°.
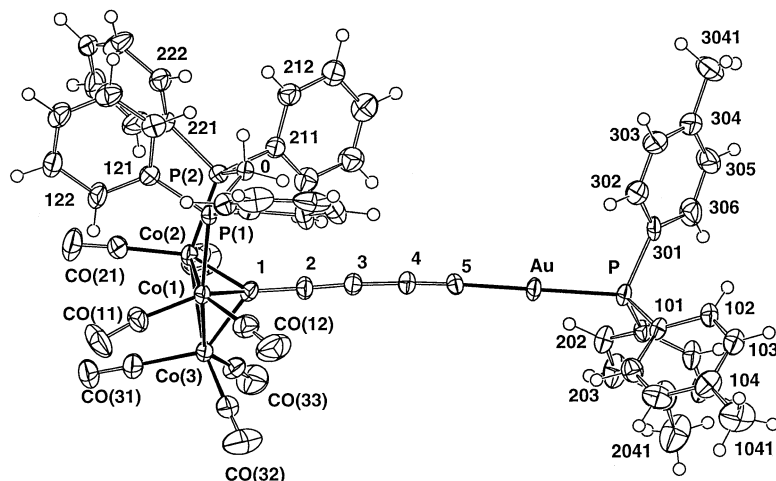
Fig. 2. Plot of a molecule of {[(tol)₃P]Au}C≡CC≡CC{Co₃(μ-dppm)(CO)₇} (**6**).

3. Conclusion

We have described a novel (phosphine)gold(I) halide-elimination reaction which can be applied to reactions involving (so far) C(sp)−Au(PR₃) derivatives and compounds containing X−C(sp) bonds. We have used it here to prepare, in good to high yield, three complexes containing metal end-caps linked by C₅ chains. Structural studies of these three complexes have shown the expected diynylcarbyne nature of the C₅ chain end-capped by the Co₃ cluster, slight elongation of the (formal) C≡C triple bonds and associated shortening of the C−C single bonds indicating that there may be a small degree of delocalisation along this chain. Further studies, including theoretical calculations and electrochemical studies, are necessary to quantify this feature.

Our concurrent studies have shown that this reaction has potentially wide application and further results, including mechanistic studies, will be communicated in due course.

4. Experimental

4.1. General experimental conditions

All reactions were carried out under dry, high purity argon using standard Schlenk techniques. Common solvents were dried, distilled under argon and degassed before use.
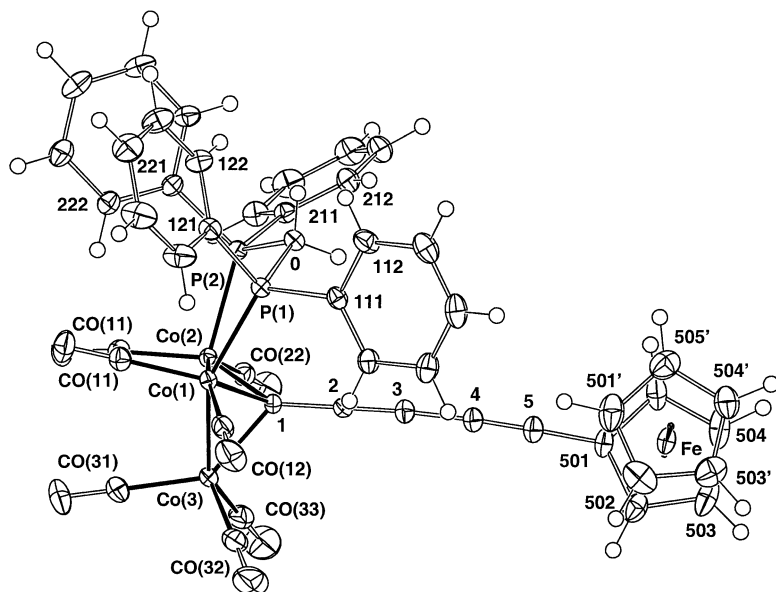

Fig. 3. Plot of a molecule of Co₃(μ₃-CC≡CC≡CFc)(μ-dppm)(CO)₇ (**8**).

4.2. Instrumentation

Infrared spectra were obtained on a Bruker IFS28 FTIR 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 Bruker AM300WB or ACP300 (^{1}H at 300.13, ^{13}C at 75.47, ^{31}P at 121.503 MHz) instruments. Samples were dissolved in $CDCl_3$, unless otherwise stated, contained in 5 mm sample tubes. Chemical shifts are given in ppm relative to internal tetramethylsilane for ^{1}H- and ^{13}C-NMR spectra and external H_3PO_4 for ^{31}P-NMR spectra. ES mass spectra: VG Platform 2 or Finnigan LCQ. Solutions were directly infused into the instrument. Chemical aids to ionisation were used as required [14]. Elemental analyses were performed by CMAS, Melbourne, Australia.

4.3. Reagents

The compounds $Co_3(\mu_3\text{-CBr})(\mu\text{-dppm})(CO)_7$ [11], $\{Cp(OC)_3W\}C{\equiv}CC{\equiv}C\{Au(PPh_3)\}$ [10], $Au(C{\equiv}CC{\equiv}CSiMe_3)\{P(tol)_3\}$ [10], $FcC{\equiv}CI$ [14] were prepared using the cited methods.

4.3.1. $\{Cp(OC)_3W\}C{\equiv}CC{\equiv}CC\{Co_3(\mu\text{-dppm})(CO)_7\}$ (5)

A mixture of $\{Cp(OC)_3W\}C{\equiv}CC{\equiv}C\{Au(PPh_3)\}$ (50 mg, 0.06 mmol), $Co_3(\mu_3\text{-CBr})(\mu\text{-dppm})(CO)_7$ (57 mg, 0.06 mmol), $Pd(PPh_3)_4$ (7 mg, 0.006 mmol) and CuI (1 mg, 0.005 mmol) in THF (7 ml) was stirred at room temperature (r.t.) for 3 h, after which time the solution had turned brown. Purification by preparative t.l.c. (acetone–hexane 3:7) gave a major brown band (R_f 0;42) from which $\{Cp(OC)_3W\}C{\equiv}CC{\equiv}CC\{Co_3(\mu\text{-dppm})(CO)_7\}$ (5) (66.4 mg, 91%) was isolated as dark red crystals ($CHCl_3$). Anal. Found: C, 45.30; H, 1.97. Calc. for ($C_{45}H_{27}Co_3O_{10}P_2W \cdot 0.5CHCl_3$): C, 45.12; H, 2.27%; M, 1150. IR (CH_2Cl_2): $v(C{\equiv}C)$ 2117w; $v(CO)$ 2058s, 2037m, 2008vs, 1955m (br) cm^{-1}. ^{1}H-NMR: δ 3.36 (m, 1H, CH_2), 4.43 (m, 1H, CH_2), 5.71 (s, 5H, Cp), 7.09–7.47 (m, 20H, Ph). ^{13}C-NMR: δ 39.13 (s, br, dppm), 91.91 (s, Cp), 210.19 (s, CO); other peaks at 53.48, 96.01, 114.03 (carbons of C_5 chain). ^{31}P-NMR: δ 34.56 (s, dppm). ESMS (positive ion, with NaOMe, m/z): 1173, $[M+Na]^+$; 1145, $[M+Na-CO]^+$; 1117, $[M+Na-2CO]^+$; (negative ion, MeOH, m/z): 1150, $[M]^-$

4.3.2. $Co_3(\mu_3\text{-CC}{\equiv}CC{\equiv}CSiMe_3)(\mu\text{-dppm})(CO)_7$ (7)

A solution containing $Au(C{\equiv}CC{\equiv}CSiMe_3)\{P(tol)_3\}$ (50 mg, 0.09 mmol), $Co_3(\mu_3\text{-CBr})(\mu\text{-dppm})(CO)_7$ (76 mg, 0.09 mmol), $Pd(PPh_3)_4$ (3 mg, 0.003 mmol) and CUI (1 mg, 0.005 mmol in THF (7 ml) was stirred at r.t.for 1 h. Work-up by preparative t.l.c. (CH_2Cl_2–hexane 1:2) gave a major brown–green band (R_f 0.59) from which

$Co_3(\mu_3\text{-CC}{\equiv}CC{\equiv}CSiMe_3)(\mu\text{-dppm})(CO)_7$ (7) (57.2 mg, 73%) was isolated as brown needles. Anal. Found: C, 53.94; H, 3.69. Calc. for ($C_{40}H_{31}Co_3O_7P_2Si$): C, 53.95; H, 3.51%; M, 890. IR (CH_2Cl_2): $v(C{\equiv}C)$ 2113w; $v(CO)$ 2061s, 2013vs, 1972 (sh) 1954 (sh) cm^{-1}. ^{1}H-NMR: δ 0.36 (s, 9H, $SiMe_3$), 3.46 (m, 1H, CH_2), 4.35 (m, 1H, CH_2), 7.26–7.43 (m, 20H, Ph). ^{13}C-NMR: δ 0.26 (s, $SiMe_3$), 43.26 (t, $J(CP)$ 35.4, CH_2–P), 90.62 (s, C_ε), 57.11 (s, C_δ), 98.58 (s, C_γ), 103.45 (s, C_β), 128.66–135.19 (m, Ph), 201.76, 209.99, 215.57 [3 × s (br), CO]. ^{31}P-NMR: δ 34.92 (s, dppm). ESMS (negative ion, with MeOH, m/z): 890, $[M]^-$; (with NaOMe, m/z): 817, $[M-SiMe_3]^-$.

4.3.3. $\{[(tol)_3P]Au\}C{\equiv}CC{\equiv}CC\{Co_3(\mu\text{-dppm})(CO)_7\}$ (6)

A solution of NaOMe (twofold excess) in MeOH (1 ml) was added to $Co_3(\mu_3\text{-CC}{\equiv}CC{\equiv}CSiMe_3)(\mu\text{-dppm})(CO)_7$ (100 mg, 0.11 mmol) in THF/MeOH (1/3, 4 ml). After 1 h at r.t., spot t.l.c. showed that all starting complex had been consumed. $AuCl\{P(tol)_3\}$ (59 mg, 0.11 mmol) was then added and the reaction mixture was stirred for 1 h to give a brown precipitate under a brown supernatant. The precipitate was filtered off, washed with MeOH and dried in air. Crystallisation (CH_2Cl_2–MeOH) gave very dark red crystals of $\{[(tol)_3P]Au\}C{\equiv}CC{\equiv}CC\{Co_3(\mu\text{-dppm})(CO)_7\}$ (6) (99.1 mg), an extra 2.3 mg (total yield 68.5%) being obtained from the mother liquor by preparative t.l.c. (acetone–hexane 3:7). Anal. Found: C, 52.86; H, 3.30. Calc. for ($C_{58}H_{43}AuCo_3O_7P_3$): C, 52.83; H, 3.27%; M, 1318. IR (CH_2Cl_2): $v(C{\equiv}C)$ 2115w; $v(CO)$ 2059s, 2010vs, 1986 (sh), 1967 (sh) cm^{-1}. ^{1}H-NMR: δ 2.46 (s, 9H, Me), 3.44, 4.46 (2 × m, 2 × 1H, CH_2), 7.16–7.56 (m, 32H, Ph+C_6H_4). ^{13}C-NMR: δ 21.43 (s, Me), 40.79 [t, $J(CP)$ 20, CH_2P], 67.92 [s(br), C_ε], 89.09 [s(br), C_δ], 92.55 [s(br), C_γ], 100.31 [s(br), C_β], 201.95, 210.21, 221.79 [3 × s (br), CO]. ^{31}P-NMR: δ 33.36 [s(br), dppm], 40.19 [s(br), $P(tol)_3$]. ESMS (negative ion, with NaOMe–MeOH, m/z): 1317, $[M-H]^-$.

4.3.4. $Co_3(\mu_3\text{-CC}{\equiv}CC{\equiv}CFc)(\mu\text{-dppm})(CO)_7$ (8)

A mixture of $\{(Ph_3P)Au\}C{\equiv}CC\{Co_3(\mu\text{-dppm})(CO)_7\}$ (75 mg, 0.06 mmol), $FcC{\equiv}CI$ (20 mg, 0.06 mmol), $Pd(PPh_3)_4$ (3.5 mg, 0.003 mmol) and CuI (1 mg, 0.006 mmol) in THF (10 ml) was stirred at r.t. for 1 h. Evaporation and purification of the residue by preparative t.l.c. (acetone–hexane 1:4) gave two bands. The faster moving (R_f 0.93) contained $FcC{\equiv}CC{\equiv}CFc$ (1.2 mg, 5%), identified by comparison with an authentic sample. The major product was contained in the brown–orange band (R_f 0.26), which gave $Co_3(\mu_3\text{-CC}{\equiv}CC{\equiv}CFc)(\mu\text{-dppm})(CO)_7$ (8) (51.7 mg, 87%) as dark red crystals (C_6H_6–hexane). Anal. Found: C, 59.22; H, 3.15. Calc. for ($C_{47}H_{31}Co_3FeO_7P_2 \cdot C_6H_6$): C, 58.88; H, 3.43%; M, 1002. IR (CH_2Cl_2): $v(C{\equiv}C)$ 2157w,

2140vw; $\nu(CO)$ 2058s, 2011vs, 1990 (sh), 1970 (sh) cm^{-1}. ^{1}H-NMR: δ 3.48, 4.40 (2 × m, 2 × 1H, CH$_2$), 4.33 (s, 5H, Cp), 4.36, 4.59 (2 × m, 2 × 2H, C$_5$H$_4$), 7.17–7.71 (m, 20H, Ph). ^{13}C-NMR: δ 42.37 [t, J(CP) 21.8, CH$_2$], 70.25 (s, Cp), 69.46, 71.63 (2 × s, C$_5$H$_4$), 65.45, 72.70, 95.17, 97.55, 100.57 (5 × s, 4 × C of C$_5$ chain + C$_{ipso}$ of C$_5$H$_4$), 127.63–135.36 (m, Ph), 201.77, 209.71, 217.17 [s (br), CO]. ^{31}P-NMR: δ 34.77 (s). ESMS (positive ion, with NaOMe–MeOH, m/z): 1025, [M + Na]$^+$; 1002, [M]$^+$; 974, [M − CO]$^+$; (negative ion, with NaOMe–MeOH, m/z): 1001, [M − H]$^+$.

4.4. Structure determinations

Full spheres of diffraction data to the indicated limits were measured at ca. 153 K using a Bruker AXS CCD area-detector instrument. N_{tot} reflections were merged to N unique (R_{int} quoted) after 'empirical'/multiscan absorption correction (proprietary software), N_o with $F > 4\sigma(F)$ being used in the full matrix least squares refinement. All data were measured using monochromatic Mo–K$_\alpha$ radiation, $\lambda = 0.71073$ Å. Anisotropic thermal parameter forms were refined for the non-hydrogen atoms, $(x, y, z, U_{iso})_H$ being constrained at estimated values. Conventional residuals R, R_w on $|F|$ are given [weights: $(\sigma^2(F) + 0.0004F^2)^{-1}$]. Neutral atom complex scattering factors were used; computation used the XTAL-3.7 program system [15]. 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 Table 1.

(5) {Cp(OC)$_3$W}C≡CC≡CC{Co$_3$(μ-dppm)(CO)$_7$} · 0.5CHCl$_3$ ≡ C$_{45}$H$_{27}$Co$_3$O$_{10}$P$_2$W · 0.5CHCl$_3$, $M = 1209.99$. Monoclinic, space group $C2/c$, $a = 33.683(1)$, $b = 12.3289(5)$, $c = 23.5287(9)$ Å, $\beta = 110.622(1)°$, $V = 9145$ Å^3, $Z = 8$. $D_{calc} = 1.75_7$ g cm^{-3}, μ(Mo–K$_\alpha$) = 3.79 mm^{-1}, $T_{min/max} = 0.77$. Crystal size 0.14 × 0.10 × 0.06 mm. $2\theta_{max} = 58°$. $N_{tot} = 59037$, $N = 12191$ ($R_{int} = 0.048$), $N_o = 8006$. $R = 0.032$, $R_w = 0.034$.

(6) Co$_3${μ$_3$-CC≡CC≡C[AuP(tol)$_3$]}(μ-dppm)(CO)$_7$ · CH$_2$Cl$_2$ ≡ C$_{58}$H$_{43}$AuCo$_3$O$_7$P$_3$ · 0.25CH$_2$Cl$_2$, $M = 1403.60$. Monoclinic, space group $P2_1/n$, $a = 18.766(5)$, $b = 16.331(5)$, $c = 18.895(5)$ Å, $\beta = 97.566(6)°$, $V = 5740$ Å^3, $Z = 4$. $D_{calc} = 1.62_4$ g cm^{-3}, μ(Mo–K$_\alpha$) = 3.63 mm^{-1}, $T_{min/max} = 0.71$. Crystal size 0.43 × 0.32 × 0.24 mm. $2\theta_{max} = 58°$. $N_{tot} = 83346$, $N = 15443$ ($R_{int} = 0.069$), $N_o = 10909$. $R = 0.056$, $R_w = 0.087$.

(8) Co$_3$(μ$_3$-CC≡CC≡CFc)(μ-dppm)(CO)$_7$ · C$_6$H$_6$ ≡ C$_{47}$H$_{31}$Co$_3$FeO$_7$P$_2$ · C$_6$H$_6$, $M = 1080.47$. Triclinic, space group $P\bar{1}$, $a = 11.7433(9)$, $b = 13.1110(9)$, $c = 16.043(1)$ Å, $\alpha = 80.381(2)$, $\beta = 72.866(2)$, $\gamma = 80.716(2)°$, $V = 2311$ Å^3, $Z = 2$. $D_{calc} = 1.55_3$ g cm^{-3}, μ(Mo–K$_\alpha$) = 1.49 mm^{-1}, $T_{min/max} = 0.84$. Crystal size 0.40 × 0.14 × 0.12 mm. $2\theta_{max} = 75°$. $N_{tot} = 45164$, $N = 23480$ ($R_{int} = 0.027$), $N_o = 17041$. $R = 0.043$, $R_w = 0.048$.

5. Supplementary material

Full details of the structure determinations (except structure factors) for **5**, **6** and **8** have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 210247–210249, respectively Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

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