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Synthesis of the square-bipyramidal cluster $[Co_4(\mu_4\text{-}SiMe)_2(CO)_{11}]$ by two routes and its reaction with $GeMe_2H_2$. The crystal structures of $[Co_4(\mu_4\text{-}SiMe)_2(CO)_{11}]$ and $[Co_4(\mu_4\text{-}SiMe)_2\{\mu\text{-}GeMe_2\}(CO)_{10}]$

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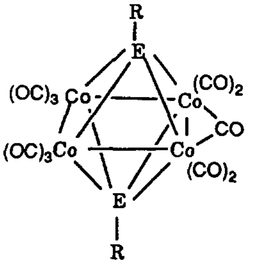
Abstract

$[Co_4(\mu_4\text{-}SiMe)_2(CO)_{11}]$ (**1a**) is the major product from the reaction of $[Co_2(CO)_8]$ with $[Fe(SiMeH_2)_2(CO)_4]$ (synthesised from $SiMeH_2Cl$ and $Na_2[Fe(CO)_4]$). An alternative, quantitative synthesis of **1a** is from $SiMeH_3$ and $[Co_4(CO)_{12}]$. **1a** reacts with an equimolar amount of $GeMe_2H_2$ to form in high yield $[Co_4(\mu_4\text{-}SiMe)_2\{\mu\text{-}GeMe_2\}(CO)_{10}]$ (**2**), in which the μ-$GeMe_2$ group has replaced the bridging carbonyl of the parent compound. Molecular structures were determined for **1a** and **2**.

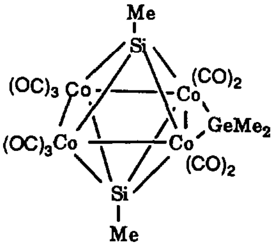
1. Introduction

There is usually a close parallel between the reactions of silicon and germanium hydrides with cobalt carbonyl, although the products often exhibit quite different stabilities. An example is the reaction of GeH_4 or SiH_4 with $[Co_2(CO)_8]$, in which spiro clusters $[\mu_4\text{-}E\{Co_2(CO)_7\}_2]$ (E = Si [1,2], Ge[3]) are formed in good yields. In both cases the clusters can be decarbonylated by gentle heating to form $[Co_3\{\mu_3\text{-}ECo(CO)_4\}(CO)_9]$. An example which demonstrates the parallels in reactivity but differences in stabilities is the reaction of Ge_2H_6 or Si_2H_6 with $[Co_2(CO)_8]$. Digermane forms the extended *spiro* cluster $[Co_2\{\mu_4\text{-}GeCo_2(CO)_7\}_2(CO)_6]$ in good yield, and only on subsequent heating does decarbonylation convert this into $[Co_4\{\mu_4\text{-}GeCo(CO)_4\}_2(CO)_{11}]$ (**1d**) [4]. In contrast disilane forms $[Co_4\{\mu_4\text{-}SiCo(CO)_4\}_2(CO)_{11}]$ (**1c**) directly at room temperature, and the intermediate $[Co_2\{\mu_4\text{-}SiCo_2(CO)_7\}_2(CO)_6]$ can only be isolated with difficulty [5,6].

There is now an extensive list of clusters incorporating E_2M_4 cores, where E is an element from Groups 14–16 and M = Co or Fe [7]. These are of interest because of the possibilities of structural isomerism (pseudo-octahedral *versus* bitetrahedral [8]), and because they have electron counts in excess of those predicted by Wade's rules; these features are now understood theoretically [8,9]. Examples of this type have also been shown to exhibit catalytic activity [10], and reactivity patterns have been established [11]. Most commonly, E is a Group 15 element. For Group 14, several examples with E = Ge have been described [4,12,13], but $[Co_4\{\mu_4\text{-}SiCo(CO)_4\}_2(CO)_{11}]$ (**1c**) is the only reported example with E = Si [5].



1a. E = Si; R = Me
1b. E = Ge; R = Me
1c. E = Si; R = $Co(CO)_4$
1d. E = Ge; R = $Co(CO)_4$



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We have recently established a number of alternative routes to clusters with a Ge_2Co_4 core [12], and now report two corresponding syntheses of the Si_2Co_4

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cluster **1a**, and describe the reaction of **1a** with $GeMe_2H_2$ to give $[Co_4(\mu_4\text{-}SiMe)_2\{\mu\text{-}GeMe_2\}(CO)_{10}]$ (**2**).

2. Results and discussion

The reaction of $[Fe(GeMeH_2)_2(CO)_4]$ with $[Co_2(CO)_8]$ produced $[Co_2\{\mu\text{-}Ge(Me)Co(CO)_4\}_2(CO)_6]$ as the major identified product [14] and subsequent mild heating gave $[Co_4(\mu_4\text{-}GeMe)_2(CO)_{11}]$ (**1b**) [12]. A similar reaction between $[Fe(GeH_3)_2(CO)_4]$ and $[Co_2(CO)_8]$ produced $[Co_2\{\mu_4\text{-}GeCo_2(CO)_7\}_2(CO)_6]$, which again could be converted to a Ge_2Co_4 cluster, $[Co_4\{\mu_4\text{-}GeCo(CO)_4\}_2(CO)_{11}]$ (**1d**) by mild heating [15]. This suggested that $[Co_4(\mu_4\text{-}SiMe)_2(CO)_{11}]$ (**1a**) could be prepared by use of the appropriate silyl-iron compound $[Fe(SiMeH_2)_2(CO)_4]$ (**3**).

2.1. *Preparation of $[Fe(SiMeH_2)_2(CO)_4]$ (3)*

Since $GeMeH_2Cl$ reacts with $Na_2[Fe(CO)_4]$ to produce good yields of $[Fe(GeMeH_2)_2(CO)_4]$ [16,17], and SiH_3I with $Na_2[Fe(CO)_4]$ gives $[Fe(SiH_3)_2(CO)_4]$ [18], the analogous formation of **3** from $SiMeH_2Cl$ and $Na_2[Fe(CO)_4]$ was investigated. The reaction proceeded smoothly (eqn. (1)).

$$Na_2[Fe(CO)_4] + 2SiMeH_2Cl \rightarrow \underset{(\mathbf{3})}{[Fe(SiMeH_2)_2(CO)_4]} + 2NaCl \qquad (1)$$

The major product was characterised as $[Fe(SiMeH_2)_2(CO)_4]$ (**3**) on the basis of the method of preparation, from its subsequent reations (see below) and from an infrared spectrum which closely matched that of the germanium analogue [17]. Full characterisation was not possible because **3** was very unstable, decomposing to an uncharacterised involatile, very air-sensitive oily liquid and $SiMeH_3$ on standing at room temperature. It is possible that $[Fe(SiMeH_2)_2(CO)_4]$ undergoes a rapid condensation reaction as outlined in eqn. (2), since $[Fe(GeMeH_2)_2(CO)_4]$ is known to undergo this type of reaction, quantitatively forming $[Fe(\mu\text{-}GeMeH)(CO)_4]_2$ and $GeMeH_3$ [17].

$$2[Fe(SiMeH_2)_2(CO)_4] \rightarrow [Fe(\mu\text{-}SiMeH)(CO)_4]_2 + 2SiMeH_3 \qquad (2)$$

The instability of **3** is not unexpected since $[Fe(GeMeH_2)_2(CO)_4]$ is less stable than $[Fe(GeH_3)_2(CO)_4]$ [17], and $[Fe(SiH_3)_2(CO)_4]$ [18] is less stable than $[Fe(GeH_3)_2(CO)_4]$, so it is reasonable to expect $[Fe(SiMeH_2)_2(CO)_4]$ to be the least stable of these four complexes.

2.2. *Preparation of $[Co_4(\mu_4\text{-}SiMe)_2(CO)_{11}]$ (1a)*

Although $[Fe(SiMeH_2)_2(CO)_4]$ was very unstable, its reaction with $[Co_2(CO)_8]$ in pentane was found to proceed rapidly. The major isolated product was $[Co_4(\mu_4\text{-}SiMe)_2(CO)_{11}]$ but there was also an unstable pentane-soluble fraction. The infrared spectrum indicated this unstable product may be $[Co_2\{\mu\text{-}Si(Me)Co(CO)_4\}(CO)_7]$ by comparison with the germanium analogue which was found in the $[Fe(GeMeH_2)_2(CO)_4] + [Co_2(CO)_8]$ reaction [12].

The overall reaction sequence is probably that outlined in eqn. (3), in parallel with the germanium system [12].

$$[Fe(SiMeH_2)_2(CO)_4] + [Co_2(CO)_8] \rightarrow [Fe\{Si(Me)[Co(CO)_4]_2\}(CO)_4] + 2H_2 \qquad (3)$$

$$\downarrow$$

$$\mathbf{1a} + 3CO \leftarrow [Co_2\{\mu Si(Me)Co(CO)_4\}_2(CO)_6] + \text{“}Fe(CO)_4\text{”} + 2CO$$

The open-chain compound $[Co_2\{\mu\text{-}Si(Me)Co(CO)_4\}_2(CO)_6]$ could not be isolated, but would be expected to condense rapidly to **1a** by analogy with the facile formation of $[Co_4\{\mu_4\text{-}SiCo(CO)_4\}_2(CO)_{11}]$ from $[Co_2\{\mu_4\text{-}SiCo_2(CO)_7\}_2(CO)_6]$ [5]. In these reactions the $Fe(CO)_4$ acts as a template, holding the $SiMeH_2$ groups in close proximity for reaction with $[Co_2(CO)_8]$. The extrusion of the $Fe(CO)_4$ unit must occur reasonably late in the reaction otherwise more mono-silyl products would be expected. The fate of the $Fe(CO)_4$ remains unclear; some was found as $Fe(CO)_5$ but this was not quantified.

The instability and difficult isolation of $[Fe(SiMeH_2)_2(CO)_4]$ make this first route to **1a** less useful than the alternative synthesis discussed below, but the method may find application in preparing mixed clusters $[Co_4(\mu_4\text{-}SiR)(\mu_4\text{-}SiR')(CO)_{11}]$ via mixed species $[Fe(SiRH_2)(SiR'H_2)(CO)_4]$ [cf. ref. 16].

The reaction of $GeRH_3$ with $[Co_4(CO)_{12}]$ has been shown to give $[Co_4(\mu_4\text{-}GeR)_2(CO)_{11}]$ in quantitative yield [12]. The parallel reaction with silanes therefore appeared to have potential as an alternative route to analogous silyl clusters. Indeed $SiMeH_3$ and $[Co_4(CO)_{12}]$ reacted together smoothly to give $[Co_4(\mu_4\text{-}SiMe)_2(CO)_{11}]$ (**1a**) as in eqn. (4) although the rate was distinctly slower than for the equivalent germane.

$$[Co_4(CO)_{12}] + 2SiMeH_3 \rightarrow \mathbf{1a} + CO + 3H_2 \qquad (4)$$

The elimination of H_2 and CO and the yield of **1a** were essentially quantitative which indicates that, as with the germanium analogue, the reaction is very specific. A reaction in a sealed tube was considerably slower than those in vessels with taps where the incondensable gases were periodically removed. The ready availability of starting materials and the high yields make this the best route to **1a**, despite the relatively long times needed for complete reaction. Although we have only investigated the reaction with one silane, this synthesis should prove to be as general for silanes as it has been shown to be for germanes. The possible reaction pathways and intermediates in the reaction have been discussed previously for the $GeMeH_3$/[$Co_4(CO)_{12}$] system [12].

2.3. *Properties of [$Co_4(\mu_4$-$SiMe)_2(CO)_{11}$]*

The carbonyl vibrations of **1a**, listed in the experimental section, match closely those of the germanium analogue **1b** [12] with a slight shift to higher frequency as is often observed for silicon compounds when compared to their germanium analogues. The highest envelope in the mass spectrum of **1a** is assigned to [P–CO]$^+$;

TABLE 1. Selected bond lengths (Å) and angles (deg.) for the structures of **1a** and **2**

1a bond lengths			
Co(1)–Co(1′)	2.690(2)	Co(2)–C(21)	1.790(6)
Co(1)–Co(2)	2.652(1)	Co(2)–C(22)	1.809(7)
Co(1)–Si(1)	2.320(2)	Co(2)–C(23)	2.509(6)
Co(1)–S(2)	2.311(2)	Si(1)–C(1)	1.862(9)
Co(1)–C(11)	1.797(7)	Si(2)–C(2)	1.872(9)
Co(1)–C(12)	1.814(6)	C(3)–O(3)	1.162(9)
Co(1)–C(23)	1.787(8)	C(11)–O(11)	1.131(8)
Co(2)–Co(2)	2.548(2)	C(12)–O(12)	1.133(7)
Co(2)–Si(1)	2.303(2)	C(21)–O(21)	1.141(7)
Co(2)–Si(2)	2.302(2)	C(22)–O(22)	1.135(7)
Co(2)–C(3)	1.917(6)	C(23)–O(23)	1.148(8)
1a bond angles			
Co(2)–Co(1)–Si(1)	54.7(1)	Co(1)–Si(1)–Co(2)	70.0(1)
Co(2)–Co(1)–Si(2)	54.7(1)	Co(2)–Si(1)–Co(2)	67.2(1)
Si(1)–Co(1)–Si(2)	72.1(1)	Co(1)–Si(2)–Co(1)	71.2(1)
Co(1)–Co(2)–Si(1)	55.3(1)	Co(1)–Si(2)–Co(2)	70.2(1)
Co(1)–Co(2)–Si(2)	55.1(1)	Co(2)–Si(2)–Co(2)	67.2(1)
Si(1)–Co(2)–Si(2)	72.6(1)	Co(2)–C(3)–Co(2)	83.3(3)
Co(1)–Si(1)–Co(1)	70.8(1)	Co(1)–C(23)–O(23)	165.4(6)
2 bond lengths			
Ge(1)–Co(1)	2.320(1)	Co(2)–Si(1)	2.325(2)
Ge(1)–Co(2)	2.352(1)	Co(2)–Si(2)	2.311(2)
Ge(1)–C(3)	1.964(7)	Co(3)–Co(4)	2.715(1)
Ge(1)–C(4)	1.941(7)	Co(3)–Si(1)	2.307(2)
Co(1)–Co(2)	2.692(1)	Co(3)–Si(2)	2.313(2)
Co(1)–Co(4)	2.634(1)	Co(4)–Si(1)	2.321(2)
Co(1)–Si(1)	2.299(2)	Co(4)–Si(2)	2.324(2)
Co(1)–Si(2)	2.291(2)	Si(1)–Si(2)	2.686(3)
Co(2)–Co(3)	2.599(1)	Si(1)–C(1)	1.870(7)
Si(2)–C(2)	1.866(8)		
2 bond angles			
Co(1)–Ge(1)–Co(2)	70.4(1)	Si(1)–Co(4)–Si(2)	70.6(1)
Co(1)–Ge(1)–C(3)	119.3(2)	Co(1)–Si(1)–Co(2)	71.2(1)
Co(1)–Ge(1)–C(4)	120.5(2)	Co(1)–Si(1)–Co(3)	108.6(1)
Co(2)–Ge(1)–C(3)	118.8(2)	Co(1)–Si(1)–Co(4)	69.5(1)
Co(2)–Ge(1)–C(4)	118.9(2)	Co(2)–Si(1)–Co(3)	68.3(1)
C(3)–Ge(1)–C(4)	106.2(3)	Co(2)–Si(1)–Co(4)	109.1(1)
Co(2)–Co(1)–Co(4)	90.5(1)	Co(3)–Si(1)–Co(4)	71.8(1)
Si(1)–Co(1)–Si(2)	71.6(1)	Co(1)–Si(2)–Co(2)	71.6(1)
Co(1)–Co(2)–Co(3)	89.9(1)	Co(1)–Si(2)–Co(3)	108.6(1)
Si(1)–Co(2)–Si(2)	70.8(1)	Co(1)–Si(2)–Co(4)	69.6(1)
Co(2)–Co(3)–Co(4)	90.8(1)	Co(2)–Si(2)–Co(3)	68.4(1)
Si(1)–Co(3)–Si(2)	71.1(1)	Co(2)–Si(2)–Co(4)	109.5(1)
Co(1)–Co(4)–Co(3)	88.7(1)	Co(3)–Si(2)–Co(4)	71.7(1)

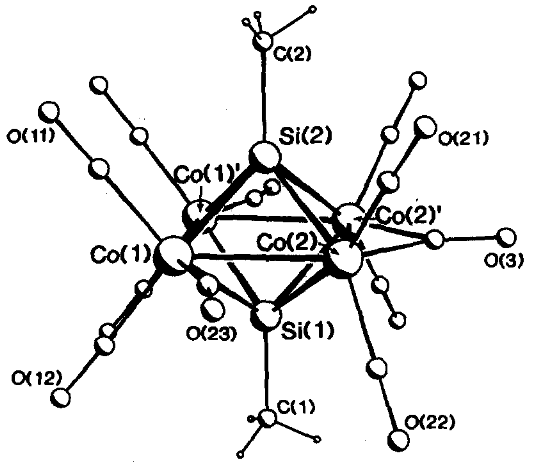

Fig. 1. The structure of [$Co_4(\mu_4$-$SiMe)_2(CO)_{11}$] (**1a**).

many related Ge/Co and Si/Co carbonyl clusters have either weak or missing parent ions. The typical stepwise loss of CO followed by limited fragmentation of the Si_2Co_4 skeleton is also observed. The ^1H NMR chemical shift of [$Co_4(\mu_4$-$SiMe)_2(CO)_{11}$] at δ 2.73 corresponds to that reported for the [$Co_4(\mu_4$-$GeMe)_2$-$(CO)_{11}$] (δ 2.75) and is about 1 ppm to low field of Me bonded to four-coordinated Si in clusters of the type (μ_3-SiMe)M_3L_n [19]. A single ^{13}C shift for the CO ligands in **1a** indicates that, in solution down to −50°C, the carbonyl groups are exchanging rapidly.

The structure of [$Co_4(\mu_4$-$SiMe)_2(CO)_{11}$] is illustrated in Fig. 1 and selected bond lengths and angles are presented in Table 1. The molecule lies on a crystallographic mirror plane which includes the two Si atoms and the bridging carbonyl. The structure is isomorphous with the germanium analogue, [$Co_4(\mu_4$-$GeMe)_2(CO)_{11}$] [12] and is only the second example of a *closo* hexanuclear cluster involving silicon.

The metal core of **1a** consists of a distorted square planar array of Co atoms quadruply-bridged on each side by a Si atom which also carries a methyl group. The Co_4 plane has three distinct Co–Co bond lengths with the length determined by the degree of carbonyl bridging. The Co(1)–Co(1′) bond, with no bridging carbonyl group, is the longest (2.690(2) Å), while the shortest is Co(2)–Co(2′)(2.548(2) Å) which accommodates a fully bridging carbonyl. The intermediate length bonds, Co(1)–Co(2) and Co(1′)–Co(2′) bonds (2.651(1) Å) are semi-bridged by carbonyl groups. The remaining eight carbonyl groups are all terminal and are evenly distributed among the four Co atoms. The Co–Co bond lengths are significantly shorter than in [$Co_4(\mu_4$-$GeMe)_2(CO)_{11}$] (2.721(2), 2.580(2) and 2.693(2) Å, respectively), while similar to those in [$Co_4\{\mu_4$-$SiCo(CO)_4\}_2(CO)_{11}$] (2.653(2), 2.569(2) and 2.623(2) Å respectively). This difference between the Si and Ge analogues is a reflection of the different size of the μ_4-group.

Both Si(1) and Si(2) are slightly displaced towards the Co(2)–Co(2)′ edge. This effect has been observed in most of the group 14 clusters of type **1** and can be attributed to the electronic imbalance between Co(1) (formally 18.5 electrons) and Co(2) (17.5 electrons) which is partially compensated for by displacement of the Si atoms, and partially by the semi-bridging carbonyls. The Si–Co bond distances of **1a** are longer than in Co–Si compounds with four-coordinate silicon (*e.g.* [μ_4-$Si\{Co_2(CO)_7\}_2$] [1,2] mean 2.288 Å), but significantly shorter than the equivalent bonds in the only other five-coordinate silicon example [$Co_4\{\mu_4$-$SiCo(CO)_4\}(CO)_{11}$] which is probably due to the different steric requirements of the apical groups.

The Si ⋯ Si non-bonded distance in **1a** (2.726 Å) is shorter than that in [$Co_4\{\mu_4$-$SiCo(CO)_4\}_2(CO)_{11}$] (2.817 Å) and considerably shorter than the Ge ⋯ Ge distance in [$Co_4(\mu_4$-$GeMe)_2(CO)_{11}$] (2.926 Å). All these are only 10–15% longer than the appropriate covalently-bonded distances, and theoretical studies [8,9] have shown that there is a weak bonding interaction between the capping main-group atoms in closely related complexes. The Si–CH_3 bond lengths (1.863(9) Å) are typical and suggest a normal covalent bond despite the five-coordination of the Si atom. The overall structure is similar but more compact than [$Co_4(\mu_4$-$GeMe)_2(CO)_{11}$] which undoubtedly is a reflection of the smaller Si atom.

2.4. Synthesis of [$Co_4(\mu_4$-$SiMe)_2\{\mu$-$GeMe_2\}(CO)_{10}$]

There are two reported cases in which μ-GeR_2 replaces the bridging CO in [$(\mu_4$-$GeR)_2Co_4(CO)_{11}$] clusters. [$Co_4(\mu_4$-$GeMe)_2\{\mu$-$Ge(Me)Co(CO)_4\}(CO)_{10}$] [20] is formed when a mixture of [$Co_2\{\mu$-$Ge(Me)Co$-$(CO)_4\}_2(CO)_6$] and [$Co_2\{\mu$-$Ge(Me)Co(CO)_4\}(CO)_x$] (x = 7 or 8) was heated and [$Co_4(\mu_4$-$GeEt)_2\{\mu$-$GeCo_2$-$(CO)_7\}(CO)_{10}$] is formed from [μ_4-$Ge\{Co_2(CO)_6(\mu$-$GeEtH)\}_2$] and [$Co_2(CO)_8$] [21]. Several reports have shown that germanes, GeR_2H_2, react with metal carbonyls to replace μ-CO groups by μ-GeR_2 groups [20,22,23] so the reaction of [$Co_4(\mu_4$-$SiMe)_2(CO)_{11}$] with $GeMe_2H_2$ was examined to see if this displacement reaction could be applied to the pseudo-octahedral clusters **1** to give extended clusters incorporating both silicon and germanium.

The reaction between $GeMe_2H_2$ and [$Co_4(\mu_4$-$SiMe)_2(CO)_{11}$] was straightforward and followed eqn. (5).

$$\mathbf{1a} + GeMe_2H_2 \rightarrow \mathbf{2} + H_2 + CO \qquad (5)$$

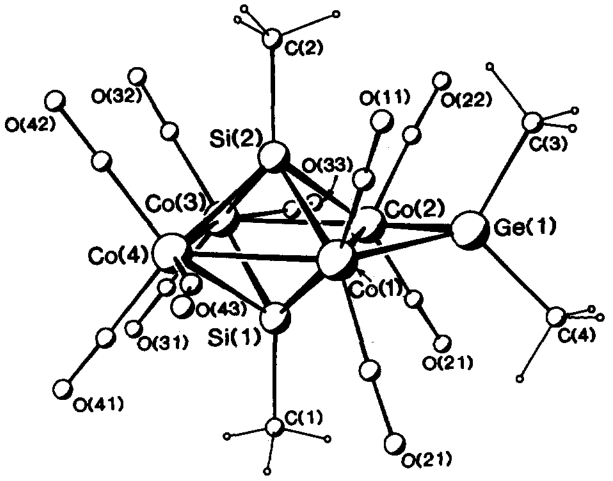

Fig. 2. The structure of $[Co_4(\mu_4\text{-}SiMe)_2(\mu\text{-}GeMe_2)(CO)_{10}]$ (2).

The yields were essentially quantitative for CO, H_2 and $[Co_4(\mu_4\text{-}SiMe)_2\{\mu\text{-}GeMe_2\}(CO)_{10}]$ which indicates the reaction is very specific. There was no evidence for the replacement of the semi-bridging carbonyl groups.

2.5. Properties of $[Co_4(\mu_4\text{-}SiMe)_2\{\mu\text{-}GeMe_2\}(CO)_{10}]$

The infrared spectrum of $[Co_4(\mu_4\text{-}SiMe)_2\{\mu\text{-}GeMe_2\}(CO)_{10}]$ in the ν(CO) region was very different from that of the parent compound **1a**, although the molecular symmetry (C_{2v}) and number of terminal carbonyl groups (ten) is unchanged. The ^{1}H NMR shift assigned to the apical methyl group on silicon (δ 2.10) has shifted upfield significantly from that of $[Co_4(\mu_4\text{-}SiMe)_2(CO)_{11}]$, while the ^{1}H NMR shift assigned to the methyl groups on the germanium bridge compare closely with those of other $GeMe_2$ groups bridging Co–Co bonds (*e.g.* $[\mu_4\text{-}Ge\{Co_2(\mu\text{-}GeMe_2)(CO)_6\}_2$ [23], δ 1.34).

The mass spectrum was consistent with the formulation showing a weak parent-ion envelope and the characteristic stepwise loss of all ten carbonyl groups. There was also a weak series corresponding to the loss of the methyl groups, as well as minor envelopes corresponding to fragmentation of the Co_4Si_2Ge core.

The structure of $[Co_4(\mu_4\text{-}SiMe)_2\{\mu\text{-}GeMe_2\}(CO)_{10}]$ is illustrated in Fig. 2 with selected bond angles listed in Table 1. This structure is the third example of an extension of the E_2M_4 skeleton [20,21] and is related to that of $[Co_4(\mu_4\text{-}SiMe)_2(CO)_{11}]$ by replacement of the symmetrical μ-CO with a μ-$GeMe_2$ group. As with $[Co_4(\mu_4\text{-}SiMe)_2(CO)_{11}]$ there are three distinct Co–Co bond lengths. The longest bond is still the unbridged Co–Co bond (2.715(1) Å) which is only slightly longer than in $[Co_4(\mu_4\text{-}SiMe)_2(CO)_{11}]$. The intermediate length Co–Co bond is the one bridged by the Ge atom (2.692(1) Å) which is considerably longer than the equivalent bond in $[Co_4(\mu_4\text{-}SiMe)_2(CO)_{11}]$. This is consistent with the lengthening of a metal–metal bond when a bridging carbonyl is replaced by a bridging group 14 element. The shortest Co–Co bonds are now those which contain the semibridging carbonyl ligands (Co(1)–Co(4) = 2.634(1), Co(2)–Co(3) = 2.599(1) Å) which are slightly shorter than the equivalent bonds in $[Co_4(\mu_4\text{-}SiMe)_2(CO)_{11}]$.

The Ge atom does not bridge the Co(1)–Co(2) bond symmetrically (Ge(1)–Co(1) = 2.320(1), Ge(1)–Co(2) = 2.352(1) Å) and the Ge atom is displaced slightly from the Co_4 plane with the dihedral angle between the Ge(1)Co(1)Co(2) triangle and the Co_4 plane being 8.1°. The Si–Co bond lengths (range 2.291(2)–2.324(2) Å) are comparable to those found in **1**. Examination of these Si–Co bond lengths shows the two Si atoms are not symmetrically positioned over the Co_4 plane. Si(1) is closer to Co(1) and Co(3) while further from Co(2) and Co(4). Si(2) is displaced towards Co(1), symmetrically positioned between Co(2) and Co(3) and slightly further from Co(4). The Si $\cdots$ Si non-bonded distance (2.686 Å) is significantly shorter than in **1** (2.726 Å). The eight terminal and two semi bridging carbonyl groups adopt the same arrangement as in **1**. Overall the structure is less symmetrical than **1** but the major structural differences can be attributed to the replacement of the bridging carbonyl by a bridging Ge atom.

3. Experimental details

Volatile compounds were handled on a conventional vacuum line system while other species were manipulated under nitrogen by use of standard Schlenk apparatus. Instrumentation, techniques, and starting materials have been described previously [4,12,14].

3.1. Reaction of $SiMeH_2Cl$ *with* $Na_2[Fe(CO)_4]$

$SiMeH_2Cl$ [24] (8.32 mmol) was condensed onto freshly prepared $Na_2[Fe(CO)_4]$ (from 2.3 g, 11.7 mmol $Fe(CO)_5$ [25]) in pentane (10 ml). The reaction was allowed to proceed for 10 min at room temperature, then the volatile fraction was recovered and fractionated through traps at −22°C and −196°C. The compound assigned as $[Fe(SiMeH_2)_2(CO)_4]$ (**3**) was collected at −22°C (0.33 g, 31%) as a slightly volatile, colourless liquid. The fraction collected at −196°C contained $SiMeH_3$, $[Fe(CO)_5]$, unchanged $SiMeH_2Cl$, and the solvent. Characterisation of **3** was by comparison of the infrared spectrum with the germanium analogue [17]. The gas phase spectrum revealed infrared bands in the carbonyl stretching region at 2092m, 2031vs, 2011s, which compare well with those of $[Fe(GeMeH_2)_2(CO)_4]$ (2089m, 2030vs, 2007s and 1985w). Compound **3** was unstable at room temperature producing $SiMeH_3$ and a non-volatile, very air-sensitive oily liquid which could not be characterised.

3.2. Reaction of [$Fe(SiMeH_2)_2(CO)_4$] with [$Co_2(CO)_8$]

The reaction of [$Fe(SiMeH_2)_2(CO)_4$] (0.291 g, 1.31 mmol) with [$Co_2(CO)_8$] (0.66 g, 1.9 mmol) in pentane (20 ml) produced 5.9 mmol of incondensable gas (H_2 = 1.9 mmol 32%; CO = 4.0 mmol, 68% based on eqn. (3)) after 48 h at room temperature. On work-up, the volatile fraction was found to contain [$HCo(CO)_4$] and [$Fe(CO)_5$], together with the solvent. A pentane extract of the involatile residue contained [$Co_4(CO)_{12}$], unreacted [$Co_2(CO)_8$], and an unstable compound which remains uncharacterised although the infrared spectrum is suggestive of [$Co_2\{\mu$-$Si(Me)Co(CO)_4\}(CO)_7$] (ν(CO) at 2092vw, 2085mw, 2066sh, 2061ms, 2052s, 2040s, 2020vs, 1996vs, 1855w,br; cf. [$Co_2\{\mu$-$Ge(Me)Co(CO)_4\}(CO)_7$] ν(CO) 2105w, 2082s, 2061sh, 2056s, 2047w, 2038s, 2017m, 2009m, 1849w [20]). A CH_2Cl_2 extract of the remaining solid was nearly pure [$Co_4(\mu_4$-$SiMe)_2(CO)_{11}$] with a small amount of [$Co_4(CO)_{12}$]. Recrystallisation from CH_2Cl_2/pentane (1:1) gave pure [$Co_4(\mu_4$-$SiMe)_2(CO)_{11}$] (0.264 g, 37%).

3.3. The reaction of $SiMeH_3$ with [$Co_4(CO)_{12}$]

3.3.1.

$SiMeH_3$ (0.166 mmol) was condensed on to [$Co_4(CO)_{12}$] (0.045 g, 0.079 mmol) in hexane (10 ml) and was allowed to react in a tube equipped with a greaseless tap at 30°C. After 11 days, incondensable gases formed were 0.228 mmol (71% H_2, 29% CO), with a further 0.059 mmol (80% H_2, 20% CO) after 20 days, 0.01 mmol (27 days), 0.008 mmol (35 days) and 0.003 mmol (49 days), making a total evolution of 0.308 mmol. There was a small amount of $SiMeH_3$ remaining in the volatile fraction which could not be separated from the solvent. The involatile residue was pure [$Co_4(\mu_4$-$SiMe)_2(CO)_{11}$] (**1a**) (0.05 g, 100%).

3.3.2.

In a second reaction carried out in a sealed ampoule for 160 days at room temperature, [$Co_4(CO)_{12}$] (0.122 g, 0.213 mmol) partially reacted with $SiMeH_3$ (0.425 mmol) to give incondensable gases (0.47 mmol, 74% H_2, 26% CO), and pure **1a** (0.051 g, 0.083 mmol, 39%). There were considerable amounts of unreacted $SiMeH_3$ and [$Co_4(CO)_{12}$].

3.4. Characterisation of [$Co_4(\mu_4$-$SiMe)_2(CO)_{11}$] (1a)

The molecular formula was confirmed by the crystal structure, see below. Pure **1a** is a dark red-black crystalline solid, slightly soluble in pentane and readily soluble in CH_2Cl_2 to form a deep red solution. Electron probe analysis gave a ratio of Si:Co of 1:2.2 (silicon is at the limits of detection for this technique which probably accounts for the slightly high Co level). IR spectrum: ν(CO)(CH_2Cl_2/pentane) 2058sh, 2048sh, 2038vvs, 2020s, 2009sh, 1993w,sh, 1857w. Mass spectrum: m/z = 604(m) $[P - CO]^+$, followed by peaks corresponding to $[P - n\text{CO}]^+$ for n = 2(m), 3(m), 4(m), 5(vs), 6(vs), 7(vs), 8(m), 9(vs), 10(vs), 11(m). There were also peaks 305(m) $[P - 11\text{CO}-\text{Me}]^+$, 292(m) $[Co_4Si_2]^+$, 264(mw) $[P - 11\text{CO} - 2\text{Me}-\text{Si}]^+$, and 236 $[Co_4]^+$. ^1H NMR spectrum ($CDCl_3$): δ 2.73(s). ^{13}C NMR spectrum ($CDCl_3$) at −50°C, δ 202.6(s).

3.5. The reaction of [$Co_4(\mu_4$-$SiMe)_2(CO)_{11}$] with $GeMe_2H_2$

3.5.1.

$GeMe_2H_2$ (0.4 mmol) was condensed onto **1a** (0.151 g, 0.24 mmol) in pentane (10 ml). The ampoule was sealed and the reaction proceeded at 30°C for 7 days. On working up 0.50 mmol of incondensable gases (H_2 = 0.24 mmol, 48%, CO = 0.26 mmol, 52%) were measured. Unreacted $GeMe_2H_2$ in the volatile fraction could not be separated from the solvent. The involatile fraction was found to be pure [$Co_4(\mu_4$-$SiMe)_2\{\mu$-$GeMe_2\}(CO)_{10}$] (**2**) (0.166 g, 0.24 mmol, 99%).

3.5.2.

In a similar reaction carried out at room temperature **1a** (0.0633 g, 0.10 mmol) reacted completely over 14 days with $GeMe_2H_2$ (1.0 mmol) to give incondensable gases (H_2, 0.08 mmol; CO, 0.09 mmol). The volatile fraction contained unreacted $GeMe_2H_2$ and solvent, while the involatile solid was pure **2** (0.066 g, 0.094 mmol, 94%).

3.6. Characterisation of [$Co_4(\mu_4$-$SiMe)_2\{\mu$-$GeMe_2\}(CO)_{10}$] (2)

The molecular formula was established from the crystal structure (see below). **2** is a red crystalline solid, moderately soluble in pentane and readily soluble in CH_2Cl_2. Electron probe analysis gave a metal ratio Ge:Si:Co of 1:2.9:3.9. The amount of silicon appears high but the technique is not sensitive for this element. IR spectrum: ν(CO)(CH_2Cl_2) 2071s, 2051vw, 2026sh, 2022vvs,br, 2009s and 1986vs. Mass spectrum: m/z = 703–708(w) P^+ followed by $[P - n\text{CO}]^+$ for n = 1(m), 2(m), 3(mw), 4(s), 5(s), 6(s), 7(w), 8(w), 9(w), 10(w). Other prominent envelopes included $[P - 10\text{CO}-n\text{Me}]^+$ for n = 1(w), 2(w), 3(w), 4(w), 362–369(w) $[P - 10\text{CO} - 4\text{Me-Si}]^+$ and 305 − 311(w) $[P - 10\text{CO} - 4\text{Me-2Si}]^+$. ^1H NMR spectrum: δ 2.10 (s, $SiCH_3$), δ 1.24 ($GeCH_3$).

TABLE 2. Final positional parameters for the structures of **1a** and **2**

Atom	x	y	z	Atom	x	y	z
1a							
Co(1)	0.1793(1)	0.0988(1)	0.2041(1)	Co(2)	0.3667(1)	0.0935(1)	0.2942(1)
Si(1)	0.2394(2)	0.0	0.3652(2)	Si(2)	0.3030(2)	0.0	0.1323(2)
C(1)	0.1964(7)	0.0	0.5244(9)	C(2)	0.3453(7)	0.0	−0.0283(8)
C(3)	0.4684(6)	0.0	0.3416(7)	O(3)	0.5519(4)	0.0	0.3754(6)
C(11)	0.1354(5)	0.1118(6)	0.0461(7)	O(11)	0.1061(4)	0.1191(5)	−0.0529(5)
C(12)	0.0681(4)	0.1149(4)	0.2886(5)	O(12)	−0.0027(3)	0.1239(3)	0.3388(4)
C(21)	0.4472(4)	0.1575(4)	0.1963(6)	O(21)	0.5027(3)	0.1955(3)	0.1369(4)
C(22)	0.3718(4)	0.1635(5)	0.4354(6)	O(22)	0.3752(3)	0.2110(4)	0.5211(4)
C(23)	0.2350(4)	0.2166(5)	0.2297(6)	O(23)	0.2511(3)	0.2992(4)	0.2378(5)
2							
Ge(1)	0.1015(1)	0.1343(1)	0.7868(1)	Co(1)	0.1688(1)	−0.1172(1)	0.8337(1)
Co(2)	0.3436(1)	0.0193(1)	0.7146(1)	Co(3)	0.5263(1)	−0.2324(1)	0.6798(1)
Co(4)	0.3519(1)	−0.3735(1)	0.7988(1)	Si(1)	0.4476(2)	−0.1860(2)	0.8286(1)
Si(2)	0.2460(2)	−0.1667(2)	0.6863(1)	C(1)	0.5835(8)	−0.2027(8)	0.9305(5)
C(2)	0.1059(9)	−0.1557(8)	0.5881(5)	C(3)	−0.0933(9)	0.2362(8)	0.7079(6)
C(4)	0.1080(9)	0.2605(7)	0.8764(5)	C(11)	−0.0354(9)	−0.0998(7)	0.8060(5)
O(11)	−0.1660(6)	−0.0876(6)	0.7871(4)	C(12)	0.1851(8)	−0.1036(7)	0.9542(5)
O(12)	0.1942(6)	−0.0899(6)	1.0306(3)	C(21)	0.4513(8)	0.1154(7)	0.7699(5)
O(21)	0.5174(6)	0.1790(6)	0.8048(4)	C(22)	0.2519(8)	0.1350(7)	0.6078(5)
O(22)	0.1941(7)	0.2130(5)	0.5415(3)	C(31)	0.727(1)	−0.3349(7)	0.7225(5)
O(31)	0.8540(7)	−0.4009(6)	0.7504(5)	C(32)	0.5076(9)	−0.3023(8)	0.5744(5)
O(32)	0.4976(8)	−0.3474(6)	0.5073(4)	C(33)	0.5685(9)	−0.0656(8)	0.6293(5)
O(33)	0.6350(6)	0.0088(5)	0.5862(4)	C(41)	0.5252(9)	−0.4961(7)	0.8640(5)
O(41)	0.6348(7)	−0.5769(6)	0.9041(4)	C(42)	0.3029(9)	−0.4734(7)	0.7176(5)
O(42)	0.2696(8)	−0.5392(6)	0.6661(4)	C(43)	0.1972(9)	−0.3788(8)	0.8838(5)
O(43)	0.1123(7)	−0.4150(5)	0.9374(4)				

3.7. X-Ray crystallography

For both compounds **1** and **2** the space groups were determined by precession photography. The cell dimensions and intensity data were collected on a Nicolet P3 diffractometer using monochromated Mo Kα X-rays ($\lambda = 0.7107$ Å). The data were corrected for absorption (using a numerical method based on indexed faces for **1**, and an empirical method based on ϕ-scans for **2**) and the structures were solved by direct methods, routinely developed and refined using the SHELX programs [26].

3.8. Structure of $[Co_4(\mu_4\text{-}SiMe)_2(CO)_{11}]$

3.8.1. Crystal data

$C_{13}H_6Co_4O_{11}Si_2$, $M = 630.1$, monoclinic, space group $C2/m$, $a = 13.445(3)$, $b = 13.618(3)$, $c = 10.905(4)$ Å, $\beta = 93.33(2)°$, $U = 1993(1)$ Å^3 (from 25 automatically centred reflections), $Z = 4$, $D_c = 2.10$ g cm^{-3}, dark red-black crystals from CH_2Cl_2/pentane, $0.24 \times 0.24 \times 0.06$ mm, transmission factors 0.814 (max), 0.476 (min), μ(Mo Kα) = 33 cm^{-1}, $F(000) = 1232$, T = 173 K.

A total of 1373 unique data was collected by θ–2θ scans in the range $4 < 2\theta < 45$, $+h$, $+k$, $\pm l$, 1106 with $I > 2\sigma(I)$ were used. All non-hydrogen atoms anisotropic, H atoms included in calculated positions, full-matrix least-squares refinement converged with $R = 0.0364$ and $R_w = 0.0373$ with $w = [\sigma^2(F) + 0.00040F^2]^{-1}$. Largest final Δ/σ 0.5, largest residual peak was 0.72 e Å^{-3}. Final positional parameters are given in Table 2, and selected bond lengths and angles are given in Table 1.

3.9. Structure of $[Co_4(\mu_4\text{-}SiMe)_2\{\mu\text{-}GeMe_2\}(CO)_{10}]$

3.9.1. Crystal data

$C_{14}H_{12}Co_4GeO_{10}Si_2$, M = 704.74, triclinic, space group $P\bar{1}$, $a = 8.638(2)$, $b = 9.717(4)$, $c = 14.437(5)$ Å, $\alpha = 80.26(3)°$, $\beta = 87.96(2)°$, $\gamma = 72.40(3)°$, $U = 1138.2(7)$ Å^3 (from 25 automatically centred reflections), $Z = 2$, $D_c = 2.07$ g cm^{-3}, dark red-black crystals from CH_2Cl_2/pentane, $0.6 \times 0.2 \times 0.2$ mm, transmission factors 0.861 (max), 0.791 (min), μ(Mo Kα) = 45 cm^{-1}, $F(000) = 688$, T = 173 K.

A total of 4246 unique data was collected by θ–2θ scans in the range $4 < 2\theta < 52$, $+h$, $\pm k$, $\pm l$, with 3131 for which $I > 2\sigma(I)$ used in all calculations. All non-hydrogen atoms anisotropic, H atoms included in calculated positions, full-matrix least-squares refinement converged with $R = 0.043$ and $R_w = 0.040$ with $w = [\sigma^2(F) + 0.0011F^2]^{-1}$. Largest final Δ/σ 0.2, largest residual peak 0.6 eÅ^{-3}. The final positional parameters are given in Table 2, and selected bond lengths and angles are given in Table 1.

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