Convenient Syntheses of the Square-bipyramidal Cluster, $[Co_4(\mu_4\text{-}GeMe)_2(CO)_{11}]$ and the Formation of $[Co_4(\mu_4\text{-}GeMe)\{\mu_4\text{-}GeCo(CO)_4\}(CO)_{11}]$ and $[Co_4\{\mu_4\text{-}GeMn(CO)_5\}\{\mu_4\text{-}GeCo(CO)_4\}(CO)_{11}]$: New Ge_2Co_4 Clusters containing the Square-bipyramidal Skeleton; and the Crystal Structure of $[Co_4(\mu_4\text{-}GeMe)\{\mu_4\text{-}GeCo(CO)_4\}(CO)_{11}]$†

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The compound $[Co_4(\mu_4\text{-}GeMe)_2(CO)_{11}]$ **1a** results directly in high yield from the reaction of $GeMeH_3$ with $[Co_4(CO)_{12}]$ under mild conditions. It also forms near-quantitatively from the smooth decarbonylation of $[Co_2\{\mu\text{-}Ge(Me)Co(CO)_4\}_2(CO)_6]$ **3**, at 40–45 °C. The compound $[Co_2(CO)_8]$ reacts with $GeMeH_2GeMeH_2$ to give a modest yield of **1a** and with $GeMeH_2GeH_3$ forms $[Co_4(\mu_4\text{-}GeMe)\{\mu_4\text{-}GeCo(CO)_4\}(CO)_{11}]$ **4a**, also formed from the reaction of $[\mu_4\text{-}Ge\{Co_2(CO)_6(\mu\text{-}GeMeH)\}\{Co_2(CO)_7\}]$ **5** with $[Co_2(CO)_8]$. The molecular structure of compound **4a** was determined by X-ray crystallography [monoclinic, space group, *I*2/*a* (non-standard *C*2/*c*), $a = 12.852(3)$, $b = 14.528(5)$, $c = 26.566(8)$ Å, $\beta = 90.32(2)°$, $R = 0.0699$ for 1660 data with $I > 2\sigma(I)$] and is related to that of **1a** by replacing one terminal Me by terminal $Co(CO)_4$. Spectroscopic evidence indicates that other Ge_2RH_5 [R = $Mn(CO)_5$ or Et] give analogues of **4a** with the appropriate R terminal groups.

We found[1] the first example of the Ge_2Co_4 pseudo-octahedral core in $[Co_4(\mu_4\text{-}GeMe)_2(CO)_{11}]$ **1a**, which was one of a number of products from the long-duration sealed-tube reaction of $GeMeH_3$ with $[\mu_4\text{-}Ge\{Co_2(CO)_7\}_2]$. Gusbeth and Vahrenkamp[2] soon reported the Bu^t **1b** and Ph **1c** analogues as minor products from the reaction of $GeCl_3R$ with $K[Co(CO)_4]$, and also demonstrated metal exchange in the skeleton. The related structure with $Co(CO)_4$ terminal groups, **2**, was formed by loss of CO from the open cluster $[\{Co_2(CO)_7(\mu_4\text{-}Ge)\}_2Co_2(CO)_6]$.[3] Recently, we found that Si_2H_6 reacted with $[Co_2(CO)_8]$ to give the silicon analogue of **2**, probably *via* the unstable $[\{Co_2(CO)_7(\mu_4\text{-}Si)\}_2Co_2(CO)_6]$.[4] In Groups 15 and 16, clusters with the E_2M_4 skeleton have been known since Dahl's 1975 characterisations.[5] In 1985 a discussion[6] of their bonding included a list of 15 examples, the majority with carbonyl ligands. In recent years, Vahrenkamp[7] and especially Kochi and co-workers[8] have reported a range of CO-replacement reactions in E_2M_4 clusters, and their uses in catalysis have been described.[9]

All the available preparations of compound **1** gave relatively low yields,[1,2] and the route to **1a** was particularly obscure.[1] In this paper we report five syntheses of **1a** including a direct synthesis in good yield from $[Co_4(CO)_{12}]$ and a preparation *via* $[Co_2\{\mu\text{-}Ge(Me)Co(CO)_4\}_2(CO)_6]$ **3**. We also describe routes to the corresponding unsymmetrically substituted clusters $[Co_4(\mu_4\text{-}GeR^1)(\mu_4\text{-}GeR^2)(CO)_{11}]$ with R^1 = Me, R^2 = $Co(CO)_4$, **4a**, and with R^1 = $Co(CO)_4$, R^2 = $Mn(CO)_5$, **4b**, and the X-ray crystal structure of the former.

Results and Discussion

Syntheses of $[Co_4(\mu_4\text{-}GeMe)_2(CO)_{11}]$ **1a**.—The original report[1] of compound **1a** was the first synthesis of an E_2M_4 square-bipyramidal species with E = a Group 14 element. Other examples were soon found[2,3] and included a variety of terminal groups as in **1b**, **1c** and **2**. Compound **1a** was originally isolated from a reaction of $GeMeH_3$ with $[\mu_4\text{-}Ge\{Co_2(CO)_7\}_2]$ for 6 months in a sealed tube, thought[1] to proceed *via* the formation of $[\{(OC)_7Co_2\}Ge\{Co_2(\mu\text{-}GeMeH)(CO)_6\}]$ **5** followed by an extensive rearrangement involving methyl transfer to form **1a**. Since then we have substantially increased our experience with such reactions and have found a number of rearrangements of Ge_xCo_y skeletons but none which alters the x/y ratio and none which involves methyl transfer.[3,10] The re-examination[11] of the reaction of $GeMeH_3$ with $[\mu_4\text{-}Ge\{Co_2(CO)_7\}_2]$ has shown that both mono- and di-substitution of the μ-CO by μ-GeMeH does occur, but that **5** does not rearrange to **1a**.

It is with some relief that we now abandon the original assumption of a drastic reordering under mild conditions, 'einem recht komplizierten Weg' in Vahrenkamp's words,[2] and conclude that the original preparation of compound **1a** probably resulted from adventitious reaction by one of the routes that we now report. In return for loss of the original preparation, five alternative syntheses of **1a** are now described; these are summarised in Scheme 1.

The reaction of $GeMeH_3$ with $[Co_4(CO)_{12}]$ was straightforward and followed equation (1). The yields were quantitative for H_2, CO and $[Co_4(\mu_4\text{-}GeMe)_2(CO)_{11}]$ within experimental uncertainty. Thus, in contrast to the reactions of

$$2GeMeH_3 + [Co_4(CO)_{12}] \longrightarrow 3H_2 + CO + \underset{\mathbf{1a}}{[Co_4(\mu_4\text{-}GeMe)_2(CO)_{11}]} \quad (1)$$

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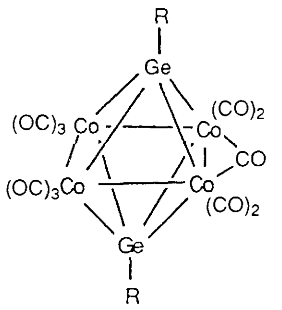
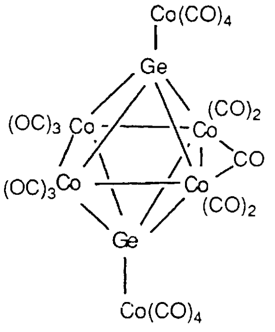
† μ-Carbonyl-1:2κ²*C*-decacarbonyl-1κ²*C*,2κ²*C*,4κ³*C*,6κ³*C*-methyl-3κ*C*-tetracarbonylcobaltio-5κ*Co*-*octahedro*-tetracobalt-3,5-digermanium.

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



R
1a Me
1b Bu^t
1c Ph



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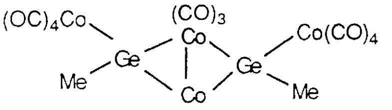

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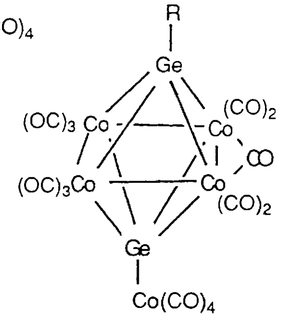
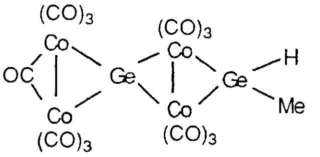


R
4a Me
4b Mn(CO)$_5$
4c Et



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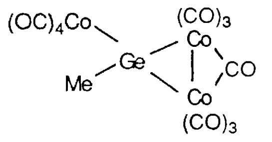

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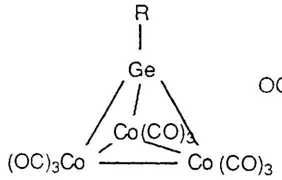
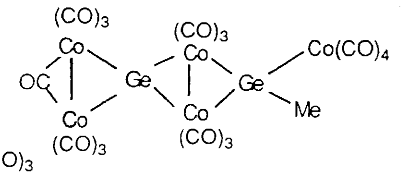


R
7a Co(CO)$_4$
7b Mn(CO)$_5$
7c Co(CO)$_3$[GeCo$_3$(CO)$_9$]$^-$
7d Me



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methylgermane with other cobalt carbonyl species, reaction (1) is very specific. There was no difference between reactions carried out in sealed tubes and in those where the evolved gases were periodically removed. Convenient reaction conditions are millimolar concentrations at 30 °C, a modest excess of $GeMeH_3$, and the reaction is terminated when gas evolution ceases after approximately 7 d.

Since the hydrogen evolution in reaction (1) is retarded relative to that of CO, as in similar germane reactions with cobalt carbonyls,[12–14] the initial step could be that postulated previously,[3,14] *i.e.* addition of Ge–H across a Co–Co bond with expulsion of a bridging CO. Later processes build up the cluster skeleton *via* elimination of H_2 and CO. Breaking one Co–Co edge of the tetrahedron would produce a 'butterfly', and this could plausibly be wingtip-bridged by a Ge(Me)H group. Attack on the hinge Co–Co by a second germane to create a similar Co–Ge(Me)H–Co unit would give a species with the heavy atoms in a suitable position to rearrange into the Ge_2Co_4 skeleton, losing the remaining hydrogens and forming the μ_4 bridges. Alternative intermediates, for example with μ_3-GeMe groups over triangular faces of the tetrahedron or butterfly, are also conceivable: such ideas are suggestive for further work.

A second route to compound **1a** is based on the ready preparation[13] of $[Co_2\{\mu\text{-}Ge(Me)Co(CO)_4\}_2(CO)_6]$ **3**, either from $[Fe(GeMeH_2)_2(CO)_4]$ and $[Co_2(CO)_8]$ in respectable yield (about 35%) or, alternatively, from the extended reaction of excess of $GeMeH_3$ with $[Co_2(CO)_8]$.[14] When **3** was heated at 45 °C until gas evolution became very slow the major reaction was loss of CO to form **1a** in high yield [equation 2]. Formation of about 20% CO in excess of that required by equation (2) was a consequence of the parallel, more drastic rearrangement to give as a by-product $[Co_4(\mu_4\text{-}GeMe)_2\{\mu\text{-}Ge(Me)Co(CO)_4\}(CO)_{10}]$,[14] which can also be formed by the extended heating of **1a**. Terminating the decarbonylation after the evolution of only three CO would further improve the yield of compound **1a**.

$$\underset{\mathbf{3}}{[Co_2\{\mu\text{-}Ge(Me)Co(CO)_4\}_2(CO)_6]} \longrightarrow \underset{\mathbf{1a}}{[Co_4(\mu_4\text{-}GeMe)_2(CO)_{11}]} + 3CO \quad (2)$$

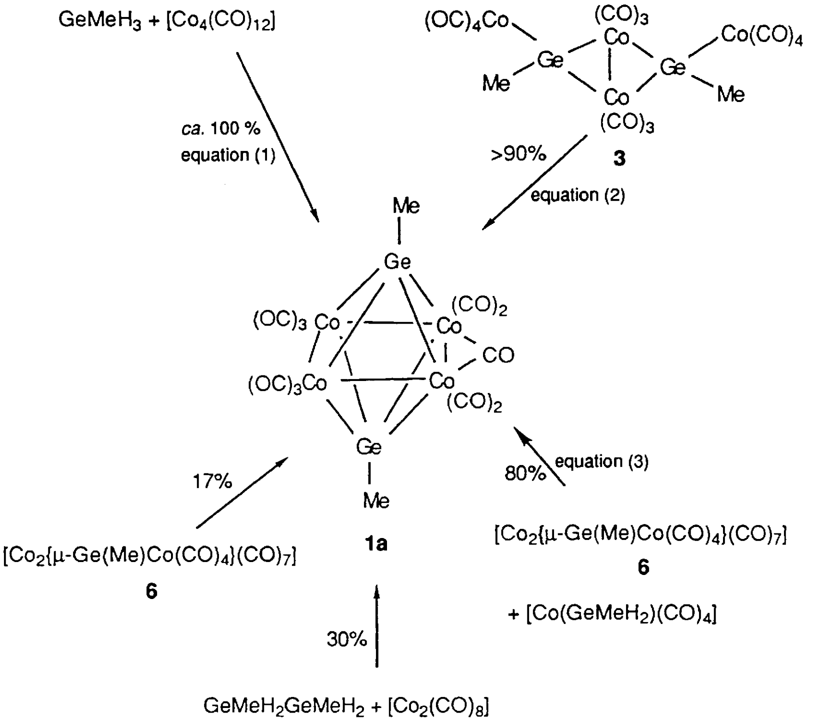
Although there is no specific information about the mechanism for the conversion of compound **3** into **1a**, the starting material is sterically crowded[13] with the $Co(CO)_4$ units close to the $(OC)_3Co–Co(CO)_3$ one; intramolecular formation of new Co–Co bonds accompanied by CO elimination would appear perfectly feasible. We note that an intermediate $Co_3(\mu_3$-GeMe) unit could form and share a Co–Co edge with a second one to give a face-bridged butterfly similar to that invoked above for a possible path in the $[Co_4(CO)_{12}]$ reaction.

Another approach to compound **1a** is from $[Co_3(\mu_3\text{-}GeMe)(CO)_{11}]$ **6** which is readily formed[14–16] in a rapid reaction of $GeMeH_3$ with $[Co_2(CO)_8]$, under conditions quite distinct from those which form **3**. The additional MeGeCo unit needed for **1a** is then supplied by $[Co(GeMeH_2)(CO)_4]$, as in equation (3). Heating the product mixture subsequently converted **3** into **1a** as in equation (2). Methylgermane may be converted even more directly into **1a** by thermolysis of the initial product, **6**. However, this route gives an unattractively low yield of **1a**.

$$\underset{\mathbf{6}}{[Co_3(\mu_3\text{-}GeMe)(CO)_{11}]} + [Co(GeMeH_2)(CO)_4] \longrightarrow H_2 + 3CO + \mathbf{1a} + \mathbf{3} \quad (3)$$

We have previously shown[3] that digermane, Ge_2H_6, reacts with cobalt carbonyl to give the open chain $[\{Co_2(CO)_7(\mu_4\text{-}Ge)\}_2Co_2(CO)_6]$, which subsequently can be decarbonylated to give $[Co_4\{\mu_4\text{-}GeCo(CO)_4\}_2(CO)_{11}]$ **2**. As an extension to this we now find $GeMeH_2GeMeH_2$ behaves similarly giving **1a**, equation (4). However in contrast to the digermane reaction no open-chain precursor to compound **1a** was seen. The preparation from 1,2-dimethyldigermane, equation (4), gives moderate yields of **1a**, with the main loss arising from separation of the two Ge atoms into the by-product $[Co_3(\mu_3\text{-}GeMe)(CO)_{11}]$ **6**. This parallels the reaction with digermane[3] which also gives the monogermanium $[\mu_4\text{-}Ge\{Co_2(CO)_7\}_2]$ as well

$$GeMeH_2GeMeH_2 + 2[Co_2(CO)_8] \longrightarrow H_2 + 3CO + \mathbf{1a} + \mathbf{6} \quad (4)$$



Scheme 1

as the digermanium species. This reaction [equation (4)] was not extensively explored as 1,2-dimethyldigermane is not very accessible, being a secondary product from the preparation of methyldigermane.[17]

Synthesis of $[\mathrm{Co_4}(\mu_4\text{-GeMe})\{\mu_4\text{-GeCo(CO)_4}\}\mathrm{(CO)_{11}}]$ *by the Reaction of* $[\mathrm{Co_2(CO)_8}]$ *with* $\mathrm{GeMeH_2GeH_3}$.—The preparation of compound **1a** from $\mathrm{GeMeH_2GeMeH_2}$, and the previously reported route[3] to **2** from $\mathrm{Ge_2H_6}$, suggested that $\mathrm{Ge_2Co_4}$ clusters with different substituents on germanium would be available from unsymmetrical digermanes. With methyldigermane, two reactions with cobalt carbonyl occurred together; separation of Ge and MeGe units as in equation (5),

$$\mathrm{Ge_2MeH_5} + 7[\mathrm{Co_2(CO)_8}] \longrightarrow 2\,\mathbf{6} + 2[\mu_4\text{-Ge}\{\mathrm{Co_2(CO)_7}\}_2] + 5\mathrm{H_2} + 6\mathrm{CO} \qquad (5)$$

$$[\mu_4\text{-Ge}\{\mathrm{Co_2(CO)_7}\}_2] \longrightarrow \underset{\mathbf{7a}}{[\mathrm{Co_3}\{\mu_3\text{-GeCo(CO)_4}\}\mathrm{(CO)_9}]} + \mathrm{CO} \qquad (5a)$$

and formation of a product molecule containing both, equation (6).

$$2\mathrm{Ge_2MeH_5} + 5[\mathrm{Co_2(CO)_8}] \longrightarrow 2\underset{\mathbf{8}}{[\{\mathrm{(OC)_7Co_2}\}(\mu_4\text{-Ge})\{\mathrm{Co_2}[\mu\text{-Ge(Me)Co(CO)_4}]\mathrm{(CO)_6}\}]} + 5\mathrm{H_2} + 6\mathrm{CO} \qquad (6)$$

$$\underset{\mathbf{8}}{[\{\mathrm{(OC)_7Co_2}\}(\mu_4\text{-Ge})\{\mathrm{Co_2}[\mu\text{-Ge(Me)Co(CO)_4}]\mathrm{(CO)_6}\}]} \longrightarrow \underset{\mathbf{4a}}{[\mathrm{Co_4}(\mu_4\text{-GeMe})\{\mu_4\text{-GeCo(CO)_4}\}\mathrm{(CO)_{11}}]} + 2\mathrm{CO} \qquad (6a)$$

For sealed-tube reactions, where the partial pressure of the evolved CO would rise to about 1 atm (*ca.* 10^5 Pa), the open clusters dominated over the closed clusters, both in equation (5) and in equation (6), while reactions (5a) and (6a) became prominent when the CO was removed in the course of the reaction. The products of equation (5)[15,16,18] and of equation (5a)[19] are known, while the products **4a** and **8** of equations (6) and (6a) are new. The formation of **4a** from **8** by equation (6a) was demonstrated separately by gentle heating in solution.

The products of equations (5) and (5a) were extracted together in non-polar solvents, allowing the isolation of pure **8**. Considering the yield and the likely losses on isolation, together with the production of the gases, the sealed-tube reactions proceeded in a ratio of at least 60:40 in favour of equation (6) over (5). Similarly, when CO was removed during the reaction, the product ratio was at least 3:1 in favour of **4a** over the monogermanium species of equations (5) and (5a).

The ^{1}H NMR study, using a large deficit of $[\mathrm{Co_2(CO)_8}]$ compared to that needed for complete substitution, showed that the initial steps of the reaction were very rapid. The appearance of three new MeGe signals in the first minutes strongly suggests that substitution at both Ge atoms occurs readily. This was further shown in the final spectrum which included signals attributable to six different partly substituted digermanes. The appearance of $\mathrm{GeMeH_3}$ shows rearrangement involving H transfer, possibly under steric pressure, and suggests one contributing path to equation (5). In general, this and earlier[15] experiments show that the first steps of the reactions of the germanium hydrides with $[\mathrm{Co_2(CO)_8}]$ are very fast, and the prolonged reaction times often needed for complete substitution result from steric and solubility effects.

Although single crystals of compound **8** could not be obtained, the spectroscopic data[20] are compatible with its formulation as the open-chain compound formally described as resulting from the replacement of one μ-CO in $[\mu_4\text{-Ge}\{\mathrm{Co_2(CO)_7}\}_2]$ by $\mu\text{-GeMe}[\mathrm{Co(CO)_4}]$. The carbonyl stretches match those observed for related molecules, and the presence of the $\mathrm{GeCo(CO)_4}$ unit is indicated particularly by the IR band at 2104 cm^{-1}. The formulation is further supported by the high-yield decarbonylation reaction (6a), which closely parallels the formation of **2**.[3]

We report elsewhere[11] that $\mathrm{GeRH_3}$ species react with $[\mu_4\text{-Ge}\{\mathrm{Co_2(CO)_7}\}_2]$[18] to replace one μ-CO by the group μ-GeRH, thus forming $[\{\mathrm{(OC)_7Co_2}\}(\mu_4\text{-Ge})\{\mathrm{Co_2}(\mu\text{-GeMeH})\mathrm{(CO)_6}\}]$ **5** when R = Me. By reaction (7), compound **5** was converted

$$\mathbf{5} + [\mathrm{Co_2(CO)_8}] \longrightarrow \mathbf{8} + [\mathrm{CoH(CO)_4}] \longrightarrow \mathbf{4a} + 2\mathrm{CO} \qquad (7)$$

into **8**, which could then be converted into **4a** on gentle heating. This sequence lends additional support for the identification of **8** as the intermediate in equation (6).

Synthesis of $[Co_4\{\mu_4\text{-}GeMn(CO)_5\}\{\mu_4\text{-}GeCo(CO)_4\}(CO)_{11}]$ **4b**.—As digermanes substituted by metal carbonyl groups are available,[21] a parallel reaction to that of equation (6) was sought. The reaction of $[Mn(GeH_2GeH_3)(CO)_5]$ with cobalt carbonyl may be represented by similar equations (8) and (9). We propose that compound **4b** is the result of a decarbonylation to a closed cluster similar to that of equation (6a), perhaps of the open-chain compound $[\{\mu\text{-}Ge[Mn(CO)_5][Co(CO)_4]\}\{Co_2(CO)_6\}(\mu_4\text{-}Ge)\{Co_2(CO)_7\}]$. Taking the yield of **4b** in the sealed-tube reaction, and the gas figures in the open-tube run, equation (9) where both Ge atoms enter the same molecule is strongly preferred over the separation of the Ge and the MnGe units into separate molecules as in equation (8). Side reactions involving fission of the Ge–Mn bond may be indicated by the observations of small amounts of $[Mn_2(CO)_{10}]$ and $[Co_6(\mu_4\text{-}Ge)_2(CO)_{20}]$. The silicon analogue of **4b** has been prepared by a similar route.[22]

$$2[Mn(GeH_2GeH_3)(CO)_5] + 7[Co_2(CO)_8] \longrightarrow 2\underset{\textbf{7b}}{[Co_3\{\mu_3\text{-}GeMn(CO)_5\}(CO)_9]} + 2[\mu_4\text{-}Ge\{Co_2(CO)_7\}_2] + 5H_2 + 10CO \tag{8}$$

$$2[Mn(GeH_2GeH_3)(CO)_5] + 5[Co_2(CO)_8] \longrightarrow 2\underset{\textbf{4b}}{[Co_4\{\mu_4\text{-}GeMn(CO)_5\}\{\mu_4\text{-}GeCo(CO)_4\}(CO)_{11}]} + 5H_2 + 10CO \tag{9}$$

A second carbonyl derivative of digermane, $[Co(GeH_2GeH_3)(CO)_4]$, was treated with $[Co_2(CO)_8]$ to give **2** in good yields according to equation (10), together with the corresponding open-chain species and some monogermanium complexes. This offers no advantages over the direct Ge_2H_6 + $[Co_2(CO)_8]$ reaction but indicates the generality of using metal-substituted digermanes.

$$2[Co(GeH_2GeH_3)(CO)_4] + 5[Co_2(CO)_8] \longrightarrow 2\underset{\textbf{2}}{[Co_4\{\mu_4\text{-}GeCo(CO)_4\}_2(CO)_{11}]} + 5H_2 + 10CO \tag{10}$$

An alternative synthesis of compound **4b** by replacing one $Co(CO)_4$ group from **2**, by the action of $[Mn(CO)_5]^-$, is suggested by the similar synthesis[23] of $[Co_3\{\mu_3\text{-}GeMn(CO)_5\}(CO)_9]$ **7b** from $[Co_3\{\mu_3\text{-}GeCo(CO)_4\}(CO)_9]$ **7a**, and by the general displacement series found[24] in simpler germylmetal carbonyls [*e.g.* equation (11)]. However, a preliminary study of the reaction of compound **2** with $[Mn(CO)_5]^-$ gave no indication of a similar displacement; instead formation of a new compound with a Mn:Ge:Co ratio of *ca.* 1:2:6 was observed. The ion $[Co(CO)_4]^-$ was formed in the early stages, so its reaction with **2** was also examined. In this case a known[25] anionic cluster **7c**, was formed [equation (12)]. The structure[25] of **7c** comprises two $GeCo_3(CO)_9$ trigonal pyramids linked *trans* about a common $Co(CO)_3$ unit, apical to both Ge atoms. The product of the $[Mn(CO)_5]^-$ reaction may well be an analogue of **7c** with one Co replaced by Mn, probably in the central unit.

$$[Co(GeH_3)(CO)_4] + [Mn(CO)_5]^- \longrightarrow [Mn(GeH_3)(CO)_5] + [Co(CO)_4]^- \tag{11}$$

$$\textbf{2} + [Co(CO)_4]^- \longrightarrow \underset{\textbf{7c}}{[Co\{\mu_4\text{-}GeCo_3(CO)_9\}_2(CO)_3]^-} \tag{12}$$

General Remarks on the Syntheses.—As this range of reactions demonstrates, $[Co_4(GeR)_2(CO)_{11}]$ clusters are readily formed under mild conditions by a variety of combinations of species providing two Ge and four Co atoms. The five reactions of Scheme 1, together with the Gusbeth and Vahrenkamp route,[2] provide a good choice of methods, which are expected to be readily modifiable to provide a range of analogues of **1**, **2** and **4**. As hydride reactions are relatively slow, the halide coupling[2] has the advantage of speed and ready variation of R, but produces species of type **1** mixed with the corresponding smaller clusters **7**, with R = alkyl or aryl.

Of the hydride reactions, equation (1) is probably the most useful, controlled, small-scale route to the cluster **1a** and should be even more convenient for other compounds **1** as the higher solubility of other $GeRH_3$ species would lead to faster reactions. This route also provides the possibility of forming Ge-functional clusters using $GeXH_3$.

Although the route to **1a** *via* equation (2), is the least direct it gives a good combination of speed and yield and $[Fe(GeMeH_2)_2(CO)_4]$ is readily formed[26] from simple materials. As we would expect other $[Fe(GeRH_2)_2(CO)_4]$ species to be readily accessible, including compounds with two different R groups,[26] this route should give analogues of **3** which, *via* equation (2), would lead to a variety of analogues of **1a**. The alternative formation of **3** by extended reaction of $GeRH_3$ with $[Co_2(CO)_8]$ is less attractive as the reaction is slow.

The route to compound **1a** *via* equation (3) provides a useful path as both starting materials are readily accessible from $GeMeH_3$. It has no advantages over equations (1) and (2) for the formation of **1a**, but could clearly be easily adapted to form analogues with two different alkyl substituents.

Similarly, equation (4) offers no advantage in the formation of **1a**. However, use of a disubstituted digermane like $[(OC)_5MnGeH_2GeH_2Mn(CO)_5]$ in equation (4) is likely to be the most feasible route to analogues of **2** with other ML_x substituents in the apical positions, as any anion route is likely to lead to skeletal rearrangements.

The best synthesis of clusters **4**, with one organic and one metal carbonyl substituent, should follow the route (6) used for $[Co_4(\mu_4\text{-}GeMe)\{\mu_4\text{-}GeCo(CO)_4\}(CO)_{11}]$ **4a**. This is attractive since monoalkyldigermanes may be produced in good yield[17] by a two-step synthesis from Ge_2H_6 and is further illustrated by the preliminary study with Ge_2EtH_5, indicating the formation of **4c**. The alternative path (7) to mixed-substituent analogues of **4a** has the advantage of using more readily available monogermanium reagents, but is much slower.

Finally, we note that the $[Mn(GeH_2GeH_3)(CO)_5]$ reaction (9) is, at present, the only path to Ge_2Co_4 bipyramids with different metal carbonyl substituents as in **4b**. Equations (9) and (10) suggest that other $[M(GeH_2GeH_3)L_x]$ would behave similarly. The plausible exchange route based on equation (11) appears to give only products with transformed skeletons or, at best, mixtures including these.

Properties of Compound **4a** *and Related Species.*—As Table 1 shows, the carbonyl vibrations of the mixed-ligand square bipyramid **4a** correlate nicely with those of the two symmetrically substituted species, **1a** and **2**. Similarly, the vibrations of the proposed $Mn(CO)_5$ analogue, **4b**, compare well with those of analogous manganese species (Table 2), and with those of Table 1. To a good approximation, the vibrations may be seen as the sum of those of the apical $M(CO)_x$ units and the central $Co_4(CO)_{11}$ unit.

In these molecules, the mass spectral data listed in the Experimental section are as expected with **4a**, **4b** and **8** resembling the majority of relatively complex Ge/Co cluster

Table 1 Carbonyl stretching bands (IR, cm^{-1}) for [$Co_4(\mu_4$-GeR)(μ_4-GeR')$(CO)_{11}$] where R = R' = $Co(CO)_4$ **2** or Me **1a**; R = Me, R' = $Co(CO)_4$ **4a**

2	**4a**		**1a**
(CH_2Cl_2)	CH_2Cl_2	Nujol mull	(CH_2Cl_2)
2100s	2102s	2106s	
	2072s	2072s	
2065w(sh)	2064(sh)w		
2050s	2050(sh)w	2051(sh)	
		2040(sh)	
2037vs	2038vvs	2038s	2034vs
		2029vs	
2014m	2017m	2015ms	2016m
		2012(sh)	
2003w(sh)	2004(sh)	2001s	2004(sh)
		1994(sh)	
1990w(sh)		1991(sh)	
		1966(sh)	
1844w(br)	1845w(br)	1854m	1835w(br)

Table 2 Carbonyl stretching bands (IR, cm^{-1}) for [$Co_4\{\mu_4$-GeMn$(CO)_5\}\{\mu_4$-GeCo$(CO)_4\}(CO)_{11}$] compared with those of the trigonal-pyramidal analogue [$Co_3\{\mu_3$-GeMn$(CO)_5\}(CO)_9$] **7b**

4b		**7b**
CH_2Cl_2	Nujol mull	(hexane, from ref. 23)
2120(sh)		
2117m	2113(sh)	2115w
2104(sh)		
2099mw	2105s	
2087(sh)	2090w	
2076m		2078m
2061(sh)		
2053m	2048(sh)m	
	2037(sh)	
2038vvs	2030s	2041vs
	2026(sh)	
2024(sh)	2024(sh)	2022ms
	2018(sh)	
	2014(sh)m	
	2002(sh)	
	2000ms	
	1997(sh)	
1851w(br)	1845m	

The very strong band about 2035, with a weaker companion about 2015 and the bridging frequency at 1850 cm^{-1}, are characteristic of the central $Co_4(CO)_{11}$ unit. The terminal $Co(CO)_4$ unit gives a sharp band due to the high-frequency a mode at 2105, while the second a mode contributes at *ca.* 2070 cm^{-1}. The analogous bands from the $Mn(CO)_5$ group are at 2115 and perhaps a contribution in the 2070–2090 cm^{-1} region. The strong e bands of the apical groups occur in the 2030 cm^{-1} region, contributing to the absorptions there.

carbonyl molecules in showing weak or missing parent ions, stepwise loss of CO and limited loss or fragmentation of GeR groups.

The NMR chemical shifts of compound **4a** are the same as the corresponding ones of **1a** and **2**. The ^1H shifts at δ 2.75–2.77 are about 1 ppm to low field of Me on four-co-ordinated Ge, as in **6**, **7d** or **8**.[15,16] The ^{13}CO shifts at δ 202.6 and 195.9 are essentially identical to those of **2**[3] but with half the relative intensity ratio of the latter, corresponding to the presence of only one $Co(CO)_4$ group. Both the $Co_4(CO)_{11}$ and $Co(CO)_4$ carbonyl groups are exchanging rapidly among themselves at −50 °C, the lowest temperature accessible to us. Values compare with δ 208 for the analogous phosphorus cluster [$Co_4(\mu_4$-PPh$)_2(CO)_{10}$] where exchange slows sufficiently only at −100 °C, giving resonances[8] at δ 204 and 238. The exchange slowed sufficiently to separate bridging and terminal signals at 263 K only when some of the CO groups in [$Co_4(\mu_4$-PPh$)_2(CO)_{10}$] were replaced by phosphines,[27] and complete resolution of terminal positions occurred only at 183 K.

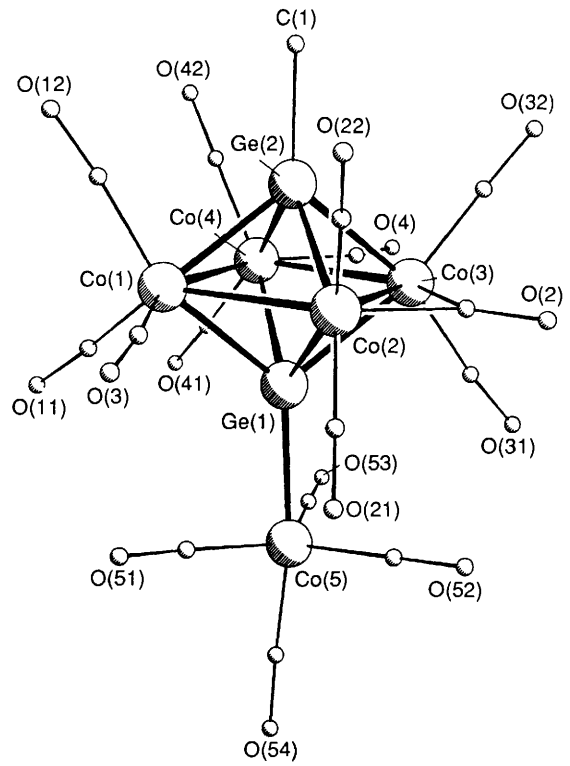


Fig. 1 A PLUTO diagram of the structure of [$Co_4(\mu_4$-GeMe$)\{\mu_4$-GeCo$(CO)_4\}(CO)_{11}$]

The structure of compound **4a** is illustrated in Fig. 1. Atomic coordinates and selected bond parameters are listed in Tables 3 and 4. The metal core of the cluster consists of two Ge atoms quadruply bridging a distorted square-planar array of Co atoms. One Ge is further bonded to a terminal $Co(CO)_4$ unit, while the other carries a methyl group. The structure is therefore intermediate between those of [$Co_4(\mu_4$-GeMe$)_2(CO)_{11}$] **1a** and [$Co_4\{\mu_4$-GeCo$(CO)_4\}_2(CO)_{11}$] **2**, and the detailed bond parameters reflect this median position (Table 5).

The carbonyl ligands on the cluster core are distributed to give one symmetrical carbonyl bridge across Co(2)–Co(3), two fully terminal carbonyls on each of the cobalt atoms and a further carbonyl on each of Co(1) and Co(4) in the plane of the four cobalt atoms, which are semibridging to the adjacent Co(2) or Co(3) respectively. This general arrangement is also found in other [$Co_4(\mu_4$-X$)_2(CO)_{11}$] clusters and is presumably the best way of sharing eleven CO ligands about four, otherwise-equivalent, cobalt atoms. The precise degree of semibridging, as judged by the longer Co • • • C distance and the Co–C–O angles, varies for the two sides of compound **4a**, and as well as in **1a** and **2**, which suggests the semibridging CO ligands are readily displaced within the plane defined by the Co_4 unit.

In compound **4a** the germanium atom with the methyl substituent forms shorter Ge(2)–Co bonds (average 2.385 Å, *cf.* 2.387 Å in **1a** than does the germanium with the $Co(CO)_4$ group [average Ge(1)–Co 2.412 Å, *cf.* 2.414 Å in **2**], while the Ge(1)–Co(5) bond to the external cobalt atom [2.399(4) Å] is intermediate in length.

The detailed skeletal bond distances for compounds **1a**, **2** and **4a** are compared in Table 5. As Me is replaced by $Co(CO)_4$ in the apex positions, the Ge • • • Ge distance lengthens a little, reflected also by the Ge–Co distances. While the two Co atoms carrying a bridging CO are consistently a little closer to the apex Ge than are the non-bridged ones, the differences are small,

Table 3 Final positional parameters for $[Co_4(\mu_4\text{-}GeMe)\{\mu_4\text{-}GeCo(CO)_4\}(CO)_{11}]$

Atom	*x*	*y*	*z*
Ge(1)	−0.0026(2)	0.2964(2)	0.1229(1)
Ge(2)	−0.0035(2)	0.0930(2)	0.1236(1)
Co(1)	−0.0630(2)	0.1943(2)	0.1886(1)
Co(2)	−0.1327(2)	0.1927(2)	0.0916(1)
Co(3)	0.0560(2)	0.1926(2)	0.0576(1)
Co(4)	0.1333(2)	0.1929(2)	0.1498(1)
Co(5)	−0.0114(3)	0.4607(2)	0.1154(1)
C(11)	−0.017(2)	0.269(2)	0.233(1)
O(11)	0.016(1)	0.320(1)	0.2652(7)
C(12)	−0.065(2)	0.090(2)	0.2243(9)
O(12)	−0.063(2)	0.028(1)	0.2504(7)
C(21)	−0.226(2)	0.283(2)	0.0854(9)
O(21)	−0.288(1)	0.341(1)	0.0813(6)
C(22)	−0.214(2)	0.095(2)	0.0880(9)
O(22)	−0.270(1)	0.031(1)	0.0871(6)
C(31)	0.096(2)	0.292(2)	0.0205(8)
O(31)	0.125(1)	0.348(1)	−0.0067(6)
C(32)	0.094(2)	0.096(2)	0.0203(9)
O(32)	0.113(1)	0.034(1)	−0.0044(6)
C(41)	0.198(2)	0.279(2)	0.184(1)
O(41)	0.246(1)	0.335(1)	0.2060(7)
C(42)	0.184(2)	0.093(2)	0.1796(9)
O(42)	0.221(1)	0.028(1)	0.1999(6)
C(51)	−0.096(2)	0.450(2)	0.167(1)
O(51)	−0.157(2)	0.444(1)	0.1996(7)
C(52)	−0.073(2)	0.447(1)	0.0543(8)
O(52)	−0.109(1)	0.440(1)	0.0157(6)
C(53)	0.123(2)	0.453(2)	0.1119(9)
O(53)	0.213(1)	0.448(1)	0.1072(7)
C(54)	−0.015(2)	0.584(2)	0.119(1)
O(54)	−0.018(2)	0.665(1)	0.1227(8)
C(1)	−0.010(2)	−0.043(1)	0.1246(9)
C(2)	−0.086(2)	0.190(2)	−0.0251(8)
O(2)	−0.115(1)	0.191(1)	−0.0165(6)
C(3)	0.213(2)	0.193(2)	0.0939(8)
O(3)	0.291(1)	0.192(1)	0.0743(5)
C(4)	−0.198(2)	0.218(2)	0.1878(9)
O(4)	−0.285(2)	0.234(1)	0.1935(7)

Table 4 Selected bond lengths (Å) and angles (°) for $[Co_4(\mu_4\text{-}GeMe)\{\mu_4\text{-}GeCo(CO)_4\}(CO)_{11}]$

Ge(1) ··· Ge(2)	2.955(3)	Ge(2)–Co(2)	2.360(4)
Ge(1)–Co(1)	2.421(4)	Ge(2)–Co(3)	2.402(4)
Ge(1)–Co(2)	2.396(4)	Ge(2)–Co(4)	2.380(4)
Ge(1)–Co(3)	2.421(4)	Ge(2)–C(1)	1.97(2)
Ge(1)–Co(4)	2.410(4)	Co(1)–Co(2)	2.725(4)
Ge(1)–Co(5)	2.399(4)	Co(1)–Co(4)	2.731(4)
Ge(2)–Co(1)	2.398(4)	Co(2)–Co(3)	2.592(4)
Co(3)–Co(4)	2.637(4)		
Co(1)–Ge(1)–Co(2)	68.9(1)	Co(2)–Ge(2)–Co(4)	104.4(1)
Co(1)–Ge(1)–Co(3)	103.8(1)	Co(2)–Ge(2)–C(1)	126.2(8)
Co(1)–Ge(1)–Co(4)	68.8(1)	Co(3)–Ge(2)–Co(4)	66.9(1)
Co(1)–Ge(1)–Co(5)	130.9(2)	Ge(1)–Co(1)–Ge(2)	75.6(1)
Co(2)–Ge(1)–Co(3)	65.1(1)	Co(2)–Co(1)–Co(4)	86.7(1)
Co(2)–Ge(1)–Co(4)	102.4(1)	Ge(1)–Co(2)–Ge(2)	76.8(1)
Co(2)–Ge(1)–Co(5)	124.4(2)	Co(1)–Co(2)–Co(3)	91.5(1)
Co(3)–Ge(1)–Co(4)	66.2(1)	Ge(1)–Co(3)–Ge(2)	75.6(1)
Co(3)–Ge(1)–Co(5)	125.0(2)	Co(2)–Co(3)–Co(4)	91.5(1)
Co(4)–Ge(1)–Co(5)	132.8(2)	Ge(1)–Co(4)–Ge(2)	76.2(1)
Co(1)–Ge(2)–Co(2)	69.9(1)	Co(1)–Co(4)–Co(3)	90.4(1)
Co(1)–Ge(2)–Co(3)	105.0(1)	Co(2)–C(2)–O(2)	142(2)
Co(1)–Ge(2)–Co(4)	69.7(1)	Co(3)–C(2)–O(2)	133(2)
Co(1)–Ge(2)–C(1)	126.2(7)	Co(3)–C(3)–O(3)	126(2)
Co(2)–Ge(2)–Co(3)	66.0(1)	Co(4)–C(3)–O(3)	152(2)
Co(1)–C(4)–O(4)	171(2)		

Table 5 A summary of the variation in the skeletal interatomic distances (Å) in three $[Co_4(\mu_4\text{-}GeR)(\mu_4\text{-}GeR')(CO)_{11}]$ species where R = R′ = Me **2**, or $Co(CO)_4$ **2**, and R = Me, R′ = $Co(CO)_4$ **4a**

	1a	**4a**	**2**
Ge ··· Ge	2.926	2.955	2.995
Ge–Co(non-bridged)	2.392	2.402	2.429
(bridged)	2.382	2.395	2.398
Co–Co(bridged)	2.580	2.592	2.605
(semi-bridged)	2.693	2.725	2.672
	2.693	2.637	2.736
(non-bridged)	2.721	2.731	2.694

suggesting that the germanium electrons are almost equally shared among the four central Co atoms. Thus the formal electron count at bridged Co is 17.5 and at non-bridged Co is 18.5, and the semibridging occurs to compensate. While the bridged Co–Co distance is the shortest in each molecule, and the three values are similar, the non-bridged and semibridged Co–Co distances are longer, more variable, and show no systematic change with apex group. Thus, the Ge_2Co_4 skeleton expands slightly but systematically with change of apical substituent while the compensation for the formal electron-count difference between the equatorial Co atoms, as shown by the semibridging and the Co–Co distances, occurs in a different manner in each molecule. A related system involving the uneven distribution of carbonyl groups about a metal core for $[M_6C(CO)_{13}]^{2-}$ (M = Co or Rh) has recently been discussed in some detail.[28]

Experimental

General methods and instruments were as used earlier.[3,13,26] A safe and convenient scale for sealed-tube experiments was in dry hexane (10 cm^3) in a 50 cm^3 tube. It was not possible quantitatively to separate unreacted methylgermane from the solvent. Incondensable gases were removed by a Toepler pump and measured by pressure and volume. Approximate gas compositions were determined from the average molecular weight, measured by weighing a sample at known pressure in a fixed volume. The total amount of gas could be measured accurately for reasonable quantities, but the H_2/CO ratio was uncertain to ±5%. Known compounds were identified principally by infrared spectroscopy.

The substituted digermanes were prepared by first synthesising the chlorodigermane from Ge_2H_6 and $SnCl_4$, using a deficit of $SnCl_4$ for the monochloride and an excess to form the dichloride.[17] The Ge_2RH_5 species were then formed by treating the chloride with excess of Mg(Me)I, Mg(Et)Br, $Na[Co(CO)_4]$[21] or $Na[Mn(CO)_5]$[21] respectively.

The Reaction of $GeMeH_3$ *with* $[Co_4(CO)_{12}]$.—(*a*) Methylgermane (0.141 mmol by volume) was condensed on to $[Co_4(CO)_{12}]$ (23 mg, 0.041 mmol) in hexane (30 cm^3) and was allowed to react in a tube equipped with a greaseless tap at 20 °C. After 4 d, incondensable gases (0.130 mmol, 69% H_2) were removed, after 8 d a further 0.02 mmol (78% H_2) (plus a small sample lost), after 9d, a further 0.005 mmol, and after 13 d a final 0.001 mmol, making the total evolution a little over 0.156 mmol [*ca.* 95% based on equation (1)]. There was no sign of unreacted $[Co_4(CO)_{12}]$ in the IR spectrum after 13 d. Work-up yielded $[Co_4(\mu_4\text{-}GeMe)_2(CO)_{11}]$ **1a** (31 mg, 0.043 mmol, 105%).

(*b*) In a similar reaction, carried out in a sealed tube for 60 d, $[Co_4(CO)_{12}]$ (0.026 mmol) reacted completely (accorded to IR spectroscopy) with $GeMeH_3$ (0.152 mmol) to give incondensable gases (0.101 mmol, 97%; 77% H_2) and $[Co_4(\mu_4\text{-}GeMe)_2(CO)_{11}]$ **1a** (19.9 mg, 0.026 mmol, 100%).

(*c*) When larger quantities {$[Co_4(CO)_{12}]$ (0.445 mmol), $GeMeH_3$ (0.96 mmol)} were used in the sealed-tube reaction much of the $[Co_4(CO)_{12}]$ remained undissolved. There was recovered after 120 d at 20 °C: gases (1.06 mmol; 79% H_2, 21%

CO); recrystallised $[Co_4(\mu_4\text{-GeMe})_2(CO)_{11}]$ (188 mg, 0.262 mmol); and unreacted $[Co_4(CO)_{12}]$ containing 5–10% **1a** (123 mg, *ca.* 0.2 mmol). Yields based on $[Co_4(CO)_{12}]$ consumed were *ca.* 105% $[Co_4(\mu_4\text{-GeMe})_2(CO)_{11}]$, 110% total gases and 92% CO.

(*d*) A sealed-tube reaction between $[Co_4(CO)_{12}]$ (0.021 mmol) and $GeMeH_3$ (0.084 mmol) was carried out for 7 d at 30 °C to give gases (0.079 mmol, 93%, containing 81% H_2), $[Co_4(\mu_4\text{-GeMe})_2(CO)_{11}]$ {0.016 mmol, 75% based on initial $[Co_4(CO)_{12}]$} together with a mixed sample of $[Co_4(CO)_{12}]$ and **1a** estimated to contain 5–10% of the initial $[Co_4(CO)_{12}]$.

Decarbonylation of $[Co_2\{\mu\text{-Ge(Me)Co(CO)}_4\}_2(CO)_6]$.—The compound $[Co_2\{\mu\text{-Ge(Me)Co(CO)}_4\}_2(CO)_6]$[13] **3** (50 mg, 0.062 mmol) was heated in hexane at 45 °C. The solution darkened and a black solid precipitated after 7 d. After 40 d, evolution of CO had virtually ceased. There were formed CO (0.22 mmol), a small pentane-soluble fraction (7 mg) containing a trace of **1a**, from which a small sample of $[Co_4(\mu_4\text{-GeMe})_2\{\mu\text{-GeMeCo(CO)}_4\}(CO)_{10}]$[14] was recrystallised. The major fraction was soluble in CH_2Cl_2 and was mainly (**1a**) with a trace of $[Co_4(\mu_4\text{-GeMe})_2\{\mu\text{-GeMeCo(CO)}_4\}(CO)_{10}]$ (31 mg, corresponding to 0.043 mmol, 70%, if taken as **1a**). A pure sample of compound **1a** was obtained by recrystallisation from pentane–CH_2Cl_2 (1:1).

Other Routes to Compound **1a**.—(*a*) The compound $[Co_3(\mu_3\text{-GeMe})(CO)_{11}]$ **6** (143 mg, 0.25 mmol) and $[Co(GeMeH_2)(CO)_4]$ (60 mg, 0.24 mmol) reacted in hexane (5 cm^3) in a sealed tube for 8 weeks at ambient temperature. Work-up gave incondensable gases (0.93 mmol, 72% CO), no volatiles apart from solvent, unreacted **6** (minor amount), and a mixed fraction of compounds **1a** and **3**. The whole involatile sample was gently decarbonylated by heating at 40 °C for 7 d, converting **3** into **1a**, and **6** into $[Co_3(\mu_3\text{-GeMe})(CO)_9]$ **7d**.[16] Recrystallisation from dichloromethane–hexane gave pure **1a** (143 mg, 0.20 mmol, 83%).

(*b*) The compound $GeMeH_2GeMeH_2$ (27 mg, 0.15 mmol) and $[Co_2(CO)_8]$ (112 mg, 0.33 mmol) in hexane (10 cm^3) for 10 d gave incondensable gases (0.68 mmol, 74% CO) and an involatile fraction containing **1a**, **6**, unreacted $[Co_2(CO)_8]$ and $[Co_4(CO)_{12}]$. Fractional crystallisation from hexane at −15 °C gave pure compound **1a** (33 mg, 0.047 mmol, 31% based on digermane).

(*c*) Compound **6** (50 mg, 0.09 mmol) refluxed in hexane (10 cm^3) under nitrogen for 8 h completely reacted to give **1a** (11 mg, 0.024 mmol, 17%) together with non-carbonyl black deposits.

Properties of $[Co_4(\mu_4\text{-GeMe})_2(CO)_{11}]$ **1a**.—The X-ray crystal structure has been described previously.[1] The mass spectrum showed a very weak parent ion and the whole series $[P - n\text{CO}]^+$ for n = 0(vw), 1(m), 2(m), 3(w), 4(m), 5(s), 6(m), 7(w), 8(mw), 9(m), 10(mw) and 11(ms) together with $[MeGe_2Co_x]^+$ for x = 4(ms), 3(w), 2(w) and 1(vw) and $[Ge_2Co_x]^+$ x = 4(ms), 3(w) and 2(w), $[MeGeCo_2]^+$(m), and $[GeCo_2]^+$(vw). All envelopes showed isotope intensity patterns appropriate to the number of Ge atoms.

The ^1H NMR spectrum showed a singlet, δ 2.75. The ^{13}CO NMR resonance of an enriched sample was also a singlet at δ 203.2 (−50 °C), or at δ 202.6 (23 °C), all in $CDCl_3$.

The IR spectrum shows one very strong absorption centred at 2031 cm^{-1} with a shoulder at 2010 cm^{-1} and a very weak broad band centred at 1838 cm^{-1} in CH_2Cl_2. Better resolution was obtained in hexane–CH_2Cl_2 (1:1), 2063vw(sh), 2034vs, 2016m, 2005mw(sh) and 1843w(br), while a CsI disc showed bands at 2083w, 2040s(sh), 2024vs, 2000s(sh), 1995s, 1963w(sh) and 1827s cm^{-1}.

Decarbonylation of Compound **1a**.—A preliminary study showed that when compound **1a** (0.11 mmol) was heated at 75 °C for 45 d in hexane solution, 0.27 mmol of CO formed, and the very dark red solution was a mixture of **1a** and the edge-bridged species $[Co_4(\mu_4\text{-GeMe})_2\{\mu\text{-Ge(Me)Co(CO)}_4\}(CO)_{10}]$ according to IR spectroscopy.[14]

Reaction of $GeMeH_2GeH_3$ *with* $[Co_2(CO)_8]$.—(*a*) *Closed-tube reactions.* The compounds $GeMeH_2GeH_3$ (137 mg, 0.83 mmol) and $[Co_2(CO)_8]$ (668 mg, 1.98 mmol) were sealed in a glass ampoule with hexane (10 cm^3) and kept in the dark at room temperature for 6 months. The tube was opened and the incondensable gases were measured (4.10 mmol, 46% H_2 and 54% CO). The hexane, which contained a little $[CoH(CO)_4]$ (IR spectroscopy) and no germane, was removed. The involatile products were redissolved in hexane, and an infrared spectrum indicated the presence of $[\mu_4\text{-Ge}\{Co_2(CO)_7\}_2]$[18] (and a trace of its condensation product, $[Co_3\{\mu_3\text{-GeCo(CO)}_4\}(CO)_9]$ **7a**),[19] together with a new species **8** characterised as below. This mixture was washed with small portions of hexane until only **8** remained {413 mg, 0.444 mmol, 56% based on $[Co_2(CO)_8]$}. Compound **8** is slightly soluble in hexane, so this yield is a minimum figure, and is soluble in CH_2Cl_2. Other runs, similar in ratio and scale, but for shorter times, gave similar results, except that $[Co_3\{\mu_3\text{-GeCo(CO)}_4\}(CO)_9]$ was not seen. Complete reaction took *ca.* 39 d.

One run with a large excess of $[Co_2(CO)_8]$ (ratio of about 1:6) gave $[Co_2\{\mu\text{-Ge(Me)Co(CO)}_4\}(CO)_7]$ **6**[14] and $[\mu_4\text{-Ge}\{Co_2(CO)_7\}_2]$ as the major products, together with $[Co_4(CO)_{12}]$, presumably from the excess of $[Co_2(CO)_8]$, while **8** was only a minor product.

(*b*) *Open-tube reaction.* The reaction of $[Co_2(CO)_8]$ (1.63 mmol) and $GeMeH_2GeH_3$ (0.64 mmol) was carried out similarly but in a vessel equipped with a greaseless tap, allowing the incondensable gas evolutions to be monitored. Half (0.20) of the total gas evolution had taken place in 14 h, three-quarters (0.41) after 10 d, and the last 10% required from week 6 (0.49) to week 8 (0.51), where the proportion of H_2 to CO at each time is given in parentheses. The run was stopped after 57 d when 4.71 mmol gases (overall composition 34% H_2, 66% CO) had evolved. The solution contained no $[CoH(CO)_4]$, but a little $[Co_4(CO)_{12}]$ was present. Minor products were **6**, **7a**[19] and **5**. All of these were removed by repeated washing with hexane to leave a red-brown solid, identified below as $[Co_4(\mu_4\text{-GeMe})\{\mu_4\text{-GeCo(CO)}_4\}(CO)_{11}]$ **4a**. This was recrystallised from CH_2Cl_2 at −16 °C giving 418 mg, 73% based on $[Co_2(CO)_8]$.

(*c*) 1:1 *Reaction ratio, followed by* ^1H *NMR spectroscopy.* The changes in the ^1H NMR spectrum of a 1:1 mixture (each 0.036 mmol) of $[Co_2(CO)_8]$ and $GeMeH_2GeH_3$ in $SiCl_4$ (acting as an inert solvent) were followed at −20 °C for 100 min, and subsequently for 10 min at 20 °C. Within 3 min there were three new signals in the methyl region and a broad, poorly featured resonance at δ 4.6–5.2 attributable to GeH_x resonances.

There was about 50% reduction of signal intensity in these first 3 min, matching the precipitation of solids. The GeH_x signal broadened further, weakened and was undetectable after 90 min. After 12 min a signal at δ −11.4 {$[CoH(CO)_4]$} was detected and this increased then diminished, up to 40 min. By this time, seven methyl signals were detectable, including a quartet at δ 0.29 from $GeMeH_3$; a sharp signal at δ 4.6 attributable to H_2 was clear as the GeH_x band weakened, and the total signal intensity had decreased to about 10% of the initial value. Further changes were minor and the spectrum remained unchanged after a further 5 d at room temperature. At this point, identifiable species were (*i*) unreacted $GeMeH_2GeH_3$ (δ 0.19, 3.24 and 3.61), (*ii*) H_2, (*iii*) $GeMeH_3$ and (*iv*) a minor amount of $[Co_3(\mu_3\text{-GeMe})(CO)_9]$ **7d** (δ 1.59, singlet).[15,16] New products were indicated by methyl signals at δ 0.47 (triplet, J = 4.3 Hz), overlapping doublets at δ 0.90 (J = 4.3 and *ca.* 5 Hz) and a singlet at δ 1.28 together with two minor singlets at δ 1.44 and 1.75. The triplet signal is compatible with β substitution, possibly in $[Co_2(GeMeH_2GeH)(CO)_7]$ while the doublets indicate $MeGeH[Co(CO)_4]GeH_xCo_{3-x}$ species and the singlets require complete α substitution. Such tentative identifications depend on the pattern of shifts for established compounds and the absence of resonances from [Co(GeMeH_2)(Co)$_4$], [{Co(CO)$_4$}$_2$GeMeH], [{Co_2(CO)$_7$}GeMeH] or **6**.

Characterisation of Compounds **4a** *and* **8**.—(*a*) *Electron probe analysis.* Within the accuracy of the technique electron probe analysis showed both compounds **4a** and **8** contained the heavy atoms Ge and Co in the ratio 2:5.

(*b*) *Mass spectra.* The mass spectrum of compound **8** was obtained only for a sample containing some [μ_4-Ge{Co_2(CO)$_7$}$_2$]. A parent-ion envelope at m/z = 926–938, relative intensity 5, with an isotope pattern showing 2Ge, indicates the 17-carbonyl formula, $C_{18}H_3Co_5Ge_2O_{17}$; $[P' - CO]^+$ was too weak to see, but the remaining CO-loss fragments $[P - n\text{CO}]^+$ was seen for n = 2 (8), 3 (26), 4 (29), 5 (5), 6 (16), 7 (100), 8 (87), 9 (47), 10 (34), 11 (48), 12 (29), 13 (31), 14 (26), 15 (19), 16 (27) and 17 (61) with relative intensities in parentheses. As the overlap with fragments from [μ_4-Ge{Co_2(CO)$_7$}$_2$] involves only the ^{76}Ge isotope of the latter, these fragment ions are clear. Methyl loss and skeletal fragmentation were probably minor processes but the presence of ions from [μ_4-Ge{Co_2(CO)$_7$}$_2$] makes this statement tentative.

The mass spectrum of compound **4a** showed similar features with the strongest fragment ions those retaining nine and eight CO units. The parent-ion family contains two Ge at m/z = 870–882 corresponding to the 15-carbonyl formula $C_{16}H_3Co_5Ge_2O_{15}$ and showing 15 carbonyl loss fragments. The sample used was a pure single crystal, but the very first scan showed ions arising from [Co_3(μ_3-GeMe)(CO)$_9$] and these increased in relative intensity on repeated scans, showing a rearrangement was occurring on the probe.

(*c*) *Infrared spectra.* In hexane solution, the carbonyl stretching bands of compound **8** are at 2104w, 2089s, 2066s, 2056s, 2046vs, 2026s, 2006(sh), 1998w and 1843m cm^{-1}. Those of **4a** are given in Table 1.

(*d*) *NMR data.* In $CDCl_3$ the ^{1}H signal at 27 °C was a singlet, δ 2.77. The ^{13}CO resonances appeared at δ 203.2 (intensity 3) and 195.3 (1) at 0 °C, and at δ 202.6 and 195.9 at −50 °C. The peaks broadened slightly on cooling but showed no sign of splitting.

(*e*) *Thermal decarbonylation of compound* **8** *to* **4a**. Compound **8** (122 mg, 0.131 mmol) was heated in cyclohexane solution at 55 °C for 18 h. Carbon monoxide (0.236 mmol, 1.80 mol equivalents) was evolved, and an IR spectrum of a small sample showed **4a** as the dominant component. A further 4 d at 75 °C produced 0.158 mmol CO (1.21 mol equivalents). No compound other than **4a** was seen in the infrared spectrum, but a small amount of insoluble deposit formed.

Ethyldigermane and [Co_2(CO)$_8$], *a Preliminary Study*.—A similar sealed-tube reaction for 25 weeks between [Co_2(CO)$_8$] (2.56 mmol) and $GeEtH_2GeH_3$ (1.04 mmol) gave a mixture of hexane-soluble products together with a fraction (401 mg) soluble in CH_2Cl_2 whose infrared spectrum [ν(CO) (CH_2Cl_2) 2105m, 2069m, 2050(sh)w, 2037vs, 2022(sh), 2004(sh) and 1845(br)w cm^{-1}] showed a carbonyl stretching region almost identical to that of **4a**, together with bands in the 1250–900 cm^{-1} region characteristic of the ethyl group. Assuming this product is [Co_4(μ_4-GeEt){μ_4-GeCo(CO)$_4$}(CO)$_{11}$] **4c**, the ethyl analogue of **4a**, the yield is 44%. The carbonyl stretches of the hexane fraction [2102m, 2088ms, 2079s, 2068(sh), 2063vs, 2054vs, 2044vs, 2040(sh), 2030(sh), 2027vs, 2023(sh), 2004w, 1865mw, 1854(sh), 1847m, and 1836(sh) cm^{-1}] can be assigned to a mixture of [Co_3(μ_3-GeEt)(CO)$_{11}$], [μ_4-Ge{Co_2(CO)$_7$}$_2$], [Co_4(μ_4-GeEt){μ_4-GeCo(CO)$_4$](CO)$_{11}$], [{(OC)$_7$$Co_2$($\mu_4$-Ge)}$_2$$Co_2(CO)_6$]^3 and [$Co_4(CO)_{12}$].

Reaction of [Mn(GeH_2GeH_3)(CO)$_5$] *with* [Co_2(CO)$_8$].—The compounds [Mn(GeH_2GeH_3)(CO)$_5$]^{21} (512 mg, 1.50 mmol) and [Co_2(CO)$_8$] (1252 mg, 3.66 mmol) were sealed with hexane and were kept in the dark at room temperature for 1 year. Incondensable gases (10.1 mmol, 35% H_2 and 65% CO) and then hexane containing a little [CoH(CO)$_4$] and some [Mn_2(CO)$_{10}$] (IR spectroscopy) were pumped away, together with a further volatile component which decomposed readily and showed IR bands at 2116w, 2056s, 2045m*, 2024vs, 2014s*, 2002w, 1994m and 1983w* cm^{-1}. The asterisked bands are assigned to [Mn_2(CO)$_{10}$] but the main component was not identified, although the simple spectrum suggests a high-symmetry molecule.

The involatile products were washed with hexane, removing a relatively small fraction whose infrared and mass spectra indicated the presence of [Co_3{μ_3-GeMn(CO)$_5$}(CO)$_9$] **7b**,^{23} less [μ_4-Ge{Co_2(CO)$_7$}$_2$] and [Co_4(CO)$_{12}$] and a trace of [{Co_2(CO)$_7$(μ_4-Ge)}$_2$$Co_2(CO)_6$].^{3} The fraction soluble in CH_2Cl_2 weighed 1247 mg and had an infrared spectrum characteristic of a closed hexanuclear cluster. For the formulation of this product as [Co_4{μ_4-GeMn(CO)$_5$}{μ_4-GeCo(CO)$_4$}(CO)$_{11}$] **4b**, the weight corresponds to a 79% yield.

In a similar reaction carried out in an open tube the gases evolved from [Mn(GeH_2GeH_3)(CO)$_5$] (495 mg, 1.43 mmol) and [Co_2(CO)$_8$] (1240 mg, 3.63 mmol) showed an initial lag in hydrogen evolution as is common in such reactions [0.30 mmol total gases containing 35% H_2 after 0.1 h, a further 4.20 mmol with 35% H_2 after 0.5 h, then additions of 0.36 (42%) after 1.3 h, 0.29 (46%) after 3.7 h, 0.41 (49% after 9.2 h, 0.28 (62%) after 16 h, 0.80 (61%) after 1.1 d, and 0.86 mmol (71%) after 1.7 d]. In the later stages the CO content started to rise again (0.31 mmol gas of 68% H_2 content after 2.6 d; a further 1.12 mmol with 57% H_2 after 4.5 d). After 6 d there was a leak in the system and the reaction was ended.

The total recovery of incondensable gas was 9.14 mmol with an overall composition of 36% H_2 to 64% CO. With the solvent hexane was recovered an inseparable trace of [CoH(CO)$_4$] and, on prolonged pumping, a fraction (20 mg) containing [Mn_2(CO)$_{10}$], [Co_4(CO)$_{12}$], and the same unidentified species as in the sealed-tube run. The hexane-soluble fraction consisted of **7b**,^{23} [μ_4-Ge{Co_2(CO)$_7$}$_2$],^{19} [Co_4(CO)$_{12}$], [{Co_2(CO)$_7$(μ_4-Ge)}$_2$$Co_2(CO)_6$]^3 and the unknown, all shown by infrared spectra. The mass spectra of various fractions confirmed the three major products and showed a further very weak ion at m/z 858 and a series of low-intensity peaks at m/z 718, 690, 634 and 606 with a two Ge isotope pattern. These could be ions $[HGe_2Co_4Mn(CO)_x]^+$ for x = 18 and 10, 9, 7 and 6.

The fraction insoluble in hexane readily dissolved in CH_2Cl_2. The infrared spectrum showed small amounts of compound **7b** and [{Co_2(CO)$_7$(μ_4-Ge)}$_2$$Co_2(CO)_6$], together with the major component which was the same as that in the sealed-tube experiment, **4b**.

Characterisation of Compound **4b**.—This compound was red-brown, gradually decomposed in air, and gave only a powder in attempts at recrystallisation. Electron probe analysis showed Ge:Mn:Co in the ratio 2:1:5. The only mass spectrum obtained was from a CH_2Cl_2 extract which contained some [Co_3{μ_3-GeMn(CO)$_5$}(CO)$_9$] and [{Co_2(CO)$_7$(μ_4-Ge)}$_2$$Co_2(CO)_6$]. By observing intensity changes from different samples, ions attributable to **4b** were those of the series $[Ge_2Co_5Mn(CO)_x]^+$ for (relative intensities in brackets) x = 18 (4), 17 (10), 16 (33), 15 (80), 14 (11), 13 (4), 12 (100), 11 (96), 10 (87), 9 (44), 8 (62), 7 (60), 6 (49), 5 (57), 4 (37), 3 (49), 2 (35), 1 (42) and 0 (77). The carbonyl stretches in the infrared spectrum are compared with those of related molecules in Table 2.

Reaction of [Co(GeH_2GeH_3)(CO)$_4$] *with* [Co_2(CO)$_8$].—The compounds [Co(GeH_2GeH_3)(CO)$_4$]^{21} (171 mg, 10.53 mmol) and [Co_2(CO)$_8$] (417 mg, 1.22 mmol) were sealed and kept in the dark at room temperature for 67 d. Incondensable gases were not measured. The hexane fraction contained only a little [CoH(CO)$_4$]. The involatile products could be only partly separated by solvent extractions. The IR spectra of successive fractions clearly identified compound **2** (*ca.* 50%), [μ_4-Ge{Co_2(CO)$_6$(μ_4-Ge)Co_2(CO)$_7$}$_2$]^{10} (*ca.* 40%), [μ_4-Ge{Co_2(CO)$_7$}$_2$] (*ca.* 10%) and [Co_4(CO)$_{12}$] (<2%).

In a similar reaction carried out in an open tube the gases evolved from $[Co(GeH_2GeH_3)(CO)_4]$ (198 mg, 0.62 mmol) and $[Co_2(CO)_8]$ (507 mg, 1.48 mmol) showed 1.06 mmol total gases containing 33% H_2 after 0.1 h, a further 0.66 mmol with 33% H_2 after 2 h, then additions of 0.41 (36%) after 21 h, 0.32 (41%) after 2 d, 0.55 (47%) after 6 d, 0.70 (55%) after 2 weeks, 0.20 (55%) after 3 weeks and 0.24 mmol (56%) after 4 weeks. The evolution is similar, but slower, than for the manganese analogue. The total recovery of incondensable gas was 4.14 mmol with an overall composition of 36% H_2 to 64% CO. The solvent fraction contained only a trace of $[CoH(CO)_4]$. The involatile fraction was a mixture of at least six components, which could be only partially separated. Infrared spectra of fractions indicated as main components **2**, $[\{Co_2(CO)_7(\mu_4\text{-}Ge)\}_2Co_2(CO)_6]$[3] and $[\mu_4\text{-}Ge\{Co_2(CO)_6(\mu_4\text{-}Ge)Co_2(CO)_7\}_2]$[10] (in approximately equal amounts), and as minor components $[\mu_4\text{-}Ge\{Co_2(CO)_7\}_2]$, $[Co_3\{\mu_3\text{-}GeCo(CO)_4\}(CO)_9]$ and $[Co_4(CO)_{12}]$.

Anion Reactions: Preliminary Study.—Compound **2** (428 mg, 0.42 mmol) and $[N(PPh_3)_2][Mn(CO)_5]$ (885 mg, 1.6 mmol, 1:4 ratio) in dichloromethane (20 cm^3) showed almost immediate formation of $[Co(CO)_4]^-$, by infrared monitoring. Changes ceased within 3 h, and successive extractions of the mixture yielded (*i*) a small amount of $[Mn_2(CO)_{10}]$ in hexane, (*ii*) a new species (400 mg) in diethyl ether and (*iii*) a mixture (670 mg) of unreacted $[N(PPh_3)_2][Mn(CO)_5]$ with $[N(PPh_3)_2][Co(CO)_4]$ in CH_2Cl_2. The solid from the ether extract was dissolved in CH_2Cl_2 and showed infrared bands at 2100m, 2076w, 2047(sh), 2037mw, 2022vs and 1984s(br) cm^{-1}. Although there was some reaction when a Nujol mull was prepared, this allowed the identification of $[N(PPh_3)_2]^+$. Electron probe analysis showed Mn:Ge:Co = 11.4:21.7:66.9 or 1:2:6 (±0.3).

In a similar reaction, compound **2** (443 mg, 0.43 mmol) and $[NEt_4][Co(CO)_4]$ (400 mg, 1.63 mmol, 1:3 ratio) in dichloromethane (20 cm^3) yielded after 3 h unreacted $[NEt_4][Co(CO)_4]$ (*ca.* 0.3 mmol) mixed with a little insoluble, purple powder and a fraction soluble in ether. This was identified as $[NEt_4][Co\{\mu_4\text{-}GeCo_3(CO)_9\}_2(CO)_3]$ **7c** by its metal ratio, infrared spectrum and handling properties[25] (310 mg, 0.24 mmol, 57% based on **2**). A second run, in a 1:2 ratio, was similar yielding 53% $[NEt_4][Co\{\mu_4\text{-}GeCo_3(CO)_9\}_2(CO)_3]$, and less unreacted $[NEt_4][Co(CO)_4]$. The dark-coloured product, **7c**, was very sensitive to oxidation in solution, giving purple insoluble deposits, presumably cobalt(II) compounds. It was less sensitive as a solid. Electron probe analyses gave Ge:Co = 2:6.9 (±0.2) and the carbonyl stretches were seen at 2065mw, 2052w, 2025vs and 2003w cm^{-1}, essentially identical to the reported[25] values.

X-Ray Crystal Structure of $[Co_4(\mu_4\text{-}GeMe)\{\mu_4\text{-}GeCo(CO)_4\}(CO)_{11}]$ **4a**.—The space group was defined by precession photography, which clearly eliminated an orthorhombic space group despite the *ca.* 90° β angle. Cell dimensions and intensity data were collected on a Nicolet P3 diffractomer, using monochromated Mo-Kα X-rays (λ 0.7107 Å). Data were corrected for absorption [based on ψ-scans, transmission factors 0.99 (maximum), 0.57 (minimum)], and the structure was solved by direct methods, routinely developed and refined using the SHELX programs.[29]

Crystal data. $C_{16}H_3Co_5Ge_2O_{15}$, M_r 875.2, monoclinic, space group *I*2/*a* (non-standard setting of *C*2/*c*), $a = 12.852(3)$, $b = 14.528(5)$, $c = 26.566(8)$ Å, $\beta = 90.32(2)°$, $U = 4960(2)$ Å^3, $D_c = 2.34$ g cm^{-3} for $Z = 8$, $F(000)$ 3344, μ(Mo-Kα) 111 cm^{-1}, $T = 173$ K.

3252 Unique data ($4 < 2\theta < 45°$) collected by ω scans, 1660 with $I > 2\sigma(I)$ being used in the refinement. Metal atoms anisotropic, C and O atoms isotropic, H atoms not included, R 0.0699, R' 0.0602 with $w = [\sigma^2(F) + 0.000\,327F^2]^{-1}$, largest final Δ/σ 0.04, largest residual peak 1.2 e Å^{-3} adjacent to O atoms.

Final parameters are given in Table 3 and selected bond lengths and angles in Table 4.

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters and remaining bond lengths and angles.

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