The Reactions of Methylgermanes with $[\mu_4\text{-Ge}\{Co_2(CO)_7\}_2]$: Extending the Chain of Linked $GeCo_2$ Triangles†

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Methylgermanes $GeMeRH_2$ (R = H or Me) react with $[\mu_4\text{-Ge}\{Co_2(CO)_7\}_2]$ **1** to form $[\mu_4\text{-Ge}\{Co_2(CO)_7\}\{Co_2(\mu\text{-GeMeR})(CO)_6\}]$ (R = H **2a** or Me **2b**) and $[\mu_4\text{-Ge}\{Co_2(\mu\text{-GeMeR})(CO)_6\}_2]$ (R = H **3a** or Me **3b**), depending on reaction ratio and time. An alternative synthesis of **2a** is from $GeMeH_3$ and $[\mu_4\text{-Ge}\{Co(CO)_4\}Co_3(CO)_9]$. Corresponding reactions of **1** with silanes or stannanes do not give compounds of type **2** or **3**, while the silicon analogue of **1** undergoes fragmentation with germanes, rather than cluster extension. ^{13}CO-Exchange, CO-addition, and thermolysis reactions of **1**, **2** and **3** are compared. An X-ray structure analysis of **3b** [triclinic, space group $P\bar{1}$, $a = 9.607(3)$, $b = 14.796(4)$, $c = 9.476(3)$ Å, $\alpha = 95.83(2)$, $\beta = 91.94(2)$, $\gamma = 98.83(2)°$, $R = 0.044$, for 3353 data with $I > 2\sigma(I)$] confirms the extended core of four $GeCo_2$ triangles linked through the Ge apices and the Co–Co edges.

The reaction of a hydride, GeR_3H, with $[Co_2(CO)_8]$ was one of the earliest routes[1] to Ge–Co bonded species $[Co(GeR_3)(CO)_4]$. Further work showed that two or more Ge–H bonds could be replaced by Ge–Co bonds, and polyhydrides were therefore a source of polymetallic species. Thus, some twenty years ago it was shown that GeR_2H_2 reacted to form products containing the $GeCo_2$ triangle by formally replacing μ-CO in $[Co_2(CO)_8]$ with μ-GeR_2. Examples are the syntheses of $[Co_2(\mu\text{-GePh}_2)(CO)_7]$ by Fieldhouse *et al.*[2] and of $[Co_2(\mu\text{-GeMe}_2)_2(CO)_6]$ by Adams *et al.*[3] With $GeRH_3$, there was a ready reaction to form $[Co_2\{\mu\text{-Ge(R)Co(CO)}_4\}(CO)_7]$ which contains both a Ge–$Co(CO)_4$ and a μ-$GeCo_2(CO)_7$ unit, established for R = Ph[4] or Me.[5] A fuller study of the $GeMeH_3$ reaction[6] showed a much slower subsequent reaction involving a second formal replacement of μ-CO by μ-$Ge(Me)Co(CO)_4$. Finally, GeH_4 reacted with two $[Co_2(CO)_8]$ molecules to form $[\mu_4\text{-Ge}\{Co_2(CO)_7\}_2]$ **1**, which contains two $GeCo_2$ triangles linked through a *spiro*-Ge.[7]

As the geometry of the $[Co_2(CO)_7]$ units of **1** is very similar to that of $[Co_2(CO)_8]$, it was of interest to examine the reactions of **1** with germanes to discover whether controlled chain extensions of molecules such as **1** were possible using germanes containing the GeH_2 group to replace the μ-CO. In an initial study[8] of **1** with $GeMe_2H_2$ formation of $[\mu_4\text{-Ge}\{Co_2(\mu\text{-GeMe}_2)(CO)_6\}\{Co_2(CO)_7\}]$ **2b** was indicated. We now describe fully the reactions of $GeMeH_3$ and $GeMe_2H_2$ with **1**, and show monosubstitution is followed by disubstitution. We have also briefly examined the reactions of $SiMeH_3$, $SiMe_2H_2$ and $SnMe_2H_2$ with **1**.

Results and Discussion

General Features of the Reactions.—The products formed by $GeMeH_3$ and $GeMe_2H_2$ on reaction with **1** are very similar, and are formulated (see below) as arising from the replacement of one or both of the μ-CO groups of **1** in a two-step substitution [equations (1) and (2)].

$$GeRMeH_2 + \underset{\mathbf{1}}{[\mu_4\text{-Ge}\{Co_2(CO)_7\}_2]} \longrightarrow H_2 + CO + [\mu_4\text{-Ge}\{Co_2(\mu\text{-GeRMe})(CO)_6\}\{Co_2(CO)_7\}] \quad (1)$$

$$\mathbf{2a}\ R = H \qquad \mathbf{2b}\ R = Me$$

$$GeRMeH_2 + \mathbf{2} \longrightarrow H_2 + CO + [\mu_4\text{-Ge}\{Co_2(\mu\text{-GeRMe})(CO)_6\}_2] \quad (2)$$

$$\mathbf{3a}\ R = H \qquad \mathbf{3b}\ R = Me$$

The early formation of **2** and its later decline in favour of **3**, as implied by these equations, was clearly shown by the IR spectra of samples taken in the course of the reaction. In addition, a separate experiment demonstrated that **2b** reacted quantitatively according to equation (2), when a modest excess of dimethylgermane was used.

Reactions with $GeMeH_3$.—In contrast to its reaction with $[Co_2(CO)_8]$, $GeMeH_3$ reacted very slowly with **1** at room temperature. At a reaction ratio of 1:1, in a sealed tube, 60% conversion to **2a** was found after half a year (further conversion may have been inhibited by the CO evolved, see below). There was no sign of the disubstituted compound **3a**. By increasing the temperature to 30 °C, a conversion of about 50% of **1** to **2a** occurred over two weeks. At 35 °C the reaction rate was further enhanced but overall yields were diminished because of the parallel condensation with loss of CO of **1** to $[\mu_4\text{-Ge}\{Co(CO)_4\}Co_3(CO)_9]$ **4**, a well established reaction [equation (3)].[9]

$$\mathbf{1} \longrightarrow CO + \underset{\mathbf{4}}{[\mu_4\text{-Ge}\{Co(CO)_4\}Co_3(CO)_9]} \quad (3)$$

Finally, heating above 40 °C reduced the time for *ca.* 50% conversion to 4 d, but **2a** was accompanied by **4** and even by a small amount of the pseudo-octahedral cluster $[Co_4(\mu_4\text{-GeMe})_2(CO)_{11}]$.[10]

Attempts to push the conversion of **1** to **2a** further towards completion at 30 °C, by increasing the amount of methyl-

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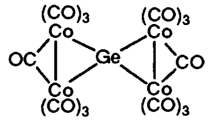
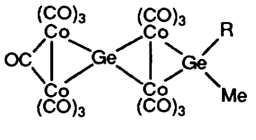
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

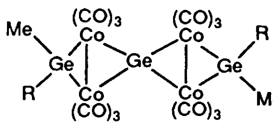
Non-SI unit employed: atm = 101 325 Pa.



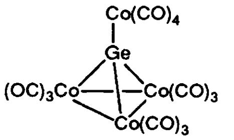
1



2a R = H
2b R = Me



3a R = H
3b R = Me



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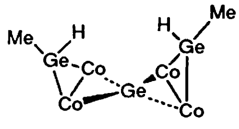
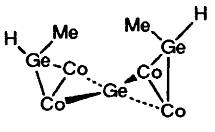
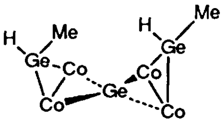


5a



5b



5c

germane in solution, led to complete reaction of **1** but gave formation of both **2a** and **3a**.

Because of the difficulties of getting complete reaction, and with separating mixed products, the sealed-tube routes were not very satisfactory. In previous related studies, reactions carried out with regular removal of incondensable gases have tended to give essentially the same products as those in sealed tubes, though with some shift in products towards more condensed species. In this study, a faster and more complete reaction occurred in tubes equipped with taps so that regular removal of gases could be performed. Thus, using a 1.5:1 ratio of $GeMeH_3$ to **1**, all of **1** was consumed and gas evolution ceased after 21 weeks, with the formation of **2a** plus **3a**. The reaction could be pushed to complete conversion to **3a** in 78% yield by adding further methylgermane. A minor amount of decomposition product and an unidentified less-soluble by-product were also found but these did not interfere with the purification of **3a**.

High conversion to the disubstituted product **3a** could therefore be achieved, but the monosubstituted species, **2a**, could only be formed mixed with unreacted **1** and/or with **3a** and separation was difficult.

The presence of **4** in the higher-temperature runs with $GeMeH_3$ led us to examine the reaction between these two, and this fortunately turned out to give a convenient, though slow, direct route to **2a** in high yield [equation (4)]. A minor amount

$$GeMeH_3 + \mathbf{4} \longrightarrow H_2 + \mathbf{2a} \qquad (4)$$

of decomposition occurred giving a little CO and an insoluble by-product.

This raises the question of whether **2a** arises directly from **1** or indirectly *via* the formation of **4**. Although the latter may contribute in the higher-temperature runs where **4** was seen among the products, it is likely that, at lower temperatures, the reaction of equation (1) is followed directly as the rate of formation of **4** is very slow, and the reaction of equation (4) is also slower than that of equation (1). In addition, the reaction of equation (2) establishes that μ-GeMeH from $GeMeH_3$ can replace the very similar μ-CO in **2a** and this argument is reinforced by the observations with $GeMe_2H_2$ where **2b** clearly forms according to equation (1).

In contrast to the reaction of $GeMeH_3$ with $[Co_2(CO)_8]$, there was no indication of further reaction of the last Ge–H bond: no Ge–$Co(CO)_4$ species was detected. This strongly suggests that the reaction of **1** takes place keeping the central Ge–Co bonds intact, so that there is no free cobalt carbonyl species, such as $[HCo(CO)_4]$, available to react (either directly or *via* its decomposition product $[Co_2(CO)_8]$, *cf.* ref. 11) with the Ge–H bonds in **2a** or **3a**.

It is interesting that reaction (4), which is essentially a reversal of the cluster-closing of equation (3), occurs in high yield under mild conditions, since the CO-induced reversal does not occur[12] up to 100 atm pressure of CO. Reaction (4) may be envisaged as proceeding *via* Ge–H addition to cleave a Co–Co bond of **4**, followed by H_2 elimination and reformation of Co–Co. In contrast to the reverse of (3), reaction (4) has a substantial driving energy in the elimination of H_2 and the high enthalpy of the H–H bond.

Reactions with $GeMe_2H_2$.—Dimethylgermane reacted with **1** distinctly faster than did methylgermane, though still very slowly by comparison with the corresponding $[Co_2(CO)_8]$ reactions. Sealed-tube reactions with a large excess of $GeMe_2H_2$ showed that disubstitution of **1** went to completion in about 20 weeks at room temperature, giving $[\mu_4\text{-Ge}\{Co_2(\mu\text{-GeMe}_2)(CO)_6\}_2]$ **3b**. Lower reaction ratios and shorter reaction times give mainly the monosubstituted species **2b**, with smaller proportions of **3b**. Though not as difficult to separate as the monomethyl analogues, pure samples of **2b** could only be produced along with substantial mixed fractions. Gentle warming and removing CO during the reaction speeded up the conversion and a modest excess of $GeMe_2H_2$ gave complete reaction of **1** within a few days.

As sealed-tube syntheses require little attention, the long-term reaction of a five-fold excess of $GeMeH_3$ or $GeMe_2H_2$ is the synthesis of the disubstituted compounds, **3**, most economical in experimenter's time. An open-tube reaction with removal of CO and addition of successive increments of hydride is most economical of material. Equation (4) offers much the best synthesis of **2a**, despite the relatively long reaction time. The most convenient synthesis of **2b** is to use a 2- to 2.5-fold excess of dimethylgermane in a sealed tube for around 8 weeks. This gives relatively low proportions of **1** and **3b**, allowing around 50% recovery of **2b**.

Related Systems.—When **1** was sealed under similar conditions with $SiMeH_3$ or $SiMe_2H_2$ no products analogous to **2** or **3** were found. The only change seen was limited conversion of **1** to **4**.

Similarly, **1** reacted only slightly with $SnMe_2H_2$ in the time available before complete decomposition of the hydride. The product identified,[13] $[SnMe_2\{Co(CO)_4\}_2]$, resulted from the abstraction of $Co(CO)_4$ units from **1**.

These observations indicate that, under these mild conditions, the $GeCo_2$ triangles in **1** may be bridged by GeMeH or $GeMe_2$ groups but not by SiMeH, $SiMe_2$ or $SnMe_2$. This is in accord with the classical chemistry of $[Co_2(CO)_8]$ where species formally formed by replacing μ-CO by μ-GeR_2 dominate the lists of dicobalt compounds with Group 14 element bridges.[1]

Spectroscopic Characterisation.—Both monosubstituted molecules, **2a** and **2b**, showed the parent ion and stepwise loss of 13 CO as the major series in the mass spectra, accompanied by a weaker series $[P - CH_x - n\text{CO}]^+$, and a prominent $Ge_2Co_4{}^+$ ion. The disubstituted GeMeH derivative **3a** also showed a parent ion, and the major series of fragments represented the loss of 12 CO. Loss of CH_x occurred only after losses of 10 CO. In contrast, the $GeMe_2$ species, **3b**, showed $(P - CH_x)^+$ as the ion of highest mass. Ions attributed to the series $(P - CH_x - n\text{CO})^+$ were seen for $n = 1$–12. Under the low-resolution conditions available, the loss of 2 CH_x could not be distinguished from CO loss. Somewhat extended envelopes suggested overlap of ions arising from loss of $GeMe_2$ units.

In the vibrational spectra there were no μ-CO modes for the disubstituted derivatives **3a** or **3b**. The bis-$GeMe_2$ derivative, **3b**, whose structure is established crystallographically, and the corresponding GeMeH molecule, **3a**, have very similar terminal CO stretches with frequencies shifted 5 cm^{-1} to higher wave number for the hydride. There is a general complementarity of intensities between the infrared and Raman spectra of **3b** which reflects the close approach of the μ_4-Ge$\{Co_2(CO)_6\}_2$ central units to D_{2d} symmetry.

The monosubstituted derivatives, **2**, each show a bridging mode, and more resolved carbonyl-stretching bands than **3**, reflecting the different bridging groups at the two ends of the molecule. There is a shift of about 10 cm^{-1} in mean values to lower frequency from **1** to **2b** and between **2b** and **3b** paralleling the changes of about 25 and 20 cm^{-1} from $[Co_2(CO)_8]$ to $[Co_2(\mu\text{-}GeMe_2)(CO)_7]$[14] and $[Co_2(\mu\text{-}GeMe_2)_2(CO)_6]$.[3] The GeMeH-substituted species have frequencies 2–5 cm^{-1} above those of the $GeMe_2$ analogues.

The middle region shows Co–C–O and $GeCH_3$ modes as expected. Four prominent bands between 180 and 265 cm^{-1} in the Raman spectrum of **3b** are in the region appropriate for heavy-atom stretches, while the five below 120 cm^{-1} will have more deformation character. This compares with three bands in each of these regions for **1**, reflecting the less extended heavy-atom skeleton. For comparison, the simple M–M stretches are ν(Ge–Co) at 221 cm^{-1} in $[CoGeH_3(CO)_4]$[15] and ν(Co–Co) at 229 cm^{-1} in $[Co_2(CO)_8]$.[16] Similarly, the totally symmetric stretch of the Co–$GeCo_2$ skeleton of $[\mu_3\text{-}GeMe\{Co(CO)_4\}\text{-}Co_2(CO)_7]$ is found[6] at 255 cm^{-1}.

In the NMR spectra there was only one ^{13}C NMR resonance at δ 202 for the CO groups of **1** down to 220 K. This shows there is a rapid CO exchange between terminal and bridging sites for **1**. For **2b** a single ^{13}CO resonance on an enriched sample was also observed, shifting slightly from δ 202.5 at 268 K to δ 199.8 at 223 K. For this example there are two interpretations. The first is that there is rapid exchange between CO ligands on the two ends of the molecule as well as between terminal and bridging sites. The second, more probable, explanation is that the ^{13}CO enrichment has only occurred at the $Co_2(CO)_7$ end of the molecule, with the consequence that the natural-abundance signal from the $Co_2(\mu\text{-}GeMe_2)(CO)_6$ part of the molecule was not detected. This is consistent with the observation that ^{13}CO exchange does not occur with the disubstituted **3b**, and is further supported by the close similarity of the signal observed for **2b** with that of **1**; if the μ-$GeMe_2$ part of the molecule was involved a more significant chemical shift would be expected. The ^{13}CO NMR spectrum of **2a** also shows only a single peak at δ 203 over the 213–273 K temperature range, and can be interpreted similarly.

In the ^1H NMR spectra of **2b** and **3b** the CH_3 signals are single, which indicates rapid averaging, since the instantaneous structures give different environments for the Me groups on the $GeMe_2$ bridges. For these examples averaging can be envisaged in terms of a rotation of the bridging group about the Co–Co bond—a sort of inside-out flapping. A similar analysis holds for **2a**, where again the NMR data show one signal for each of the CH_3 and GeH groups. A more complex averaging process must be involved for **3a** where the CH_3 and GeH signals are also apparently from one environment. For **3a** three distinct isomers, **5a**–**5c**, can be envisaged. A flapping-type fluxionality could interchange the two symmetric species **5a** and **5b**, but the unsymmetrical **5c** could only be interchanged with the symmetrical forms with breaking and reforming of Ge–Co bonds.

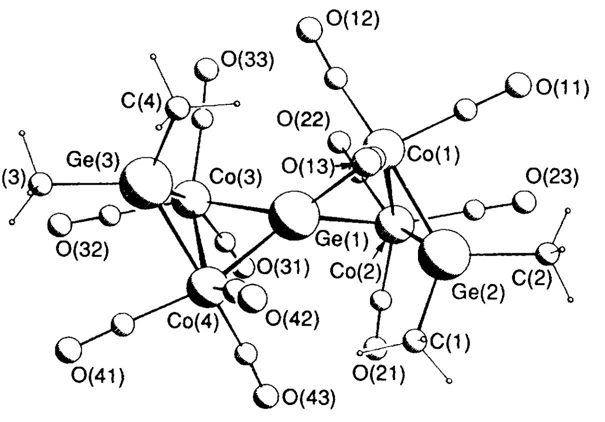


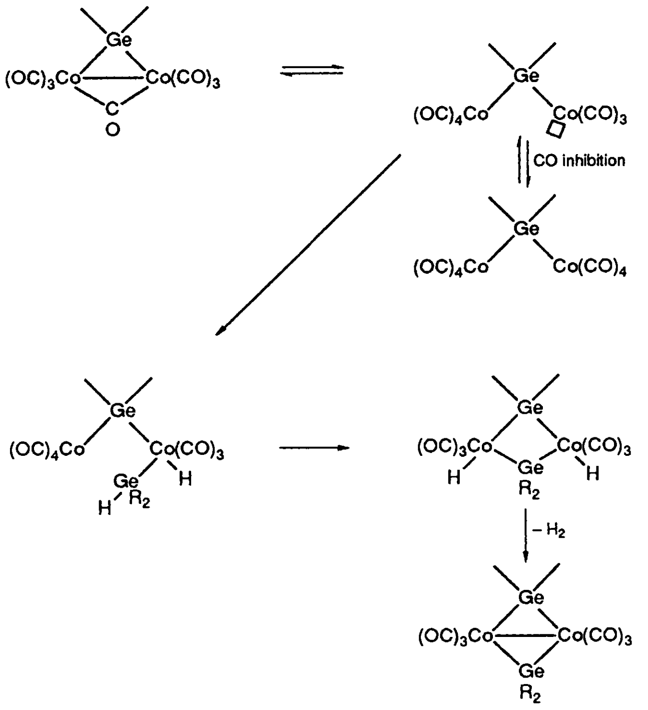
Fig. 1 The structure of $[\mu_4\text{-}Ge\{Co_2(\mu\text{-}GeMe_2)(CO)_6\}_2]$ **3b**

Crystal Structures of **2b** *and* **3b**.—The hydride species, **2a** and **3a** could not be obtained as single crystals, while the dimethyl compounds **2b** and **3b** were more manageable. Unfortunately, crystals of **2b** were twinned so that the poor X-ray data set obtained revealed only the metal skeleton, and refinement below $R = 0.18$ was not achieved. However the overall features were clear, consisting of a *spiro*-Ge linking two Co–Co units, one of which is further bridged by a Ge atom, so the apparent structure is therefore fully consistent with that proposed on spectroscopic grounds for **2b**.

The structure of **3b** is illustrated in Fig. 1 and consists of a chain of four linked triangles sharing Co–Co edges and a Ge apex. The compound is clearly related to **1** with the bridging CO ligands replaced by $GeMe_2$ groups. The dihedral angle between the planes of the triangles sharing the common apex at Ge(1) is 101°, compared with a corresponding angle of 96.5° in **1**. The dihedral angles between the triangles sharing a common Co–Co edge are both 105°, a value that is adopted to maintain a reasonable Ge • • • Ge non-bonded distance of 3.13 Å, which is still less than the van der Waals distance. There is a small lengthening of the central Ge–Co bonds (average 2.38 Å compared with 2.36 Å in **1**[7]). The main effect of substitution is to increase Co–Co from 2.56 Å in **1** to 2.64 Å in **3b**; this is the expected effect for a bond bridged by two Ge atoms, compared to one with Ge and C atom bridges.[17] Another useful comparison is of **3b** with $[Ge_3Co_8(CO)_{26}]$,[18] **6**. In this structure there is the central $GeCo_4$ unit of **1**, with the Co–Co edges bridged by μ-$GeCo_2(CO)_7$ units. The central Co–Co distances in **6**, at 2.664 Å, are very similar to those in **3b**, as are the central Ge–Co distances. However the dihedral angles between the outer $GeCo_2$ triangles are greater in **6**, at 120°, reflecting the greater bulk of the μ-$GeCo_2(CO)_7$ groups compared to μ-$GeMe_2$.

Because of the orientation of the $GeMe_2$ groups, one of the Me groups is directed over the central Ge atom so that the Ge(1) • • • C(1) distance is only 3.75 Å, which may explain the transfer of an Me group from one Ge to another which is observed on thermolysis (see below).

Reaction Pathways.—The mechanism of replacement of a μ-CO by a μ-GeR_2 group *via* the appropriate germane is not established. Some indication comes from the observation that the presence of CO (1 atm) completely inhibits the reaction between **1** and $GeMeH_3$, which suggests CO dissociation to give a vacant site at a Co atom is a key step in the reaction. Consistent with this the gas evolution follows what has become the standard pattern[6,10] for germane–metal-carbonyl reactions: the gases formed in the earlier stages are relatively enriched in CO, while the proportion of H_2 builds up later. Allowing for



Scheme 1

some CO from the small amounts of condensation or decomposition products, the overall gas formation corresponds to equations (1) and (2). The retardation of H_2 evolution accords with the mechanism outlined in Scheme 1, where the early stage is oxidative addition of Ge–H at the vacant site on a cobalt atom generated by opening of the Co–Co bond; then follows addition of the other Ge–H at the adjacent Co atom, and finally 1,2 elimination of H_2 and reformation of the Co–Co bond bridged by the μ-GeR$_2$ unit.

Some Reactions of **2**.—(*a*) *With* CO. In a study of the synthesis of [μ_4-Ge{Co(CO)$_4$}$_4$] from $GeCl_4$ it was found[19] that CO was readily lost to give **1**. The reverse, **1** reacting with CO under pressure to form [μ_4-Ge{Co(CO)$_4$}$_4$], has now been demonstrated. Similarly, the monosubstituted derivatives **2a** and **2b** also reacted with CO under pressure to form similar products. Their infrared spectra showed no μ-CO stretch and are compatible with species formed by opening the CO bridged Co–Co bond in **2a** or **2b**, *i.e.* [{Co$_2$(μ-GeMeR)(CO)$_6$}-Ge{Co(CO)$_4$}$_2$] for R = H or Me. These products readily lost CO and reverted to **2a** or **2b** respectively.

(*b*) *With* $SiMe_2H_2$. Although the reaction of **2b** with $GeMe_2H_2$ according to equation (2) was complete in 13 weeks, there was no analogous reaction of **2b** with an excess of dimethylsilane, even after 8 months. In this, **2b** matches the parent compound, **1**.

(*c*) ^{13}CO *Exchange*. The exchange of ^{13}CO occurs readily with **1** and with the monosubstituted compounds **2**, with up to 50% exchange after 2 weeks at 1 atm of ^{13}CO. In contrast the disubstituted compounds **3** do not exchange under similar conditions. This strongly indicates that the exchange mechanism relies on the presence of μ-CO.

(*d*) *Thermolysis*. Cluster **1** loses CO steadily under gentle heating to form the more closed cluster **4** [equation (3)],[7,9] a conversion that appears to take place by breaking and reforming Co–Co bonds without fission of the Ge–Co ones. It was therefore of interest to see what bridge-substitution does to this behaviour. For **2b** CO was not lost very easily, and the critical temperature for significant reaction seems to be 30–50 °C. One set of changes corresponded to the overall reaction of equation (5).

$$\underset{\mathbf{2b}}{2[\mu_4\text{-Ge}\{Co_2(\mu\text{-GeMe}_2)(CO)_6\}\{Co_2(CO)_7\}]} \longrightarrow \underset{\mathbf{3b}}{[\mu_4\text{-Ge}\{Co_2(\mu\text{-GeMe}_2)(CO)_6\}_2]} + \underset{\mathbf{1}}{[\mu_4\text{-Ge}\{Co_2(CO)_7\}_2]} \quad (5)$$

Clusters **3b** and **1** were detected together, and in similar amounts, at the earliest points monitored. Reaction (5) involves intermolecular exchange of μ-CO and μ-GeMe$_2$ but it is not clear how this occurs. As elimination of CO continued, the quantities of **1**, **2b** and **3b** decreased, but **1** and **3b** were lost more rapidly than **2b**, and their proportions remained equal.

The parallel formation of the closed cluster [Co$_4$(μ_4-GeMe)$_2$(CO)$_{11}$] can be regarded as formally occurring *via* equation (6). This cluster is well known[10,20] and contains an

$$\underset{\mathbf{2b}}{[\mu_4\text{-Ge}\{Co_2(\mu\text{-GeMe}_2)(CO)_6\}\{Co_2(CO)_7\}]} \longrightarrow 2\,CO + [Co_4(\mu_4\text{-GeMe})_2(CO)_{11}] \quad (6)$$

irregular square-bipyramidal Ge_2Co_4 skeleton. While the stoichiometry of equation (6) fits the conversion of **2b**, the pathway may well involve **1** and/or **3b**, as these species declined relative to **2b** in the later stages. There was no sign of **4**, the usual condensation product of **1**, which would be expected to form under these conditions. The transfer of Me between Ge atoms required by equation (6) is unusual under such mild conditions, and may reflect the very close approach of the central Ge to the bridging GeMe$_2$, indicated by the crystal structure of **3b**.

Experimental

Compounds were handled on vacuum lines or in Schlenk equipment under dry N_2 with the same general methods as previously.[7,10] Reactants were dissolved in dry hexane (usually 10 cm^3), sealed in glass ampoules and held in the dark, usually at ambient temperature (20–23 °C). Alternatively they were contained in vessels fitted with greaseless taps, so that the evolved H_2–CO could be measured at intervals using a Toepler pump and gas burette.

Reactions of Methylgermane with [μ_4-Ge{Co$_2$(CO)$_7$}$_2$] **1**.—(*a*) *Sealed tube reactions*. Methylgermane (0.15 mmol) and **1** (105 mg, 0.15 mmol) were allowed to react for 42 d at 20 °C, forming a dark solution and a reddish brown solid. The solvent and unreacted $GeMeH_3$ were removed. The involatile residue could be partially separated into its components by extracting with successive small amounts of hexane. Infrared spectra of the fractions showed each was a mixture of **2a** and **1**, with the proportion of **1** increasing in the later fractions. Attempts at chromatographic separation led only to decomposition, so pure **2a** could not be obtained. The yield of **2a** was estimated as around 10%. A 70 d run, on a 0.5 mmol scale, gave a similar partly separable mixture of **2a** and **1**, somewhat richer in **2a**. When the reaction time was extended to 196 d at 20 °C, $GeMeH_3$ (1.2 mmol) and **1** (848 mg, 1.21 mmol) produced 1.51 mmol of incondensable gases (60% CO), and a volatile fraction containing solvent and unreacted $GeMeH_3$, but no [HCo(CO)$_4$]. From the involatile products (890 mg) separate samples of **1** and **2a** could be isolated by repeated extraction and crystallisation from hexane. The infrared spectrum of the most soluble fraction showed a very weak shoulder at 2086 cm^{-1}, characteristic of **3a**, otherwise the sample was entirely **1** and **2a**. The weight of involatiles indicated that the product mix contained **2a** in a yield of *ca.* 57% matching the yield estimated from the incondensable gas volume (63%).

In a similar reaction, $GeMeH_3$ (0.71 mmol) and **1** (247 mg, 0.35 mmol) were gently heated for 11 d at 35 °C. Several cycles of extraction with hexane and crystallisation yielded **2a**

(105 mg, 1.38 mmol, 39%) and a mixture of **1** and **2a**, together with a small amount of **4**, formed by decarbonylation of **1** (characteristic[9] IR bands at 2112w, 2083s, 2045vs, 2029m and 2008vw cm^{-1}). Reaction times could be reduced to as little as 4 d at temperatures up to 43 °C, giving up to 70% **2a** but mixed with **4** and some **1** which were equally difficult to separate. At the higher temperatures, the *closo*-cluster $[Co_4(\mu_4\text{-}GeMe)_2(CO)_{11}]$ was detected by IR spectroscopy in the product mixes.[10]

Among the better compromises was a reaction for 16 d at 30 °C, with occasional shaking, using $GeMeH_3$ (0.63 mmol) and **1** (260 mg, 0.38 mmol). The ampoule was held at 0 °C for several hours before opening to improve the separation of unreacted **1**. Several recrystallisations from dichloromethane–hexane gave pure **2a** (127 mg, 0.167 mmol, 44%). The incondensable gases (0.40 mmol, 51% H_2) contained 0.21 mmol H_2, corresponding to a crude yield of 53% if **2a** is the only product.

A more separable product mix was sought in similar runs at 30 °C, using a larger excess of methylgermane. Such runs gave product mixtures which contained no unreacted **1** but which contained both the monosubstituted and disubstituted products **2a** and **3a**. These two also could not be cleanly separated, and did not survive chromatography.

(*b*) *Open tube reactions.* Methylgermane (0.61 mmol) and **1** (306 mg, 0.44 mmol) were allowed to react in the dark at room temperature. The evolution of incondensable gases (mmol per day) was 0.03 for 4 d, rising to 0.06 for a further 3 d, then falling to 0.05 for 8 d, 0.03 for 12 d then steadily dropping till significant evolution ceased after 145 d (accumulated gas total, 1.81 mmol). Work-up yielded a hexane-soluble fraction containing **2a** and **3a** and a CH_2Cl_2-soluble fraction which showed a relatively weak IR spectrum of **2a** plus **3a** and no other significant absorption. However, a mass spectrum of the dichloromethane fraction showed a weak but clear series of envelopes with the intensity pattern for 2Ge headed by *m*/*z* 865, and with 15 CO-loss envelopes which match the spectrum of the closed cluster $[MeGe_2Co_5(CO)_{15}]$. The fraction could not be crystallised, and was not studied further, leaving open the question whether the cluster was formed in the initial reaction or arose from a rearrangement on the mass spectrometer probe.

In a similar run, $GeMeH_3$ (0.59 mmol) and **1** (327 mg, 0.47 mmol) were allowed to react, with the incondensable gases and the solution examined at intervals. After 227 d, further $GeMeH_3$ (1.13 mmol) was added to complete the disubstitution. From the intensities of the indicated IR bands were determined the relative amounts in the hexane fraction of **1** (2079 cm^{-1}), monosubstituted product **2a** (2098 cm^{-1}), and disubstituted product **3a** (2086 cm^{-1}). After 32 d, 0.46 mmol of gas had evolved, only 0.078 mmol being H_2, and the ratio of the **1** and **2a** bands was 5:1. Compound **3a** appeared after 45 d when gases totalled 0.63 mmol (20% H_2), and the ratio of **1** to **2a** was 3:1. By 181 d, the gas evolution was quite slow, the H_2–CO ratio was about 50:50, and the ratio of **1**:**2a**:**3a** was 0.6:1:0.6. Cluster **1** had disappeared by 211 d, giving equal amounts of **2a** and **3a**, while gases totalled 1.67 mmol. The proportion of **3a** was twelve times that of **2a** after 228 d, and was the only species detectable after 238 d. The final total gas evolution was 1.22 mmol CO and 0.785 mmol H_2. The work-up yielded a hexane-soluble fraction consisting entirely of **3a** (300 mg, 78%), a fraction insoluble in hexane but soluble in dichloromethane (*ca.* 20 mg) whose IR spectrum showed only a poorly resolved broad feature at 2042 cm^{-1}, and a fraction insoluble in either solvent (*ca.* 20 mg).

Several similar experiments using reaction ratios up to a 17-fold excess of $GeMeH_3$, and run at 10 °C or room temperature for 2 to 8 weeks, all give mixtures of **2a** and **3a**, in ratios that limited isolation of a pure sample.

A room-temperature reaction using a 10-fold excess of $GeMeH_3$ but with added CO (1 atm) gave only complete recovery of the reagents.

Specific synthesis of **3a**. Measurement of incondensable gases from $GeMeH_3$ (0.45 mmol) and **1** (63 mg, 0.09 mmol) showed that reaction had ceased after 90 d. The total gas evolution was 0.23 mmol, containing 60% CO. Unreacted $GeMeH_3$ (0.2 mmol) was recovered, together with a small amount of dark material showing no CO stretching band in the infrared. The sole hexane-soluble product was **3a** (61 mg, 0.074 mmol, 82%).

Reaction of $GeMeH_3$ *with* **4** *in a Sealed Tube.*—After 20 weeks at 20 °C $GeMeH_3$ (0.3 mmol) and **4** (67 mg, 0.1 mmol) yielded: incondensable gases (0.09 mmol, 11% CO); unreacted $GeMeH_3$ (*ca.* 0.15 mmol); a trace of dark decomposition product; and a fraction soluble in hexane which contained only the monosubstituted species **2a** (67 mg, 0.09 mmol, 88% yield based on **4**).

Characterisation of **2a** *and* **3a**.—The cluster $[\mu_4\text{-}Ge\{Co_2(\mu\text{-}GeMeH)(CO)_6\}\{Co_2(CO)_7\}]$ **2a** was a brownish agglomerate, soluble in hexane, which did not yield a well crystalline material while $[\mu_4\text{-}Ge\{Co_2(\mu\text{-}GeMeH)(CO)_6\}_2]$ **3a** formed thin yellow needles which were soluble in hexane. ν(CO) (hexane solution): **2a**, 2098w, 2068vs, 2056s, 2047vs, 2030m, 2020m and 1842w; **3a**, 2085w, 2059s, 2042vs, 2019m and 2010ms cm^{-1}. ^1H NMR: **2a**, δ 1.37 (d) and 5.72 (q); **3a**, δ 1.36 (d) and 5.70 (q). The ^{13}CO signal from **2a** was a relatively broad singlet at δ 202.8 at 0 °C which showed only a slight shift to δ 203.8 on cooling to −60 °C.

The mass spectrum of **2a** shows a weak parent-ion family, with intensities appropriate to 2Ge, centred at *m*/*z* 762 (P^+, $C_{14}H_4Co_4Ge_2O_{13}$ requires 756–768) and a major series of fragment ions $(P - nCO)^+$ for n = 1 (w), 2 (w), 3 (m), 4 (m), 5 (w), 6 (s), 7 (s), 8 (vs), 9 (s), 10 (s), 11 (m), 12 (w) and 13 (s). Fragments arising from loss of Me were minor.

The mass spectrum of **3a** shows a relatively weak parent-ion family, with intensities appropriate to 3Ge, centred at *m*/*z* 822 ($P^+ = C_{14}H_8Co_4Ge_3O_{12}$ requires 814–832) and a major series of fragment ions $(P - nCO)^+$ for n = 1 (ms), 2 (m), 3 (w), 4 (w), 5 (w), 6 (mw), 7 (w), 8 (w), 9 (w), 10 (w), 11 (w) and 12 (w). Loss of CH_x occurs only with loss of 11 (w) and 12 (w) CO, and similarly for loss of 2 CH_x. A group of four strong families between *m*/*z* 400 and 448 probably arise from loss of 1 Co, 11 and 12 CO and 1 or 2 CH_x groups.

Reactions of Dimethylgermane with $[\mu_4\text{-}Ge\{Co_2(CO)_7\}_2]$ **1**. —*Excess* $GeMe_2H_2$ *with* **1** *in a sealed tube.* An initial study with $GeMe_2H_2$ (0.9 mmol) and **1** (63 mg, 0.09 mmol) showed unreacted **1** after 3 weeks. The tube was opened at this point, yielding incondensable gases (0.14 mmol: 68% CO, 32% H_2). The reaction was allowed to continue with measurement of the incondensable gases at intervals. This showed that the reaction slowed over a further 10 weeks (0.18 mmol gas). In a further 2 weeks only 0.008 mmol gas formed, and the reaction was terminated. The CO content dropped to 50%, in the last samples. The total evolution of incondensable gases was 0.33 mmol (59% CO).

The volatile fraction contained only hexane and unreacted $GeMe_2H_2$ (*ca.* 0.7 mmol). The involatile product was completely soluble in hexane, apart from a trace of dark material which showed no CO absorptions. Crystallisation yielded bright orange $[\mu_4\text{-}Ge\{Co_2(\mu\text{-}GeMe_2)(CO)_6\}_2]$ **3b**, which was stable at room temperature in the absence of air.

From a similar reaction of $GeMe_2H_2$ (0.65 mmol) and **1** (65 mg, 0.093 mmol) in a sealed tube for 20 weeks, there were recovered: incondensable gases (0.34 mmol, 52% CO), unreacted $GeMe_2H_2$ (0.47 mmol), a trace of insoluble dark material, and $[\mu_4\text{-}Ge\{Co_2(\mu\text{-}GeMe_2)(CO)_6\}_2]$ **3b** (68 mg, 0.08 mmol, 86% yield).

Reactions at lower ratios. Similar sealed-tube reactions for 30–60 d gave yields of recrystallised **2b** of 38% ($GeMe_2H_2$ ratio 1.5:1) and 52% (ratio 2.7:1) together with mixed fractions of **2b** and **3b**. The higher ratios and longer reaction times, within this range, left less unreacted **1**, allowing a higher recovery of recrystallised **2b**.

A small scale run followed by ^1H NMR spectroscopy in C_6D_6 (2.5:1 ratio of $GeMe_2H_2$ to **1**) showed the rapid formation of **2b**, followed by a slower generation of **3b**. Changes were complete in 38 d at room temperature. The final mixture contained unreacted $GeMe_2H_2$ (10% of original), and **2b** and **3b** in a ratio of 1:9 from ^1H NMR and from IR intensities.

Reaction of $GeMe_2H_2$ *with* **2b**.—The cluster $[\mu_4\text{-Ge}\{Co_2(\mu\text{-GeMe}_2)(CO)_6\}\{Co_2(CO)_7\}]$ **2b** (112 mg, 0.145 mmol) and $GeMe_2H_2$ (0.36 mmol) in hexane (10 cm^3) were sealed and shaken for 13 weeks at room temperature. The solution became orange, and yellow diamond-shaped crystals were present. The volatile fraction of unreacted $GeMe_2H_2$ and solvent was removed to leave **3b** (124 mg, 0.145 mmol, 100%).

^{13}CO*-Exchange Reactions and* ^{13}C *NMR Spectra*.—Hexane solutions of **1**, **2b** and **3b** were exposed to 95%-enriched CO at 1 atm pressure in a 250 cm^3 vessel, and exchange was monitored by IR spectroscopy. Under these conditions about 10% enrichment occurred within 1 d, and 30–50% in 8–14 d, both for **1** and for **2b**, but no significant exchange occurred for **3b**.

When the ^{13}CO NMR spectra were run, the ^{13}CO enriched sample of **2b** gave a singlet at δ 199.8 at −50 °C, and at δ 202.5 at −5 °C; **1** showed a singlet at δ 201.9 at room temperature and at −50 °C.

Characterisation of **2b**.—The cluster $[\mu_4\text{-Ge}\{Co_2(\mu\text{-GeMe}_2)(CO)_6\}\{Co_2(CO)_7\}]$, formed red crystals, soluble in hexane, which were invariably twinned. A preliminary X-ray crystal structure determination indicated a tetragonal space group, $P4_12_12$ or $P4_32_12$, $a = 11.93$, $c = 34.01$ Å. Solution of the data revealed the Ge_2Co_4 skeleton of **2b**, which refined to $R = 0.18$. However the Me and CO groups were poorly defined and did not refine sensibly, presumably because of poor data from a twinned crystal. The analysis was therefore abandoned. ν(CO) (IR hexane solution): 2096w, 2064vs, 2054ms, 2049(sh), 2043vs, 2027m, 2021(sh), 2017ms, 2003w and 1843w cm^{-1}; (IR, solid CsI disc) 2098m, 2074s, 2063s, 2058s, 2052vs, 2048(sh), 2033vs, 2028(sh), 2019w, 2002m, 1991m, 1981w and 1826s cm^{-1}; (Raman, single crystal) 2110s, 2084w, 2060vw, 2040vs, 2021m, 2012s, 2006vs, 2000m, 1986vw and 1828w cm^{-1}. ^1H NMR ($CDCl_3$) δ 1.31 (s); (C_6D_6) δ 1.2 (s).

The mass spectrum of **2b** showed a relatively weak parent ion and all members of the $(P - n\text{CO})^+$ series from $n = 0$ to 13. Relative intensities were 17, 14, 17, 25, 23, 34, 100, 93, 57, 23, 42, 51, 39 and 77% for $n = 0$ to 13 respectively. The much weaker series $(P - n\text{CO} - \text{CH}_x)^+$ occurred with only 1–10% of these intensities apart from $n = 3$ and 2 (20) and $n = 0$ (73%). The only other significant ions were $Ge_2Co_4^+$(71), $Me_2Ge_2Co_3^+$(15), $MeGe_2Co_3^+$(24), $Ge_2Co_3^+$(27), $MeGe_2Co_2^+$(20), $Ge_2Co_2^+$(23), Ge_2Co^+(19), Me_2Ge^+(19) and $MeGe^+$(31%).

Characterisation of **3b**.—The compound formed yellow crystals, stable indefinitely at 20 °C under nitrogen, and able to be handled in air for brief periods. ν(CO) (IR, hexane solution) 2081w, 2054vs, 2037vvs, 2015m and 2002m cm^{-1}; [CsI disc (mull similar)] 2082ms, 2058s, 2053(sh), 2041(sh), 2030vvs, 2018vw, 2008w, 1996s and 1988vw, 1982w, 1961(sh) cm^{-1}; (Raman, solid) 2081ms, 2056w, 2036w, 2010s, 2006vs, 2000(sh), 1997s, 1990s, 1982s, 1976vw and 1973w cm^{-1}.

At lower frequencies, a Nujol mull showed IR bands at 851s, 800vs, 767mw and 717w [ρ(Me)]; 622m and 580m [ν(GeC)]; 563m, 537vvs, 509vs, 463w, 448m and 418m (Co–C–O modes). The Raman spectrum showed lower frequency bands at 583w [ν(GeC)]; 570m, 520w, 470m and 420w (Co–C–O modes); and heavy-atom skeletal modes at 265s, 230s, 200vs, 180m, 120m, 110s, 90vs, 75s and 60m cm^{-1}. These latter should be compared with the skeletal modes of **1** found at 221s, 201w, 181w, 148m, 136m and 93w cm^{-1}. ^1H NMR ($CDCl_3$) δ 1.34 (s).

The highest envelope of peaks in the mass spectrum of **3b** was centred at *m*/*z* 838 (relative intensity 48%) with intensities corresponding to 3Ge. The envelope is thus assigned to the loss of CH_x ($x = 2$, 3 or 4 cannot be distinguished) from **3b**: $(P - \text{CH}_x)^+ = C_{15}H_{10-8}Co_4Ge_3O_{12} = 826\text{–}846$. The major series of fragment ions corresponded to $(P - \text{CH}_x - n\text{CO})^+$ (relative intensities in brackets) for $n = 1$ (41), 2 (69), 3 (76), 4 (61), 5 (74), 6 (100), 7 (80), 8 (94), 9 (50), 10 (36), 11 (12) and 12 (9%). A further series is assigned to $(P - 2\ \text{CH}_x - n\text{CO})^+$, weak for $n = 2$–8 and more prominent for $n = 9$ (26), 10 (17), 11 (41) and 12 (54). Peaks due to $CH_xGe_3Co_y^+$ [$y = 4$ (59) and 3 (20%)] and $Ge_3Co_y^+$ [$y = 4$ (81) and 3 (34%)] are also seen. Alternative assignments with one less CO and two more CH_x groups are also possible.

X-Ray Crystal Structure of **3b**.—A suitable single crystal was obtained from hexane at −10 °C. Preliminary precession photography showed triclinic symmetry. Cell dimensions and intensity data were obtained on a Nicolet P3 diffractometer, using Mo-Kα X-rays (λ = 0.710 69 Å). The data were corrected for absorption (based on φ scans), and the structure was solved by direct methods and refined using the SHELX programs.[21]

Crystal data. $C_{16}H_{12}Co_4Ge_3O_{12}$, $M = 849.77$, triclinic, space group $P\bar{1}$ (no. 2), $a = 9.607(3)$, $b = 14.796(4)$, $c = 9.476(3)$ Å, $\alpha = 95.83(2)$, $\beta = 91.94(2)$, $\gamma = 98.83(2)°$, $U = 1322.4(6)$ Å^3, $Z = 2$, $D_c = 2.14$ g cm^{-3}, transmission 0.949(max.), 0.736(min.), μ(Mo-Kα) 57 cm^{-1}, $F(000) = 816$, T 293 K.

5192 Unique reflections were collected by θ–2θ scans, in the range 4 < 2θ < 45°, with 3353 [$I > 2\sigma(I)$] used in calculations. All non-H atoms anisotropic, H atoms included as calculated CH_3 groups, full-matrix least-squares refinement converged to $R = 0.044$, $R' = 0.0399$ with $w = [\sigma^2(F) + 0.000\,322F^2]^{-1}$. Largest final Δ/σ (not involving CH_3 orientation) was 0.08, largest residual peak 0.5 e Å^{-3}. Final positional parameters are given in Table 1, selected bond parameters in Table 2 and the structure is illustrated in Fig. 1.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Effect of CO *under Pressure on* **1**, **2a** *or* **2b**.—The cluster $[\mu_4\text{-Ge}\{Co_2(CO)_7\}_2]$ **1** (40 mg, 0.05 mmol) in hexane (5 cm^3) was sealed in a bomb under CO (30 atm) for 24 h. The sample was cooled to 0 °C before opening, and an infrared spectrum showed the presence of $[Ge\{Co(CO)_4\}_4]$,[19] as well as **1**. The cluster $[Ge\{Co(CO)_4\}_4]$ reverted to **1** within 5 min at room temperature.

For **2a**, after 16 h under 30 atm CO, an infrared spectrum of the hexane solution at atmospheric pressure showed that $[\mu_4\text{-Ge}\{Co_2(\mu\text{-GeMeH})(CO)_6\}\{Co_2(CO)_7\}]$ **2a**, was completely converted to a new species showing ν(CO) bands at 2080w, 2068w, 2039m, 2020vs, 1998vs and 1962w cm^{-1}. Pumping off the hexane and dissolved CO led to complete reversion to **2a**.

In a similar experiment, **2b** was partly converted to a species showing ν(CO) bands at 2080w, 2070w, 2044(?) (overlapping band from **2b**), 2022vs, 1999vs and 1962w cm^{-1}. This new compound was more stable than the product from **1**, but was converted completely to **2b** on warming the hexane solution at 35 °C for 72 h.

Reactions with MMe_2H_2 (M = Si *or* Sn).—Cluster **1** (485 mg, 0.69 mmol) and $SiMe_2H_2$ (3.7 mmol) were combined in hexane in a sealed tube in the dark for 18 weeks. The solution turned pale purple and showed weak additional IR bands at 2081s, 2043vs and 2026m cm^{-1} characteristic of the closed cluster $[\mu_4\text{-Ge}\{Co(CO)_4\}Co_3(CO)_9]$.[9] Recrystallisation led to the recovery of unchanged **1** (470 mg, 0.67 mmol). Similarly **2b** showed no reaction with $SiMe_2H_2$ over 8 months.

A corresponding reaction between $SnMe_2H_2$ and **1** in a 1.2:1 ratio for 3 weeks led to 98% recovery of **1**. Extra IR bands indicated minor formation of $[SnMe_2\{Co(CO)_4\}_2]$.[13]

Table 1 Final positional parameters for $[\mu_4\text{-Ge}\{Co_2(\mu\text{-GeMe}_2)(CO)_6\}_2]$ **3b**

Atom	x	y	z	Atom	x	y	z
Ge(1)	0.2182(1)	0.2426(1)	0.7664(1)	C(43)	0.131(1)	0.1222(6)	0.4971(9)
Ge(2)	0.2009(1)	0.4238(1)	0.6265(1)	C(1)	0.236(1)	0.3677(7)	0.4398(9)
Ge(3)	0.4326(1)	0.1064(1)	0.8050(1)	C(2)	0.190(1)	0.5517(6)	0.597(1)
Co(1)	0.3181(1)	0.3973(1)	0.8399(1)	C(3)	0.5217(9)	−0.0057(6)	0.803(1)
Co(2)	0.0467(1)	0.3437(1)	0.7749(1)	C(4)	0.5818(9)	0.2037(6)	0.888(1)
Co(3)	0.1928(1)	0.0974(1)	0.8587(1)	O(11)	0.2770(7)	0.5830(4)	0.9549(8)
Co(4)	0.2881(1)	0.1261(1)	0.6060(1)	O(12)	0.3906(8)	0.3490(5)	1.1210(7)
C(11)	0.2938(8)	0.5099(6)	0.9096(9)	O(13)	0.5802(7)	0.4178(5)	0.6970(7)
C(12)	0.3583(9)	0.3637(6)	1.009(1)	O(21)	−0.1418(7)	0.2440(5)	0.5477(9)
C(13)	0.4748(9)	0.4080(6)	0.7506(9)	O(22)	−0.0365(7)	0.2763(4)	1.0455(7)
C(21)	−0.0625(9)	0.2812(6)	0.635(1)	O(23)	−0.0747(6)	0.5134(4)	0.8259(7)
C(22)	−0.0035(9)	0.3008(5)	0.941(1)	O(31)	−0.1115(6)	0.0780(4)	0.7904(7)
C(23)	−0.0232(8)	0.4481(5)	0.8061(8)	O(32)	0.1891(7)	−0.1009(4)	0.8523(8)
C(31)	0.0063(9)	0.0872(5)	0.8171(8)	O(33)	0.2400(8)	0.1629(5)	1.1587(7)
C(32)	0.1914(8)	−0.0240(5)	0.8537(9)	O(41)	0.3222(7)	−0.0623(4)	0.5038(7)
C(33)	0.2245(9)	0.1409(6)	1.041(1)	O(42)	0.5173(7)	0.2393(4)	0.4837(8)
C(41)	0.3086(9)	0.0108(6)	0.5455(9)	O(43)	0.0368(8)	0.1157(5)	0.4224(7)
C(42)	0.4277(9)	0.1977(6)	0.5358(9)				

Table 2 Selected bond lengths (Å) and angles (°) for $[\mu_4\text{-Ge}\{Co_2(\mu\text{-GeMe}_2)(CO)_6\}_2]$ **3b**

Ge(1)–Co(1)	2.366(1)	Ge(2)–C(2)	1.960(8)
Ge(1)–Co(2)	2.387(1)	Ge(3)–Co(3)	2.363(1)
Ge(1)–Co(3)	2.383(1)	Ge(3)–Co(4)	2.372(1)
Ge(1)–Co(4)	2.372(1)	Ge(3)–C(3)	1.979(7)
Ge(2)–Co(1)	2.378(1)	Ge(3)–C(4)	1.951(8)
Ge(2)–Co(2)	2.349(1)	Co(1)–Co(2)	2.640(1)
Ge(2)–C(1)	1.939(9)	Co(3)–Co(4)	2.644(1)
Co(1)–Ge(1)–Co(2)	67.5(1)	Ge(1)–Co(1)–Co(2)	56.6(1)
Co(1)–Ge(1)–Co(3)	138.3(1)	Ge(2)–Co(1)–Co(2)	55.6(1)
Co(1)–Ge(1)–Co(4)	133.1(1)	Ge(1)–Co(2)–Ge(2)	82.8(1)
Co(2)–Ge(1)–Co(3)	125.4(1)	Ge(1)–Co(2)–Co(1)	55.9(1)
Co(2)–Ge(1)–Co(4)	138.5(1)	Ge(2)–Co(2)–Co(1)	56.6(1)
Co(3)–Ge(1)–Co(4)	67.6(1)	Ge(1)–Co(3)–Ge(3)	82.6(1)
Co(1)–Ge(2)–Co(2)	67.9(1)	Ge(1)–Co(3)–Co(4)	56.0(1)
C(1)–Ge(2)–C(2)	103.9(4)	Ge(3)–Co(3)–Co(4)	56.2(1)
Co(3)–Ge(3)–Co(4)	67.9(1)	Ge(1)–Co(4)–Ge(3)	82.6(1)
C(3)–Ge(3)–C(4)	103.3(4)	Ge(1)–Co(4)–Co(3)	56.4(1)
Ge(1)–Co(1)–Ge(2)	82.6(1)	Ge(3)–Co(4)–Co(3)	55.9(1)

Dihedral angles (°)

Ge(1)Co(1)Co(2)/Ge(1)Co(3)Co(4)	101
Ge(1)Co(1)Co(2)/Ge(2)Co(1)Co(2)	105
Ge(1)Co(3)Co(4)/Ge(3)Co(3)Co(4)	105

Related Reactions.—The cluster $[\mu_4\text{-Si}\{Co_2(CO)_7\}_2]$, the Si analogue of **1** (444 mg, 0.68 mmol) and $GeMe_2H_2$ (4.25 mmol) in hexane (10 cm^3) were sealed and left to react in the dark with shaking for 4 months. The colour changed from red to dark purple in 2 months. There were recovered incondensable gases (0.57 mmol, 23% CO) and a hexane-soluble fraction with an IR spectrum showing $[Co_2(\mu\text{-GeMe}_2)(CO)_7]$,[14] $[Co_2(\mu\text{-GeMe}_2)_2(CO)_6]$[3] and $[GeMe_2\{Co(CO)_4\}_2]$[5,13] together with the closed cluster $[\mu_4\text{-Si}\{Co(CO)_4\}Co_3(CO)_9]$.[22] There was no indication of any analogue of **2** or **3**.

In a similar reaction of $[\mu_4\text{-Si}\{Co_2(CO)_7\}_2]$ (280 mg, 0.43 mmol) and $SiMe_2H_2$ (1.8 mmol) the mixture turned purple after a few days. After several months the mixture yielded incondensable gases (1.63 mmol, 99% H_2) and a hexane-soluble fraction containing, in decreasing amounts, $[SiMe_2H\{Co(CO)_4\}]$,[23] $[SiMe_2\{Co(CO)_4\}\{OCCo_3(CO)_9\}]$,[24] $[Co_4(CO)_{12}]$, and $[Co_2(CO)_8]$, based on infrared bands. Solubilities were too similar to allow useful separation.

Mild Heating of **2b**.—A sample of **2b** (73 mg, 0.094 mmol) was dissolved in hexane (5 cm^3) and heated in a 20 cm^3 tube at 30 °C. The colour changed from orange-red, through yellow-brown to dark red-brown and gas was evolved very slowly, totalling only 0.029 mmol after 70 d. The temperature was raised to 49 °C, giving a further 0.06 mmol of gas quite rapidly but then tapering off over the next 8 weeks. After a total of 136 d the accumulated gas was *ca.* 1.5 mol equivalent. The hexane-soluble fraction contained **1** and **3** as well as **2**, with approximately equal intensities of the diagnostic IR bands, while the CH_2Cl_2-soluble fraction was a red solid showing IR bands at 2063(sh), 2032vs, 2010m (sh), 1841–1833vw (br) cm^{-1} which indicate the closed cluster[10] $[Co_4(\mu_4\text{-GeMe})_2(CO)_{11}]$.

Heating **2b** (0.109 mmol) in hexane at 50 °C for 59 d evolved 0.15 mmol gas. Work-up gave a hexane-soluble mixed fraction of 50 mg, containing **2b**, **3b** and **1**, and a dichloromethane fraction of pure $[Co_4(\mu_4\text{-GeMe})_2(CO)_{11}]$ (34 mg, 0.047 mmol, 43%).

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