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The preparation and characterisation of monomeric and linked metal carbonyl clusters containing the *closo*-Si_2Co_4 pseudo-octahedral core

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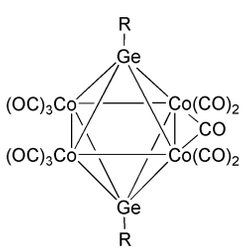
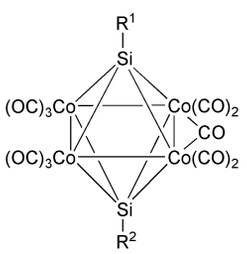
$PhSiH_3$ reacts with $[Co_4(CO)_{12}]$ at 50 °C in hydrocarbon solvents to give $[(\mu_4\text{-SiPh})_2Co_4(CO)_{11}]$, **2c**, shown by an X-ray crystal structure determination to have a pseudo-octahedral Si_2Co_4 core. Substituted aryl-silanes behaved similarly. Mixtures of $PhSiH_3$, $H_3SiC_6H_4SiH_3$ and $[Co_4(CO)_{12}]$ in a *ca.* 2 : 1 : 2 ratio gave the dimeric cluster $[\{Co_4(\mu_4\text{-SiPh})(CO)_{11}Si\}_2C_6H_4]$, **3a**, which has the two Si_2Co_4 cores linked by a C_6H_4 group to give a rigid molecule which an X-ray structure analysis shows to be over 23 Å long. Related dimers linked by $-(CH_2)_8-$ groups were isolated from mixtures of $PhSiH_3$, α,ω-$(H_3Si)_2(CH_2)_8$ and $[Co_4(CO)_{12}]$. Electrochemical studies show the two cluster units in **3a** do not interact electronically.

Introduction

There is an extensive family of metal clusters incorporating a pseudo-octahedral E_2M_4 core, where E is a main group element from Groups 14–16 and M is a transition metal, usually Co, Fe or Ru although others can be involved.[1,2] Representative examples include $[Co_4(\mu_4\text{-PPh})_2(CO)_{10}]$, $[Fe_4(\mu_4\text{-PPh})_2(CO)_{11}]$, $[Mn_4(\mu_4\text{-Te})_2(CO)_{12}]^{2-}$ and $[Fe_4(\mu_4\text{-AsPh})_2(CO)_{11}]$.[3–6] For Group 14 elements there are several examples of the type $[Co_4(\mu_4\text{-GeR})_2(CO)_{11}]$, (**1**, R = Me, Ph, Bu, $Co(CO)_4$),[7,8] but for silicon the only reports are of $[Co_4\{\mu_4\text{-Si}[Co(CO)_4]\}_2(CO)_{11}]$ (**2a** from Si_2H_6 and $[Co_2(CO)_8]$),[9] and $[Co_4(\mu_4\text{-SiMe})_2(CO)_{11}]$, (**2b**, originally by an indirect route from $[Fe(SiMeH_2)_2(CO)_4]$ and $[Co_2(CO)_8]$ though a more systematic synthesis from $MeSiH_3$ was subsequently developed).[10]



(**1**)



(**2**)

2a $R^1 = R^2 = Co(CO)_4$
2b $R^1 = R^2 = Me$
2c $R^1 = R^2 = Ph$
2d $R^1 = R^2 = p\text{-}MeOC_6H_4$
2e $R^1 = R^2 = p\text{-}Me_2NC_6H_4$
2f $R^1 = Ph$ $R^2 = p\text{-}MeOC_6H_4$
2g $R^1 = Ph$ $R^2 = p\text{-}Me_2NC_6H_4$
2h $R^1 = R^2 = (CH_2)_3OMe$

Interest in clusters with the E_2M_4 core stems partly from their catalytic activity,[11] and also from their electronic properties since both 7- and 8-SEP (SEP = skeletal electron pairs) versions are known, with the latter more common despite the expectation for 7-SEP for a *closo*-E_2M_4 core.[2] This has been analysed theoretically,[12] and electrochemically for $[Fe_4(\mu_4\text{-PPh})_2(CO)_x]$ (x = 11 or 12) and corresponding cobalt clusters.[13,14]

In this present paper we report the synthesis and structures of some new silicon examples of type **2**, including oligomeric clusters linked through the apical groups.

Experimental

All reactions were carried out in re-distilled solvents under nitrogen, using standard Schlenk techniques. $[Co_4(CO)_{12}]$ was prepared using a literature procedure.[15] $PhSiH_3$ was prepared by $LiAlH_4$ reduction of $PhSiCl_3$ in Et_2O. p-$MeOC_6H_4SiCl_3$ and p-$Me_2NC_6H_4SiCl_3$ were prepared by combining the Grignard reagent from the respective aryl bromides with excess $SiCl_4$, and reduction of these chlorides with $LiAlH_4$ gave the appropriate silanes.[16] p-$(H_3Si)_2C_6H_4$ was prepared using a modified literature procedure,[17] coupling the di-Grignard $C_6H_4(MgBr)_2$ with a large excess of $SiCl_4$ in Et_2O. Reduction of the resulting p-$(Cl_3Si)_2C_6H_4$ with $LiAlH_4$ in Et_2O gave the di-silylbenzene. This was purified by pumping the product and the solvent *in vacuo* at room temperature into a trap cooled to 77 K, and then evaporating the Et_2O by heating the crude mixture in an open container over a water bath at 60–80 °C. The remaining liquid was shown by NMR spectroscopy to be sufficiently pure for further use. **CAUTION!** Attempted vacuum distillation of crude p-$(H_3Si)_2C_6H_4$ on one occasion led to an explosion, presumably as the result of SiH_4 formation by thermal rearrangement. $MeO(CH_2)_3SiH_3$[18] and $H_3Si(CH_2)_8SiH_3$ (bp 33–37 °C/0.5 mmHg) were prepared by $LiAlH_4$ reduction of commercially available (Gelest Inc.) $MeO(CH_2)_3Si(OMe)_3$ and $Cl_3Si(CH_2)_8SiCl_3$, respectively.

Electrospray mass spectra were recorded on a VG Platform II spectrometer, operated as detailed elsewhere.[19] NMR spectra were recorded on a Bruker DRX-400 and IR on a Digilab FTS-40 instrument.

Preparations of monomeric clusters

(a) $[Co_4(\mu_4\text{-SiPh})_2(CO)_{11}]$ (2c). $PhSiH_3$ (0.265 g, 2.45 mmol) was condensed into an ampoule (*ca.* 50 mL) containing $[Co_4(CO)_{12}]$ (0.70 g, 1.23 mmol) in hexane (10 mL). The ampoule was evacuated, sealed and placed in an oil bath at 40 °C for 2 months. The ampoule was opened and the contents transferred to a Schlenk tube, washing with CH_2Cl_2. Solvent was removed under vacuum. Unreacted $[Co_4(CO)_{12}]$ was extracted from the residue with hexane (3 × 5 mL). The remaining solid was recrystallised at −20 °C from toluene to give $[Co_4(\mu_4\text{-SiPh})_2(CO)_{11}]$, (**2c**, 0.792 g, 86%). Found: C 35.95, H 1.90;

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$C_{23}H_{10}Co_4O_{11}Si_2$ requires C 36.63, H 1.34%. Mp 106–110 °C (dec.), ν_{CO} (CH_2Cl_2, cm^{-1}): 2085 w, 2046 s, 2030 m, 2016 m, 1855 w, br. NMR: ^1H δ 8.16, 7.69 (m, C_6H_5); ^{13}C δ 203.0 (br, CO), 139.3 (C1) 134.4 (C2) 132.0 (C4) 128.9 (C3). FAB-MS: *m/z* 754 w $(M)^+$ followed by 11 peaks corresponding to CO loss. ESI-MS: *m/z* 754 $(M)^+$.

The reaction could also be carried out using toluene as solvent at *ca.* 50 °C over periods of 2–14 d.

(b) $[Co_4(\mu_4\text{-}SiC_6H_4OMe)_2(CO)_{11}]$ (2d). Following the same procedure a toluene solution (20 mL) of *p*-$MeOC_6H_4SiH_3$ (170 µL, 0.166 g, 1.12 mmol) and $[Co_4(CO)_{12}]$ (0.212 g, 0.37 mmol) was sealed in a glass ampoule under vacuum and heated to 50 °C for 2 weeks. The product was purified by column chromatography using a 3 : 1 petroleum spirits–CH_2Cl_2 solvent mixture. $[Co_4(\mu_4\text{-}SiC_6H_4OMe)_2(CO)_{11}]$ (**2d**, 0.157 g, 0.19 mmol, 52%) was obtained as orange–red crystals from a 1 : 1 petroleum spirits–toluene solution at −20 °C. Found: C 42.24, H 2.38; $C_{25}H_{14}Co_4O_{13}Si_2{\cdot}C_7H_8$ requires C 42.40, H 2.45%. Mp 98–104 °C (dec.), ν_{CO} (CH_2Cl_2, cm^{-1}): 2082 w, 2044 s, 2027 m,sh, 2013 m,sh, 1849 w, br. NMR: ^1H δ 8.11, 7.24 (m, C_6H_4), 3.97 (s, CH_3); ^{13}C δ 203.3 (br, CO), 164.5 (C4), 136.3 (C2), 130.9 (C1), 114.6 (C3), 55.4 (CH_3). ESI-MS: *m/z* 814 $(M)^+$.

(c) $[Co_4(\mu_4\text{-}SiC_6H_4NMe_2)_2(CO)_{11}]$ (2e). Similarly $Me_2NC_6H_4SiH_3$ (0.18 g, 1.2 mmol) was added to a toluene solution (20 mL) of $[Co_4(CO)_{12}]$ (0.3 g, 0.52 mmol), sealed in a glass ampoule under vacuum and heated to 50 °C for 3 weeks. The ampoule was opened and the contents transferred to a Schlenk flask. Solvent was removed under vacuum and the sample extracted into CH_2Cl_2. Column chromatography using a 3 : 1 petroleum spirits–CH_2Cl_2 solvent mixture gave (i) an unidentified purple band [ν_{CO} (petroleum spirits, cm^{-1}): 2102w, 2052s, 2038m, 2018w]; (ii) unreacted $[Co_4(CO)_{12}]$ and (iii) orange $[Co_4(\mu_4\text{-}SiC_6H_4NMe_2)_2(CO)_{11}]$ (**2e**, 0.056 g, 0.07 mmol, 13%). An analytical sample was obtained from a 1 : 1 petroleum spirits–toluene solution at −20 °C. Found: C 38.23, H 2.58, N 2.97; $C_{27}H_{20}Co_4N_2O_{11}Si_2$ requires C 38.59, H 2.40, N 3.33%. Mp 108–112 °C (dec.) ν_{CO}, (CH_2Cl_2, cm^{-1}): 2073 w, 2040 s, 2027 m,sh, 2011 m,sh, 1976 w, 1848 w, br. NMR: ^1H δ 8.00, 6.92 (m, C_6H_4), 3.10 (s, CH_3);^{13}C δ 204.0 (CO), 152.3 (C4), 136.0 (C2), 126.0 (C1), 111.5 (C3), 40.0 (CH_3). ESI-MS: *m/z* 841 $(M + H)^+$.

(d) $[Co_4(\mu_4\text{-}SiPh)(\mu_4\text{-}SiC_6H_4OMe)(CO)_{11}]$ (2 f). Following the same procedure a toluene solution (20 mL) of $PhSiH_3$ (0.09 g, 0.79 mmol), *p*-$MeOC_6H_4SiH_3$ (0.11 g, 0.79 mmol) and $[Co_4(CO)_{12}]$ (0.45 g, 0.78 mmol) was sealed in a glass ampoule under vacuum and heated to 50 °C for 2 weeks. Column chromatography (3 : 1 petroleum spirits–CH_2Cl_2 solvent mixture) gave three orange bands. The first and third were $[Co_4(\mu_4\text{-}SiPh)_2(CO)_{11}]$ (**2c**) and $[Co_4(\mu_4\text{-}SiC_6H_4OMe)_2(CO)_{11}]$ (**2d**) respectively, while the middle band was $[Co_4(\mu_4\text{-}Ph)(\mu_4\text{-}SiC_6H_4OMe)(CO)_{11}]$ (**2f**, 0.12 g, 26%). Mp 91–101 °C (dec.), ν_{CO} (petroleum spirits, cm^{-1}): 2082 vw, 2044 s, 2029 m, 2015 m, 1979 vw, 1864 w, br. NMR: ^1H δ 8.16–7.22, (m, C_6H_5 and C_6H_4), 3.96 (s, CH_3); ^{13}C δ 203.1 (br, CO), 162.5 (C4), 136.3 (C2), 130.8 (C1), 114.6 (C3), 55.4 (CH_3), 139.4 (C1′), 134.4 (C2′), 131.9 (C4′), 128.9 (C3′). ESI-MS: *m/z* 784 $(M)^+$.

(e) $[Co_4(\mu_4\text{-}SiPh)(\mu_4\text{-}SiC_6H_4NMe_2)(CO)_{11}]$ (2g). Similarly a toluene solution (20 mL) of $PhSiH_3$ (0.06 g, 0.56 mmol), *p*-$Me_2NC_6H_4SiH_3$ (0.09 g, 0.56 mmol) and $[Co_4(CO)_{12}]$ (0.32 g, 0.56 mmol) at 50 °C for 2 weeks gave $[Co_4(\mu_4\text{-}SiPh)_2(CO)_{11}]$ (**2c**) and $[Co_4(\mu_4\text{-}SiC_6H_4NMe_2)_2(CO)_{11}]$ (**2e**), together with $[Co_4(\mu_4\text{-}SiPh)(\mu_4\text{-}SiC_6H_4NMe_2)(CO)_{11}]$ (**2g**, 0.04 g, 8%). Mp 78–85 °C (dec.), ν_{CO} (petroleum spirits, cm^{-1}): 2075 vw, 2042 s, 2029 m, 2014 m, 1861 w, br. NMR: ^1H δ 8.22–6.94, (m, C_6H_5 and C_6H_4), 3.13 (s, CH_3); ^{13}C δ 203.4 (br, CO), 152.3 (C4), 135.9 (C2), 125.7 (C1), 111.3 (C3), 39.9 (CH_3), 138.7 (C1′), 134.5 (C2′), 131.8 (C4′), 128.8 (C3′). ESI-MS: *m/z* 798 $(M + H)^+$.

(f) Preparation of $[Co_4\{\mu_4\text{-}Si(CH_2)_3OMe\}_2(CO)_{11}]$ (2h). Similarly, a 50% solution of $MeO(CH_2)_3SiH_3$ (250 µL, *ca.* 0.135 g, 1.3 mmol) in Et_2O was sealed with a toluene solution (10 mL) of $[Co_4(CO)_{12}]$ (0.28 g, 0.5 mmol) and heated to 50 °C for 4 days. The ampoule was opened and the contents transferred to a Schlenk flask. Solvent was removed under vacuum and the sample extracted into CH_2Cl_2. Column chromatography using a 1 : 1 petroleum spirits–CH_2Cl_2 solvent mixture gave an orange fraction of $[Co_4\{\mu_4\text{-}Si(CH_2)_3OMe\}_2(CO)_{11}]$ (**2h**, 0.067 g, 0.09 mmol, 18%). The compound was significantly less stable than other clusters in this series so no attempt was made to recrystallise the sample. ν_{CO}, (CH_2Cl_2, cm^{-1}): 2083 w, 2039 s, 2019 m, sh, 2006 m,sh, 1979 m,sh, 1851 w. NMR: ^1H δ 3.69 (m, $-CH_2O$), 3.45 (m, CH_3), 2.92 (m, CH_2Si), 2.45 (m, $-CH_2-$); ^{13}C δ 203.3 (CO), 74.4 (CH_2O), 58.9 (CH_3), 28.3 ($-CH_2-$), 26.0 (CH_2Si).

Preparation of dimeric clusters

(a) $[\{Co_4(\mu_4\text{-}SiPh)(CO)_{11}Si\}_2C_6H_4]$ (3a). To a toluene solution (20 mL) of $[Co_4(CO)_{12}]$ (0.50 g, 0.88 mmol) was added $PhSiH_3$ (110 µL, 0.100 g, 0.93 mmol) and *p*-$(H_3Si)_2C_6H_4$ (13 µL, 0.010 g, 0.072 mmol). The mixture was sealed in an ampoule under vacuum and heated to 50 °C for 3 d. Column chromatography using a 4 : 1 petroleum spirits–CH_2Cl_2 solvent mixture gave (i) $[Co_4(CO)_{12}]$, (ii) orange $[Co_4(\mu_4\text{-}SiPh)_2(CO)_{11}]$ and (iii) orange $[\{Co_4(\mu_4\text{-}SiPh)(CO)_{11}Si\}_2C_6H_4]$ (**3a**, 0.030 g, 28%). Mp 88–96 °C. ν_{CO}, (CH_2Cl_2 cm^{-1}): 2086 vw, 2048 s, 2028 m, 2014 m, 1854 w. NMR: ^1H δ 8.51–7.68 (m, 14H, C_6H_5 and C_6H_4), ^{13}C δ 202.8 (br, CO), 139.7 (C1), 134.4 (C2), 132.1 (C4), 128.9 (C3), 140.9 (C1′), 125.8 (C2′). ESI-MS: *m/z* 1430 $(M)^+$. This compound was also identified by an X-ray crystal structure determination (see below).

(b) $[\{Co_4(\mu_4\text{-}SiC_6H_4OMe)(CO)_{11}Si\}_2C_6H_4]$ (3b). This was prepared similarly from *p*-$MeOC_6H_4SiH_3$ (0.06 g, 0.43 mmol), *p*-$(H_3Si)_2C_6H_4$ (0.03 g, 0.23 mmol) and $[Co_4(CO)_{12}]$ (0.30 g, 0.53 mmol) in toluene (20 mL) at 50 °C for two weeks. Yield of **3b**, 0.010 g, 3%. Mp 87–94 °C (dec.). ν_{CO}, (CH_2Cl_2, cm^{-1}): 2084 vw, 2046 s, 2027 m, 2012 m, 1854 w. NMR: ^1H δ 8.50–7.24 (m, C_6H_4), 3.98 (s, CH_3); ^{13}C δ 203.0 (br, CO), 160.4 (C4), 136.3 (C2), 130.1 (C1), 114.7 (C3), 141.5 (C1′), 125.8 (C2′), 55.4 (CH_3). ESI-MS: *m/z* 1490 $(M)^+$.

(c) $[\{Co_4(\mu_4\text{-}SiC_6H_4NMe_2)(CO)_{11}Si\}_2C_6H_4]$ (3c). Using the same procedure *p*-$Me_2NC_6H_4SiH_3$ (0.08 g, 0.53 mmol), *p*-$(H_3Si)_2C_6H_4$ (0.039 g, 0.28 mmol) and $[Co_4(CO)_{12}]$ (0.303 g, 0.53 mmol) in toluene (20 mL) at 50 °C for two weeks yielded after chromatography **3c**, 0.003 g, 1%. Mp 79–88 °C (dec.). ν_{CO}, (CH_2Cl_2, cm^{-1}): 2083 vw, 2045 s, 2024 m, 2012 m, 1850 w. ESI-MS: *m/z* 1516 $(M)^+$.

(d) $[\{Co_4(\mu_4\text{-}SiPh)(CO)_{11}Si\}_2(CH_2)_8]$ (4a). To a toluene solution (20 mL) of $[Co_4(CO)_{12}]$ (0.38 g, 0.67 mmol) was added $PhSiH_3$ (60 µL, 0.051 g, 0.47 mmol) and $H_3Si(CH_2)_8SiH_3$ (96 µL, 0.083 g, 0.47 mmol), and the mixture sealed in an ampoule under vacuum. The mixture was heated to 50 °C for 2 weeks. The ampoule was opened, the contents transferred to a Schlenk flask and solvent removed under vacuum. Column chromatography using a 5 : 1 petroleum spirits–CH_2Cl_2 solvent mixture gave (i) unreacted $[Co_4(CO)_{12}]$, (ii) $[Co_4(\mu_4\text{-}SiPh)_2(CO)_{11}]$ and (iii) an orange microcrystalline solid tentatively characterised as $[\{Co_4(\mu_4\text{-}SiPh)(CO)_{11}Si\}_2(CH_2)_8]$ (**4a**, 0.012 g, 0.008 mmol, 2%). ν_{CO}, (CH_2Cl_2, cm^{-1}): 2083 w, 2065 w, 2043 s, 2026 m,sh, 1835 w,br. NMR: δ ^1H 8.55–7.70 (m, 10H, C_6H_5), 0.8–1.9 (m, 16H, CH_2); ^{13}C δ 204.5 (CO), 134.6 (C2), 132.0 (C4), 129.1 (C3), 35.4 (C_γ), 31.0 (C_δ), 30.8 (C_β), 10.1 (C_α) (C1 was not detected).

(e) [{$Co_4(\mu_4$-$SiC_6H_4OMe)(CO)_{11}Si\}_2(CH_2)_8$] (4b). To a toluene solution (20 mL) of [$Co_4(CO)_{12}$] (0.35 g, 0.61 mmol) was added $MeOC_6H_4SiH_3$ (86 µL, 0.084 g, 0.61 mmol) and $H_3Si(CH_2)_8SiH_3$ (65 µL, 0.053 g, 0.31 mmol). The resultant mixture was sealed in an ampoule under vacuum and heated to 50 °C for 2 weeks after which the ampoule was opened, the contents transferred to a Schlenk flask and solvent removed under vacuum. TLC indicated the presence of unreacted [$Co_4(CO)_{12}$], [$Co_4(\mu_4$-$SiC_6H_4OMe)_2(CO)_{11}$], [{$Co_4(\mu_4$-$SiC_6H_4OMe)(CO)_{11}Si\}_2(CH_2)_8$] and an immobile orange product. These were separated by column chromatography using a 3 : 1 petroleum spirits–CH_2Cl_2 solvent mixture. The second orange fraction afforded [{$Co_4(\mu_4$-$SiC_6H_4OMe)(CO)_{11}Si\}_2(CH_2)_8$] (**4b**, 0.018 g, 0.012 mmol, 4%). ν_{CO}, (CH_2Cl_2, cm^{-1}): 2045 s, 2025 m,sh, 2010 m, sh, 1840 w,br. NMR δ ^1H 8.50, 7.55 (m, 8H, C_6H_4), 3.95 (s, 6H, CH_3), 0.7–2.0 (m, 16*H*); ^{13}C δ 205.3 (CO), 136.3 (C2), 114.8 (C3), 54.7 (CH_3), 36.0 (C_γ), 28.8 (C_δ), 28.6 (C_β), 9.3 (C_α).

(f) Attempted synthesis of [{$Co_4(\mu_4$-$SiC_6H_4NMe_2)(CO)_{11}$-$Si\}_2(CH_2)_8$]. To a toluene solution (10 mL) of [$Co_4(CO)_{12}$] (0.35 g, 0.6 mmol) was added $Me_2NC_6H_4SiH_3$ (0.1 g, 0.66 mmol) and $H_3Si(CH_2)_8SiH_3$ (50 µL, 0.42 g, 0.3 mmol), in an ampoule which was heated to 50 °C for 2 weeks. An electrospray mass spectrum of the crude reaction mixture showed a weak peak at *m*/*z* 1573, corresponding to the $(M + H)^+$ ion of the dimer **4c**, but work up gave only unreacted [$Co_4(CO)_{12}$] and [$Co_4(\mu_4$-$SiC_6H_4NMe_2)_2(CO)_{11}$].

X-Ray crystallography

Structure of [$Co_4(\mu_4$-$SiPh)_2(CO)_{11}$]·0.5C_7H_8. Intensely red crystals of **2c** were obtained from toluene. Data were collected on a Nicolet P3 four-circle diffractometer. Crystal data: $C_{23}H_{10}Co_4O_{11}Si_2$·0.5$C_7H_8$, M = 800.28, monoclinic, a = 9.460(10), b = 21.580(10), c = 14.850(10) Å, β = 90.09(10)°, U = 3032(4) Å^3, T = 173 K, space group $P2_1/n$, Z = 4, μ(Mo-Kα) = 2.28 mm^{-1}, 6401 reflections collected, 5960 unique (R_{int} = 0.015) used after correction for absorption ($T_{max,min}$ = 0.547, 0.297). Crystal dimensions 0.70 × 0.70 × 0.30 mm^3. Refinement on F^2 gave R_1 = 0.0365 [4328 data with $I > 2\sigma(I)$] and wR_2 = 0.0958 (all data). Structure solution and refinement were straightforward, except for the toluene molecule of crystallisation which was disordered about an inversion centre. The hydrogen atoms of the main molecule were included in calculated positions, but those of the solvent were omitted.

Structure of [{$Co_4(\mu_4$-$SiPh)(CO)_{11}(\mu_4$-$Si\}_2C_6H_4$]·1.5CH_2Cl_2. Deep orange crystals of **3a** were obtained from CH_2Cl_2–petroleum spirits. Data were collected on a Bruker CCD diffractometer. Crystal data: $C_{40}H_{14}Co_8O_{22}Si_4$·1.5$CH_2Cl_2$, M = 1557.7, monoclinic, a = 9.323(4), b = 18.192(7), c = 16.890(7) Å, β = 103.340(5)°, U = 2787(2) Å^3, T = 158 K, space group $P2_1$, Z = 2, μ(Mo-Kα) = 2.62 mm^{-1}, 34955 reflections collected, 11041 unique (R_{int} = 0.0456) used after correction for absorption ($T_{max,min}$ = 1.000, 0.825). Crystal dimensions 0.38 × 0.22 × 0.02 mm^3. Refinement on F^2 gave R_1 = 0.0469 [6524 data with $I > 2\sigma(I)$] and wR_2 0.1108 (all data). The asymmetric unit contained one ordered CH_2Cl_2 molecule and one disordered half-molecule of CH_2Cl_2. All non-hydrogen atoms were treated anisotropically except for C(92) of the disordered solvent molecule. Hydrogen atoms were included in calculated positions.

The structures of **2c** and **4a** are illustrated in Figs. 1 and 2 respectively, with selected bond parameters included in the captions to the figures.

The crystal structures were solved and refined using the SHELX programs.[20]

CCDC reference numbers 193182 and 193183.

See http://www.rsc.org/suppdata/dt/b2/b208347b/ for crystallographic data in CIF or other electronic format.

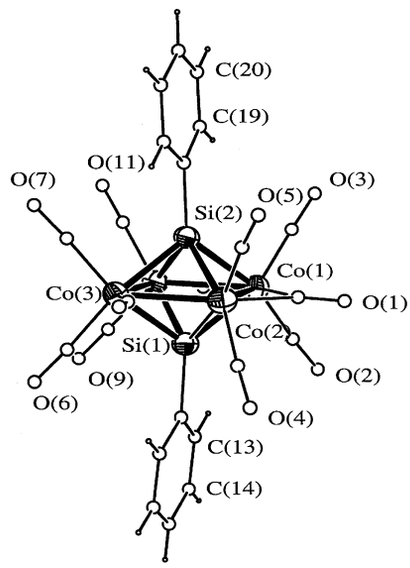


Fig. 1 The structure of the [$Co_4(\mu_4$-$SiPh)_2(CO)_{11}$] cluster **2c**. Selected bond lengths (Å): Co(1)–Co(2) 2.566(2), Co(2)–Co(3) 2.647(2), Co(3)–Co(4) 2.725(2), Co(1)–Co(4) 2.684(2), Co–Si (av.) 2.314(2), Si–C (av.) 1.870(3), Si ··· Si 2.705(2).

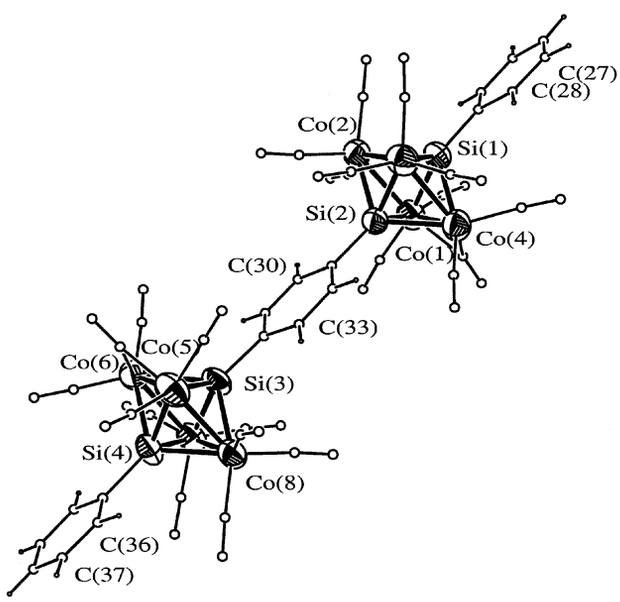


Fig. 2 The structure of the linked cluster **3a**, showing atom labelling. Selected bond lengths (Å): Co(1)–Co(2) 2.619(2), Co(2)–Co(3) 2.710(2), Co(3)–Co(4) 2.707(2), Co(1)–Co(4) 2.573(2), Co(5)–Co(6) 2.574(2), Co(6)–Co(7) 2.684(2), Co(7)–Co(8) 2.723(2), Co(5)–Co(8) 2.625(2), Co–Si (av.) 2.319(3), Si–C (av.) 1.870(9), Si ··· Si 2.729(3).

Results and discussion

Synthesis of [$Co_4(\mu_4$-$SiR)_2(CO)_{11}$] clusters

Following on from the earlier reports of [$Co_4(\mu_4$-$GePh)_2(CO)_{11}$] and [$Co_4(\mu_4$-$SiMe)_2(CO)_{11}$] from [$Co_4(CO)_{12}$] and $PhGeH_3$ or $MeSiH_3$ respectively,[7,10] we now report that $PhSiH_3$ reacts with [$Co_4(CO)_{12}$] to give reasonable yields of [$Co_4(\mu_4$-$SiPh)_2(CO)_{11}$] (**2c**). The reactions were carried out in either hexane or toluene solvent maintained at temperatures between 45–55 °C for periods of at least two days and up to two weeks. Reactions in hexane gave higher yields but required longer times. Although the reactions could be carried out in normal Schlenk apparatus, we found it more convenient to use sealed evacuated ampoules.

Spectroscopic characterisation of [$Co_4(\mu_4$-$SiPh)_2(CO)_{11}$] **2c** was straightforward, with an infrared spectrum matching that of the germanium analogue.[8] Under FAB conditions, the mass

spectrum showed a weak parent ion and others from CO-loss. Under electrospray ionisation mass spectral (ESI-MS) conditions a parent ion at *m*/*z* 754 corresponding to an $(M)^+$ ion generated by oxidation at the electrospray probe tip could sometimes be observed, but this was not always reproducible. We have shown that ESI-MS is a useful technique for analysing anionic clusters directly,[21] and neutral clusters with appropriate chemical ionisation,[19] since intact parent ions with little fragmentation are the norm under the gentle conditions possible. However, the use of Na(OMe) reagent for ionisation[19] did not lead to sensible results in the case of $[Co_4(\mu_4\text{-SiPh})_2(CO)_{11}]$. In order to facilitate the monitoring of the chemistry of the clusters by ESI-MS we extended the idea of introducing protonatable groups into the molecule so that $(M + H)^+$ ions could be readily formed, an approach that has been successful with derivatised "electrospray-friendly" ligands such as $(p\text{-}Me_2NC_6H_4)_3P$.[22] To this end, we explored both *p*-NMe_2 and *p*-OMe substituted phenyl silanes as substrates for cluster formation.

Following the method for the unsubstituted analogues, the symmetrical $[Co_4(\mu_4\text{-}SiC_6H_4X)_2(CO)_{11}]$ (**2d**,**e**) as well as the unsymmetrical $[Co_4(\mu_4\text{-}SiC_6H_4X)(\mu_4\text{-SiPh})(CO)_{11}]$ (**2f**,**g**) (X = OMe, NMe_2) clusters were readily prepared. The clusters with NMe_2 groups behaved as expected and gave strong $(M + H)^+$ ions under ESI-MS conditions, but surprisingly those with the less basic OMe groups did not give the corresponding signals. Unfortunately, although the NMe_2 was the functional group of choice to facilitate ESI-MS studies, the Si_2Co_4 clusters were significantly lower-yielding, with more side-products than for the other silanes used.

The cluster with $\mu_4\text{-}Si(CH_2)_3OMe$ capping groups, (**2h**), was also prepared by the same method, but this was less readily handled than the aryl examples, and did not give $(M + H)^+$ signals in the ESI-MS, so it was not developed further.

All of the Si_2Co_4 clusters formed are electron-rich 8-SEP examples, showing no tendency to eliminate CO and adopt 7-SEP forms. In this they parallel Ge_2Co_4 clusters and contrast with P_2Fe_4 analogues.[2,12]

Linked clusters

There is interest in linking metal carbonyl clusters together to give dimers and (potentially) higher oligomers because of the unusual electronic and other properties the materials might have.[23] Previously Jaeger and Vahrenkamp[24] have linked two and three $[Fe_4(\mu_4\text{-PPh})_2(CO)_{10}]$ clusters together *via* the di-functional Lewis bases *p*-$[(MeO)_2P]_2C_6H_4$ and *p*-$(CN)_2C_6H_4$, and a dimer of C_2Co_3 clusters linked by a di-alkyne unit has been examined in detail for $[Me_3SiCCo_3(Cp)_3C\text{–}C{\equiv}C\text{–}]_2$.[25]

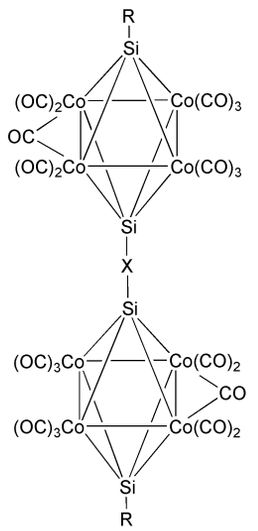
We envisaged that the use of di-functional silanes would possibly lead to linked clusters, where the linking atoms were part of the cluster core. This proved to be the case. When a mixture of $PhSiH_3$ (as capping group), *p*-$(H_3Si)_2C_6H_4$ (as linking moiety), and $[Co_4(CO)_{12}]$ was heated in toluene, the linked cluster **3a** could be isolated in up to 28% yields, together with the monomeric cluster **2c**. The dimer **3a** showed a CO-region infrared spectrum essentially the same as that of the monomer and an NMR spectrum consistent with the proposed structure. The ESI-MS gave a clear signal at *m*/*z* 1430 corresponding to the $(M)^+$ ion of the dimer, and full characterisation was by an X-ray crystal structure determination, discussed below.

The corresponding dimers **3b** and **3c** with substituted terminal aryl groups were similarly obtained from *p*-$XC_6H_4SiH_3$, *p*-$(H_3Si)_2C_6H_4$ and $[Co_4(CO)_{12}]$.

Another linking reagent, $H_3Si(CH_2)_8SiH_3$, was also explored and the dimers **4a** and **4b** were isolated and tentatively characterised, but yields were never more than 5%.

Other than the coupled $C_2Co_3Cp_3$ example mentioned above,[25] clusters **3** and **4** are the first examples of clusters linked in such a way that the organic backbone is incorporated into the oligomer chain of the cluster itself. Other carbonyl examples link clusters using a di-functional Lewis base which becomes part of the ligand sphere of the clusters,[24] ostensibly a more labile arrangement.

Potentially, higher oligomers should be possible by varying the ratio of capping to linking silanes, but we were not able to demonstrate other than dimers from any of the reactions.



3a X = -C_6H_4- R = -Ph
3b X = -C_6H_4- R = -C_6H_4OMe
3c X = -C_6H_4- R = -$C_6H_4NMe_2$
4a X = -$(CH_2)_8$- R = -Ph
4b X = -$(CH_2)_8$- R = -C_6H_4OMe
4c X = -$(CH_2)_8$- R = -$C_6H_4NMe_2$

Structural determinations

The structures of the monomer **2c** and the dimer **3a** were determined for comparison. They are illustrated in Figs. 1 and 2.

The monomer **2c** has the expected quadrilateral plane of four cobalt atoms, quadruply bridged on each side by SiPh groups. The eleven CO groups are distributed so that there are two terminal COs on each cobalt atom, there is one fully bridging CO across the Co(1)–Co(2) edge, while the remaining two COs are semi-bridging the Co(1)–Co(4) and Co(2)–Co(3) edges. This arrangement affects the Co–Co distances so that Co(1)–Co(2) < Co(1)–Co(4) ≅ Co(2)–Co(3) < Co(3)–Co(4). Despite the inequivalence of the cobalt atoms, the Si–Co distances are all similar (average 2.314 Å), marginally longer than the corresponding bonds in the $Co_4(\mu_4\text{-SiMe})_2(CO)_{11}$ cluster (2.309 Å).[10] The formally non-bonded Si ··· Si distance of 2.705(2) Å is remarkably short, and only marginally longer than the Si–Si bond of 2.686 Å in $Si_2(Bu^t)_6$.[26]

The structure of the dimer **3a** is shown in Fig. 2. Despite the potential symmetry of the molecule, it crystallised in the non-centrosymmetric space group $P2_1$. However, the molecules do have approximate inversion symmetry. As expected, there are two cluster units, each with a capping (μ_4-SiPh) group, linked together by a Si–C_6H_4–Si moiety. This generates a long molecule, over 23 Å from end-to-end.

The two Si_2Co_4 cores in **3a** are each similar to the same unit in the monomeric compound **2c**, with no statistically significant differences in corresponding Si–Co or Co–Co bond lengths. The only differences are in a slightly longer Si ··· Si distance [2.729(3) Å average], and a less symmetrical arrangement of the bridging and semi-bridging CO ligands around the equatorial plane. Within the bridging unit the Si–C and C–C distances are all normal, showing no indication of any delocalised bonding between the two halves. The three phenyl rings are coplanar to within ±6°, but this is presumably due to steric interactions between the rings and the terminal CO ligands on the clusters, rather than to any electronic requirements.

Electrochemistry of $[Co_4(\mu_4\text{-}SiR)_2(CO)_{11}]$ clusters

Cyclic and square wave voltammetry was performed on $[Co_4(\mu_4\text{-}SiC_6H_4R)_2(CO)_{11}]$ (R = H, OMe, NMe_2) clusters **2c–f** in CH_2Cl_2 with potentials referenced against decamethylferrocene. Primary voltammetric profiles were remarkably similar for all clusters. In each case there was a one-electron oxidation process at ~0.95 V, **A** and a non-Nernstian reduction wave at ~−1.2V, **B** with a current relative to **A** greater than one-electron (the relative current varies with scan rate). The chemical reversibility of **A** was dependent on scan rate, temperature, the condition of the electrode and the cluster; $i_c/i_c = 1$ at 200 mV s^{-1} for **2e** and 0.3 for **2c**. A cathodic scan subsequent to **A** produced a new reduction wave **C** at ~−0.4 V the current of which was linked to the reversibility of **A**. The reduction step **B** was irreversible at all scan rates and a shape consistent with two or more steps with E_{pc} close to −1.2 V.

OTTLE spectra were used to assist in the identification of the decomposition and ECE products. Electrochemical oxidation generated new bands at 2063, 2055 and 2035 cm^{-1} attributed to the decomposition product $[Co_4(CO)_{12}]$, which is also responsible for the reduction wave **C** and bands due to $[Co(CO)_4]^-$; on the timescale of the OTTLE experiment we were unable to identify the ν(CO) bands due to $\mathbf{2e}^+$. IR analysis during the reduction of **2e** at −1.2 V displayed (Fig. 3) a decrease in the intensity of the signals attributed to the parent cluster (2079, 2039, 2023, 2008 and 1849 cm^{-1}), with new signals detected at 1943, 1923, 1909 and 1751 cm^{-1}. In essence, the spectrum of the reduced species is similar to that of the parent cluster but shifted to lower wavenumber, the shift attributed to the formation of a radical anionic species, possibly $[Co_4(\mu_4\text{-}SiR)_2(CO)_{11}]^{-\bullet}$ (the Group 14 analogue of $[Co_4(\mu_4\text{-}PPh)_2(CO)_{10}]^{-\bullet}$).[14]

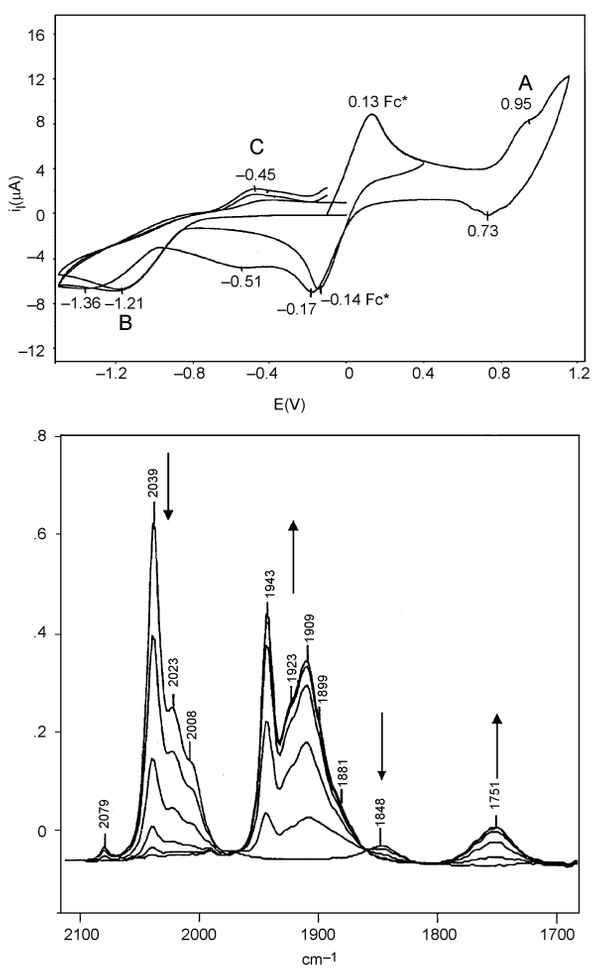
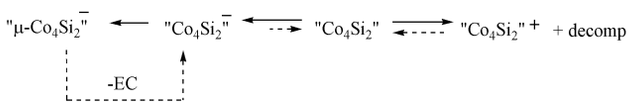


Fig. 3 The cyclic voltametric scan of $[Co_4(\mu_4\text{-}SiC_6H_4NMe_2)_2(CO)_{11}]$ (**2e**) (upper) and FTIR spectrum of the first reduction process (lower).

The formation of this radical anion accounts for the observed signals, especially the 1751 cm^{-1} absorbance attributed to μ-CO in an anionic cluster (a similar pattern was reported for the radical anion of $[Fe_4(\mu_4\text{-}PPh)_2(CO)_{11}]$).[13] These OTTLE and voltammetric data for the reduction process are consistent with a fast structural conversion to a μ species which is oxidized at a potential close to −1.2 V (Scheme 1).



Scheme 1

The dimeric cluster **3a** was also examined under the same conditions. Electrochemical responses were essentially the same as for the monomer, indicating that the two cluster units were acting independently, and that there was no electronic communication across the linking $Si–C_6H_4–Si$ group. This contrasts with the linked $C_2Co_3Cp_3$ examples where electronic interaction *via* the linking alkyne chain was significant.[25]

Conclusion

Synthesis of $[Co_4(\mu_4\text{-}SiR)_2Co_4(CO)_{11}]$ clusters is clearly general for a range of R groups. The use of bi-functional silanes $H_3Si–X–SiH_3$ provides a systematic way of linking clusters together. By using different X groups rigid or flexible molecules are accessible, and suitable choices of X should lead to products where the cluster centres are either interacting or isolated electronically. It seems likely that a suitable choice of ratios of capping : linking : $[Co_4(CO)_{12}]$ will lead to higher oligomers (or even polymers in the absence of capping silanes) although we have not yet found conditions to achieve this. Extension to linking $[Co_4(\mu_4\text{-}GeR)_2(CO)_{11}]$ or $[Fe_4(\mu_4\text{-}PR)_2(CO)_{10}]$ using appropriate difunctional germanes and phosphines are obvious.

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