Transition-metal Carbonyl Derivatives of the Germanes. Part 17.† Tetracarbonylgermyl(trimethylgermyl)iron, $[Fe(CO)_4(GeH_3)(GeMe_3)]$, its Conversion into $[\{Fe(CO)_4(GeH_2)\}_2]$, and hence to $[Co_4Fe_2Ge_2(CO)_{21}]$ (characterised by *X*-Ray Crystallography)‡ *via* $[Co_4Fe_2Ge_2(CO)_{22}]$

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The synthesis and spectroscopic characterisation of the mixed germane derivative $[Fe(CO)_4(GeH_3)(GeMe_3)]$ (**3**) are described. This compound eliminates $GeMe_3H$ to give quantitatively $[\{Fe(CO)_4(GeH_2)\}_2]$ (**4**), which has a Fe_2Ge_2 four-membered ring. The GeH_2 units of (**4**) react with $[Co_2(CO)_8]$, eliminating H_2 and CO, to give $[Co_4Fe_2Ge_2(CO)_{22}]$ (**7**). Quantitative loss of CO from (**7**) gives $[Co_4Fe_2Ge_2(CO)_{21}]$ (**8**) which has been shown by an *X*-ray crystal structure determination to contain linked Co_2Ge and Fe_2Ge triangles.

The thermal stability under vacuum at room temperature of $[Fe(CO)_4(GeH_3)_2]$ (**1**)[1,2] and of $[Fe(CO)_4(GeMe_3)_2]$ (**2**)[3,4] is good, although (**2**) is very oxygen-sensitive and also forms $(Me_3Ge)_2O$ on prolonged standing. The silicon analogues of (**1**)[5] and (**2**)[6,7] are also well established despite initial uncertainty[6] about the latter.

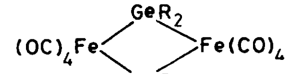
Compounds containing the linkages H–Ge–metal are useful precursors to polymetallic clusters,[8,9] exploiting the ready elimination of H on reaction with metal carbonyls such as $[Co_2(CO)_8]$. Among such precursors, it was interesting to explore compounds of type (**1**) containing two different germyl groups; $[Fe(CO)_4(GeH_3)(GeMe_3)]$ (**3**) was an obvious target in view of the stability of (**1**) and (**2**).

A route to such mixed germane compounds was established in the preparation[2,10] of $[Fe(CO)_4(GeH_3)(Ge_2H_5)]$ where one GeH_3 group was displaced from (**1**) with $[Mn(CO)_5]^-$ and then Ge_2ClH_5 was used to add Ge_2H_5.

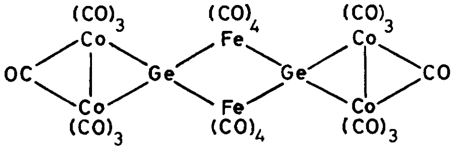
We report here the synthesis of compound (**3**) and its ready self-condensation to the four-membered ring compound $[\{Fe(CO)_4(GeH_2)\}_2]$, (**4**), in a similar reaction to those reported earlier[11] to form $[\{Fe(CO)_4(GeMeH)\}_2]$ (**5**) and $[\{Fe(CO)_4(GeMe_2)\}_2]$ (**6**). The relationships between the species (**1**)—(**6**) are explored, and the reaction of the hydride (**4**) with $[Co_2(CO)_8]$ is shown to generate the polymetallic catenated species (**7**) and (**8**).

$[Fe(CO)_4(GeR_3)(GeR'_3)]$

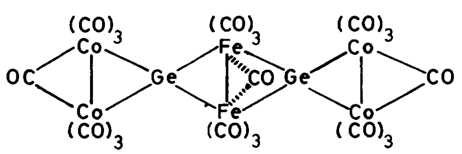
(**1**) R = R′ = H
(**2**) R = R′ = Me
(**3**) R = H; R′ = Me



	R_2
(**4**)	H_2
(**5**)	MeH
(**6**)	Me_2



(**7**)



(**8**)

Experimental

Volatile compounds were handled under vacuum in a conventional line, while non-volatile species were maintained under a nitrogen atmosphere in Schlenk apparatus. The spectroscopic methods were outlined recently.[2] The compound $[Fe(CO)_4(GeH_3)_2]$ (**1**) was prepared by the established method.[1,2] The literature route to $[Fe(CO)_4(GeMe_3)_2]$ (**2**)[3] was improved by using CH_2Cl_2 as solvent for the coupling of $GeClMe_3$ with $[Fe(CO)_4]^{2-}$, and by using contact times of 15—45 min. White crystals of (**2**) (48—70%) were sublimed from the red-brown oily residue after removal of the solvent from the reaction mixture. Spectroscopic values compared well with literature data.[3,4]

Preparation of $[Fe(CO)_4(GeH_3)(GeMe_3)]$ (**3**).—From compound (**1**) (940 mg, 2.94 mmol) and $Na[Mn(CO)_5]$ {from $[Mn_2(CO)_{10}]$ (584 mg, 1.49 mmol)} in Et_2O (2 cm^3) was recovered after 30 min at 20 °C $[Mn(CO)_5(GeH_3)]$ (675 mg, 84%), together with traces of incondensable gases (*ca.* 0.07 mmol), GeH_4 (*ca.* 0.2 mmol), Et_2O and a trace of $[Fe(CO)_4(GeH_3)_2]$ or $[Fe(CO)_4(GeH_3)H]$.

The compound $GeClMe_3$ (449 mg, 2.93 mmol) and Et_2O (0.8 cm^3) were added to the red residue, presumed to be $[Fe(CO)_4(GeH_3)]^-$. After 30 min, there were recovered GeH_4 (*ca.* 0.15 mmol), a fraction containing Et_2O plus $GeMe_3H$ and a little $GeMe_3Cl$, $[Mn(CO)_5(GeH_3)]$ plus (**1**) (*ca.* 3 mg), together with a sample identified as (**3**) {210 mg, 0.58 mmol, 23% based on $[Mn(CO)_5(GeH_3)]$} which had transferred to a cooled preweighed U-trap after pumping for 3 h at diffusion pump vacuum. Cyclohexane extraction of the residues yielded a species later shown to be $[\{Fe(CO)_4(GeH_2)\}_2]$ (**4**) {352 mg, 0.73 mmol, 58% based on $[Mn(CO)_5(GeH_3)]$}. In further runs, recovery of (**4**) was as high as 86% (especially with excess of Et_2O and longer reaction times). The yield of compound (**3**) varied inversely with that of (**4**), dropping to 9%.

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† For Part 16 see ref. 2.

‡ *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii—xx.

Ready self-condensation of compound (**3**) limited the characterisation but satisfactory ^{1}H n.m.r. spectra were obtained at 8—10 °C (singlets at δ 0.55 and 3.47 in ratio 3.06:1 averaged over six samples). Its identification as *tetracarbonylgermyl(trimethylgermyl)iron* was also supported by the mass spectrum, the vibrational spectrum, and by the quantitative self-condensation to (**4**) plus $GeMe_3H$ (see below). Although $GeMe_3H$ built up and had to be removed intermittently, a reasonable mass spectrum was obtained when temperatures were kept as low as possible: $GeMe_3^+$ dominated but was shown to be a by-product from its varying relative intensity. Consistent relative intensities established a very weak parent-ion envelope showing the isotope pattern for two Ge atoms at m/z = 368—353 ($C_7H_{12}FeGe_2O_4$ requires 368—356:$[P - n\text{H}]^+$ overlapping). Families of fragment ions corresponded to $[Fe(CO)_xGe_2Me_3H_y]^+$ for x = 3(m), 2(w), 1(m), and 0(w), $[Fe(CO)_xGe_2Me_2H_y]^+$ for x = 4(vw), 3(vw), 2(ms), 1(m), and 0(vs), $[Fe(CO)_xGeH_y]^+$ for x = 2(m), 1(s), and 0(s) and $[Fe(CO)_x]^+$ for x = 4(s), 3(s), 2(s), and 1(s). Other prominent ions were $[FeGe_2MeH_y]^+$(s), $[FeGe_2H_y]^+$(vs), $[FeGeMe_3]^+$(mw), $[FeGeCH_y]^+$(m), and two doubly charged species appearing very weakly, $[Fe(CO)_2GeH_y]^{2+}$ and $[FeGe_2MeH_y]^{2+}$. Discounting $[GeMe_3]^+$, the bulk of the ion current was carried by ions retaining Fe and two Ge.

The i.r. spectrum was observed on a solid film on a window cooled by liquid nitrogen, and in the gas phase with fairly rapid scans and repeated overlapping sections. Gas-phase wavenumbers were 2 085m, 2 036s, 2 023s, and 2 004vs [all ν(CO), characteristic pattern for *cis* isomer], 829(sh), 817s [$\delta(GeH_3)$], 666w,br, and 624s cm^{-1} (FeCO modes). Additional bands were detected for the solid at 878 [$\rho(CH_3)$] and 534 cm^{-1} [$\rho(GeH_3)$]. After 10 min, an orange solid started to deposit from a gas sample, leaving a new gas-phase product which was probably[1] $[Fe(CO)_4(GeH_3)H]$, with bands at: 2 114(*R*), 2 110(*Q*), 2 106(*P*) (m) [ν(GeH)], 2 048(sh), 2 044vs, 2 039vs [ν(CO)], 825(*R*), 821(*Q*), 818(*P*) [$\delta(GeH_3)$], 727m, 597mw, and 572w cm^{-1}.

Changes in compound (**3**) *on standing*. A sample of the colourless oily liquid (**3**) (77.2 mg, 0.214 mmol) was allowed to stand in a pre-weighed U-tube in the dark for 64 h at ambient temperature. An orange solid was formed and no incondensable gases were seen. Recovered unchanged were (**3**) (27.5 mg, 36%), GeH_4 (0.3 mg), $GeMe_3H$ (14.8 mg, 91%), and (**4**) [34.6 mg, 102% based on (**3**) consumed], all identified spectroscopically.

In a similar experiment carried out for 16 h in the presence of a trace of Et_2O, only 28 mg (0.08 mmol) remained unreacted from (**3**) (155 mg, 0.43 mmol). Also formed were *ca.* 0.1 mmol incondensable gases, $GeMe_3H$ plus Et_2O (39 mg), and (**4**) (88 mg, 100%).

A reaction in benzene was followed by ^{1}H n.m.r. spectroscopy. After 30 min at 7 °C, a yellow tinge appeared which later deepened through orange. The solution was allowed to warm to 17 °C and the signals from $GeMe_3H$ were distinct after 1 h. The reaction was then allowed to proceed at room temperature and the relative intensities (%) of the methyl signals of compound (**3**) and $GeMe_3H$ were: 1 h, 87:12; 6 h, 79:20; 42 h, 54:45; 30 d, 18:82 (GeH_4 now distinguishable, *ca.* 6% relative to $GeMe_3H$: see Figure 1); 43 d, 12:88 (plus very weak singlets at 0.67, 3.57, and 3.77) (<1% in total): 170 d, 0.5:99.5 (GeH_4 *ca.* 5% of $GeMe_3H$). After 1 h the singlet from (**4**) was also observable (δ 3.29) and increased with time but this compound started to precipitate from 6 h onwards. A second pair of singlets about 2 Hz to low field of the signals from (**3**) (δ 0.53 and 3.51) were distinguished at about 15% of the intensity of (**3**) after 42 h. These signals diminished as the reaction proceeded, but more slowly than those from (**3**), rising to a relative intensity of 50% at 43 d.

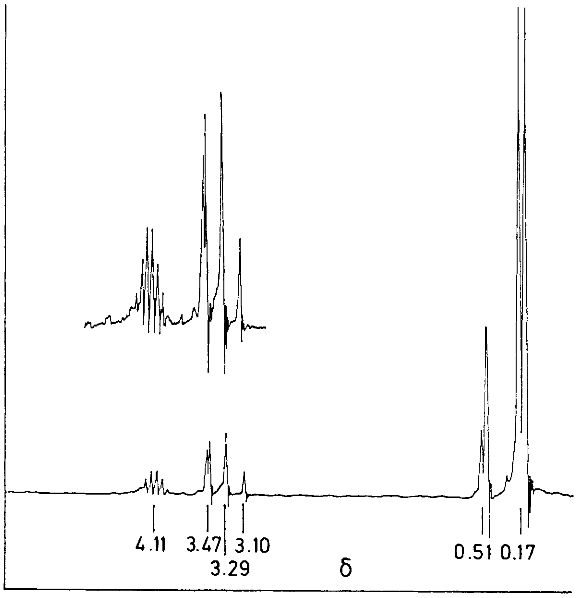


Figure 1. Proton n.m.r. signals at 60 MHz from $[Fe(CO)_4(GeH_3)(GeMe_3)]$ (**3**), after 30 d at room temperature in benzene. Only 18% of (**3**) (δ 0.51 and 3.47) remains, the main signal is the doublet (δ 0.17) and decet (δ 4.11, ^3J = 3.2 Hz) of $GeMe_3H$. Much of the $[\{Fe(CO)_4(GeH_2)\}_2]$ (**4**) has precipitated so the signal at δ 3.29 is not quantitative. At this late stage GeH_4 (δ 3.10) is observable, as are the additional signals close to those of (**3**) (*ca.* δ 0.55 and 3.52)

The orange-red self-condensation product (**4**) was characterised as $[\{Fe(CO)_4(GeH_2)\}_2]$ by spectroscopic means. It showed a very weak parent ion with the isotope pattern of two Ge atoms, m/z = 490—480 ($C_8H_4Fe_2Ge_2O_8$ requires 492—480) together with the $[P - n\text{CO}]^+$ series of fragments: n = 1(s), 2(m), 3(m), 4(ms), 5(s), 6(ms), 7(m), and 8(vs, base peak). Loss of one Ge gave rise to only very weak ions corresponding to $[Fe_2(CO)_nGeH_x]^+$ for n = 6, 4, and 3: germanium-free ions were limited to m/z = 168(m) $\{[Fe_2(CO)_2]^+$ or $[Fe(CO)_4]^+\}$ and 112(w) $\{Fe_2^+$ or $[Fe(CO)_2]^+\}$.

The ^{1}H n.m.r. spectrum showed a singlet at δ 3.29 in benzene and at 3.35 in CS_2.

The i.r. spectrum showed a characteristic carbonyl stretching region with only two very strong bands in CH_2Cl_2 solution at 2 066 and 2 015 cm^{-1}: the latter was resolved in C_6H_{12} to bands at 2 026vs, 2 017vvs, 1 981w(sh), and 1 964w cm^{-1}. At lower frequencies, a weak feature could be attributed to GeH_2 deformation at 830(sh) and 800 cm^{-1}, and bands from FeCO vibrations occurred at 683m, 618s, and 609vs cm^{-1}.

At room temperature, under vacuum, and in subdued light, compound (**4**) slowly turned brown and evolved incondensable gases over a period of several days.

Reaction of Compound (**4**) *with* $[Co_2(CO)_8]$.—The reaction of compound (**4**) with $[Co_2(CO)_8]$ in a 1:2 ratio has been described.[12] In the ratio 1:2.5, (**4**) (110 mg, 0.22 mmol) and $[Co_2(CO)_8]$ (190 mg, 0.54 mmol) in hexane (10 cm^3) gave 0.99 mmol of incondensable gases ($CO:H_2$ = 1.68:1, 84% H_2) after 36 h. Only 0.01 mmol $[Co_2(CO)_8]$ was recovered, along with $[Co_4(CO)_{12}]$ (0.03 mmol) and $[Co(CO)_4H]$ (0.01 mmol). Work-up gave compounds (**7**) (52.8 mg, 21%) and (**8**) (88 mg, 36%). Reaction in the ratio 1:1.75 similarly yielded gases ($CO:H_2$ = 1.09:1, 92% H_2), small amounts of $[Co(CO)_4H]$, $[Co_2(CO)_8]$, and $[Co_4(CO)_{12}]$, (**7**) (18%), and (**8**) (37%). In all reactions evolution of hydrogen was smooth, 70% complete at 40 min and complete in 2 h. Evolution of CO was rapid for 20 min, then slowed, but continued at a slow rate for several hours. In a similar reaction in a sealed tube for 4 d in the dark {ratio of (**4**) to $[Co_2(CO)_8]$ 1:2.35} the yields of (**7**) and (**8**) were 37 and 36% respectively.

Characterisation of compounds (**7**) *and* (**8**). Compound (**7**) was a light brown powder, insoluble in CH_2Cl_2, whose i.r. spectrum has been reported.[12] Electron-probe analysis showed a metal ratio Ge:Co:Fe = 1:1.96:0.93 (average over four samples). The compound gave a clean mass spectrum up to the instrument limit (m/z = 1 100) for $[Co_4Fe_2Ge_2(CO)_x]^+$ for $x = 21$; m/z centred at 1 078(w), 20(mw), 19(w), 18(mw), 17?(w), 16?(w), 14(m), 13(mw), 12(ms), 11(m), 10(mw), 9(mw), 8(s), 7(mw), 6(mw), 5(m), 4(m), 3(mw), 2(m), 1(w), and 0(mw). It was insoluble in all common organic solvents, stable under nitrogen, and unchanged by brief exposure to air. When a suspension in CH_2Cl_2 was stirred for 12 h, the solvent became orange, the solid volume decreased, gas was evolved, and compound (**8**) was identified. This reaction was rapid at 30 °C. Gas evolution was monitored from (**7**) (140 mg, 0.126 mmol) suspended in CH_2Cl_2 (10 cm^3) at room temperature. Only CO was evolved, smoothly up to 17 h (0.106 mmol) and then slowly to 30 h (0.119 mmol, 94% assuming a 1:1 stoicheiometry) at which point no solid remained in the deep orange solution.

The i.r. spectrum of the dark orange compound (**8**) has been reported.[12] Electron-probe analysis of two crystalline and two powdered samples showed an average heavy atom ratio Ge:Co:Fe of 1:2.05:0.92. The mass spectrum run under the same conditions as for (**7**) was difficult to obtain. An extremely weak envelope at m/z 1 047—1 051 indicates $[Co_4Fe_2Ge_2(CO)_{20}]^+$ and weak or very weak envelopes corresponding to $[Co_4Fe_2Ge_2(CO)_n]^+$ were seen for all the fragments n = 20—4, and medium-intensity ions with n = 3—0. Broadening suggests overlap from n = 9 with $[Co_3Fe_2Ge_2(CO)_m]^+$ for m = 11—2, and clear envelopes for m = 1 and 0 were resolved, together with $[CoFe_2Ge_2]^+$.

Compound (**8**) is stable indefinitely under N_2 at −4 °C and has moderate stability in air. It is readily soluble in CH_2Cl_2 and slightly soluble in hexane forming bright orange-red solutions which are air-sensitive.

Experimental details of the crystallographic characterisation of (**8**) have been reported previously;[12] the structure is illustrated in Figure 2, and bond parameters are given in the Table. Additional material available from the Cambridge Crystallographic Data Centre comprises atomic co-ordinates and remaining bond lengths and angles.

Results

Because of the ready self-condensation of compound (**3**) to (**4**), and of the air sensitivity of these two compounds, their characterisation depends on the spectroscopic evidence. The 1:3 ratio of proton n.m.r. intensities is compatible with (**3**) and the values show slight shifts from those[1,3] for (**1**) and (**3**), though not enough to preclude a 1:1 mixture of these. The i.r. spectrum, however, indicates only one species. In the gas phase, there is a shift of about 40 cm^{-1} to lower frequencies for the ν(CO) modes from those of compound (**1**) to (**2**). The values for (**3**) lie nicely in the middle. The symmetric deformation of the GeH_3 group of (**3**) at 817 cm^{-1} lies a little below the average wavenumber of the two symmetric modes of (**1**),[1] at 835 and 809 cm^{-1}. Similar consistencies are found for the other modes of compounds (**1**)—(**3**). Unfortunately (**3**) was too unstable to yield a Raman spectrum.

These observations are further supported by the mass spectrum of compound (**3**), where the major features parallel those observed for (**1**) and (**2**). Despite the ready elimination of $GeMe_3H$, the ions characteristic of (**3**) may be picked out by their constant relative intensities in different scans. The characteristic series of fragments are $[P - nCO]^+$ and $[P - Me - nCO]^+$ with H loss not analysable in detail. By comparison with (**1**), the $[Fe(CO)_x]^+$ series is more prominent. If $[GeMe_3]^+$ is excluded, the bulk of the ion current was carried by ions retaining the three heavy atoms. Loss of Me was a significant process, as for compound (**2**) and similar species,[11] but there was no sign of ions containing six, five, or four Me groups and ions with no Me were minor. Thus the spectrum is not compatible with a mixture of (**1**) and (**2**). Although $GeMe_3H$ elimination undoubtedly occurs in the mass spectrometer, compound (**4**) is so much less volatile than (**3**) that ions from (**4**) were not observed in the presence of (**3**).

This characterisation of (**3**) is further supported by its quantitative conversion, within experimental error, into $GeMe_3H$ plus (**4**). Side reactions are minor and occur only to the extent of about 5—7% in the last stages of the reaction.

In characterising compound (**4**), the singlet in the ^1H n.m.r. spectrum shows a similar shift from (**3**) as was observed[11] for $[\{Fe(CO)_4(GeMeH)\}_2]$ (**5**) compared with $[Fe(CO)_4(GeMeH_2)_2]$.

In cyclohexane, the i.r. spectrum of (**4**) fits nicely into the series already noted[11] for (**5**) and $[\{Fe(CO)_4(GeMe_2)\}_2]$ (**6**). The axial carbonyl stretch of (**6**) occurs at 2 052 cm^{-1} and the other three carbonyl modes fall under one very strong contour at 2 001 cm^{-1}. For (**5**) these wavenumbers increase and the lower one splits so that the main vibrations are found at 2 060, 2 012, and 2 008 cm^{-1}. For (**4**) the higher wavenumber increases by a further 6 cm^{-1} and the lower ones separate further to 2 026 and 2 017 cm^{-1}. The shift to higher wavenumbers as H replaces Me is as expected and parallels, for example, the changes from compound (**1**) to (**3**) to (**2**). The GeH_2 deformations of (**4**) were observed only as weak modes, certainly less prominent than the GeH_3 modes of (**1**) and (**3**).

For the mass spectra as well, there is a clear parallel between the three ring compounds (**4**)—(**6**). In each case, P^+ is very weak and $[P - CO]^+$ is prominent, paralleling the bulk reaction where $[\{Fe(CO)_4(GeR_2)\}_2]$ loses CO and forms $[Fe_2(CO)_7(GeR_2)_2]$; this is a facile reaction for all Group 4–iron group compounds $[\{M(CO)_4(M'R_2)\}_2]$. The $[Fe_2Ge_2(CO)_n]^+$ families carry the major part of the ion current for (**4**), and few other fragment ions were found. Hydrogen loss was less prominent than for (**1**). In all its spectroscopic properties compound (**4**) closely resembles (**5**), (**6**), and other $[\{Fe(CO)_4(GeR_2)\}_2]$ species.[13,14]

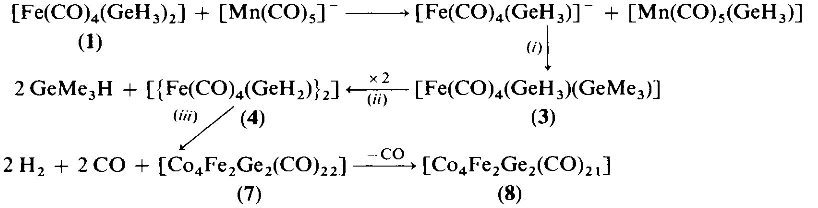
Although $[Fe(CO)_4]^{2-}$ reacts with GeR_2X_2 to form $[\{Fe(CO)_4(GeR_2)\}_2]$,[14] the parallel reaction with $GeBr_2H_2$ to yield (**4**) does not seem to occur.[15] Higher-molecular-weight compounds, some containing Br, were indicated. These observations probably reflect the instability of $GeBr_2H_2$, with its ready formation of HBr.

The major reaction of compound (**4**) with $[Co_2(CO)_8]$ is probably the formation of (**7**) as the insoluble product, with this converting into (**8**) as shown by the two stages of CO evolution. Varying proportions of (**7**) and (**8**) were observed under different conditions and CO loss from (**7**) was demonstrated separately. The best combined yield of (**7**) plus (**8**) was 76% using a $[Co_2(CO)_8]$:(**4**) ratio of 2:1. In the sealed-tube experiment with reaction CO present, the yield of (**7**) increased from 21 in 37% in runs with a reaction ratio of 2.5:1. A significant side reaction yielded $[Co_4(CO)_{12}]$.

The cluster (**8**) has been fully characterised by an *X*-ray structure determination[12] which confirms its formulation as $[Co_4Fe_2Ge_2(CO)_{21}]$, hence the CO loss strongly indicates the formula of (**7**) to be $[Co_4Fe_2Ge_2(CO)_{22}]$. In the mass spectra of (**7**) and (**8**) the highest mass ion is $[P - CO]^+$ in each case. Although these high masses were near our limit of observation, it is clear that (**7**) and (**8**) gave mass spectra under the same conditions that were different in both absolute and relative intensities. Taken with the other spectroscopic data, compound (**7**) thus differs from (**8**) and is most reasonably $[Co_4Fe_2Ge_2(CO)_{22}]$.

Discussion

The principal reactions occurring are shown in the Scheme. The anion, $[Fe(CO)_4(GeH_3)]^-$, was not directly characterised. The reaction (**3**) ⟶ (**4**) occurred during the preparation and isolation of compound (**3**), but was also demonstrated starting with pure (**3**), when it occurred quantitatively at least up to two-thirds conversion. When account is taken of the yield of (**4**), the reaction (**1**) ⟶ (**3**) was also quantitative within experimental errors. While the alternative synthesis of (**3**) from (**2**) should be feasible, the handling problems and lower volatility of (**2**) make it a poorer choice of starting material.



Scheme. (*i*) $GeMe_3Cl$; (*ii*) room temperature; (*iii*) $[Co_2(CO)_8]$

Reaction (**7**) ⟶ (**8**) also occurred during the preparation and was demonstrated quantitatively in a separate experiment. Allowing for the minor formation of $[Co(CO)_4H]$, the hydrogen in (**4**) was accounted for completely within the limits of accuracy. The total mass recovery ranged from 65 to 120% of the input, reasonable for work under these conditions when one product is insoluble. The reaction (**4**) ⟶ (**7**) + (**8**) appeared to be without major side reactions apart from the formation of $[Co_4(CO)_{12}]$, implying in turn that (**4**) ⟶ (**7**) was the major primary reaction.

The properties of (**3**) and (**4**) compare well with those of related species like (**1**) and (**2**), or (**5**) and (**6**), and are placed in the context of an extended series in the following paper.[16]

A number of side-reactions were observed but all were very minor. While partial self-condensation of compound (**3**) with elimination of GeH_4 could occur to produce $[(Me_3Ge)(OC)_4FeGeH_2Fe(CO)_4(GeMe_3)]$, this seems a less probable source of the observed GeH_4 since the latter occurred only on long standing and there seems no reason why this alternative condensation of (**3**) should not take place from the beginning. We note also that (**1**) does not eliminate GeH_4 at room temperature. It is more likely that the GeH_4, and the very minor extra ^1H n.m.r. signals, all reflect a slow further condensation of (**4**) perhaps to multiple-ring compounds as seen in the iron–tin systems.[14]

The formation of incondensable gases may also indicate formation of more condensed compounds. We would also expect some formation of $[Fe_2(CO)_7(GeH_2)_2]$ with elimination of CO.

A different process in the gas phase was indicated by the observation of $[Fe(CO)_4(GeH_3)H]$. No iron hydride compounds were detected in the liquid phase or in solution, but the hydride could react readily with (**3**) to yield (**4**).

An interesting near-parallel to the condensation of (**3**), and to the formation of the hydride, is given by work[17] on $[Fe(CO)_4(SiMe_3)_2]$. Here, abstraction of one $SiMe_3$ group by reaction with Me_2O yielded the iron alkyl $[Fe(CO)_4Me(SiMe_3)]$ and this was shown to eliminate $SiMe_4$.

Since GeH_4 was not eliminated between two GeH_3 groups in compound (**1**),[1] nor was $GeMe_4$ from two $GeMe_3$ groups in (**2**),[3] the self-condensation of (**3**) must occur only when GeH_3 on one molecule is close to a $GeMe_3$ on a second, assuming a bimolecular mechanism. Such an approach would be favoured sterically. Elimination of one $GeMe_3H$ molecule would give an intermediate (**A**) $[(Me_3Ge)(OC)_4FeGeH_2Fe(CO)_4(GeH_3)]$, which would readily extrude a second $GeMe_3H$ molecule from an all-*cis* arrangement of the skeleton. It is possible, in the solution condensation of (**3**), that the additional ^1H n.m.r. signals, very close to those of (**3**), are those of (**A**). The GeH_3 and $GeMe_3$ environments are very similar in (**A**) and (**3**) and the GeH_2 resonance could coincide with that of (**4**).

Leaving these minor species aside, the major system is that shown in the Scheme. The identification of compounds (**3**) and (**4**) depends on the spectroscopic properties and comparisons which ultimately extend back to $[Fe(CO)_4(M'R_3)_2]$ and $[\{Fe(CO)_4(M'R_2)\}_2]$ species whose structures have been confirmed crystallographically for a number of combinations of M′ and R.[13,14]

The reaction of compound (**4**) to form (**7**) may readily be seen as the conversion of $Co_2(\mu\text{-}CO)$ into Co_2Ge by reaction with the GeH_2 units of (**4**), in accord with similar reactions, such as those of $[Co_2(CO)_8]$[18] or $[\{Co_2(CO)_7\}_2Ge]$[19] with $GeMe_2H_2$. If (**7**) contains two $GeCo_2$ triangles linked to a Ge_2Fe_2 square, then the closure of the square to the linked $GeFe_2$ triangles of (**8**), with elimination of CO, parallels many known conversions of compounds of the type $[\{Fe(CO)_4X\}_2]$ into $[Fe_2(\mu\text{-}CO)(CO)_6(\mu\text{-}X)_2]$.[14] One feature of note is the sharp i.r. band in the bridging carbonyl region of (**7**), compared with the weak, broad feature in the same region for (**8**), reflecting the different bridging CO environments.

The Crystal Structure of Compound (**8**).—The crystallographic details have been reported, without discussion, previously.[12] The structure is illustrated in Figure 2 which shows it to have a metal framework made up of four linked GeM_2 triangles with two spiro Ge atoms. Each of the Co–Co and Fe–Fe bonds are bridged by CO ligands, and each transition metal carries three terminal CO groups. Ignoring irregularities, the overall symmetry is approximately C_2, with the two-fold axis coincident with the μ-CO across the Fe–Fe bond. The central portion of the molecule is clearly related to $[Fe_2(CO)_9]$, with two of the bridging CO groups replaced by bridging $Ge[Co_2(CO)_7]$ units. The related structures $[Fe_2(CO)_7(\mu\text{-}GePh_2)_2]$[20] and $[Fe_2(CO)_6(\mu\text{-}GeMe_2)_3]$[21] have been described and provide a useful comparison.

In the Ge_2Fe_2 unit of (**8**) the edge-linked triangles are unsymmetrical so that Ge(1) lies closer to Fe(1) while Ge(2) lies closer to Fe(2); the individual Ge–Fe distances range from 2.365(4) to 2.437(4) Å. The dihedral angle between the two $GeFe_2$ triangles is surprisingly only 111°, with a non-bonded Ge ••• Ge distance of 3.302 Å, whereas in $[Fe_2(CO)_7(\mu\text{-}GePh_2)_2]$ the equivalent angle is 128° with Ge ••• Ge of 3.645 Å, and in $[Fe_2(CO)_6(\mu\text{-}GeMe_2)_3]$ the corresponding values are 120° and 3.403 Å. This suggests that the tendency to maximise Ge ••• Ge distances is less important than the need to prevent

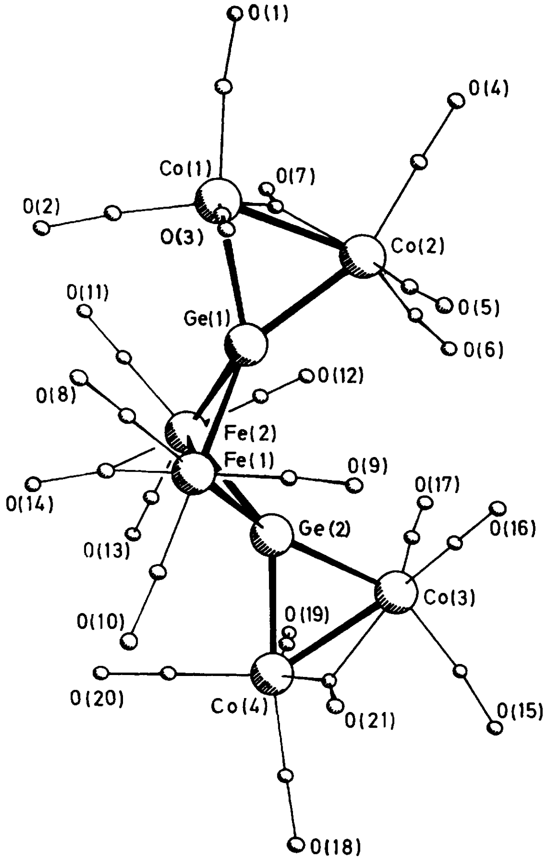


Figure 2. A PLUTO diagram of the structure of $[Co_4Fe_2Ge_2(CO)_{21}]$ (**8**)

Table. Selected bond lengths (Å) and angles (°) for $[Co_4Fe_2Ge_2(CO)_{21}]$

Ge(1)–Co(1)	2.383(5)	Ge(1)–Co(2)	2.351(4)
Ge(2)–Co(3)	2.309(5)	Ge(2)–Co(4)	2.399(4)
Ge(1)–Fe(1)	2.365(4)	Ge(1)–Fe(2)	2.437(4)
Ge(2)–Fe(1)	2.421(4)	Ge(2)–Fe(2)	2.399(4)
Co(1)–Co(2)	2.528(5)	Co(3)–Co(4)	2.491(5)
Fe(1)–Fe(2)	2.678(5)	Co(1)–C(7)	1.90(3)
Co(2)–C(7)	1.92(3)	Co(3)–C(21)	2.29(3)
Co(4)–C(21)	1.86(3)	Fe(1)–C(14)	1.97(3)
Fe(2)–C(14)	1.94(3)	Ge(1) ··· Ge(2)	3.30(2)
Co(1)–Ge(1)–Co(2)	64.5(1)	Co(3)–Ge(2)–Co(4)	63.8(1)
Ge(1)–Co(1)–Co(2)	57.1(1)	Ge(2)–Co(3)–Co(4)	59.8(1)
Ge(1)–Co(2)–Co(1)	58.4(1)	Ge(2)–Co(4)–Co(3)	56.3(1)
Fe(1)–Ge(1)–Fe(2)	67.8(1)	Fe(1)–Ge(2)–Fe(2)	67.5(1)
Ge(1)–Fe(1)–Fe(2)	57.4(1)	Ge(2)–Fe(1)–Fe(2)	55.9(1)
Ge(1)–Fe(2)–Fe(1)	54.8(1)	Ge(2)–Fe(2)–Fe(1)	56.6(1)

Dihedral angles

Ge(1)Co(1)Co(2)/Ge(1)Fe(1)Fe(2)	84.4
Ge(2)Fe(1)Fe(2)/Ge(2)Co(3)Co(4)	88.4
Ge(1)Fe(1)Fe(2)/Ge(2)Fe(1)Fe(2)	111.4
Ge(1)Fe(1)Fe(2)/Fe(1)Fe(2)C(14)	128.3
Ge(2)Fe(1)Fe(2)/Fe(1)Fe(2)C(14)	120.3
Ge(1)Co(1)Co(2)/Co(1)Co(2)C(7)	97.1
Ge(2)Co(3)Co(4)/Co(3)Co(4)C(21)	93.6

excessive interactions between CO ligands on neighbouring parts of the molecule.

The $Ge[Co_2(CO)_7]$ moieties can be related to a number of molecules which incorporate this grouping.[22] In compound (**8**) the two ends are formally chemically identical but packing effects have imposed quite distinct geometries. The Ge(1)Co(1)-Co(2) triangle is only slightly unsymmetrical with nearly equal Ge–Co bonds, and the CO group bridging the Co(1)–Co(2) edge is similarly regular. However the Ge(2)Co(3)Co(4) triangle is strongly distorted, with the Ge(2)–Co(4) bond 0.090(5) Å longer than Ge(2)–Co(3). The corresponding bridging CO across the Co(3)–Co(4) bond is displaced in the opposite sense, lying 0.4 Å closer to Co(4) than to Co(3). The long Co(3)–C(21) distance of 2.29(3) Å is more in the range expected for semi-bridging CO ligands and it is interesting that the nominally terminal C(19)–O(19) ligand on Co(4) is bent towards Co(3) to give a Co(3) ··· C(19) distance of 2.82 Å, significantly shorter than any other Co ··· C distance in the molecule. This may help to redress the electronic imbalance induced by the other asymmetry. If CO(19) were to become fully bridging and CO(21) terminal on Co(4) this would correspond to the other isomer of (**8**) (formally C_s, with both µ-CO pointing to the same side of the molecule*). The difference between the two ends is also evident in the Co–Co bond lengths [2.491(5) and 2.528(5) Å] and the $GeCo_2/C_bCo_2$ dihedral angles (94 and 97°). The dihedral angles between the triangles sharing a common apex at the spiro-Ge atoms also differ (84 and 88°).

The CO ligands are obviously crowded in (**8**), with a number of short O ··· O distances between ligands on different metal atoms, for example O(6) ··· O(12) 2.9 Å, O(2) ··· O(11) and O(5) ··· O(9) 3.0 Å. The overall structural details are consistent with a flexible chain of metal triangles embedded in a fairly crowded matrix of carbonyl ligands. The observed distortions from regular geometry will be imposed by the need to minimise non-bonded interactions between CO groups on neighbouring metals.

The crystal structures of $[\{Co_2(CO)_7\}_2Ge]$ and $[Co_8Ge_3(CO)_{26}]$ also showed linked MCo_2 triangles. The intermediate member of the series, $[Co_6Ge_2(CO)_{20}]$, has not yielded single crystals but has the same electron count as (**8**) and similar spectroscopic properties, reinforcing the suggestion[23] that it too has the analogous linked triangle skeleton.

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* The possibility that the irregularity arises because of a disordered packing of both isomers in the crystal can be discounted since the thermal parameters for all atoms were normal.

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