Formation and Reactions of Mono- and Di-substituted Derivatives of $[\mu_4\text{-Ge}\{Co_2(CO)_7\}_2]$, containing Functional μ-GeRH or μ-GeRCl Groups[†]

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The reaction of $[\mu_4\text{-Ge}\{Co_2(CO)_7\}_2]$ **1** with $GeRH_3$ (R = Et or Ph) has been found to give $[\mu_4\text{-Ge}\{Co_2(CO)_7\}\{Co_2(CO)_6(\mu\text{-GeRH})\}]$ **2** or $[\mu_4\text{-Ge}\{Co_2(CO)_6(\mu\text{-GeRH})\}_2]$ **3** depending on the stoichiometries and conditions. Analogues of **2** or **3** with μ-GeMeCl groups form from **1** and $GeMe(Cl)H_2$. Reaction of **2** with $[Co_2(CO)_8]$ gives an open cluster with a $\mu\text{-Ge(R)Co(CO)}_4$ group which readily condenses to a *closo*-cluster with a Ge_2Co_4 core. Analogous reactions of **3** with $[Co_2(CO)_8]$ ultimately give clusters $[Co_4(\mu_4\text{-GeR})_2\{\mu\text{-GeCo}_2(CO)_7\}(CO)_{10}]$ again *via* more-open intermediates. Corresponding species are obtained from the μ-GeMeCl compounds and $[Co(CO)_4]^-$. An X-ray structure analysis of $[Co_4(\mu_4\text{-GeEt})_2\{\mu\text{-GeCo}_2(CO)_7\}(CO)_{10}]$ has been performed: triclinic, space group $P\bar{1}$, $a = 10.617(1)$, $b = 16.895(3)$, $c = 9.822(4)$ Å, $\alpha = 104.22(2)$, $\beta = 94.40(2)$, $\gamma = 102.03(1)°$, $Z = 2$, $R = 0.027$, for 3516 data with $I > 2\sigma(I)$. It reveals a structure consisting of a pseudo-octahedral Ge_2Co_4 unit, with one of the Co–Co bonds edge-bridged by a $\mu\text{-GeCo}_2(CO)_7$ moiety.

The reaction of GeH_4 with $[Co_2(CO)_8]$ yields $[\mu_4\text{-Ge}\{Co_2(CO)_7\}_2]$ **1**, which contains two $GeCo_2$ triangles linked through a spiro-Ge.[1] Use of polygermanes gives larger open clusters of linked triangles, such as $[Ge_3Co_8(CO)_{26}]$ prepared[2] from Ge_3H_8. An alternative approach to an extended chain of triangles was the reaction of $GeMeRH_2$ with **1** to form both the monosubstituted product $[\mu_4\text{-Ge}\{Co_2(CO)_7\}\{Co_2(CO)_6(\mu\text{-GeMeR})\}]$ (R = H **2a** or Me **2d**) and disubstituted $[\mu_4\text{-Ge}\{Co_2(CO)_6(\mu\text{-GeMeR})\}_2]$ (R = H **3a** or Me **3d**).[3] The crystal structure of **3d** revealed four $GeCo_2$ triangles linked alternately by the germanium vertices and the Co–Co edges.[3]

A significant reaction of compound **1** is the facile loss of CO to form $[\mu_4\text{-Ge}\{Co(CO)_4\}\{Co_3(CO)_9\}]$ **4** a *closo*-cluster with a $GeCo_3$ trigonal-pyramidal core.[1,4] The next congener of **1**, $[Co_2\{(\mu_4\text{-Ge})Co_2(CO)_7\}_2(CO)_6]$, readily decarbonylates to *closo*-$[Co_4\{\mu_4\text{-GeCo(CO)}_4\}_2(CO)_{11}]$ **5a** which has a square-bipyramidal Ge_2Co_4 core.[5]

For comparison with the reactions involving methylgermanes,[3] we now report on reactions of other $GeRH_3$ (R = Et or Ph) with **1** to give the corresponding products of types **2** and **3**. The Ge–H bonds of **2a**–**2c** or **3a**–**3c** are themselves functional[6] and we have examined the reactions of these with $[Co_2(CO)_8]$ as a route to more complex clusters. We have also found clusters containing the Ge–Cl functionality from the reaction with **1** of $GeMe(Cl)H_2$. Finally, decarbonylation of such products has given new clusters based on the Ge_2Co_4 skeleton.

Results and Discussion

Reactions.—In direct parallel with the previously reported[3] reactions of $GeMeH_3$ or $GeMe_2H_2$, the reaction of $GeEtH_3$ with compound **1** in hexane proceeds slowly at room temperature, and more rapidly at 30 °C, to give the mono- or disubstituted species **2b** or **3b**, according to equations (1) and (2)

$$\mathrm{GeRH_3} + \underset{\mathbf{1}}{[\mu_4\text{-Ge}\{\mathrm{Co_2(CO)_7}\}_2]} \longrightarrow \underset{\mathbf{2}}{[\mu_4\text{-Ge}\{\mathrm{Co_2(CO)_7}\}\{\mathrm{Co_2(CO)_6}(\mu\text{-GeRH})\}]} + \mathrm{H_2} + \mathrm{CO} \qquad (1)$$

$$\mathrm{GeRH_3} + \underset{\mathbf{2}}{[\mu_4\text{-Ge}\{\mathrm{Co_2(CO)_7}\}\{\mathrm{Co_2(CO)_6}(\mu\text{-GeRH})\}]} \longrightarrow \underset{\mathbf{3}}{[\mu_4\text{-Ge}\{\mathrm{Co_2(CO)_6}(\mu\text{-GeRH})\}_2]} + \mathrm{H_2} + \mathrm{CO} \qquad (2)$$

(R = Et). The products depend mainly on the initial stoichiometry. With a small excess of $GeEtH_3$ over a 1:1 ratio, the monosubstituted species **2b** is the main product, with some unreacted **1** even after 10 weeks. At higher reactant ratios, or at slightly elevated temperatures, increasing amounts of the disubstituted compound **3b** are formed. This compound becomes the only product with a large excess of $GeEtH_3$ and intermittent removal of CO and H_2 during the reaction. With $GePhH_3$ and **1**, directly analogous reactions to give **2c** and **3c** occur, although overall conversions are slower than for the $GeEtH_3$ system.

The stepwise nature of the reaction, according to equations (1) and (2), was confirmed by a separate experiment in which compound **1** was converted into **2b** with $GeEtH_3$, and was then treated with $GePhH_3$ to provide a disubstituted compound **3f**, with a μ-GeEtH at one end and a μ-GePhH at the other.

These reactions give chain-extended species which incorporate a GeH functional group. An alternative functionality, GeCl, results from the reaction of **1** with $GeMe(Cl)H_2$, where again either mono- or di-substituted derivatives **2e** and **3e** can be produced in reasonable yields. It was noticeable that $GeMe(Cl)H_2$ reacted at a significantly faster rate than did alkyl- or aryl-germanes under the same conditions. A compound with $\mu\text{-GeMe}_2$ and μ-GeMeCl groups at opposite ends of the molecule, **3g**, was formed from **2d** and $GeMe(Cl)H_2$.

For each of these systems the reactions were relatively slow, requiring a few weeks in sealed tubes. The rates were increased by slight warming to *ca.* 30 °C but higher temperatures were avoided to prevent alternative reactions. The main limiting factor on isolated yields is the ease of separation of the mixtures of compounds **1** and **2** or of **2** and **3** that are produced. In

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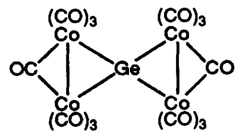
[†] *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.



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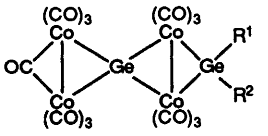
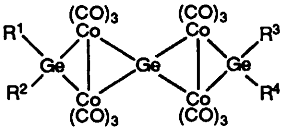
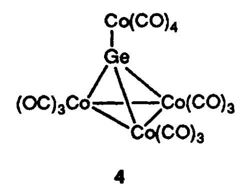


2

	R1	R2
2a	Me	H
2b	Et	H
2c	Ph	H
2d	Me	Me
2e	Me	Cl
2f	Me	Co(CO)4
2g	Ph	Co(CO)4



3a $R^1 = R^3 = Me$, $R^2 = R^4 = H$
3b $R^1 = R^3 = Et$, $R^2 = R^4 = H$
3c $R^1 = R^3 = Ph$, $R^2 = R^4 = H$
3d $R^1 = R^2 = R^3 = R^4 = Me$
3e $R^1 = R^3 = Me$, $R^2 = R^4 = Cl$
3f $R^1 = Ph$, $R^3 = Et$, $R^2 = R^4 = H$
3g $R^1 = R^2 = R^3 = Me$, $R^4 = Cl$
3h $R^1 = R^3 = Et$, $R^2 = R^4 = Co(CO)_4$
3i $R^1 = R^3 = Me$, $R^2 = R^4 = Co(CO)_4$



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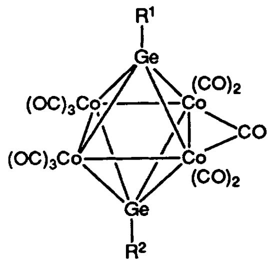
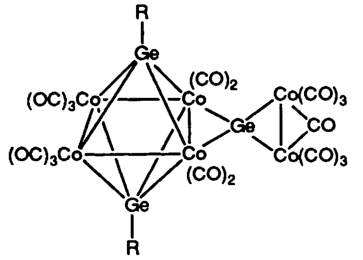


5a $R^1 = R^2 = Co(CO)_4$
5b $R^1 = Me$, $R^2 = Co(CO)_4$
5c $R^1 = Ph$, $R^2 = Co(CO)_4$



	R
6a	Me
6b	Et

Table 1 The CO fundamentals (cm^{-1}) in the infrared spectra of $[\mu_4\text{-Ge}\{Co_2(CO)_7\}\{Co_2(CO)_6(\mu\text{-GeR}^1R^2)\}]$ **2**

R^1R^2

MeH **2a**[3]	EtH **2b**	PhH **2c**	Me_2 **2d**[3]	MeCl **2e**
2098w	2097w	2097w	2096w 2093w	2099w 2097 (sh) 2076ms
2068vs	2068vs	2068vs	2064s	2070s
2056s	2057s	2056s	2054ms 2049 (sh)	2059vs
2047vs	2046vs	2048vs	2043vs	2054s
2030mw	2030mw	2031mw	2026m 2021 (sh)	2032s
2020m	2019m	2020m	2017ms	2022s
1842w	1842w	1842w	1843w	1842w

this respect the reactions described in this paper are more manageable than those[3] of $GeMeH_3$ or $GeMe_2H_2$ because of bigger differences in relative solubilities. With careful control of stoichiometry and conditions any of the mono- or di-substituted species **2** or **3** is available in respectable isolated yields.

The actual mechanism by which a μ-CO is replaced by a μ-GeR_2 group on reaction with GeR_2H_2 is not known. A suggested route consistent with the observations that (*i*) no $[CoH(CO)_4]$ is found and (*ii*) evolution of CO precedes that of H_2 is discussed elsewhere.[3]

Table 2 The CO fundamentals (cm^{-1}) in the infrared spectra of $[\mu_4\text{-Ge}\{Co_2(CO)_6(\mu\text{-GeR}^1R^2)\}_2]$ **3**

R^1R^2

MeH **3a**[3]	EtH **3b**	PhH **3c**	Me_2 **3d**[3]	EtH/PhH **3f**	MeCl **3e**
2085w	2086w	2085w	2081w	2085vw 2071 (sh)	2092w
2059s	2059s	2061vs	2054s	2059m	2066ms
2042vs	2042vs	2042vs	2037vs	2043vs 2026 (sh)	2050vs
2019m	2019m	2020m	2015m	2019w	2026m
2010ms	2009ms	2008ms	2003ms	2011mw	2016ms

Characterisations.—None of the compounds of type **2** was obtained as crystals suitable for full X-ray structure determination. However the spectroscopic data, and the further reactions to give species of type **3** where a structure for **3d** is available for comparison,[3] provide unambiguous characterisation.

All the products studied showed the appropriate ^1H NMR spectra. The chemical shifts were characteristic of the RGeH group with little change between the monosubstituted **2** and disubstituted **3** species, including the mixed-substituent molecule **3f**. Changing R from Ph to Me to Et shifted δ (GeH) to higher field as expected, while the GeMeCl groups gave resonances shifted by the effect of the Cl. As found[3] for **2a** and **2d**, ^{13}CO exchange occurred readily for **2c** and **2e** but not for disubstituted species like **3c**, suggesting ready interchange among CO groups only when μ-CO is present. Although all these molecules have possible isomers resulting from the orientation of the two groups on the Ge, and of the dihedral angles about the Co–Co bonds, all the spectra indicate fast exchange on the NMR time-scale, apart from the MeGeCl compound, **2e**. Here, at −50 °C, both the ^1H and the ^{13}CO signals showed two shifts in a 2:1 intensity ratio. These can be assigned to isomers with either the Me or the Cl group pointing inwards towards the rest of the molecule.

In the mass spectra, all the molecules **2**, except the chloride **2e**, showed parent ions and stepwise loss of 13CO as the major series. For **2e**, the first clear ion was $[P - 2CO]^+$. The ethyl compound, **2b**, showed ions arising from loss of CH_x after eight CO groups had been lost. Otherwise, loss or fragmentation of R groups occurred only after all CO had gone. Among the disubstituted species, only **3c** and **3g** showed a parent ion. The others showed loss of CH_x, CO or Cl in the ion of highest mass. Stepwise loss of the remaining CO was seen for all.

The infrared absorptions in the carbonyl stretching region are presented in Tables 1 and 2, for hexane solutions. These data show the expected pattern of changes, very little effect of changing R in the GeRH species, a shift of about 5 cm^{-1} to lower frequency on replacing H by Me, and of some 8 cm^{-1} to higher frequency on replacing H by Cl.

These molecules **2** and **3** provide, with **1** and related species, the most extensive set of compounds with a geometry based on linked $GeCo_2$ triangles. They are part of a wider range of compounds based on EM_2 units (E = main group and M = transition-metal elements) which originated with the 1967 report[7] of the $SnFe_4$ analogue of **1**. Examples are included in recent reviews,[8] and later papers have reported several analogues of **1** such as an $InRe_4$ species,[9] and several compounds with the AsM_4 skeleton.[10] A few larger E_2M_6 homologues of **1** have also been found, *e.g.* with E = As or Sb and M = Fe,[11] E = S and M = Ru,[12] or E = Ge or Sn and M = Fe.[13] While the range of examples is growing, none provides the opportunity for further reaction under mild conditions represented by the GeH and the GeCl functionalities of **2a**–**2c**, **2e**, **3a**–**3c** and **3e**–**3g**.

Reactions of the Substituted Species **2** *or* **3**.—The initial product of the reaction of $[\mu_4\text{-Ge}\{Co_2(CO)_7\}\{Co_2(CO)_6(\mu\text{-GeMeH})\}]$ **2a** with $[Co_2(CO)_8]$ at 0 °C was the same as that formed by $[\mu_4\text{-Ge}\{Co_2(CO)_7\}\{Co_2(CO)_6(\mu\text{-GeMeCl})\}]$ **2e**, with $[Co(CO)_4]^-$, or from $GeMeH_2(GeH_3)$ with $[Co_2(CO)_8]$.[14] This product may be plausibly formulated as $[\mu_4\text{-Ge}\{Co_2(CO)_7\}\{Co_2(CO)_6[\mu\text{-Ge(Me)Co(CO)}_4]\}]$ **2f**. When **2a** was allowed to react for a longer period, or at room temperature, the main product observed was the closed-cluster decarbonylation product[15] $[Co_4(\mu_4\text{-GeMe})\{\mu_4\text{-GeCo(CO)}_4\}(CO)_{11}]$ **5b**.

Similarly the reaction of $[\mu_4\text{-Ge}\{Co_2(CO)_7\}\{Co_2(CO)_6(\mu\text{-GePhH})\}]$ **2c** with $[Co_2(CO)_8]$ gives a product postulated to be $[Co_4(\mu_4\text{-GePh})\{\mu_4\text{-GeCo(CO)}_4\}(CO)_{11}]$ **5c** from the close match of its properties with those of **5b**. It is reasonable to suppose that the greater steric demand of the Ph group would mean that the open-chain phenyl analogue of **2f** would lose CO under the conditions of the experiment.

In directly analogous procedures, the initial product of the quite fast reaction of compound **3a** with $[Co_2(CO)_8]$, or of **3e** with $[Co(CO)_4]^-$, was formulated as $[\mu_4\text{-Ge}\{Co_2(CO)_6[\mu\text{-Ge(Me)Co(CO)}_4]\}_2]$ **3i**, with $Co(CO)_4$ groups added to both germanium bridges. The initial product **3i** was not particularly robust and readily lost CO to give a new species, characterised as **6a**. When the GeEtH analogue **3b** was used with $[Co_2(CO)_8]$ only the decarbonylation product **6b** was found without obvious sign of the presumed intermediate species **3h**.

For all of these systems the same basic processes are occurring. Initially the GeH units of **2a**, **2c** (or both GeH of **3a**, **3b**) are converted into the corresponding $GeCo(CO)_4$ species *via* the normal[6] hydrogen-elimination reaction. Alternatively the Ge–Cl bonds of **2e** or **3e** undergo salt elimination with $[Co(CO)_4]^-$. In each case the resulting molecules **2f**, **2g** or **3h**, **3i** will be sterically crowded and undergo elimination of CO, to form a *closo* cluster. For the monosubstituted species **2f** the $Co_2GeCo_2GeMeCo$ skeleton rearranges to give μ_4-GeMe and μ_4-GeCo units at the apices of the square-bipyramidal Ge_2Co_4 core of **5b**. A similar rearrangement is also indicated starting from **2e** to give **5c**.

For the disubstituted species a more complex rearrangement occurs. In the presumed intermediate species **3h** or **3i**, we have the core structure $(RGeCo)Co_2GeCo_2(GeCoR)$ which gives, for R = Et, the structure found in **6b** (see below) with two μ_4-GeEt apices to the core Ge_2Co_4 unit which now shares a Co–Co edge with a Co_2GeCo_2 unit equivalent to the skeleton of **1**. The methyl analogue behaves similarly.

There are now five, crystallographically established examples of molecules with the basic pseudo-octahedral core of the form $[Co_4(\mu_4\text{-GeR})(\mu_4\text{-GeR}')(CO)_{10}(\mu\text{-X})]$: (*i*) R = R′ = Me; X = CO;[14,16] (*ii*) R = R′ = $Co(CO)_4$; X = CO **5a**;[5] (*iii*) R = Me, R′ = $Co(CO)_4$; X = CO **5b**;[14] (*iv*) R = R′ = Me, X = $Ge(Me)Co(CO)_4$;[15] (*v*) R = R′ = Et, X = $GeCo_2(CO)_7$ **6b**, see below. A number of related species are indicated by their parallel preparations and spectroscopic properties. All five types may be prepared by CO loss from open clusters the core structures of which are linked $GeCo_2$ triangles. In all cases, GeR groups are conserved, and the number of Co atoms does not change. Cobalt atoms from $Co(CO)_4$ groups in the open clusters may be incorporated into the core, while $Co_2(CO)_7$ units may split and contribute both to the core and to apical $Co(CO)_4$ substituents. Reaction pathways may be devised which involve mainly Co–Co bond breaking and making with minimum changes in Ge–Co bonds. It is noteworthy that all these rearrangements occur under mild conditions in non-polar solvents at 0–50 °C. We have no direct evidence on the pathway from **3h** to **6b** but note that models show that the $Co(CO)_4$ terminal unit on each $\mu\text{-Ge(Et)Co(CO)}_4$ is close to the Co–Co bond at the other end of the molecule. By breaking these Co–Co bonds, and reforming Co–Co links incorporating one Co from each and the two Co atoms from the $Co(CO)_4$ units, it would be possible to form the $EtGeCo_4GeEt$ core while the remaining two Co atoms, still bonded to the original central Ge, reform a Co–Co link to complete the $GeCo_2$ bridge. Thus the rearrangement probably does not involve Et–Ge cleavage and requires replacement of two Ge–Co bonds by two others.

Properties and Crystal Structure of Compound **6b**.—The limit of our mass spectrometer meant we did not see the parent ion, otherwise the dominant pattern is the loss of the 17CO with no fragmentation of the Et groups until the majority of the CO had gone. The infrared spectrum showed a relatively simple pattern of CO stretches in solution, including a bridging mode. The stretches of the 10 terminal CO units of $[Co_4(\mu_4\text{-GeMe})_2(CO)_{11}]$ also heavily overlap to give a very simple-looking spectrum with one very strong band at 2034 cm^{-1} accompanied by only two other distinguishable terminal modes.[14,16] The observed spectrum of **6b** is reasonable for a superimposition of such a pattern with that of the $\mu\text{-GeCo}_2(CO)_7$ unit. The solid-state spectrum allows at least 12 of the 16 terminal modes to be distinguished. The ^{13}C NMR spectrum shows three CO environments at −50 °C, which can be explained from the crystal structure. There will be rapid exchange among the seven CO of the bridged $Co_2(CO)_7$ giving the δ 199 signal (*cf.* δ 202 for **1**[3]). We would expect the four axial and the two semi-bridging CO on the non-bridged edge of the Ge_2Co_4 unit to exchange readily, and the third environment is that of the four axial CO on the Ge-bridged edge. These two similar environments give the signals at δ 202.2 and 202.8. The intensities and shifts are in accord; compare δ 202.6 for $[Co_4(\mu_4\text{-GeMe})_2(CO)_{11}]$ where all the CO exchange rapidly.

The structure of compound **6b** determined by X-ray crystallography is shown in Fig. 1 and represents a novel combination of familiar units. First there is a Co_2GeCo_2 unit, analogous to that in the parent molecule **1**,[1] but now with one Co–Co shared with the square-bipyramidal unit analogous to those of clusters of type **5**. The bridging group is twisted slightly so that the dihedral angle between the Co(1)Co(2)Co(3)Co(4) and the Ge(3)Co(3)Co(4) planes is 8.6°, while the dihedral angle between the two $GeCo_2$ triangles sharing the spiro-Ge is 85.5°, essentially the same as that in **1**.

The Ge–Co distances to the outer Co atoms are equal at 2.384 Å, close to those in compound **1**[1] and in **3d**.[3] The distances to the shared Co atoms are much shorter at 2.316 Å, distinctly less than the 2.34 Å found for the equivalent bonds in the only other edge germanium-bridged cluster, $[Co_4(\mu_4\text{-GeMe})_2(CO)_{10}\{\mu\text{-Ge(Me)Co(CO)}_4\}]$.[14] The external Co–Co distance of 2.53 Å compares with 2.56 Å in **1**, and is shorter than the value of 2.64 Å in the Me_2Ge-bridged **3d**. The Ge(1)···Ge(3) and Ge(2)···Ge(3) non-bonded distances (average 3.49 Å) are greater than the equivalent distances in open-chain linked triangles related to **3** {*e.g.* 3.13 Å in **3d** or 3.22 Å in $[Ge_3Co_8(CO)_{26}]^{2,3}$} presumably because in **6b** the core Ge atoms are held firmly within the cluster. On the other hand the non-bonded Ge(3)···C(56) distance of 2.65 Å is *ca.* 0.1 Å shorter than in analogous compounds.[1,2]

The other unit for general comparison is the Ge_2Co_4 core. Taking the bridging group as a two-electron source, the skeletal electron pair count is eight, and the species is formally electron-precise. The distances from the apex Ge to the Co atoms, at 2.39 Å, are very similar to those of the other five structures listed above, while the Ge(1)···Ge(2) non-bonded distance of 2.89 Å is at the shorter end of the range found for Ge_2Co_4 clusters. For the central Co_4 unit the formal localised electron count is 17.5 at the bridged Co atoms and 18.5 at the non-bridged ones, and all five molecules adapt to this by in-plane CO groups moving into semi-bridging positions along the edges joining the Co atoms with two different electron counts. In the present case, as with (*iii*) and (*iv*) above, the two edges show different degrees of semi-bridging and the Co–Co distances differ by up to 0.05 Å. In contrast, (*i*) and (*ii*) have identical semi-bridging along the two edges. When the Co–Co distances are compared the main effect is the difference of some 0.1 Å in the fully bridged edge between

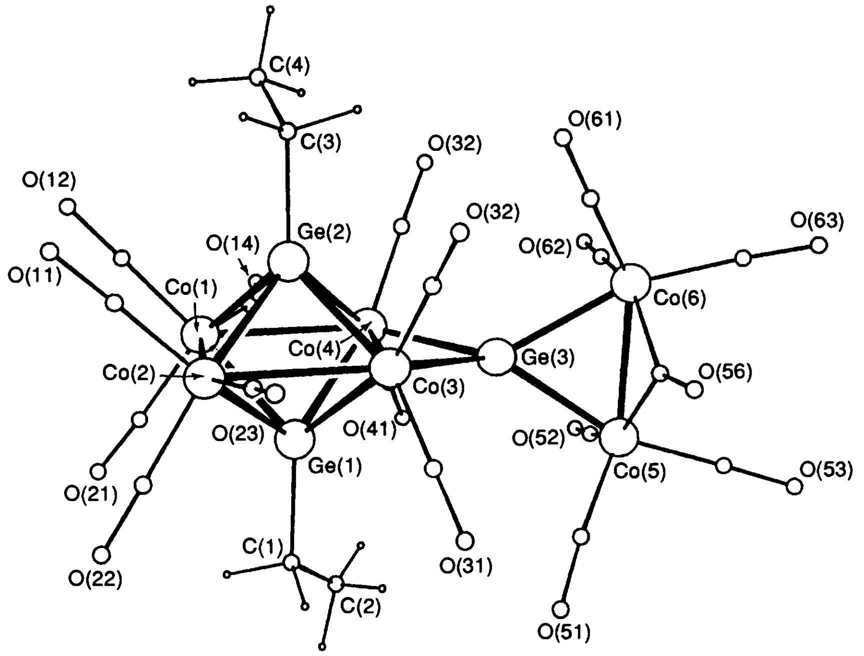


Fig. 1 The structure of $[Co_4(\mu_4\text{-GeEt})_2\{\mu\text{-GeCo}_2(CO)_7\}(CO)_{10}]$ **6b**

Table 3 Final positional parameters for $[Co_4(\mu_4\text{-GeEt})_2\{\mu\text{-GeCo}_2(CO)_7\}(CO)_{10}]$

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Ge(1)	0.694 17(5)	0.148 63(3)	0.327 75(6)	O(32)	0.960 2(6)	0.172 4(3)	−0.089 7(5)
Ge(2)	0.963 95(5)	0.204 48(3)	0.295 62(5)	C(41)	0.688 2(6)	0.331 6(4)	0.449 8(6)
Ge(3)	0.723 07(5)	0.294 09(3)	0.144 61(6)	O(41)	0.613 7(6)	0.360 8(4)	0.508 5(6)
Co(1)	0.880 68(7)	0.187 93(4)	0.507 57(7)	C(42)	0.945 2(6)	0.378 6(3)	0.375 9(6)
Co(2)	0.847 50(7)	0.062 09(4)	0.265 61(7)	O(42)	1.026 1(4)	0.435 1(2)	0.378 6(5)
Co(3)	0.779 89(7)	0.166 70(4)	0.119 76(7)	C(51)	0.433 4(6)	0.233 3(4)	0.017 2(9)
Co(4)	0.812 47(6)	0.290 72(4)	0.365 24(7)	O(51)	0.356 5(6)	0.175 0(3)	0.003 6(9)
Co(5)	0.541 87(7)	0.331 81(4)	0.040 63(9)	C(52)	0.523 2(7)	0.401 8(4)	0.207 7(8)
Co(6)	0.773 66(7)	0.398 76(4)	0.019 90(8)	O(52)	0.511 0(6)	0.447 3(4)	0.308 1(7)
C(11)	0.996 5(6)	0.038 8(3)	0.319 9(7)	C(53)	0.448 3(9)	0.374 4(5)	−0.069(1)
O(11)	1.089 4(5)	0.022 4(3)	0.357 3(7)	O(53)	0.388 4(9)	0.399 5(5)	−0.140(1)
C(12)	1.034 4(8)	0.181 6(5)	0.586 7(8)	C(56)	0.648 6(6)	0.309 4(3)	−0.112 4(6)
O(12)	1.129 3(7)	0.179 3(5)	0.642 1(8)	O(56)	0.636 1(4)	0.264 4(3)	−0.225 7(5)
C(14)	0.889 6(6)	0.295 2(4)	0.597 5(7)	C(61)	0.925 3(6)	0.371 6(3)	−0.004 7(6)
O(14)	0.910 1(5)	0.355 7(3)	0.686 5(5)	O(61)	1.025 3(4)	0.359 2(3)	−0.015 1(6)
C(21)	0.772 2(6)	0.131 5(4)	0.603 1(6)	C(62)	0.803 4(6)	0.482 0(4)	0.186 3(7)
O(21)	0.709 4(5)	0.095 0(3)	0.664 4(5)	O(62)	0.818 0(5)	0.532 6(3)	0.288 1(6)
C(22)	0.728 6(6)	−0.016 1(3)	0.313 0(7)	C(63)	0.760 0(6)	0.464 8(3)	−0.098 8(7)
O(22)	0.657 4(5)	−0.066 3(3)	0.344 4(6)	O(63)	0.748 7(6)	0.503 5(3)	−0.175 6(6)
C(23)	0.837 1(6)	0.016 2(3)	0.081 8(7)	C(1)	0.514 9(6)	0.105 7(4)	0.358(1)
O(23)	0.837 0(5)	−0.021 4(2)	−0.032 2(5)	C(2)	0.430(1)	0.150(1)	0.364(3)
C(31)	0.632 8(7)	0.108 7(4)	0.007 8(7)	C(3)	1.145 9(6)	0.244 7(4)	0.271 0(8)
O(31)	0.544 2(6)	0.069 0(3)	−0.069 0(6)	C(4)	1.230 8(8)	0.303 4(6)	0.399(2)
C(32)	0.893 8(6)	0.173 9(3)	−0.005 3(6)				

the cases X = CO and X = Ge. Otherwise the average Co–Co distances for the five cases fall into a range from 2.67 to 2.71 Å, while the overall range of non- and semi-bridged distances is 2.65–2.77 Å. The longest edge is the non-bridged one in three cases, a semi-bridged one in one case, and the fully bridged one in this molecule. These variations suggest that the overall size of the Ge_2Co_4 unit is relatively invariant and the different steric and electronic demands of the apical substituents R, R′ and of the bridging groups X are met by adjustments to the Co_4 quadrilateral and the in-plane semi-bridging CO groups within an overall tendency to compensate for the distinctive cobalt environments.

The preparation of the $(Ge_2Co_4)GeCo_2$ edge-extended skeleton suggests ways in which more complex units could be built up. Mixed-metal species should be accessible by reaction of other metal carbonyl anions with the GeCl species **2e** or **3e**, or by hydrogen-elimination reactions with the GeH-containing complexes. Further elaboration of clusters of the type **6** by substituting the μ-CO group in the bridge group, using reactions analogous to equation (1), should be feasible. This would allow introduction of further GeH or GeCl functions, leading in turn to more extended clusters.

Experimental

Methods and equipment were as described recently.[3,14,15]

Reactions of $GeEtH_3$ *with Compound* **1** *in a Sealed Tube.*—The compounds $GeEtH_3$ (0.40 mmol) and **1** (215 mg, 0.31 mmol) were shaken in hexane (10 cm^3) for 10 weeks at 20 °C. The tube was opened to yield: incondensable gases (CO, 0.19 mmol; H_2, 0.13 mmol); unreacted $GeEtH_3$ (not

Table 4 Selected bond lengths (Å) and angles (°) for $[Co_4(\mu_4\text{-}GeEt)_2\{\mu\text{-}GeCo_2(CO)_7\}(CO)_{10}]$

Ge(1)–Ge(2)	2.890(1)	Ge(2)–C(3)	1.964(5)
Ge(1)–Co(1)	2.413(1)	Ge(3)–Co(3)	2.315(1)
Ge(1)–Co(2)	2.422(1)	Ge(3)–Co(4)	2.317(1)
Ge(1)–Co(3)	2.360(1)	Ge(3)–Co(5)	2.383(1)
Ge(1)–Co(4)	2.390(1)	Ge(3)–Co(6)	2.385(1)
Ge(1)–C(1)	1.962(5)	Co(1)–Co(2)	2.715(1)
Ge(2)–Co(1)	2.379(1)	Co(1)–Co(4)	2.656(1)
Ge(2)–Co(2)	2.400(1)	Co(2)–Co(3)	2.703(1)
Ge(2)–Co(3)	2.373(1)	Co(3)–Co(4)	2.722(1)
Ge(2)–Co(4)	2.415(1)	Co(5)–Co(6)	2.531(1)
Ge(1) · · · Ge(2)	2.889	Ge(1) · · · Ge(3)	3.363
Ge(2) · · · Ge(3)	3.628	Ge(3) · · · C(56)	2.647
Ge(2)–Ge(1)–Co(1)	52.4(1)	Ge(1)–Co(2)–Ge(2)	73.6(1)
Ge(2)–Ge(1)–Co(2)	52.8(1)	Ge(1)–Co(2)–Co(1)	55.7(1)
Ge(2)–Ge(1)–Co(3)	52.6(1)	Ge(1)–Co(2)–Co(3)	54.5(1)
Ge(2)–Ge(1)–Co(4)	53.4(1)	Ge(2)–Co(2)–Co(1)	55.0(1)
Co(1)–Ge(1)–Co(2)	68.3(1)	Ge(2)–Co(2)–Co(3)	55.0(1)
Co(1)–Ge(1)–Co(4)	67.2(1)	Co(1)–Co(2)–Co(3)	88.6(1)
Co(2)–Ge(1)–Co(3)	68.8(1)	Ge(1)–Co(3)–Ge(2)	75.3(1)
Co(3)–Ge(1)–Co(4)	69.9(1)	Ge(1)–Co(3)–Ge(3)	92.0(1)
Ge(1)–Ge(2)–Co(1)	53.4(1)	Ge(1)–Co(3)–Co(2)	56.7(1)
Ge(1)–Ge(2)–Co(2)	53.5(1)	Ge(1)–Co(3)–Co(4)	55.6(1)
Ge(1)–Ge(2)–Co(3)	52.2(1)	Ge(2)–Co(3)–Ge(3)	101.4(1)
Ge(1)–Ge(2)–Co(4)	52.6(1)	Ge(2)–Co(3)–Co(2)	56.0(1)
Co(1)–Ge(2)–Co(2)	69.2(1)	Ge(2)–Co(3)–Co(4)	56.1(1)
Co(1)–Ge(2)–Co(4)	67.3(1)	Ge(3)–Co(3)–Co(2)	143.5(1)
Co(2)–Ge(2)–Co(3)	69.0(1)	Ge(3)–Co(3)–Co(4)	54.0(1)
Co(3)–Ge(2)–Co(4)	69.3(1)	Co(2)–Co(3)–Co(4)	90.4(1)
Co(3)–Ge(3)–Co(4)	72.0(1)	Ge(1)–Co(4)–Ge(2)	73.9(1)
Co(3)–Ge(3)–Co(5)	132.3(1)	Ge(1)–Co(4)–Ge(3)	91.2(1)
Co(3)–Ge(3)–Co(6)	131.2(1)	Ge(1)–Co(4)–Co(1)	56.8(1)
Co(4)–Ge(3)–Co(5)	139.3(1)	Ge(1)–Co(4)–Co(3)	54.5(1)
Co(4)–Ge(3)–Co(6)	129.9(1)	Ge(2)–Co(4)–Ge(3)	100.1(1)
Co(5)–Ge(3)–Co(6)	64.1(1)	Ge(2)–Co(4)–Co(1)	55.7(1)
Ge(1)–Co(1)–Ge(2)	74.2(1)	Ge(2)–Co(4)–Co(3)	54.6(1)
Ge(1)–Co(1)–Co(2)	56.0(1)	Ge(3)–Co(4)–Co(1)	142.6(1)
Ge(1)–Co(1)–Co(4)	56.0(1)	Ge(3)–Co(4)–Co(3)	54.0(1)
Ge(2)–Co(1)–Co(2)	55.7(1)	Co(1)–Co(4)–Co(3)	89.4(1)
Ge(2)–Co(1)–Co(4)	57.0(1)	Ge(3)–Co(5)–Co(6)	58.0(1)
Co(2)–Co(1)–Co(4)	91.5(1)	Ge(3)–Co(6)–Co(5)	57.9(1)

separated) in the solvent fraction; and an involatile fraction which was extracted with hexane, leaving almost pure **1**. Concentration and cooling of the hexane extract yielded an initial crop of purple $[\mu_4\text{-}Ge\{Co(CO)_4\}\{Co_3(CO)_9\}]$ **4**[4] (11 mg, 6%). Then $[\mu_4\text{-}Ge\{Co_2(CO)_7\}\{Co_2(CO)_6(\mu\text{-}GeEtH)\}]$ **2b** (96 mg, 40% based on initial **1**) was recovered after recrystallisation from dichloromethane–hexane. The calculated conversion into **2b** based on the measured H_2 was 44%. A similar run where the reaction mixture was warmed to 30 °C for 5 d after 65 d at room temperature gave no $[\mu_4\text{-}Ge\{Co(CO)_4\}\{Co_3(CO)_9\}]$, and showed the formation of $[\mu_4\text{-}Ge\{Co_2(CO)_6(\mu\text{-}GeEtH)\}_2]$ **3b**, as well as **2b**. The former could not be isolated pure, but 51% of recrystallised **2b** was recovered, together with a mixed fraction of **2b** and **3b**.

A further experiment aimed at complete conversion into compound **3b** involved shaking a four-fold excess of $GeEtH_3$ (1.33 mmol) with **1** (233 mg, 0.33 mmol) at room temperature for 30 d. A yellow-brown mixture of compounds **1**, **2b** and **3b** resulted, together with CO (0.47 mmol) and H_2 (0.45 mmol). This hydrogen evolution showed that the extent of reaction was *ca.* 70% so all the involatile products were resealed with an additional portion of $GeEtH_3$ (0.33 mmol) and hexane (10 cm^3) and warmed at 30 °C for 5 d. The infrared spectrum of the resulting yellow solution showed it was entirely **3b**, and yellow crystals (270 mg, 96%) were obtained by recrystallising from dichloromethane–hexane.

Characterisation of Compounds **2b** *and* **3b**.—The compound $[\mu_4\text{-}Ge\{Co_2(CO)_7\}\{Co_2(CO)_6(\mu\text{-}GeEtH)\}]$ **2b** was a brown oil or waxy solid, soluble in hexane, which did not yield a well crystalline material. Crystals of $[\mu_4\text{-}Ge\{Co_2(CO)_6(\mu\text{-}GeEtH)\}_2]$ **3b** formed as thin yellow plates, very soluble in hydrocarbons. X-Ray precession photographs indicated a triclinic unit cell, $a = 12.89$, $b = 22.93$, $c = 9.12$ Å, $\alpha = 99.5$, $\beta = 94.5$, $\gamma = 93.2°$, $U = 2644$ Å^3, $Z = 4$, $D_c = 2.13$ g cm^{-3}. The crystal did not survive full data collection, and no other untwinned crystal could be found. For vibrational spectra see Tables 1 and 2.

^1H NMR ($CDCl_3$): **2b** δ 1.39 (t, CH_3), 1.89 (d of q, CH_2) and 5.55 (t, GeH); **3b** δ 1.38 (t), 1.90 (m) and 5.55 (m). Compound **2b** showed a signal at δ 200.8 (s) at −50 °C in the ^{13}C NMR spectrum. An electron probe analysis for **3b** gave a Co : Ge ratio of 3.95 : 3 (calc. 4 : 3), averaged over several points on the crystal. The mass spectrum of **2b** showed all members of the $[P - n\mathrm{CO}]^+$ series from $n = 0$ to 13, weak or medium weak for $n = 0$ to 9 and medium or strong for the remaining members. After loss of eight CO a second series $[P - n\mathrm{CO} - \mathrm{CH}_x]^+$ was seen for each of $n = 9$–13. Loss of Et (or 2 CH_x) and of Co occurred only after all the CO had been lost. For **3b** no parent ion was observed. A well resolved series, with a 3Ge isotope pattern, was found for $[P - \mathrm{CH}_x - n\mathrm{CO}]^+$ for $n = 0$–12. The base peak had $n = 7$, and ions with $n = 9, 6, 5, 3$ and 2 were also prominent. The ion $[Ge_3Co_4]^+$ was strong, while $[EtGe_3Co_4]^+$ and $[Ge_3Co_3]^+$ were medium.

Reactions of $GePhH_3$ *with Compound* **1** *in a Sealed Tube*.—(*a*) A ratio of $GePhH_3$: **1** = 1.5 : 1 in hexane after 4 months at room temperature gave *ca.* 30% conversion into $[\mu_4\text{-}Ge\{Co_2(CO)_7\}\{Co_2(CO)_6(\mu\text{-}GePhH)\}]$ **2c**, from which pure **2c** was recrystallised in 8% overall yield. (*b*) A similar run for 2 months at 30 °C gave complete conversion of compound **1**, allowing the isolation of 24% **2c**, a similar quantity of a mixed fraction of **2c** and $[\mu_4\text{-}Ge\{Co_2(CO)_6(\mu\text{-}GePhH)\}_2]$ **3c**, and a brown CH_2Cl_2-soluble species which has not been identified. (*c*) A 3 : 1 ratio of $GePhH_3$: **1** shaken at room temperature for 4 months gave 55% **2c** and 10% **3c**. (*d*) A sample of compound **2c** (171 mg, 0.21 mmol) warmed for 2 months at 30 °C with a four-fold excess of $GePhH_3$ (0.78 mmol) gave CO (0.19 mmol), H_2 (0.17 mmol), and a brown solution. Work-up yielded pure **3c** (20 mg, *ca.* 10%), a mixed fraction of **2c** and **3c** (150 mg), and *ca.* 20 mg of a species soluble in CH_2Cl_2 the infrared spectrum of which was too poorly resolved for analysis. Neglecting this last, the gas figure suggests *ca.* 80% overall conversion of **2c** into **3c**.

Characterisation of Compounds **2c** *and* **3c**.—The compound $[\mu_4\text{-}Ge\{Co_2(CO)_7\}\{Co_2(CO)_6(\mu\text{-}GePhH)\}]$ **2c** was a waxy brown solid, soluble in hexane, while $[\mu_4\text{-}Ge\{Co_2(CO)_6(\mu\text{-}GePhH)\}]$ **3c** was a similar yellow material, very soluble in hydrocarbons. For vibrational spectra see Tables 1 and 2. ^1H NMR ($CDCl_3$): **2c** δ 6.04 (s, GeH), 7.49 (m, 3 H) and 7.79 (m, 2 H); **3c** δ 6.10 (s, GeH), 7.48 (m, 3 H) and 7.78 (m, 2 H). The mass spectrum of **2c** showed all members of the $[P - n\mathrm{CO}]^+$ series: $n = 0$ (m), 1 (m), 2 (s), 3 (s), 4 (m), 5 (m), 6 (w), 7 (m), 8 (s), 9 (m), 10 (m), 11 (m), 12 (m) and 13 (s). Loss or fragmentation of Ph was seen only after loss of all CO, and then only to give weak peaks apart from $[Ge_2Co_4]^+$ (vs) and $[Ge_2Co_3]^+$ (ms). Compound **3c** showed only a weak, poorly resolved mass spectrum with a weak parent-ion family and envelopes corresponding to $[P - n\mathrm{CO}]^+$ for $n = 3, 5, 7, 9, 11$ and 12.

Reaction of $GePhH_3$ *with* $[\mu_4\text{-}Ge\{Co_2(CO)_7\}\{Co_2(CO)_6(\mu\text{-}GeEtH)\}]$ **2b**.—The compounds $GePhH_3$ (0.43 mmol) and **2b** (150 mg, 0.19 mmol) in hexane (10 cm^3) were shaken for 5 weeks at room temperature, with measurement of the incondensable gases at intervals. At this point, 0.116 mmol gas had been formed (48% CO, 52% H_2) amounting to about 30% reaction, if the second μ-CO was being substituted. The reaction was continued at 30 °C. After another 6 weeks, 0.14 mmol gas (60% CO) had evolved. Evolution slowed and ceased after another 11 weeks, at which time the total of the incondensable gases was 0.33 mmol and the overall CO content was 54%, corresponding, within experimental limits, to essentially complete substitution.

Two involatile products were isolated; a light-brown fraction soluble in hexane, and a dark brown one which was insoluble in hexane but soluble in CH_2Cl_2. No unreacted **2b** remained. The dark brown fraction showed CO stretches in the IR spectrum at 2050s, 2039s, 2002ms and 1830vw cm^{-1} and was not identified. The hexane-soluble product was recrystallised from CH_2Cl_2–hexane as a yellow species which had spectroscopic properties consistent with formulation as the mixed disubstituted product $[\mu_4\text{-Ge}\{Co_2(CO)_6(\mu\text{-GePhH})\}\{Co_2(CO)_6(\mu\text{-GeEtH})\}]$ **3f**. Yields: recrystallised **3f**, 120 mg (69%); dichloromethane-soluble species, 38 mg. For the ν_{CO} of **3f** see Table 2. ^{1}H NMR ($CDCl_3$): δ 1.38 (CH_3), 1.85 (CH_2), 5.52 (GeH in EtGeH), 6.10 (GeH in PhGeH) and 7.48 and 7.78 (Ph), all with appropriate intensities and multiplicities.

Reactions of $GeMe(Cl)H_2$ *with Compound* **1** *in a Sealed Tube*.—Compound **1** (298 mg, 0.425 mmol) and $GeMe(Cl)H_2$ (0.86 mmol) were shaken in hexane (10 cm^3) in a sealed tube in the dark at room temperature for 2 weeks, when dark red needles had formed in a red solution. Incondensable gases evolved were H_2 (0.43 mmol) and CO (0.30 mmol). Work-up gave red crystals which were fairly soluble in hexane and very soluble in dichloromethane, together with a small amount of **1** and some black insoluble material. The red compound was recrystallised from hexane–CH_2Cl_2 at −35 °C and identified as monosubstituted $[\mu_4\text{-Ge}\{Co_2(CO)_7\}\{Co_2(CO)_6(\mu\text{-GeMeCl})\}]$ **2e** (300 mg, 89%). In a similar run, **1** (647 mg, 0.92 mmol) and $GeMe(Cl)H_2$ (1.175 mmol) were shaken for 30 d, then left standing for 30 d. The products were H_2 (0.91 mmol), CO (1.11 mmol), recrystallised **2e** (356 mg, 49%), impure **1** (36 mg, *ca.* 5%), an an orange oil (303 mg) which was quite soluble in CH_2Cl_2 and containing some **2e**.

At a higher ratio, **1** (614 mg, 0.88 mmol) and $GeMe(Cl)H_2$ (1.43 mmol) reacted for 75 d to form incondensable gases (0.97 mmol H_2, 1.23 mmol CO), red crystalline **2e** (550 mg, 79%), a yellow non-crystalline solid shown below to be the disubstituted **3e** (130 mg, 16%), and dark insoluble material (12 mg). The yellow solid was obtained from CH_2Cl_2 solution. Based on the hydrogen recovery, assuming only **2e** and **3e** were formed, the calculated amount of the latter is 21%. When the gas evolution was followed in a tube fitted with a tap, **1** (276 mg, 0.394 mmol) and $GeMe(Cl)H_2$ (0.488 mmol) showed a slow and steady gas formation for 10 d, forming a total of 0.547 mmol, containing 25% H_2. The evolution slowed and the hydrogen content rose to 34% after another 22 d, when the cumulated total of gases was 0.917 mmol. At this point, further $GeMe(Cl)H_2$ (1.1 mmol) was added, and incondensable gas evolution increased to give a total of 1.56 mmol after 58 d. The hydrogen content of the increments rose to 44% H_2. The reaction tapered off and was ended after a total of 67 d when the total gas formation was 1.63 mmol. A red oil was present. Work-up gave yellow disubstituted **3e** (241 mg, 69%), a mixed fraction of **2e** and **3e** (77 mg) and a red oil (215 mg) showing poorly resolved CO stretches in the IR spectrum at 2050, 2045, 2034 and 1973 cm^{-1}.

When monosubstituted compound **2e** (271 mg, 0.341 mmol) was treated with $GeMe(Cl)H_2$ (1.41 mmol) in hexane (10 cm^3) in a sealed tube in the dark at room temperature for 2 months an orange-red solution resulted. Work-up gave a mixed fraction of **2e** and **3e** which could not be separated. The infrared spectrum suggested about 50% conversion.

Characterisation of Compounds **2e** *and* **3e**.—Infrared spectra are given in Tables 1 and 2. A Raman spectrum of compound **2e** gave bands at 2103m, 2077w, 2041vs, 2035 (sh), 2028m, 2016m, 2009w, 2003 (br, sh) and 1836w cm^{-1}. ^{1}H NMR ($CDCl_3$): **2e** δ 1.80 (s) at room temperature, which broadened on cooling to give a singlet at δ 1.85 with a shoulder at δ 1.77 at −30 °C, separating at −50 °C to singlets at δ 1.87 and 1.74 (ratio 2:1); **3e** δ 1.82 (s) at room temperature. Only weak ^{13}C NMR spectra could be obtained but **2e** gave a singlet at δ 202.4 with a weak shoulder at δ 198 at room temperature which separated more clearly into singlets at δ 202.7 and 197.4 (intensities 1:2) at −50 °C.

In the mass spectrum of compound **2e** the ion $[P - CO]^+$ was possibly present but the first envelope to show a clear isotope pattern was centred at m/z = 738 (m) and assigned to $[P - 2CO]^+$. All the remaining members of the $[P - nCO]^+$ series were clear: n = 3 (m), 4 (w), 5 (w), 6 (w), 7 (vs), 8 (s), 9 (s), 10 (m), 11 (s), 12 (w) and 13 (s). The ions $[P - 13CO - Me]^+$ and $[P - 13CO - Cl]^+$ were of medium intensity, and all other polymetallic fragment ions were very minor. For **3e** the highest-mass ion detected was $[P - Cl - nCO]^+$ for $n = 1$, and the rest of the series from n = 2–12 were present; base peak $n = 7$. Overlapping with these were envelopes arising from loss of 2Cl, and from loss of Me, which could not be further resolved on our instrument. Most prominent of the lower-mass fragments was $[MeGe_2Co_4(CO)_x]^+$, x = 1 (mw) and 0 (s); all the others were weak or very weak. An electron probe analysis for **2e** showed an atom ratio Cl:Co:Ge of 0.8:3.9:2.0 (calc. 1:4:2) averaged over several sites on the crystal.

The Reaction of Compound **2d** *with* $GeMe(Cl)H_2$.—The compounds $[\mu_4\text{-Ge}\{Co_2(CO)_7\}\{Co_2(CO)_6(\mu\text{-GeMe}_2)\}]$ **2d** (40 mg, 0.052 mmol) and $GeMe(Cl)H_2$ (0.24 mmol) were allowed to react in hexane (30 cm^3) in the dark at room temperature. Incondensable gases were evolved mainly in the first 5 d (0.079 mmol, 59% CO), with only 0.016 mmol forming in the next 4 weeks. A yellow product was isolated (*ca.* 59 mg, 0.05 mmol, *ca.* 100% by weight, 80% by gas measurement). This is provisionally identified as $[\mu_4\text{-Ge}\{Co_2(CO)_6(\mu\text{-GeMe}_2\}\{Co_2(CO)_6(\mu\text{-GeMeCl})\}]$ **3g** by the following observations. The product shows CO stretches at 2081w, 2069 (sh), 2054s, 2037vs, 2015m and 2003ms cm^{-1}, very similar to those of **3d** and **3e**. The mass spectrum showed two series of ions, $[P - nCO]^+$ and $[P - nCO - Me]^+$, with intensities w, m, m, ms, w, w, w, w, w, w, w, w, w in each species for n = 0–12 respectively, apart from a little more intense methyl-loss peak for n = 5. The only other prominent fragments were $[Ge_3Co_4]^+$ and $[MeGeCo_4]^+$.

Reaction of $[\mu_4\text{-Ge}\{Co_2(CO)_7\}\{Co_2(CO)_6(\mu\text{-GePhH})\}]$ **2c** *with* $[Co_2(CO)_8]$.—Compound **2c** (121 mg, 0.15 mmol) and $[Co_2(CO)_8]$ (30 mg, 0.09 mmol) in hexane (5 cm^3) were allowed to react for 40 d at room temperature, with measurement of the incondensable gases at intervals. At this point, CO (0.23 mmol) had evolved at a gently decreasing rate. In the next 44 d further evolution of CO (0.32 mmol) occurred with a little H_2 (0.05 mmol). A trace of $[CoH(CO)_4]$ was observed. Extraction with hexane yielded a dark brown solution and a red-brown solid insoluble in hexane, which gave a red solution in CH_2Cl_2. No unreacted **2c** remained. The red solid showed aromatic protons in the NMR and CO stretches in the IR spectrum at 2105mw, 2061mw, 2050 (sh), 2038vvs, 2015m, 2005m, 1969 (sh), 1845vw (solution) and 2106m, 2071mw, 2054 (sh), 2043–2038s (sh), 2032 (sh), 2029vs, 2016s, 2008s, 2000s, 1970 (sh) and 1853mw cm^{-1} (CsI disc). This is similar to the spectrum of $[Co_4(\mu_4\text{-GeMe})\{\mu_4\text{-GeCo(CO)}_4\}(CO)_{11}]$ **5b** and thus the red product was provisionally identified as $[Co_4(\mu_4\text{-GePh})\{\mu_4\text{-GeCo(CO)}_4\}(CO)_{11}]$ **5c** (51 mg, 37%). From its IR spectrum the dark brown fraction in hexane (0.1 g) contained **5c** and $[Co_4(CO)_{12}]$.

Reaction of $[\mu_4\text{-Ge}\{Co_2(CO)_7\}\{Co_2(CO)_6(\mu\text{-GeMeH})\}]$ **2a** *with* $[Co_2(CO)_8]$.—In a similar experiment, compound **2a** (210 mg, 0.22 mmol), contaminated by about 20% **1**, and $[Co_2(CO)_8]$ (50 mg, 0.15 mmol) were allowed to react for 45 d. Carbon monoxide (0.11 mmol) was evolved at a decreasing rate. Work-up yielded a brown hexane-soluble species, a red-brown solid insoluble in hexane but soluble in CH_2Cl_2, and an insoluble fraction. The hexane-soluble fraction (150 mg) contained **1**, its condensation product **4**, a little $[Co_2(CO)_8]$, and a compound the IR spectrum of which indicated it to be $[\mu_4\text{-Ge}\{Co_2(CO)_7\}\{Co_2(CO)_6[\mu\text{-Ge(Me)Co(CO)}_4]\}]$ **2f**. Recrystallisation gave a small amount of red $[Co_4(\mu_4\text{-GeMe})\{\mu_4\text{-GeCo(CO)}_4\}(CO)_{11}]$ **5b**. The dark red CH_2Cl_2 fraction was solely **5b** (80 mg, 42%). The insoluble fraction (20 mg) gave a weak mass spectrum with no clear patterns of loss of Ge or CO and was not further studied. A similar run, for 21 d at 0 °C, gave only **2f** in 85% yield.

Characterisation of $[Co_4(\mu_4\text{-GeMe})\{\mu_4\text{-GeCo(CO)}_4\}(CO)_{11}]$ **5b**.—Electron probe analysis gave Ge:Co = 2:5.2 (calc. 2:5). The IR spectrum showed CO stretches at 2106m, 2067m, 2050 (sh), 2037vvs, 2013ms, 2004 (sh), 1965 (sh), 1843vw (br) (hexane solution) and 2106m, 2072m, 2051w (sh), 2037s (sh), 2029vs, 2015ms, 2012 (sh), 2001s, 1994 (sh), 1991 (sh), 1966 (sh) and 1854m cm^{-1} (CsI disc). The mass spectrum showed the full series of ions $[MeGe_2Co_5(CO)_n]^+$ for n = 15 (m), 14 (mw), 13 (ms), 12 (vw), 11 (vw), 10 (m), 9 (vs), 8 (ms), 7 (m), 6 (m), 5 (m), 4 (m), 3 (m), 2 (w), 1 (m) and 0 (s). The last three overlapped the $[MeGeCo_3(CO)_n]^+$ series, from n = 9, most of the members of which were clear. NMR ($CDCl_3$): ^1H, δ 2.77 (s); ^{13}C, two signals in a 3:1 ratio at δ 203.2 and 195.5, which remained essentially unchanged down to −50 °C. All these data agree closely with those reported[14] for **5b** prepared from $GeMeH_2(GeH_3)$, and crystallographically defined.

Characterisation of $[\mu_4\text{-Ge}\{Co_2(CO)_7\}\{Co_2(CO)_6[\mu\text{-Ge(Me)Co(CO)}_4]\}]$ **2f**.—Electron probe analysis gave Ge:Co = 1.9:5 (calc. 2:5). The IR spectrum in hexane–CH_2Cl_2 showed CO stretches at 2105w, 2088vs, 2064s, 2055ms, 2046vs, 2026s, 2023 (sh), 2015 (sh), 2004 (sh), 1997w and 1845w cm^{-1}, very similar to those obtained[14] for the product from the reaction of Ge_2MeH_5 and $[Co_2(CO)_8]$. The mass spectrum also agreed, showing 17CO loss steps and methyl loss. The compound also lost CO readily to give **5b**. These properties, and the preparations, allow the formulation as given.

Reaction of $[\mu_4\text{-Ge}\{Co_2(CO)_6(\mu\text{-GeEtH})\}_2]$ **3b** *with* $[Co_2(CO)_8]$.—In a similar experiment, compounds **3b** (90 mg, 0.11 mmol) and $[Co_2(CO)_8]$ (44 mg, 0.13 mmol) were allowed to react for 82 d. Incondensable gases were evolved at a decreasing rate (0.037 mmol in 4 h, 0.102 mmol in 10 d, 0.200 mmol in 73 d, 0.204 mmol in 82 d). After 26 d an IR spectrum showed the presence of $[Co_4(CO)_{12}]$ and a new compound, shown below to be $[Co_4(\mu_4\text{-GeEt})_2\{\mu\text{-GeCo}_2(CO)_7\}(CO)_{10}]$ **6b**, together with traces of a further species which may be $[\mu_4\text{-Ge}\{Co_2(CO)_6[\mu\text{-Ge(Et)Co(CO)}_4]\}_2]$ **3h**. After 82 d a trace of $[CoH(CO)_4]$ was present and this, with $[Co_2(CO)_8]$, was removed by pumping. Work-up yielded a dark brown hexane-soluble fraction, and a red-brown solid insoluble in hexane but soluble in CH_2Cl_2. The dark red CH_2Cl_2 solution was concentrated, hexane added, and cooled to give long dark crystals of $[Co_4(\mu_4\text{-GeEt})_2\{\mu\text{-GeCo}_2(CO)_7\}(CO)_{10}]$ (70 mg, 0.063 mmol, 58%). The first crop from the hexane solution was also **6b** (20 mg, 17%), while a second crop (20 mg) contained **6b** and $[Co_4(CO)_{12}]$.

Reaction of $[\mu_4\text{-Ge}\{Co_2(CO)_6(\mu\text{-GeMeH})\}_2]$ **3a** *with* $[Co_2(CO)_8]$.—In a similar experiment, compounds **3a** (250 mg, 0.30 mmol) and $[Co_2(CO)_8]$ (131 mg, 0.38 mmol) reacted much more rapidly giving incondensable gases as follows: 0.236 mmol (5% H_2, 95% CO) in 6 d, 0.042 mmol in 2 d more, and 0.073 mmol (now 91% H_2) in 7 d more. After these 15 d an IR spectrum showed no unreacted **3a**, $[Co_4(CO)_{12}]$ and the compounds shown below to be $[Co_4(\mu_4\text{-GeMe})_2\{\mu\text{-GeCo}_2(CO)_7\}(CO)_{10}]$ **6a** and $[\mu_4\text{-Ge}\{Co_2(CO)_6[\mu\text{-Ge(Me)Co(CO)}_4]\}_2]$ **3i**. Work-up yielded hexane and CH_2Cl_2 soluble fractions. The CH_2Cl_2 solution gave crystals of **6a** (100 mg, 30%). Crops from the hexane solution were $[Co_4(CO)_{12}]$ (30 mg) and $[\mu_4\text{-Ge}\{Co_2(CO)_6[\mu\text{-Ge(Me)Co(CO)}_4]\}_2]$, contaminated with some $[Co_4(CO)_{12}]$ (200 mg, *ca.* 57%).

Reaction of $[\mu_4\text{-Ge}\{Co_2(CO)_7\}\{Co_2(CO)_6(\mu\text{-GeMeCl})\}]$ **2e** *with* $[Co(CO)_4]^-$.—In CH_2Cl_2, compounds **2e** (284 mg, 0.36 mmol) and $K[Co(CO)_4]$ {prepared from $[Co_2(CO)_8]$ (81 mg, 0.24 mmol) and Na/K alloy} were stirred vigorously for 15 min, the solvent removed, and products separated from KCl by extraction with hexane. There were isolated a fraction of pure $[\mu_4\text{-Ge}\{Co_2(CO)_7\}\{Co_2(CO)_6[\mu\text{-Ge(Me)Co(CO)}_4]\}]$ **2f** (127 mg, 38%) and a mixed fraction contaminated with some $[Co_4(CO)_{12}]$ (207 mg).

Reaction of $[\mu_4\text{-Ge}\{Co_2(CO)_6(\mu\text{-GeMeCl})\}_2]$ **3e** *with* $[Co(CO)_4]^-$.—Hexane extraction of the products of a similar experiment using compound **3e** (190 mg, 0.21 mmol), containing a little **2e**, and $K[Co(CO)_4]$ {from $[Co_2(CO)_8]$ (92 mg, 0.27 mmol)} gave a mixed fraction of **2f** (arising from the **2e**?) contaminated with some $[Co_4(CO)_{12}]$ (77 mg). A hexane–CH_2Cl_2 extract of the residue produced a pure sample of $[\mu_4\text{-Ge}\{Co_2(CO)_6[\mu\text{-Ge(Me)Co(CO)}_4]\}_2]$ **3i** (182 mg, 0.156 mmol, 85%); no unreacted **3e** remained.

Provisional Characterisation of $[\mu_4\text{-Ge}\{Co_2(CO)_6[\mu\text{-Ge(Me)Co(CO)}_4]\}_2]$ **3i**.—The substitution of Cl in compound **3e** or of H in **3a** each gives a product with matching IR spectrum which readily loses CO under vacuum to form the species identified below as $[Co_4(\mu_4\text{-GeMe})_2\{\mu\text{-GeCo}_2(CO)_7\}(CO)_{10}]$. The mass spectrum up to our instrument limit of m/z about 1000 shows ions of the $[P - n\text{CO}]^+$ and $[P - n\text{CO} - \text{Me}]^+$ series with intensity patterns appropriate to 3Ge for n = 5–20. The overall pattern of intensities is very similar to those of the corresponding ions from **6b** (characterised crystallographically below) suggesting decarbonylation on the probe. The IR spectrum in solution shows no μ-CO mode and terminal CO stretches at 2090s, 2072mw, 2058s, 2043vs, 2018s and 1995 (br, sh) cm^{-1}. While not substantive, these observations are compatible with the formulation given, and as expected from the preparation reactions.

Characterisation of $[Co_4(\mu_4\text{-GeR})_2\{\mu\text{-GeCo}_2(CO)_7\}(CO)_{10}]$ (R = Me **6a** *or* Et **6b**).—The product from compound **3b** was characterised crystallographically as $[Co_4(\mu_4\text{-GeEt})_2\{\mu\text{-GeCo}_2(CO)_7\}(CO)_{10}]$ **6b**. The product from **3a** is therefore the methyl analogue as the spectra match closely: in CH_2Cl_2, bands at 2089mw, 2062s, 2053s, 2039vs, 2016m and 1837w for **6a** and 2092mw, 2063vs, 2052s, 2034vs, 2017s, 1988 (sh) and 1827w cm^{-1} for **6b**. More detail appears in other media, exemplified by the CsI disc spectrum of **6b**: 2115vw, 2095m, 2067 (sh), 2060s, 2053 (sh), 2046m, 2033 (sh), 2027m, 2016 (sh), 2013vs, 2008 (sh), 1993m, 1981m and 1826m cm^{-1}. For **6b**, in the ^1H NMR spectrum the Et protons were at δ 1.96 (t, 3 H) and 3.29 (q, 2 H) while the ^{13}C NMR resonances (CO) were singlets at δ 202.7 and (broader) 199.2 (ratio 2:1) at 27 °C and at δ 202.8, 202.2 and 199.0 (ratio 1.5:1:1.5) at −50 °C.

Crystal Structure of $[Co_4(\mu_4\text{-GeEt})_2\{\mu\text{-GeCo}_2(CO)_7\}(CO)_{10}]$ **6b**.—A suitable single crystal was obtained from CH_2Cl_2 at −10 °C. Preliminary precession photography showed triclinic symmetry. Cell dimensions and intensity data were obtained on an Enraf-Nonius CAD4 diffractometer, using monochromated Mo-Kα X-rays (λ = 0.710 69 Å). The data were corrected for absorption (based on ψ scans), and the structure was solved by direct methods and refined using the SHELX programs.[17]

Crystal data. $C_{21}H_{10}Co_6Ge_3O_{17}$, M = 1105.2, triclinic, space group $P\bar{1}$ (no. 2), a = 10.617(1), b = 16.895(3), c = 9.822(4) Å, α = 104.22(2), β = 94.40(2), γ = 102.03(2)°, U = 1655.1 Å^3, Z = 2, D_c = 2.22 g cm^{-3}, transmission factors 0.99 (maximum), 0.66 (minimum), μ(Mo-Kα) 55 cm^{-1}, $F(000)$ = 1060, T = 293 K.

4395 Unique reflections were collected by θ–2θ scans, in the range $2 < 2\theta < 56°$, with 3516 $[I > 2\sigma(I)]$ used in calculations. All non-H atoms anisotropic, H atoms included in calculated positions; full-matrix least-squares refinement converged with $R = 0.0274$, $R' = 0.0274$ with $w = [\sigma^2(F) + 0.0004F^2]^{-1}$. Largest final Δ/σ (not involving the ethyl groups) was 0.03, largest residual peak 0.5 e Å^{-3}. The ethyl groups did not converge properly, and showed large thermal parameters and unrealistic bond lengths due to partial disorder.

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

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