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Biscarbynetricobalt clusters with alkyne functionality: structure and redox processes

S.M. Elder, B.H. Robinson * and J. Simpson *

Chemistry Department, University of Otago, P.O. Box 56, Dunedin (New Zealand)

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Abstract

Steric and/or electronic factors preclude the direct coupling of two CCo_3Cp_3C units via the carbyne cap by classical alkyne-coupling procedures but the compounds $[Me_3SiCCo_3(Cp)_3C-(C\equiv C)_n]_2$, $n = 1, 2$, have been prepared from appropriate alkynes $Me_3SiCCo_3(Cp)_3C-(C\equiv C)_nH$. The crystal structure of $[Me_3SiCCo_3(Cp)_3C-(C\equiv C)]_2$ has been determined by X-ray diffraction. Compared with clusters with only one CCo_3Cp_3C unit per molecule, compounds with two units per molecule display intense colours and electrochemical responses indicative of electronic interaction between the redox centres via the alkyne chain.

The physical properties of materials in which redox-active low-valent metal clusters are incorporated via unsaturated linkages have been described for clusters containing the $CCo_3(CO)_9$ unit [1,2]. While thermal decomposition of these carbonyl clusters shows promise for the controlled production of conducting materials [2] this instability is a hindrance to a fundamental study of the electronic interactions between capped cluster-units incorporating a carbyne capping atom [3,4] which have a delocalised core. Bi-capped clusters containing a $CCo_3(Cp)_3C$ core are thermally stable [2] to at least 200 ° C and display reversible one-electron oxidation processes [5,6].

It was therefore of interest to prepare materials with a number of these cores inserted into an unsaturated link, a concept which offers the possibility of directional electron transfer. Alkyne linked bis-carbyne clusters have been identified in the preparation of trimethylsilyl capped derivatives [7] but only as minor products. The aim of the work described in this paper was to devise a rational synthesis of multi-cluster compounds of the type $[RCCo_3Cp_3C-(C\equiv C)_n]_2$ and to investigate the degree of interaction between the redox centres.

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Results and discussion

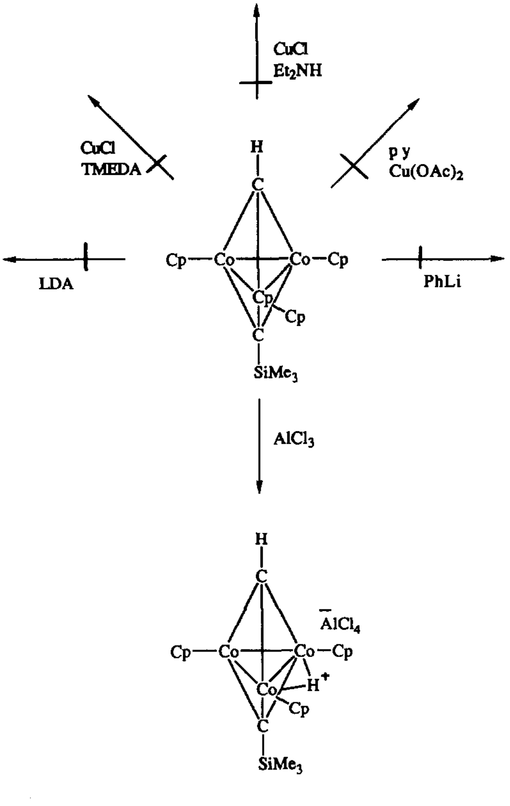
Copper-catalysed coupling reactions have been successfully used to synthesise alkyne-linked $CCo_3(CO)_9$ complexes [8] (eqn. 1). For analogous reactions involving the CCo_3Cp_3C moiety the initial strategy was to use a biscarbyne cluster with one

$$(CO)_9Co_3CBr + RC{\equiv}CH \longrightarrow (CO)_9Co_3C{-}C{\equiv}CR + HBr \qquad (1)$$

blocked capping group and a reactive C–H cap; specifically $Me_3Si{-}CCo_3(Cp)_3C{-}H$, **1**.

Unfortunately self-coupling to produce $Me_3Si{-}C|C{-}C|C{-}SiMe_3$ *, **2**, an analogue of the known $(CO)_9Co_3C{-}CCo_3(CO)_9$ [1,9] could not be induced by any of the reagents shown in Scheme 1. Similarly, coupling between **1** and $RC{\equiv}CH$ or $RC{\equiv}CI$ was unsuccessful.

Given that there are no inherent steric constraints to the formation of clusters like **2** (**2** is one of the trace products found in the preparation of **1**) [7] the lack of reactivity of the C–H functionality in **1** could be electronic in origin or due to steric congestion with respect to the attacking metallation reagents. Horn and Volhardt



Scheme 1

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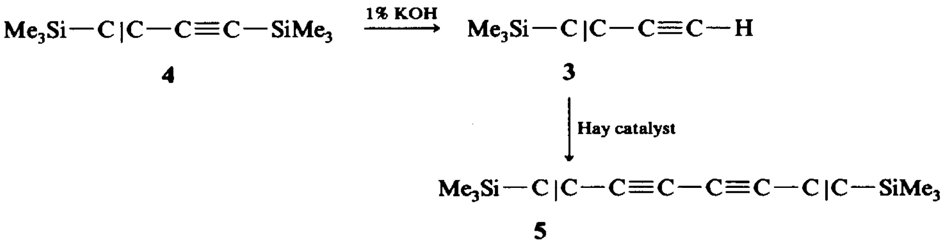
* To simplify the formula for these clusters we represent triangular $Co_3(Cp)_3$ core as: |.

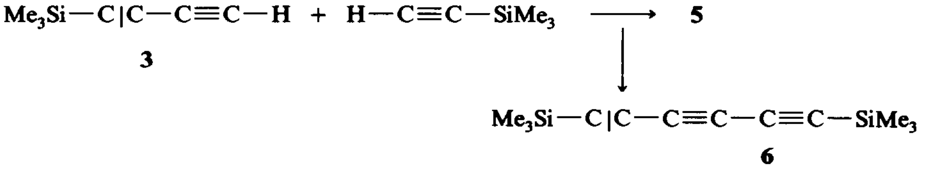
[10] have suggested that electrophilic attack at the cluster carbyne–H functionality occurs via prior attack at the electron-rich edge of the Co_3 moiety and they identified a green, edge-protonated species $[(Bu^n{-}C|C{-}Bu^n)H^+]CF_3SO_3^-$. During Lewis-acid coupling reactions of **1** using $AlCl_3$ we observed a colour change from purple to green and suggest that the green colour is due to the Lewis acid complex shown in Scheme 1. Bands at 385 nm and 455 nm(sh) in the electronic spectrum of this complex are similar to those in the spectrum of the protonated species and are consistent with a product in which electron density has been removed from the upper bonding levels of the cluster [5]. Models suggest that the capping hydrogen is directly accessible to coupling reagents but, if the site of initial attack by the coupling or metallation reagents is at the edge of the Co_3 triangle, then steric congestion from the peripheral cyclopentadienyl rings may well prevent the self-coupling or coupling reactions with metallated alkynes. In this context it is noteworthy that the coupling reaction was also unsuccessful where the capping hydrogen atom was replaced by an iodo substituent which is a better leaving group, vis-à-vis $Me_3Si{-}C|C{-}I$.

Successful coupling reactions were carried out with the cluster $Me_3Si{-}C|C{-}C{\equiv}C{-}H$, **3**, where an alkyne function separates the hydrogen capping substituent from the cluster unit (eqn. 2). This cluster was generated in situ by the base desilylation of $Me_3Si{-}C|C{-}C{\equiv}C{-}SiMe_3$, **4**, as **3** is unstable under coupling conditions.



$$\begin{tikzcd} \underset{\mathbf{4}}{Me_3Si{-}C|C{-}C{\equiv}C{-}SiMe_3} \arrow[r, "1\%\ KOH"] & \underset{\mathbf{3}}{Me_3Si{-}C|C{-}C{\equiv}C{-}H} \arrow[d, "\text{Hay catalyst}"] \\ & \underset{\mathbf{5}}{Me_3Si{-}C|C{-}C{\equiv}C{-}C{\equiv}C{-}C|C{-}SiMe_3} \end{tikzcd} \tag{2}$$

Self-coupling of **3** with the Hay catalyst, CuCl : TMEDA, gave **5** in good yield. The stoichiometry was confirmed by ^1H NMR, mass spectra and X-ray structure analysis (see below). The most significant feature of **5** is the intense *dark green* color compared to the usual purple color of CCo_3Cp_3C compounds. An alternative synthesis of **5** is from a coupling of **3** and $H{-}C{\equiv}C{-}SiMe_3$ (eqn. 3) although cluster **6** is a major product from this reaction.



$$\begin{tikzcd} \underset{\mathbf{3}}{Me_3Si{-}C|C{-}C{\equiv}C{-}H} + H{-}C{\equiv}C{-}SiMe_3 \arrow[r] \arrow[dr, phantom] & \mathbf{5} \\ & \underset{\mathbf{6}}{Me_3Si{-}C|C{-}C{\equiv}C{-}C{\equiv}C{-}SiMe_3} \end{tikzcd} \tag{3}$$

Cluster **6** was also the major product, but in poor yield, from a coupling reaction between **3** and $I{-}C|C{-}SiMe_3$. The synthesis of **6** offered the opportunity to extend the series $\mathrm{Me_3Si{-}C|C{-}(C{\equiv}C)_{\mathit{n}}{-}C|C{-}SiMe_3}$ and a self-coupling reaction gave the $n = 4$ cluster, **7** (eqn. 4). **7** is unstable in both solid and solution, a direct analogy

$$\begin{array}{ccc} \mathrm{Me_3Si{-}C|C{-}(C{\equiv}C)_2{-}SiMe_3} & \xrightarrow{\mathrm{KOH}} & \mathrm{Me_3Si{-}C|C{-}(C{\equiv}C)_2{-}H} \\ & & \Big\downarrow{\scriptstyle [\mathrm{Cu}]} \\ & & \mathrm{Me_3Si{-}C|C{-}(C{\equiv}C)_4{-}C|C{-}SiMe_3} \\ & & \mathbf{7} \end{array} \qquad (4)$$

[11] with $\mathrm{Me_3Si{-}(C{\equiv}C)_{\mathit{n}}{-}SiMe_3}$ compounds which decrease in stability with increasing n, and suitable crystals for a structural analysis were not obtained. Note that **7**, like **5**, is a very intense dark green colour.

As an aside to the question of how steric factors impinge on the reactivity of this type of cluster we were surprised to find that $\mathrm{Co_2(CO)_8}$ did not react with the triple bond of **3** or **4** (eqn. 5) although it reacted exclusively with the terminal alkyne function of **6** (eqn. 6).

$$\mathrm{Me_3Si{-}C|C{-}C{\equiv}C{-}SiMe_3} + \mathrm{Co_2(CO)_8} \longrightarrow \text{no reaction} \qquad (5)$$

$$\begin{array}{l} \mathrm{Me_3Si{-}C|C{-}C{\equiv}C{-}C{\equiv}C{-}SiMe_3} + \mathrm{Co_2(CO)_8} \longrightarrow \\ \qquad\qquad \mathrm{Me_3Si{-}C|C{-}C{\equiv}C{-}C{=}C[Co_2(CO)_6]\}{-}SiMe_3} \qquad (6) \\ \qquad\qquad\qquad\qquad\qquad \mathbf{8} \end{array}$$

This contrasts with $\mathrm{(CO)_9Co_3C{-}C{\equiv}C{-}SiMe_3}$ which gave the dicobalt-alkyne complex within five minutes [8]. The peripheral carbonyl groups provide a much more effective steric umbrella for the substituent on the apical carbyne atom than the cyclopentadienyl groups and steric factors would not explain this difference in reactivity. It seems likely that orbital interaction between the bis-carbyne cluster and apical alkyne function reduces the electron density at the alkyne thus reducing its reactivity.

Structure of 5

The molecular structure of **5** can be described as that of two bipyramidal bis-carbynetricobalt cluster units linked through a butadiyne chain attached to one of the carbyne carbon atoms from each cluster unit (Fig. 1). The outer carbyne atoms of the bipyramids carry trimethylsilyl substituents. Selected bond lengths and angles are detailed in Table 1. The molecule has a crystallographically imposed mirror plane of symmetry passing through both silicon atoms, the Co(1) and Co(3) atoms of the cobalt triangles, the carbon atoms of the bis-carbyne units, and the diyne chain.

Both $\mathrm{Co_3}$ triangles are symmetrical and the mean Co–Co distance 2.373(5) Å is not exceptional [12]. Similarly the Co–C(carbyne) bonds show no significant variation (mean 1.86(1) Å) indicating that neither the steric requirements of the carbyne substituents nor electron release by the dialkyne bridging system contribute substantially to the minimum energy configurations of the cluster units. The distances between the capping C atoms across the $\mathrm{Co_3}$ triangles are unremarkable, C(1) $\cdots$ C(2) 2.54(3)Å and C(7) $\cdots$ C(8) 2.50(3)Å. Each Co atom carries a cyclopentadienyl

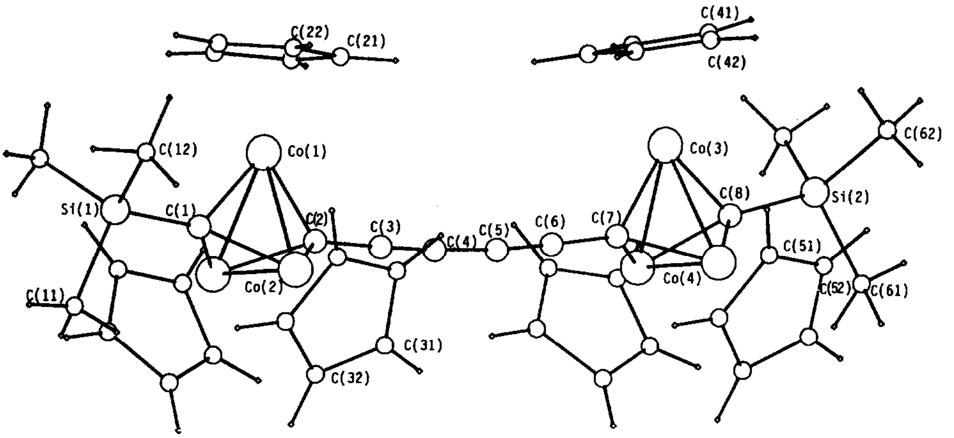


Fig. 1. Structure of **5** showing the atom numbering scheme. For clarity only one of each pair of symmetry related atoms and the first two atoms of the consecutively numbered cyclopentadienyl rings have been labelled.

and the mean Co–C(ring), distances 2.07(1)Å, are similar to those reported for analogous systems [12–15]. The cyclopentadienyl ligands are orthogonal to the Co_3 ring plane indicating little or no steric interaction between the rings and the substituents on the carbyne atoms. This contrasts with the situation for $FcCCo_3(Cp)_3CH]$ where the rings are skewed away from the bulkly ferrocenyl substituent [12]. The terminal trimethylsilyl substituents show normal Si–C bond lengths (mean 1.87(1)Å) and angles close to the tetrahedral angle (mean 109.4(9)°). The orientation of these groups is such that they adopt a staggered conformation with respect to the Co atoms and their η^5-Cp ligands. This serves to minimise non-bonded contacts involving these relatively bulky substituents.

The C–C–C angles vary slightly from 180° along the alkyne chain causing it to "bow" in the direction of the Co(2)–Co(2)′ and Co(4)–Co(4)′ bonds. The C–C bonds linking the chain to the apical C atoms of the clusters are short, C(2)–C(3) 1.42(3) Å, C(6)–C(7) 1.43(2) Å, in comparison to bonds to methyl substituents [15], but are similar to those observed for an alkyne substituted bis-carbyne complex [13] and in tricobalt–carbon clusters with alkyne and diyne apical substituents [1]. In the ferrocenyl substituted complexes $FcCCo_3(CO)_9$ and $FcCCo_3(Cp)_3CH$ where delocalisation between the cluster core and the apical substituent was clearly indicated [12], the comparable C–C bond lengths were 1.45(3) and 1.448(9) respectively. In **5**, bond lengths along the chain clearly identify the two C≡C bonds (C(3)–C(4) 1.19(2), C(5)–C(6) 1.21(3) Å) although the central "single" bond is also short, C(4)–C(5) 1.36(2) Å, supporting the possibility of delocalisation between the cluster units.

Interaction between cluster units

The synthesis of **5** and **7** provided examples of multi-centre clusters in which each cluster redox centre could 'see' each other via the unsaturated linkage. As noted above both **5** and **7** are characterised by intense dark colours, a classical indication of closely spaced energy levels [16]. In contrast to **3**, **4** and **6** which have bands at

Table 1

Selected bond lengths Å and angles (°) for **5**

Co(1)–Co(2)	2.373(3)	Co(3)–C(43)	2.06(1)
Co(1)–C(1)	1.89(2)	Co(4)–Co(4)′	2.366(4)
Co(1)–C(2)	1.88(2)	Co(4)–C(7)	1.85(1)
Co(1)–C(21)	2.09(2)	Co(4)–C(8)	1.85(2)
Co(1)–C(22)	2.08(2)	Co(4)–C(51)	2.08(2)
Co(1)–C(23)	2.08(2)	Co(4)–C(52)	2.06(2)
Co(2)–Co(2)′	2.380(4)	Co(4)–C(53)	2.06(2)
Co(2)–C(1)	1.86(1)	Co(4)–C(54)	2.05(2)
Co(2)–C(2)	1.86(2)	Co(4)–C(55)	2.09(2)
Co(2)–C(31)	2.08(2)	Si(1)–C(11)	1.87(2)
Co(2)–C(32)	2.06(2)	Si(1)–C(12)	1.87(2)
Co(2)–C(33)	2.10(2)	Si(1)–C(1)	1.86(2)
Co(2)–C(34)	2.07(2)	Si(2)–C(61)	1.87(2)
Co(2)–C(35)	2.08(2)	Si(2)–C(62)	1.87(2)
Co(3)–Co(4)	2.375(3)	Si(2)–C(8)	1.90(2)
Co(3)–C(7)	1.87(2)	C(2)–C(3)	1.43(3)
Co(3)–C(8)	1.85(2)	C(3)–C(4)	1.18(2)
Co(3)–C(41)	2.11(2)	C(4)–C(5)	1.36(2)
Co(3)–C(42)	2.07(2)	C(5)–C(6)	1.21(2)
		C(6)–C(7)	1.44(2)
Co(2)–Co(1)–C(1)	50.2(4)	C(61)–Si(2)–C(8)	111.2(9)
Co(2)–Co(1)–C(2)	50.3(4)	C(62)–Si(2)–C(8)	109.9(6)
Co(2)–Co(1)–C(21)	135.8(5)	Co(1)–C(1)–Co(2)	78.5(7)
Co(2)–Co(1)–C(22)	168.5(5)	Co(1)–C(1)–Si(1)	129(1)
Co(2)–Co(1)–C(23)	151.3(4)	Co(2)–C(1)–Co(2)′	79.5(7)
Co(2)–Co(1)–Co(2)′	60.2(1)	Co(2)–C(1)–Si(1)	134.5(6)
C(1)–Co(1)–C(2)	84.7(8)	Co(1)–C(2)–Co(2)	78.8(7)
Co(1)–Co(2)–C(1)	51.3(6)	Co(1)–C(2)–C(3)	130(1)
Co(1)–Co(2)–C(2)	50.9(6)	Co(2)–C(2)–Co(2)′	79.5(8)
C(1)–Co(2)–C(2)	86.0(7)	Co(2)–C(2)–C(3)	133.7(8)
Co(4)–Co(3)–C(7)	50.0(4)	C(2)–C(3)–C(4)	178(2)
Co(4)–Co(3)–C(8)	50.0(4)	C(3)–C(4)–C(5)	177(2)
Co(4)–Co(3)–Co(4)′	59.8(1)	C(4)–C(5)–C(6)	175(2)
C(7)–Co(3)–C(8)	84.3(8)	C(5)–C(6)–C(7)	178(2)
Co(3)–Co(4)–C(7)	50.8(6)	Co(3)–C(7)–Co(4)	79.2(7)
Co(3)–Co(4)–C(8)	50.0(6)	Co(3)–C(7)–C(6)	130(1)
C(7)–Co(4)–C(8)	84.9(7)	Co(4)–C(7)–Co(4)′	79.4(7)
C(11)–Si(1)–C(12)	108.6(6)	Co(4)–C(7)–C(6)	133.7(8)
C(11)–Si(1)–C(1)	109.0(9)	Co(3)–C(8)–Co(4)	80.0(7)
C(12)–Si(1)–C(1)	109.5(6)	Co(3)–C(8)–Si(2)	127(1)
C(61)–Si(2)–C(62)	108.5(7)	Co(4)–C(8)–Co(4)′	79.6(8)
		Co(4)–C(8)–Si(2)	134.2(6)

750–670 nm ($\epsilon = 400$–1400) and 520–500 nm ($\epsilon \sim 4000$) in their electronic spectrum **5** and **7** display intense bands at 610 and 635 nm ($\epsilon \approx 10{,}000$) respectively (Fig. 2). This bathochromic shift in the bands and increase in intensity is consistent with a decrease in the energy gap between the upper bonding levels and the LUMO, both centred in the cluster. However, there is an ambiguity in assignment as the formally forbidden $\sigma^\star$(HOMO) → $\sigma^\star$(LUMO), $^1A_1' \rightarrow {}^1E''$, excitation (the lowest energy band in purple clusters [5]) could be allowed in **5** and **7**. The intense band in **5** and **7** is

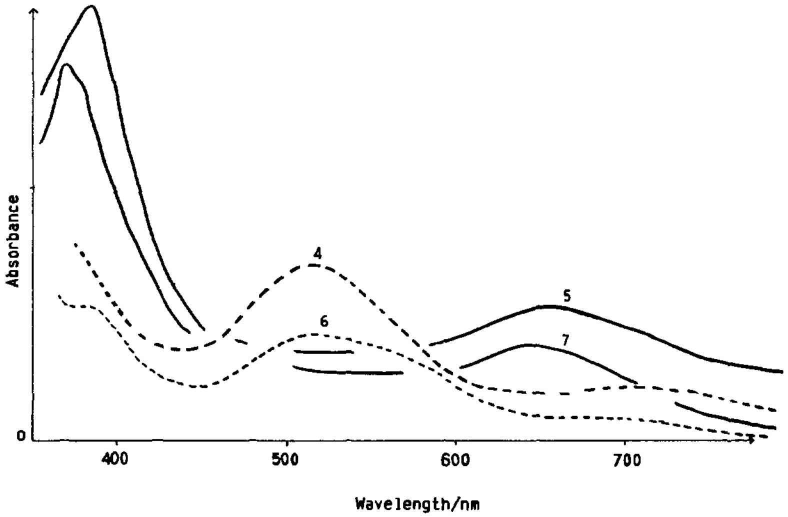


Fig. 2. Electronic spectrum of clusters 4–7 in CH_2Cl_2 at 20° C. Absorbance scale for 5 and 7 is approximately 3 × that for 4 and 6.

best assigned to an allowed excitation from perturbed upper bonding levels of the cluster to the LUMO with a small band gap due to the perturbation of one cluster unit by the other.

The redox chemistry 5 and 7 provided further evidence for interaction between the cluster units. Clusters with one CCo_3Cp_3C unit display [5] a single chemically reversible one-electron oxidation process at ~ 0.60 V vs Ag/AgCl in CH_2Cl_2 [2]. In contrast 5 and 7 undergo two reversible oxidation processes separated by (~ 0.14 V (Fig. 3)). Molecules with equivalent, non-interacting electroactive centres have only one voltammetric wave with a magnitude determined by the number of electroactive centres. Conversely, molecules with interaction between equivalent electroactive centres have as many voltammetric waves with one-electron diffusion currents as there are centres [17]. Thus in 5 and 7 the two oxidisable CCo_3C centres

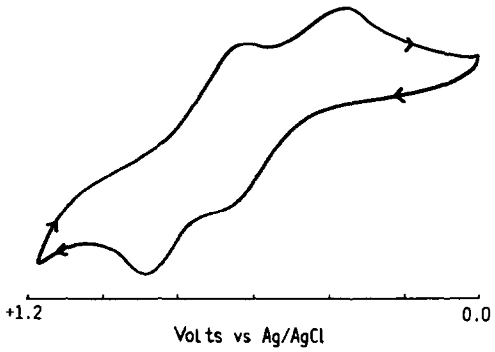


Fig. 3. Cyclic voltammogram of 5 at Pt in CH_2Cl_2/TBAP (0.1 mol dm^{-3}) 200 mV s^{-1}, 20 °C.

are interacting via the –C≡C– bridge(s) (eqn. 7); this is similar behaviour to that found in the $FcCCo_3(Cp)_3CFc$ where these oxidation processes are observed and Class II mixed-valency behaviour has been demonstrated [5,6]. Oxidation of **5** by

$$\{[Me_3Si{-}C\,|\,C{-}C{\equiv}C]_2\}^{2+} + e \rightleftharpoons \{[Me_3Si{-}C\,|\,C{-}C{\equiv}C]_2\}^{+} + e \rightleftharpoons \mathbf{5} \qquad (7)$$

one mole Ag^+ gave an unstable pale yellow compound but a titration indicated that the reaction with Ag^+ was not of a simple 1 : 1 or 1 : 2 stoichiometry. The instability of the system precluded further study of what are presumably disproportionation or conproportionation reactions involving $\mathbf{5}^+$ or $\mathbf{5}^{2+}$ in solution.

Conclusion

Steric and/or electronic constraints reduce the reactivity of capping groups in clusters containing the CCo_3Cp_3C core which made the rational synthesis of alkyne-linked multicluster compounds difficult. The discrete cluster redox centres in these compounds are weakly coupled and unlike the analogous $Co_3(CO)_9$ system [8] there is evidence from this study that the valence/conduction band gap is reduced. This provides an incentive to incorporate the CCo_3Cp_3C unit in conducting materials, and we have shown that these complexes provide a measure of thermal stability to solid materials [2].

Experimental

All reactions were carried out under argon. Trimethylsilylacetylene was prepared from a Grignard reaction with acetylene and Me_3SiCl and bistrimethylsilyl-1,3-butadiyne from hexachlorobutadiene and Me_3SiCl [18]. The clusters **1** and **4** were prepared from $CpCo(CO)_2$ and the appropriate alkyne using literature procedures [13,19] and characterised by analysis, mass spectra and NMR. Iodination of **1** was achieved using Volhardt's procedure [10]. The "Hay catalyst" used in the coupling reactions was prepared by adding 1.00 g CuCl to a stirred mixture of 0.5 cm^3 TMEDA (*N,N,N′,N′*-tetramethylethylenediamine) in 20 cm^3 degassed acetone. A fresh mixture was used for each reaction. Electrochemical instrumentation and reference were as described previously [5]. All processes were non-Nernstian because of the slow electrode kinetics associated with this type of cluster.

Preparation of 5

4 (0.213 g, 0.376 mmol) was dissolved in 40 cm^3 1% KOH/EtOH. The reaction mixture was heated to 55 °C to effect quantitative desilylation. After 1.5 h the reaction mixture was poured over 30 cm^3 H_2O and extracted into 20 cm^3 hexane, aqueous extracts were washed with 2 × 20 cm^3 hexane; the organic layers were combined, dried over $MgSO_4$, filtered and evaporated to ~ 20 cm^3. The brown product **3** was reacted with 15 cm^3 of freshly prepared "Hay catalyst". The reaction mixture was heated to 40 °C for 1 h during which the solution changed from purple to dark green. Evaporation of the solvent and separation of the products by preparative silica gel chromatography gave a pale-pink band (0.002 g), brown band (0.003 g) and the green product band. The green film obtained by evaporation of the last band was recrystallised from hexane/CH_2Cl_2 (~ 10 : 1) to give dark crystals of

5 (0.122 g, 34%). Found: C, 52.16; H, 4.78. $C_{43}H_{48}Co_6Si_2$ requires: C, 53.54; H, 4.91%. *m/e* (M^+) 950. ^{1}H NMR ($CDCl_3$) 0.84 (CH_3, s, 18 H); 4.66 (C_5H_5, s, 30H).

*Reaction of **4** with trimethylsilylacetylene*

4 (0.080 g, 0.141 mmol) was dissolved in 30 cm^3 1% KOH/EtOH as described for the selfcoupling reaction, except the reaction was heated to 40 ° C. When **4** had largely disappeared (from tlc analysis, 1–2 h) the cluster was extracted into 20 cm^3 hexane, washed with 20 cm^3 H_2O, dried over $MgSO_4$ and evaporated to ~ 20 cm^3. $Me_3Si–C{\equiv}C–H$ (0.195 mmol), and CuCl:TMEDA (5 cm^3) were added to the reaction mixture which was left to stir at 40 ° C over 1.5 hours. The solvent was evaporated and the products separated by ptlc to give a violet band and green **5**. Recrystallisation of the violet compound gave **6** (0.058 g) as purple crystals. *m/e* (M^+): 567; ^{1}H NMR ($CDCl_3$): 0.35 (CH_3, s, 9H), 0.77 (CH_3, s, 9H), 4.47 (C_5H_5, s, 15H). λ_{max}, 519 nm.

*Reaction of **3** with I–C|C–SiMe*

4 (0.090 g, 0.159 mmol) and $Me_3Si–C|C–I$ (0.013 g, 0.021 mmol) were dissolved in 40 cm^3 CH_2Cl_2 and placed in a pressure-equalised dropping funnel. $AlCl_3$ (0.054 g, 0.405 mmol) was dissolved in 20 cm^3 CH_2Cl_2 and the clusters added to this solution dropwise. The reaction mixture was heated to 35 ° C when no reaction was visible at room temperature. When all the reactants had been added (~ 1.5 h) the solvent was evaporated. The analysis revealed that there were 7 different bands, only one being present in sufficient quantity to isolate and characterise. This purple band gave a purple solid; *m/e* (M^+) 962. ^{1}H NMR ($CDCl_3$): 0.33 (CH_3, s, 9H), 0.77 (CH_3, s, 9H), 4.42 (C_5H_5, s, 15H) [13] consistent with **6**.

*Coupling reaction of **6***

Coupling of **6** following the same procedure as outlined for **4**, i.e. desilylation followed by treatment with CuCl : TMEDA, gave a 20% yield of **7** as dark green crystals. *m/e* (M^+) 1064, ^{1}H NMR: 0.48 (CH_3, s, 18H), 4.52 (C_5H_5, s, 30H).

*Reaction of **4** and **6** with $Co_2(CO)_8$*

An excess of $Co_2(CO)_8$ (0.126 mmol) was added to a hexane solution of **4** (0.053 mmol). The solution became more brown in colour but tlc and infrared analysis of the solution after one hour confirmed that only starting reagents and $Co_4(CO)_{12}$ were present. The absence of a reaction was confirmed by a ^{1}H NMR experiment involving the same reagents in CD_2Cl_2. A similar reaction with **6** instead of **4** gave an immediate deep brown colour. The hexane was removed and the residue separated on preparative thin layer plates (eluant hexane). The slow-moving purple-brown band was collected and recrystallised from hexane to give **8** in quantitative yield. *m/e* (M^+) 849; ν(CO) 2080 (m), 2060 (vs), 2031 (m), 1980 (w) cm^{-1}.

*Structural analysis of **5***

Crystals of **5** were grown from hexane/CH_2Cl_2, and a dark purple plate was used for data collection. Precession photography (Cu-K_α radiation) indicated a C-centred, orthorhombic unit cell and the space group was confirmed as $Cmc2_1$ by the success of the structure refinement. The low-temperature unit-cell dimensions and orientation matrices were calculated from 25 accurately centred reflections on a

Table 2

Crystal data, data collection and refinement of $Me_3SiCCo_3(\eta^5\text{-}C_5H_5)_3CSiMe_3 \cdot 2CH_2Cl_2$

Crystal Data	Data Collection and Refinement
Empirical formula: $C_{46}H_{52}Si_2Cl_4Co_6$	Diffractometer: Nicolet $P\bar{3}$
Formula weight: 1156.51 g mol^{-1}	Temperature: 133 ± 5 K
Crystal system: orthorhombic	Radiation: Mo-K_α ($\lambda = 0.71069$ Å)
Space group: $Cmc2_1$ (No 36) [24]	Scan type ($\omega-2\theta$)
$a = 15.781(3)$ Å	Scan speed: 7.32 deg min^{-1}
$b = 17.090(8)$ Å	Data limits: $5 < 2\theta < 50°$
$c = 17.538(4)$ Å	Reflections measured: h, k, l
$V = 4730(2)$ Å^3	Crystal decay: $< 2\%$ [a]
$D_c = 1.62$ g cm^{-3}	Absorption correction: empirical [b]
$Z = 4$	Transmission: 0.784 (maximum)
Crystal size $3.0 \times 1.0 \times 0.5$ mm	0.631 (minimum)
μ(Mo-K_α) = 24.40 cm^{-1}	Total observed data: 2338
$F(000) = 2344$	Unique data: 1762 ($I > 2\sigma(I)$)
	Number of variables: 197
	$R(\Sigma \| \|F_o\| - \|F_c\| \| / \|F_o\|) = 0.0593$
	$R_w[\Sigma w(\Delta F)^2/\Sigma wF_o^2]^{1/2} = 0.0593$ [c]
	$w = [1.0742/(\sigma^2 F + 0.001591 F^2)]$

[a] Standard reflections (400)(060)(008) measured after every 100 reflections. [b] Lorentz and polarisation corrections and empirical absorption corrections were applied using the SHELXTL system [21]. [c] Refinement, minimising $w(F_o - F_c)^2$, was performed using SHELX-76 [23].

Nicolet $P\bar{3}$ fully automated diffractometer. Details of the crystal, data collection and structure refinement are summarized in Table 2. Data were processed and empirical absorption corrections applied using programs from the SHELXTL package [21].

The structure was solved using the TREF option of the program SHELXS-86 [22]. The E-map revealed two cobalt atoms, the silicon atoms, the carbon atoms of the bis-alkyne bridge and the tricobalt carbyne moieties on the special positions 0, y, z (a for $Cmc2_1$ in Wycoff notation) [24]. The two additional Co atoms required to define the metal triangles of the tricobalt bis-carbyne units were found in general positions. The remaining non-hydrogen atoms were found by successive difference Fourier syntheses and least-squares refinements [23]. The C atoms C(11) and C(61) from the trimethylsilyl groups and C(21) and C(41) of the cyclopentadienyl ligands were also on the mirror plane and their coordinates were constrained appropriately. A difference Fourier synthesis at this stage of the refinement showed high peaks on general positions consistent with the presence of CH_2Cl_2 molecules of crystallisation. Inclusion of these solvent atoms improved the overall model significantly. The cobalt, silicon and methyl C atoms and the non-hydrogen atoms of the solvate molecules were assigned anisotropic temperature factors and a weighting scheme introduced. A difference Fourier synthesis at this point revealed electron density in appropriate positions and orientations for H atoms. These were included in calculated positions with fixed isotropic temperature factors. This model for the structure converged with $R = 0.0602$, $R_w = 0.0606$. Two peaks of intensity ~ 1.3 e Å^{-3} were found in the final difference Fourier map in the vicinity of the cobalt triangles.

Table 3

Final positional and equivalent thermal parameters for 5

Atom	x	y	z	U_{eq}/U_{iso}
Co(1)	0.0000	0.5013(2)	0.3085(1)	0.019
Co(2)	0.0754(1)	0.4585(1)	0.4179(2)	0.019
Co(3)	0.0000	0.0460(1)	0.0775(2)	0.016
Co(4)	−0.0750(1)	−0.0221(1)	0.1744(2)	0.017
Si(1)	0.0000	0.6451(3)	0.4412(3)	0.029
C(11)	0.0000	0.647(1)	0.548(1)	0.047
C(12)	0.0980(10)	0.6951(9)	0.4062(9)	0.049
Si(2)	0.0000	−0.1461(3)	0.0342(3)	0.023
C(61)	0.0000	−0.241(1)	0.088(2)	0.043
C(62)	−0.0960(10)	−0.1429(9)	−0.0277(9)	0.037
C(1)	0.0000	0.542(1)	0.409(1)	0.022(4)
C(2)	0.0000	0.403(1)	0.357(1)	0.023(4)
C(3)	0.0000	0.326(1)	0.326(1)	0.020(4)
C(4)	0.0000	0.2633(9)	0.298(1)	0.017(4)
C(5)	0.0000	0.192(1)	0.263(1)	0.020(4)
C(6)	0.0000	0.132(1)	0.227(1)	0.016(4)
C(7)	0.0000	0.061(1)	0.183(1)	0.020(4)
C(8)	0.0000	−0.059(1)	0.102(1)	0.022(5)
C(21)	0.0000	0.601(1)	0.240(1)	0.039(6)
C(22)	−0.072(10)	0.558(1)	0.226(1)	0.043(4)
C(23)	−0.045(10)	0.4835(9)	0.1988(9)	0.037(4)
C(31)	0.163(10)	0.4995(9)	0.4973(9)	0.033(4)
C(32)	0.134(10)	0.4241(9)	0.5173(9)	0.036(4)
C(33)	0.157(10)	0.3725(9)	0.4611(9)	0.032(4)
C(34)	0.197(10)	0.4159(9)	0.4026(9)	0.036(4)
C(35)	0.2016(9)	0.493(1)	0.425(1)	0.037(4)
C(41)	0.0000	0.046(1)	−0.043(1)	0.039(6)
C(42)	−0.0720(10)	0.0840(9)	−0.0138(9)	0.039(4)
C(43)	0.0431(9)	0.1480(8)	0.0284(8)	0.028(3)
C(51)	−0.204(10)	0.002(1)	0.182(1)	0.054(5)
C(52)	−0.1910(10)	−0.074(1)	0.157(1)	0.045(5)
C(53)	−0.1470(10)	−0.1148(9)	0.2118(9)	0.038(4)
C(54)	−0.1290(10)	−0.0647(9)	0.2726(9)	0.037(4)
C(55)	−0.1680(10)	0.010(1)	0.2531(9)	0.040(4)
Cl(1)	0.2327(3)	0.2211(3)	0.2809(3)	0.058
Cl(2)	0.2465(4)	0.2207(3)	0.1151(3)	0.065
C(10)	0.1870(10)	0.252(1)	0.194(1)	0.053

However no chemical significance could be attached to this observation. The remainder of the map was flat with the highest peak corresponding to 0.8 e Å^{-3}.

Final positional and equivalent thermal parameters are given in Table 3. A full listing of bond lengths and angles, thermal parameters of the non-hydrogen atoms, positional and thermal parameters for the calculated H atoms, observed and calculated structure factors and meanplane data are available from the authors (JS).

Coupling reactions with 1

(*a*) Approximately 0.1 cm^3 of CuCl : TMEDA solution (Hay catalyst) [20] was added to an acetone solution of **1** (0.03 mmol). Air was bubbled through the stirred solution for two hours but work-up recovered unchanged **1**.

(*b*) A similar reaction to (*a*) but with excess CuCl and Et_2NH (0.2 cm^3) gave no reaction.

(*c*) An excess of copper(II) acetate was added to **1** (0.03 mmol) dissolved in anhydrous pyridine (20 cm^3). The solution was heated to 60 ° C for one hour but tlc analysis showed that no reaction had occurred. At this point excess trimethylsilylacetylene was added but apart from insoluble black material forming there was no tlc or spectroscopic evidence for coupling between the alkyne and cluster.

(*d*) Phenyllithium in THF (0.023 mmol) was added at ambient temperature to **1** (0.023 mmol) in THF (30 cm^3). After 30 min the work-up gave quantitative recovery of **1**. Similarly, phenyllithium (0.228 mmol) added to trimethylsilylacetylene (0.023 mmol), followed by the addition of **1** (0.034 mmol) gave no reaction. These reactions were repeated at lower and higher temperatures without result.

(*e*) **1** (0.093 mmol), lithium diisopropylamide (0.093 mmol) and iodine (0.093 mmol) were added to 35 cm^3 of hexane at $-78\,^\circ C$. Work-up gave quantitative recovery of **1**.

(*f*) An excess of powdered $AlCl_3$ was gradually added to a stirred solution of **1** (0.032 mmol) in CH_2Cl_2 at ambient temperature. A colour change from purple to brown was observed over 5 min, then to green over 30 min. Removal of the solvent gave a green solid but attempts to remove excess $AlCl_3$ invariably gave **1**. An IR spectrum of the green solid was virtually identical to that of **1**; NMR spectra were inconclusive.

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