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Preliminary communication

$[\mu_4\text{-SiCo(CO)}_4]_2\text{Co}_4\text{(CO)}_{11}$, a cobalt carbonyl cluster incorporating five-coordinate silicon

Martin Van Tiel, Kenneth M. Mackay* and Brian K. Nicholson*
School of Science, University of Waikato, Hamilton (New Zealand)

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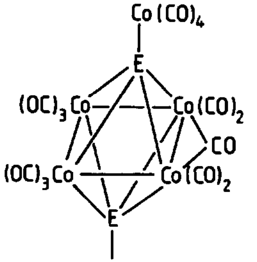
Abstract

Si_2H_6 reacts with $Co_2(CO)_8$ to form $Si_2Co_6(CO)_{19}$, shown by X-ray structure analysis to contain a pseudo-octahedral *trans*-Si_2Co_4 core with terminal $Co(CO)_4$ groups on the silicon atoms. This is the first silicon example of a compound with the E_2M_4 type with M = transition metal and E = main group element, and has the silicon in a distorted square-pyramidal configuration, with a Si...Si distance of 2.817 Å.

Germanium hydrides react with cobalt carbonyl under mild conditions to yield an interesting range of open and closed clusters. For example, Ge_2H_6 gave the pseudo-octahedral cluster of the E_2M_4 type, $[\mu_4\text{-GeCo(CO)}_4]_2\text{Co}_4\text{(CO)}_{11}$, (**1a**), via the facile decarbonylation of the open species $Ge_2Co_6(CO)_{20}$, [1]. Similar reactions of silicon hydrides have been less studied, but SiH_4 parallels GeH_4 in yielding the open cluster $Si[Co_2(CO)_7]_2$ (**2**), with a *spiro*-silicon [2], which readily loses CO to give the closed cluster [3] $(CO)_4CoSiCo_3(CO)_9$ (**3**), an example of the pyramidal EM_3 class [4].



1a E = Ge
1b E = Si

While E_2M_4 species are well established for E = P and M = Co, Fe, Ru [5–7], and examples have been described for E = S, As and Te [8–10], the only Group IV

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examples described are Ge_2Co_4 species [1,11,12]. This communication describes the first example with E = Si.

The slow reaction of disilane with cobalt carbonyl in hexane proceeds as in eq. 1 *:

$$\mathrm{Si_2H_6 + Co_2(CO)_8 \rightarrow \underset{(\mathbf{1b})}{Si_2Co_6(CO)_{19}} + \underset{(\mathbf{2})}{Si[Co_2(CO)_7]_2} + \underset{(\mathbf{3})}{(CO)_4CoSiCo_3(CO)_9} + 3H_2 + \mathit{n}(CO)} \tag{1}$$

In different runs 30–50% of the silicon ended up in **1b** and the rest was found in the mono-silicon species **2** and **3**. Purification of **1b** makes use of its lower solubility compared with the lower molecular mass co-products.

The new complex was characterised by the close similarity of the carbonyl-region infrared spectrum to that of the germanium analogue and by mass spectrometry, while the geometry of the new cluster was further defined by a single-crystal X-ray study **.

The molecular structure of $[\mu_4\text{-SiCo(CO)}_4]_2Co_4(CO)_{11}$, is shown in Fig. 1, which also includes selected bond parameters. The central Co_4 quadrilateral coincides with a crystallographic mirror plane, and is capped on both sides by μ_4 silicon atoms, each of which bears a terminal $Co(CO)_4$ unit. Two of the cluster cobalt atoms carry three terminal carbonyl ligands, while the other two have two terminal carbonyls and share one edge-bridging CO; there are therefore two pairs of chemically inequivalent cobalt atoms. To compensate for the lower electron count on Co(1) and Co(4) the equatorial carbonyl ligands on Co(2) and Co(3) are bent into semi-bridging positions, and the silicon atoms lie further from the electron-rich cobalt atoms. The overall structure is closely related to that of the isomorphous germanium analogue, the main difference being that the smaller silicon atom leads to a more compact cluster (Si–Co(av.) 2.336, Co–Co(av) 2.635 Å) than the corresponding

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* In a typical run Si_2H_6 and $Co_2(CO)_8$ in a 1 to 2.9 ratio were sealed in an ampoule with hexane, and left for 4 months. After pumping off the hexane the residue was repeatedly extracted with small amounts of hexane then CH_2Cl_2 to remove the monosilicon species **2** and **3**, identified spectroscopically [2,3]. The residue was recrystallised from warm CH_2Cl_2 to give $Si_2Co_6(CO)_{19}$ (**1b**) in 30% yield. Infrared: ν(CO) (CH_2Cl_2) 2101s, 2074w, 2053s,sh, 2041vs, 2019m, 2004m, 1850w,br cm^{-1}. The mass spectrum showed the parent ion and all fragment ions corresponding to nineteen consecutive losses of carbonyl groups to $Si_2Co_6^+$. Another prominent series starting at m/e 600 can be assigned to $Si_2Co_4(CO)_x^+$, $x = 11–0$.

** A dark-orange diamond-shaped crystal 0.56×0.36×0.14 mm was obtained from CH_2Cl_2. Preliminary precession photography showed orthorhombic symmetry. Intensity data were obtained on a Nicolet XRD P3 diffractometer using monochromated Mo-K_α X-rays.

Crystal data. $C_{19}Co_6O_{19}Si_2$, M = 941.97, orthorhombic, space group *Cmca*, a 17.527(2), b 12.585(1), c 26.179(4) Å, U 5774.5 Å^3. D_c 2.17 g cm^{-1} for $Z = 8$. $F(000)$ 3648, μ(Mo-K_α) 34 cm^{-1}. T 133 K. Intensity data in the range $4° < 2\theta < 55°$ were collected using a θ–2θ scan technique. Absorption corrections were applied (max, min transmission factors 0.98, 0.72, respectively). A total of 3421 unique reflexions were collected and those 2609 for which $I > 3\sigma(I)$ were used in all calculations.

The structure was developed using the atom positions of the isomorphous germanium compound [1]. Full-matrix least-squares refinement with all atoms anisotropic, converged at $R = 0.0575$, $R_w = 0.0693$ where $w = [\sigma^2(F) + 0.00655F^2]^{-1}$. The highest peak in a final difference map was < 0.7 e Å^{-3} near a Co atom. All calculations were performed with SHELX-76 [13]. Atomic coordinates and a list of bond lengths and angles has been deposited with the Cambridge Crystallographic Data Centre.

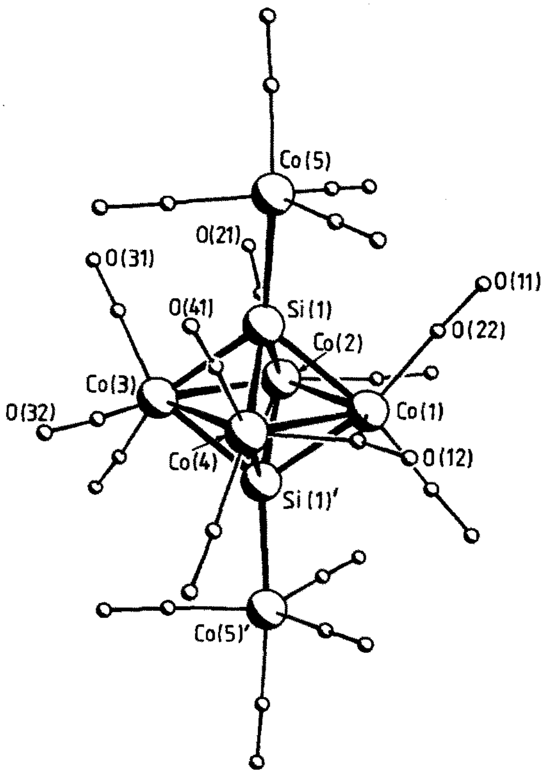

Fig. 1. A PLUTO diagram of the structure of $[\mu_4\text{-SiCo(CO)}_4]_2\text{Co}_4\text{(CO)}_{11}$ (**1b**). Bond lengths: Si(1)–Co(1) 2.330(2), Si(1)–Co(2) 2.351(2), Si(1)–Co(3) 2.360(2), Si(1)–Co(4) 2.308(2), Si(1)–Co(5) 2.347(2), Co(1)–Co(2) 2.623(2), Co(1)–Co(4) 2.569(2), Co(2)–Co(3) 2.653(2), Co(3)–Co(4) 2.696(2), Si(1)...Si(1)' 2.817 Å.

Ge_2Co_4 core (Ge–Co(av) 2.413, Co–Co(av) 2.676 Å [1]). The silicon example is also less symmetric, particularly in the arrangement of the bridging and semi-bridging carbonyl ligands, but the high thermal parameters found for these atoms in the crystal structure (even at 133 K) suggest that they are easily displaced; distortions from a regular geometry are therefore probably not significant.

There are no other examples where a silicon atom participates in five Si–M bonds. As expected, the Si–Co bond lengths in **1b** are longer (by 0.12 Å) than those in $(CO)_4CoSiCo_3(CO)_9$, (3), in which the silicon atom is four-coordinate [3].

The Si...Si distance of 2.817 Å is much less than twice the Van der Waals radius of Si, although significantly longer than an Si–Si bond (ca. 2.35 Å). Some interaction is therefore probable between the two silicon atoms, and by comparison with the results of a detailed theoretical analysis of P_2Co_4 clusters [14] it can be assumed to be bonding, although perhaps less so than for the phosphorus complex, in which the P...P distances are comparatively shorter (ca. 2.4 Å).

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