A Further Study of the Reaction of Methylgermane with $[Co_2(CO)_8]$, and some Interconversions of the Products. Crystal and Molecular Structures of $[Co_2\{\mu\text{-}Ge(Me)Co(CO)_4\}(CO)_7]$ and $[Co_4(\mu_4\text{-}GeMe)_2\{\mu\text{-}Ge(Me)Co(CO)_4\}(CO)_{10}]$,† an Edge-bridged Square-bipyramidal Ge_2Co_4 Species

Skelte G. Anema, Siew Kim Lee, Kenneth M. Mackay,* Brian K. Nicholson* and Miranda Service
School of Science, University of Waikato, Private Bag, Hamilton, New Zealand

The compound $[CoH(CO)_4]$ has been established as a stoichiometric product in the fast reaction of $GeMeH_3$ with $[Co_2(CO)_8]$ to form $[Co_2\{\mu\text{-}Ge(Me)Co(CO)_4\}(CO)_7]$ **1**. A prolonged reaction with an excess of $GeMeH_3$ yields $[Co_2\{\mu\text{-}Ge(Me)Co(CO)_4\}_2(CO)_6]$ **2**, accompanied by a hydride species $[Co_2(GeMeH)(CO)_x]$ (x = 7 or 8) when the excess is large. Heating this latter mixture yields $[Co_4(\mu_4\text{-}GeMe)_2\{\mu\text{-}Ge(Me)Co(CO)_4\}(CO)_{10}]$ **3**, shown by X-ray crystallography to contain the $Co_4(\mu_4\text{-}GeMe)_2$ square-bipyramid core, edge-bridged by a μ-Ge(Me)[Co(CO)$_4$] unit. The bridged Co atoms carry two terminal CO groups, and the non-bridged ones, three. The crystal structures of compound **1** [triclinic, space group $P\bar{1}$, $Z = 2$, $a = 8.626(6)$, $b = 8.656(5)$, $c = 13.381(9)$ Å, $\alpha = 88.25(5)$, $\beta = 84.72(5)$, $\gamma = 66.26(4)°$, $R = 0.0649$ for 1614 reflections with $I > 3\sigma(I)$] and **3** [monoclinic, space group $C2/m$, $Z = 4$, $a = 12.330(6)$, $b = 12.302(3)$, $c = 18.815(9)$ Å, $\beta = 92.93(3)°$, $R = 0.0344$ for 1136 reflections with $I > 3\sigma(I)$] have been determined and are compared with that of **2**, and spectroscopic properties are discussed, including heavy-atom vibrations of **1**

Nearly twenty years ago[1] we treated $GeMeH_3$ with $[Co_2(CO)_8]$ in the hope of forming $[Co(GeMeH_2)(CO)_4]$, by analogy with an earlier study by MacDiarmid and co-workers[2] where $SiMeH_3$ reacted with $[Co_2(CO)_8]$ to form $[Co(SiMeH_2)(CO)_4]$ in 50% yield. Instead, a very rapid reaction with $GeMeH_3$ ensued[1,3] in which all the Ge–H bonds were replaced by Ge–Co to yield $[Co_2\{\mu\text{-}Ge(Me)Co(CO)_4\}(CO)_7]$ **1**. The reaction was complete in a few minutes at ambient temperature and gave a good yield of **1** plus CO and H_2; $[CoH(CO)_4]$ was also found but not quantified. The reaction proceeded *via* partly substituted intermediates of which $[Co(GeMeH_2)(CO)_4]$ was fully characterised and shown[1,3] to form compound **1** in a similar reaction. The compounds $[\{Co(CO)_4\}_2GeMeH]$ and $[Co_2(\mu\text{-}GeMeH)(CO)_7]$ were proposed as the disubstituted intermediates, and traces of two further $MeGeCo_3$ species were also seen: none of these minor products was characterised. The carbonyl stretching frequencies of **1** were almost identical to those reported earlier by Graham and co-workers[4] for $[Co_2\{\mu\text{-}Ge(Ph)Co(CO)_4\}(CO)_7]$, so the same structure was attributed to **1**, in which one μ-CO of $[Co_2(CO)_8]$ was replaced by μ-Ge(Me)[Co(CO)$_4$]. An alternative synthesis of **1** was reported by Etzrodt and Schmid.[5]

We have re-examined this reaction, because our recent experience[6,7] with room-temperature reactions between $[Co_2(CO)_8]$ and germanium polyhydrides suggested that further, much slower, reactions might occur and increase the yield of some of the minor species found earlier.[1,3] In addition, we now know that $[Co_2\{\mu\text{-}Ge(Me)Co(CO)_4\}_2(CO)_6]$ **2**, the disubstituted analogue of **1** where both μ-CO are replaced, can be prepared by a quite different reaction.[8] Clearly, **2** is one possible product from a more prolonged methylgermane reaction. We report here the results of this study.

Results and Discussion

The Reaction of $GeMeH_3$ *and* $[Co_2(CO)_8]$.—The present experiments demonstrate that the reaction of methylgermane with octacarbonyldicobalt is a complex one whose products depend mainly on reaction ratio and, to some extent, on reaction time. The disubstituted $[Co_2(CO)_8]$ derivative **2** has been established as a second product and conditions have been defined for directing the conversion into either **1** or **2**.

The overall equation for the original reaction[3] was (1) when

$$2\,GeMeH_3 + 3[Co_2(CO)_8] \longrightarrow 3H_2 + 2CO + 2[Co_2\{\mu\text{-}Ge(Me)Co(CO)_4\}(CO)_7] \quad (1)$$

there was an interval before work-up, though reactions followed by proton NMR spectroscopy showed substantial initial conversion into $[CoH(CO)_4]$ and $[Co(GeMeH_2)(CO)_4]$. The $[CoH(CO)_4]$ is now established as a primary product. Equation

$$GeMeH_3 + 2[Co_2(CO)_8] \longrightarrow H_2 + CO + [CoH(CO)_4] + [Co_2\{\mu\text{-}Ge(Me)Co(CO)_4\}(CO)_7] \quad (2)$$

(2) was followed when the reaction was carried out in an open tube with removal of gases, the reactant ratio was 1 : 1, and the reaction time was around half a day at 10–20 °C. The measured quantities match well, making modest allowance for incomplete recovery of $GeMeH_3$ from the solvent and some decomposition of $[CoH(CO)_4]$ during the reaction. Equations (1) and (2) are compatible if there is enough time for the reaction (3) to occur

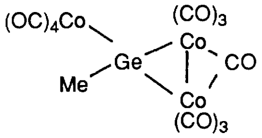
$$2\,[CoH(CO)_4] \longrightarrow H_2 + [Co_2(CO)_8] \quad (3)$$

and the reformed $[Co_2(CO)_8]$ reacts further by equation (2).[9]

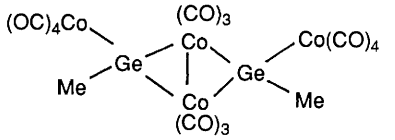
---

† μ-Carbonyl-1:2κ^2C-decacarbonyl-1κ^3C, 2κ^3C, 3κ^4C-μ_3-methylgermanetriyl-tricobalt(*Co*^{1}–*Co*^{2}) and decacarbonyl-1κ^3C, 2κ^3C, 4κ^2C, 6κ^2C-dimethyl-3κC, 5κC-μ-methyl(tetracarbonylcobaltio)germanediyl-4:6κ^2*Ge*-*octahedro*-tetracobalt-3,5-digermanium.

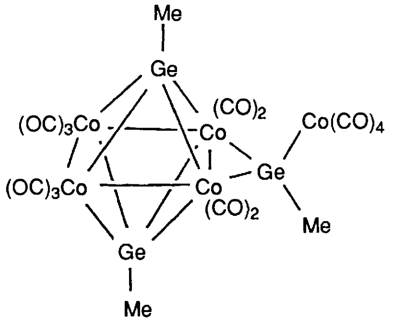
Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.



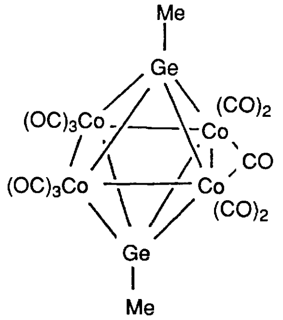
1



2



3



4

The contribution of $[CoH(CO)_4]$ in such reactions is seldom clear,[2,3,9] as it is very difficult to separate quantitatively from the solvent, and it decomposes steadily by equation (3) under experimental conditions. It is thus usually estimated by infrared intensities. Here, $[CoH(CO)_4]$ was shown to be a stoichiometric reagent by removing it, together with solvent, and allowing the quantitative conversion into $[Co_4(CO)_{12}]$ in the absence of CO, which could then be weighed. On the other hand, all the H_2 does not arise from equation (3), as the rate of hydrogen evolution in the course of the reaction was much higher than that of (3) under similar conditions. From the earlier work,[3] the overall reaction (2) undoubtedly proceeds *via* compounds like $[Co(GeMeH_2)(CO)_4]$, $[Co_2(\mu\text{-}GeMeH)(CO)_7]$ and $[\{Co(CO)_4\}_2GeMeH]$.

In a sealed tube for 6 months, a 2:1 reagent ratio of $[Co_2(CO)_8]$ to $GeMeH_3$ gave essentially the same reactions as found for short periods, equations (1)–(3). The excess of cobalt carbonyl formed $[Co_4(CO)_{12}]$ and the *ca.* 4% $[Co_4(\mu_4\text{-}GeMe)_2(CO)_{11}]$[7] **4** probably resulted[10] from the reaction of this with $GeMeH_3$. No $[CoH(CO)_4]$ was observed, as expected from the long reaction time. However, substantial $[Co_4(CO)_{12}]$ formation, despite the presence of free CO, suggests that the conversion of the excess of $[Co_2(CO)_8]$ involved reaction with $[CoH(CO)_4]$. The trace of the closed cluster $[Co_3(\mu_3\text{-}GeMe)(CO)_9]$ was to be expected from the decarbonylation of **1** during the long reaction.[4,5]

In contrast, when the $[Co_2(CO)_8]$: $GeMeH_3$ ratio was reversed to 1:2 in long-term sealed-tube runs, the main reaction followed equation (4), giving compound **2** where the remaining

$$\begin{aligned}2\,GeMeH_3 + 2[Co_2(CO)_8] &\longrightarrow 3H_2 + 2CO\\ &+ [Co_2\{\mu\text{-}Ge(Me)Co(CO)_4\}_2(CO)_6]\\ &+ [Co_2(GeMeH)(CO)_x]\ (x = 7 \text{ or } 8) \quad (4)\end{aligned}$$

μ-CO is replaced by μ-Ge(Me)$[Co(CO)_4]$; only a trace of **1** was found. As the product mixture could not be separated, the yields were assessed indirectly to be about 60% **2** and 40% $[Co_2(GeMeH)(CO)_x]$. For the latter, the NMR intensities showed a 2:1 split and it is thought the major component has $x = 8$. About 2% $[Co_3(\mu_3\text{-}GeMe)(CO)_9]$ was also found.

In contrast to the short-term open-tube reactions, in the sealed-tube run with a 1:1 ratio of $[Co_2(CO)_8]$ to $GeMeH_3$, equations (1)–(3) and (4) were followed to similar extents. Thus the longer reaction time produced a substantial proportion of compound **2**, while the initial fast reactions[3] yielded only **1**. The structure of **2**[8] shows that the two bridging groups are very close, which no doubt accounts for the marked difference in the rates of the two substitution steps. The formation of **2** in good yield required a 2:1 or higher ratio of $GeMeH_3$ to $[Co_2(CO)_8]$, and the much longer reaction times. Such conditions produced a number of other products, making separation difficult, and giving poor recoveries of pure **2**. Thus, the best route to **2** is probably the indirect one[8] *via* the reaction of $[Fe(GeMeH_2)_2(CO)_4]$ with $[Co_2(CO)_8]$.

In an NMR experiment $[Co_2(CO)_8]$ reacted with a large excess of $GeMeH_3$. Monitoring showed the rapid initial formation of $[Co(GeMeH_2)(CO)_4]$, a $GeMeHCo_2$ species, **1**, and $[CoH(CO)_4]$ as in the earlier work[3] with a lower reagent ratio. However, as $GeMeH_3$ continued to react, $[Co(GeMeH_2)(CO)_4]$ was produced more rapidly than **1** and the minor di- and tri-substituted components changed. The major divergence from the observations at lower $GeMeH_3$ ratio came in the second and third days of reaction where **1** disappeared, along with the minor components and $[CoH(CO)_4]$, to leave as main products H_2, $[Co(GeMeH_2)(CO)_4]$ and a new $GeMeHCo_2$ species giving a doublet at δ 1.41, $J = 3.17$ Hz. Since all the initial $[Co_2(CO)_8]$ was consumed in the first stages, these later changes suggest that the slowly produced $[Co_2(CO)_8]$ from equation (3) reacts with the excess of methylgermane to form principally $[Co(GeMeH_2)(CO)_4]$. Then, in what appears to be the critical step, **1** reacted with either $GeMeH_3$ or $[Co(GeMeH_2)(CO)_4]$ to give the, as yet unidentified, $GeMeHCo_2$ species. This is neither of the species (provisionally identified as $[Co_2(GeMeH)(CO)_7]$ or $[\{Co(CO)_4\}_2GeMeH]$) formed in the early stages and with lower methylgermane ratios. Compound **2** was probably represented by the weak singlet at δ 1.8 which appeared in the first day. Its later disappearance may signal further reaction, but more probably precipitation. While there are a number of possibilities for this later reaction, one is the formation of $[Co_2(\mu\text{-}GeMeH)\{\mu\text{-}Ge(Me)Co(CO)_4\}(CO)_6]$ by replacement of the μ-CO in **1**, equation (5). Such μ-GeMeH

$$\mathrm{GeMeH_3 + 1 \longrightarrow H_2 + CO + [Co_2(\mu\text{-}GeMeH)\{\mu\text{-}Ge(Me)Co(CO)_4\}(CO)_6]} \quad (5)$$

species could well be intermediates in the formation of **2** under the conditions of the long-term sealed-tube reactions.

The separate reaction of $GeMeH_3$ and compound **1** supports this picture. These reacted in the ratio 1 : 1, while a little less than 1 H_2 and a little more than 1 CO were evolved. The main product had CO vibrations similar to those of **2**, and reacted with $[Co_2(CO)_8]$ to form $[Co_4(\mu_4\text{-}GeMe)_2(CO)_{11}]$ **4**,[7] a known reaction of **2**. These observations are compatible with the formation of $[Co_2(\mu\text{-}GeMeH)\{\mu\text{-}Ge(Me)Co(CO)_4\}(CO)_6]$, and subsequent replacement of GeH with $GeCo(CO)_4$.

Further products not previously identified in the methylgermane reaction were $[Co_4(\mu_4\text{-}GeMe)_2(CO)_{11}]$ **4** and $[Co_3(\mu_3\text{-}GeMe)(CO)_9]$, both formed in the sealed-tube experiments. Compound **4** is discussed in the following paper,[10] and is likely to arise from the reaction of $GeMeH_3$ with by-product $[Co_4(CO)_{12}]$; the alternative path[8] by decarbonylation of **2** *via* equation (6a), is less likely at room temperature and in the presence of CO. The always small yield of $[Co_4(\mu_4\text{-}GeMe)_2(CO)_{11}]$ decreased as the $[Co_4(CO)_{12}]$ yield decreased. The compound $[Co_3(\mu_3\text{-}GeMe)(CO)_9]$ is quantitatively formed from **1** by decarbonylation at around 50 °C. The very long reaction times probably allowed its formation in trace amounts here.

The Formation of $[Co_4(\mu_4\text{-}GeMe)_2\{\mu\text{-}Ge(Me)Co(CO)_4\}(CO)_{10}]$ **3**.—With the aim of clarifying the composition of the mixed-product fraction of equation (4) the crude mixture was heated at 55 °C in hexane. However this produced a completely new compound type in which the large excess of $GeMeH_3$ is reflected by the incorporation of three GeMe residues in the molecule, extending the $GeCo_3$ and Ge_2Co_4 formulae of **1** and **2** to Ge_3Co_5. This last product, **3**, has a structure (see below) in which the μ-CO of $[Co_4(\mu_4\text{-}GeMe)_2(CO)_{11}]$ **4** is replaced by a $\mu\text{-}GeMe[Co(CO)_4]$ unit. The first stage of gas evolution at 55 °C produced only CO, then H_2 evolved for a stage, and finally only the slow release of CO continued. This indicates the decarbonylation of **2**, equation (6a) (a known reaction[10]), followed by the reaction of the hydride species with the $[Co_4(\mu_4\text{-}GeMe)_2(CO)_{11}]$ so produced. In equation (6b) it is probable

$$\mathbf{2} \longrightarrow \mathrm{[Co_4(\mu_4\text{-}GeMe)_2(CO)_{11}]}\ \mathbf{4} + \mathrm{3CO} \quad (6a)$$

$$\mathbf{4} + \mathrm{[Co_2(GeMeH)_y(CO)_x]} \longrightarrow \mathbf{3} + \mathrm{H_2} + ? \quad (6b)$$

that CO is also evolved as the μ-CO is replaced, and the missing $Co(CO)_x$ presumably contributes to the black residue. While this scheme is speculative it does tie up with the quantities observed. Further study of similar μ-CO replacement reactions of compound **4** is underway.

Reaction Paths.—Different paths have been proposed for the formation of Group 14 E–Co bonds from E–H. The first suggestion by Chalk and Harrod[11] and by Baay and MacDiarmid[12] was that the initial step in the reaction of silanes SiR_3H was cleavage of $[Co_2(CO)_8]$, to give $[Co(SiR_3)(CO)_4]$ and $[CoH(CO)_4]$. The latter was assumed to react as in equation (3), or with another equivalent of silane *via* equation (7). Either way the overall effect was the formation of two

$$\mathrm{[CoH(CO)_4] + SiR_3H \longrightarrow [Co(SiR_3)(CO)_4] + H_2} \quad (7)$$

$[Co(SiR_3)(CO)_4]$ molecules plus H_2. This approach, applied to germanium polyhydrides, would repeat to give a $Ge[Co(CO)_4]_2$ unit which would then eliminate CO to form the $\mu\text{-}GeCo_2(CO)_7$ unit, the commonest structural feature of the products. For example, it has been found that this condensation occurs readily in $[Ge\{Co(CO)_4\}_4]$ which starts to lose CO at 0 °C to yield $[\mu_4\text{-}Ge\{Co_2(CO)_7\}_2]$.[13]

An alternative path, for the direct formation of $\mu\text{-}GeCo_2(CO)_7$, was suggested by Brooks and Cross[14] in their seminal review. Here the Co–Co bond remains intact and the Ge–H adds with loss of a bridging CO to give a Ge–Co–Co–H intermediate. This then loses H_2 by further reaction between the Co–H and Ge–H to form the $\mu\text{-}GeCo_2(CO)_7$ unit. This pathway is consistent with our observations that evolution of H_2 is retarded relative to formation of CO. Further support came from the observation by O'Brien and co-workers[15] that $GePh_2H_2$ reacted with $[Co_2(CO)_8]$ to produce directly $[Co_2(\mu\text{-}GePh_2)(CO)_7]$ under conditions where the stepwise-addition product $[\{Co(CO)_4\}_2GePh_2]$ would not undergo CO elimination. Also suggestive are the recent observations of the reactions[16] of SiH_4 or GeH_4 with $[Os_3(CO)_{11}(NCMe)]$ where $[Os_3\{Ge(\text{or }Si)H_3\}(\mu\text{-}H)(CO)_{11}]$ is produced, with the H retained in the product and bonded to the transition metal.

More light has been thrown on the above speculative mechanisms by a recent kinetic study by Marko and co-workers.[17] They have shown that $[CoH(CO)_4]$ is not an intermediate in the reaction of $SiEt_3H$ with $[Co_2(CO)_8]$, carried out under an atmosphere of CO, and that the reaction (7) does not take place. Instead, the cobalt carbonyl cleaves to $Co(CO)_4$ and the reaction proceeds *via* this and other radical intermediates. In the absence of added CO, the hydride does form[11,12] but the reaction is complicated by intermediates rapidly formed from the cobalt carbonyls, including paramagnetic species. In the earlier NMR studies[1,3] only broad signals were seen in the first few minutes, which may reflect the presence of paramagnetic species. As the reaction proceeds, CO and $[CoH(CO)_4]$ definitely occur together.

In the present work, the time-scale for the bulk reactions is longer than that of the kinetic work and there was no initial pressure of CO. Even in the short-term NMR observations in sealed tubes, CO would be present only after the initial stages. Thus there is no conflict between our observation of a stoichiometric ratio of $[CoH(CO)_4]$ and Marko's more rigorous study. It is interesting that a $Et_3SiCo\text{–}Co\text{–}H$ species is proposed as an intermediate in the kinetic scheme, since this can only eliminate H_2 with a second $SiEt_3H$ molecule, to form the final $[Co(SiEt_3)(CO)_4]$ product.

In the case of $GeMeH_3$, it is reasonable to suggest that a similar 'Brooks and Cross' intermediate containing $GeMeH_2\text{–}Co\text{–}Co\text{–}H$ could internally eliminate H_2 to form the $(\mu\text{-}GeMeH)Co_2$ unit of compound **1** or **2** and the remaining single Ge–H can then be converted into $Ge\text{–}Co(CO)_4$ *via* a Chalk and Harrod type reaction [equation (3)]. This is supported by the identification of approximately one $[CoH(CO)_4]$ for every two $[Co_2(CO)_8]$ which suggests that the two pathways make similar contributions. This would mean that about 10% of the $[CoH(CO)_4]$ had decayed in the time the reaction took, which is reasonable. The compounds $[Co(GeMeH_2)(CO)_4]$, $[\{Co(CO)_4\}_2GeMeH]$ and $[Co_2(\mu\text{-}GeMeH)(CO)_7]$ all appear rapidly, suggesting the two paths occur together. This is also indicated by the pattern of incondensable gas evolution, where the formation of H_2 is retarded relative to that of CO, but is much faster than reaction (3) on its own. We conclude that these observations may be most simply rationalised by equal contributions from the two classical speculative mechanisms, but that they are also reconcilable with the reaction scheme proposed from the kinetic study.

The observation of the second product, **2**, from this reaction system opens up further speculation about the various species containing $GeMeHCo_2$ units, indicated in the NMR experiments. Various $[Co_2(\mu\text{-}GeR_2)_2(CO)_6]$ compounds are probable with different permutations of $GeR_2 = GeMeH$ or $GeMe[Co(CO)_4]$.

Structure of Compound **1**.—While earlier work[3,5] adequately characterised compound **1** spectroscopically, the more recent preparation and structural characterisation of two other species with $\mu\text{-}GeMe[Co(CO)_4]$ groups bridging Co–Co, namely **2**[8]

Table 1 Selected bond lengths (Å) and Angles (°) for $[Co_2\{\mu\text{-}Ge(Me)Co(CO)_4\}(CO)_7]$ **1**

Ge–Co(1)	2.383(2)	Ge–C(1)	2.01(1)
Ge–Co(2)	2.378(2)	Co(1)–Co(2)	2.587(2)
Ge–Co(3)	2.426(2)		
Co(1)–Ge–Co(2)	65.8(1)	Co(2)–Ge–C(1)	118.3(5)
Co(1)–Ge–Co(3)	123.1(1)	Co(3)–Ge–C(1)	106.8(5)
Co(1)–Ge–C(1)	116.7(6)	Ge–Co(1)–Co(2)	57.0(1)
Co(2)–Ge–Co(3)	121.9(1)	Co(1)–C(2)–Co(2)	83.1(6)

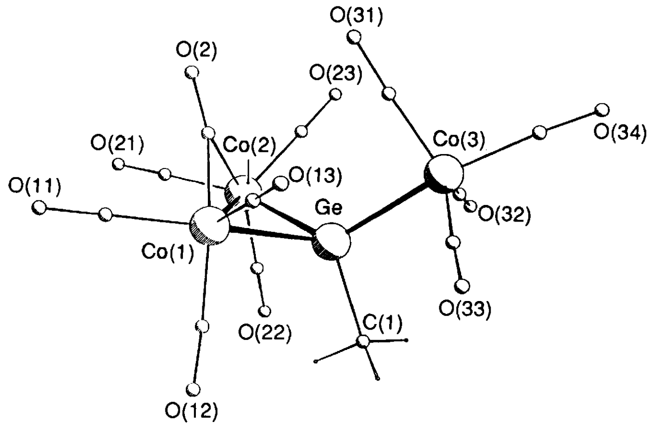


Fig. 1 A view of $[Co_2\{\mu\text{-}Ge(Me)Co(CO)_4\}(CO)_7]$ **1**

and 3, made it desirable to determine the crystal structure of **1** for comparison. Bond parameters are in Table 1 and the structure is shown in Fig. 1; as expected it is very similar to that[4] of the phenyl analogue. For both, the isomer isolated is that with the bulky $Co(CO)_4$ group on the side of the $GeCo_2$ triangle directed towards the μ-CO, which is perhaps unexpected on steric grounds. However there is infrared spectral evidence in solution for a second isomer [presumably that with $Co(CO)_4$ directed away from μ-CO] so the form found in the X-ray experiments is presumably that which crystallises most readily, and the observed O(2) ⋯ O(31) distance of 3.03 Å does not indicate excessive interactions between the two halves of the molecule. Within the $GeCo_2$ triangle, the Co–Co distance has increased by 0.06 Å from that[18] in $[Co_2(CO)_8]$, but is 0.15 Å less than in **2** which has two μ-Ge atoms. The Ge–Co distances within the triangle average 2.380 Å, much shorter than the external Ge–Co(3) bond length of 2.426 Å. These are as expected from comparison with the phenyl analogue, and with **2**. The main structural difference between compound **1** and the corresponding phenyl analogue is in the dihedral angle between the $GeCo_2$ triangle and the plane containing the μ-CO; this is 119.5° in **1**, while only 95° in the phenyl compound.[4] Reasons for this difference are not obvious, but it has been shown that butterfly angles are quite flexible in other clusters[19] and a range of values has been found for $[Co_2(\mu\text{-}X)_2(CO)_6]$ species.[13,20] The actual values are not apparently determined by the bulk of the bridging groups, as might be expected, since the value of 130° for $[Co_2(CO)_8]$ is especially wide.[18]

The Spectroscopic Properties of Compound **1**.—A Raman spectrum of compound **1** as a solid was obtained, one of the first for a fairly complex GeCo cluster. The lower-frequency Raman shifts are assignable to the heavy-element stretches, comparable with ν(Ge–Co) of 221 cm^{-1} of $[Co(GeH_3)(CO)_4]$[21] and $[Co(GeMeH_2)(CO)_4]$,[3] and the Co–Co stretch of 229 cm^{-1} of solid $[Co_2(CO)_8]$.[22] The Raman shift at the relatively high frequency of 255 cm^{-1} is assigned to the in-phase stretch of the external Ge–Co with the expanding mode of the $GeCo_2$ triangle. The shifts at 204 and 182 cm^{-1} are further stretching modes, while the lower frequencies are skeletal deformations. The shift at 585 cm^{-1}, matching the IR band at 577 cm^{-1}, is attributed to the Ge–C stretch (compare ref. 3).

The CO modes of compound **1**, together with those of **2**, may be attributed as in Table 2 by comparison with $[Co(GeH_3)(CO)_4]$[21] and $[Co(GeMeH_2)(CO)_4]$,[3] and using the Bor analysis[23] for doubly bridged $M_2(CO)_6$ units. Compounds **1** and **2** are related to $[Co_2(CO)_8]$ by replacement of the μ-CO, and thus the CO stretching modes may be seen in a simple way as the superposition of the $M_2(CO)_6$ vibrations and those of the $Co(CO)_4$ unit, assuming interaction between the two $Co(CO)_4$ groups in **2** may be neglected. Table 2 also includes the comparison with the two related μ-$GeMe_2$ analogues.[24] While disubstitution in the $GeMe_2$ derivatives moves the Bor frequencies down by 10–14 cm^{-1}, substitution of the second $GeMe[Co(CO)_4]$ unit leads to an increase in frequency by around 10 cm^{-1}. Although a more detailed analysis is not feasible for these complex species, this assignment of the terminal modes is satisfactory, except in the 2000–2025 cm^{-1} region where the intensities are unexpected and suggest interaction between ν and the a″ mode. The overall assignment is further supported by the Raman intensities (see Table 2). While the IR spectrum of compound **1**,[3,5] and of the phenyl analogue,[4] shows two bands in the μ-CO region [presumably reflecting the presence of two isomers with the $Co(CO)_4$ group directed either towards or away from the μ-CO] only one was found in the Raman.

In the ^1H NMR spectrum only one signal is found for the Me group, suggesting the two isomers interconvert rapidly. The ^{13}C NMR spectrum of a ^{13}CO-enriched sample showed two signals, assignable to the carbonyl ligands of the $Co(CO)_4$ unit (δ 195.4) and the $Co_2(CO)_7$ unit (δ 203.5) which are interchanging within themselves but not between groups on the NMR time-scale.

Spectroscopic Properties of Compound **3**.—The NMR shifts[10] of $[Co_4(\mu_4\text{-}GeMe)_2(CO)_{11}]$ are a proton singlet at δ 2.75 and a singlet for the ^{13}CO resonance at δ 203.2 at room temperature and at δ 202.6 at −50 °C. Although the latter is broadened, there is no resolution into separate signals at accessible temperatures. Similarly, $[Co_4(\mu_4\text{-}PPh)_2(CO)_{10}]$ showed[25] a ^{13}CO singlet at 0 °C, and differentiation only occurred at −100 °C, and even then only into two signals at δ 238 and 204 with intensity ratio 1:4. In the NMR spectrum of compound **3** at −50 °C the replacement of the bridging CO by Ge slows down most of the exchange processes, and the shifts reflect the environments resulting from the two different substituents on this Ge. The proton shifts are assigned as δ 1.97 to the Me on the bridge, and 2.47 and 2.56 to the apical Me groups. The ^{13}CO signal at δ 197 must arise from the $Co(CO)_4$ carbonyls, which would continue to undergo fast scrambling among themselves at −50 °C, compare δ 195.4 for **1**. The other resonances, from their intensities, are assigned to the six CO on the two non-bridged Co(δ 203.4), while the signals at δ 200.5 and 199.6 are attributed to the two pairs of CO on the bridged edge, one pair 'up' and one pair 'down'. The mean shift for the $Co_4(CO)_{10}$ carbonyls is 202 ppm, compared with 203 ppm for the parent cluster **4** which includes the μ-CO in the fast exchange.

Structure of Compound **3**.—The molecular structure of compound **3** is shown in Fig. 2, and bond lengths and angles are given in Table 3. The molecule lies on a crystallographic mirror plane which includes the three Ge atoms and Co(3). This structure is the first example of an extension of the E_2M_4 skeleton, and is simply related to that[7] of $[Co_4(\mu_4\text{-}GeMe)_2(CO)_{11}]$ **4** by substituting the symmetrical μ-CO by a μ-$GeMe[Co(CO)_4]$ group. The Ge(3) atom is displaced slightly from the Co_4 plane, with the dihedral angle between the Ge(3)Co(2)Co(2′) and the Co_4 planes being 8.6°. This is presumably because of greater steric interactions of the terminal $Co(CO)_4$ group, compared with those of the methyl group, with the main cluster.

Table 2 Terminal carbonyl stretches (cm^{-1}) of compounds **1**, **2** and their dimethylgermyl analogues

$[Co_2(CO)_6(\mu\text{-}CO)(\mu\text{-}Z)]$			$[Co_2(CO)_6(\mu\text{-}Z)_2]$		
Z = $GeMe_2$ Ref. 24	Z = $Ge(Me)Co(CO)_4$ **1**	Raman	Z = $Ge(Me)Co(CO)_4$ **2**	Z = $GeMe_2$ Ref. 24	Assignment
	2105m	2103s	2097w		a′
2088s	2082s	2081m	2087s	2072s	q
2048vs	2056s	2057m	2067m	2035vs	s
	2046w (sh)	2040vs			a′
2026vs	2030s		2039s	2014vs	u
	2025m(br)	2021vs	2029s		a′
	2017m	2013vs	2017vs		a″
2008vs	2007w (sh)		2002w	1994vs	v
1998(sh) w	1998w	1997vs	1989mw	1984m	w
	1993w	1990m			*

All data from infrared spectrum except those labelled Raman for compound **1**: a′, a″ refer to vibrations of the $Ge(Me)Co(CO)_4$ unit with respect to the local plane of symmetry. Compare 2106(a′), 2047(a′), 2017 and 2012 (a′ and a″) for $[Co(GeMeH_2)(CO)_4]$.[3] Designations q,s,u,v and w are as defined by Bor:[23] the band marked*, which is weak in the infrared and in the Raman, is perhaps the a_2 mode of the C_{2v} $M_2(CO)_6X_2$ molecules which becomes active in this C_s compound.

Table 3 Selected bond lengths (Å) and angles (°) for $[Co_4(\mu_4\text{-}GeMe)_2\{\mu\text{-}Ge(Me)Co(CO)_4\}(CO)_{10}]$ **3**

Ge(1)–Ge(2)	2.880(2)	Ge(2)–C(3)	1.97(2)
Ge(1)–Co(1)	2.398(2)	Ge(3)–Co(2)	2.340(2)
Ge(1)–Co(2)	2.372(2)	Ge(3)–Co(3)	2.438(3)
Ge(1)–C(1)	1.99(2)	Ge(3)–C(2)	2.01(2)
Ge(2)–Co(1)	2.405(2)	Co(1)–Co(1)	2.719(4)
Ge(2)–Co(2)	2.389(2)	Co(1)–Co(2)	2.671(2)
Ge(2)–Co(2)	2.735(3)		
Co(1)–Ge(1)–C(1)	126.2(4)	Co(2)–Ge(2)–Co(2)	69.8(1)
Co(1)–Ge(1)–Co(1)	69.1(1)	Co(2)–Ge(3)–Co(3)	122.3(1)
Co(2)–Ge(1)–C(1)	127.5(4)	Co(2)–Ge(3)–Co(2)	71.5(1)
Co(2)–Ge(1)–Co(2)	70.4(1)	Co(3)–Ge(3)–C(2)	105.0(5)
Co(1)–Ge(2)–Co(2)	67.7(1)	Ge(1)–Co(1)–Ge(2)	73.7(1)
Co(1)–Ge(2)–C(3)	125.1(4)	Ge(1)–Co(2)–Ge(2)	74.4(1)
Co(1)–Ge(2)–Co(1)	68.9(1)	Ge(1)–Co(2)–Ge(3)	91.9(1)
Co(2)–Ge(2)–C(3)	129.3(4)	Ge(2)–Co(2)–Ge(3)	100.5(1)
Ge(3)–Co(2)–Co(1)	143.2(1)		

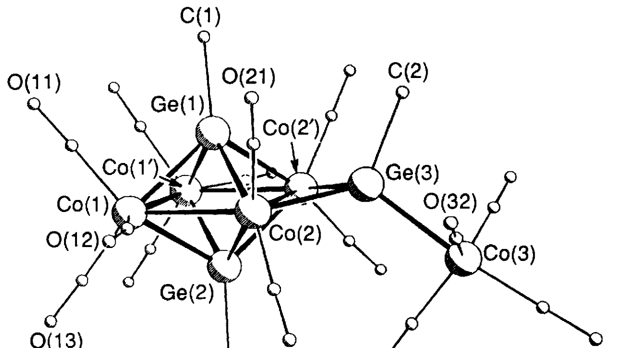


Fig. 2 The molecular structure of $[Co_4(\mu_4\text{-}GeMe)_2\{\mu\text{-}Ge(Me)Co(CO)_4\}(CO)_{10}]$ **3**. A crystallographic mirror plane includes the three germanium atoms

A comparison of the μ-GeMe$[Co(CO)_4]$ unit of compound **3** with the equivalent group in **1** shows strong similarities. The Ge(3)–C(2) and the Ge(3)–Co(3) distances, and the C(2)–Ge(3)–Co(3) angle, are indistinguishable within the accuracy of the determinations. However the bonds between Ge(3) and the core Co atoms [2.340(2) Å] are markedly shorter than the corresponding distances in **1** [average 2.380(2) Å]. This presumably arises because of a difference in the orbitals presented for bonding to Ge(3) by the two cobalt atoms in the respective complexes, since in **3** the Co–Co bond is part of a larger cluster while in **1** the Co atoms are only otherwise bonded to carbonyl groups. The Ge–Co distances involving Ge(3) are also much shorter than the Ge–Co bonds within the main cluster unit [2.385(2) Å], but this is not unexpected since Ge(3) is only four-co-ordinate while Ge(1) and Ge(2) are both five-co-ordinate. Both Ge(1) and Ge(2) are closer to the bridged Co(2)–Co(2′) edge of the cluster than to the Co(1)–Co(1′) edge, presumably partially to compensate for the electronic imbalance between Co(2) (which formally has 17.5 electrons) and Co(1) (which has an 18.5-electron count); the semibridging C(12)O(12) groups which lie in the Co_4 plane also act to redistribute the electron count more evenly. All these features are also found in the Ge_2Co_4 unit of other clusters of the type $[Co_4(\mu_4\text{-}GeR)_2(CO)_{11}]$ such as **4**.[6,7,10] The main difference between the Ge_2Co_4 units of **3** and **4** is in the bridged Co–Co bond length which has increased from 2.580 Å in **4** with a μ–CO, to 2.735 Å in **3** with a μ-Ge group, reflecting the increase in size of the bridging atom.

Experimental

Materials were handled on a conventional vacuum line, or in Schlenk equipment under nitrogen. Instrumentation and hydride preparation have been described elsewhere.[8,26]

Preliminary Study by NMR Spectroscopy.—The compound $GeMeH_3$ (0.52 mmol) was sealed with $[Co_2(CO)_8]$ (0.12 mmol) in C_6D_6 in an NMR tube and changes in the proton resonance followed at 10 °C for 72 h. In the first observation, after 5 min, the most prominent product signals were of $[Co(GeMeH_2)(CO)_4]$ (δ 0.76, 4.47, J = 3.42 Hz), **1** (δ 1.96), $[CoH(CO)_4]$ (δ -11.6), and a doublet at δ 0.87 J = 2.44 Hz, appropriate for a MeGeH species {possibly $[Co_2(GeMeH)_2(CO)_6]$. The GeH_x signals for these species were not observed. Weak, ill resolved signals were also present in the MeGe region at δ 1.1 and 1.4. As the reaction proceeded up to 24 h all the signals increased at the expense of those of $GeMeH_3$, except for the doublet at δ 0.87 which diminished until it disappeared at 5 h. The weak signals were resolved as irregular doublets at δ 1.11, J = 3.42 Hz, and δ 1.41, J = 3.17 Hz (with indications of a singlet on the low-field edge). The major product was $[Co(GeMeH_2)(CO)_4]$, with **1** the next most important, and two further much weaker singlets appearing at δ 1.8 and *ca*. 2. Between 24 and 72 h compound **1** and the weak singlets all disappeared, and $GeMeH_3$ diminished relative to $[Co(GeMeH_2)(CO)_4]$ and the doublet at δ 1.41. From 5 to 72 h a singlet at δ 4.71 grew and is assigned as H_2, while the $[CoH(CO)_4]$ decreased and disappeared.

Open-tube Reactions in 1:1 *Ratio.*—Quantities are listed below. Gases were monitored at regular intervals: the overall composition was between 60:40 and 51:49 CO:H_2 with hydrogen evolution retarded relative to CO. The compound $[CoH(CO)_4]$ was measured by separating the solvent + $[CoH(CO_4]$ cut which was heated in an ampoule to convert it into $[Co_4(CO)_{12}]$, which was then weighed. Unreacted $GeMeH_3$ was fractionated from solvent as far as possible, and the quantity remaining in the solvent fraction estimated from infrared intensities. The involatile fraction, soluble in dichloromethane and in hexane, was almost entirely **1**. Two yields for compound **1** are listed: the first based on initial $[Co_2(CO)_8]$ less the amount converted into $[CoH(CO)_4]$ and the second one based on $GeMeH_3$ consumed: the latter is more approximate because of the need to estimate the portion remaining with the solvent.

Run 1. $[Co_2(CO)_8]$ (340 mg, 1.00 mmol); $GeMeH_3$ (added, 1.00 mmol, recovered unreacted *ca.* 0.41 mmol); hexane (5 cm^3) for 9 h at 20 °C; produced incondensable gases [0.98 mmol total over 9 h of which 45% (30% H_2) in 1.5 h and 90% in 4 h]; $[CoH(CO)_4]$ {0.44 mmol by decomposition to $[Co_4(CO)_{12}]$ (64 mg, 0.11 mmol)}; **1** (284 mg, 0.50 mmol, 96%, *ca.* 85%).

Run 2. $[Co_2(CO)_8]$ (667 mg, 1.98 mmol); $GeMeH_3$ (added, 1.96 mmol, recovered unreacted 0.98 mmol); hexane (10 cm^3) for 13 h at 10 °C; produced incondensable gases [1.99 mmol total over 13 h of which 50% (35% H_2) in 2 h and 90% in 7 h]; $[CoH(CO)_4]$ {0.88 mmol from 127 mg, 0.22 mmol $[Co_4(CO)_{12}]$}; **1** (509 mg, 0.89 mmol, 88%, *ca.* 98%).

Run 3. $[Co_2(CO)_8]$ (677 mg, 1.98 mmol); $GeMeH_3$ (added, 1.98 mmol, recovered unreacted *ca.* 0.91 mmol); hexane (5 cm^3) for 9 h at 10 °C; produced incondensable gases [2.25 mmol total over 9 h of which 55% (40% H_2) in 1.5 h and 90% in 4h]; $[CoH(CO)_4]$ {0.88 mmol from $[Co_4(CO)_{12}]$, 124 mg, 0.22 mmol}; **1** (516 mg, 0.90 mmol, 88%, *ca.* 84%).

Sealed-tube, long-term Reactions.—For reactions in sealed tubes (volume 50 cm^3, 10 cm^3 hexane) for 6 months at 20 °C, reagent ratios of $[Co_2(CO)_8]$: $GeMeH_3$ were approximately 2:1 (run 1: 876 mg, 2.56 mmol with 1.31 mmol), 1:1 (run 2: 1069 mg, 3.13 mmol with 2.72 mmol), and 1:2 (run 3:675 mg, 1.98 mmol with 3.95 mmol) where the $GeMeH_3$ was measured by volume. The system gave a red-brown solution and a red solid. Gases and volatiles were removed and involatile products were separated by extraction with hexane then dichloromethane, to give the following products.

Run 1. Gases (3.18 mmol containing 60% H_2); **1** (350 mg, 0.61 mmol, 47%); $[Co_4(CO)_{12}]$ (50 mg, 0.09 mmol); $[Co_2(CO)_8]$ (25 mg, 0.07 mmol); $[Co_4(\mu_4\text{-}GeMe)_2(CO)_{11}]$ **4** (30 mg, 0.04 mmol); and a mixed fraction of **1** and $[Co_4(CO)_{12}]$ (450 mg, *ca.* 0.79 mmol, M_r of each component almost the same). The contributions from the mixed fraction and the pure sample bring the yield of compound **1** to over 80% based on equation (2). Based on the MeGe-containing species recovered, the H_2 yield is 100 ± 10%.

Run 2. Gases (5.24 mmol containing 68% H_2); **1** (732 mg, 1.28 mmol, 47%); an oily mixed fraction (474 mg); $[Co_4(\mu_4\text{-}GeMe)_2(CO)_{11}]$ (31 mg, 0.04 mmol, 1%); and traces of $[Co_4(CO)_{12}]$ and $[Co_3(\mu_3\text{-}GeMe)(CO)_9]$. The infrared spectrum of the oil in CH_2Cl_2–hexane showed CO vibrations at 2102w, 2094vw, 2083s, 2079vs, 2070w, 2065mw, 2053s, 2038s, 2029vs, 2017vvs, 2012 vvs, 2002m (sh), 1967vw (sh), 1847w and 1835vw cm^{-1}. These, together with a mass spectrum, indicate a mixture of **1**, $[(Co_2MeGeH)(CO)_x]$ for $x = 7$ and/or 8,[3] and **2**. In the ^1H NMR spectrum of an extract of the oil into $CDCl_3$ these three components gave respectively a singlet at δ 1.95, a distorted doublet at δ 1.39 plus multiplets at δ 5.18 and 5.68, and a singlet at δ 1.71. The relative intensities were 4:3:10, and the weak GeH signals were in the ratio of 3 (attributed to $x = 8$): 1 ($x = 7$). From the IR and NMR intensities, a rough partition of the oily fraction suggests that the approximate conversion into the major products was 60% **1**, 15–20% **2**, and 25–20% mixed hydride species.

Run 3. Gases (3.34 mmol containing 57% H_2); $[Co_3(\mu_3\text{-}GeMe)(CO)_9]$ (20 mg, *ca.* 2%), **1** (trace); insoluble material [13 mg, no ν(CO)]; and a mixed fraction containing substantial amounts of **2** and $[Co_2(GeMeH)(CO)_x]$, and a smaller proportion of a species giving a strong infrared band at 2004 cm^{-1} with a shoulder at 2000 cm^{-1}. This was not identified, but was removed by pumping, leaving the inseparable mixed fraction of **2** and $[Co_2(GeMeH)(CO)_x]$ (673 mg).

This fraction was further investigated by heating to 55 °C in hexane and measuring evolved gases. The first stage (2 weeks) was marked by the steady evolution of 2.33 mmol CO. In the next stage (12 d) H_2 formed (0.18 mmol) together with CO (0.19 mmol). The third stage (5 weeks) was marked by a very slow evolution of both gases giving an overall total of 0.24 mmol H_2 and 2.64 mmol CO to this point. In the last stage only CO formed, and very slowly, increasing the overall total of CO to 2.79 mmol after 22 weeks. Heating for a further 40 d at 75 °C produced only a further 0.02 mmol CO. Work-up showed no unchanged compound **2** or hydride fraction; a pure fraction of the species identified below as $[Co_4(\mu_4\text{-}GeMe)_2\{\mu\text{-}Ge(Me)Co(CO)_4\}(CO)_{10}]$ **3** (335 mg, 0.311 mmol), a mixed fraction (100 mg), made up of **3** and **4**, *ca.* 2:1, and an insoluble black powder (150 mg) showing very weak ν(CO) modes indicating only a trace of **3** together with a non-carbonyl species. Calculating back from the hydrogen figure suggests 0.48 ± 0.06 mmol $[Co_2(GeMeH)(CO)_7]$, 150 ± 25 mg of the starting mixture. This leaves *ca.* 0.7 ± 0.1 mmol **2**, which would account for most of the initial 2.33 mmol CO by conversion into $[Co_4(\mu_4\text{-}GeMe)_2(CO)_{11}]$. Thus the mixed fraction would have been about 60% **2** and 40% hydride by mass.

The formation of the new compound **3** (*ca.* 0.37 mmol) would appear to indicate a 1:1 reaction between $[Co_4(\mu_4\text{-}GeMe)_2(CO)_{11}]$ and the hydride species. Other by-products, and probably the slow later decarbonylation stages, produced the insoluble black powder.

Reaction of Compound **1** *with* $GeMeH_3$.—A prolonged reaction in a sealed tube in hexane between $GeMeH_3$ (2.43 mmol by volume) and compound **1** (346 mg, 0.60 mmol) yielded incondensable gases (1.1 mmol, 40% CO), unreacted $GeMeH_3$ (1.7 mmol + small fraction remaining with the solvent), and an oily involatile fraction which gave a bright orange hexane solution. This could not be separated by extraction or fractional crystallisation, but the IR spectrum [2102m, 2094s, 2083vs, 2079w (sh), 2073s, 2070w (sh), 2065s, 2053w (sh), 2038vs (br), 2017vs (br), 1966w, 1954w, 1847w, and 1834vw cm^{-1}] indicated a small proportion of **1** and a species greatly resembling **2**.

A portion of this product mixture (131 mg) was allowed to react with $[Co_2(CO)_8]$ (40mg, 0.12 mmol) in hexane to form an orange-brown solution with red-brown crystals. Apart from a small amount of unreacted $[Co_2(CO)_8]$, and a little **1**, the product consisted of $[Co_4(\mu_4\text{-}GeMe)_2(CO)_{11}]$, confirmed[10] by IR and mass spectroscopy.

Characterisation of $[Co_2\{\mu\text{-}Ge(Me)Co(CO)_4\}(CO)_7]$ **1**.—The CO stretches in the IR spectrum (Table 2), and the mass spectrum, agreed with those reported.[3,5] A Nujol mull also showed weak IR bands at 577, 555 and 529 cm^{-1}. A Raman spectrum of the solid showed the terminal CO modes listed in Table 2 together with bands at: 1834m, 585m, 565m, 495m, 473s, 448s, 413vs, 383vs, 363m, 255m, 204m, 182s, 103vs and 80m cm^{-1}.

The ^1H NMR shift in $CDCl_3$ was δ 1.95 at 27 °C, compared with δ 1.93[3] at −20 °C in $SiCl_4$. The ^{13}C NMR spectrum at −40 °C showed two singlets from a ^{13}CO-enriched sample at δ 203.5 and 195.4 in approximate intensity ratio 1:2. These are assigned respectively to the $Co_2(CO)_7$ and $Co(CO)_4$ units, each undergoing fast exchange among themselves.

The crystal structure of compound **1** was also determined by X-ray methods, see below.

Characterisation of $[Co_2\{\mu\text{-}Ge(Me)Co(CO)_4\}_2(CO)_6]$ **2**.—

Table 4 Final positional parameters for $[Co_2\{\mu\text{-}Ge(Me)Co(CO)_4\}(CO)_7]$ **1**

Atom	*x*	*y*	*z*
Ge	0.0851(2)	0.7306(2)	0.7213(1)
Co(1)	0.3002(2)	0.7946(2)	0.6275(1)
Co(2)	0.3620(2)	0.5845(2)	0.7753(1)
Co(3)	−0.1437(2)	0.9352(2)	0.8278(1)
C(11)	0.492(2)	0.803(2)	0.564(1)
O(11)	0.389(1)	1.193(2)	0.4765(8)
C(12)	0.280(2)	0.663(2)	0.530(1)
O(12)	0.274(1)	0.585(1)	0.4654(9)
C(13)	0.154(2)	1.007(2)	0.618(1)
O(13)	0.063(1)	1.146(2)	0.607(1)
C(21)	0.590(2)	0.478(2)	0.777(1)
O(21)	0.733(1)	0.408(1)	0.7758(9)
C(22)	0.336(2)	0.400(2)	0.736(1)
O(22)	0.325(2)	0.277(1)	0.716(1)
C(23)	0.291(2)	0.622(2)	0.906(1)
O(23)	0.250(1)	0.643(2)	0.9893(9)
C(2)	0.392(2)	0.797(2)	0.754(1)
O(2)	0.443(1)	0.882(1)	0.7952(9)
C(31)	−0.003(2)	1.024(2)	0.862(1)
O(31)	0.085(1)	1.089(2)	0.886(1)
C(32)	−0.139(2)	0.751(2)	0.891(1)
O(32)	−0.139(2)	0.634(2)	0.932(1)
C(33)	−0.230(2)	1.000(2)	0.710(1)
O(33)	−0.290(1)	1.050(1)	0.6378(9)
C(34)	−0.334(2)	1.071(2)	0.903(1)
O(34)	−0.456(1)	1.153(2)	0.947(1)
C(1)	−0.017(2)	0.599(2)	0.650(2)

Table 5 Final positional parameters for $[Co_4(\mu_4\text{-}GeMe)_2\{\mu\text{-}Ge(Me)Co(CO)_4\}(CO)_{10}]$ **3**

Atom	*x*	*y*	*z*
Ge(1)	0.8395(1)	0.0	0.3366(1)
Ge(2)	0.6203(1)	0.0	0.2758(1)
Ge(3)	0.8435(1)	0.0	0.1568(1)
Co(1)	0.6918(1)	0.1105(1)	0.3727(1)
Co(2)	0.7682(1)	0.1111(1)	0.2423(1)
Co(3)	0.7772(2)	0.0	0.0324(1)
C(11)	0.772(1)	0.125(1)	0.4551(7)
O(11)	0.8215(9)	0.140(1)	0.5062(6)
C(12)	0.712(1)	0.240(1)	0.3351(7)
O(12)	0.7158(8)	0.3313(9)	0.3249(5)
C(13)	0.554(1)	0.128(1)	0.3974(7)
O(13)	0.4691(8)	0.144(1)	0.4149(5)
C(21)	0.893(1)	0.183(1)	0.2497(7)
O(21)	0.9715(8)	0.2323(9)	0.2555(6)
C(22)	0.683(1)	0.186(1)	0.1806(7)
O(22)	0.6347(9)	0.238(1)	0.1404(6)
C(31)	0.641(2)	0.0	0.059(1)
O(31)	0.551(1)	0.0	0.0760(8)
C(32)	0.843(2)	−0.132(2)	0.0344(9)
O(32)	0.885(1)	−0.212(1)	0.0364(8)
C(33)	0.743(2)	0.0	−0.062(1)
O(33)	0.724(2)	0.0	−0.122(1)
C(1)	0.990(1)	0.0	0.380(1)
C(2)	1.006(1)	0.0	0.154(1)
C(3)	0.468(1)	0.0	0.239(1)

The spectroscopic properties matched closely with those of the product of the alternative synthesis,[8] where the molecular formula was established from the crystal structure. A weaker mass spectrum showed a very weak parent ion, with the dominant high-mass fragment ion family being $[P - Co(CO)_4]^+$. The carbonyl stretches are listed in Table 2. The proton NMR spectrum showed a singlet at δ 1.71, which compares with δ 1.95 for **1**.

Characterisation of $[Co_4(\mu_4\text{-}GeMe)_2\{\mu\text{-}Ge(Me)Co(CO)_4\}(CO)_{10}]$ **3**.—The molecular formula was established from the crystal structure, see below.

The mass spectrum showed no parent ion, and the highest-mass family at m/z = 923–929(vvw) was attributed to $[P - CO]^+$. There followed $[P - 3CO]^+$ (mw) and $[P - 4CO]^+$ (vvw) and then the series $[P - Me - nCO]^+$ for n = 4 (vw), 5 (w), 6 (s), 7 (s), 8 (vs), 9 (m), 10 (m), 11 (mw), 12 (w), and 13 (vvw). A family at m/z = 520–545 (vs) may, within the limits of the instrument, correspond to $[P - 14CO - 2Me]^+$ or to $[P - Co - 13CO]^+$ [possibly $P - Co(CO)_4 - 9CO$]. Other low-mass ions were weak or very weak, and could be assigned similarly.

The ^1H NMR spectrum showed three equal-intensity singlets at δ 1.97, 2.47 and 2.56. The ^{13}CO NMR spectrum at −50 °C showed singlets at δ 203.4, 200.5, 199.6, and 196.8 of relative intensities 3:1:1:2. At 30 °C the first three signals merged to a broad peak at δ 201, while a sharp singlet remained at δ 197.

In CH_2Cl_2, the CO stretches were poorly resolved showing bands at 2091mw, 2061ms, and 2012vs with 2021 (sh) and 1972 (sh), in hexane–CH_2Cl_2, (1:1) at 2092m, 2062s, 2023s, 2016vs, 2010ms (sh), 1994w, and 1980w, and a KBr disc at 2097mw, 2058ms, 2043w, 2001vs (sh), 1992vs and 1963m cm^{-1}.

X-Ray Crystallography.—For both structures **1** and **3** the space group was defined by precession photography. Cell dimensions and intensity data were collected on a Nicolet P3 (for **1**) or an Enraf-Nonius CAD4 (for **3**) diffractometer, using monochromated Mo-Kα X-rays (λ 0.7107 Å). Data were corrected for absorption (based on ψ scans), and structures were solved by direct methods, routinely developed and refined using the SHELX programs.[27] Details for each are as follows:

Structure of compound **1**. *Crystal data*. $C_{12}H_3Co_3GeO_{11}$, M = 572.54, triclinic, space group $P\bar{1}$ (no. 2), a = 8.626(6), b = 8.656(5), c = 13.381(9) Å, α = 88.25(5), β = 84.72(5), γ = 66.26(4)°, U = 911 $Å^3$ (from 25 automatically centred reflections), Z = 2, D_c = 2.09 g cm^{-3}, orange crystals from hexane, 1.0 × 0.8 × 0.16 mm, transmission 0.96 (maximum), 0.47 (minimum), μ(Mo-Kα) = 43.5 cm^{-1}, F(000) 552, T 173 K.

A total of 2171 unique data were collected by θ–2θ scans, in the range $4 < 2\theta < 45°$, $+h$, $\pm k$, $\pm l$, with 1614 for which $I > 3\sigma(I)$ used in calculations. All non-hydrogen atoms anisotropic, H atoms in calculated positions, full-matrix least-squares refinement converged with R = 0.0649, R' = 0.0642 with $w = [\sigma^2(F) + 0.001\ 854F^2]^{-1}$. Largest final Δ/σ (not involving CH_3 orientation) 0.15, largest final peak 1.5 e $Å^{-3}$, adjacent to Ge. Positional parameters are given in Table 4, and selected bond lengths and angles in Table 1.

Structure of compound **3**. *Crystal data*: $C_{17}H_9Co_5Ge_3O_{14}$, M = 949.8, monoclinic, space group $C2/m$(no. 12), a = 12.330(6), b = 12.302(3), c = 18.815(9) Å, β = 92.93(3), U = 2850 $Å^3$ (from 25 automatically centred reflections), Z = 4, D_c = 2.21 g cm^{-3}, intensely coloured dark red crystals from CH_2Cl_2–hexane, 0.5 × 0.3 × 0.1 mm, transmission 0.99 (maximum), 0.86 (minimum), μ(Mo-Kα) = 58 cm^{-1}, F(000) 1816, T 294 K.

A total of 1814 unique data were collected by θ–2θ scans, in the range $2 < 2\theta < 48°$, $+h$, $+k$, $\pm l$, with 1136 for which $I > 3\sigma(I)$ used in all calculations. All non-hydrogen atoms anisotropic, H atoms not included, full-matrix least-squares refinement converged with R = 0.0344, R' = 0.0354 with $w = [\sigma^2(F) + 0.000\ 683F^2]^{-1}$. Largest final Δ/σ 0.03, largest final peak 0.6 e $Å^{-3}$. Positional parameters are given in Table 5, and selected bond lengths and angles in Table 3.

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

Acknowledgements

We thank Dr. Ward T. Robinson, University of Canterbury, and Dr. C. Rickard, University of Auckland, for collection of

X-ray intensity data. Financial support from the New Zealand Universities Grants Committee, and from the Petroleum Research Fund, administered by the American Chemical Society, is also gratefully acknowledged.

References

1 B. W. L. Graham, D.Phil. Thesis, University of Waikato, 1973.
2 S. K. Gandal, A. G. MacDiarmid, F. E. Saalfeld and M. V. McDowell, *Inorg. Nucl. Chem. Lett.*, 1969, **5**, 413.
3 R. F. Gerlach, B. W. L. Graham and K. M. Mackay, *J. Organomet. Chem.*, 1979, **182**, 285.
4 R. Ball, M. A. Bennett, E. H. Brooks, W. A. G. Graham, J. Hoyano and S. M. Illingworth, *Chem. Commun.*, 1970, 592.
5 G. Etzrodt and G. Schmid, *J. Organomet. Chem.*, 1979, **169**, 259.
6 S. G. Anema, K. M. Mackay, L. C. McLeod, B. K. Nicholson and J. Whittaker, *Angew. Chem., Int. Ed. Engl.*, 1986, **25**, 759; S. P. Foster, K. M. Mackay and B. K. Nicholson, *Inorg. Chem.*, 1985, **24**, 909.
7 S. P. Foster, K. M. Mackay and B. K. Nicholson, *J. Chem. Soc., Chem. Commun.*, 1982, 1156.
8 S. G. Anema, K. M. Mackay and B. K. Nicholson, *J. Organomet. Chem.*, 1989, **371**, 233.
9 F. Ungavary and L. Marko, *J. Organomet. Chem.*, 1980, **193**, 383; I. Kovacs, A. Sisak, F. Ungavary and L. Marko, *Organometallics*, 1989, **8**, 1873.
10 S. G. Anema, S. K. Lee, K. M. Mackay, L. C. McLeod, B. K. Nicholson and M. Service, following paper.
11 A. J. Chalk and J. F. Harrod, *J. Am. Chem. Soc.*, 1967, **89**, 1640.
12 Y. L. Baay and A. G. MacDiarmid, *Inorg. Chem.*, 1969, **8**, 986.
13 R. F. Gerlach, K. M. Mackay, B. K. Nicholson and W. T. Robinson, *J. Chem. Soc., Dalton Trans.*, 1981, 80.
14 E. H. Brooks and R. J. Cross, *Organomet. Chem. Rev., A*, 1970, **6**, 227.
15 S. A. Fieldhouse, B. H. Freeland and R. J. O'Brien, *Chem. Commun.*, 1969, 1297.
16 A. T. Brooker, S. B. Colbran, B. F. G. Johnson, J. Lewis and P. R. Raithby, 13th International Conference on Co-ordination Chemistry, Turin, 1988, Abstract 396–1.
17 A. Sisak, F. Ungavary and L. Marko, *Organometallics*, 1986, **5**, 1019.
18 G. Sumner, H. Klug and L. Alexander, *Acta Crystallogr.*, 1964, **17**, 732; P. C. Leung and P. Coppens, *Acta Crystallogr., Sect. B*, 1983, **39**, 535.
19 M. I. Bruce and B. K. Nicholson, *J. Organomet. Chem.*, 1983, **250**, 627.
20 D. N. Duffy, K. M. Mackay, B. K. Nicholson and W. T. Robinson, *J. Chem. Soc., Dalton Trans.*, 1981, 381.
21 R. D. George, K. M. Mackay and S. R. Stobart, *J. Chem. Soc., Dalton Trans.*, 1972, 974.
22 S. Onaka and D. F. Shriver, *Inorg. Chem.*, 1976, **15**, 915.
23 G. J. Bor, *J. Organomet. Chem.*, 1975, **94**, 181.
24 R. C. Job and M. D. Curtis, *Inorg. Chem.*, 1973, **12**, 2514: R. D. Adams, F. A. Cotton, W. R. Cullen, D. L. Hunter and L. Mihichuk, *Inorg. Chem.*, 1975, **14**, 1395.
25 M. G. Richmond and J. K. Kochi, *J. Organomet. Chem.*, 1987, **323**, 219.
26 S. G. Anema, K. M. Mackay and B. K. Nicholson, *Inorg. Chem.*, 1989, **28**, 3158.
27 G. M. Sheldrick, SHELX 76, program for crystal structure determination, University of Cambridge, 1976; SHELXS 86; program for solving crystal structures, University of Göttingen, 1986.

Received 23rd *August* 1990; *Paper* 0/03850D