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A new approach to the synthesis of carbon chains capped by metal clusters

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Abstract

Reactions of $Co_3(\mu_3\text{-CBr})(\mu\text{-dppm})(CO)_7$ with $\{Au[P(tol)_3]\}_2\{\mu\text{-}(C\equiv C)_n\}$ ($n = 2$–4) have given $\{Co_3(\mu\text{-dppm})(CO)_7\}\{\mu_3{:}\mu_3\text{-}C(C\equiv C)_nC\}$ [$n = 2$ (**1**), 3 (**2**), 4 (**3**)] containing carbon chains capped by the cobalt clusters. Tetracyanoethene reacts with **2** to give $\{Co_3(\mu\text{-dppm})(CO)_7\}_2\{\mu_3{:}\mu_3\text{-}C(C\equiv C)_2C[{=}C(CN)_2]C[{=}C(CN)_2]C\}$ (**4**). X-ray structural characterisation of **1**, **3** and **4** are reported, that for **3** being the first of a cluster-capped C_{10} chain.

Keywords: Carbon chains; Cobalt clusters; Capped clusters; C_{10} chains

1. Introduction

The chemistry of molecules containing chains of sp carbon atoms continues to excite interest, both from their intrinsic properties and as potential precursors for nanoscale components [1,2]. Although most studies have been carried out with compounds containing C_2 or C_4 chains linking two metal centres, species with longer carbon chains have also been prepared, including the C_{20} derivative, $\{Re(NO)(PPh_3)Cp^*\}_2\{\mu\text{-}(C\equiv C)_{10}\}$ [3]. More recently, platinum complexes containing between eight and 12 carbons have been used as templates for the construction of novel helical systems in which the strands have no bonded contacts with each other [4].

Complexes in which metal clusters act as end-caps to carbon chains are less common and usually involve the terminal carbons interacting with three metal atoms. Recent examples include $\{Co_3(CO)_9\}_2\{\mu_3{:}\mu_3\text{-}C(C\equiv C)_nC\}$ ($n = 0$–2) [5–7], $\{(\mu_3\text{-}Me_3SiC)Co_3Cp_3\}_2\{\mu_3{:}\mu_3\text{-}C(C\equiv C)_nC\}$ ($n = 0$–2, 4) [8,9] and $\{Cu_3(\mu\text{-dppm})_3\}_2\{\mu_3{:}\mu_3\text{-}(C\equiv C)_2Au(C\equiv C)_2\}$ [10]. In general, however, these compounds are accessed with difficulty, reported yields often being low as a result of side reactions occurring when conventional coupling reactions (e.g. Sonogashira) are used.

We report here a new approach to the synthesis of this type of molecule, which arose out of our studies of reactions designed to prepare cluster-capped chains containing odd-numbers of carbon atoms.

2. Results

We chose to use the μ_3-bromocarbyne precursor $Co_3(\mu_3\text{-CBr})(\mu\text{-dppm})(CO)_7$, which is readily obtained from a reaction of dppm with $Co_3(\mu\text{-CBr})(CO)_9$ in the presence of Me_3NO (tmno) [11], in which the dppm ligand helps preserve the Co_3 cluster against degradation. Copper(I)–palladium(0)-catalysed reactions of this complex with the gold(I)–phosphine derivatives $\{Au[P(tol)_3]\}_2\{\mu\text{-}(C\equiv C)_n\}$ ($n = 2$–4) [12] afforded the corresponding cluster-capped C_n chains $\{Co_3(\mu\text{-dppm})(CO)_7\}\{\mu_3{:}\mu_3\text{-}C(C\equiv C)_nC\}$ (Scheme 1; $n = 2$ (**1**), 3 (**2**), 4 (**3**)) in good to excellent yields. Mild conditions are employed, reactions generally being complete within 3 h at room temperature. The new compounds form

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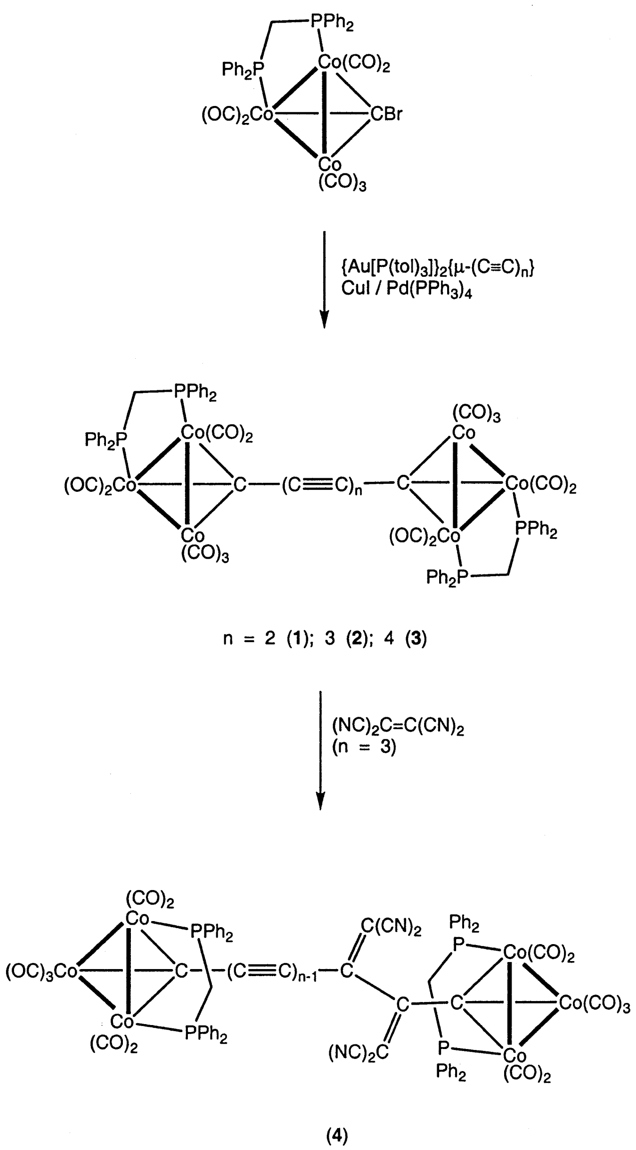

Scheme 1.

dark brown, almost black crystals which are stable in air.

The IR ν(CO) spectra contain two strong broad bands with shoulders to lower frequencies and are similar to those found for $Co_3(\mu_3\text{-}CBr)(\mu\text{-}dppm)(CO)_7$ [2064s, 2014vs, 1987 (sh), 1973 (sh) cm^{-1}] [11]. The ν(CO) bands of **1**–**3** were found at similar frequencies, with additional very weak absorptions at 2128 (**1**), 2098 (**2**) and 2112 and 2104 cm^{-1} (**3**) being assigned to ν(C≡C). In general, the bands associated with the C≡C triple bond are very weak and were only recorded with a Nujol mull. For **1**, the ^{1}H-NMR spectrum contains resonances for the dppm ligand at δ 3.41 and 4.43 (CH_2) and between 7.20 and 7.46 (Ph); the ^{31}P-NMR spectrum contains a resonance at δ 35.06. The ^{13}C-NMR spectrum of **1** contains two resonances at δ 97.56 and 117.96, which we assign to the two types of triply-bonded carbons; as for all complexes described herein, the resonances for the μ_3-C atoms was not detected. Complex **2** was too insoluble to record a satisfactory ^{13}C-NMR spectrum, while for **3**, singlet resonances at δ 71.63, 82.74, 97.56 and 103.13 are assigned to the carbons of the C_8 chain which links the two μ_3-C atoms. The electrospray (ES) mass spectra were recorded with added NaOMe. For **1**, the molecular ion at m/z 1586 was accompanied by adduct ions $[M+Na-nCO]^+$ ($n=0$–8). For **2**, a strong $[Co_3C_4(CO)_7(dppm)]^+$ ion is found at m/z 805, together with a weak adduct $[M+Na]^+$ at m/z 1633. The negative ion spectrum contains $[M-H]^-$ and $[M+I]^-$, the latter arising from CsI reference in the spectrometer. Similar ions are present in the spectrum of **3**.

The molecular structures of **1** and **3** were determined by single-crystal X-ray diffraction studies. Plots of molecules of **1** and **3** are given in Figs. 1 and 2, respectively, with selected structural data being collected in Table 1. As can be seen, the centrosymmetric molecules consist of two $Co_3(\mu\text{-}dppm)(CO)_7$ moieties end-capping the C_6 or C_{10} chains. In both complexes, the dppm ligands bridge two of the cobalts [Co–P 2.1961(6) to 2.2164(5) Å] in equatorial positions and on opposite sides of the molecule. The Co_3 base is almost equilateral, with Co–Co separations being somewhat longer in **1** [2.4857, 2.4890, 2.4969(4) Å] than in **3** [2.4732, 2.4844, 2.4893(4) Å]. Two Co–C distances from cobalt atoms bearing the dppm ligand are shorter [1.897, 1.902(2) (**1**); 1.914, 1.898(2) Å (**3**)] than from the third cobalt [1.933, 1.936(2) Å].

The carbon chains are almost linear with alternating long–short–long separations [1.377, 1.225, 1.346(3) (**1**); 1.376, 1.226, 1.345, 1.221, 1.347(3) Å (**3**)] which, however, are respectively shorter and longer than purely organic C(sp)–C(sp) single and triple bonds, suggesting some degree of delocalisation occurs along the chain. The C–C–C angles vary between 173.3 and 178.4(2)°. The most significant deviations from linearity are at atoms having close contacts to the shrouding hydrogen atoms of the chelate ligand, C(1)–C(2)–C(3) 175.6(2)°, with associations C(2)···H(0a, 216) 2.63(2), 2.64(2) Å in **1**, and C(1)–C(2)–C(3), C(2)–C(3)–C(4) 176.1(2), 173.3(2)° with associations H(116)···C(2,3) 2.62, 2.52 Å (est.) in **3** (see Figs. 1 and 2).

We have so far been unsuccessful in obtaining X-ray quality crystals of **2**. Previously, we have used the formation of adducts with tetracyanoethene (tcne) to confirm the presence of long C(sp) chains [13]. Accordingly, we examined the reaction between **2** and tcne, which occurred overnight at room temperature. Separation of the products afforded black crystals of the major product (42%), which was determined to be the mono-adduct (**4**) by analysis, spectroscopy and a single-crystal X-ray structure. In the IR spectrum, the usual ν(CO) bands were accompanied by ν(CN) at 2214 and ν(CC)

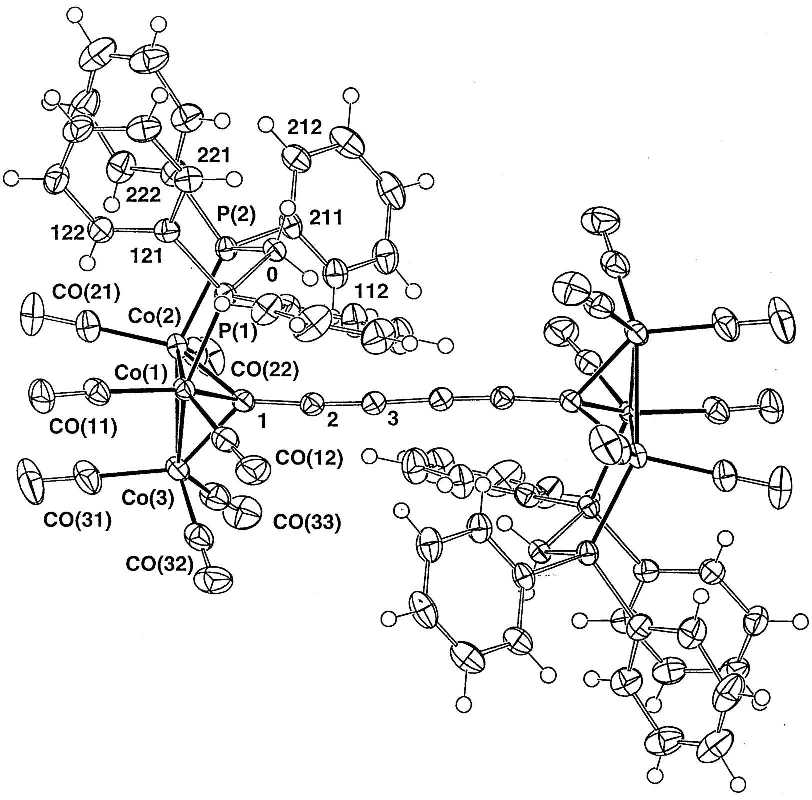

Fig. 1. Plot of a molecule of $\{Co_3(\mu\text{-dppm})(CO)_7\}_2\{\mu_3{:}\mu_3\text{-}C(C{\equiv}C)_2C\}$ (**1**).

at 2099 cm^{-1}, while the ^1H-NMR spectrum contained only resonances due to the dppm ligand at δ 3.90, 4.28 (CH_2) and between 7.06 and 7.60 (Ph). The ^{31}P-NMR spectrum contained a singlet at δ 35.19 and an AB quartet centred at δ 32.64, both having relative intensity 1. The ^{31}P-NMR data confirmed the formation of an asymmetric adduct, atoms P(21) and P(22) being differentiated by virtue of the (different) $C(CN)_2$ groups nearby. Atoms P(11) and P(12) are sufficiently distant to give only one resonance. Both positive and negative ion

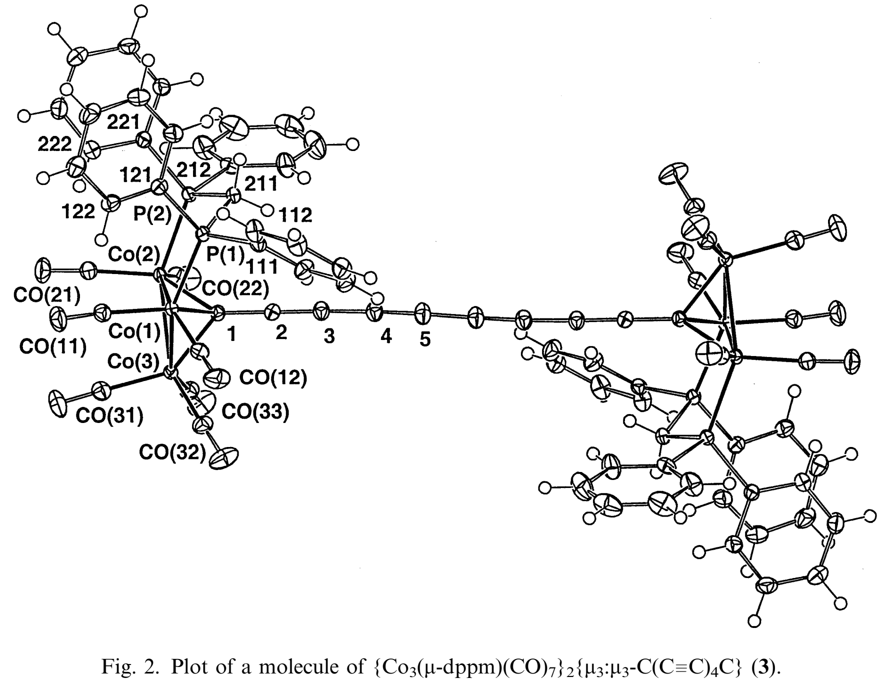

Fig. 2. Plot of a molecule of $\{Co_3(\mu\text{-dppm})(CO)_7\}_2\{\mu_3{:}\mu_3\text{-}C(C{\equiv}C)_4C\}$ (**3**).

Table 1
Selected structural data for $\{Co_3(\mu\text{-dppm})(CO)_7\}\{\mu_3{:}\mu_3\text{-}C(C{\equiv}C)_nC\}$ [$n = 2$ (**1**), 4 (**3**)]

	1	**3**
Bond distances (Å)		
Co(1)–Co(2)	2.4969(4)	2.4732(4)
Co(1)–Co(3)	2.4893(4)	2.4893(2)
Co(2)–Co(3)	2.4857(4)	2.4844(3)
Co(1)–P(1)	2.1961(6)	2.2164(5)
Co(2)–P(2)	2.2035(6)	2.2032(5)
Co(1)–C(1)	1.897(2)	1.914(2)
Co(2)–C(1)	1.902(2)	1.898(2)
Co(3)–C(1)	1.933(2)	1.936(2)
C(1)–C(2)	1.377(3)	1.376(2)
C(2)–C(3)	1.225(3)	1.226(3)
C(3)–C(4)	1.346(3) [C(3′)]	1.345(3)
C(4)–C(5)		1.221(3)
C(5)–C(5′)		1.347(3)
Bond angles (°)		
C(1)–C(2)–C(3)	175.6(2)	176.1(2)
C(2)–C(3)–C(4)	177.9(2) [C(3′)]	173.3(2)
C(3)–C(4)–C(5)		176.8(2)
C(4)–C(5)–C(5′)		178.4(2)

Table 2
Selected structural data for $\{Co_3(\mu\text{-dppm})(CO)_7\}_2\{\mu_3{:}\mu_3\text{-}C(C{\equiv}C)_2C[{=}C(CN)_2]C[{=}C(CN)_2]C\}$ (**4**)

Bond distances (Å)			
Co(11)–Co(12)	2.4733(5)	Co(21)–C(8)	1.908(2)
Co(11)–Co(13)	2.4749(5)	Co(22)–C(8)	1.899(3)
Co(12)–Co(13)	2.4845(5)	Co(23)–C(8)	1.955(2)
Co(21)–Co(22)	2.4799(6)	C(1)–C(2)	1.380(3)
Co(21)–Co(23)	2.4965(5)	C(2)–C(3)	1.226(3)
Co(22)–Co(23)	2.4796(5)	C(3)–C(4)	1.345(3)
Co(11)–P(11)	2.2041(7)	C(4)–C(5)	1.219(4)
Co(12)–P(12)	2.2078(6)	C(5)–C(6)	1.410(3)
Co(21)–P(21)	2.2316(7)	C(6)–C(7)	1.483(3)
Co(22)–P(22)	2.2048(6)	C(6)–C(81)	1.376(4)
Co(11)–C(1)	1.907(3)	C(7)–C(8)	1.451(4)
Co(12)–C(1)	1.901(2)	C(7)–C(71)	1.391(5)
Co(13)–C(1)	1.927(2)		
Bond angles (°)			
C(1)–C(2)–C(3)	179.3(3)	C(6)–C(7)–C(8)	118.8(3)
C(2)–C(3)–C(4)	177.5(3)	C(5)–C(6)–C(81)	120.7(2)
C(3)–C(4)–C(5)	178.2(3)	C(7)–C(6)–C(81)	122.2(2)
C(4)–C(5)–C(6)	169.8(3)	C(6)–C(7)–C(71)	113.3(2)
C(5)–C(6)–C(7)	117.1(2)	C(8)–C(7)–C(71)	128.0(2)

ES mass spectra were obtained with addition of NaOMe, the ions at m/z 1739 ($[M+H]^+$) and at 1769 ($[M+OMe]^-$) confirming the formulation.

Fig. 3 is a plot of a molecule of **4**, selected structural data being presented in Table 2. Dimensions of the Co_3C clusters are similar to those found for **1** and **3**. The second dppm ligand is aligned so that the two P atoms are in different environments, as indicated by the ^{31}P-NMR spectrum. Atoms C(1)–C(5) form an approximately linear chain [C–C 1.380, 1.226, 1.345, 1.219(3) Å]. Here the C···H contacts are slightly longer [C(2)···H(10a, 1122), C(3)···H(1222, 2222) 2.88, 2.90, 2.88, 2.73 Å; C(4)···H(20a, 2122, 2222) 2.83, 2.72, 2.87 Å]; the chain is generally straighter [C–C(2–4)–C > 177.5(3)°, except at C(5), which is 169.8(3)°. The only contact in this molecule is long [C(5)···H(20a) 2.83 Å] and seemingly unlikely to be the cause of the distortion, which may originate, rather, in packing constraints of

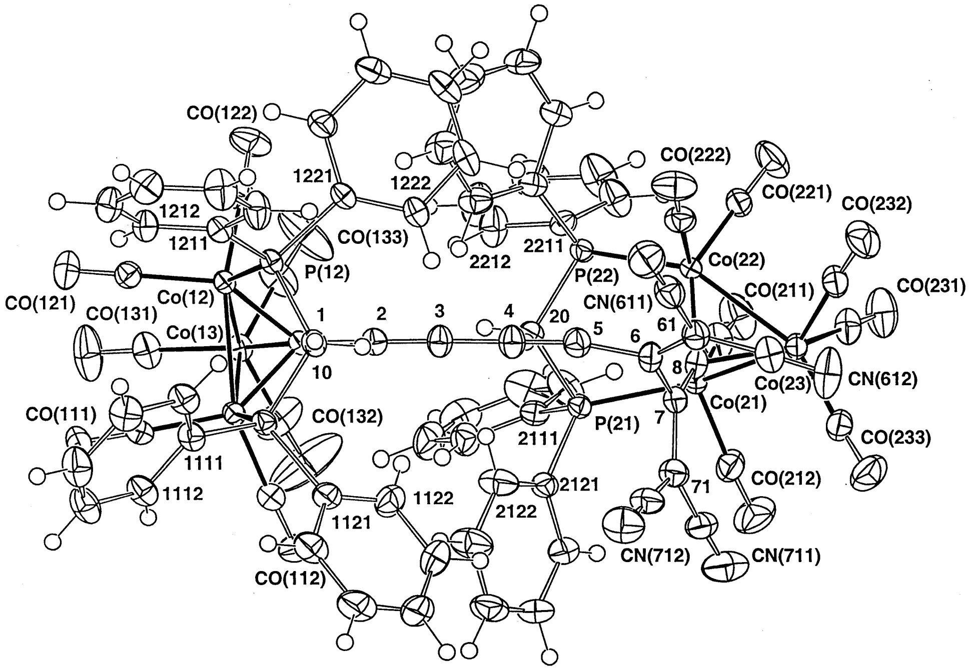

Fig. 3. Plot of a molecule of $\{Co_3(\mu\text{-dppm})(CO)_7\}_2\{\mu_3{:}\mu_3\text{-}C(C{\equiv}C)_2C[{=}C(CN)_2]C[{=}C(CN)_2]C\}$ (**4**).

the neighbouring CN groups against the nearby carbonyls, e.g. N(612)···C,O(232), C,O(233) 3.216(4), 3.335(4), 3.309(4), 3.379(4), N(711)···C,O(212), C,O(233) 3.009(5), 3.007(4), 3.460(5), 3.350(4) Å. The tcne molecule has added to the C(6)–C(7) triple bond to give a 1,3-diene, in which atoms C(6) and C(7) are separated by a single bond [1.483(3) Å] and form shorter bonds to C(5) [1.410(3) Å] and C(8) [1.451(4) Å]. Within the diene system, the double bonds are C(6)–C(61) and C(7)–C(71) [1.376, 1.391(4) Å], with angles at C(6) of 120.7 and 122.2(2) and at C(7) of 113.3 and 128.0(2)°. As found with other tetracyano-dienes, there is a considerable torsion angle between the two $C(CN)_2$ groups [88.5(3)°].

3. Discussion

In contrast with previous syntheses of carbon chain complexes involving the $Co_3(CO)_9(\mu_3\text{-}C)$ system, which have used conventional coupling reactions between $Co_3(\mu\text{-}CCl)(CO)_9$ and terminal alkynes in amine solvents catalysed by Cu(I)–Pd(0) [5–7], elimination of $AuBr\{P(tol)_3\}$ with concomitant transfer of the carbon chain to the μ_3-C atom has resulted in considerably higher yields in the present study. The presence of the μ-dppm ligand undoubtedly also contributes to the stability of the Co_3C cluster under these reaction conditions. The resulting complexes contain two $Co_3(\mu\text{-dppm})(CO)_7$ clusters bridged by C_6, C_8 or C_{10} chains. Although a complex containing a C_{10} chain capped by $\{Co_3Cp_3\}{\equiv}CSiMe_3$ moieties was briefly described in an earlier study [9a], **3** is the first crystallographically characterised example of a C_{10} chain end-capped by cluster moieties,

The course of the reaction involves elimination of $AuBr(PR_3)$ and transfer of the carbon chain to the cluster-bonded carbon of the precursor. The pseudo-metal attributes of cluster carbynes have been noted before [14] and are a factor in the success of this reaction. The nature of the carbon chain is revealed by the structural determination, the cluster being attached to a carbon with carbynic character, resulting in the familiar long–short–long alternation of bond lengths. The dimensions suggest that partial delocalisation occurs along the chain, in turn suggesting that some electronic communication between the cluster moieties might occur. However, preliminary cyclic voltammetry studies have shown that while two reduction waves are found for **1** at $E_{1/2}$ −1.11 and −1.26 V, respectively (referenced to $[FcH]^{0/1+}$ at +0.46 V), only a single reduction wave is found for **3** at $E_{1/2}$ −1.025 V, suggesting that there is some electronic communication in the former, but little if any in **3**. Oxidation processes occur at higher potentials (between +0.50 and +1.20 V) in both complexes.

While we were not able to get single crystals of **2** for X-ray studies, we have demonstrated the presence of the C_8 chain in **2** by a structural study of the tcne adduct. While the initial addition often proceeds via an intensely coloured, paramagnetic adduct, this did not occur in the reaction of tcne with **2**. The first formed cyclo-adduct is the cyclobutenyl compound, which undergoes a more or less rapid ring-opening to the tetracyano diene of the type found in **4**. Complex **4** is the first adduct of the latter type, since, to our knowledge, there is no report of addition of tcne to non-metallic alkynes, although recently addition of tcne to ferrocenyl-alkynes and diynes was described [15]. This contrasts with the extensive studies that have been reported with σ-alkynyl derivatives of transition metals [13,16]. At present, we have no evidence for the formation of a bis-adduct; inspection of Fig. 3 suggests that approach to the C(2)–C(3) triple bond is sterically hindered by the dppm phenyl groups.

As detailed above, distortions in the carbon chain, which have been the source of some discussion recently, occur at carbons which have some close contacts to H atoms, which collectively shroud the chain, suggesting that these interactions are not unimportant in determining the final conformation.

4. Conclusions

This work has described a novel coupling reaction between a gold(I)–phosphine derivative of a poly-yne with the halo derivative of a tricobalt cluster carbyne to give complexes containing long carbon chains end-capped by the clusters. The formal description of the carbon chains as $\equiv C{-}(C{\equiv}C)_n{-}C\equiv$ units triply-bonded to an M_3 cluster is consistent with the observed alternation of C–C bonds, although detailed inspection of the dimensions of these suggests that a degree of electron delocalisation occurs along the chain. The complexes that we have described are novel examples of long C_n chains ($n \geq 4$) linking cluster groups. The convenience and high yields obtained here have encouraged us to extend these reactions successfully to other halocarbyne systems, which will be described elsewhere.

5. Experimental

5.1. General

Reactions were carried out under an atmosphere of nitrogen, but no special precautions were taken to exclude oxygen during work-up. Common solvents were dried and distilled under nitrogen before use. Elemental analyses were performed by the Chemical and Microanalytical Services (CMAS), Belmont, Vic.

Preparative TLC was carried out on glass plates (20 × 20 cm) coated with silica gel (Merck 60 GF254, 0.5 mm thickness).

5.1.1. Instrumentation

IR: Perkin–Elmer 1720X FTIR. Spectra of solutions in CH_2Cl_2 held in a 0.05 mm path-length NaCl cell were recorded. NMR: Bruker CXP300 or ACP300 (^{1}H- at 300.13 MHz, ^{13}C- at 75.47 MHz) or Varian Gemini 200 (^{1}H- at 199.8 MHz, ^{13}C- at 50.29 MHz) spectrometers. Unless otherwise stated, spectra were recorded using solutions in $CDCl_3$ in 5 mm sample tubes. ES mass spectra: Finnegan LCQ. Solutions were directly infused into the instrument. Chemical aids to ionisation were used as required [17]. Cyclic voltammograms were recorded for 1.0 mM solution in CH_2Cl_2, with 0.1 M $[NBu_4][BF_4]$ as supporting electrolyte, using a Maclab 400 instrument. A three-electrode system was used, consisting of a Pt-dot working electrode and Pt counter and reference electrodes. Potentials are given in V versus SCE, the ferrocene–ferricinium couple being used as internal calibrant for the measured potentials ($E_0 = 0.46$ V vs. SCE) [18].

5.1.2. Reagents

$Co_3(\mu_3\text{-CBr})(CO)_9$ was made from $Co_2(CO)_8$ and CBr_4 via a modified literature procedure [19]. Addition of dppm (one equivalent) in the presence of tmno afforded $Co_3(\mu_3\text{-CBr})(\mu\text{-dppm})(CO)_7$ (70–80%). The Au(I)–phosphine complexes $\{Au[P(tol)_3]\}_2\{\mu\text{-}(C{\equiv}C)_n\}$ were obtained from reactions between $AuCl\{P(tol)_3\}$ and $SiMe_3(C{\equiv}C)_nSiMe_3$ ($n = 2$–4) carried out in MeOH in the presence of NaOH [12].

5.2. Preparation of $\{Co_3(\mu\text{-dppm})(CO)_7\}_2\{\mu_3{:}\mu_3\text{-}C(C{\equiv}C)_nC\}$

*5.2.1. (a) $n = 2$ (**1**)*

Tetrahydrofuran (10 ml) was added to a solid mixture of $\{Au[P(tol)_3]\}_2\{\mu\text{-}(C{\equiv}C)_2\}$ (105 mg, 0.1 mmol), $Co_3(\mu_3\text{-CBr})(\mu\text{-dppm})(CO)_7$ (170 mg, 0.2 mmol), $Pd(PPh_3)_4$ (14 mg, 0.012 mmol) and CuI (2 mg, 0.01 mmol) and the whole was stirred at room temperature (r.t.) for 3 h. The filtered solution was evaporated under vacuum and the residue was extracted with CH_2Cl_2. Separation by preparative TLC (C_3H_6O–C_6H_{12} 3/7) gave one major brown band (R_f 0.51) which contained $\{Co_3(\mu\text{-dppm})(CO)_7\}_2\{\mu_3{:}\mu_3\text{-}C(C{\equiv}C)_2C\}$ (**1**) (142 mg, 89.3%), isolated as dark brown crystals. Anal. Found: C, 52.89; H, 2.85. Calc. for $C_{70}H_{44}Co_6O_{14}P_4$: C, 52.99; H, 2.80%; M, 1586. IR (cm^{-1}) (Nujol): ν(C≡C) 2128vw; (CH_2Cl_2) ν(CO) 2053s, 2007vs, 1967 (sh). ^{1}H-NMR: δ 3.41, 4.43 (2 × m, 2 × 1H, CH_2), 7.20–7.46 (m, 20H, Ph). ^{13}C-NMR: δ 44.59 (s, br, dppm), 97.56 [s, C(3)], 117.96 [s, C(2)], 128.55–135.34 (m, Ph); 202.25, 209.44 (s, br, CO). ^{31}P-NMR: δ 35.06 (s, dppm). ES–MS (positive ion, with NaOMe, m/z): 1609, $[M+Na]^+$; 1586, $[M]^+$; 1581–1385, $[M+Na-nCO]^+$ ($n = 1$–8); (negative ion, MeOH, m/z): 1585, $[M-H]^-$.

*5.2.2. (b) $n = 3$ (**2**)*

A similar reaction to (a) above used $\{Au[P(tol)_3]\}_2\{\mu\text{-}(C{\equiv}C)_3\}$ (50 mg, 0.05 mmol), $Co_3(\mu_3\text{-CBr})(\mu\text{-dppm})(CO)_7$ (89.6 mg, 0.1 mmol), $Pd(PPh_3)_4$ (5 mg, 0.004 mmol) and CuI (1 mg, 0.005 mmol) in THF (25 ml). After stirring at r.t. for 2 h, a new brown band (R_f 0.38) was present. Purification by running the solution through a short silica column gave $\{Co_3(\mu\text{-dppm})(CO)_7\}_2\{\mu_3{:}\mu_3\text{-}C(C{\equiv}C)_3C\}$ (**2**) (61.5 mg, 77%) as a dark brown solid, only moderately soluble in THF and other organic solvents. Anal. Found: C, 51.25; H, 2.49 (consistent analyses could not be obtained as a result of the insolubility of this complex). Calc. for $C_{72}H_{44}Co_6O_4P_4$: C, 53.69; H, 2.75%; M, 1610. IR (cm^{-1}) (Nujol): ν(C≡C) 2089vw; (CH_2Cl_2) ν(CO) 2064 (sh), 2045s, 2014vs, 1991 (sh), 1974w. ES–MS (negative ion, with NaOMe–MeOH, m/z): 1737, $[M+I]^-$ (I from CsI calibrant); 1609, $[M-H]^-$; (positive ion, NaOMe–MeOH, m/z): 1633, $[M+Na]^+$; 805, $[Co_3C_4(CO)_7(dppm)]^+$.

*5.2.3. (c) $n = 4$ (**3**)*

A mixture of $\{Au[P(tol)_3]\}_2\{\mu\text{-}(C{\equiv}C)_4\}$ (65 mg, 0.06 mmol), $Co_3(\mu_3\text{-CBr})(\mu\text{-dppm})(CO)_7$ (100 mg, 0.12 mmol), $Pd(PPh_3)_4$ (7 mg, 0.006 mmol) and CuI (1 mg, 0.005 mmol) in THF (25 ml) was stirred at r.t. for 1 h. Purification by preparative TLC gave an orange–brown band (R_f 0.50) from which dark red crystals (CH_2Cl_2–MeOH) of $\{Co_3(\mu\text{-dppm})(CO)_7\}_2\{\mu_3{:}\mu_3\text{-}C(C{\equiv}C)_4C\}$ (**3**) (88 mg, 91%) were obtained. Anal. Found: C, 54.42; H, 2.81. Calc. for $C_{74}H_{44}Co_6O_{14}P_4$: C, 54.37; H, 2.71%; M, 1634. IR (cm^{-1}) (Nujol): 2112vw, 2104vw ν(C≡C); (cyclohexane): ν(C≡C) 2112vw, 2104w; ν(CO) 2060s, 2056 (sh), 2017vs, 1990 (sh), 1981w, 1960vw (br). ^{1}H-NMR: δ 3.45, 4.33 (2 × m, 2 × 1H, CH_2), 7.22–7.49 (m, 20H, Ph). ^{13}C-NMR: δ 43.95 [t, J(CP) 22 Hz, dppm], 71.63 [s, C(5)], 82.74 [s, C(4)], 97.56 [s, C(3)], 103.13 [s, C(2)], 128.84–135.05 (m, Ph), 201.67, 209.92 (s, br, CO). ^{31}P-NMR: 34.75 (s, dppm). ES–MS (negative ion, NaOMe–MeOH, m/z): 1761, $[M+I]^+$ (I from CsI calibrant); 1633, $[M-H]^-$; (positive ion, NaOMe–MeOH, m/z): 1657, $[M+Na]^+$.

5.3. Reaction of $\{Co_3(\mu\text{-dppm})(CO)_7\}_2\{\mu_3{:}\mu_3\text{-}C(C{\equiv}C)_3C\}$ with tcne

Tcne (4 mg, 0.03 mmol) was added to a solution of $\{Co_3(\mu\text{-dppm})(CO)_7\}_2\{\mu_3{:}\mu_3\text{-}C(C{\equiv}C)_3C\}$ (50 mg, 0.03 mmol) in THF (40 ml). After stirring overnight, the solution had turned black. Evaporation, extraction with CH_2Cl_2 and purification by preparative TLC (C_3H_6O–C_6H_{12} 3/7) afforded a black band (R_f 0.29) which contained $\{Co_3(\mu\text{-dppm})(CO)_7\}_2\{\mu_3{:}\mu_3\text{-}C(C{\equiv}C)_2C[{=}C(CN)_2]C[{=}C(CN)_2]C\}$ (**4**) (brown crystals from C_6H_6–C_6H_{12}; 22 mg, 41%). Anal. Found: C, 53.80; H, 2.49; N, 3.18. Calc. for $C_{78}H_{44}Co_6N_4O_{14}P_4$: C, 53.88; H, 2.55; N, 3.22%; *M*, 1738. IR (cm^{-1}) (CH_2Cl_2): ν(CN) 2214w (br); ν(CO) 2099m, 2068s, 2024vs, 1985 (sh). ^1H-NMR ($CDCl_3$): δ 3.45, 3.90 (2 × m, 2 × 1H, CH_2), 4.28 (m, 2H, CH_2), 7.06–7.60 (m, 20H, Ph). ^{31}P-NMR ($CDCl_3$): δ 35.19 (s, 2P, dppm), 32.64 [AB q, *J*(PP) 103.76, 45.56, 2P, dppm]. ES–MS (positive ion, MeOH, *m*/*z*): 1739, $[M+H]^+$; (negative ion, with NaOMe, *m*/*z*): 1769, $[M+OMe]^-$; 1741–1657, $[M+OMe-nCO]^-$ ($n=1$–4).

5.4. Structure determinations

Full spheres of CCD area-detector diffractometer data (Bruker AXS instrument, *T* ca. 150 K; monochromatic Mo–K_α radiation $\lambda = 0.71073$ Å) were measured yielding N_{tot} reflections, merged to *N* unique (R_{int} quoted), N_o with $F > 4\sigma(F)$ considered 'observed' and used in the full-matrix least-squares refinements. Anisotropic displacement parameter forms were refined for the non-hydrogen atoms, $(x, y, z, U_{iso})_H$ constrained at estimates. Conventional residuals R, R_w on $|F|$ are cited at convergence [weights: $(\sigma^2(F)+0.0004F^2)^{-1}$]. Neutral atom complex scattering factors were employed within the XTAL 3.7 program system [20]. Results are presented in tables and figures, the latter showing 50% displacement amplitude ellipsoids for the non-hydrogen atoms, hydrogen atoms having arbitrary radii of 0.1 Å.

5.4.1. Crystal/refinement data

5.4.1.1. Compound ***1***. $\{Co_3(\mu\text{-dppm})(CO)_7\}_2\{\mu_3{:}\mu_3\text{-}C(C{\equiv}C)_2C\} \equiv C_{70}H_{44}Co_6O_{14}P_4$, $M = 1586.6$. Monoclinic, space group $P2_1/n$ [C_{2h}^5, No. 14 (variant)], $a = 12.9902(7)$, $b = 12.7052(6)$, $c = 20.563(1)$ Å, $\beta = 94.806(1)^\circ$, $V = 3382$ Å^3. ρ_c ($Z = 2$) $= 1.555$ g cm^{-3}, $\mu_{Mo} = 1.60$ mm^{-1}, $T_{min/max} = 0.75$. Crystal: 0.39 × 0.22 × 0.08 mm. $2\theta_{max} = 60^\circ$; $N_{tot} = 44868$, $N = 9877$ ($R_{int} = 0.044$), $N_o = 7142$, $R = 0.035$, $R_w = 0.037$. $|\Delta\rho_{max}| = 0.63(6)$ e Å^3.

Variata: $(x, y, z, U_{iso})_H$ were refined.

5.4.1.2. Compound ***3***. $\{Co_3(\mu\text{-dppm})(CO)_7\}_2\{\mu_3{:}\mu_3\text{-}C(C{\equiv}C)_4C\}\cdot 2CH_2Cl_2 \equiv C_{74}H_{44}Co_6O_{14}P_4\cdot 2CH_2Cl_2$, $M = 1804.5$. Monoclinic, space group $P2_1/c$ [C_{2h}^5, No. 14], $a = 12.824(1)$, $b = 12.118(1)$, $c = 23.300(2)$ Å, $\beta = 91.750(2)^\circ$, $V = 3619$ Å^3. ρ_c ($Z = 2$) $= 1.656$ g cm^{-3}, $\mu_{Mo} = 1.65$ mm^{-1}, $T_{min/max} = 0.90$. Crystal: 0.28 × 0.20 × 0.14 mm. $2\theta_{max} = 65^\circ$; $N_{tot} = 74361$, $N = 12793$ ($R_{int} = 0.041$), $N_o = 10158$, $R = 0.035$, $R_w = 0.044$. $|\Delta\rho_{max}| = 0.94(5)$ e Å^3.

5.4.1.3. Compound ***4***. $\{Co_3(\mu\text{-dppm})(CO)_7\}_2\{\mu_3{:}\mu_3\text{-}C(C{\equiv}C)_2C[{=}C(CN)_2]C[{=}C(CN)_2]C\}\cdot 2C_6H_6 \equiv C_{78}H_{44}Co_6N_4O_{14}P_4\cdot 2C_6H_6$, $M = 1894.9$. Triclinic, space group $P\bar{1}$ [C_i^1, No. 2], $a = 12.150(1)$, $b = 13.138(1)$, $c = 27.651(1)$ Å, $\alpha = 79.099(3)$, $\beta = 79.967(3)$, $\gamma = 74.864(3)^\circ$, $V = 4147$ Å^3. ρ_c ($Z = 2$) $= 1.517$ g cm^{-3}, $\mu_{Mo} = 1.32$ mm^{-1}, 'T'$_{min/max} = 0.81$. Crystal: 0.16 × 0.12 × 0.06 mm. $2\theta_{max} = 75^\circ$; $N_{tot} = 85859$, $N = 42717$ ($R_{int} = 0.040$), $N_o = 23890$, $R = 0.050$, $R_w = 0.054$.

Variata: Disorder was resolved in two of the three cobalt atoms of the Co(2*n*) array, site occupancies refining to 0.883(1) and complement. Co(2*n*)–Co(2*n*′) distances ($n = 1$, 2) are 0.896(4), 0.965(3) Å.

6. Supplementary material

Crystallographic data for the structural determinations have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos 195450–195452 for compounds **1**, **3** and **4**, 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).

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