Transition-metal Carbonyl Derivatives of the Germanes. Part 13.† Preparation, Spectroscopic Properties, and the Crystal and Molecular Structure of Bis[μ-carbonyl-bis(tricarbonylcobaltio)(*Co–Co*)]germanium (4*Co–Ge*), [Ge{$Co_2(CO)_7$}$_2$]; a New Type of Group 4–Tetracobalt Species

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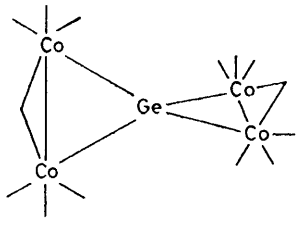
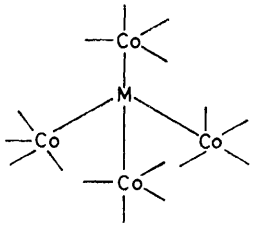
Reaction between GeI_4 and $[Co(CO)_4]^-$ or between GeH_4 and $[Co_2(CO)_8]$ gives [Ge{$Co_2(CO)_7$}$_2$] (1). The crystal and molecular structure of (1) has been obtained by *X*-ray methods. Crystals are triclinic, with a = 10.396(2), b = 16.495(3), c = 12.879(2) Å, α = 90.33(2), β = 97.68(2), γ = 95.03(2)°, space group $P\bar{1}$, and Z = 4. The structure was solved by direct methods and refined by least-squares techniques to R = 0.056 for 2 852 reflections [$I \geqslant 5\sigma(I)$]. The molecule exhibits approximate C_2 symmetry with the Ge atom bridging the Co–Co bonds of two $Co_2(CO)_7$ units. The Ge bridge is unsymmetric with unequal Ge–Co bond lengths (average 2.38, 2.34 Å); the correspondong μ-CO in each unit is asymmetrically disposed in the opposite sense. Infrared and mass spectral data for [Ge{$Co_2(CO)_7$}$_2$] are also discussed.

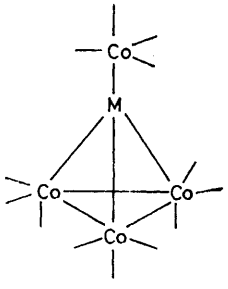
UNTIL recently compounds containing a heavier Group 4 atom bonded to four cobalt atoms fell into two classes. The larger Sn and Pb atoms formed only fully open molecules [M{$Co(CO)_4$}$_4$] (2) containing terminal $Co(CO)_4$ groups, and attempts to form Co–Co bonded species by CO elimination were unsuccessful.[1-3]



(1)



(2)
(M=Sn, Pb, or Ge)



(3)
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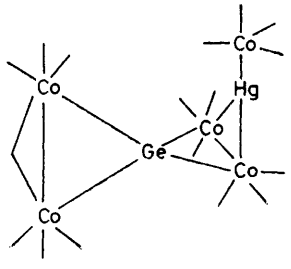


(4)

On the other hand, the analogous compounds of Si and Ge were thought [4-6] to be unstable towards CO elimination and Co–Co bond formation giving [$(OC)_4CoMCo_3(CO)_9$] (3) with cluster structures related to the well known $RCCo_3(CO)_9$ species.[7] These differences have been discussed in terms of the size of the Group 4 atom.[3] We have previously reported [8] that Ge forms a third type of tetracobalt derivative of formula [Ge{$Co_2(CO)_7$}$_2$] (1) that is intermediate between the fully open and cluster examples. We now report preparative and spectroscopic details, together with the results of an *X*-ray structure determination of [Ge{$Co_2(CO)_7$}$_2$].

† Part 12, F. S. Wong and K. M. Mackay, *J. Chem. Res.*, 1980, (S) 109, (M) 1761.

EXPERIMENTAL

All reactions were carried out either in nitrogen-flushed or evacuated apparatus using standard inert-atmosphere techniques. The compounds GeI_4 (Laramie Chemical Co.) and $[Co_2(CO)_8]$ (Pressure Chemicals) were used as received. Infrared spectra were recorded using a Perkin-Elmer model 180 spectrometer and mass spectra using a Varian MAT CH5 instrument.

Preparation of [Ge{$Co_2(CO)_7$}$_2$] (1).—(*a*) *From* GeI_4 *and* $[Co(CO)_4]^-$. A solution of $[Co_2(CO)_8]$ (3.4 g, 10 mmol) in tetrahydrofuran (40 cm^3) was reduced with 1% sodium amalgam. After decantation from excess of amalgam the solution of $Na[Co(CO)_4]$ was evaporated under vacuum. The residue was suspended in benzene–hexane (1 : 2, 60 cm^3) and GeI_4 (1.9 g, 3.6 mmol) was added. After stirring for 3 h at 25 °C the solution was filtered and solvents were pumped off. Recrystallisation of the residue from CH_2Cl_2 afforded dark red crystals of [Ge{$Co_2(CO)_7$}$_2$] (1) (1.3 g, 52% based on GeI_4). The solid from the reaction mixture was extracted with CH_2Cl_2 to give a mixture of anionic species containing both Ge and Co. These will be discussed in detail elsewhere.[9]

(*b*) *From* [$GeCl\{Co(CO)_4\}_3$] *and* $[Co(CO)_4]^-$. A diethyl ether solution containing an excess of $Na[Co(CO)_4]$ and [$GeCl\{Co(CO)_4\}_3$] (0.16 g, 0.25 mmol) was stirred for 20 min at 25 °C. After solvent was removed, only a small proportion of the residue was soluble in hexane. This fraction contained [Ge{$Co_2(CO)_7$}$_2$] as the major component together with $[Co_2(CO)_8]$ and a species which is probably [$Ge\{Co(CO)_4\}_4$] from its i.r. spectrum 2 079s, 2 032m (sh), 2 020vs, 2 000w cm^{-1}. A similar reaction between [$GeCl_3\{Co(CO)_4\}$] and $[Co(CO)_4]^-$ also gives [Ge{$Co_2(CO)_7$}$_2$] but again in low yields.[10]

(*c*) *From* GeH_4 *and* $[Co_2(CO)_8]$. A mixture of $[Co_2(CO)_8]$ (0.43 g, 1.26 mmol), GeH_4 (*ca.* 0.65 mmol), and hexane (5 cm^3) was sealed in a tube which was left in the dark for 15 weeks at ambient temperature. On opening, unchanged

GeH_4 (*ca.* 0.08 mmol) was recovered. The solid product was mainly $[Ge\{Co_2(CO)_7\}_2]$ together with small amounts of $[(OC)_4CoGeCo_3(CO)_9]$ (ref. 4) and unreacted $[Co_2(CO)_8]$, identified by i.r.

X-Ray Structure of $[Ge\{Co_2(CO)_7\}_2]$.—*Data collection.* Deep red crystals were obtained on recrystallization from CH_2Cl_2 at −30 °C. Preliminary precession and Weissenberg photographs indicated triclinic symmetry. A single crystal of dimensions 0.12 × 0.70 × 0.40 mm was sealed in a glass capillary for data collection on a Hilger and Watts automatic four-circle diffractometer using zirconium-filtered Mo-K_α radiation.

Solution and refinement. Initial solution using direct methods gave the positions of the 10 metal atoms in the asymmetric unit. Subsequent Fourier syntheses revealed all other atoms. Blocked full-matrix refinement using 2 852 reflections for which $I \geqslant 5\sigma(I)$ and a model with the O atoms anisotropic and all other atoms isotropic converged at $R = 0.056$, $R' = 0.058$. A structure-factor calculation using 3 690 reflections with $I \geqslant 3\sigma(I)$ gave $R = 0.067$, $R' = 0.073$. There were no serious discrepancies between $|F_o|$ and $|F_c|$ for reflections not used in the refinement.

The final positional parameters are listed in Table 1. The co-ordinates of corresponding atoms of the two molecules in the asymmetric unit show an approximate relationship $X_1 = X_2 - 0.5$, $Y_1 = 0.5 - Y_2$, $Z_1 = 1 - Z_2$; however, we are unable to relate these to a unit cell of higher symmetry than $P\bar{1}$. Selected bond lengths and angles are given in Table 2. A full listing of thermal parameters and tables of observed and calculated structure factors have been deposited as Supplementary Publication No. SUP 22902 (42 pp.).‡

TABLE 1

Final positional parameters (× 10^4)

	Molecule 1			Molecule 2		
Atom	*X*	*Y*	*Z*	*X*	*Y*	*Z*
Ge	625(1)	3 646(1)	7 600(1)	5 175(1)	1 353(1)	2 537(1)
Co(1)	−1 241(2)	3 033(1)	8 264(1)	3 253(2)	1 965(1)	1 869(1)
Co(2)	−1 347(2)	4 079(1)	6 790(1)	3 350(2)	934(1)	3 348(1)
Co(3)	2 728(2)	4 089(1)	8 416(1)	6 877(2)	922(1)	1 714(1)
Co(4)	2 332(2)	3 053(1)	6 890(1)	7 290(2)	1 953(1)	3 232(1)
C(B1) *	−1 787(14)	2 902(10)	6 794(10)	3 173(15)	2 132(10)	3 321(11)
O(B1)	−2 183(11)	2 387(8)	6 186(8)	3 112(10)	2 628(8)	3 935(8)
C(B2)	2 834(14)	2 899(10)	8 343(10)	7 355(15)	2 124(11)	1 804(11)
O(B2)	3 085(11)	2 397(8)	8 930(8)	7 584(11)	2 620(8)	1 185(8)
C(11)	−982(18)	3 741(13)	9 379(14)	2 875(17)	1 209(12)	853(12)
C(12)	−430(18)	2 135(13)	8 586(13)	4 245(17)	2 813(12)	1 522(12)
C(13)	−2 891(18)	2 709(13)	8 506(13)	1 637(18)	2 331(12)	1 560(12)
C(21)	−816(19)	5 088(14)	7 339(14)	3 268(17)	−71(13)	2 723(13)
C(22)	−924(17)	4 088(12)	5 472(13)	4 283(17)	917(12)	4 599(12)
C(23)	−3 067(19)	4 281(13)	6 562(13)	1 677(18)	792(12)	3 650(12)
O(11)	−890(15)	4 172(11)	10 059(10)	2 637(13)	716(9)	194(10)
O(12)	80(16)	1 592(12)	8 835(13)	4 859(12)	3 383(9)	1 258(10)
O(13)	−3 885(12)	2 500(10)	8 700(11)	645(12)	2 564(9)	1 317(10)
O(21)	−526(17)	5 716(10)	7 623(10)	3 176(13)	−687(9)	2 337(10)
O(22)	−712(15)	4 123(9)	4 637(7)	4 858(13)	896(8)	5 424(9)
O(23)	−4 123(17)	4 387(12)	6 399(14)	642(14)	680(10)	3 848(11)
C(31)	2 531(17)	5 044(13)	7 802(12)	6 639(17)	−43(13)	2 262(12)
C(32)	2 294(17)	4 135(12)	9 687(13)	5 990(17)	919(12)	447(13)
C(33)	4 494(18)	4 262(12)	8 717(12)	8 506(17)	792(12)	1 428(12)
C(41)	2 273(17)	3 789(12)	5 843(13)	7 467(16)	1 174(12)	4 218(12)
C(42)	1 260(18)	2 162(13)	6 524(13)	6 503(17)	2 774(12)	3 717(12)
C(43)	3 828(18)	2 709(12)	6 640(13)	8 948(18)	2 344(12)	3 495(12)
O(31)	2 396(17)	5 699(8)	7 480(12)	6 508(14)	−714(9)	2 595(10)
O(32)	2 105(12)	4 155(10)	10 559(8)	5 426(13)	885(9)	−377(9)
O(33)	5 573(15)	4 404(11)	8 917(13)	9 527(13)	664(9)	1 226(11)
O(41)	2 278(15)	4 238(10)	5 207(10)	7 596(14)	662(9)	4 813(10)
O(42)	604(16)	1 605(12)	6 209(13)	6 079(12)	3 294(8)	4 084(9)
O(43)	4 777(17)	2 533(12)	6 417(13)	10 046(12)	2 563(10)	3 720(10)

* B indicates bridging atom.

*Crystal data.** $C_{14}Co_4GeO_{14}$, $M = 700.47$, Triclinic, space group $P\bar{1}$, $a = 10.396(2)$, $b = 16.495(3)$, $c = 12.879(2)$ Å, $\alpha = 90.33(2)$, $\beta = 97.68(2)$, $\gamma = 95.03(2)°$, $D_m = 2.11$ g cm^{-3} (by flotation), $Z = 4$, $D_c = 2.13$ g cm^{-3}, $F(000) = 1\,344$, $\mu = 46.1$ cm^{-1} (Mo-K_α radiation). A total of 6 629 unique reflections for which $2\theta \leqslant 50°$ were collected by the θ—2θ scan technique. Three standard reflections monitored regularly showed significant variations due to power fluctuations; the data were scaled accordingly. There was no indication of crystal decomposition. The data were corrected for Lorentz and polarisation effects and for absorption.†

* Cell dimensions measured at 23 °C.

† Initial processing of the data was done using the program HILGOUT, absorption corrections were from ABSORB, and the diagrams were obtained using ORTEP2. All other computing was carried out with the SHELX '76 package. See ref. 11 for details.

DISCUSSION

Preparation.—The most efficient preparation of $[Ge\{Co_2(CO)_7\}_2]$ involves the reaction of $[Co(CO)_4]^-$ with GeI_4 [equation (1)]; best yields (*ca.* 50%) are achieved using a small excess of $[Co(CO)_4]^-$ and the benzene–hexane mixed solvent suggested by the work of Schmid

‡ For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1979, Index issue.

and Etzrodt on related chemistry.[4] If lower Co : Ge

$$GeI_4 + 5\,Na[Co(CO)_4] \xrightarrow[\leqslant 25^\circ C]{\text{benzene–hexane}} [Ge\{Co_2(CO)_7\}_2] + \text{ionic products} \quad (1)$$

ratios are used, partially substituted species result, while higher Co : Ge ratios increase the yield of ionic products at the expense of $[Ge\{Co_2(CO)_7\}_2]$. Partially substituted germanium halides can be used [*e.g.* equation (2)] but

$$[GeCl\{Co(CO)_4\}_3] + [Co(CO)_4]^- \xrightarrow{\text{diethyl ether}} [Ge\{Co_2(CO)_7\}_2] \quad (2)$$

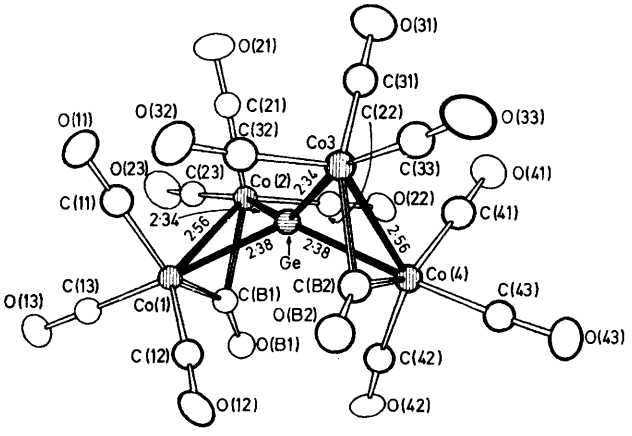
yields are no better. The alternative preparation by hydrogen elimination between GeH_4 and $[Co_2(CO)_8]$ [equation (3)] also shows promise. Shorter reaction

$$GeH_4 + 2\,[Co_2(CO)_8] \longrightarrow [Ge\{Co_2(CO)_7\}_2] + 2\,H_2 \quad (3)$$

times should lead to a product free of $[(OC)_4CoGeCo_3(CO)_9]$.

The compound $[Ge\{Co_2(CO)_7\}_2]$ is a dark red crystalline compound soluble in most organic solvents although only poorly so in hexane. It can be handled briefly in air as the solid without apparent decomposition and is indefinitely stable under nitrogen at 0 °C. On heating above *ca.* 40 °C in solution or as a solid $[Ge\{Co_2(CO)_7\}_2]$ loses CO to give quantitatively the previously characterised [4,6] $[(OC)_4CoGeCo_3(CO)_9]$. We are at present unable to speculate on the mechanism of this rather unusual rearrangement which involves the cleavage of one Co–Co bond, formation of two new Co–Co bonds, and elimination of CO. We are currently examining the interconversion in the series $[Ge\{Co(CO)_4\}_4] \rightleftharpoons [Ge\{Co_2(CO)_7\}_2] \rightleftharpoons [(OC)_4CoGeCo_3(CO)_9]$ and will report details later.

Structure.—The structure of $[Ge\{Co_2(CO)_7\}_2]$ consists of discrete molecules with no intermolecular distances less than 3 Å. There are only minor differences in the structural parameters found for the two molecules in the asymmetric unit. A perspective view of $[Ge\{Co_2(CO)_7\}_2]$ is given in the Figure, which also shows the atom-labelling system used. The molecule contains a common



A perspective view of the molecular structure of $[Ge\{Co_2(CO)_7\}_2]$

Ge atom bridging the Co–Co bonds of two equivalent $Co_2(CO)_7$ units, each of which has one bridging and six terminal CO ligands. There are two mutually perpendicular (dihedral angle 96°) closed $GeCo_2$ triangular units with a shared apex. There is an idealised C_2 axis passing through the Ge atom and bisecting the angle between the

TABLE 2

Selected bond lengths and bond angles in $[Ge\{Co_2(CO)_7\}_2]$

	Molecule 1	Molecule 2
(*a*) Bond lengths (Å)		
Ge–Co(1)	2.372(3)	2.379(3)
Ge–Co(2)	2.344(2)	2.341(3)
Ge–Co(3)	2.348(2)	2.339(2)
Ge–Co(4)	2.381(3)	2.387(2)
Co(1)–Co(2)	2.570(3)	2.559(3)
Co(3)–Co(4)	2.564(3)	2.552(3)
Co(1)–C(B1)	1.91(1)	1.90(1)
Co(2)–C(B1)	1.96(2)	2.00(1)
Co(3)–C(B2)	1.98(2)	2.00(2)
Co(4)–C(B2)	1.90(1)	1.87(1)
C(B1)–O(B1)	1.16(2)	1.15(2)
C(B2)–O(B2)	1.15(2)	1.18(2)
Other Co–C distances are 1.76—1.83 Å (average 1.80 Å)		
Other C–O distances are 1.10—1.19 Å (average 1.14 Å)		
(*b*) Bond angles (°)		
Co(1)–Ge–Co(2)	66.0(1)	65.7(1)
Co(3)–Ge–Co(4)	65.7(1)	65.4(1)
Ge–Co(1)–Co(2)	56.5(1)	56.4(1)
Ge–Co(2)–Co(1)	57.5(1)	57.9(1)
Ge–Co(3)–Co(4)	57.8(1)	58.2(1)
Ge–Co(4)–Co(3)	56.5(1)	56.4(1)
Co(1)–C(B1)–Co(2)	83.4(6)	81.8(6)
Co(3)–C(B2)–Co(4)	82.8(6)	82.4(6)
(*c*) Dihedral angles (°)		
Ge–Co(1)–Co(2)–Ge–Co(3)–Co(4)	96	97
Ge–Co(1)–Co(2)–Co(1)–Co(2)–C(B1)	107	109
Ge–Co(4)–Co(4)–Co(3)–Co(4)–C(B2)	106	106

two bridging C–O bonds. The individual $Co_2(CO)_7$ units are related to the bridged isomer of $[Co_2(CO)_8]$ with one μ-CO replaced by the Ge atom giving $GeCo_2$–Co_2C_b dihedral angles of 107°. The structure is also related to those [12,13] of $[GePh\{Co(CO)_4\}\{Co_2(CO)_7\}]$ and $[Sn(acac)_2\{Co_2(CO)_7\}]$(acac = acetylacetonate); a closer comparison of the $[M\{Co_2(CO)_7\}]$ units (M = Sn or Ge) is given later. There are also similarities [14,15] to $[Sn\{Fe_2(CO)_8\}_2]$ and $[As\{Co_2(CO)_2(\eta\text{-}C_5H_5)_2\}_2]^+$ which likewise have two mutually perpendicular triangular units containing the metal atoms.

The average Co–Co bond length (2.56 Å) and average Co–Ge–Co angle (66°) are very similar to those reported [12] for $[GePh\{Co(CO)_4\}\{Co_2(CO)_7\}]$ (2.55 Å and 65° respectively). This suggests there is little extra strain imposed at the Ge atom when it is bridging two Co–Co bonds, despite the two acute Co–Ge–Co angles. This is consistent with a bonding scheme which does not place the main orbital overlap along the Ge–Co vector (*cf.* ref. 16). However the Co–Co bond lengths in $[Ge\{Co_2(CO)_7\}_2]$ are significantly longer than that in $[Co_2(CO)_8]$ (2.52 Å).[17] As previously noted,[18] replacing a μ-CO by a Group 4 atom does lead to lengthening of the bridged bond, presumably to accommodate the larger atom. Consistent with this the Co–Co bond in $[Sn(acac)_2\{Co_2(CO)_7\}]$ is longer still (2.63 Å).[13] Nevertheless, the Co–Co

distances in all these molecules are significantly shorter than unbridged Co–Co bonds *e.g.* 2.66 Å in $[Co_2(CO)_6(PBu_3)_2]$.[19]

The Ge–Co bond lengths in $[Ge\{Co_2(CO)_7\}_2]$ vary from 2.339 (1) to 2.387 (1) Å, again shorter than expected for terminal Ge–Co bonds (*ca.* 2.42 Å).[20] A more interesting feature is that the Ge atom does not bridge either of the Co–Co bonds symmetrically, the difference in the Ge–Co bond lengths in any triangle being *ca.* 0.04 Å which is ten times the estimated standard deviation in this difference. The corresponding bridging carbonyl is also unsymmetric being displaced toward the Co with the longer Ge–Co bond. Similar distortions have been observed in other related species. Triplett and Curtis [16] have discussed the asymmetry of the bridge in $[GeMe_2\{Mn_2(CO)_9\}]$ in relation to previous work on asymmetric carbonyl bridging in iron carbonyl structures.[21] This assumes that unsymmetrical bridges merely represent a 'stopped-action' intermediate stage in going from symmetrical bridges to fully terminal structures in a shallow potential well. Relatively minor steric requirements amongst the remaining ligands would therefore decide the degree of asymmetry. In $[Fe_2(CO)_7(GePh_2)_2]$ it was suggested by Elder [22] that the distortion of *both* bridging Ge atoms towards one Fe atom and the μ-CO towards the other relieved non-bonded interactions between the bridging Ge and C atoms. This seems unlikely to be the only reason since equally severe interaction between the two Ge atoms (Ge · · · Ge = 3.65 Å *cf.* Ge · · · C_b = 3.02 Å) is not only probable but is in fact indicated by an opening of the $GeFe_2$–Fe_2Ge dihedral angle (129°) at the expense of the $GeFe_2$–Fe_2C_b angle (116°). It might therefore have been expected that the Ge atoms would distort towards opposite Fe atoms.

Nevertheless an interaction between the bridging Ge and C atoms in $[Ge\{Co_2(CO)_7\}_2]$ seems a likely explanation for the asymmetry observed in the present study. In this molecule, as well as in $[GePh\{Co(CO)_4\}\{Co_2(CO)_7\}]$ [12] and $[Ge\{Co_2(CO)_7\}\{Co_2(CO)_6[HgCo(CO)_4]\}]^-$ (4),[9] the Ge · · · C_b distances are remarkably constant at 2.77 ± 0.01 Å, considerably less than the sum of the van der Waals radii for the two atoms (*ca.* 3.5 Å). The $GeCo_2$–Co_2C_b dihedral angles are apparently determined by these interactions, varying from 107° in $[Ge\{Co_2(CO)_7\}_2]$ to 95° in $[GePh\{Co(CO)_4\}\{Co_2(CO)_7\}]$. Relief of the Ge · · · C_b interaction by increasing the dihedral angle would increase the non-bonded interaction between the bridging and terminal carbonyl groups.

The Co–C and C–O bond lengths in $[Ge\{Co_2(CO)_7\}_2]$ average 1.80 Å and 1.14 Å respectively; these are typical for cobalt carbonyl complexes.

Spectral Studies.—The i.r. spectrum of $[Ge\{Co_2(CO)_7\}_2]$ in hexane shows terminal carbonyl stretching absorptions at 2 079s, 2 061vs, 2 040m, 2 032m, 2 023w, 2 005w and a bridging mode at 1 848 cm^{-1} (resolution 1 cm^{-1}). Assuming that the C_2 structure found in the solid persists in solution a total of 12 terminal and two bridging modes would be expected. The observed modes match those predicted for the idealised D_{2d} species where all Ge–Co bonds are equal and μ-CO is coplanar with $GeCo_2$. Thus, the dipole changes for vibrations in phase between the two $Co_2(CO)_7$ units, zero for D_{2d}, must remain very small in the real molecule. Alternatively, coupling across Ge between vibrations in the two $Co_2(CO)_7$ units must be weak. Certainly the observed spectrum is deceptively simple.

The mass spectrum of $[Ge\{Co_2(CO)_7\}_2]$ showed the whole series of ions $[Ge\{Co_4(CO)_x\}]^+$ (x = 0—14) arising from typical stepwise loss of CO ligands; 73% of the total ion current is carried by ions with the $GeCo_4$ unit intact. However some early cleavage of Ge–Co bonds is evidenced by the series of ions $[Ge\{Co_3(CO)_x\}]^+$ (x = 0—7) as a minor feature. Except for the peaks at *m/e* 698—704, attributable to the parent ion, the mass spectrum of $[Ge\{Co_2(CO)_7\}_2]$ is similar to that reported for $[(OC)_4CoGeCo_3(CO)_9]$ although the higher mass ions have significantly greater relative intensities.

Conclusion.—The full characterisation of $[Ge\{Co_2(CO)_7\}_2]$ provides a link between the open and cluster MCo_4 species (M = Si, Ge, Sn, or Pb). In view of the similar sizes of Si and Ge the silicon analogue of $[Ge\{Co_2(CO)_7\}_2]$ should also be obtainable, especially since R_2Si bridged Co–Co species are known.[23] On the other hand, tin analogues must be doubtful; it is probably significant that $[SnMe_2\{Co_2(CO)_7\}]$ is 'exceedingly unstable'.[24] In $[Sn\{Fe_2(CO)_8\}_2]$ the Fe–Fe bond is exceptionally long; [14] a similar stretching of the Co–Co bond in the $[Sn\{Co_2(CO)_7\}]$ unit would undoubtedly destabilise the μ-CO which is a necessary feature. Stable tin-bridged $Co_2(CO)_7$ units are only found with six-co-ordinate tin,[13] which is smaller and able to accommodate more acute bond angles than when it is four-co-ordinate.

The compound $[Ge\{Co_2(CO)_7\}_2]$ promises to be a useful precursor in the synthesis of novel, mixed germanium–cobalt species. In particular, we have prepared several anionic clusters by reaction with $[Co(CO)_4]^-$; full details will be reported in a future paper.

We wish to thank the New Zealand University Grants' Committee for financial support and a Scholarship (to R. F. G.) and Ruakura Agricultural Research Centre for use of mass spectrometer facilities. Assistance from Mr. D. N. Duffy is also gratefully acknowledged.

[0/590 *Received, 22nd April,* 1980]

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