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Reactions of $HCCo_3(CO)_9$ with silanes; synthesis and electrochemistry of $X[SiMe_2CCo_3(CO)_9]_2$ ($X=O$, 1,4-C_6H_4)

Jan Borgdorff, Noel W. Duffy, Brian H. Robinson*, Jim Simpson

Department of Chemistry, University of Otago, PO Box 56, Dunedin, New Zealand

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Abstract

Reactions between Ph_nSiH_{4-n} or $HR_2SiXSiR_2H$ and $HCCo_3(CO)_9$ are described. Both the monocluster, $HMe_2SiXSiMe_2CCo_3(CO)_9$, and the dicluster, $(CO)_9Co_3CMe_2SiXSiMe_2CCo_3(CO)_9$, complexes were obtained from the silanes $HMe_2SiXSiMe_2H$ ($X=O$, 1,4-C_6H_4). $RSiH_2CCo_3(CO)_9$ ($R=Ph$, Me) or sterically demanding silanes do not couple with $HCCo_3(CO)_9$. Generally with Ph_nSiH_{4-n} ($n=1$, 2) electrophilic attack on the cluster core resulted in the formation of the novel μ-silylene complexes $HCCo_3(CO)_8(\mu\text{-}SiR_2)$, and fragmentation of the Co_3C unit, instead of the expected silicon-bridged diclusters. Electrochemical investigation of the dicluster compounds and their phosphite derivatives showed there was no interaction between the cluster redox centres.

Keywords: Cobalt complexes; Carbonyl complexes; Silane complexes; Electrochemistry

1. Introduction

Our interest [1] in the electron-transfer properties and thermodynamic stability of redox-active organometallic clusters linked by Group 14 elements arises from the possibility of using these molecules as precursors for technologically useful materials and/or preveniens for chemical vapour deposition. Previous papers have dealt with molecules in which the CCo_3C [2,3] or Co_3C [4–6] cluster is linked through the capping non-metal atom by a carbyne chain or by a ferrocenylsilicon group [7]. Where two clusters are linked directly to another redox centre, or via an unsaturated group, there was evidence for a modification of the electron transfer properties of the reducible [4,8] (Co_3C) or oxidisable [2,3] (CCo_3C) core. In the case of the carbyne-linked systems thermal decomposition gave conducting materials [9].

In this paper we examine systems in which a silicon group $\mu\text{-}SiR_2$, μ-Si–O–Si or μ-Si–C_6H_4–Si functions as the link between two $CCo_3(CO)_9$ redox sites. Two possible synthetic routes to $RR'Si[CCo_3(CO)_9]_2$ are shown in Eqs. (1) and (2). The first route [10] is of limited use because the trichloromethyl reagents are often difficult to prepare.

$$RR'Si(CCl_3)_2 + Co_2(CO)_8 \longrightarrow RR'Si[CCo_3(CO)_9]_2 \quad (1)$$

$$RR'SiH_2 + 2HCCo_3(CO)_9 \longrightarrow RR'Si[CCo_3(CO)_9]_2 + 2H_2 \quad (2)$$

In contrast, the versatility of the reaction between suitably functionalised silanes R_3SiH and $HCCo_3(CO)_9$ has been amply demonstrated [11] and has been used inter alia to synthesise optically active derivatives [12]. Reaction with Ph_2SiH_2 has been reported [11] to give decomposition products. The objective of the work described herein was to investigate the effect of an interpolated silicon functionality in the carbyne linkage between two clusters, and to produce clusters which could provide a source of silicon in ceramic or conducting materials. Modification of the redox properties by substitution of CO by a Lewis base is also explored.

2. Experimental

All reactions were carried out in an atmosphere of dry argon in oven-dried glassware. Solvents were purified as described previously [13]. The starting cluster

*Corresponding author.

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$HCCo_3(CO)_9$, was prepared by the published procedure [14], Me_3SiCCl_3 and $Ph_2Si(CCl_3)_2$ from the reaction of trimethylchlorosilane or diphenylchlorosilane with trichloromethyllithium [10], Ph_2SiH_2 and $PhSiH_3$ by lithium aluminium hydride reduction of the appropriate chlorosilane [15] and $(Me_3Si)_3SiH$ according to the method of Gilman and Smith [16]. $LiAlH_4$ and Et_3N (Merck); $P(OPh)_3$ (Strem); $Co_2(CO)_8$ (Aldrich or Strem); $MeSiHCl_2$, Ph_2SiCl_2 and $PhSiCl_3$ (ROC/RIC), and Me_2SiHCl, 1,1,2,2-tetramethyl-disiloxane, 1,4-bis-(dimethylsilyl)benzene, 1,1,2-trimethyldisilane, Et_3SiH and tris(dimethylsilyl)amine (Petrarch Systems Inc.) were used as received. n-Butyllithium (Aldrich or Merck) was standardised before use [17]. Na-BPK in THF solution was produced as a by-product of the purification of THF [13]. Polarography and cycle voltammetry studies were carried out with the reference solid Ag/AgCl electrode immersed directly in the solution and calibrated in situ with $[\text{ferrocene}]^{+/0}$ taken as $E_{1/2}=0.68$ V in CH_2Cl_2 [13]; solutions were $\sim 10^{-3}$ M in electroactive material and 0.10 M (TBAP) in supporting electrolyte. IR spectra were recorded on a Nicolet MX-S; ^1H, $^{31}P\{^1H\}$ and $^{39}Si\{^1H\}$(DEPT) NMR on a VXR-300 spectrometer; and ESR spectra on a Varian E3 spectrometer with in situ electrochemical generation of radical anions [18]. Elemental analyses were performed by the Campbell Microanalytical Laboratory, University of Otago.

2.1. Preparation of 1 and 2

$HCCo_3(CO)_9$ (0.72 g, 1.6 mmol) and $(HMe_2Si)_2O$ (0.10 g, 0.75 mmol) were dissolved in toluene (35 cm^3) and the solution was heated under reflux for 60 min. Preparative TLC (silica gel, hexane) showed 13 bands with only three products present in significant amounts. Band 3 (purple) was removed and recrystallised from hexane to give purple–black crystals of $HMe_2SiOSiMe_2CCo_3(CO)_9$ (**1**); yield ~45%. *Anal.* Calc. for $C_{14}H_{13}Co_3O_{10}Si_2$: C, 29.28; H, 2.28. Found: C, 29.24; H, 2.76%. IR (CCl_4, cm^{-1}) ν(CO): 2103(w), 2057(s), 2040(s), 2023(w). ^1H NMR (CCl_4): 0.02 (s, 6H), 0.37 (d, 6H). Band 12 (green), $Co_4(CO)_9[\eta^6\text{-}(C_6H_5CH_3)]$, was identical to that produced in the reaction of Ph_2SiH_2 with $HCCo_3(CO)_9$ (see below); yield <5%. Band 13 recrystallised from hexane gave purple–black crystals of $[(OC)_9Co_3CSiMe_2]_2O$, (**2**); yield 10%. *Anal.* Calc. for $C_{24}H_{12}Co_6O_{19}Si_2$: C, 28.42; H, 1.19. Found: C, 28.35; H, 0.89%. IR (CCl_4, cm^{-1}) ν(CO): 2102(w), 2060(s), 2041(s), 2002(w). ^1H NMR ($CDCl_3$): 0.46. ^{13}C NMR ($CDCl_3$): 5.0 ($SiCH_3$), 199.8 (CO). $E_{pa}=0.66$ V, $\Delta E=135$ mV, in acetone at 100 mV s^{-1}.

2.2. Preparation of 3 and 4

$HCCo_3(CO)_9$ (0.92 g, 2.1 mmol) and 1,4-bis(dimethylsilyl)benzene (0.20 g, 1.0 mmol) were dissolved in toluene (30 cm^3) and the solution was heated under reflux for 45 min. After cooling, the mixture was filtered and the precipitate washed, first with hexane, then with dry diethyl ether. The precipitate was dried in vacuo to give $1,4\text{-}[Me_2SiCCo_3(CO)_9]_2C_6H_4$, (**4**) as a dull red powder; yield 0.609 g (55%). *Anal.* Calc. for $C_{30}H_{16}Co_6O_{18}Si_2$: C, 33.54; H, 1.50. Found: C, 33.84; H, 2.24%. IR (CCl_4, cm^{-1}) ν(CO): 2101(w), 2054(s), 2037(s), 2020(w). ^1H NMR: 0.67 (s, 12H), 7.69 (s, 4H). ^{21}Si NMR: −4.7. $E_{pa}=0.61$ V, $\Delta E=210$ mV in acetone at 100 mV s^{-1} at 25 °C. This compound is stable to air and water, sparingly soluble in warm hexane and chlorinated solvents. In a separate experiment with a 1:1 silane:cluster mole ratio, the solvent was stripped and the residue separated to give 3 bands (in descending R_f, $HCCo_3(CO)_9$, red and **4**). Workup of the red band gave purple crystals of $Me_2Si(H)\text{–}O\text{–}Si(Me_2)CCo(CO)_9$ (**3**). Mass spectrum: $m/e=634$ (M^+), followed by M^+-9CO. IR (CCl_4, cm^{-1}) ν(CO): 2101(w), 2052(s), 2037(s), 2020(w). ^1H NMR (CCl_4): 0.30 (s, 6H), 0.68 (s, 6H), 3.70 (septet, Si–H), 7.55, 7.60 (d, 4H).

2.3. Reaction of 4 with $P(OPh)_3$

4 (0.100 g, 0.0931 mmol) and $P(OPh)_3$ (0.060 g, 0.19 mmol) were dissolved in THF (~20 cm^3) and the solution heated under reflux for 20 min. After cooling, the solvent was removed under vacuum and the residue dissolved in a small volume of dichloromethane. Preparative TLC (silica gel, CH_2Cl_2) resulted in two bands in addition to unreacted **4**. Band 1 yielded brown crystals of $([Me_2SiCCo_3(CO)_9]C_6H_4[Me_2SiCCo_3(CO)_8P(OPh)_3])$, (**5**); yield ~60%. *Anal.* Calc. for $C_{47}H_{31}Co_6O_{20}PSi_2$: C, 41.62; H, 2.30. Found: C, 42.37; H, 3.24%. IR (CCl_4, cm^{-1}) ν(CO): 2101(w), 2084(w), 2053(s), 2041(s, sh) 2037(s), 2022(m). ^1H NMR ($CDCl_3$): 0.1 (s, 3H), 0.2 (s, 3H), 0.74 (s, 6H), 6.4–6.8 (m, 19 H). $^{13}P\{^1H\}$ NMR: 129. Band 2 gave green–brown crystals of $1,4\text{-}[Me_2SiCCo_3(CO)_8P(OPh)_3]_2\cdot C_6H_4$ (**6**); yield ~20%. This compound is extremely labile and good analyses were not obtained. IR (CCl_4, cm^{-1}) ν(CO): 2084(w), 2042(s), 2028(m), 2022(m). ^1H NMR ($CDCl_3$): 1.29 (s, 12H, $(SiCH_3)_4$); 6.88–6.96, 7.1–7.3, 7.5 (m, 34H, $2\times P(OC_6H_5)_3$ and SiC_6H_4Si). $^{31}P\{^1H\}$ NMR: 142.

2.4. Reaction of $HCCo_3(CO)_9$ and $PhSiH_3$

Typically, $HCCo_3(CO)_9$ (1.0 g, 2.3 mmol) and $PhSiH_3$ (0.244 g, 2.26 mmol) were dissolved in hexane (50 cm^3) and the purple solution heated under reflux for 3 h. After the brown solution had cooled, the solvent was removed under vacuum and the residue dissolved in a small volume of dichloromethane. Preparative TLC (silica gel, hexane, argon atmosphere) showed 3 bands in addition to unreacted $HCCo_3(CO)_9$. Band 1 yielded

$PhH_2SiCCo_3(CO)_9$ (**7**) as a purple microcrystalline solid; yield ~5%. Mass spectrum (70 eV): *m/e* 548 M^+ (calc. 548). IR (CCl_4, cm^{-1}) ν(CO): 2109(w), 2062(s), 2045(s), 2032(w). The second product band was $Co_4(CO)_{12}$; yield ~10%. Band 3 gave $HCCo_3(CO)_8(\mu\text{-SiHPh})$ (**8**) as an orange powder; yield ~10%. *Anal.* Calc. for $C_{15}H_7Co_3O_8Si$: C, 36.64; H, 1.36. Found: C, 36.73; H, 1.76%. Mass spectrum (70 eV): *m/e* 520 (M^+, 520, $M^+ - 8CO$, $M^+ - 8CO - H$, $M^+ - 8CO - H - SiPh$). IR (CCl_4, cm^{-1}) ν(CO): 2084(w), 2046(vs), 2043(sh), 2029(m), 2027(sh), 2017(m), 1861(w). ^1H NMR (CCl_4): 6.50 (s, 1H, Si–*H*), 7.60–8.40 (m, 5H, C_6H_5). Compounds **7** and **8** decomposed slowly to give insoluble, green–brown, non-carbonyl containing compounds. No reaction occurred between $PhSiH_3$ and $HCCo_3(CO)_9$ in hexane (room temperature, overnight or 308–318 K for 2 h). In toluene (under reflux) a precipitate was produced more quickly, and the product yields were much lower than in hexane.

2.5. Reaction of $HCCo_3(CO)_9$ and Ph_2SiH_2

$HCCo_3(CO)_9$ (0.50 g, 1.1 mmol) and Ph_2SiH_2 (0.21 g, 1.1 mmol) were dissolved in toluene (~30 cm^3) and heated under reflux for 3 h. After cooling, the solvent was removed in vacuo and the residue dissolved in a small volume of dichloromethane. Preparative TLC (silica gel, hexane) showed a large number of products of which only one (green; R_f~0.1) was present in sufficient quantity to permit characterisation and was shown to be $Co_4(CO)_9(\eta^6\text{-}C_6H_5CH_3)$ (**9**) by comparison with the published spectroscopic data [19] and mass spectroscopic analysis; yield ~10% (slightly higher yield when reaction was carried out at ~70 °C). Reactions in hexane gave similar results to those in toluene but fewer products were separated. The main product (green crystals; ~10% yield) was shown by its IR and NMR spectra [19], and unit cell dimensions [20], to be $Co_4(CO)_9(\eta^6\text{-}C_6H_6)$ (**10**). An orange compound is also produced in this reaction (R_f~0.40) which decomposed quickly during chromatography to produce an insoluble green solid. Comparison with the orange products obtained from the $PhSiH_3/HCCo_3(CO)_9$ reaction, vide supra, suggests that it may be $HCCo_3(CO)_8(\mu\text{-SiPh}_2)$. Analytical TLC confirmed that no reaction occurred between $HCCo_3(CO)_9$ and Ph_2SiH_2 in dry diethyl ether.

2.6. Preparation of $MeCl_2SiCCo_3(CO)_9$ (11)

$HCCo_3(CO)_9$ (1.5 g, 3.4 mmol) and $MeSiHCl_2$ (2.0 g, 17 mmol) were dissolved in toluene (~30 cm^3) and the solution was heated under reflux for 30 min. The solvent and excess silane were removed in vacuo. The purple–black solid remaining was washed with hexane to remove traces of $HCCo_3(CO)_9$, leaving small purple–black crystals of $MeCl_2SiCCo_3(CO)_9$ (**11**); yield >90%. *Anal.* Calc. for $C_{11}H_3Cl_2Co_3O_9Si$: C, 23.81; H, 0.54. Found: C, 23.63; H, 1.28%. Mass spectrum (70 eV): *m/e* 554 (M^+, 554). IR (CCl_4, cm^{-1}) ν(CO): 2108(w), 2064(s), 2045(s), 2031(w). ^1H NMR (CCl_4): 0.67 (s, 3H).

2.7. Preparation of $MeH_2SiCCo_3(CO)_9$ (12)

$LiAlH_4$ (0.024 g, 0.63 mmol) was suspended in dry diethyl ether (~20 cm^3) at 195 K. $MeCl_2SiCCo_3(CO)_9$ (0.176 g, 0.317 mmol) dissolved in toluene (~40 cm^3) was added dropwise over ~20 min. The mixture was stirred at 195 K for 1 h, warmed to room temperature, stirred for a further 2 h and then hydrolysed by the careful addition of cold dilute hydrochloric acid (~50 cm^3). The purple product was extracted into diethyl ether and the solvent removed in vacuo. The solid product was dissolved in warm toluene, the solution layered with hexane to give purple–black crystals of $MeH_2SiCCo_3(CO)_9$ (**12**); yield 0.116 g (75%). *Anal.* Calc. for $C_{11}H_5Co_3O_9Si$: C, 27.18; H, 1.04. Found: C, 27.39; H, 0.99%. Mass spectrum (70 eV): *m/e* 486 (M^+, 486). IR (CCl_4, cm^{-1}) ν(CO): 2101(w), 2053(s), 2040(s), 2022(w). ^1H NMR (CCl_4): 0.43 (m, 3H, CH_3), 4.72 (m, 2H, Si–*H*). The compound is stable both in air and in solution.

2.8. Attempts to prepare other silicon-bridged dicluster compounds

Only decomposition or very small amounts of cluster products were obtained from the following reactions. (a) $MeH_2SiCCo_3(CO)_9$ (0.086 g, 0.16 mmol) and $HCCo_3(CO)_9$ (0.235 g, 0.532 mmol) in toluene (~20 cm^3) heated under reflux for 5 h. (b) $Co_2(CO)_8$ (1.50 g, 4.39 mmol) and $Ph_2Si(CCl_3)_2$ (0.50 g, 1.2 mmol) in THF (40 cm^3) at reflux for 30 min. (c) $HCCo_3(CO)_9$ (1.24 g, 2.81 mmol) and tris(dimethylsilyl)amine (0.18 g, 0.94 mmol) in toluene (~60 cm^3) heated under reflux for 1 h; reactants recovered unchanged. (d) $HCCo_3(CO)_9$ (1.0 g, 2.3 mmol) and $(Me_3Si)_3SiH$ (0.56 g, 2.7 mmol) in hexane (~50 cm^3), stirring for 24h at room temperature followed by 2 h at 323 K; alternatively, the solution was heated under reflux for 3 h; reactants were recovered unchanged. (e) $HCCo_3(CO)_9$ + $HMe_2Si\text{–}SiMe_2H$ in toluene as for (a); a number of products including $Me_2SiCo_2(CO)_7$ and $(Me_2Si)_2Co_2(CO)_6$ (identified by mass spectra).

3. Results and discussion

Of the two possible synthetic routes to the silicon-bridged clusters, the hydrogen elimination reaction was used because of its versatility. In order to minimise steric constraints it was decided to initially examine molecules in which the tricobalt carbon redox centres were linked by linear Si–X–Si units. Reaction of 1,1,2,2-tetramethyldisiloxane (X=O) or 1,4-bis(dimethylsilyl)benzene (X=1,4-C_6H_4) with $HCCo_3(CO)_9$ in refluxing toluene gave the respective mono- (**1**, **3**) and di- (**2**, **4**) clusters in reasonable yields (Eqs. (3) and (4)). Analyses and spectroscopic data for these compounds fully support their formulation and structure. Fragmentation patterns in the mass spectra are dominated by the facile loss of CO groups followed by cleavage of the silyl species or $SiMe_2$ groups; the integrity of the CCo_3 unit is maintained. ^{29}Si NMR data were similar to those for ferrocenyl analogues [7]. As expected, there was a downfield shift on binding of the silane to the electron-withdrawing Co_3C moiety (e.g. from −16.9 for the ligand to −4.7 for **4**).

$$HCCo_3(CO)_9 + O(SiMe_2H)_2 \longrightarrow \underset{\mathbf{1}}{Me_2Si(H){-}O{-}Si(Me_2)CCo_3(CO)_9} + \underset{\mathbf{2}}{(CO)_9Co_3C{-}Si(Me_2){-}O{-}Si(Me_2)CCo_3(CO)_9} \quad (3)$$

$$HCCo_3(CO)_9 + C_6H_4(SiMe_2H)_2 \longrightarrow \underset{\mathbf{3}}{Me_2Si(H){-}C_6H_4{-}Si(Me_2)CCo_3(CO)_9} + \underset{\mathbf{4}}{(CO)_9Co_3C{-}Si(Me_2){-}C_6H_4{-}Si(Me_2)CCo_3(CO)_9} \quad (4)$$

In contrast to these smooth reactions, the anticipated products $Ph_nSi[CCo_3(CO)_9]_{4-n}$ from the reaction of $HCCo_3(CO)_9$ with Ph_2SiH_2 or $PhSiH_3$ were not observed. Furthermore, while the reaction between $PhSiH_3$ and $HCCo_3(CO)_9$ gave the phenylsilylmethylidynetricobalt complex, **7**, in low yield, (Eq. (5)) there was no evidence that substitution of a second cluster unit on the silicon atom had taken place; the cleavage products from the Ph_nSiH_{4-n} reactions are discussed below.

$$PhSiH_3 + HCCo_3(CO)_9 \longrightarrow \underset{\mathbf{7}}{PhSiH_2CCo_3(CO)_9} + H_2 \quad (5)$$

Reaction of $HCCo_3(CO)_9$ with 1,1,2,2-tetramethyldisilane also gave a number of products none of which were Co_3C derivatives; significantly, $Me_2SiCo_2(CO)_7$ and $(Me_2Si)_2Co_2(CO)_6$ [21] were among those identified, which indicates that Si–Si bond cleavage as well as cluster fragmentation takes place.

All attempts to incorporate the sterically demanding [22] tris(trimethylsilyl)silyl moiety as the apical substituent on a single cluster unit via reaction with $(Me_3Si)_3SiH$ or $(Me_2SiH)_3N$ proved unsuccessful. The generality of steric constraints and the influence of silane electrophilicity in the above reactions was further probed by seeking an indirect route to silicon bridged diclusters via the reaction of $MeH_2SiCCo_3(CO)_9$ with a further mole of $HCCo_3(CO)_9$: a methyl substituent on the silicon atom reduces the steric demands of the putative bridging unit and increases the nucleophilicity of the silylene group. The precursor $MeH_2SiCCo_3(CO)_9$ (**12**) was obtained from the dichloromethylsilyl compound, **11** (Eq. (6)) in excellent yields providing the lithiation reaction was carried out at low temperatures in an arene/ether solvent system to minimise the alternative reaction of nucleophilic attack at the carbonyl ligands. This results in complete decomposition of

$$MeCl_2SiH + HCCo_3(CO)_9 \longrightarrow \underset{\mathbf{11}}{MeCl_2SiCCo_3(CO)_9} \longrightarrow \underset{\mathbf{12}}{MeH_2SiCCo_3(CO)_9} \quad (6)$$

the cluster unit [23]. However, no reaction between **12**, or indeed any other $RSiH_2CCo_3(CO)_9$ cluster, and $HCCo_3(CO)_9$ in toluene was observed. Another attempt to produce a μ-SiR_2 bridged dicluster involved a reaction between bis(trichloromethyl)diphenylsilane and dicobalt octacarbonyl (cf. Eq. (1)) but again no carbonyl-containing products were obtained.

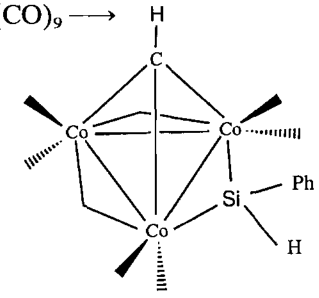
Computer-generated models show that there would be considerable non-bonded interactions if two bulky cluster units were forced into close proximity by the necessity for tetrahedral coordination about a central silicon atom and it is clear that the inability to bond a second $CCo_3(CO)_9$ unit to silicon is a result of steric hindrance. The stereochemical demands of the six equatorial carbonyl ligands on the cobalt triangle are well documented [24,10b], and there are few instances in which a capping group with more than a single bulky substituent is bound to the apical carbon atom. Even in compounds such as $FcCCo_3(CO)_9$ [5], and the archetypal dicluster $[CCo_3(CO)_9]_2$ [25], the effects of the steric interactions between the apical substituent and the equatorial carbonyl groups are manifest. It is notable in this context that the chlorosilane **11** is unusually resistant to hydrolysis and may be shaken in CCl_4/H_2O, at ambient temperature [1], without reaction. This low reactivity can be attributed to the steric protection to nucleophilic attack at the silicon centre afforded by the equatorial carbonyl groups of the cluster unit.

As noted above other products were obtained from the reactions of Ph_nSiH_{4-n} with $HCCo_3(CO)_9$ in toluene. The only isolable carbonyl-containing product with Ph_2SiH_2 was the green complex $Co_4(CO)_9(\eta^6\text{-}C_6H_5CH_3)$

[1] Hydrolysis and alcoholysis of chlorosilyl derivatives can be achieved in benzene at 80 °C.

(**5**), previously characterised from the reaction of toluene with $Co_4(CO)_{12}$, or from the decomposition of $R_2C_2Co_2(CO)_6$ complexes in toluene in the presence of norbornadiene [19] (**5** was also found among the minor products from the reaction with $C_6H_4(SiMe_2H)_2$). The equivalent reaction in refluxing hexane surprisingly produced the analogous benzene derivative $Co_4(CO)_9(\eta^6\text{-}C_6H_6)$ (**6**). With $PhSiH_3$ the major products were $Co_4(CO)_{12}$, the ubiquitous result of cobalt carbonyl cluster fragmentation, and the novel orange silylene bridged complex $HCCo_3(CO)_8(\mu\text{-SiHPh})$ (**8**). The mass spectrum of **8** showed the parent molecular ion with subsequent loss of 8 CO groups and the silylene ligand to leave the Co_3C unit intact. ^1H NMR confirmed the presence of phenyl and Si–H groups and the observation of the $\nu(CO)$ in-phase A_1 band at 2084 cm^{-1} is consistent with replacement of a single CO on the cluster unit [26]. A weak absorption in the bridging carbonyl region at 1861 cm^{-1} parallels those observed in the silylene and germylene bridged dicobalt complexes $(\mu\text{-}R_2M)Co_2(CO)_7$, (R = Ph, Me, Cl, M = Si; R = Me, M = Ge) [21,27]. A possible structure which maintains the appropriate electronic configuration for each cobalt is depicted in Eq. (7).

$PhSiH_3 + HCCo_3(CO)_9 \longrightarrow$



8

$+ PhH_2SiCCo_3(CO)_9$ (7)
7

To our knowledge this is the first reported example of silylene bridging in a tricobalt carbon cluster but attempts to obtain a ^{29}Si NMR or crystals suitable for X-ray analysis have been unsuccessful. A transient, orange compound observed during the workup of the reaction with Ph_2SiH_2 is thought from the spectroscopic data to be a related silylene bridged complex $HCCo_3(CO)_8(\mu\text{-}SiPh_2)$ but it decomposed rapidly during chromatography.

Products from the reactions above are all derived from fragmentation of the cluster and are consistent with the mechanism proposed [11] for the hydrogen-elimination reaction whereby a 'bond-opened' intermediate results from oxidative-addition of the silane to the Co_3C unit. Recent work by Richmond and co-workers [28] has lent support to the notion of a hapticity change during the reaction involving Co–C rather than, or as well as, Co–Co cleavage. Isolation of the μ_2-silylene derivative is interesting in this context and the concomitant Si–Si bond cleavage that was noted is understandable given this mechanism. The result for the reaction of Ph_2SiH_2 in hexane suggests that both Si–H and Si–C bonds of a silane cluster are cleaved as the phenyl substituent on silicon is the most likely source of the initial arene ($Co_4(CO)_9(\eta^6$-arene)) product – coordinated benzene would then be replaced by the solvent toluene. Since the fragmentation pathway is dependent upon the nature of the silicon substituent acting as an electrophile, it may be possible to isolate μ_2-derivatives using electron-withdrawing groups on the silicon.

3.1. Redox properties of the complexes 1–4

$Me_3SiCCo_3(CO)_9$ (**13**) was used as the reference one-electron transfer cluster. As expected [29] it undergoes a chemically and electrochemically reversible one-electron process on Pt and Hg, with $E_{1/2} = -0.59$ V, and a further irreversible reduction at -1.5 V (the separation between the first and the second reduction processes is larger than normal for $RCCo_3(CO)_9$ compounds so an assignment of the second wave to the formation of the dianion is uncertain). In situ electrochemical reduction of the cluster in CH_2Cl_2 at 233 K gave the characteristic [18] ESR spectrum of a radical anion, $Me_3SiCCo_3(CO)_9^{\cdot -}$ ($g_{iso} = 2.012$, $A = 35.2$) in which the electron occupies the a_2^* antibonding orbital.

The electrochemistry of **1** and **3** was almost identical to that of **13**. Polarography and the CV profiles of the dicluster compounds **2** and **4** were also similar to **13**. Thus, $E_{1/2} = -0.60$ and -0.53 V for **2** and **4**, respectively, but the diffusion currents were larger for the first reduction process than those for **13**. The relative magnitude of the diffusion current parameters for the first reduction process for **2** and **4** confirm that there is an overall two-electron transfer. A plot of v versus $i_d - i/i$ had a slope of 37 mV and the ratio of the diffusion currents compared with that for equimolar in situ ferrocene is 2:1 assuming that the ratio of the diffusion coefficients of ferrocene and a large Co_3C cluster is approximately 0.6 [13]. A separation of 35.6 mV in the two peak potentials for *i–E* plots is predicted [30] for two one-electron reduction waves of two identical redox centres, but is rarely resolved, and so the *i–E* responses observed are essentially the superposition of two physically distinct redox centres. This contrasts sharply with the carbyne-linked cluster $[(CO)_9Co_3CC]_2$ or other molecules where two cluster redox sites are linked by delocalized C–C bonds [4]; in these molecules two one-electron waves are observed separated by >200 mV. Clearly, the silicon groups are functioning as effective insulators, a conclusion reached for molecules where the cluster is linked via silicon to ferrocene as the alternate redox site [7].

$$(CO)_9Co_3CSi(Me_2)\text{–}C_6H_4\text{–}Si(Me_2)CCo_3(CO)_9 + 2e \longrightarrow$$
$$(CO)_9\overset{\cdot -}{Co_3}CSi(Me_2)\text{–}C_6H_4\text{–}Si(Me_2)C\overset{\cdot -}{Co_3}(CO)_9 \quad (8)$$

To investigate the effectiveness of this insulation, molecules with non-identical cluster sites were desired. This was achieved by substituting one or more CO groups by a tertiary phosphite. Reaction of **4** with triphenylphosphite in THF gave two phosphite derivatives, **5** and **6**, in good yields (Eq. (9)). **10** was identified as the monosubstituted complex by the appearance of two A_1 ν(CO) bands, the first at 2101 cm^{-1} characteristic of an unsubstituted $CCo_3(CO)_9$ fragment, while the lower frequency 2084 cm^{-1} band typifies those of a cluster unit carrying a single phosphite substituent [26]. Weak bands in the bridging ν(CO) region for both **5** and **6** suggest that a bridged/non-bridged equilibrium [31] is established in solution, commensurate with considerable steric crowding in the cluster units. i–E responses of **5** and **6** are complex because of facile ligand dissociation and rapid $\vec{E}C\vec{E}$ processes [1]. For the symmetrically-substituted derivative **6**, they were chemically irreversible at ambient temperature but reversible at low temperatures. At 203 K a single two-electron couple is observed at $E_{1/2} \sim -0.84$ V giving the anticipated cathodic shift in potential characteristic [13,32] of a $CCo_3(CO)_8L$ species. By comparison, the unsymmetrical derivative **5** has two primary reduction processes; below 270 K two distinct couples are seen but the current of the second is less than that of the first. The first couple at $E_{1/2} \sim -0.65$ V is readily assigned to the unsubstituted redox centre and the second at $E_{1/2} \sim -0.86$ V to the $CCo_3(CO)_8P(OPh)_3$ redox centre. Because of the accompanying $\vec{E}C\vec{E}$ processes in the reduced species it is not possible to derive n for each transfer step but the electrochemical parameters and a comparison of i_{pc} with equimolar in situ ferrocene are not inconsistent with $n=1$ for the first reduction step. It is clear that the two redox sites in **5** and **6** are non-interacting in the electrochemical sense. If the cluster moieties in **1–4** are functioning as a single redox site then they should undergo $\vec{E}C\vec{E}$ (or ETC) reactions [1] with tertiary phosphites with consequent substitution of CO. Quantitative ETC synthesis in which up to one CO per cluster unit was substituted by a range of phosphine and phosphite ligands was indeed achieved using sodium benzophenoneketal as reductant in THF [33].

$$\mathbf{4} + L \longrightarrow$$
$$\underset{\mathbf{5}}{(CO)_9Co_3C(Me_2)Si\text{–}C_6H_4\text{–}Si(Me_2)CCo_3(CO)_8L}$$
$$+ \underset{\mathbf{6}}{[L(CO)_9Co_3C(Me_2)Si]_2\text{–}C_6H_4} \quad (9)$$

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