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Novel acetylene-linked di-cobalt and tetra-cobalt carbonyl clusters

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Abstract

$\{\text{Co}_2(\text{CO})_6\}$ groups were attached to *p*-diethynylbenzene-based acetylenes giving complexes of general formula $[\{\text{Co}_2(\text{CO})_6\}(\mu_2\text{-}\eta^{2:2}\text{-RC}_2\text{C}_6\text{H}_4\text{C}_2\text{R}')] ((4): \text{R} = \text{R}' = \text{H}; (4\text{a}): \text{R} = \text{SiMe}_3, \text{R}' = \text{H}; (4\text{b}): \text{R} = \text{R}' = \text{SiMe}_3); [\{\text{Co}_2(\text{CO})_6\}_2(\mu_4\text{-}\eta^{2:2:2:2}\text{-RC}_2\text{C}_6\text{H}_4\text{C}_2\text{R}')] ((3): \text{R} = \text{R}' = \text{H}; (3\text{a}): \text{R} = \text{SiMe}_3, \text{R}' = \text{H}; (3\text{b}): \text{R} = \text{R}' = \text{SiMe}_3); [\{\text{Co}_2(\text{CO})_6\}_4(\mu_8\text{-}\eta^{2:2:2:2:2:2:2:2}\text{-R}_2\text{C}_6\text{H}_4\text{C}_2\text{C}_6\text{H}_4\text{C}_2\text{R})] ((5): \text{R} = \text{H}; (5\text{b}): \text{R} = \text{SiMe}_3)$. The addition of $\text{Co}_4(\text{CO})_{12}$ to *p*-diethynylbenzene and to **4** was also investigated, producing $[\{\text{Co}_4(\text{CO})_8(\mu\text{-CO})_2\}(\mu_4\text{-HC}_2\text{C}_6\text{H}_4\text{C}_2\text{H})]$ (**6**) and $[\{\text{Co}_2(\text{CO})_6\}(\{\text{Co}_4(\text{CO})_8(\mu\text{-CO})_2\}(\mu_8\text{-HC}_2\text{C}_6\text{H}_4\text{C}_2\text{H}))]$ (**7**). The syntheses of the acetylenic derivatives of C_{60} $[(\text{trimethylsilyl})\text{ethynyl}]\text{hydrofullerene}[60]$ (**8a**) and $(\text{phenylethynyl})\text{hydrofullerene}[60]$ (**9**) and the new ligand $[(\text{trimethylsilyl})\text{diethynylbenzene}]\text{hydrofullerene}[60]$ (**10a**) were performed and the resulting acetylenes were reacted with dicobaltotetracarbonyl giving the corresponding complexes $[(\text{trimethylsilyl})(\text{dicobalthexacarbonyl})\text{ethynyl}]\text{hydrofullerene}[60]$ (**11a**), $(\text{phenylethynyl})(\text{dicobalthexacarbonyl})\text{hydrofullerene}[60]$ (**12**) and $[(\text{trimethylsilyl})\text{bis}(\text{dicobalthexacarbonyl})\text{diethynylbenzene}]$ (**13a**). The reaction of 1-bromo-3,5-diethynylbenzene and 1,3,5-triethynylbenzene with dicobaltotetracarbonyl resulted in the formation of $[\text{HC}_2\{\text{Co}_2(\text{CO})_6\}]_2\text{C}_6\text{H}_2\text{Br}$ (**16**) and $[\text{HC}_2\{\text{Co}_2(\text{CO})_6\}]_2\text{C}_6\text{H}_3$ (**15**) as expected. Crystals of **3a**, **3b**, **4**, **4b**, **15** and **16** suitable for single-crystal X-ray diffraction were grown and the molecular structures of these compounds are discussed. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

The interaction of alkynes with $\text{Co}_2(\text{CO})_8$ is well documented [1]. There has been a recent resurgence of interest in the resulting complexes, $[\{\text{Co}_2(\text{CO})_6\}(\mu, \eta^{2:2}\text{-RC}_2\text{R}')]]$. This is partly due to the use of similar compounds in the formation of cyclopentenones (Pauson–Khand reaction) [2], in the generation of $[2 + 2 + 2]$ cycloadditions (via an intramolecular Heck reaction) [3] and in the stabilization of propargyl cations (Nicholas carbocations) [4]. There is considerable scope for modifying these transformations by changing the cobalt source (e.g. $\text{Co}_4(\text{CO})_{12}$) [11] or the substituents on the alkyne [5]. This work represents the first in a series of studies on the synthesis and photochemistry of modified cobalt carbonyl complexes.

Π -conjugated polyynes are attractive materials for non-linear optics [6]. Free polyynes are constructed via stepwise multi-coupling reactions but are generally unstable [7]. Previous researchers have used metal–acetylene complexes as building blocks in the generation of stabilized polyynes [8]. In this work we adopted di- and tri- ethynylbenzene as the metal carbonyl linking unit. The benzene ring is a suitable alkyne spacer because it forms an electron-rich π -conjugated system, which can be extended in a linear (disubstituted) or network (trisubstituted) fashion. Recent advances in the syntheses of fullerene–acetylenes suggested C_{60} as an alternative source of conjugated C_6 rings [9].

2. Results and discussion

$\text{Co}_2(\text{CO})_8$ addition to ethynyls can be achieved by stoichiometric addition of the reagents, in CH_2Cl_2 , and

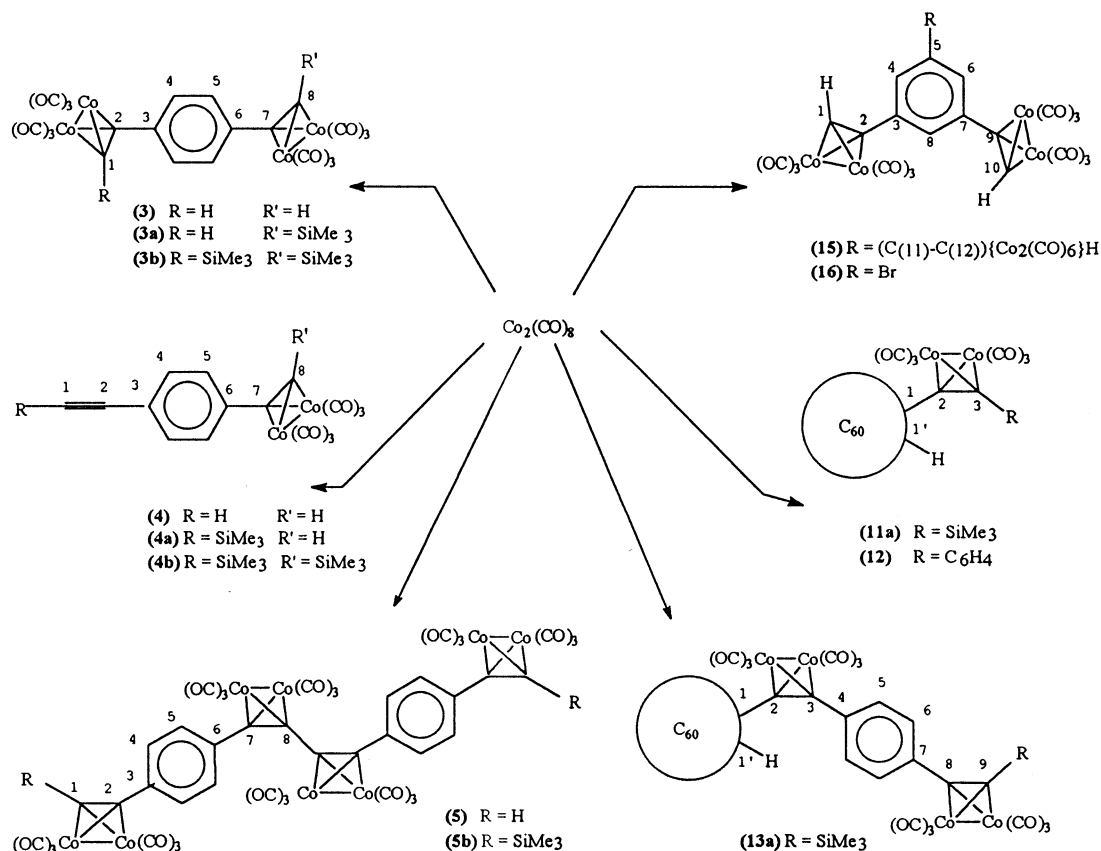
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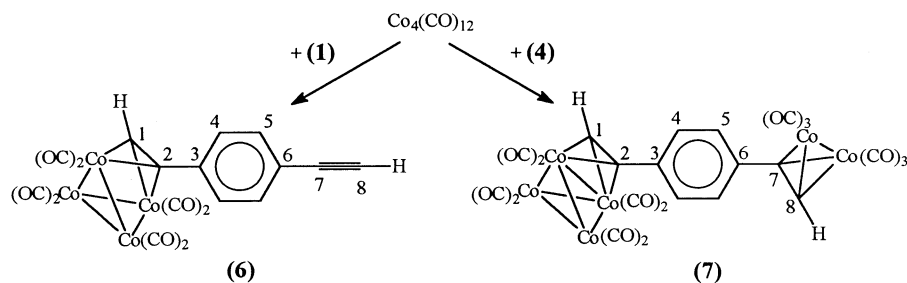
in most cases under an inert atmosphere at room temperature (see Scheme 1). In the process two equivalents of CO are lost, allowing the retention of the 18 e⁻ count in the alkynyl products. In this work, {Co₂(CO)₆} groups were attached to substituted diethynylbenzene giving complexes [{Co₂(CO)₆}(μ_4 - $\eta^{2:2:2:2}$ -RC₂C₆H₄C₂R')] ((4): R = R' = H; (4a): R = SiMe₃, R' = H; (4b): R = R' = SiMe₃). The addition of two {Co₂(CO)₆} units to substituted diethynylbenzene gave [{Co₂(CO)₆}₂(μ_8 - $\eta^{2:2:2:2:2:2:2:2}$ -RC₂C₆H₄C₂R')] ((3): R = R' = H; (3a): R = SiMe₃, R' = H; (3b): R = R' = SiMe₃). Coupled diethynylbenzene gave the corresponding substituted compounds 5 and 5b.

The addition of Co₄(CO)₁₂ to *p*-diethynylbenzene (1) and to the complex [{Co₂(CO)₆}(μ_4 - $\eta^{2:2:2:2}$ -HC₂C₆H₄-C₂H)] (4) was also investigated, producing [{Co₄(CO)₈-(μ -CO)₂}(μ_4 -HC₂C₆H₄C₂H)] (6) and [{Co₂(CO)₆}-(Co₄(CO)₈(μ -CO)₂)(μ_8 -HC₂C₆H₄C₂H)] (7) (see Scheme 2). These derivatives are extremely air-sensitive and can only be isolated by inert atmosphere chromatography and work-up.

Alternative ligand sets were examined. These included the trisubstituted benzene system, 1,3,5-triethynylbenzene (14) and 1-bromo-3,5-ethynylbenzene (14c) and the acetylenic derivatives of C₆₀ [(trimethylsilyl)ethynyl]hydrofullerene[60] (8a), (phenylethynyl)-



Scheme 1. Schematic representation of the complexes containing exclusively {Co₂(CO)₆} units. The C atom numbers are consistent with the NMR assignments and the X-ray crystallography atom labelling.



Scheme 2. Schematic representation of the complexes containing {Co₄(CO)₈(μ -CO)₂} units. The bridging carbonyl ligands have been removed for clarity. The atom labels are consistent with the NMR assignments.

hydrofullerene[60] (**9**), [(trimethylsilyl)diethynylbenzene]hydrofullerene[60] (**10a**). These were reacted with $\text{Co}_2(\text{CO})_8$ and the resulting fully coordinated complexes were spectroscopically characterised.

2.1. Infrared spectra

The solution IR spectra in hexane of all cobalt carbonyl compounds gave rise to the expected strong C–O absorptions in the carbonyl region. In particular, the IR spectra of **4**, **4a**, **4b** and **11a** show a similar and characteristic pattern for terminal carbonyl stretches as was observed previously for $[\{\text{Co}_2(\text{CO})_6(\mu, \eta^2\text{-RC}_2\text{R}')\}]$ complexes [10].

For the complexes that possess more than one dimetallatetrahedrane core, the IR carbonyl region results from the superposition of the IR carbonyl stretching bands corresponding to each core. There is little difference in the overall carbonyl pattern mentioned above. However, the presence of two bands arising from the totally symmetric C–O stretching vibration ($\nu_1\text{CO}$) for complexes **3a**, **5**, **5b** and **13a** confirms the presence of more than one type of dimetallatetrahedrane core in these molecules.

The IR spectra of **6** and **7** were conducted in Nujol using mounting plates designed for air-sensitive compounds. Terminal and bridging C–O bands are visible and the carbonyl pattern for **7** is similar to the one previously published for $[\{\text{Co}_4(\text{CO})_8(\mu\text{-CO})_2\}(\mu_4\text{-HC}_2\text{H})]$ (*n*-heptane) [11], indicating a similar coordination mode of the alkyne.

2.2. NMR spectroscopy

The coordination of the alkynes to $\{\text{Co}_2(\text{CO})_6\}$ is evident from the downfield shift of the terminal protons in the ^1H -NMR spectra [10]. Clearly this does not relate to the fullerenyl protons of **8a**, **9** and **10a**, which are in a different electronic environment and experience an upfield shift from δ 7.2 to 6.8 upon coordination. In addition, the carbon $\text{H-}^{13}\text{C}_1\equiv\text{C-Ar}$ experiences a shielding effect in ^{13}C -NMR, whereas the carbon $\text{H-C}\equiv^{13}\text{C}_2\text{-Ar}$ signal is moved downfield (e.g. see complexes **4a**, **5**, **6**).

A Coloc long-range ^1H - ^{13}C -COSY was performed on *p*-trimethylsilyl diethynylbenzene (**1a**) (CDCl_3) in order to determine the resonances of the acetylenic carbons. The signal at δ 104.6 was assigned to the carbon $^{13}\text{C}_2$ atom next to the phenyl ring, whereas the carbon $^{13}\text{C}_1$ attached to the $\text{Si}(\text{CH}_3)_3$ group resonates at δ 96.2.

Comparison of the signals of $\text{R-}^{13}\text{C}_1$ and $\text{R-C}\equiv^{13}\text{C}_2$ ($\text{R} = \text{H}$, $\text{Si}(\text{CH}_3)_3$) suggests that the $\text{Si}(\text{CH}_3)_3$ group is electron withdrawing when attached to an aromatic ring. It has been suggested that this results from back-donation $\text{Si} \leftarrow \text{C}_\pi$ that originates from interactions between the perpendicular acetylenic π -orbitals and the

empty d orbitals on the Si atom [12]. These downfield shifts are no longer observed on metal coordination e.g. **5b**. It would appear that formation of the dimetallatetrahedrane alters the electronic environment of $\text{R-}^{13}\text{C}_1$. As expected, the other carbon signal on which it has a significant influence is $^{13}\text{C}_3$, which does not form part of the dimetallatetrahedrane core but is directly attached to it.

The ^{13}C chemical shifts of the carbonyls in the $[\{\text{Co}_2(\text{CO})_6\}(\mu\text{-RC}_2\text{R}')]$ complexes appear as one signal at around δ 199, suggesting that they are rapidly interchanging on the NMR scale. The complexes containing two different types of $\{\text{Co}_2(\text{CO})_6\}$ cores exhibit in their ^{13}C -NMR spectra two carbonyl signals.

For **6** and **7**, each ^{13}C -NMR spectrum only exhibits six peaks. The ^{13}C chemical shifts of the carbon atoms $\text{H-}^{13}\text{C}_1^{13}\text{C}_2\text{-Ar}$ coordinated to a $\{\text{Co}_4(\text{CO})_{10}\}$ group could not be detected. This is thought to be a relaxation effect.

2.3. Description of the molecular structures

Crystallisation of products **3a**, **3b**, **4**, **4b**, **15** and **16** from hexane– CH_2Cl_2 solutions at -25°C gave light-red to dark-red air-stable crystalline solids. The molecular structures of **3a**, **4b**, and **16** are shown in Figs. 1–3, respectively. The core structure of one molecule of **15** can be seen in Fig. 4 and results from an incomplete data set collected on a plate-like crystal of this compound.

The interaction of the $\text{Co}_2(\text{CO})_6$ units lengthens the alkyne bond, as is consistent with the loss of C $\equiv$ C bond character resulting from the delocalisation of electron density onto the Co_2 unit (see Table 1). The deviation from sp hybridisation on metallisation is also clearly seen in the pivotal angles C(6)–C(7)–C(8) (**3a**: $142.9(4)^\circ$; **3b**: $142.2(2)^\circ$; **4b**: $141.6(3)^\circ$) and C(3)–C(2)–C(1) (**3a**: $142.5(4)^\circ$; **4**: $142.2(3)^\circ$; **16**: $141.1(8)^\circ$) about C(7) and C(2). These angles are similar to that already reported for $[\{\text{Co}_2(\text{CO})_6\}_2(\text{H}_2\text{C}_2\text{C}_6\text{H}_4\text{C}_2\text{H})]$ ($141.9(7)^\circ$) and imply that this angle is independent of the substituents attached to the phenyl ring within crystallographic error. The C–C bond is twisted out of the plane containing the aryl ring in each case. The maximum bend out of the plane defined by the benzene ring for the diethynyl benzene systems is observed in **3a** for the trimethylsilyl-substituted portion of the alkyne (C(8)–C(7)–C(6)–C(5) 163.3° , C(8)–C(7)–C(6)–C(4) 18.0°) as opposed to the proton-terminated portion C(1)–C(2)–C(3)–C(10) 166.8° , C(1)–C(2)–C(3)–C(4) 14.2°). The free alkyne unit in **4b** and **4** retains its linearity as expected and the relevant bond lengths are consistent with the retention of significant triple-bond character C(1)–C(2) (**4**: $1.155(5)$; **4b**: $1.196(5)$). The hydrogen-terminated alkyne bond is considerably shorter than in the trimethylsilyl case, but within crystallographic error this does not

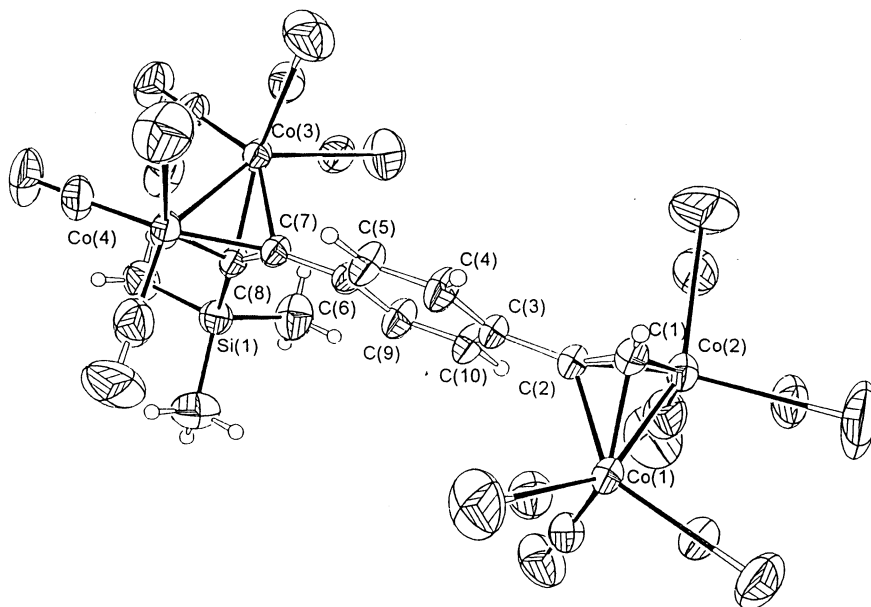


Fig. 1. ORTEX drawing of the molecular structure of **3a** (thermal ellipsoids have been drawn at 40% probability level, hydrogen atoms have been omitted for clarity).

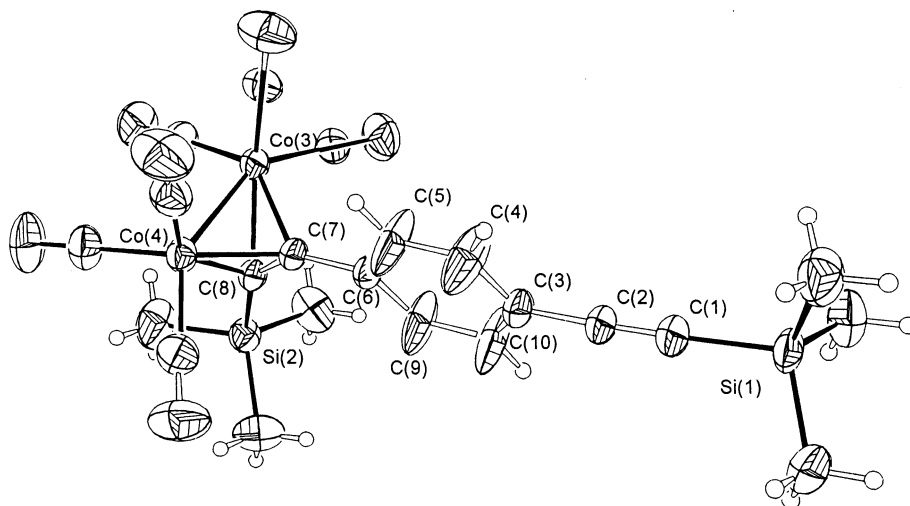


Fig. 2. ORTEX drawing of the molecular structure of **4b** (thermal ellipsoids have been drawn at 40% probability level, hydrogen atoms have been omitted for clarity).

significantly affect the length of the adjacent C(2)–C(3) bond (**4b**: 1.442(5); **4**: 1.450(4)).

The Co–Co bond lengths are shorter than that observed in the parent carbonyl (2.52 Å) and lie in the range 2.46–2.48 Å [13]. This observation agrees with previously reported dicobalt systems that are bridged by perpendicular alkynes [14]. A common feature of all the molecular structures obtained is the presence of distorted Co₂C₂ cores. An interesting feature of these cores is the nature of the asymmetry of the Co–C distances. Unlike the Co–Co bonds, these are sensitive to the substituents on the alkyne. For all systems containing a terminal proton on the alkyne the

H–C–Co bonds (e.g. C(1)–Co in **3a**) are on average shorter than those close to the phenyl ring (e.g. C(2)–Co in **3a**). The two Co₂C₂ tetrahedra in the molecular structure of **16** also illustrate this feature. However, those dimetallatetrahedra terminated by a SiMe₃ group show a reversal of this trend, the C–Co bonds next to the phenyl ring being the shortest (e.g. C(7)–Co in **3a**). In addition the asymmetry of the dimetallatetrahedra is most clearly seen in the disparity of the (Ar)C–Co bond lengths, which show a long–short relationship.

As expected, **3b** which is symmetrically substituted has a crystallographic centre of symmetry that lies at

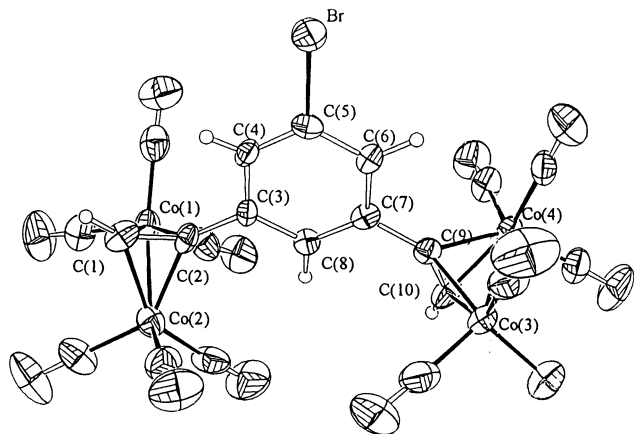


Fig. 3. ORTEX drawing of the molecular structure of **16** (thermal ellipsoids have been drawn at 40% probability level, hydrogen atoms have been omitted for clarity).

the centre of the aryl ring. The overall geometry of the system is very similar to that already reported for **3** [10].

A number of systems have recently reported molecular structures of metallised derivatives of 1,3,5-triethynylbenzene [15]. However, none possesses the characteristic distorted metallahedranes reported in this work. The molecular structure of **16** contains two distinct dimetallatetrahedranes that twist out of the plane associated with the benzene ring. The respective dihedral angles are C(10)–C(9)–C(7)–C(6) 167.6°, C(10)–C(9)–C(7)–C(8) 12.5° and C(1)–C(2)–C(3)–C(8) 161.0°, C(1)–C(2)–C(3)–C(4) 19.8°. The core structure

of **15** is sufficient to illustrate the manner in which the system can accommodate three metallahedrane units. Interestingly there is no three-fold axis of rotation about the centre of the benzene ring. In fact the bent three-legged structure in which the legs radiate from the central ring is reminiscent of a ‘hopping’ triskelion.

3. Conclusions

The selective synthesis of $[\{\text{Co}_2(\text{CO})_6\}(\mu, \eta^2\text{-SiMe}_3\text{C}_2\text{C}_6\text{H}_4\text{C}_2\text{H})]$ (**4a**) indicates that the addition of $\{\text{Co}_2(\text{CO})_6\}$ groups to alkynes can be controlled. Clearly one of the factors that influences the degree and position of the metallisation is the bulk of the substituents on the alkyne. The work described details the structural affects associated with proton or trimethylsilyl termination of the alkyne, but a number of substituents can be envisaged [16], e.g. ferrocene or fullerene.

It has recently been shown that non-polar molecules with a three-fold rotation symmetry can have non-zero β values [17]. As such we are interested in the synthesis of polymers derived from 1,3,5-triethynylbenzene. Multiple acetylation of C_{60} would generate a three-dimensional carbon-rich framework on which to support metal complexes. Possible targets are the polymers derived from Fullerene[60] and *p*-diethynylbenzene or 1,3,5-triethynylbenzene (see Scheme 3). We are in the process of examining the non-linear optical responses of such systems. In addition we intend to exploit pho-

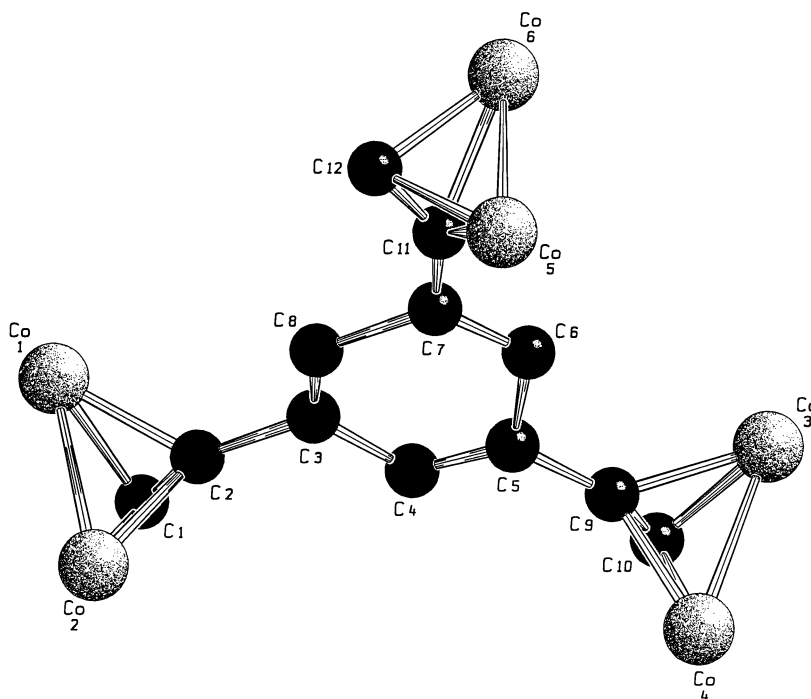
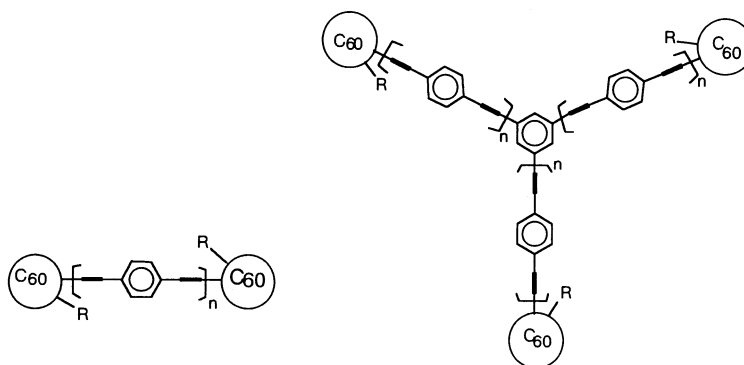


Fig. 4. SHAKAL drawing of the core molecular structure of **15**. Only one of the two molecules contained in the unit cell is depicted.

Table 1
Bond lengths (Å) present in the different 'Co₂C₂' cores of **3a**, **3b**, **4**, **4b**, **16**

Complexes	Co ₁ –Co ₂	C ₂ –C ₁ –H	(H)C ₁ –Co		(Ar)C ₂ –Co	
3a	2.4718(10)	1.345(6)	1.953(5)	1.950(5)	1.977 [4]	1.962 [4]
4	2.4649(8)	1.325(5)	1.949(3)	1.946(5)	1.983 [2]	1.953 [3]
16	2.485(2)	1.327(12)	1.954(10)	1.942(9)	1.972[9]	1.940[9]
	Co ₃ –Co ₄	C ₇ –C ₈ (SiMe ₃)	(Me ₃ Si)C ₈ –Co		(Ar)C ₇ –Co	
3a	2.4820(10)	1.333(6)	1.993(4)	1.989(4)	1.982 [4]	1.957 [4]
3b	2.4828(5)	1.334(3)	1.996(2)	1.993(2)	1.984 [2]	1.957 [2]
4b	2.4733(9)	1.341(5)	1.996(3)	1.993(4)	1.966 [3]	1.955 [3]
	Co ₃ –Co ₄	C ₉ –C ₁₀ (H)	(H)C ₁₀ –Co		(Ar)C ₉ –Co	
16	2.471(2)	1.325(12)	1.947(10)	1.931(10)]	1.938[9]	1.975[8]



Scheme 3. Polymers derived from Fullerene[60] and *p*-diethynylbenzene or 1,3,5-triethynylbenzene (R = alkyl or aryl chain).

tolytic carbonyl loss from dicobalt hexacarbonyl systems incorporating phenyl or diphenyl acetylene: the first step in the normally thermally initiated Pauson–Khand reaction [18].

4. Experimental

4.1. General considerations

Infrared measurements were performed on a Perkin–Elmer Paragon 1000 FT-IR spectrophotometer. NMR measurements were performed on a Bruker MSL 300 FT spectrometer or on a Bruker DPX 400 FT spectrometer. ¹H-NMR (300 and 400 MHz, respectively) were standardised with respect to TMS set at δ 0.0. ¹³C-NMR spectra (75 and 100 MHz, respectively) were standardised with respect to TMS. UV–vis spectra were performed on a Unicam UV–vis UV4 spectrometer. The FAB mass spectra were obtained using a VG Autospec instrument using 3-NOBA as matrix. The melting points were recorded using a Griffin melting point apparatus.

The reactions involving organometallic compounds were carried out using standard Schlenk line techniques under an atmosphere of argon. All solvents were dried and degassed before use.

4.2. Syntheses of the ligands

The ligands *p*-diethynylbenzene (**1**), 1,3,5-triethynylbenzene (**14**) and 1-bromo-3,5-ethynylbenzene (**14a**) were prepared following the literature procedures [19]. The trimethylsilyl derivatives (**1a**) and *p*-bis(trimethylsilyl)diethynylbenzene (**1b**) were obtained by reacting **1** with *n*-BuLi in THF at -78°C , in 1:1 and 1:2 ratios, respectively, followed by treatment with Me₃SiCl. The three ligands were purified through controlled sublimation under reduced pressure. *p*-Trimethylsilyldiethynylbenzene (**1a**) was coupled under Hay's conditions [20] (CuCl, TMEDA, acetone) to give the protected dimer **2b**. Subsequent treatment of the later with anhydrous potassium carbonate in anhydrous methanol at 25°C afforded the deprotected dimer bis(*p*-diethynylbenzene) (**2**) (see Scheme 4). The detailed experimental conditions used are given below.

4.2.1. [Me₃SiC≡CC₆H₄C≡C]₂ (**2b**)

Acetone (25 ml), TMEDA (2 ml, 1% in acetone, 0.13 mmol) and CuCl (13 mg, 0.13 mmol) were stirred at 28°C while oxygen was bubbled through the solution. After 15 min, the colour of the solution changed from colourless to green. (Trimethylsilyl)diethynylbenzene (0.525 g, 2.65 mmol) was dissolved in acetone (20 ml) and added drop-wise to the above mixture. Bis[(trimethylsilyl)diethynylbenzene] precipitated

from the solution during strong stirring and as oxygen was still bubbling through the solution over 3 h. The white precipitate was filtered, washed with acetone, with dilute HCl (1 ml of concentrated HCl in 20 ml H₂O) and acetone. The product was dissolved in benzene, the organic layer was washed with water, and removal of the solvent yielded bis[(trimethylsilyl)diethynylbenzene] as a yellowish shiny and flaky powder (0.421 g, 81%); m.p. = 218–222°C (dec.). TLC: *R_f* 0.6 (Al₂O₃, hexane). ¹H-NMR (CDCl₃, 300 MHz): δ 7.43 (d, ³*J* = 9 Hz, 4H, H₄/H₅), 7.46 (d, ³*J* = 9 Hz, 4H, H₄/H₅), 0.27 (s, 18H, H_{CH₃}). ¹³C-NMR (CDCl₃, 75 MHz): δ 132.26/131.92 (C₄/C₅), 104.26 (C₂), 124.00 (C₃), 121.56 (C₆), 97.33 (C₁), 81.96 (C₇), 75.55 (C₈), –0.14 (C_{CH₃}). IR (KBr, cm^{–1}): 2957 (m), 2896 (w), ν(C–H aryl); 2152 (m), ν(C≡C); 1492 (m), ν(C=C aryl); 1254 (m), ν(Si–Me). Anal. Calc. for C₂₆H₂₆Si₂ (394.66): C, 79.1; H, 6.6. Found: C, 79.2; H, 6.9.

4.2.2. [HC≡CC₆H₄C≡C]₂ (2)

Bis[(trimethylsilyl)diethynylbenzene] (0.294 g, 0.75 mmol) was treated with K₂CO₃ (81 mg, 0.59 mmol) in MeOH (30 ml) with strong stirring for 5 days. MeOH was removed under vacuum, and the residue was treated with NaHCO₃ (150 mg) in water (20 ml) for 15 min. Bis[diethynylbenzene] was filtered, washed with water, cold chloroform and acetone. It was isolated as a dark yellow powder (0.168 g, 90%). M.p. > 360°C. TLC: *R_f* 0.2 (SiO₂, hexane). IR (KBr, cm^{–1}): 3267 (m), ν(≡C–H); 2961 (w), ν(H–C aryl); 2151 (w), ν(C≡C₈); 2100 (w), ν(C₁≡C₂); 1492 (m), ν(C=C aryl); 832 (s), *p*-substitution. Anal. Calc. for C₂₀H₁₀ (250.30): C, 96.0; H, 4.0. Found: C, 95.4; H, 3.6.

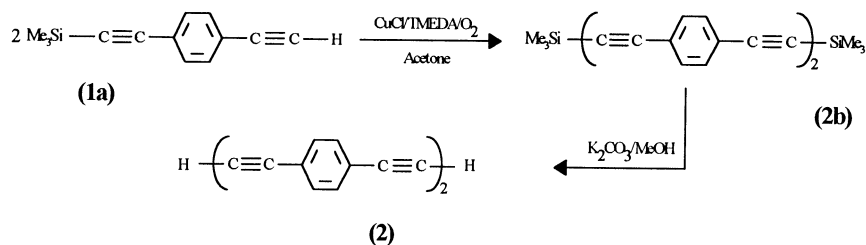
The syntheses of the acetylenic derivatives of C₆₀, [(trimethylsilyl)ethynyl]hydrofullerene[60] (8a) and (phenylethynyl)hydrofullerene[60] (9), have been reported using refluxing toluene [21]. However, the formation of 1-octynylhydrofullerene[60] was more recently carried out in THF [22], and this method was preferred here as it allows for higher yields of the monoacetylene derivatives of C₆₀ and simplifies the procedure. The new ligand [(trimethylsilyl)diethynylbenzene]hydrofullerene[60] (10a) was obtained similarly by reacting lithiated *p*-(trimethylsilyl)diethynylbenzene with C₆₀ in THF as detailed below.

4.2.3. 1-Hydro-9-[(trimethylsilyl)diethynylbenzene]-fullerene[60] (10a)

A 0.28 M solution of [(trimethylsilyl)diethynylbenzene]lithium (IV) was prepared by first dissolving (trimethylsilyl)diethynylbenzene (0.170 mg, 0.86 mmol) into THF (2.3 ml). This solution was left stirring at –78°C for 5 min before *n*-BuLi (0.51 ml, 1.54 N, 0.79 mmol) was added to it drop-wise. The mixture was left stirring for 40 min at 0°C and 5 min at room temperature. [(Trimethylsilyl) diethynylbenzene]lithium (1 ml, 0.29 mmol) was added drop-wise to a vigorously stirred suspension of C₆₀ (35 mg) in THF (35 ml) over 10 min. The resulting dark-green solution was left stirring for an extra 10 min, and was then quenched with CF₃COOH (0.3 ml, 3.9 mmol) to give a brown/orange solution. Extraction in cyclohexane of the residue, followed by flash chromatography (SiO₂, cyclohexane) afforded C₆₀ (3 mg, 9%) and 1-hydro-9-[(trimethylsilyl)diethynylbenzene]fullerene[60] (20 mg, 45%, *R_f* 0.3). The presence of the bis adduct was indicated by TLC (*R_f* 0.2). M.p. > 360°C. ¹H-NMR (CDCl₃/CS₂ (1:1), 400 MHz): δ 7.16 (s, 1H, C₆₀H), 7.75 (d, ³*J* = 8 Hz, 2H, H₅), 7.56 (d, ³*J* = 8 Hz, 2H, H₆), 0.33 (s, 9H, H_{CH₃}). ¹³C-NMR (CDCl₃/CS₂ (1:1), 75 MHz): [23] δ 131.90/131.78 (C₅/C₆), 123.76 (C₇), 122.27 (C₄), 104.44 (C₈), 96.89 (C₉), 93.97 (C₂), 83.27 (C₃), 61.67 (C₁), 54.99 (C₁), –0.18 (C_{CH₃}); 151.20, 150.88, 147.46, 147.18, 146.47, 146.27, 146.24, 146.08, 145.64, 145.56, 145.44, 145.36, 145.30, 145.21, 144.55, 144.36, 143.07, 142.47, 142.45, 141.96, 141.91, 141.88, 141.71, 141.57, 141.49, 140.23, 135.91, 135.05 (28 signals, sp² C on the C₆₀ core). IR (KBr, cm^{–1}): 2953 (w), 2920 (w), ν(C–H aryl); 2154 (w), ν(C≡CTMS); 1436 (w), 1428 (w), 1424 (w), 1418 (w), 1188 (w), 1176(w), 586 (w), 575 (w), 566 (w), 549 (w), 545 (w), 526 (s), C₆₀ bands. MS (FAB⁺): *m/z* 919 (M⁺), 720 (C₆₀).

4.3. Syntheses of the complexes

The dicobalt hexacarbonyl complexes based on diethynylbenzene and its dimers were obtained by the standard methods of stirring the ligand and dicobaltotetracarbonyl under argon for 1 h in hexane or dichloromethane. In the case of the products resulting from the coordination of {Co₂(CO)₆} to C₆₀ acetylenes,



Scheme 4. Schematic representation of the synthesis of coupled ethynylbenzene.

toluene was used as the solvent. The fullerene-based ligands **8a**, **9** and **10a** were reacted with dicobaltocarbonyl in toluene and isolated by flash chromatography (SiO₂, cyclohexane) to yield the corresponding complexes [(trimethylsilyl)(dicobalthexacarbonyl)ethynyl]hydrofullerene[60] (**11a**), (phenylethynyl)(dicobalthexacarbonyl)hydrofullerene[60] (**12**) and [(trimethylsilyl)bis(dicobalthexacarbonyl)diethynylbenzene] (**13a**).

Suitable elemental analyses could not be obtained for all the metal complexes [23]. This was due to difficulties in separating the pure product from unreacted ligand: prolonged or repeated column chromatography results in the degradation of the product to metal residues that stick to the silica and free ligand that travels at the same rate as the product. In these cases mass spectra were obtained.

4.3.1. [$\{Co_2(CO)_6\}(\mu_2-\eta^{2:2}-HC_2C_6H_4C_2H)$] (**4**)

Isolated as a bright red product by flash chromatography (Al₂O₃, hexane). TLC: *R_f* 0.5. Yield: 28%. M.p. = 78–80°C. ¹H-NMR ((CD₃)₂CO, 300 MHz): δ 7.63 (d, ³*J* = 8 Hz, H₅), 7.51 (d, ³*J* = 8 Hz, H₄) (4H), 6.89 (s, 1H, H₈), 3.75 (s, H₁). ¹³C-NMR ((CD₃)₂CO, 75 MHz): δ 199.46 (C_{CO}), 138.93 (C₆), 132.86 (C₄), 130.64 (C₅), 122.38 (C₃), 89.22 (C₇), 83.56 (C₂), 79.88 (C₁), 73.97 (C₈). IR (CsI) (cm^{−1}): 3315 (s), ν(H–C≡); 3118 (w), ν(terminal H–C). IR (ν_(CO), hexane) (cm^{−1}): 2096 (m), 2059 (s), 2034 (s), 2031 (s), 2018 (w), 1987 (w). MS (FAB⁺): *m/z* 412 [M⁺].

4.3.2. [$\{Co_2(CO)_6\}_2(\mu_4-\eta^{2:2:2:2}-Me_3SiC_2C_6H_4C_2H)$] (**3a**)

Flash chromatography (SiO₂, hexane) isolated a red brown fraction. TLC: *R_f* 0.3. Yield 19%. M.p. = 128–130°C. ¹H-NMR ((CD₃)₂CO, 300 MHz): δ 7.62 (d, ³*J* = 8 Hz)/7.59 (d, ³*J* = 8 Hz) (4H, H₄/H₅), 6.84 (s, 1H, H₁), 0.42 (s, 9H, H_{CH₃}). ¹³C-NMR ((CD₃)₂CO, 75 MHz): δ 200.41 (C_{CO}), 200.07 (C_{CO}), 138.20/138.71 (C₆/C₃), 131.29/130.86 (C₄/C₅), 105.04 (C₇), 89.77 (C₂), 80.50 (C₈), 74.28 (C₁), 0.62 (C_{CH₃}). IR (CsI) (cm^{−1}): 2965 (w), ν(H–C aryl); 3119 (w), ν(terminal H–C). IR (ν_(CO), hexane) (cm^{−1}): 2096 (w), 2088 (m), 2060 (s), 2054 (m), 2028 (s), 2011 (w), 1983 (w). MS (FAB⁺): *m/z* 698 [M⁺].

4.3.3. [$\{Co_2(CO)_6\}(\mu_2-\eta^{2:2}-Me_3SiC_2C_6H_4C_2H)$] (**4a**)

Isolation of the product as a bright red solid via flash chromatography (SiO₂, hexane). TLC *R_f* 0.2. Yield 35%. M.p. = 77–79°C. ¹H-NMR (CDCl₃, 400 MHz) δ 7.47(d, ³*J* = 8 Hz)/7.44 (d, ³*J* = 8 Hz) (H₄/H₅, 4H), 6.38 (s, 1H, H₁), 0.28 (s, 9H, H_{CH₃}). ¹³C-NMR (CDCl₃, 100 MHz) δ 199.20 (C_{CO}), 137.97 (C₃), 132.41 (C₅), 129.96 (C₄), 122.80 (C₆), 104.88 (C₇), 95.76 (C₈), 88.83 (C₂), 72.59 (C₁), −0.09 (C_{CH₃}). IR (CsI) (cm^{−1}): 2962 (m), ν(C–H aryl); 2160 (m), ν(C≡CH). IR (ν_(CO), hexane) (cm^{−1}): 2095 (m), 2059 (s), 2033 (s), 2031 (s), 2018 (w), 1986 (w); 2160 (w), ν(C≡C). MS (FAB⁺) *m/z* 485 [M⁺].

4.3.4. [$\{Co_2(CO)_6\}_2(\mu_4-\eta^{2:2:2:2}-Me_3SiC_2C_6H_4C_2SiMe_3)$] (**3b**)

A brown product, isolated by flash chromatography (SiO₂, hexane). TLC: *R_f* 0.3. Yield 29%. M.p. = 103–105°C. ¹H-NMR (CDCl₃, 400 MHz): δ 7.47 (s, 4H, H₄), 0.45 (s, 18H, H_{CH₃}). ¹³C-NMR (CDCl₃, 75 MHz): δ 199.91 (C_{CO}), 138.15 (C₃), 130.39 (C₄), 104.28 (C₂), 79.92 (C₁), 0.95 (C_{CH₃}). IR (CsI) (cm^{−1}): 2964 (w), ν(C–H aryl). IR (ν_(CO), hexane) (cm^{−1}): 2091 (w), 2086 (m), 2054 (s), 2027 (s), 2010 (w), 1979 (w). MS (FAB⁺): *m/z* 839 [M⁺ − 3H]. Anal. Calc. for C₂₈H₂₂O₁₂Si₂Co₄ (842.38): C, 39.9; H, 2.6; Co, 28.0. Found C, 40.1; H, 2.9; Co, 27.8.

4.3.5. [$\{Co_2(CO)_6\}(\mu_2-\eta^{2:2}-Me_3SiC_2C_6H_4C_2SiMe_3)$] (**4b**)

Isolated as a red solid yield via flash chromatography (SiO₂, hexane) TLC: *R_f* 0.3. Yield 22%. M.p. = 112–114°C. ¹H-NMR (CDCl₃, 300 MHz): δ 7.45 (s, 4H), 0.42 (s, 9H, H_{CH₃}), 0.27 (s, 9H, H_{CH₃}). ¹³C-NMR (CDCl₃, 75 MHz) δ 199.74 (C_{CO}), 138.82 (C₆), 132.46 (C₄), 129.65 (C₅), 122.55 (C₃), 104.78 (C₂), 104.11 (C₇), 95.76 (C₁), 79.86 (C₈), 0.82 (C_{CH₃}), −0.10 (C_{CH₃}). IR (ν_(CO), hexane) (cm^{−1}): 2089 (m), 2053 (s), 2027 (s), 2025 (s), 2011 (w), 1980 (w); 2160 (w), ν(C≡C); MS (FAB⁺): *m/z* 557 [M⁺]. Anal. Calc. for C₂₂H₂₂O₆Si₂Co₂ (556.45): C, 47.5; H, 4.00; Co, 21.2. Found C, 47.3; H, 4.00; Co, 21.0.

4.3.6. [$\{Co_2(CO)_6\}_4(\mu_8-\eta^{2:2:2:2:2:2:2:2}-Me_3SiC_2C_6H_4C_2-C_2C_6H_4C_2SiMe_3)$] (**5b**)

Isolated via flash chromatography (SiO₂, hexane) as a brown solid. TLC: *R_f* 0.6. Yield: 52%. M.p. > 360°C. (Al₂O₃, hexane). ¹H-NMR (CDCl₃, 300 MHz) δ 7.47 (s, 8H, H₄/H₅), 0.43 (s, 18H, H_{CH₃}). ¹³C-NMR (CDCl₃, 75 MHz): δ 199.79 (C_{CO}), 198.56 (C_{CO}), 138.56/138.29 (C₃/C₆), 130.07/129.62 (C₄/C₅), 104.26 (C₂), 99.41 (C₈), 93.47 (C₇), 79.83 (C₁), 1.00 (C_{CH₃}). IR (CsI) (cm^{−1}): 2962 (w), 2925 (w), 2859 (w), ν(C–H aryl); 1250 (m), ν(Si–Me); IR (ν_(CO), hexane) (cm^{−1}): 2101 (w), 2086 (m), 2083 (m), 2063 (s), 2053(s), 2038 (w), 2027 (s), 2011 (w), 1983 (w). MS (FAB⁺): *m/z* 1538 [M⁺].

4.3.7. [$\{Co_2(CO)_6\}_4(\mu_8-\eta^{2:2:2:2:2:2:2:2}-HC_2C_6H_4C_2-C_2C_6H_4C_2H)$] (**5**)

Purified as a brown solid through flash chromatography (Al₂O₃, hexane). TLC: *R_f* 0.5. Yield: 21%. M.p. > 360°C. ¹H-NMR (CDCl₃, 300 MHz): δ 7.48 (d, ³*J* = 8 Hz, 2H, H₄/H₅)/7.42 (d, ³*J* = 8 Hz, 2H, H₄/H₅), 6.39 (s, 1H, H₁). ¹³C-NMR (CDCl₃, 75 MHz): δ 199.20 (C_{CO}), 198.58 (C_{CO}), 138.64 (C₆), 137.47 (C₃), 130.38/129.69 (C₄/C₅), 98.85 (C₈), 93.78 (C₇), 88.87 (C₂), 72.61 (C₁). IR (CsI) (cm^{−1}): 2961 (m), 2924 (m), 2859 (w), ν(C–H aryl). IR (ν_(CO), hexane) (cm^{−1}): 2102 (w), 2094 (m), 2083 (m), 2064 (s), 2032 (s), 2018 (w), 1985 (w). MS (FAB⁺): *m/z* 1366 [M⁺ − CO].

4.3.8. [$\{Co_4(CO)_8(\mu-CO)_2\}(\mu_4-HC_2C_6H_4C_2H)$] (6)

Dicobaltoctacarbonyl (0.410 g, 1.2 mmol) was heated in hexane (70 ml) at 50°C for 3 h when TLC (SiO₂, hexane) indicated that all dicobaltoctacarbonyl had transformed into tetracobaltdodecacarbonyl. The reaction vessel was left to cool down. The solvent was removed under vacuum to give a black solid and was replaced with CH₂Cl₂ (40 ml). The dark brown solution was added via cannula to a solution of diethynylbenzene (0.076 g, 0.6 mmol) in CH₂Cl₂ (20 ml) and left stirring at room temperature wrapped in tin foil under argon flow. The solution was followed by TLC (SiO₂, hexane) and allowed to continue for 4 days before it was considered complete. The solvent was removed under vacuum and (tetracobalt)decacarbonyl was recovered as a blue solid. TLC: *R_f* 0.1 (SiO₂, hexane). Yield 48%. ¹H-NMR (CDCl₃, 300 MHz): δ 8.43 (s, 1H, H₁), 7.33 (d, ³*J* = 8 Hz, 2H, H₅), 7.07 (d, ³*J* = 8 Hz, 2H, H₄), 3.14 (s, H₈). ¹³C-NMR (CDCl₃, 75 MHz): δ 151.83 (C₃), 131.87 (C₅), 125.74 (C₄), 122.35 (C₆), 82.76 (C₇), 78.70 (C₈). IR (ν_{CO} , Nujol, cm⁻¹): 2091 (w), 2053 (s), 2040 (s), 2020 (w, sh), 1996 (w), 1980 (w, sh), (terminal CO); 1879 (w), 1858 (w), (bridging CO); MS (FAB⁺): *m/z* 643 [M⁺].

4.3.9. [$\{Co_2(CO)_6\}\{Co_4(CO)_8(\mu-CO)_2\}(\mu_6-HC_2-C_6H_4C_2H)$] (7)

Tetracobaltdodecacarbonyl was prepared as above from dicobaltoctacarbonyl (0.067 g, 0.2 mmol) and was reacted with dicobalthexacarbonyl diethynylbenzene (0.041 g, 0.1 mmol) in CH₂Cl₂ (40 ml). The mixture was allowed to stir under argon flow and wrapped in tin foil for 3 days. Flash chromatography (SiO₂, hexane) was performed under argon with dry and degassed hexane, and isolated (tetracobaltdodecacarbonyl)(dicobalthexacarbonyl)diethynylbenzene as a dark blue solid. TLC: *R_f* 0.1 Yield: 0.061 g, 66%. ¹H-NMR (CDCl₃, 300 MHz) δ 8.42 (s, 1H, H₁), 7.34 (d, ³*J* = 8 Hz, 2H, H₅), 7.06 (d, ³*J* = 8 Hz, 2H, H₄), 6.37 (s, 1H, H₈). ¹³C-NMR (CDCl₃, 75 MHz) δ 199.11 (C_{CO}, {Co₂(CO)₆}), 151.33 (C₃), 138.31 (C₆), 129.71 (C₅), 126.24 (C₄), 88.28 (C₇), 72.75 (C₈). IR (ν_{CO} , Nujol, cm⁻¹) 2093 (w), 2090 (w), 2058 (s), 2032 (s), 2016 (w, sh), 1996 (w), 1980 (w, sh), (terminal CO); 1879 (w), 1865 (w), (bridging CO); MS (FAB⁺): *m/z* 927 [M⁺].

4.3.10. HC₆₀[C₂{Co₂(CO)₆}]₂SiMe₃ (11a)

Purified by column chromatography (SiO₂, loaded with CS₂ and eluted with hexane) to give a black powder. TLC: *R_f* 0.4. Yield 80%. ¹H-NMR (300 MHz, CS₂/CDCl₃) δ 6.74 (s, 1H), 0.59 (s, 9H). ¹³C-NMR (75.47 MHz, CS₂/CDCl₃) δ 79.2 (C₁), 80.5 (C₂), 1.2 (C₃), 67.5 (C₄), 64.0 (C₅), 199.4 (C_{CO}), C₆₀ core: δ 134.91, 135.85, 140.05, 140.16, 141.54, 141.71, 141.85, 141.99, 142.16, 142.46, 142.5, 142.83, 142.99, 144.29, 144.56, 145.19, 145.27, 145.32, 145.44, 146.0, 146.03, 146.21,

146.27, 147.11, 147.37, 152.13, 154.71. IR (KBr, cm⁻¹): 2963(m), 2911(w), 2848 (w), 2088s, 2051 (s), 2025 (s), 2019 (s), 1261 (vs), 1183 (w) (C₆₀), 1098 (vs), 1022 (vs) 801 (s), 576 (w) (C₆₀), 526 (m) (C₆₀). IR (ν_{CO} , hexane, cm⁻¹): 2092 (w), 2056 (s), 2032 (s), 2026 (s).

4.3.11. 1-hydro-9-[(dicobalthexacarbonyl)phenyl-acetylene]fullerene[60] (12)

Purified by flash chromatography (SiO₂, cyclohexane) to give a red-brown powder. TLC: *R_f* 0.3. Yield: 71%. M.p. > 360°C. ¹H-NMR (CDCl₃/CS₂ (1:1), 400 MHz): δ 6.75 (s, C₆₀H), 8.12 (m, H₅), 7.56 (m, H₆/H₇). ¹³C-NMR (CDCl₃/CS₂ (1:1), 100 MHz): δ 198.90 (C_{CO}), 137.59 (C₄), 129.81/129.36 (C₅/C₆), 128.48 (C₇), 108.21 (C₂), 93.05 (C₃), 65.80 (C₁), 62.88 (C₁); 154.77, 152.58, 147.63, 147.38, 146.44, 146.47, 146.28, 146.22, 145.92, 145.70, 145.50, 145.43, 144.76, 144.52, 143.22, 142.71, 142.66, 142.35, 142.18, 142.08, 141.90, 141.80, 141.71, 140.36, 140.30, 136.04, 135.17 (27 signals due to the sp² carbon atoms on in the C₆₀ core). IR (KBr, cm⁻¹): 2960 (w), 2921 (w), 2850 (w), ν (C–H aryl); 1436 (w), 1429 (w), 1424 (w), 1189 (w), 1182 (w), 1176 (w), 578 (w), 574 (w), 526 (s), 518 (m), 512 (m), C₆₀ bands. IR (ν_{CO} , cyclohexane, cm⁻¹): 2094 (m), 2058 (s), 2036 (s), 2028 (s), 2016 (w), 1983 (w). Anal. Calc. for C₇₄H₆O₆Co₂ (1108.7): C, 80.2; H, 0.5. Found C, 79.7; H, 1.0.

4.3.12. 1-hydro-9-[bis(dicobalthexacarbonyl)(trimethylsilyl)diethynylbenzene]fullerene[60] (13a)

Purified as a red-brown solid via flash chromatography (SiO₂, cyclohexane). TLC: *R_f* 0.2. Yield: 65%. M.p. > 360°C. ¹H-NMR (CDCl₃/CS₂ (1:1), 400 MHz): δ 6.78 (s, C₆₀H), 8.07 (d, ³*J* = 8 Hz, H₅), 7.66 (d, ³*J* = 8 Hz, H₆), 0.42 (s, 18H, H_{CH₃}). ¹³C-NMR (CDCl₃/CS₂ (1:1), 100 MHz) δ 199.56 (C_{CO}), 198.73 (C_{CO}), 139.05 (C₄), 137.48 (C₇), 130.26/130.66 (C₅/C₆), 108.46 (C₂), 103.72 (C₈), 91.77 (C₃), 80.00 (C₉), 65.54 (C₁), 62.93 (C₁), 0.92 (C_{CH₃}); 154.55, 152.39, 147.58, 147.33, 146.43, 146.39, 146.23, 146.18, 145.78, 145.67, 145.63, 145.48, 145.46, 145.37, 144.71, 144.46, 143.16, 142.68, 142.61, 142.31, 142.16, 142.03, 141.85, 141.75, 141.67, 140.31, 140.29, 135.95, 135.13 (29 signals due to sp² carbons on the C₆₀ core). IR (CsI) (cm⁻¹): 2961 (w), 2925 (m), 2851 (w), ν (C–H aryl); 1437 (w), 1430 (w), 1425 (w), 1419 (w), 580 (w), 574 (w), 526 (w), 514 (m), C₆₀ bands. IR (ν_{CO} , cyclohexane, cm⁻¹): 2094 (m), 2088 (m), 2060 (s), 2052 (s), 2036 (m), 2028 (s), 2010 (w), 1988 (w). Anal. Calc. for C₈₅H₁₄O₁₂SiCo₄ (1490.9): C, 68.5; H, 0.9. Found C, 69.0; H, 1.4.

4.3.13. [HC₂{Co₂(CO)₆}]₂C₆H₂Br (16)

Red compound, isolated by flash chromatography (SiO₂/hexane). TLC: *R_f* 0.4. Yield 92%. M.p. 101–102°C (dec.). ¹H-NMR (400 MHz, CDCl₃): δ 6.36(s, 2H), 7.55 (s, 2H), 7.60 (s, 1H). ¹³C (100 MHz, CDCl₃):

Table 2

Crystallographic data for **3a**, **3b**, **4**, **4b**, **16** and **15**^a

	3a	3b	4	4b	16	15
Molecular formula	C ₂₅ H ₁₄ Co ₄ O ₁₂ Si	C ₂₈ H ₂₂ Co ₄ O ₁₂ Si ₂	C ₁₆ H ₆ Co ₂ O ₆	C ₂₂ H ₂₂ Co ₂ O ₆ Si ₂	C ₂₂ H ₅ BrCo ₄ O ₁₂	C ₃₀ H ₆ Co ₆ O ₁₈
Crystal dimensions (mm)	0.5 × 0.2 × 0.4	0.4 × 0.5 × 0.4	0.7 × 0.5 × 0.5	0.3 × 0.4 × 0.4	0.1 × 0.3 × 0.5	0.05 × 0.2 × 0.5
Colour	Red	Brown	Bright-red	Red	Red	Deep-red
Habit	Prism	Prism	Prism	Prism	Plate	Plate
Crystal system	Triclinic	Triclinic	Triclinic	Triclinic	Monoclinic	Orthorhombic
<i>a</i> (Å)	8.655(3)	8.3652(8)	7.776(3)	8.953(2)	12.747(3)	13.204(3)
<i>b</i> (Å)	12.840(4)	8.7213(8)	7.772(2)	11.807(3)	7.958(1)	42.53(2)
<i>c</i> (Å)	14.242(5)	12.765(1)	14.277(3)	12.950(2)	27.509(6)	13.428(6)
α (°)	92.700(2)	79.694(7)	101.00(1)	90.65(2)	90	90
β (°)	95.375(3)	87.358(6)	90.32(2)	98.69(1)	101.433(9)	90
γ (°)	99.067(5)	73.839(8)	97.96(2)	96.28(2)	90	90
<i>V</i> (Å ³)	1552.9(9)	880.0(2)	838.4(4)	1344.5(5)	2735.3(9)	7451(5)
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>n</i>	<i>Pmna</i>
<i>Z</i>	2	1	2	2	4	8
Theta range (°)	1.44–24.99	1.62–24.97	1.45–24.95	1.59–24.97	1.51–24.97	1.44–20.00
<i>D</i> _{calc.} (g cm ^{−3})	1.647	1.589	1.632	1.374	1.887	1.839
<i>F</i> ₀₀₀	764	422	408	568	1504	
μ (Mo–K α) (cm ^{−1})	2.194	1.976	2.005	1.354	3.902	
Total no. of reflections	5636	3232	2175	5053	4578	
Independent reflections	5263	3012	1948	4722	4481	
<i>R</i> _{int}	0.0197	0.0088	0.0123	0.0168	0.0257	
<i>R</i> ₁ ^b	0.0477	0.0314	0.0334	0.0411	0.0496	
<i>wR</i> ₂ ^b	0.1110	0.0793	0.0802	0.1022		
Goodness of fit	1.105	1.213	1.245	1.122	0.0789	
Largest diff. peak and hole (e Å ^{−3})	1.208 −0.502	0.673 −0.339	0.761 −0.381	0.762 −0.285	0.584 −0.548	

^a For solution, refinement procedures and treatment of hydrogen atoms see Section 5.^b For *I* > 2 σ (*I*).

δ 72.5 (C₁) 87.1 (C₂) 122.6 (C₃) 131.3 (C₄) 140.8 (C₃) 198.8 (C₆, broad). IR (ν_{CO} , hexane, cm^{−1}) 2096 (s), 2064 (s), 2033 (s). Anal. Calc. for C₂₂H₅BrO₁₂Co₄ (776.9): C, 34.0; H, 0.6. Found C, 34.0; H, 0.5.

4.3.14. [HC₂{Co₂(CO)₆}]₃C₆H₃ (**15**)

Red product, isolated by flash chromatography (SiO₂/hexane). TLC: *R*_f 0.32. Yield 93%. M.p. 100–102°C (dec.). ¹H-NMR (300 MHz, CDCl₃) δ 6.40 (s, 3H), 7.55 (s, 3H). ¹³C-NMR (75 MHz, CDCl₃): δ 130.7 (C₄) 139.3 (C₃) 72.8 (C₁) 88.4 (C₂) 199.1 (C₅, broad). IR (ν_{CO} , hexane, cm^{−1}) 2093 (s), 2064 (s), 2031 (s). Calc. for C₃₀H₆O₁₈Co₆ (1007.97): C, 35.7; H, 0.6. Found C, 36.0; H, 1.0.

5. X-ray structure determination

The crystal structure data were collected on an Enraf–Nonius CAD-4 diffractometer. The crystal data and experimental parameters are summarised in Table 2. No decay or absorption corrections were applied to the data collected. The data were reduced to give the number of unique reflections and those with $F \geq |4\sigma|F$

were used in structure solution and refinement. The structures were solved by automatic direct methods using SHELXS-86 [24] and refined by full-matrix least-squares analysis on *F*² with SHELXL [25]. Final electron density difference maps showed no regions of significant electron density. All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were treated differently in each case. All the hydrogen atoms of **16**, the benzene protons of **3b**, and the terminal ‘acetylenic’ protons of **4** and **3a** were located from subsequent Fourier difference maps and refined isotropically with individual temperature factors. The remaining hydrogen atoms of these structures and all those of **4b** were placed in calculated positions riding on the appropriate carbon atom. The ORTEP diagrams were presented using ORTEX [26].

The crude crystallographic data obtained for **15** resulted only in the location and refinement of the core atoms. The crystal and cell dimensions were not suitable for the diffractometer or the source available. The core atoms were refined anisotropically. For the molecular representation, the graphics programme SCHAKAL 93 was used [27].

6. Supplementary material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 124699, 124700, 124701, 124702 and 124703 for compounds **3a**, **3b**, **4**, **4b**, **16**. Copies of this information may be obtained free of charge from The Director, CCDC, 12, Union Road, Cambridge CB2 1EZ (Fax: +44-1223-336-033; email: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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