Substitution reactions of $[Ge_2Co_4Fe_2(CO)_{21}]$ with methylgermanes, and its decarbonylation. Structures of $[Fe_2\{\mu_4\text{-}GeCo_2(CO)_6(\mu\text{-}GeMe_2)\}_2(CO)_7]$ and $[Fe_3\{\mu_3\text{-}GeCo(CO)_4\}_2(CO)_9]$

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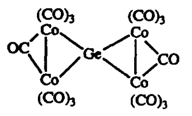
The compound $GeMe_2H_2$ reacted with $[Fe_2\{\mu_4\text{-}Ge[Co_2(CO)_7]\}_2(CO)_7]$, to replace only the μ-CO on the Co–Co bonds, forming $[Fe_2\{\mu_4\text{-}Ge[Co_2(CO)_6(\mu\text{-}GeMe_2)]\}_2(CO)_7]$. The monosubstituted product $[Fe_2\{\mu_4\text{-}Ge[Co_2(CO)_7]\}\{\mu_4\text{-}Ge[Co_2(CO)_6(\mu\text{-}GeMe_2)]\}(CO)_7]$ and similar products from $GeMeH_3$ are also indicated. A crystal structure analysis of $[Fe_2\{\mu_4\text{-}Ge[Co_2(CO)_6(\mu\text{-}GeMe_2)]\}_2(CO)_7]$ confirmed an extended core of six GeM_2 triangles, linked through the germanium apices and the Co–Co or Fe–Fe edges. Heating $[Fe_2\{\mu_4\text{-}Ge[Co_2(CO)_7]\}_2(CO)_7]$ at 50–60 °C for 4–7 weeks yielded as major product $[Fe_2Co_4Ge_2(CO)_n]$ (n = 19 or 20) whose spectroscopic properties indicate a square-bipyramidal cluster with a $Fe_2Co_2Ge_2$ core. The minor product was the crystallographically characterised *closo*-trigonal-bipyramidal cluster $[Fe_3\{\mu_3\text{-}GeCo(CO)_4\}_2(CO)_9]$ with a Ge_2Fe_3 core.

An increasing range of open clusters is known whose structures are a series of EM_2 (E = main group, M = transition element) triangles linked by alternate sharing of the E apices and the M–M edges.[1] Archetypes are found among germanium–cobalt compounds. Classical cases[2] are substituted dicobalt octacarbonyl species, $[Co_2(\mu\text{-}GeR_2)_2(CO)_6]$, which can be seen as two $GeCo_2$ triangles sharing the Co–Co edge, while[3] $[\{Co_2(CO)_7\}_2(\mu_4\text{-}Ge)]$ **1** represents the alternative case where the two $GeCo_2$ triangles share the germanium apex. An important feature of **1** is that the geometry of the outer $Co_2(\mu\text{-}CO)$ edges is very similar to that of dicobalt octacarbonyl, suggesting that further substitution to extend the chain of triangles is feasible. We have indeed recently shown[4,5] that **1** reacts with $GeR(R')H_2$ to convert the $Co_2(\mu\text{-}CO)$ unit into a Co_2Ge triangle by formally replacing μ-CO by μ-GeR(R′). Both mono- and di-substituted products were found, including the crystallographically characterised[4] $[\{Co_2(\mu\text{-}GeMe_2)(CO)_6\}_2(\mu_4\text{-}Ge)]$, and related species containing $\mu\text{-}GeR_2$, μ-GeR(R′) (R,R′ = Me, Et or Ph), μ-GeR(H) or μ-GeR(Cl) units. These products consist of three and four, respectively, linked triangles with both edge and apex sharing.

The molecule $[\{Co_2(CO)_7\}_2(\mu_4\text{-}Ge)]$ **1** is the first member of a homologous series $Ge_nCo_{2n+2}(CO)_{6n+8}$ formed by treating polygermanes with dicobalt octacarbonyl. The compounds with n = 2 (**2**) and 3 have also been characterised.[6,7] The core structures of all these molecules are linked chains of $GeCo_2$ triangles: a crystal structure[7] of the third member, $[Ge_3Co_8(CO)_{26}]$, shows six such triangles with the two terminal $(OC)_3Co\text{–}Co(CO)_3$ edges bridged by CO in a configuration very similar to that of **1**. Unfortunately **2** did not give single crystals though chemical and spectroscopic properties are fully in accord with the linked-triangle structure. This was further reinforced by the extension of the series[7,8] to mixed iron–cobalt species and the crystallographic characterisation[7] of the analogue of **2**, $[Ge_2Co_4Fe_2(CO)_{21}]$ **3**, whose structure relates to that expected for **2**, but with the central $Co_2(CO)_6$ unit replaced by the analogous $Fe_2(CO)_6(\mu\text{-}CO)$ one.

Since substitution reactions had been found which extended the chain of triangles in compound **1**, it was interesting to see if the higher homologues would behave similarly. Unpublished studies in our laboratory[9] have indicated, from the mass balance and IR spectra, that $GeMe_2H_2$ and $GeMeH_3$ react with the second homologue **2** to form the disubstituted derivative $[Co_2\{\mu_4\text{-}Ge\{Co_2(\mu\text{-}GeMeR)(CO)_6\}\}_2(CO)_6]$ **4** (R = H or Me) and also indicated a similar reaction for the third homologue $[Ge_3Co_8(CO)_{26}]$. Unfortunately, the products could only be partially characterised as they were too involatile for mass spectroscopy and did not form single crystals.



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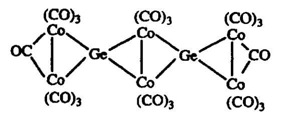

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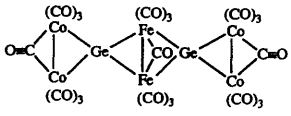

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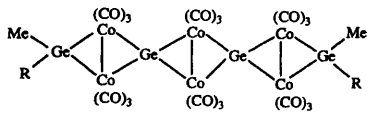
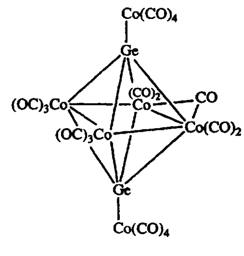


4 R = H, Me



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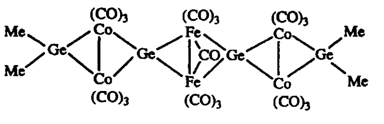

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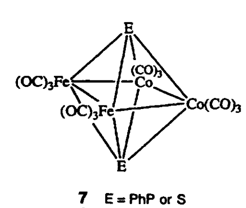
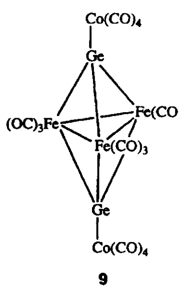


7 E = PhP or S

8 E = GeCo(CO)$_4$



9

As the results from the all-cobalt compounds were inconclusive, we extended these studies to the analogue of **2**, $[Ge_2Co_4Fe_2(CO)_{21}]$ **3**. The structure of **3** presents very similar outer $Co_2(CO)_6(\mu\text{-}CO)$ units and there is also additional interest in whether substitution of the central μ-CO bridging Fe–Fe occurs more or less readily than substitution of the CO bridging Co–Co. This paper reports the results including the crystal structure of the major product from reaction of **3** with $GeMe_2H_2$, the disubstituted product **5**.

A further reaction characteristic of compounds **1** and **2** is the loss of a CO group under very mild heating, and the condensation of the open skeleton into a *closo* one. A terminal $Co(CO)_4$ unit attaches to each Ge and the remaining Co atoms make up the cluster skeleton. From **1** the trigonal-pyramidal $[Co_3\{\mu_3\text{-}GeCo(CO)_4\}(CO)_9]$ forms[3,10] while **2** yields[6] the analogous square-bipyramidal cluster **6**. While mixed-metal analogues of **6**, such as $[Fe_2Co_2(\mu_4\text{-}E)_2(CO)_{12}]$ **7** (E = PPh or S) or $[Fe_nRu_{4-n}(\mu_4\text{-}E)_2(CO)_{11}]$ (n = 1–4; E = PPh, Se or Te) are known,[11] no mixed-metal species capped by Group 14 elements has been reported. Thus we also investigated the decarbonylation of **3**.

Results

Reactions of $[Fe_2\{\mu_4\text{-}Ge[Co_2(CO)_7]\}_2(CO)_7]$ 3

The reaction of a five-fold excess of $GeMe_2H_2$ with compound **3** proceeded smoothly over 10 d according to equation (1) to

$$2GeMe_2H_2 + \mathbf{3} \longrightarrow 2CO + 2H_2 + \mathbf{5} \qquad (1)$$

give a quantitative yield of the product **5**. The crystal study below shows that the CO units bridging the two outer Co–Co edges of **3** are both substituted by μ-$GeMe_2$ in **5**. Even when the $GeMe_2H_2$: **3** ratio was raised to 10 : 1, and the reaction left for 6 months, there was no sign of a trisubstituted species where the CO bridging the central Fe–Fe bond was replaced; warming cannot be used as condensation reactions supervene. At a 1 : 1 reaction ratio about 40% of **3** remained unreacted and an inseparable mixture of products resulted. Within experimental uncertainties, the reaction obeyed equation (1) to around 90%. The second component was probably the monosubstituted product $[Fe_2\{\mu_4\text{-}Ge[Co_2(CO)_7]\}\{\mu_4\text{-}Ge[Co_2(CO)_6(\mu\text{-}GeMe_2)]\}(CO)_7]$, indicated by extra bands in the IR spectrum. The very poor solubility of **3** in the pentane solvent probably led to the low production of the monosubstituted species which would be expected to be more soluble, and therefore more available for further substitution.

Survey experiments suggest that $GeMeH_3$ reacts with compound **3** to form the μ-GeMe(H) analogue of **5** in a similar, somewhat slower, reaction but that $SiMe_2H_2$ did not react.

Crystal structure of compound 5

The structure of compound **5** is shown in Fig. 1, and selected bond parameters are in Table 1. The molecule lies on a crystallographic two-fold axis coincident with the bridging CO group and bisecting the Fe–Fe bond. It has a chain of six linked GeM_2 triangles, and has been formed by replacing the μ-CO on the two Co–Co bonds in **3** by μ-$GeMe_2$ groups.

The geometry of the central Ge_2Fe_2 is similar[7] to that of the same unit in compound **3**. The Fe–Fe bond at 2.641(4) Å is slightly shorter than the comparable bonds in **3** [2.678(5) Å] or in $[Fe_2(\mu\text{-}GePh_2)_2(CO)_7]$ [2.666(3) Å][12] and the dihedral angle between the two $GeFe_2$ planes is 3° smaller than in **3**. For the outer Ge_2Co_2 parts of the molecule the Co–Co distance is longer than in **3**, as expected, but similar to other Co–Co where there are two μ-GeR_2 units.[4] The *spiro*-dihedral angle for Fe_2GeCo_2 is 7° smaller than the average value in **3**. The M–CO and Ge–Me distances and angles fall within normal ranges, while the Ge(2) ··· Ge(2′) non-bonded distance at 3.360 Å is longer than the 3.302 Å in **3**, despite the smaller dihedral angle, because of the longer Ge–Fe bonds in **5** (0.04 Å longer on average than in **3**). The outer Ge(1) ··· Ge(2) distance is much shorter at 3.132 Å (the same as in the equivalent[4] part of $[\{Co_2(CO)_6(\mu\text{-}GeMe_2)\}_2(\mu_4\text{-}Ge)]$) reflecting both the shorter Ge–Co distances compared with Ge–Fe, and the more acute dihedral angle between the triangles with a common Co–Co edge.

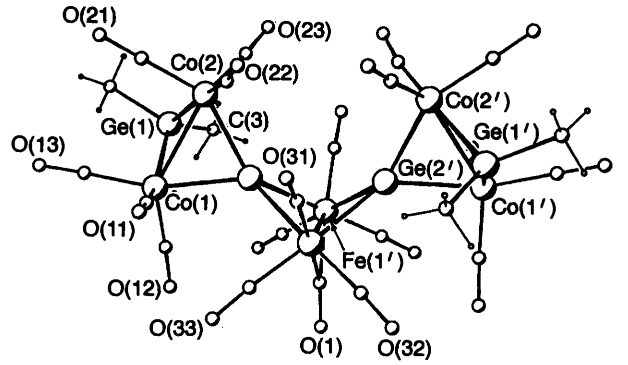


Fig. 1 A view of $[Fe_2\{\mu_4\text{-}Ge[Co_2(CO)_6(\mu\text{-}GeMe_2)]\}_2(CO)_7]$ **5**. There is a two-fold axis coincident with the O(1)–C(1) vector and bisecting the Fe–Fe bond

Table 1 Selected bond lengths (Å) and angles (°) for $[Fe_2\{\mu_4\text{-}Ge[Co_2(CO)_6(\mu\text{-}GeMe_2)]\}_2(CO)_7]$ **5**

Ge(1)–Co(1)	2.348(3)	Ge(1)–Co(2)	2.386(2)
Ge(1)–C(2)	1.98(2)	Ge(1)–C(3)	1.94(2)
Ge(2)–Co(1)	2.382(2)	Ge(2)–Co(2)	2.346(2)
Ge(2)–Fe(1)	2.471(2)	Co(1)–Co(2)	2.636(3)
Fe(1)–Fe(1′)	2.641(4)		
Co(1)–Ge(1)–Co(2)	67.7(1)	C(2)–Ge(1)–C(3)	102.0(8)
Co(1)–Ge(2)–Co(2)	67.8(1)	Co(1)–Ge(2)–Fe(1)	123.4(1)
Co(2)–Ge(2)–Fe(1)	140.4(1)	Ge(1)–Co(1)–Ge(2)	82.9(1)
Ge(1)–Co(1)–Co(2)	56.9(1)	Ge(2)–Co(1)–Co(2)	55.5(1)
Ge(1)–Co(2)–Ge(2)	82.9(1)	Ge(1)–Co(2)–Co(1)	55.5(1)
Ge(2)–Co(2)–Co(1)	56.8(1)		

As in compounds **1**,[4] **3**[7] and $[Ge_3Co_8(CO)_{26}]$,[7] the $GeCo_2$ and $GeFe_2$ triangles are all asymmetric with the difference between corresponding Ge–Fe and Ge–Co distances being 0.05 and 0.04 Å respectively. All of these variations are in accord with earlier ideas[3,7] that the linked-triangle core in these clusters is quite flexible and readily undergoes small deformations under the influence of intra- or inter-molecular interactions.

Characterisation of related products

The reaction stoichiometries and the spectroscopic properties are consistent with the formulation of the product from the reaction of $GeMeH_3$ with **3** as the μ-GeMe(H) analogue of **5**. The CO stretching region in the IR spectrum (Table 2) shows the close match. Comparison with **3** shows significant changes, and a narrowing of the band in the μ-CO bridging region. The broad band of **3** suggests that the stretches of the CO groups bridging Fe–Fe and Co–Co bonds overlap, and this is replaced by the sharper band due only to stretch of the CO bridging Fe–Fe.

Also included in Table 2 are the CO stretches[9] of species resulting from the reaction of an excess of $GeMe_2H_2$ or $GeMeH_3$ with **2**. The bands are compatible with disubstituted products analogous to **5**.

Decarbonylation of compound 3

Carbon monoxide was lost slowly and smoothly on gentle heating of compound **3** in hexane, with the formation of a major and a minor product. The major product accounts for over 90% of the reaction, but did not form single crystals. The simplest rationalisation of the reaction and spectroscopic data is that the open cluster **3** condenses according to equation (2) to a *closo*-

Table 2 Carbonyl stretching bands (cm^{-1}) of compound **5** and related species

5[a]	**3** + GeMeH$_3$[a]	**3**[a,b]	**2** + GeMe$_2$H$_2$[c,d]	**2** + GeMeH$_3$[d,e]
2083mw	2082w		2087vw	2086w
	f			*g*
2063s	2057ms	2086s	2065ms	2071ms
2048vs	2040vs	2064vs	2053vs	2055vs
2039vs	2036s	2050vs	2041vs	2038vvs
			2034 (sh)	2022 (sh)
2012m	2013s	2020m (br)	2013m (sh)	2010s
2004 (sh)				
1996s	2001m (sh)	2008m (br)	2008ms	2003 (sh)
1989 (sh)	1973mw		1985 (sh)	1985 (sh)
1834m	1840mw	1844–1826w (br)		

[a] In hexane–CH$_2$Cl$_2$. [b] Ref. 7. [c] Ref. 13; postulated to be $[Co_2\{\mu_4\text{-}Ge[Co_2(CO)_6(\mu\text{-}GeMe_2)]\}_2(CO)_6]$. [d] In hexane. [e] Ref. 14; postulated to be $[Co_2\{\mu_4\text{-}Ge[Co_2(CO)_6(\mu\text{-}GeMeH)]\}_2(CO)_6]$. [f] Absorption at 2070 cm^{-1} assigned as ν(Ge–H). [g] Absorption at 2071 cm^{-1} assigned as ν(Ge–H).

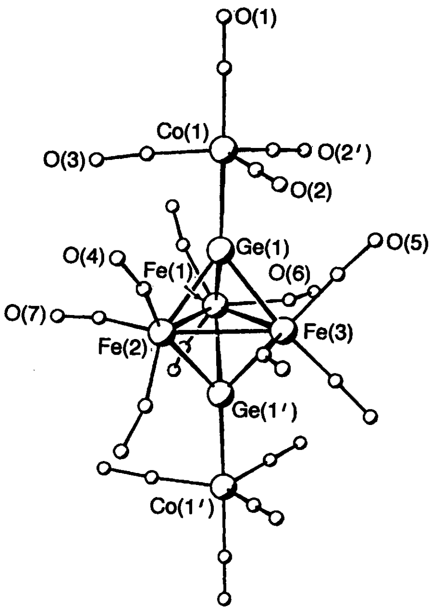


Fig. 2 The structure of $[Fe_3\{\mu_3\text{-}GeCo(CO)_4\}_2(CO)_9]$ **9**. Only one of the disordered configurations is shown. Selected bond lengths (accuracy diminished by disorder) include: Fe(1)–Fe(2) 2.75(1), Fe(1)–Fe(3) 2.76(1), Fe(2)–Fe(3) 2.75(1), Ge(1)–Fe(1) 2.369(6), Ge(1)–Fe(2) 2.331(6), Ge(1)–Fe(3) 2.329(5) and Ge(1)–Co(1) 2.325(4) Å

$$\underset{\mathbf{3}}{[Fe_2\{\mu_4\text{-}Ge[Co_2(CO)_7]\}_2(CO)_7]} \longrightarrow CO + \underset{\mathbf{8}}{[Fe_2Co_2\{\mu_4\text{-}GeCo(CO)_4\}_2(CO)_{12}]} \quad (2)$$

square-bipyramidal Ge$_2$M$_4$ species analogous[6] to the condensation of $[Ge_2Co_6(CO)_{20}]$ **2** to $[Ge_2Co_6(CO)_{19}]$ **6**.

The characterisation of the product **8** depends on the mass balance during the reaction and on spectroscopic data. Since the formation of the minor product **9**, and any partial decomposition, would increase the evolution of CO, the formation of approximately 1.5 CO per molecule is compatible with **8** as the major product. A good mass spectrum, up to our instrument limits, was obtained for 19 CO losses, and a very weak ion family centred at *m*/*z* 1050 was tentatively identified as the parent ion. While this could have arisen from a trace of the starting material, the intensity pattern in the rest of the spectrum was quite different from that found[8] for **3**, *e.g.* the base peak is the ion $[Ge_2Co_4Fe_2(CO)_{12}]^+$ for **8** but was $[Ge_2Co_4Fe_2(CO)_8]^+$ for **3**. The CO stretching region in the IR spectrum is also compatible, although all these species give similar spectra with only two main, broad, absorptions. Of course, **8** is not the only possible square-bipyramidal product, for example the isomer with the alternative FeCoFeCo central plane is conceivable. More significantly, while **8** is an eight skeletal electron pair (SEP) species isoelectronic with $[Fe_2Co_2S_2(CO)_{11}]$ or $[Fe_2Co_2(PPh)_2(CO)_{11}]$,[11] the evidence does not preclude the presence of a 19-carbonyl, seven SEP species isostructural with **6** and corresponding to the well established[15] $[Fe_4(\mu_4\text{-}PPh)_2(CO)_{11}]$ which readily interconverts with the eight SEP $[Fe_4(\mu_4\text{-}PPh)_2(CO)_{12}]$. However, the fully terminal **8** is presumably the dominant product as a 19-carbonyl species would be expected to show a distinct bridging-CO stretch, while at best there is only an extremely weak, broad absorption at *ca.* 1830 cm^{-1}.

The minor product, **9**, was characterised by X-ray crystallography. It arises from a much more drastic reorganisation, formally as in equation (3). While crystals of **9**

$$3\,[Fe_2\{\mu_4\text{-}Ge[Co_2(CO)_7]\}_2(CO)_7] \longrightarrow [Fe_3\{\mu_3\text{-}GeCo(CO)_4\}_2(CO)_9] + \text{‘}Ge_2Co_8(CO)_{29}\text{’} \quad (3)$$

could be picked out for analysis, **8** and **9** were not quantitatively separable but **9** was estimated to form no more than 10% of the total product. The maximum contribution of equation (3) to the measured CO would then correspond to between one- and two-thirds of that involved in the ‘$Ge_2Co_8(CO)_{29}$’ of equation (3), depending on the proportion of **3** in the soluble material. The amount of insoluble material would also approximate to the ‘$Ge_2Co_8(CO)_{29}$’ of equation (3).

Structure of compound 9

The black crystals turned out to be one of the still relatively rare class[1,16,17] of E$_2$M$_3$ *closo*-trigonal bipyramids formed by main-group, E, and transition-metal, M, atoms. The structure is shown in Fig. 2, and selected bond lengths are given in the caption. The molecule lies on a site which includes two crystallographic mirror planes, one through the equatorial plane of Fe$_3$ atoms and one bisecting this plane and including the Co atoms. There is disorder across this latter plane leading to two half-occupied sites for each Fe atom, about 0.9 Å apart (see Fig. 3). This gives two orientations of the Fe$_3$ triangles, related by a rotation of *ca.* 31° within the polyhedron of CO ligands. Interestingly the related trigonal-bipyramidal clusters $[Fe_3(\mu_3\text{-}As)_2(CO)_9]$, $[Fe_3(\mu_3\text{-}Bi)_2(CO)_9]$ and $[Fe_3(\mu_3\text{-}CF)_2(CO)_9]$ (refs. 18 and 19) also crystallise in the same space group (*Cmcm*) and show the same disorder, whereas $[Fe_3(\mu_3\text{-}ER)_2(CO)_9]$ with lower-symmetry capping groups are fully ordered [*e.g.* ER = GeEt, GeFe(CO)$_2$(cp), GeRe(CO)$_5$ or PMn(CO)$_2$(cp)(cp = η-C$_5$H$_5$)].[17,20,21] However $[Ru_3(\mu_3\text{-}Bi)_2(CO)_9]$ is also ordered despite being isostructural with the Fe$_3$ analogue,[22] highlighting the difficulties with predicting crystal structures based on molecular structures. The disorder in **9** leaves the oxygen atoms of the carbonyl ligands in the same

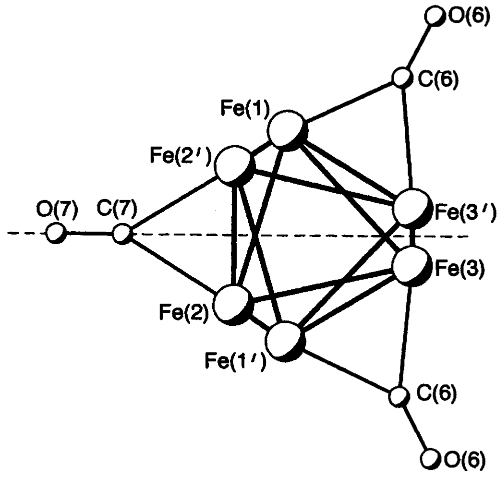


Fig. 3 The equatorial plane of the structure of $[Fe_3\{\mu_3\text{-}GeCo(CO)_4\}_2(CO)_9]$ **9**, showing the disorder of the iron atoms across the crystallographic mirror plane

positions for each orientation but divides the carbon atoms into two half-weighted positions; these could not be separately resolved in the present study. Note that this disorder is distinct from that found for other M_3 (or M_4) carbonyl clusters which exhibit a 'Star-of-David' metal core with the two orientations related by a 60° rotation.[23]

The disorder for compound **9** reduces the accuracy of the bond parameters. Within this uncertainty, the mean bond lengths, Ge–Fe (2.342 Å) and Fe–Fe (2.75 Å), of the Ge_2Fe_3 core are the same as those found for the other characterised $[Fe_3(\mu_3\text{-}GeR)_2(CO)_9]$ species, R = Et,[17] $Re(CO)_5$[20] or $Fe(CO)_2(cp)$,[17] with average Ge–Fe 2.321, 2.379 or 2.378 Å and average Fe–Fe 2.732, 2.718 or 2.726 Å, respectively.

The bond to the external group, Ge–Co 2.325 Å, is similar to that found in the trigonal-pyramidal[10] $[Co_3\{(\mu_3\text{-}GeCo(CO)_4\}(CO)_9]$ (2.349 Å) but distinctly shorter than in the square-pyramidal configurations $[Co_4(\mu_4\text{-}GeR)(\mu_4\text{-}GeR')(CO)_{11}]$ with Ge–Co(CO)$_4$ 2.399 Å (ref. 24) for R = Me, R′ = Co(CO)$_4$ and 2.405 Å (ref. 6) for R = R′ = Co(CO)$_4$. While both the μ_3-Ge and μ_4-Ge atoms formally provide three electrons for their respective clusters, there is clearly a moderate difference in their bonding to the external group, reflecting different contributions to the cluster units.

Discussion

The chain-extension reaction (1) exactly parallels previously observed reactions. The structure of compound **5**, with six linked triangles, is the second one of this length, after $[Ge_3Co_8(CO)_{26}]$, to be fully characterised. Many structures for a linked pair of triangles are known,[1,3,16] and crystal structures of several four-triangle chains have been reported.[8,16,25] In addition, spectroscopic and other evidence for monosubstitution of **1**, **2**, and related compounds indicates chain lengths of three and five triangles. The indications[9] of substitution in $[Ge_3Co_8(CO)_{26}]$ suggest that even longer chains are possible. While the relatively small dihedral angles about the M–M bonds could allow such molecules gradually to bend around and even link ends into a coronet if there were enough triangles, the steric hindrance between CO groups leads to a preference for 'linear' rather than curved arrangements. The two-fold axis in **5** neatly confirms the transoid orientation of the two $GeMe_2$ groups with respect to each other.

In parallel with reported reactions of $[Fe_2(CO)_9]$ the last μ-CO was not replaced. While triply substituted bridges are known, they are all formed indirectly, from $[Fe_3(CO)_{12}]$ or at elevated temperatures when $[Fe_3(CO)_{12}]$ would be produced.

The trigonal-bipyramidal condensation product from **3** is the fourth Ge_2Fe_3 species to be reported. As with the trigonal-pyramidal GeM_3 and square-bipyramidal Ge_2M_4 compounds, the apical substituent can be Co(CO)$_4$ or a similar metal residue or else an organic group. These three mixed main group–transition element *closo* structures are thus broadly related in type and range of substituents. However, all the syntheses of trigonal bipyramids so far found with Group 14 elements in the capping positions are undirected ones, as in this case. The most direct is the formation[17] of $[Fe_3(\mu_3\text{-}GeR)_2(CO)_9]$ from $GeRH_3$ and $[Fe(CO)_5]$ but even here there are two other products and the yield is variable and unpredictable.

Conclusion

The clean substitution of μ-CO by μ-GeR$_2$ in compound **3** confirms earlier observations that replacement of the bridging carbonyl of a $Co_2(\mu\text{-}CO)$ unit with GeR_2 is a general, specific reaction. This has value in chain-extending reactions of the type reported here, but also has potential for introducing active sites for more complex cluster build-up by using germanes with additional functionality, *e.g.* $GeRH_3$ or $GeR(Cl)H_2$. Of the elements of Group 14, germanium is the one of choice in this process; equivalent reactions with silanes or stannanes are not as successful.

Experimental

Compounds were handled on vacuum lines or under dry N_2 with the same general methods as previously.[24] Reactants were dissolved in dry pentane or hexane (usually 10 cm^3) and sealed in glass ampoules and shaken in the dark, usually at ambient temperature (23–25 °C). Alternatively they were held in vessels fitted with greaseless taps, and the evolved H_2/CO measured at intervals using a Toepler pump and gas burette. The synthesis of **3** has been reported elsewhere.[8]

Reaction of dimethylgermane with compound 3

In a sealed tube, $GeMe_2H_2$ (0.44 mmol) and compound **3** (103 mg, 0.095 mmol) were shaken together at 20 °C. The solubility of orange **3** is low. The initially very pale solution became progressively more orange while the amount of solid **3** decreased and had all reacted after 10 d. The reaction was worked up after 26 d to yield: incondensable gases (0.38 mmol; H_2, 49%, 0.188 mmol; CO, 51%, 0.192 mmol), solvent and unreacted $GeMe_2H_2$ (0.16 mmol recovered: more inseparable from solvent), and an involatile product which was soluble in pentane. Recrystallisation yielded a species whose electron-probe analysis showed a Ge:Co:Fe ratio of 2.0:2.1:0.96. This, the crystal structure, and the spectroscopic properties detailed below show the product to be $[Fe_2\{\mu_4\text{-}Ge[Co_2(CO)_6(\mu\text{-}GeMe_2)]\}_2(CO)_7]$ **5** (116 mg, 0.094 mmol, 99%).

In a similar experiment using $GeMe_2H_2$ (0.11 mmol) and compound **3** (98 mg, 0.091 mmol) there remained unreacted orange solid after 30 d, and no unreacted $GeMe_2H_2$ was found. Gases measured: H_2 (53%, 0.105 mmol) and CO (47%, 0.094 mmol). The insoluble residue was washed, and the total pentane-soluble fraction collected (58 mg). The remaining solid was soluble in CH_2Cl_2 and was shown to be pure starting material, **3** (44 mg, 0.036 mmol). The components of the mixture could not be separated. The infrared spectrum showed all the bands of **5** (see below) and additional maxima at 2087m, 2074m, 2058vs and 2033vs cm^{-1}, attributable to a monosubstituted species.

A similar experiment using $GeMe_2H_2$ (1.09 mmol) and compound **3** (105 mg, 0.097 mmol) was left on a shaker for 6 months. Gases measured, H_2 (52%, 0.21 mmol) and CO (48%, 0.195 mmol), corresponded to disubstitution. Again there was only partial separation of unreacted $GeMe_2H_2$ (0.55 mmol) from the solvent. The involatile product was pure **5** (115 mg, 0.091 mmol, 93%) with no trace of any second species.

Characterisation of compound 5. The product **5** is a bright orange crystalline solid, slightly lighter than **3**. It is readily soluble in pentane, CH_2Cl_2 and Et_2O, and decomposes in tetrahydrofuran. The solid was stable to short exposures to air but the solutions rapidly oxidised. Solid and solution were stable indefinitely under nitrogen at −20 °C.

The ^1H NMR spectrum showed a singlet at δ 1.37, very similar to those of other $Co_2(\mu\text{-}GeMe_2)$ species,[4] and indicating that the methyl groups are all equivalent in solution. The IR spectrum of the CO stretching region is included in Table 2.

Crystal structure of compound 5. Crystals from pentane or CH_2Cl_2 were twinned, but suitable crystals of a regular needle habit could be obtained from diethyl ether. Such crystals slowly broke up over 48 h on the precession camera, attributed to the slow loss of solvent of crystallisation. At −110 °C on the diffractometer there was no evidence of decomposition. Intensity data were collected on a Nicolet P4 diffractometer with monochromated Mo-Kα X-rays (λ = 0.710 73 Å).

Crystal data. $C_{23}H_{12}Co_4Fe_2Ge_4O_{19}\cdot C_4H_{10}O$, $M = 1304.25$, orthorhombic, space group *Pccn*, $a = 15.721(8)$, $b = 14.597(6)$, $c = 17.533(9)$ Å, $U = 4023(3)$ Å^3, $D_c = 2.15$ g cm^{-3} for $Z = 4$, $F(000) = 2528$, μ(Mo-Kα) = 55 cm^{-1}, $T = 163$ K. Orange crystals from Et_2O, 0.06 × 0.06 × 1.06 mm.

3956 Unique reflections collected for $4 < 2\theta < 52°$, $T_{max,min}$ 0.962, 0.239 (empirical absorption correction based on ψ-scans). Calculations used the 2016 reflections with $I > 3\sigma(I)$. The coordinates of the heavy atoms were located using the TREF routine of SHELXS 86[26] and subsequent difference maps located the 10 unique CO groups and the two Me carbons. Areas of large residual electron density led to the location of $(C_2H_5)_2O$ of crystallisation on the two-fold axis. The two C and the O of the unique part were included and all H placed in calculated positions. All non-H atoms anisotropic and refinement (based on *F*) converged to $R = 0.063$, $R' = 0.060$ where $w = [\sigma^2(F) + 0.001\,35F^2]^{-1}$. Three areas of residual electron density (1–2 e Å^{-3}) adjacent to metal atoms were attributed to an imprecise absorption correction for the very long thin needle.

Reaction of methylgermane with compound 3

In a similar reaction, $GeMeH_3$ (1.1 mmol) and compound **3** (118 mg, 0.11 mmol) were shaken together in a sealed tube for 4 months in the dark. The solid disappeared more slowly than for $GeMe_2H_2$, but otherwise the reaction proceeded similarly. This produced incondensable gases (0.42 mmol, 54% CO), a volatile fraction containing only solvent and unreacted $GeMeH_3$, and an involatile product (115 mg) which was free from **3**. Electron-probe analysis showed Ge:Co:Fe in the ratio 2.0:2.3:1.1. If this was entirely the GeMe(H) analogue of **5** it would amount to 0.096 mmol (88% yield).

The IR spectrum of the CO stretching region of the $GeMeH_3$ product is included in Table 2. The 1840 cm^{-1} maximum in the μ-CO region is appropriate for CO bridging Fe–Fe. The GeMe(H) frequencies average about 5 cm^{-1} lower than the $GeMe_2$ values as expected, and the 2070m cm^{-1} band is a possible candidate for ν(GeH).

In a similar sealed-tube reaction, $SiMe_2H_2$ (1.6 mmol) and compound **3** (108 mg, 0.10 mmol) were held for 6 months at room temperature. No changes were observed, no incondensable gases were found when the tube was opened, and **3** was recovered quantitatively.

Decarbonylation of compound 3

Compound **3** (144 mg, 0.133 mmol) was heated in hexane (20 cm^3) at 50 °C for 60 d, and the evolved gases were measured at intervals. The solution darkened rapidly and was quite black after 12 h, but gas evolution was slow. The evolved gas was entirely CO (mmol cumulatively): 2 d, 0.058; 9 d, 0.123; 27 d, 0.197; 50 d, 0.205. After about 10 d a black deposit appeared on the glass walls which increased as the reaction proceeded. When the reaction was worked up there was no volatile product and no pentane-soluble fraction, and the total CO corresponded to 1.5 mol per mol of **3**. Cold CH_2Cl_2 removed 11 mg, mainly starting material with a little product. At 45 °C most of the solid (83 mg) dissolved in CH_2Cl_2, leaving an insoluble black deposit on the walls of the tube. Controlled cooling to −20 °C over 7 d yielded black crystals of $[Fe_3\{\mu_3\text{-}GeCo(CO)_4\}_2(CO)_9]$ **9** together with a black powder, **8**. The crystals could not be cleanly separated but the yield of **9** was around 10%.

A run using compound **3** (148 mg, 0.137 mmol) at 60 °C for 30 d proceeded similarly but with less decomposition: CO (0.22 mmol); starting material recovered (44 mg); soluble product (92 mg), accounting in all for 142 mg (96%). A run at one-third scale for 48 d at 60 °C gave a higher yield (72% by weight) of soluble product. In both runs the black soluble material was mainly the powder **8**, with the crystals as only a minor proportion.

The crystalline product **9** gave a Ge:Co:Fe ratio of 2.0:2.2:2.6 on electron-probe analysis; a mass spectrum could not be obtained. The infrared spectrum in CH_2Cl_2 showed CO stretches at 2118w, 2102m, 2042 (sh), 2016vvs (br) and 1970s (sh) cm^{-1} and no bridging group. This is compatible with an overlap of $Co(CO)_4$ absorptions with the very simple spectrum seen[17] for the MeGe analogue, $[Fe_3(\mu_3\text{-}GeMe)_2(CO)_9]$ (2013vvs and 1966s cm^{-1}). A crystal structure determination provided full characterisation (see below).

The second product **8**, did yield a mass spectrum with a very weak ion family, at the limit of our range, with $m/z = 1048$–1051. Below this there was a well resolved, well defined series of ion families with a pattern of isotope intensities appropriate to 2Ge, for the species $Co_4Fe_2Ge_2(CO)_x{}^+$ with (relative intensities) x = 19s, 18s, 17s, 16m, 15s, 14s, 13s, 12vs, 11ms, 10s, 9s, 8s, 7s, 6s, 5s, 4s, 3s, 2s, 1s and 0s. In addition $Co_yFe_2Ge_2{}^+$ ions were strong for y = 3, 2 and 1. The infrared spectrum in dichloromethane showed CO stretches at 2099s and 2064s [attributable to Ge–$Co(CO)_4$ vibrations] and 2050vs, 2032s, 1990 (sh) and 1830vw (br) cm^{-1}, a pattern similar to those reported for other E_2M_4 clusters.

Crystal structure of compound 9. A flask containing a warm CH_2Cl_2 solution of compound **9** was placed in a closed Dewar flask in a freezer at −20 °C and left for 7 d. Black crystals were obtained. Data collection was on a Nicolet P4 diffractometer.

Crystal data. $C_{17}Co_2Fe_3Ge_2O_{17}$, $M = 906.767$, orthorhombic, space group *Cmcm*, $a = 18.19(2)$, $b = 12.949(8)$, $c = 11.09(1)$ Å, $U = 2612(4)$ Å^3, $D_c = 2.31$ g cm^{-3} for $Z = 4$, $F(000) = 1736$, μ(Mo-Kα) = 52 cm^{-1}, $T = 153$ K, crystal size *ca.* 0.1 × 0.1 × 0.1 mm, 1195 unique reflections collected for $4 < 2\theta < 42°$, $T_{max,min}$ = 0.914, 0.784 (empirical absorption correction based on ψ-scans). Of these, 560 with $I > 2\sigma(I)$ were used in the refinement.

The EEES routine of SHELX 76[26] located Ge, Co and Fe atoms. One crystallographic mirror plane contains six half-Fe atoms of a disordered trigonal bipyramid while the second bisects the Fe-containing plane and passes through Ge and Co. The subsequent difference maps located the seven unique CO groups. With all metal atoms anisotropic and light atoms isotropic the refinement (based on *F*) converged to $R = 0.0742$, $R' = 0.0650$ where $w = [\sigma^2(F) + 0.000\,738F^2]^{-1}$. A small amount of residual electron density (1.4 e Å^{-3}) was located close to the metal atoms.

Atomic coordinates, thermal parameters and bond lengths and angles for both structures have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/192.

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