Articles

Synthesis and Structure of Co_3C Clusters with Alkyne Functionality

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Tricobalt carbon clusters with alkyne functionality $R(C{\equiv}C)_nCCo_3(CO)_9$ ($R = Me_3Si$, $n = 1, 2$; $R = Ph$, $(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4)$ (Fc), and H, $n = 1$) have been prepared by Cadiot–Chodkiewicz, Grignard, or $AlCl_3$-assisted coupling reactions between an alkyne and $BrCCo_3(CO)_9$. The scope for these reactions has been delineated. X-ray structure analysis of the compounds $Me_3SiC{\equiv}CCCo_3(CO)_9$ ($P\bar{1}$, $a = 9.261$ (2) Å, $b = 15.092$ (6) Å, $c = 15.739$ (8) Å, $\alpha = 76.12$ (4)°, $\beta = 88.33$ (3)°, $\gamma = 77.73$ (2)°, $Z = 4$), $FcC{\equiv}CCCo_3(CO)_9$ ($P2_12_12_1$, $a = 11.658$ (3) Å, $b = 13.826$ (3) Å, $c = 14.625$ (3) Å, $Z = 4$), and $Me_3Si(C{\equiv}C)_2CCo_3(CO)_9$ ($P\bar{1}$, $a = 9.117$ (3) Å, $b = 9.386$ (4) Å, $c = 15.191$ (4), $\alpha = 95.40$ (3)°, $\beta = 93.42$ (3)°, $\gamma = 93.38$ (3)°, $Z = 2$) have assisted spectroscopic characterization. The structural analysis of $Me_3Si(C{\equiv}C)_2CCo_3(CO)_9$ revealed the presence of polymeric material in the crystal, consistent with topochemical polymerization of the monomer units in the solid state. $Co_2(CO)_6$ derivatives of these clusters ($R = Me_3Si$, Ph) are minor products and have been independently synthesized from the alkyne clusters; regioisomers of $Me_3Si(C{\equiv}C)_2[Co_2(CO)_6]CCo_3(CO)_9$ were identified.

Low-valency transition-metal clusters can function as redox centers and as electron-transfer entities.[1-3] Cooperative interactions within these clusters as well as inductive/mesomeric effects allow tuning of the redox potential, and it is possible to have both reducible and oxidizable centers within one structural framework.[4] These facets of cluster chemistry have not been exploited in any technological sense although the concept of clusters as ETC catalysts is firmly established.[2,5-7] Is it possible to incorporate these advantageous redox properties into multicluster arrays, in particular materials which might have cooperative catalytic and electronic/magnetic properties? Incorporation of cluster units could increase the mechanical strength of these materials or give materials with modified electrical or magnetic properties. In searching for some answers to this question, we have utilized clusters which have a functional main-group atom as part of the cluster skeleton.[8] Conceptually, utilization of a carbyne atom for example is the simplest way to link cluster units into arrays. Moreover, extensive investigations in a number of laboratories[9] have shown that organo-carbyne materials such as doped polyacetylenes can have one-dimensional conductivities which rival metals.

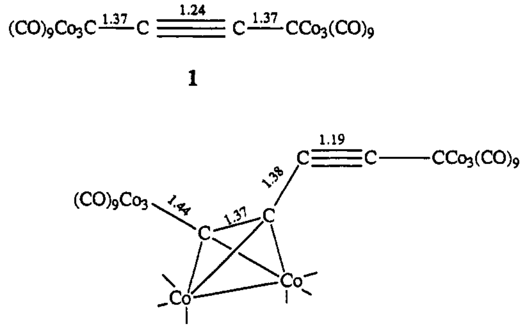

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Figure 1. Structures of $(CO)_9Co_3CC{\equiv}CCCo_3(CO)_9$[10] (**1**) and $(CO)_9Co_3C(C{\equiv}C)_2[(Co_2(CO)_6]CCo_3(CO)_9$[11] (**2**), showing the bond-length variations in the alkyne chains.

Some years ago,[8] we isolated several tricobalt carbon clusters including **1**, $(CO)_9Co_3CC{\equiv}CCCo_3(CO)_9$,[10] and **2**, $(CO)_9Co_3C(C{\equiv}C)_2[(Co_2(CO)_6]CCo_3(CO)_9$,[11] in which the Co_3C units were linked by carbon–carbon bonds. Short C–C bond distances suggested that there was electron delocalization along the cluster-carbyne chain (Figure 1), but at the time there was no other evidence indicative of especial cooperative features which may be associated with two cluster units in close proximity. Subsequently, the recognition of the well-defined redox character of a low-valency polymetallic framework and its ability to function as an electron reservoir[12] indicated that clusters **1** and **2**,

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or relatives in which the Co_3C moiety was incorporated in the alkyne backbone, may be suitable precursors for conducting materials. The early preparation of the clusters **1** and **2** and their derivatives was a serendipitous process with low and inconsistent yields.[10,11,13] In this paper we present some synthetic strategies directed toward a more rational synthesis of $(CO)_9Co_3C(C{\equiv}C)_nR$ clusters in which the Co_3C unit has alkyne functionality and may include a cluster unit as the second alkyne substituent. The redox[14] and conduction properties[15] of these compounds are discussed elsewhere.

Results and Discussion

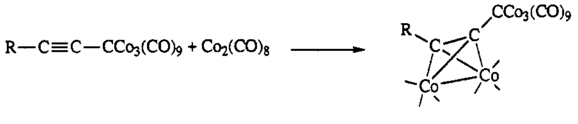
Copper-Catalyzed Reactions. $BrCCo_3(CO)_9$ reacts with the terminal alkynes $RC{\equiv}CH$ [R = $SiMe_3$, phenyl (Ph), ferrocenyl (Fc)] in the presence of ethylamine and a catalytic amount of CuCl to produce the cluster-substituted alkynes **3**–**5** in moderate yields (eq 1). Cluster **4**, $PhC{\equiv}CCo_3(CO)_9$, rapidly undergoes a novel rearrangement on standing in concentrated solutions or in the solid to a cyclopentadienone derivative $Ph_2C_4C(O)[CCo_3(CO)_9]_2$; the synthesis and structure of this compound has been described in detail elsewhere.[16] Neither **3**, $Me_3SiC{\equiv}CCCo_3(CO)_9$, nor **5**, $FeC{\equiv}CCCo_3(CO)_9$, undergo the same rearrangement as **4**, a fact which may be attributed to the steric bulk of the terminal Me_3Si or Fc substituents in these clusters.

$$BrCCo_3(CO)_9 + R{-}C{\equiv}C{-}H \xrightarrow[EtNH_2]{Cu(I)} R{-}C{\equiv}C{-}CCo_3(CO)_9 \quad (1)$$

R = Me_3Si, Ph, Fc
3 **4** **5**

Originally reported in 1957 the Cadiot–Chodkiewicz procedure is widely used as a method for the controlled coupling of unsymmetric acetylenes.[17] Reaction 1 displayed the same limitations shown by classical organic substrates. Thus, the yields decreased in order for the amine 1° ≫ 2° > 3° and products from reaction 1 with acetylenes bearing an electron-withdrawing group (e.g. CF_3) could not be isolated. Acetylenes with two –I substituents are normally kinetically unstable,[18] so the latter observation is consistent with the electron-withdrawing capability of the CCo_3 cluster.[4,12]

Reaction 1 has a narrow temperature regime; while it is inhibited below ~24 °C, temperatures above 29 °C cause decomposition of the cluster, presumably producing cobalt carbonyl fragments, which then react with either the free alkyne, to give $RC{\equiv}C[Co_2(CO)_6]H$ (R = Me_3Si, Ph, Fc),[19] or with the alkyne-substituted cluster products, yielding the dicobalt bis(carbyne) derivatives $RC{\equiv}C[Co_2(CO)_6]CCo_3(CO)_9$ (R = Me_3Si (**6**), Ph (**7**)). Both classes of compound are isolated from the reaction as minor products. Alternatively, the complexes **6** and **7** could arise from the direct reaction of excess alkyne with **3** and **4**, although this process normally requires more severe reaction conditions[20] than those utilized in the coupling reactions. Clusters **6** and **7** were independently synthesized from $Co_2(CO)_8$ and **3** and **4** respectively (eq 2).



(2)

R = Me_3Si, Ph
6 **7**

Reactions of $BrCCo_3(CO)_9$ with $HC{\equiv}CH$ and $H(C{\equiv}C)_2H$ according to eq 3 resulted in the formation of both

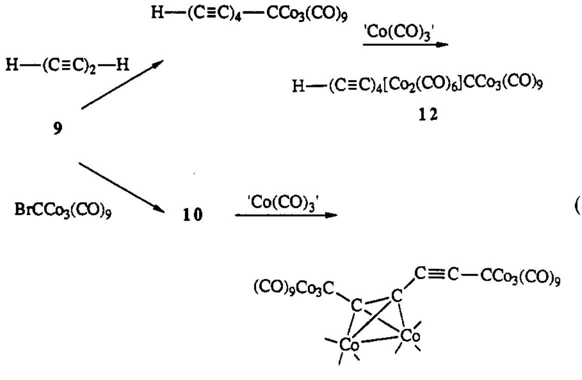
$$BrCCo_3(CO)_9 + H{-}(C{\equiv}C)_n{-}H \xrightarrow[EtNH_2]{Cu(I)}$$

$$H{-}(C{\equiv}C)_n{-}CCo_3(CO)_9 \quad n = 1,\ \mathbf{8};\ n = 2,\ \mathbf{9}$$

$$+ \quad (3)$$

$$(CO)_9Co_3C{-}(C{\equiv}C)_n{-}CCo_3(CO)_9 \quad n = 1,\ \mathbf{1};\ n = 2,\ \mathbf{10}$$

mono, **8**, $HC{\equiv}CCCo_3(CO)_9$, and **9**, $H(C{\equiv}C)_2CCo_3(CO)_9$, and dicluster, **1** and **10**, $(CO)_9Co_3C(C{\equiv}C)_2CCo_3(CO)_9$, products. These compounds could only be identified tentatively in solution due to their instability, but confirmation of their existence came from the characterization of $Co_2(CO)_6$ derivatives. Thus, the green complex **11**, $HC{\equiv}C[Co_2(CO)_6]CCo_3(CO)_9$,[13] was a minor product of the reaction between acetylene and $BrCCo_3(CO)_9$, together with the butterfly cluster $HC{\equiv}CHCo_4(CO)_{10}$.[19] The corresponding reaction with diacetylene leads to the isolation of two dicobalt bis(carbyne) complexes **12**, $H(C{\equiv}C)_4[Co_2(CO)_6]CCo_3(CO)_9$, and **2**, $(CO)_9Co_3C(C{\equiv}C)_2[(Co_2(CO)_6]CCo_3(CO)_9$[11] (eq 4). **12** may be derived from a cluster formed by an in situ coupling reaction of the diacetylene itself or, more likely, from an equivalent coupling reaction between **9** and diacetylene. Similarly, coupling of **9** with a second mole of the bromo cluster and adventitious "Co(CO)$_3$" leads to the isolation of **2**. There was no evidence for the formation of blue butterfly complexes in the diacetylene reactions.



(4)

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The low yields in reaction 3 are also partly due to the low solubility of the copper acetylide complexes, which in both cases separate out as red precipitates during the reaction. Significantly, a considerable amount of black insoluble material was also obtained upon work up, which had the typical ν(CO) profile of a $Co_3(CO)_9$ unit. Similar insoluble products were also formed in the corresponding reactions of the alkyne-Grignard reagent $HC{\equiv}CMgBr$

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(vide infra). Analysis indicated that there were approximately 0.6 cluster units per $-C\equiv C-$ bond, and we believe these materials to be polyacetylene derivatives formed by the random nonstoichiometric condensation of acetylene and **8**.[21]

In an effort to extend the alkyne chain of the $Co_2(CO)_6$ derivatives, $BrCCo_3(CO)_9$ was reacted in the presence of copper catalysts with the substituted alkynes $R(C\equiv C)_n[Co_2(CO)_6]H$ ($R = CCo_3(CO)_9$, $SiMe_3$, C_6H_5; $n = 1, 2$). However, the products $R(C\equiv C)_n[Co_2(CO)_6]CCo_3(CO)_9$ were only obtained in low to negligible yields.

Self-coupling reactions of 1-bromoalkynes have been employed to produce symmetrical polyacetylenes.[17] By analogy it seemed possible that self-coupling of $BrCCo_3(CO)_9$ would provide a more efficient route to the cluster dimer $(CO)_9Co_3CCCo_3(CO)_9$;[22] an alternative synthesis could be provided by coupling $BrCCo_3(CO)_9$ with $HCCo_3(CO)_9$. The requisite reaction did not occur in either instance and, in hindsight, this is not surprising given the steric bulk of the cluster unit.

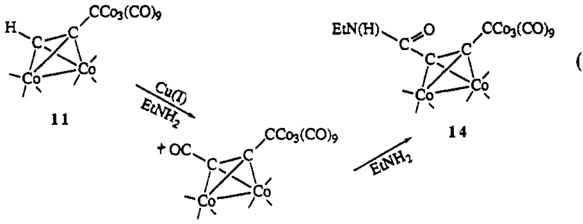
In all of the Cadiot–Chodkiewicz reactions, a competing process (eq 5) involving the amine and CuCl occurs to

$$BrCCo_3(CO)_9 + EtNH_2 \xrightarrow{Cu(I)} \underset{\textbf{13}}{EtN(H)CCo_3(CO)_9} + HBr \qquad (5)$$

produce the amino complex **13**, $EtN(H)CCo_3(CO)_9$. Although the formal elimination of HX (X = halogen) has been recognized in the base-induced reactions of $BrCCo_3(CO)_9$ with arenethiols,[23] or in reactions with silanes,[24] the addition of Lewis acids such as aluminum chloride or nucleophiles normally accelerates the formation of acyl derivatives, in which a CO is inserted between the carbyne cap and the cluster apical substituent. For example, the reaction of $BrCCo_3(CO)_9$ with Et_2NH, with *or without* a Lewis acid gives the amide product $Et_2NC(O)CCo_3(CO)_9$. Intramolecular CO insertion is known to proceed through the formation of the acylium cation $^+OCCCo_3(CO)_9$,[25] possibly involving the intermediate formation of the (μ-oxo)tetracobalt(II) species $OCo_4[O_2CCo_3(CO)_9]_6$.[26] In aryl Friedel–Crafts[27] or radical-initiated reactions[28] of halotricobalt carbon clusters, intramolecular CO insertion is not the preferred reaction. By analogy with the chemistry of the alkynes, the role of CuCl in reaction 5 may be to accelerate halide loss from the cluster moiety and subsequent nucleophilic attack on the apical carbyne atom via a Cu(I)-stabilized carbonium ion[29] or through an intermediate complex involving electron transfer and oxidation of Cu(I).

Whatever the precise mechanistic details for eq 5, the absence of CO insertion suggests that reactions with other Lewis bases in the presence of CuCl could offer a facile route to novel apical substituents in $RCCo_3(CO)_9$ chemistry.

In contrast to reaction 5, a complex resulting from intramolecular CO insertion, **14**, $Et(H)N(CO)C\equiv C[Co_2(CO)_6]CCo_3(CO)_9$,[30] was a major product in the attempted coupling reaction between **11** and $BrCCo_3(CO)_9$ (eq 6).



(6)

Subsequent work revealed that **14** arose from the direct reaction between **11** and $EtNH_2$ and that a stoichiometric amount of the Cu(I) reagent was required. Products which arise from the combination of a single alkyne substrate and one CO molecule are relatively uncommon, as the CO insertion reaction is usually part of a multistep process whereby one or more carbonyl groups and alkyne units are incorporated into lactones, cyclopentadienones, etc.[19] Indeed a reaction of this type was observed for $PhC\equiv CCCo_3(CO)_9$ (**4**).[16] The intriguing question is why oligomeric products were not formed in reaction 6. Direct nucleophilic attack at the alkyne functionality is unlikely, and we suggest that an acylium cation, $^+OCC\equiv C[Co_2(CO)_6]CCo_3(CO)_9$, is formed by a nucleophile-assisted CO insertion reaction. The cation subsequently reacts with the nucleophile to give the product, **14**. This acylium cation is stabilized to oligomerization due to the steric protection afforded by the bulky hexacarbonyl dicobalt and cluster substituents.

Grignard Reactions. Girgnard reagents have been used to synthesize aryl- (but not alkyl-) methinyltricobalt enneacarbonyls from the halo clusters.[31] For these reactions a ratio of 10 mol of Grignard reagent to 1 mol of cluster is required, because initial attack occurs at the carbonyl ligands. There have been no reports on the reactivity of alkyne-Grignard reagents toward these clusters, but conceptually this is a route to diacetylene-coupled clusters. $BrCCo_3(CO)_9$ reacted with alkynylmagnesium bromides to give **3** and **4** in low yields (eq 7); there was no

$$BrCCo_3(CO)_9 + R{-}C\equiv CMgBr \xrightarrow{THF} \underset{\substack{R\,=\,Me_3Si,\ Ph\\ \textbf{3}\quad\ \textbf{4}}}{R{-}C\equiv C{-}CCo_3(CO)_9} \qquad (7)$$

improvement in yield using $ICCo_3(CO)_9$. $HCCo_3(CO)_9$ was the major product from reaction 7. Hydrogen transfer commonly occurs in reactions of alkynyl bromides with an alkynyl Grignard,[32] so the formation of $HCCo_3(CO)_9$ (eq 8) was not unexpected given the similarity between the tricobalt carbyne–halide and alkynyl–halide bond.

$$BrCCo_3(CO)_9 + RMgBr \xrightarrow{THF} BrMgCCo_3(CO)_9 + RBr \xrightarrow{H_2O} HCCo_3(CO)_9 \qquad (8)$$

The major cluster products, other than $HCCo_3(CO)_9$, from the reaction of HC_2MgBr with $BrCCo_3(CO)_9$ were the known compounds $HC\equiv C[Co_2(CO)_6]CCo_3(CO)_9$[13] (**11**) and $(CO)_9Co_3CC\equiv CCCo_3(CO)_9$[10] (**1**). The latter could arise from a coupling reaction involving $HC\equiv CCCo_3(CO)_9$, or from the dimagnesium-Grignard species, which is in equilibrium with $HC\equiv CMgBr$ in solution.[33]

Friedel–Crafts Reactions. A problem with the preceding synthetic routes is that polyacetylenes, which would

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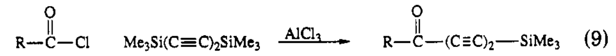
be suitable precursors for complexes with two cluster units linked by an unsaturated bridge, are difficult to handle. Bis(trimethylsilyl)alkynes offer a source of stable polyacetylene derivatives and are known to undergo Lewis acid assisted desilylation reactions (eq 9) with acyl chlorides.[34]



$$\mathrm{R{-}C({=}O){-}Cl} \quad \mathrm{Me_3Si(C{\equiv}C)_2SiMe_3} \xrightarrow{\mathrm{AlCl_3}} \mathrm{R{-}C({=}O){-}(C{\equiv}C)_2{-}SiMe_3} \qquad (9)$$

Furthermore tricobalt carbon clusters with halo capping substituents are also known to participate readily in Friedel–Crafts arylation reactions.[27,35] This route gave $\mathrm{Me_3Si(C{\equiv}C)_2CCo_3(CO)_9}$ (**15**) in good yield (eq 10); similar reactions with $\mathrm{Me_3SiC{\equiv}CSiMe_3}$ or $\mathrm{Me_3Si(C{\equiv}C)_4SiMe_3}$ were unsuccessful.

$$\mathrm{BrCCo_3(CO)_9 + Me_3Si{-}(C{\equiv}C)_2{-}SiMe_3} \xrightarrow[\mathrm{CH_2Cl_2}]{\mathrm{AlCl_3}} \underset{\textbf{15}}{\mathrm{Me_3Si{-}(C{\equiv}C)_2{-}CCo_3(CO)_9}} \qquad (10)$$

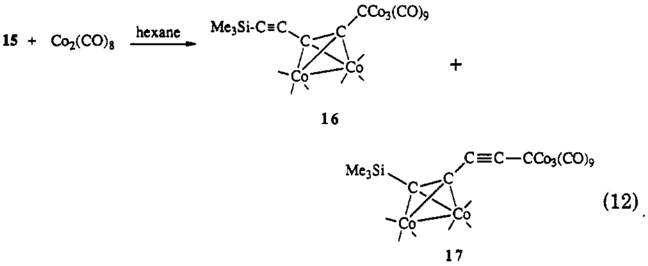
Electrophilic attack at the alkyne to give a carbocation is a reasonable mechanism (eq 11); the positive charge on

$$\mathrm{BrCCo_3(CO)_9 + AlCl_3} \longrightarrow \mathrm{Cl_3Al}^{\delta-}{-}\mathrm{Br}{-}{}^{\delta+}\mathrm{CCo_3(CO)_9} \equiv \mathrm{Cl_3AlBr^{-}\,{}^{+}CCo_3(CO)_9}$$

$$\begin{array}{c} \mathrm{Me_3Si{-}(C{\equiv}C)_2{-}SiMe_3 + Cl_3AlBr^{-}\,{}^{+}CCo_3(CO)_9} \\ \downarrow \\ \mathrm{Me_3Si{-}(C{\equiv}C)_2{-}CCo_3(CO)_9 + Me_3SiBr + AlCl_3} \\ \textbf{15} \end{array} \qquad (11)$$

the carbonium ion $^{+}\mathrm{CCo_3(CO)_9}$ is stabilized by delocalization onto the $\mathrm{Co_3C}$ core, and this species was implicated in Friedel–Crafts reactions of the haloclusters.[27,29,35] The steric demands of the cluster carbonium ion probably prohibit electrophilic attack on $\mathrm{Me_3SiC{\equiv}CSiMe_3}$ and the higher congeners of $\mathrm{R(C{\equiv}C)_nCCo_3(CO)_9}$ are apparently very unstable.

Reaction of **15** with $\mathrm{Co_2(CO)_8}$ gave both regioisomers of the (μ_2-alkyne)hexacarbonyldicobalt complex in good yield (eq 12). Assignment of the regioisomers is based on the



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(12)

chemical shift of the ^{13}C resonance for the terminal $\mathrm{Me_3Si}$ group of **16**, $\mathrm{Me_3SiC{\equiv}CC{\equiv}C[Co_2(CO)_6]CCo_3(CO)_9}$, which is the same as that for **15**, whereas coordination of a $\mathrm{Co_2(CO)_6}$ moiety to the proximal alkyne in **17**, $\mathrm{Me_3SiC{\equiv}C[Co_2(CO)_6]C{\equiv}CCCo_3(CO)_9}$, moves the resonance downfield.

Spectroscopic and Structural Characterization. Elemental analyses do not readily characterize this type of cluster so the molecular masses were obtained from FAB mass spectra. Carbonyl loss was the primary fragmentation process in all spectra, and it was interesting that $\mathrm{Co_3C^+}$ and $\mathrm{Co_2C^+}$ fragments were at low abundance. The latter are predominant in the spectra of other $\mathrm{RCCo_3(CO)_9}$ compounds, presumably because of the particular stability of the $\mathrm{Co_3C}$ unit.[36] It seems that cobalt–carbon cleavage is facile in the alkynyl clusters due to the stability of the CoC_n fragments.

The long relaxation times of the alkyne carbon atoms and the absence of a definitive $\nu(\mathrm{C{\equiv}C})$ in the infrared spectra meant that detection of the alkyne functionality was difficult. All clusters display the typical four-band $\nu(\mathrm{CO})$ envelope of $\mathrm{CCo_3(CO)_9}$ clusters,[37] which may obscure any $\nu(\mathrm{C{\equiv}C})$ bands. The $\nu(\mathrm{CO})$ profile for **6**, **7**, **11**, **12**, **16**, and **17** is a superposition of the $\mathrm{Co_3(CO)_9}$ and $\mathrm{Co_2(CO)_6}$ profiles, which leads to easy identification of these derivatives. As expected, the methylidyne capping group ^{13}C NMR resonance was not detected, but weak resonances for the sp alkyne carbons were found over a wide range, 78–133 ppm. This is downfield from most organic alkyne resonances and reflects the electron-withdrawing character and deshielding influence of the $\mathrm{Co_3(CO)_9}$ unit (the deshielding extends to the β triple bond; see the data for **16**).

With the paucity of definitive spectroscopic data, three structures were determined by X-ray methods, **3**, an example of a cluster with only one redox center, **5**, representative of a multiple redox site system in which the substituent on the alkyne could interact with cluster via the π system of the alkyne,[38] and **15**, a diacetylene.

Structures of 3, 5, and 15. Selected bond length and angle data for **3**, **5**, and **15** are given in Table I. Compound **3** crystallizes with two unique molecules in the asymmetric unit of the triclinic unit cell. Perspective views of both molecules of **3** are shown in Figure 2. These molecules differ in slight distortions of the $\mathrm{Co_3C}$ cluster unit and in the relative positions of the trimethylsilyl substituent of the alkyne capping group with respect to the $\mathrm{Co_3}$ triangle. In molecule 1 the Co(11)–Co(12) bond is significantly shorter (2.458 (1) Å) than the other two [Co(11)–Co(13) = 2.470 (1) Å; Co(12)–Co(13) = 2.470 (1) Å]. By contrast in molecule 2, the Co triangle is symmetrical. The Co–$\mathrm{C_{ap}}$ (ap = apical) bonds do not differ significantly from one another in either molecule [mean Co–$\mathrm{C_{ap}}$ = 1.906 (6) Å]. In molecule 1, the approximately linear alkyne chain is at right angles to the plane of the $\mathrm{Co_3}$ triangle, with the Si atom located above the centroid of the triangle. In contrast, the ∠C–C–C angles of the alkyne chain in molecule 2 incline the apical substituent so as to position the Si atom above the Co(21)–Co(22) bond. It is most likely that these differences result from the effect of molecular packing in the solid state.

Compound **5** consists of well-separated monomeric molecules with no unusual intermolecular contacts. A perspective view of the molecule is shown in Figure 3.

The structure of the diacetylene cluster **15** is shown in Figure 4. Refinement of **15** revealed the presence of a possible diacetylene polymer in the crystal lattice, as detailed in the Experimental Section. The incorporation of polymer units in crystalline samples of diacetylene molecules is well documented[21] and can generally be ascribed to lattice-controlled photopolymerization reactions occurring in the solid state.[39] For **15** the packing arrangement of the unique molecules in the triclinic unit cell (Figure 5) does not preclude the possibility of topochemical polymerization in this system. However, the intermolecular contact distances between the triple bonds of adjacent monomer molecules is greater than 3–4 Å, which is the accepted norm for the promotion of solid-state polymerization reactions in diacetylene systems.[40] The

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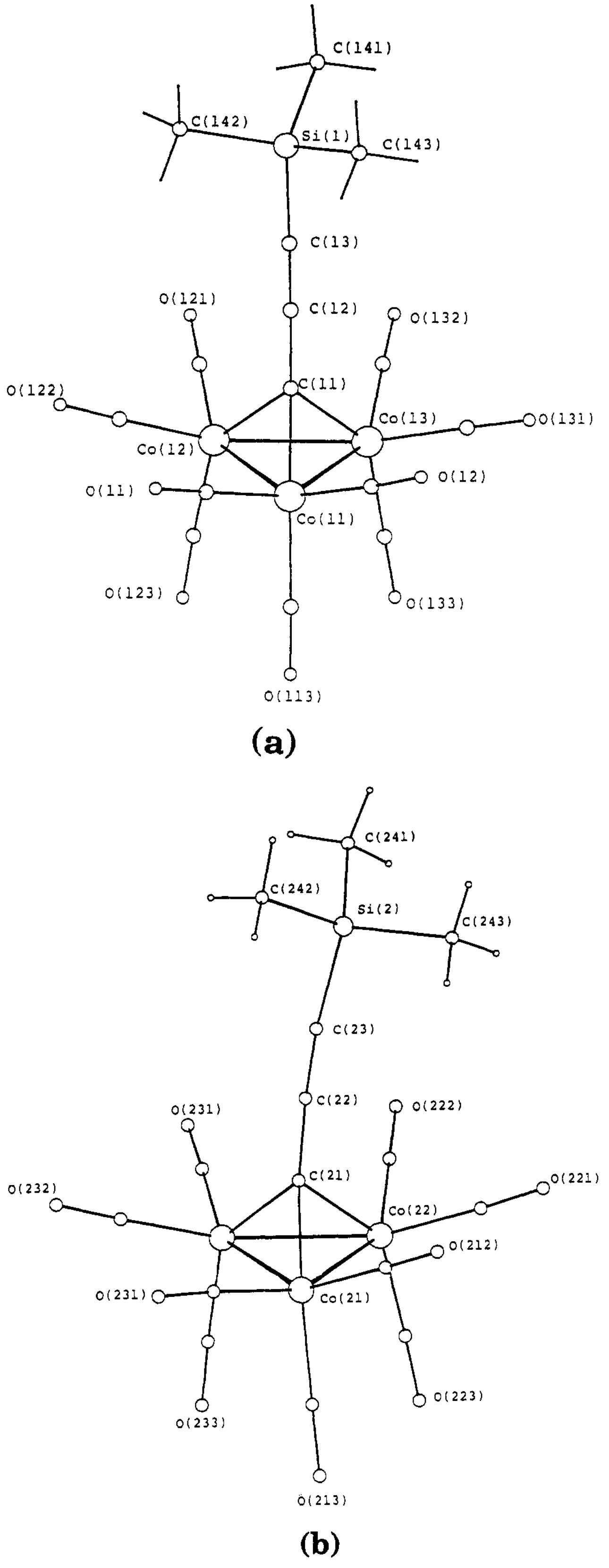

Figure 2. Perspective views of the two unique molecules of Me$_3$SiC≡CCCo$_3$(CO)$_9$ (**3**), showing the atom-numbering scheme: (a) molecule 1; (b) molecule 2.

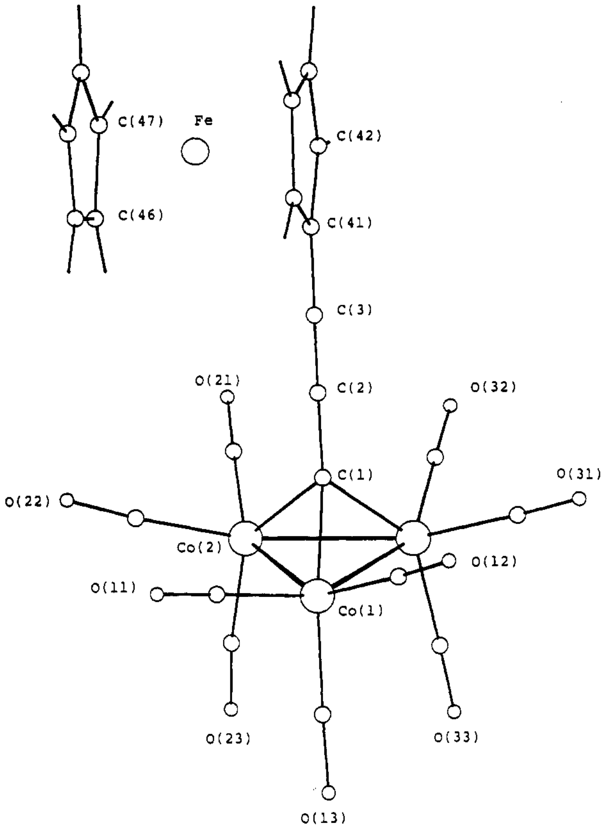

Figure 3. Perspective view of FcC≡CCCo$_3$(CO)$_9$ (**5**), showing the atom-numbering scheme.

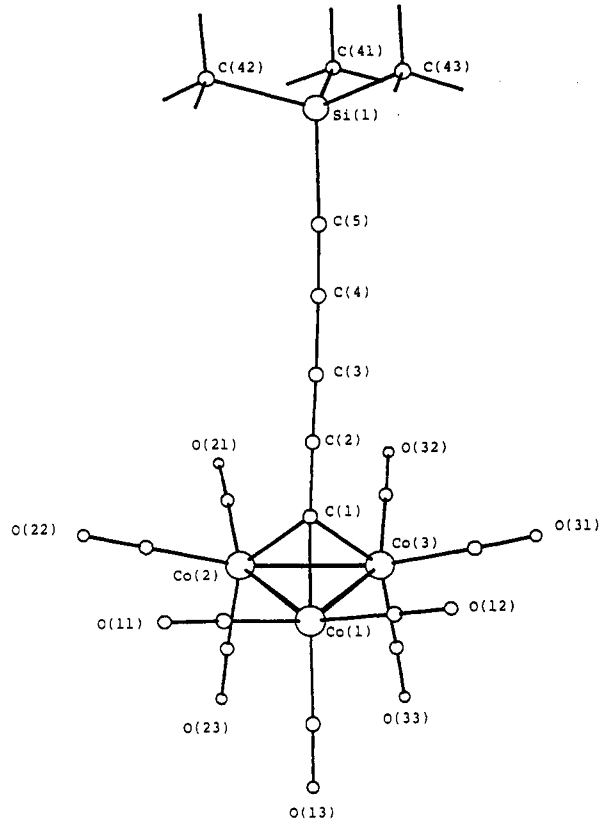

Figure 4. Perspective view of Me$_3$Si(C≡C)$_2$CCo$_3$(CO)$_9$ (**15**), showing the atom-numbering scheme.

detailed nature of the polymer is not fully revealed in this investigation, and further work is underway[41] to fully identify both the polymer structure and the source of the polymerization process.

Structures **3**, **5**, and **15** consist of approximately tetrahedral tricobalt carbon cluster moieties, apically substi-

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Table I. Selected Bond Lengths and Angles for 3, 5, and 15

molecule 1		molecule 2	
Bond Lengths (Å) for $Me_3SiC{\equiv}CCo_3(CO)_9$ (3)			
Co(11)–Co(12)	2.458 (1)	Co(21)–Co(22)	2.463 (1)
Co(11)–Co(13)	2.470 (1)	Co(21)–Co(23)	2.467 (1)
Co(11)–C(111)	1.792 (4)	Co(21)–C(211)	1.795 (6)
Co(11)–C(112)	1.786 (5)	Co(21)–C(212)	1.804 (4)
Co(11)–C(113)	1.829 (5)	Co(21)–C(213)	1.816 (5)
Co(11)–C(11)	1.913 (5)	Co(21)–C(21)	1.906 (4)
Co(12)–Co(13)	2.470 (1)	Co(22)–Co(23)	2.467 (1)
Co(12)–C(121)	1.794 (6)	Co(22)–C(221)	1.803 (4)
Co(12)–C(122)	1.804 (4)	Co(22)–C(222)	1.786 (5)
Co(12)–C(123)	1.823 (5)	Co(22)–C(223)	1.815 (5)
Co(12)–C(11)	1.902 (4)	Co(22)–C(21)	1.909 (5)
Co(13)–C(131)	1.793 (5)	Co(23)–C(231)	1.781 (5)
Co(13)–C(132)	1.789 (6)	Co(23)–C(232)	1.796 (6)
Co(13)–C(133)	1.822 (5)	Co(23)–C(233)	1.829 (5)
Co(13)–C(11)	1.916 (4)	Co(23)–C(21)	1.895 (4)
C(111)–O(111)	1.137 (5)	C(211)–O(211)	1.129 (7)
C(112)–O(112)	1.138 (6)	C(212)–O(212)	1.123 (5)
C(113)–O(113)	1.133 (6)	C(213)–O(213)	1.130 (6)
C(121)–O(121)	1.130 (7)	C(221)–O(221)	1.127 (5)
C(122)–O(122)	1.130 (5)	C(222)–O(222)	1.134 (6)
C(123)–O(123)	1.137 (6)	C(223)–O(223)	1.135 (6)
C(131)–O(131)	1.132 (6)	C(231)–O(231)	1.140 (6)
C(132)–O(132)	1.127 (7)	C(232)–O(232)	1.131 (7)
C(133)–O(133)	1.128 (6)	C(233)–O(233)	1.129 (6)
C(11)–C(12)	1.389 (6)	C(21)–C(22)	1.407 (6)
C(12)–C(13)	1.205 (7)	C(22)–C(23)	1.205 (6)
C(13)–Si(1)	1.838 (5)	C(23)–Si(2)	1.842 (5)
Si(1)–C(141)	1.862 (7)	Si(2)–C(241)	1.852 (6)
Si(1)–C(142)	1.835 (6)	Si(2)–C(242)	1.835 (8)
Si(1)–C(143)	1.844 (6)	Si(2)–C(243)	1.852 (6)
Bond Angles (deg) for $Me_3SiC{\equiv}CCo_3(CO)_9$ (3)			
Co(12)–Co(11)–Co(13)	60.20 (1)	Co(22)–Co(21)–Co(23)	60.00 (1)
Co(12)–Co(11)–C(11)	49.7 (1)	Co(22)–Co(21)–C(21)	49.8 (1)
Co(13)–Co(11)–C(11)	49.9 (1)	Co(23)–Co(21)–C(21)	49.3 (1)
C(111)–Co(11)–C(112)	95.7 (2)	C(211)–Co(21)–C(212)	97.5 (2)
C(111)–Co(11)–C(113)	101.6 (2)	C(211)–Co(21)–C(213)	99.8 (2)
C(111)–Co(11)–C(11)	103.5 (2)	C(211)–Co(21)–C(21)	105.9 (2)
C(112)–Co(11)–C(113)	103.9 (2)	C(212)–Co(21)–C(213)	103.6 (2)
C(112)–Co(11)–C(11)	100.5 (2)	C(212)–Co(21)–C(21)	97.3 (2)
C(113)–Co(11)–C(11)	142.7 (2)	C(213)–Co(21)–C(21)	144.2 (2)
Co(11)–Co(12)–Co(13)	60.10 (1)	Co(21)–Co(22)–Co(23)	60.10 (1)
Co(11)–Co(12)–C(11)	50.1 (1)	Co(21)–Co(22)–C(21)	49.7 (1)
Co(13)–Co(12)–C(11)	50.0 (1)	Co(23)–Co(22)–C(21)	49.3 (1)
C(121)–Co(12)–C(122)	96.2 (2)	C(221)–Co(22)–C(222)	95.7 (2)
C(121)–Co(12)–C(123)	102.3 (2)	C(221)–Co(22)–C(223)	102.3 (2)
C(121)–Co(12)–C(11)	102.7 (2)	C(221)–Co(22)–C(21)	101.7 (2)
C(122)–Co(12)–C(123)	104.2 (2)	C(222)–Co(22)–C(223)	103.6 (2)
C(122)–Co(12)–C(11)	99.8 (2)	C(222)–Co(22)–C(21)	100.8 (2)
C(123)–Co(12)–C(11)	142.9 (2)	C(223)–Co(22)–C(21)	143.6 (2)
Co(11)–Co(13)–Co(12)	59.70 (1)	Co(21)–Co(23)–Co(22)	59.90 (1)
Co(11)–Co(13)–C(11)	49.8 (1)	Co(21)–Co(23)–C(21)	49.7 (1)
Co(12)–Co(13)–C(11)	49.4 (1)	Co(22)–Co(23)–C(21)	49.8 (1)
C(131)–Co(13)–C(132)	96.2 (2)	C(231)–Co(23)–C(232)	95.9 (2)
C(131)–Co(13)–C(133)	101.6 (2)	C(231)–Co(23)–C(233)	99.5 (2)
C(131)–Co(13)–C(11)	103.6 (2)	C(231)–Co(23)–C(21)	107.0 (2)
C(132)–Co(13)–C(133)	102.9 (2)	C(232)–Co(23)–C(233)	104.6 (2)
C(132)–Co(13)–C(11)	101.3 (2)	C(232)–Co(23)–C(21)	101.3 (2)
C(133)–Co(13)–C(11)	142.6 (2)	C(233)–Co(23)–C(21)	140.4 (2)
Co(11)–C(111)–O(111)	177.8 (4)	Co(21)–C(211)–O(211)	176.9 (4)
Co(11)–C(112)–O(112)	176.8 (5)	Co(21)–C(212)–O(212)	178.4 (4)
Co(11)–C(113)–O(113)	177.8 (4)	Co(21)–C(213)–O(213)	179.2 (4)
Co(12)–C(121)–O(121)	178.7 (4)	Co(22)–C(221)–O(221)	177.1 (4)
Co(12)–C(122)–O(122)	177.8 (5)	Co(22)–C(222)–O(222)	176.6 (5)
Co(12)–C(123)–O(123)	177.7 (4)	Co(22)–C(223)–O(223)	177.9 (5)
Co(13)–C(131)–O(131)	177.7 (4)	Co(23)–C(231)–O(231)	178.5 (3)
Co(13)–C(132)–O(132)	178.4 (4)	Co(23)–C(232)–O(232)	178.0 (4)
Co(13)–C(133)–O(133)	179.0 (5)	Co(23)–C(233)–O(233)	177.5 (5)
Co(11)–C(11)–C(12)	131.4 (3)	Co(21)–C(21)–C(22)	129.8 (3)
Co(12)–C(11)–C(12)	131.6 (3)	Co(22)–C(21)–C(22)	127.6 (3)
Co(13)–C(11)–C(12)	132.4 (3)	Co(23)–C(21)–C(22)	137.0 (3)
C(11)–C(12)–C(13)	178.7 (5)	C(21)–C(22)–C(23)	176.4 (5)
C(12)–C(13)–Si(1)	176.0 (5)	C(22)–C(23)–Si(2)	174.5 (4)
C(13)–Si(1)–C(141)	108.9 (3)	C(23)–Si(2)–C(241)	109.2 (2)
C(13)–Si(1)–C(142)	108.0 (3)	C(23)–Si(2)–C(242)	109.9 (2)
C(13)–Si(1)–C(143)	107.4 (2)	C(23)–Si(2)–C(243)	107.1 (3)

Table I (Continued)

$FcC\equiv CCo_3(CO)_9$ (**5**)		$Me_3Si(C\equiv C)_2CCo_3(CO)_3$ (**15**)	
Bond Lengths (Å)			
Co(1)–Co(2)	2.474 (2)	Co(1)–Co(2)	2.476 (1)
Co(1)–Co(3)	2.473 (3)	Co(1)–Co(3)	2.469 (1)
Co(1)–C(11)	1.82 (2)	Co(1)–C(11)	1.795 (7)
Co(1)–C(12)	1.79 (2)	Co(1)–C(12)	1.796 (7)
Co(1)–C(13)	1.80 (2)	Co(1)–C(13)	1.810 (7)
Co(1)–C(1)	1.91 (1)	Co(1)–C(1)	1.914 (6)
Co(2)–Co(3)	2.472 (3)	Co(2)–Co(3)	2.461 (1)
Co(2)–C(21)	1.85 (2)	Co(2)–C(21)	1.810 (7)
Co(2)–C(22)	1.80 (2)	Co(2)–C(22)	1.789 (8)
Co(2)–C(23)	1.83 (2)	Co(2)–C(23)	1.824 (7)
Co(2)–C(1)	1.92 (1)	Co(2)–C(1)	1.911 (5)
Co(3)–C(31)	1.83 (2)	Co(3)–C(31)	1.796 (7)
Co(3)–C(32)	1.80 (2)	Co(3)–C(32)	1.800 (7)
Co(3)–C(33)	1.80 (2)	Co(3)–C(33)	1.826 (6)
Co(3)–C(1)	1.91 (1)	Co(3)–C(1)	1.908 (6)
C(11)–O(11)	1.11 (2)	C(11)–O(11)	1.136 (8)
C(12)–O(12)	1.14 (2)	C(12)–O(12)	1.127 (8)
C(13)–O(13)	1.17 (2)	C(13)–O(13)	1.146 (7)
C(21)–O(21)	1.09 (2)	C(21)–O(21)	1.119 (8)
C(22)–O(22)	1.12 (2)	C(22)–O(22)	1.142 (8)
C(23)–O(23)	1.14 (2)	C(23)–O(23)	1.119 (7)
C(31)–O(31)	1.11 (2)	C(31)–O(31)	1.129 (8)
C(32)–O(32)	1.13 (2)	C(32)–O(32)	1.131 (8)
C(33)–O(33)	1.13 (2)	C(33)–O(33)	1.126 (7)
C(1)–C(2)	1.37 (2)	C(1)–C(2)	1.376 (8)
C(2)–C(3)	1.23 (2)	C(2)–C(3)	1.212 (8)
C(3)–C(41)	1.39 (2)	C(3)–C(4)	1.367 (8)
C(41)–C(42)	1.41 (2)	C(4)–C(5)	1.183 (9)
C(41)–C(45)	1.43 (2)	C(5)–Si(1)	1.856 (7)
C(42)–C(43)	1.41 (2)	Si(1)–C(41)	1.84 (1)
C(43)–C(44)	1.35 (2)	Si(1)–C(42)	1.85 (1)
C(44)–C(45)	1.44 (2)	Si(1)–C(43)	1.82 (1)
C(41)–Fe(1)	2.05 (1)		
C(42)–Fe(1)	2.01 (2)		
C(43)–Fe(1)	2.06 (2)		
C(44)–Fe(1)	2.05 (2)		
C(45)–Fe(1)	2.04 (1)		
Fe(1)–C(46)	2.01 (2)		
Fe(1)–C(47)	1.98 (2)		
Fe(1)–C(48)	2.05 (2)		
Fe(1)–C(49)	2.03 (2)		
Fe(1)–C(50)	2.04 (2)		
C(46)–C(47)	1.45 (2)		
C(46)–C(50)	1.39 (2)		
C(47)–C(48)	1.38 (3)		
C(48)–C(49)	1.38 (2)		
C(49)–C(50)	1.34 92)		
Bond Angles (deg)			
Co(2)–Co(1)–Co(3)	59.9 (1)	Co(2)–Co(1)–Co(3)	59.70 (1)
Co(2)–Co(1)–C(1)	50.0 (4)	Co(2)–Co(1)–C(1)	49.6 (2)
Co(3)–Co(1)–C(1)	49.5 (4)	Co(3)–Co(1)–C(1)	49.6 (2)
C(11)–Co(1)–C(12)	96.7 (7)	C(11)–Co(1)–C(12)	96.6 (3)
C(11)–Co(1)–C(13)	100.2 (7)	C(11)–Co(1)–C(13)	102.1 (3)
C(11)–Co(1)–C(1)	105.7 (7)	C(11)–Co(1)–C(1)	103.4 (3)
C(12)–Co(1)–C(13)	107.5 (7)	C(12)–Co(1)–C(13)	103.6 (3)
C(12)–Co(1)–C(1)	97.8 (7)	C(12)–Co(1)–C(1)	101.0 (3)
C(13)–Co(1)–C(1)	141.2 (7)	C(13)–Co(1)–C(1)	141.9 (2)
Co(1)–Co(2)–Co(3)	60.0 (1)	Co(1)–Co(2)–Co(3)	60.00 (1)
Co(1)–Co(2)–C(1)	49.5 (4)	Co(1)–Co(2)–C(1)	49.7 (2)
Co(3)–Co(2)–C(21)	98.9 (5)	Co(3)–Co(2)–C(1)	49.8 (2)
Co(3)–Co(2)–C(22)	149.5 (5)	C(21)–Co(2)–C(22)	93.7 (3)
Co(3)–Co(2)–C(23)	99.4 (5)	C(21)–Co(2)–C(23)	100.5 (3)
Co(3)–Co(2)–C(1)	49.5 (4)	C(21)–Co(2)–C(1)	105.1 (3)
C(21)–Co(2)–C(22)	95.0 (7)	C(22)–Co(2)–C(23)	104.8 (3)
C(21)–Co(2)–C(23)	100.6 (7)	C(22)–Co(2)–C(1)	101.5 (3)
C(21)–Co(2)–C(1)	101.7 (6)	C(23)–Co(2)–C(1)	141.7 (3)
C(22)–Co(2)–C(23)	104.6 (7)	Co(1)–Co(3)–Co(2)	60.30 (1)
C(22)–Co(2)–C(1)	101.1 (7)	Co(1)–Co(3)–C(1)	49.9 (2)
C(23)–Co(2)–C(1)	144.1 (7)	Co(2)–Co(3)–C(1)	49.9 (2)
Co(1)–Co(3)–Co(2)	60.0 (1)	C(31)–Co(3)–C(32)	96.7 (3)
Co(1)–Co(3)–C(1)	49.6 (4)	C(31)–Co(3)–C(33)	102.5 (3)
Co(2)–Co(3)–C(1)	50.1 (4)	C(31)–Co(3)–C(1)	101.9 (2)
C(31)–Co(3)–C(32)	97.1 (6)	C(32)–Co(3)–C(33)	103.8 (3)
C(31)–Co(3)–C(33)	102.7 (7)	C(32)–Co(3)–C(1)	99.4 (3)
C(31)–Co(3)–C(1)	101.3 (7)	C(33)–Co(3)–C(1)	143.8 (3)

Table I (Continued)

$FcC{\equiv}CCo_3(CO)_9$ (5)		$Me_3Si(C{\equiv}C)_2CCo_3(CO)_9$ (15)	
Bond Angles (deg)			
C(32)-Co(3)-C(33)	102.0 (7)	Co(1)-C(11)-O(11)	178.6 (6)
C(32)-Co(3)-C(1)	102.7 (7)	Co(1)-C(12)-O(12)	178.2 (7)
C(33)-Co(3)-C(1)	142.9 (6)	Co(1)-C(13)-O(13)	178.3 (6)
Co(1)-C(11)-O(11)	177 (2)	Co(2)-C(21)-O(21)	178.3 (6)
Co(1)-C(12)-O(12)	178 (2)	Co(2)-C(22)-O(22)	178.7 (6)
Co(1)-C(13)-O(13)	178 (1)	Co(2)-C(23)-O(23)	178.4 (6)
Co(2)-C(21)-O(21)	176 (2)	Co(3)-C(31)-O(31)	178.7 (6)
Co(2)-C(22)-O(22)	175 (2)	Co(3)-C(32)-O(32)	178.0 (6)
Co(2)-C(23)-O(23)	172 (2)	Co(3)-C(33)-O(33)	178.5 (6)
Co(3)-C(31)-O(31)	178 (2)	Co(1)-C(1)-C(2)	131.5 (4)
Co(3)-C(32)-O(32)	177 (1)	Co(2)-C(1)-C(2)	133.3 (4)
Co(3)-C(33)-O(33)	178 (2)	Co(3)-C(1)-C(2)	130.4 (5)
Co(1)-C(1)-C(2)	131 (1)	C(1)-C(2)-C(3)	178.5 (7)
Co(2)-C(1)-C(2)	130 (1)	C(2)-C(3)-C(4)	177.4 (7)
Co(3)-C(1)-C(2)	132 (1)	C(3)-C(4)-C(5)	178.5 (8)
C(1)-C(2)-C(3)	177 (2)	C(4)-C(5)-Si(1)	176.5 (7)
C(2)-C(3)-C(41)	178 (1)	C(5)-Si(1)-C(41)	108.4 (4)
C(3)-C(41)-C(42)	129 (1)	C(5)-Si(1)-C(42)	106.6 (4)
C(3)-C(41)-C(45)	126 (1)	C(5)-Si(1)-C(43)	108.8 (4)
C(42)-C(41)-C(45)	104 (1)		
C(41)-C(42)-C(43)	110 (2)		
C(42)-C(43)-C(44)	108 (2)		
C(43)-C(44)-C(45)	108 (2)		
C(41)-C(45)-C(44)	108 (1)		
C(47)-C(46)-C(50)	105 (2)		
C(46)-C(47)-C(48)	109 (2)		
C(47)-C(48)-C(49)	104 (2)		
C(48)-C(49)-C(50)	113 (2)		
C(46)-C(50)-C(49)	107 (2)		

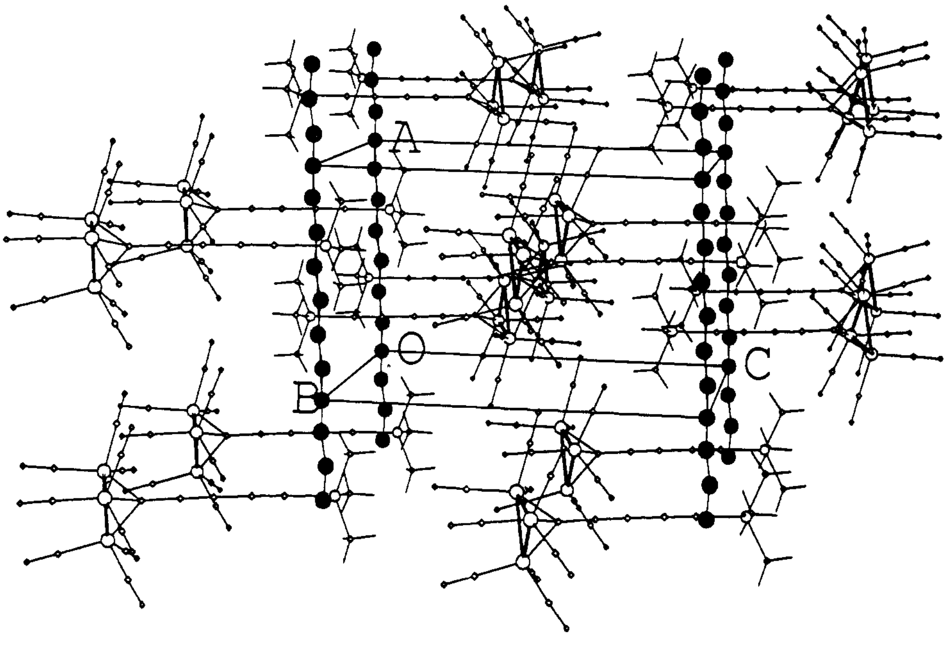
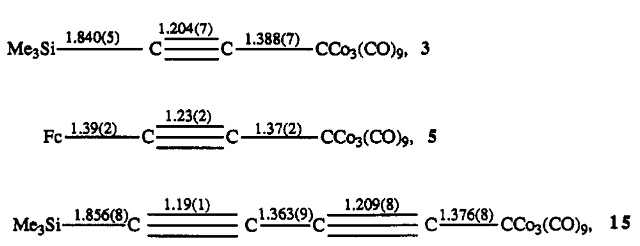


Figure 5. Unit cell contents for $Me_3Si(C{\equiv}C)_2CCo_3(CO)_9$ (15). The carbon atoms of the proposed polyacetylene chain are shown as filled circles of arbitrary radius, with the polymer units extending along the *a* axes.

tuted with (trimethylsilyl)acetylene, ferrocenylacetylene, and (trimethylsilyl)buta-1,3-diyne residues, respectively. Each cobalt atom of the cluster units carries two equatorial and one axial carbonyl ligand, and there is no indication of carbonyl bridging in any of the molecules. The dihedral angles formed by the planes of the cobalt triangles with those of the equatorial carbonyls (the C-Co-C planes) are all in the range 29-32°. These values are typical of tricobalt carbon clusters, where there is minimal steric interaction between the carbonyl ligands and the substituent on the apical carbon atom,[8] and contrast sharply with those observed in $FcCCo_3(CO)_9$,[38] in which dihedral angles as low as 25° signal the requirement to minimize interactions between the apical constituent and the Co coordination spheres. The Co-Co and Co-C_{ap} bond lengths in 5 and 15 are unremarkable, and there is no evidence for distortion of the cluster unit in these compounds.



$$Me_3Si\overset{1.840(5)}{-\!-\!-}C\overset{1.204(7)}{\equiv}C\overset{1.388(7)}{-\!-\!-}CCo_3(CO)_9,\ 3$$

$$Fc\overset{1.39(2)}{-\!-\!-}C\overset{1.23(2)}{\equiv}C\overset{1.37(2)}{-\!-\!-}CCo_3(CO)_9,\ 5$$

$$Me_3Si\overset{1.856(8)}{-\!-}C\overset{1.19(1)}{\equiv}C\overset{1.363(9)}{-\!-}C\overset{1.209(8)}{\equiv}C\overset{1.376(8)}{-\!-}CCo_3(CO)_9,\ 15$$

Figure 6. Bond-length variations in the alkyne chains of 3, 5, and 15.

The C–C bond lengths in the alkyne chains of **3**, **5**, and **15** are of particular interest (Figure 6), as they give a strong indication of the possibility of conjugation between the alkyne substituents and the CCo_3 core. The $C\equiv C$ bond lengths in all three compounds are typical of those found in other alkynes,[42,43] and the diyne chain in **15** shows the characteristic shortening of the central C–C bond, indicative of a conjugated system.[44,45] Of especial significance are the very short C–C bonds between the capping carbon of the cluster core and the adjacent alkyne. Interestingly, these bond lengths differ little from that observed for the central C–C bond in the alkyne chain of **15**, which reflects the carbyne character of the apical carbon atom and the likelihood of delocalization between the alkyne and cluster systems. Similarly short C–C bonds have been observed in compounds where two tricobalt carbon clusters are linked by alkyne chains[10,11] or where the cluster units are linked directly through the capping carbon atoms.[22] In the related molecules $Me_3SiC\equiv CCCo_3(\eta^5\text{-}C_5H_5)_3CSiMe_3$[46] and $[C\equiv CCCo_3(\eta^5\text{-}C_5H_5)_3CSiMe_3]_2$,[3] with alkyne chains linked to the apical C atoms of tricobalt bis(carbyne) clusters, the corresponding C–C bonds are longer (1.41–1.43 Å). Nonetheless electrochemical data for $[(C\equiv C)_nCCo_3(\eta^5\text{-}C_5H_5)_3CSiMe_3]_2$ ($n = 1, 2$) confirm an interaction between the cluster redox centers, pointing to significant electron delocalization along the alkyne chains.[3] The relationship between structural parameters and electrochemical response will be developed further in a paper describing the electron-transfer properties of a variety of linked cluster systems.[14]

The orientation of the ferrocene moiety in **5** with respect to the Co_3 triangle of the cluster unit contrasts sharply with that observed in the related compounds $FcCCo_3(CO)_9$ and $FcCCo_3(\eta^5\text{-}C_5H_5)_3CH$.[38] In the molecules with a direct link between the clusters and the cyclopentadiene ring of the ferrocene, there is a characteristic tilting of the ferrocene moieties toward one of the cluster cobalt atoms, believed to result from a cooperative π interation between the cluster core and the ferrocenyl substituent. In **5**, however, both Cp rings of the ferrocene are approximately orthogonal to the Co_3 ring plane [interplanar angles with the Co(1)–Co(2)–Co(3) plane, 87.7 (4)° to ring C(41)–C(45) and 86.1 (5)° to ring C(46)–C(50)]. The C(3)–C(41) bond is nonetheless short [1.39 (2) Å], and the possibility of delocalization extending via the alkyne linkage to the two redox centers cannot be discounted. Other molecular parameters within the ferrocenyl moiety are unremarkable, with mean Fe–C and C–C distances of 2.03 (2) and 1.40 (3) Å, respectively.[47] The two Cp rings are planar, and the Fe atom lies 1.649 (2) Å from the C(41)$\cdots$C(45) ring plane and 1.642 (2) Å from the C(46)$\cdots$C(50) plane. The rings are inclined at an angle of 2.2 (2)°.

Conclusion

The synthetic strategies outlined in this work do provide a route to tricobalt clusters with alkyne functionality and hence offer potential syntheses of cluster-functionalized polyacetylenes. The fragment incorporated within the unit cell of **15** is significant in this regard, as are the black polymeric materials containing cluster units which were byproducts in the reactions with acetylene and diacetylene. Conductivity and the further preparation of polymers is considered in other papers.[15,16] Limitations of the synthetic methods resulted primarily from the instability of the products when the number of carbon atoms in the alkyne chain exceeds 4 or where both substituents on the alkyne chains were cluster moieties. This suggested that in situ preparation of long-chain precursors would be the best strategy for controlled polymer production; these attempts will be described elsewhere.

Experimental Section

Infrared and electronic spectra were recorded on Digilab FX60 or Nicolet and Schimadzu spectrophotometers, respectively, and NMR spectra, on a Varian VXR-300 spectrometer; ^{13}C chemical spectra shifts were referenced to CH_2Cl_2 (δ 54.20) as an internal reference. Electron-impact mass spectra were recorded on a Varian CH-7 instrument and FAB spectra on a VG ZAB 2HF instrument at the University of Adelaide. Elemental analyses were performed by the Microanalytical Service, University of Otago.

All reactions were carried out under argon or nitrogen in purified, dried solvents. The following compounds were prepared by literature methods: $XCCo_3(CO)_9$ (X = Cl, Br, I),[48] $RC\equiv C(H)Co_2(CO)_6$ (R = H, Ph, CF_3),[19,49] C_4H_2, $PhC\equiv CMgBr$, $Me_3SiC\equiv CMgBr$, $HC\equiv CMgBr$, $Me_3SiC\equiv CH$, $Me_3SiC\equiv CSiMe_3$,[50] $Me_3Si(C\equiv C)_2SiMe_3$,[51] $FcC\equiv CH$,[52] CuCl,[53] and $NaC\equiv CH$.[54] All other reagents were from commercial sources.

Coupling Reactions Using Copper(I). A three-necked flask was fitted with a pressure-equalizing dropping funnel, thermometer, and gas inlet/outlet. Prior to the reaction, $EtNH_2$ was vacuum distilled from a 70% aqueous solution (Riedel-de Haën) and successively dried over KOH and $MgSO_4$. A weighed amount was then dissolved in the required volume of solvent and transferred to the flask.

$Me_3SiC\equiv CH$ with $BrCCo_3(CO)_9$. Anhydrous CuCl (50 mg) followed by $Me_3SiC\equiv CH$ (~0.2 cm^3) was added to a solution of dioxane (12 cm^3) containing $EtNH_2$ (190 mg) at 22 °C. An exothermic reaction occurred, increasing the temperature to approximately 24 °C. $BrCCo_3(CO)_9$ (1.0 g) dissolved in dioxane (12 mL) was added dropwise over a period of 20 min, during which time an exothermic reaction occurred to give a brown solution; the temperature was maintained below 29 °C. On occasions when the reaction ceased to occur with the addition of $BrCCo_3(CO)_9$ it was found that addition of more $Me_3SiC\equiv CH$ and/or CuCl would revive the process. The reaction mixture was stirred for another 5 min, after which time it was filtered and the residue washed with CH_2Cl_2. This left a red solid, presumed to be $CuC\equiv CSiMe_3$. The solvent was then removed under reduced pressure and the remaining solid developed on preparative TLC silica plates with hexane. Six bands were obtained: (1) *orange* (37 mg) $Me_3Si\equiv CCo_2(CO)_6H$[19] ($\nu_{CO}$ (CH_2Cl_2) 2091 (s), 2052 (vs), 2027 (vs), 2022 (vs), 2010 (sh), 1979 (mw) cm^{-1}; *m/e* 384 (M^+)); (2) *purple* (<5 mg) $HCCo_3(CO)_9$; (3) *purple* (72 mg) $BrCCo_3(CO)_9$; (4) *brown* (398 mg); (5) *green* (<5 mg); (6) *dark brown* (278 mg).

Band 4 was recrystallized from pentane and identified as $Me_3SiC\equiv CCCo_3(CO)_9$ (**3**). Anal. Calcd for $C_{15}H_9Co_3O_9Si$: C,

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Table II. Crystal Data, Data Collection, and Refinement of Compounds 3, 5, and 15

	compound		
	$Me_3SiC\equiv CCCo_3(CO)_9$ (**3**)	$FcC\equiv CCCo_3(CO)_9$ (**5**)	$Me_3Si(C\equiv C)_2CCo_3(CO)_9$ (**15**)
empirical formula	$C_{15}H_9O_9SiCo_3$	$C_{22}H_9O_9FeCo_3$	$C_{17}H_9O_9SiCo_3$
M_r	538.12	649.96	562.14
cryst system	triclinic	orthorhombic	triclinic
space group[a]	$P\bar{1}$ (No. 2)	$P2_12_12_1$ (No. 19)	$P\bar{1}$ (No. 2)[b]
a/Å	9.261 (2)	11.658 (3)	9.117 (3)
b/Å	15.092 (6)	13.826 (3)	9.386 (4)
c/Å	15.739 (8)	14.625 (3)	15.191 (4)
α/deg	76.12 (4)	90	95.40 (3)
β/deg	88.33 (3)	90	93.42 (3)
γ/deg	77.73 (2)	90	93.38 (3)
V/Å^3	2086 (2)	2357.3 (8)	1289.1 (8)
D_c (D_m)/g cm^{-3}	1.72	1.81 (1.78)	1.45
Z	4[b]	4	2
cryst size/mm	0.86 × 0.60 × 0.16	0.70 × 0.60 × 0.16	0.56 × 0.38 × 0.03
μ(Mo Kα)/cm^{-1}	24.52	27.24	19.86
F(000)	1064	1280	556
diffractometer	Nicolet R3M	Nicolet R3M	Nicolet R3M
temp/K	123 (5)	178 (5)	163 (5)
radiation (λ/Å)	Mo Kα (0.71069)	Mo Kα (0.71069)	Mo Kα (0.71069)
scan type	θ–2θ	ω	θ–2θ
scan speed/deg min^{-1}	5.86	7.32	5.86
data limits/deg	$4 < 2\theta < 45$	$4 < 2\theta < 52$	$4 < 2\theta < 53$
reflcns measd	$h,\pm k,\pm l$	h,k,l	$h,\pm k,\pm l$
cryst decay[c]	<8%	<3%	<6%
abs corr	analytical	empirical	empirical
transm	0.827 (max)	0.765 (max)	0.999 (max)
	0.538 (min)	0.380 (min)	0.563 (min)
tot. no. of reflcns[d]	5423	2524	5138
no. of unique data ($I > 2\sigma(I)$)	4490	1622	3789
method of solving	direct	Patterson	Patterson
no. of variables	265[e]	206	294
treatment of protons	calcd	calcd	calcd
R ($\sum\Delta F/\sum\lvert F_o\rvert$)	0.0361	0.0582	0.0628
R_w [$\sum w^{1/2}(\Delta F)/\sum w^{1/2}F_o$]	0.0427	0.0617	0.0770
weight (w)	$[2.7636/(\sigma^2F + 0.000176F^2)]$	$[1.0752/(\sigma^2F + 0.001293F^2)]$	$[2.0672/(\sigma^2F + 0.001471F^2)]$
resid density/e Å^{-3}	0.66, −0.61	0.82, −0.88	0.87, −0.83

[a] Reference 56. [b] Two unique molecules in the asymmetric unit. [c] Standard reflections (400), (060), and (006) for **3**, (800), (060), and (008) for **5**, and (300), (030), and (004) for **15** were measured after every 100 reflections. [d] Lorentz and polarization corrections and empirical absorption corrections were applied using the SHELXTL system.[59] [e] Individual molecules refined in alternating blocked matrix cycles.[57]

33.48; H, 1.69. Found: C, 33.66; H, 1.94. Mass spectrum: m/e 538 (M$^+$). ^{1}H NMR (CD_2Cl_2): δ 0.32 (9 H, s, Me_3Si). ^{13}C NMR (CD_2Cl_2): δ 200.38 (CO), 122.81 ($C\equiv C$), 122.28 ($C\equiv C$), 0.03 (Me_3Si). UV-visible (CH_2Cl_2): λ_{max} 515 (1440), 403 (4130), 325 (12400) nm. IR (CH_2Cl_2): ν_{CO} 2105 (m), 2050 (vs), 2041 (vs), 2027 (mw) cm^{-1}. Band 5 was identified as $Me_3SiC\equiv C[Co_2(CO)_6]CCo_3(CO)_9$ (**6**) (vide infra).

Band 6 was recrystallized from hexane and identified as $EtN(H)CCo_3(CO)_9$ (**13**). Mp: 22 °C. Anal. Calcd for $C_{12}H_6Co_3NO_9$: C, 29.69; H, 1.24; N, 2.89. Found: C, 30.19; H, 1.17; N, 2.67. Mass spectrum: m/e 485 (M$^+$). ^{1}H NMR ($CDCl_3$): δ 1.3 (3 H, t, CH_3), 3.5 (2 H, m, CH_2), 5.85 (N-H). UV-visible (CH_2Cl_2): λ_{max} 515, 380 nm. IR (CH_2Cl_2): ν_{CO} 2108 m, 2062 vs, 2045 vs, 2029 (sh) cm^{-1}; δ_{N-H} 1640 cm^{-1}.

$PhC\equiv CH$ with $BrCCo_3(CO)_9$. The reaction proceeded as with $Me_3SiC\equiv CH$. The filtered solution was reduced to a constant volume in vacuo, containing as solvent some unreacted $PhC\equiv CH$. The thick syrup was dissolved in CH_2Cl_2 and separated on silica gel plates (eluent hexane): (1) *red-brown oil* (10 mg) $PhC\equiv CCo_2(CO)_6H$[19] (ν_{CO} (CH_2Cl_2) 2095 (ms), 2056 (vs), 2031 (vs), 2016 (sh), 1984 (w) cm^{-1}); (2) *purple* (<5 mg) $HCCo_3(CO)_9$; (3) *purple* (311 mg) $BrCCo_3(CO)_9$; (4) *brown* (230 mg); (5) *green* (<5 mg) $PhC\equiv C[Co_2(CO)_6]CCo_3(CO)_9$ (**7**) (see below); (6) *dark brown* $EtN(H)CCo_3(CO)_9$ (**13**).

A mass spectrum of band 4, freshly prepared, revealed a parent molecular ion at m/e 542, indicating the expected $PhC\equiv CCCo_3(CO)_9$ (**4**). However, with time the sample was found to have undergone a transformation producing a number of other products. These are described in ref 16.

$FcC\equiv CH$ with $BrCCo_3(CO)_9$. A dioxane solution (6 cm^3) of $FcC\equiv CH$ (200 mg) and $BrCCo_3(CO)_9$ (500 mg) was added to dioxane (6 cm^3) containing CuCl (50 mg) and $EtNH_2$ (90 mg) at 24 °C over 5 min. The temperature was maintained below 29 °C. The mixture was filtered, the solvent was removed in vacuo, and preparative TLC on silica (hexane) gave the following: (1) *purple* $HCCo_3(CO)_9$; (2) *purple* $BrCCo_3(CO)_9$; (3) *green* $FcC\equiv CCo_2(CO)_6H$,[55] (4) *yellow* $FcC\equiv CH$; (5) *red*; (6) *dark brown* $EtN(H)CCo_3(CO)_9$ (**13**).

Band 5 was contaminated with traces of $FcC\equiv CH$, which proved difficult to remove and led to poor-quality analyses. After several chromatographic separations, sticky platelike crystals identified as $FcC\equiv CCCo_3(CO)_9$ (**5**) recrystallized from hexane (together with considerable decomposition). Anal. Calcd for $C_{22}H_9O_9FeCo_3$: C, 40.59; H, 1.55. Found: C, 42.57; H, 2.03. ^{13}C NMR (CD_2Cl_2): δ 117.4, 78.0, 71.8, 66.0. MS: m/e 650 (M$^+$). UV-visible (CH_2Cl_2): λ_{max} 510 (4950), 410 (6030), 340 (12700) nm. IR (CH_2Cl_2): ν_{CO} 2100 (m), 2056 (vs), 2039 (s), 2022 (mw), 2012 (mw) cm^{-1}.

Acetylene with $BrCCo_3(CO)_9$. A flow of $HC\equiv CH$, passed through H_2SO_4, and over $CaCl_2$, was bubbled into a dioxane solution (6 cm^3) of CuCl (50 mg) and $EtNH_2$ (120 mg) at 23 °C. This produced a red precipitate. $BrCCo_3(CO)_9$ (500 mg) dissolved in dioxane was added over 5 min while the temperature was maintained at ~26 °C. TLC gave the following: (1) *purple* (60 mg) $BrCCo_3(CO)_9$ and some $HCCo_3(CO)_9$—mixture not resolved; (2) *green* (5 mg) $HC\equiv C[Co_2(CO)_6]CCo_3(CO)_9$[13] (**11**) ($\nu_{CO}$ (CH_2Cl_2) 2108 (w), 2083 (s), 2064 (vs), 2058 (vs), 2049 (sh), 2043 (w), 2031 (m), 2016 (w), 1983 (w) cm^{-1}); (3) *orange* (5 mg) $(CO)_9Co_3CC\equiv CCCo_3(CO)_9$ (**1**);[10] (4) *blue* (4 mg) $H_2C_2Co_4(CO)_{10}$;[19] (5) *brown* (271 mg) $EtN(H)CCo_3(CO)_9$ (**13**).

A black precipitate which separated on filtration of the raw mixture gave variable C, H, and cobalt analyses but a consistent

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(55) Harper, M. J.; Robinson, B. H.; Simpson, J. Manuscript in preparation.

Table III. Final Positional and Equivalent[a] Thermal Parameters (Å^2) for 3, 5, and 15

atom	x/a	y/b	z/c	U_{eq}	atom	x/a	y/b	z/c	U_{eq}
				$Me_3SiC{\equiv}CCCO_3(CO)_9$ (3) (Molecule 1)					
Co(11)	0.6675 (1)	0.3098 (0)	0.9384 (0)	0.021	O(123)	0.4460 (3)	0.1593 (2)	1.1307 (2)	0.038
Co(12)	0.5041 (1)	0.2005 (0)	0.9409 (0)	0.020	C(131)	0.9576 (5)	0.1553 (3)	0.9130 (3)	0.028
Co(13)	0.7750 (1)	0.1434 (0)	0.9473 (0)	0.020	O(131)	1.0747 (4)	0.1606 (2)	0.8937 (2)	0.049
C(111)	0.5342 (5)	0.4157 (3)	0.8968 (3)	0.033	C(132)	0.7784 (5)	0.0388 (3)	0.9119 (3)	0.033
O(111)	0.4530 (4)	0.4838 (2)	0.8686 (3)	0.053	O(132)	0.7840 (4)	−0.0272 (3)	0.8892 (3)	0.057
C(112)	0.8249 (5)	0.3551 (3)	0.8955 (3)	0.034	C(133)	0.8023 (5)	0.1011 (3)	1.0655 (3)	0.028
O(112)	0.9219 (4)	0.3853 (3)	0.8644 (3)	0.057	O(133)	0.8199 (4)	0.0760 (2)	1.1386 (2)	0.048
C(113)	0.6746 (5)	0.3077 (3)	1.0549 (3)	0.027	C(11)	0.6495 (4)	0.2345 (3)	0.8589 (3)	0.022
O(113)	0.6764 (4)	0.3042 (2)	1.1276 (2)	0.043	C(12)	0.6493 (4)	0.2537 (3)	0.7681 (3)	0.023
C(121)	0.4558 (5)	0.1047 (3)	0.9076 (3)	0.030	C(13)	0.6463 (5)	0.2703 (3)	0.6893 (3)	0.034
O(121)	0.4235 (4)	0.0455 (2)	0.8853 (2)	0.047	Si(1)	0.6423 (2)	0.3041 (1)	0.5690 (1)	0.041
C(122)	0.3444 (5)	0.2869 (3)	0.8916 (3)	0.033	C(141)	0.6746 (9)	0.1967 (4)	0.5265 (4)	0.082
O(122)	0.2467 (4)	0.3415 (2)	0.8581 (3)	0.051	C(142)	0.4594 (6)	0.3769 (5)	0.5326 (5)	0.086
C(123)	0.4657 (5)	0.1746 (3)	1.0575 (3)	0.026	C(143)	0.7886 (5)	0.3705 (4)	0.5352 (3)	0.040
				$Me_3SiC{\equiv}CCCo_3(CO)_9$ (3) (Molecule 2)					
Co(21)	0.7630 (1)	0.6653 (0)	0.7433 (0)	0.020	O(223)	0.9363 (4)	0.7509 (2)	0.9403 (2)	0.043
Co(22)	0.9213 (1)	0.7760 (0)	0.7489 (0)	0.020	C(231)	1.2140 (5)	0.6329 (3)	0.7020 (3)	0.023
Co(23)	1.0337 (1)	0.6168 (0)	0.7346 (0)	0.020	O(231)	1.3306 (4)	0.6410 (2)	0.6820 (2)	0.039
C(211)	0.7154 (5)	0.5708 (3)	0.7071 (3)	0.031	C(232)	1.0363 (5)	0.5208 (3)	0.6852 (3)	0.033
O(211)	0.6822 (4)	0.5104 (3)	0.6878 (2)	0.048	O(232)	1.0387 (4)	0.4620 (3)	0.6519 (3)	0.061
C(212)	0.5997 (5)	0.7527 (3)	0.7013 (3)	0.029	C(233)	1.0711 (5)	0.5625 (3)	0.8510 (3)	0.026
O(212)	0.4995 (4)	0.8075 (2)	0.6734 (2)	0.049	O(233)	1.0946 (4)	0.5320 (2)	0.9233 (2)	0.043
C(213)	0.7292 (5)	0.6294 (3)	0.8595 (3)	0.025	C(21)	0.8972 (4)	0.7135 (3)	0.6598 (3)	0.019
O(213)	0.7066 (4)	0.6075 (2)	0.9316 (2)	0.040	C(22)	0.8770 (4)	0.7525 (3)	0.5692 (3)	0.022
C(221)	0.7870 (5)	0.8839 (4)	0.7144 (3)	0.031	C(23)	0.8576 (5)	0.7906 (3)	0.4926 (3)	0.028
O(221)	0.7069 (4)	0.9526 (2)	0.6900 (3)	0.053	Si(2)	0.8158 (2)	0.8581 (1)	0.3788 (1)	0.035
C(222)	1.0782 (5)	0.8240 (3)	0.7101 (3)	0.033	C(241)	0.9795 (6)	0.9039 (4)	0.3334 (4)	0.052
O(222)	1.1744 (4)	0.8560 (2)	0.6816 (3)	0.052	C(242)	0.7684 (8)	0.7830 (5)	0.3126 (4)	0.075
C(223)	0.9319 (5)	0.7619 (3)	0.8664 (3)	0.027	C(243)	0.6579 (6)	0.9560 (4)	0.3817 (5)	0.072
atom	x/a	y/b	z/c	U_{eq}/U_{11}	atom	x/a	y/b	z/c	U_{eq}/U_{11}
				$FcC{\equiv}CCCo_3(CO)_9$ (5)					
Co(1)	0.9200 (2)	0.1438 (2)	0.8121 (1)	0.025	O(32)	0.6231 (9)	0.1633 (9)	1.0790 (8)	0.049
Co(2)	0.7078 (1)	0.1440 (1)	0.8109 (1)	0.024	C(33)	0.815 (1)	0.321 (1)	0.936 (1)	0.036 (4)
Co(3)	0.8125 (2)	0.1917 (1)	0.9507 (1)	0.025	O(33)	0.813 (1)	0.4017 (8)	0.9254 (7)	0.052
C(11)	0.941 (1)	0.072 (1)	0.709 (1)	0.033 (4)	C(1)	0.814 (1)	0.073 (1)	0.8853 (9)	0.029 (3)
O(11)	0.958 (1)	0.028 (1)	0.6473 (9)	0.060	C(2)	0.813 (1)	−0.022 (1)	0.9133 (8)	0.020 (3)
C(12)	1.049 (2)	0.107 (1)	0.869 (1)	0.038 (4)	C(3)	0.807 (1)	−0.106 (1)	0.9400 (9)	0.029 (3)
O(12)	1.130 (1)	0.081 (1)	0.905 (1)	0.063	C(41)	0.800 (1)	−0.201 (1)	0.9717 (8)	0.022 (3)
C(13)	0.944 (1)	0.263 (1)	0.767 (1)	0.026 (4)	C(42)	0.716 (1)	−0.243 (1)	1.029 (1)	0.045 (5)
O(13)	0.961 (1)	0.342 (1)	0.7403 (8)	0.050	C(43)	0.740 (1)	−0.342 (1)	1.043 (1)	0.040 (4)
C(21)	0.569 (1)	0.111 (1)	0.863 (1)	0.027 (4)	C(44)	0.834 (1)	−0.365 (1)	0.994 (1)	0.045 (4)
O(21)	0.4899 (9)	0.087 (1)	0.8958 (9)	0.060	C(45)	0.876 (1)	−0.279 (1)	0.950 (1)	0.030 (4)
C(22)	0.692 (2)	0.064 (1)	0.715 (1)	0.037 (4)	Fe(1)	0.7133 (2)	−0.3093 (2)	0.9070 (1)	0.026
O(22)	0.682 (1)	0.0098 (9)	0.6584 (8)	0.056	C(46)	0.621 (1)	−0.249 (1)	0.806 (1)	0.039 (4)
C(23)	0.674 (1)	0.264 (1)	0.766 (1)	0.027 (4)	C(47)	0.554 (1)	−0.317 (1)	0.861 (1)	0.048 (5)
O(23)	0.661 (1)	0.3422 (9)	0.7436 (8)	0.046	C(48)	0.601 (2)	−0.408 (2)	0.853 (1)	0.057 (6)
C(31)	0.928 (1)	0.172 (1)	1.034 (1)	0.032 (4)	C(49)	0.694 (2)	−0.395 (2)	0.796 (1)	0.058 (5)
O(31)	0.9971 (9)	0.157 (1)	1.0842 (8)	0.056	C(50)	0.708 (2)	−0.304 (1)	0.768 (1)	0.049 (4)
C(32)	0.695 (1)	0.176 (1)	1.029 (1)	0.034 (4)					
				$Me_3SiC{\equiv}CC{\equiv}CCCo_3(CO)_9$ (15)					
Co(1)	0.1534 (1)	0.3175 (1)	0.4117 (1)	0.028	C(32)	0.5209 (7)	0.1339 (7)	0.3207 (5)	0.043
Co(2)	0.1828 (1)	0.0681 (1)	0.3497 (1)	0.028	O(32)	0.5939 (6)	0.0730 (6)	0.2749 (4)	0.064
Co(3)	0.4014 (1)	0.2329 (1)	0.3902 (1)	0.027	C(33)	0.4509 (7)	0.1836 (6)	0.5011 (4)	0.034
C(11)	−0.0372 (8)	0.3249 (6)	0.3764 (4)	0.038	O(33)	0.4789 (5)	0.1511 (5)	0.5693 (3)	0.049
O(11)	−0.1580 (5)	0.3319 (6)	0.3553 (4)	0.057	C(1)	0.2402 (6)	0.2461 (6)	0.3060 (4)	0.029
C(12)	0.2014 (7)	0.5063 (7)	0.4142 (5)	0.041	C(2)	0.2375 (7)	0.2922 (6)	0.2226 (4)	0.034
O(12)	0.2307 (6)	0.6244 (5)	0.4133 (4)	0.067	C(3)	0.2387 (8)	0.3336 (7)	0.1495 (4)	0.043
C(13)	0.1439 (7)	0.2891 (7)	0.5275 (4)	0.038	C(4)	0.2395(9)	0.3741 (7)	0.0654 (4)	0.052
O(13)	0.1346 (6)	0.2692 (5)	0.6002 (3)	0.056	C(5)	0.241 (1)	0.4060 (8)	−0.0081 (5)	0.060
C(21)	0.2648 (7)	−0.0673 (7)	0.2790 (4)	0.040	Si(1)	0.2425 (3)	0.4444 (2)	−0.1257 (1)	0.067
O(21)	0.3130 (6)	−0.1535 (6)	0.2359 (4)	0.065	C(41)	0.380 (1)	0.337 (1)	−0.1792 (6)	0.097
C(22)	0.0027 (8)	0.0299 (7)	0.2962 (5)	0.046	C(42)	0.057 (1)	0.390 (1)	−0.1770 (6)	0.092
O(22)	−0.1116 (6)	0.0029 (6)	0.2617 (4)	0.067	C(43)	0.286 (2)	0.636 (1)	−0.1294 (7)	0.166
C(23)	0.1777 (7)	−0.0190 (6)	0.4520 (4)	0.035	C(1)A	0.0000 (0)	1.0000 (0)	0.0000 (0)	0.17 (1)
O(23)	0.1776 (6)	−0.0707 (5)	0.5154 (3)	0.050	C(2)A	0.134 (2)	0.989 (2)	0.003 (1)	0.189 (8)
C(31)	0.4984 (7)	0.4050 (7)	0.3902 (4)	0.037	C(3)A	0.282 (3)	0.997 (2)	−0.004 (1)	0.177 (7)
O(31)	0.5615 (5)	0.5121 (5)	0.3897 (3)	0.050	C(4)A	0.429 (2)	0.997 (2)	0.006 (2)	0.181 (8)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

four-band ν_{CO} profile of variable intensity similar to 3.

Diacetylene with $BrCCo_3(CO)_9$. Diacetylene prepared from $ClCH_2C_2CH_2Cl$[50] (0.1 mol) was bubbled into dioxane (12 cm^3) containing CuCl (~50 mg) and $EtNH_2$ (160 mg) at 22 °C, producing a red-brown precipitate. $BrCCo_3(CO)_9$ (1.0 g) in dioxane (12 cm^3) was added over 15 min with a maximum temperature of 27 °C. The mixture was worked up as described previously, and the following bands separated: (1) *purple* $BrCCo_3(CO)_9$; (2)

green (m/e 823 ($M - H^+$ for $H(C{\equiv}C)_4[Co_2(CO)_6]CCo_3(CO)_9$ (**12**)); ν_{CO} (CH_2Cl_2) 2104 (m), 2089 (ms), 2063 (vs), 2059 (vs), 2042 (ms), 2035 (ms), 2029 (ms) cm^{-1}); (3) *green* (m/e 1216 (M^+ for $(CO)_9Co_3C(C{\equiv}C)_2[(Co_2(CO)_6]CCo_3(CO)_9$ (**2**));[11] ν_{CO} (CH_2Cl_2) 2104 (m), 2099 (m), 2080 (s), 2066 (vs), 2062 (vs), 2056 (s), 2043 (s), 2033 (s), 2025 (s) cm^{-1}; (4) *orange* (ν_{CO} (CH_2Cl_2) 2096 (s), 2085 (vw), 2064 (vs), 2041 (ms), 2030 (sh) cm^{-1}). Attempts to recrystallize this band resulted in the formation of $(CO)_9Co_3C(C{\equiv}C)_2[(Co_2(CO)_6]CCo_3(CO)_9$, (**2**); it was concluded that the original compound may have been $(CO)_9Co_3C(C{\equiv}C)_2[CCo_3(CO)_9]$.

Other Copper-Catalyzed Reactions of $BrCCo_3(CO)_9$. Negligible reaction occurred with $HCCo_3(CO)_9$, the major product being $EtN(H)CCo_3(CO)_9$ (**13**) plus unreacted $HCCo_3(CO)_9$. The reactants 1,5-hexadiyne, $CF_3C{\equiv}C_2H$, and $CF_3C{\equiv}CCo_2(CO)_6H$ gave various products in trace quantities, which proved too unstable to isolate. $PhC{\equiv}CCo_2(CO)_6H$ gave the products $PhC{\equiv}C[Co_2(CO)_6]CCo_3(CO)_9$ (**7**) and $PhC{\equiv}CCCo_3(CO)_9$ (**4**) but in much smaller yields than in the reaction of $PhC{\equiv}CH$. With $HC{\equiv}CCCo_3Cp_3CSiMe_3$ the major product resulted from a self-coupling reaction yielding $Me_3SiCCo_3Cp_3C(C{\equiv}C)_2Co_3Cp_3CSiMe_3$.[3]

$BrCCo_3(CO)_9$ (500 mg) in dioxane (6 cm^3) added to a dioxane solution of CuCl (50 mg) and $EtNH_2$ (120 mg) resulted in an exothermic reaction. The major product was $EtNHCCo_3(CO)_9$ (**13**) (210 mg).

Grignard Reactions. $BrCCo_3(CO)_9$ with $HC{\equiv}CMgBr$. A THF solution, (15 cm^3) of HC_2MgBr (~9.6×10^{-3} mol) was added dropwise to a THF (50 cm^3) solution of $BrCCo_3(CO)_9$ (500 mg) at −70 °C over 10 min. The mixture was slowly warmed to 0 °C while being stirred. This was then added to ice water (250 cm^3) containing 2.5 cm^3 of concentrated H_2SO_4 and extracted into CH_2Cl_2 to give a brown solution. The solvent was removed in vacuo. The CH_2Cl_2-soluble portion was plated (hexane) to give trace amounts (5 mg) of the following: (1) *purple* $HCCo_3(CO)_9$ and $BrCCo_3(CO)_9$; (2) *green* $HC{\equiv}C[Co_2(CO)_6]CCo_3(CO)_9$[13] (**11**); (3) *orange* $(CO)_9Co_3CC{\equiv}CCCo_3(CO)_9$ (**1**);[10] (4) *blue* $Co_4(CO)_{10}$-C_2H_2.[19]

Infrared spectra of the insoluble black solid confirmed that $CCo_3(CO)_9$ units were present. No X-ray powder diffraction pattern could be obtained, and elemental analysis gave the following: C, 40.73; H, 3.27; Co, 17.0.

$BrCCo_3(CO)_9$ with $RC{\equiv}CMgBr$ (R = Ph, Me_3Si). $BrCCo_3(CO)_9$ (250 mg) was reacted with PhC_2MgBr, in a 1:10 mole ratio, as described for HC_2MgBr. Chromatographic separation gave the following: (1) *purple* (85 mg) $HCCo_3(CO)_9$ and $BrCCo_3(CO)_9$; (2) *orange-brown* (<5 mg) $PhC{\equiv}C(Co_2(CO)_6H$;[19] (3) *brown* (~10 mg) $PhC{\equiv}CCCo_3(CO)_9$ (**4**); (4) *green* (<5 mg) $PhC{\equiv}CCo_2(CO)_6CCo_3(CO)_9$ (**7**); (5) *brown*. Band 5 was redeveloped in hexane/CH_2Cl_2 (5:1), which gave trace amounts of at least eight bands, all highly colored; these were not investigated further. The reaction of $BrCCo_3(CO)_9$ with Me_3SiC_2MgBr in the manner described above produced a large number of products in small quantities but not the desired $Me_3SiC{\equiv}CCCo_3(CO)_9$.

Friedel–Crafts Reactions. $BrCCo_3(CO)_9$ with $Me_3Si(C{\equiv}C)_2SiMe_3$. $BrCCo_3(CO)_9$ and Me_3SiC_4SiMe (1.7 g) in CH_2Cl_2 (20 cm^3) were added to a suspension of $AlCl_3$ (~0.2 g) in 20 mL of CH_2Cl_2 at 31 °C through which was bubbled a flow of argon. The addition proceeded dropwise over 40 min; the temperature was maintained at 31–34 °C. The mixture was stirred for another 10 min or until TLC indicated no further reaction. The mixture was filtered and then washed with CH_2Cl_2 to leave a brown solid. The brown solid partially dissolved in CH_3CN but rapidly decomposed. Tlc separation of the CH_2Cl_2-soluble component gave the following: (1) *purple* $BrCCo_3(CO)_9$ plus $Me_3SiC_4SiMe_3$; (2) *brown* (156 mg); (3) *brown* (8 mg) (ν_{CO} (CH_2Cl_2) 2103 (s), 2060 (vs), 2043 (vs), 2029 (m), 2018 (sh), 1993 (vw, sh), 1983 (vw) cm^{-1}) (unstable); (4) *yellow* (7 mg) (ν_{CO} (CH_2Cl_2) 2102 (m), 2095 (s), 2062 (vs), 2043 (s), 2929 (sh), 2018 (sh), 1993 (vw), 1983 (vw) cm^{-1}) (not identified); (5) *brown* (110 mg (ν_{CO} (CH_2Cl_2) 2103 (m), 2068 (sh), 2062 (vs), 2043 (vs), 2029 (sh) cm^{-1}) (this band was eluted with $CHCl_3$).

Band 2 was recrystallized from hexane and identified as $Me_3Si(C{\equiv}C)_2CCo_3(CO)_9$ (**15**). Anal. Calcd for $C_{17}H_9Co_3O_9Si$: C, 36.33; H, 1.61. Found: C, 37.63; H, 1.89. MS: m/e 562 (M^+). ^1H NMR ($CDCl_3$): δ 0.27 (CH_3). ^{13}C NMR (CD_2Cl_2): δ 199.8 (w), 108.8, 108.3, 99.4, 93.4, 0.20 (Me_3Si). UV–visible (CH_2Cl_2): λ_{max} 680 (570), 545 (2230), 415 (8270), 355 (23 900) nm. IR (CH_2Cl_2): ν_{CO} 2103 (s), 2060 (vs), 2043 (vs), 2029 (m), 2018 (sh), 1989 (w) cm^{-1}. Polymeric material observed in the X-ray structural analysis of this product (vide supra) may explain the poor analytical data.

$BrCCo_3(CO)_9$ with $Me_3SiC{\equiv}CSiMe_3$. $BrCCo_3(CO)_9$ (4.30 mg) and $Me_3SiC{\equiv}CSiMe_3$ (280 mg) in CH_2Cl_2 (10 cm^3) were added dropwise to a stirred solution containing $AlCl_3$ (-50 mg) over 15 at 37 °C. The mixture was heated under reflux for ~30 min, filtered, and washed with CH_2Cl_2, and the solvent was removed under reduced pressure. Only part of the solid would redissolve in CH_2Cl_2. Chromatographic separation gave only trace amounts of several carbonyl compounds, apart from $BrCCo_3(CO)_9$, which were not identified.

Reactions with $Co_2(CO)_8$. $Me_3SiC{\equiv}CCCo_3(CO)_9$. $Me_3SiC{\equiv}CCCo_3(CO)_9$ (**3**) (63 mg) and $Co_2(CO)_8$ (50 mg) were stirred together in hexane (12 cm^{-3}) at room temperature with complete reaction occurring after 45 min. Workup as above gave a single green band, which was recrystallized from hexane to give $Me_3SiC{\equiv}C[Co_2(CO)_6]CCo_3(CO)_9$ (**6**) in quantitative yield. Anal. Calcd for $C_{21}H_9Co_5O_{15}Si$: C, 30.61; H, 1.10. Found: C, 32.19; H, 1.74. MS: m/e 824 (M^+). IR: ν_{CO} 2105 (m), 2078 (s), 2060 (vs), 2041 (ms), 2024 (s), 2014 (mw), 1979 (w) cm^{-1}. ^1H NMR (CD_2Cl_2): δ 0.33 (9 H, s, Me_3Si).

$PhC{\equiv}CCCo_3(CO)_9$. An excess of $Co_2(CO)_8$ was added to a solution of freshly prepared $PhC{\equiv}CCCo_3(CO)_9$ (**4**) (~50 mg) in hexane (10 cm^3) at room temperature. Complete reaction of the cluster had occurred after 15 min. The solvent was removed in vacuo, and the products were separated on silica gel plates (hexane): (1) *brown* $Co_4(CO)_{12}$; (2) *green*; (3) *green-gray*.

Band 2, recrystallized from hexane, gave dark green crystals of $PhC{\equiv}C[Co_2(CO)_6]CCo_3(CO)_9$ (**7**).[16]

Band 3 is believed to be a $Co(CO)_3$ derivative of the cyclopentadienone cluster $Ph_2C_4C(O)[CCo_3(CO)_9]_2$ but was not identified further. IR (CH_2Cl_2): ν_{CO} 2106 (w) (typical of $CCo_3(CO)_9$), 2097 (w) (typical of $Co_2(CO)_6$), 2058 (vs), 2038 (vs), 2010 (w), 1987 (w), 1987 (w) cm^{-1}.

$Me_3Si(C{\equiv}C)_2CCo_3(CO)_9$. $Me_3Si(C{\equiv}C)_2CCo_3(CO)_9$ (**15**) (30 mg) and an excess of $Co_2(CO)_8$ were stirred together in hexane (9 cm^3) at room temperature. Complete reaction occurred after 15 min. Workup (CH_2Cl_2) gave three bands: (1) *brown-green* (10 mg); (2) *green* (8 mg); (3) *gray-green* (5 mg).

The brown-green compound from band 1 (10 mg) was recrystallized from hexane and identified as one stereoisomer, **16**, of $Me_3Si(C{\equiv}C)_2[Co_2(CO)_6]CCo_3(CO)_9$. ^1H NMR (CD_2Cl_2): δ 0.33 (Me_3Si). ^{13}C NMR (CD_2Cl_2): δ 200.1 (CO), 117.4 ($C{\equiv}$), 113.7 ($C{\equiv}C$), 0.74 (Me_3Si). MS: m/e 848 (M^+). IR (CH_2Cl_2): ν_{CO} (2105 (mw), 2089 (s), 2062 (vs), 2041 (s), 2033 (s), 2029 (s), 1983 (w) cm^{-1}. The second green band gave (8 mg) the other stereoisomer, **17**. ^1H NMR (CD_2Cl_2): δ 0.33. ^{13}C NMR (CD_2Cl_2): δ 200.0, 112.1, 102.3, 0.03. MS: m/e 848 (M^+). IR (CH_2Cl_2): ν_{CO} 2106 (mw), 2083 (s), 2066 (vs), 2060 (vs), 2051 (w), 2043 (w), 2033 (s), 1986 (w), 1981 (w) cm^{-1}. The third compound (5 mg) was not identified. IR (CH_2Cl_2): ν_{CO} 2099 (mw), 2079 (s), 2064 (s), 2033 (s), 1981 (w) cm^{-1}.

X-ray Structure Determinations of 3, 5, and 15. Samples of **3**, **5**, and **15** were prepared as detailed above and were recrystallized from pentane (**3**) and hexane (**5**, **15**). All three crystalline samples were in the form of thin plates. Precession photography (Cu Kα radiation) indicated triclinic unit cells for **3** and **15**. In both cases the structures were successfully solved in the centrosymmetric alternative $P\bar{1}$.[56] For **5** the systematic absences $h00$, $h = 2n + 1$; $0k0$, $k = 2n + 1$; and $00l$, $l = 2n + 1$, confirmed the orthorhombic space group $P2_12_12_1$.[56] Details of the crystals, data collections, and refinements are summarized in Table II.

The structure of **3** was solved by direct methods using the EEES option of SHELX-76,[57] which revealed the locations of the Co atoms for the two unique molecules in the asymmetric unit. The remaining non-hydrogen atoms were found in subsequent difference Fourier least-squares refinement cycles. The Patterson interpretation procedures of SHELXS-86[58] were used for **5** and **15**, with

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[56] *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1966; Vol. 1.

[57] SHELX-76: Sheldrick, G. M. Program for crystal structure determination. University of Cambridge, 1976.

[58] SHELXS-86: Sheldrick, G. M. A program for the solution of crystal structures from diffraction data. University of Göttingen, 1986.

all non-hydrogen atoms located in the tangent expansion procedures. Refinement minimizing $\Sigma w(|F_o| - |F_c|)^2$ was performed using SHELX-76.[57] In all cases hydrogen atoms were included in the refinements as fixed contributions to F_c, weighting schemes were introduced, and the non-hydrogen atoms were refined anisotropically, except in the case of **5**, where the data set from a weakly diffracting crystal limited anisotropic refinement to the Fe, Co, and carbonyl O atoms, and for **15**, where the C atoms of the putative polymer chain, vide infra, were refined isotropically. Final positional and equivalent thermal parameters for **3**, **5**, and **15** are given in Table III.

A difference Fourier synthesis following refinement of **15** revealed several peaks with electron density in excess of 2.0 e Å^{-3}. Inclusion of these peaks into the overall model as C atoms resulted in a considerable reduction in R. Bond distances and angles within the C atom chain were consistent with the incorporation of a diacetylene polymer in the crystal lattice.[20] High and increasing temperature factors for the polymer C atoms are consistent with extensive positional disorder in the polymer chain; furthermore the substituents require for the alkene moieties in the polymer unit were not resolved in further difference Fourier syntheses. The exact nature of the polymer residue is therefore unclear. Further work is in progress[41] to improve the resolution of the polymer and to attempt to determine whether it results from topotactic polymerization[21,39,40] of the diacetylene cluster system in the solid state.

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Supplementary Material Available: Tables of anisotropic thermal parameters, hydrogen positional and thermal parameters, least-squares planes, and bond distances and angles (20 pages); tables of structure factors (47 pages). Ordering information is given on any current masthead page.

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(59) SHELXTL: Sheldrick, G. M. An integrated system for solving, refining and displaying crystal structures from diffraction data. University of Göttingen, 1980.