Anionic Germanium Polycobalt Carbonyl Clusters. Part 2.[†] Preparation and Structure of $[NEt_4][Ge\{Co_5(CO)_{16}\}]$,[‡] a Cluster which contains Five-co-ordinate Germanium

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Addition of $[Co(CO)_4]^-$ to $[Ge\{Co_4(CO)_n\}]$ (n = 16, 14, or 13) under mild conditions gives good yields of $[Ge\{Co_5(CO)_{16}\}]^-$. This forms crystals with NEt_4^+ which are orthorhombic, space group $Pn2_1a$ with a = 12.014(1), b = 36.938(4), c = 15.249(2), and Z = 8. The crystal structure was solved by direct methods and refined, with some difficulty due to pseudo-symmetry, to R = 0.088, R' = 0.081, for 1 590 unique reflections with $F^2 > 2\sigma(F^2)$. The anion has a $GeCo_5$ metal skeleton consisting of a $GeCo_2$ triangle and a $GeCo_3$ tetrahedron sharing a common apex at Ge. The five Ge–Co bond lengths vary from 2.33 to 2.51 Å. Three of the CO ligands on the $GeCo_3$ unit bridge the three Co–Co bonds, with two terminal CO groups on each Co atom. On the $GeCo_2$ moiety there are six terminal and one bridging carbonyls.

ALTHOUGH a large number of transition-metal clusters is known,[1,2] those incorporating main-group atoms in their framework are not common. Tetrahedral species $[M'R\{Co_3(CO)_9\}]$ [M' = Si or Ge, R = $Co(CO)_4$] and $[E\{Co_3(CO)_9\}]$ (E = P, As, S, or Se) are well characterised,[2-6] and another major class is where a main-group atom, usually C but also H, N, P, S, or As, is encapsulated within a closed cage of metal atoms.[1,7] In many cases the heteroatom has a stabilising effect on the cluster framework. It is therefore of interest to develop new syntheses to extend this class of compound.

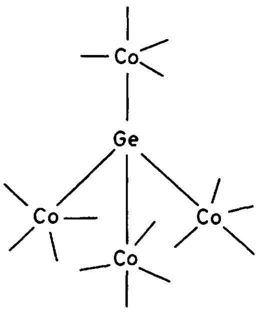
It has recently been shown that three distinct species, namely $[Ge\{Co(CO)_4\}_4]$ (1),[8] $[Ge\{Co_2(CO)_7\}_2]$ (2),[9] and $[(OC)_4CoGeCo_3(CO)_9]$ (3),[3] are obtainable from the GeI_4–$[Co(CO)_4]^-$ or GeH_4–$[Co_2(CO)_8]$ systems, and these represent increasing clusterification about the Ge atom as CO is eliminated and Co–Co bonds form. We now report that addition of $[Co(CO)_4]^-$ to the neutral $GeCo_4$ derivatives (1)—(3) occurs readily to give the anionic cluster (4) which has been shown by a full crystal-structure analysis to be the first example of a heavier Group 4 atom bonded to more than four transition-metal atoms in a discrete complex.

EXPERIMENTAL

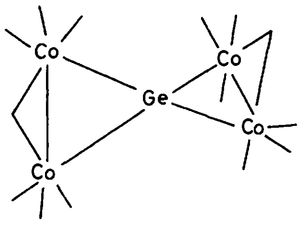
All preparations were conducted under a nitrogen atmosphere using standard Schlenk techniques. The complexes $[Ge\{Co_2(CO)_7\}_2]$ and $[(OC)_4CoGeCo_3(CO)_9]$ were prepared by standard procedures,[3,8] whilst $K[Co(CO)_4]$ was synthesised by reduction of $[Co_2(CO)_8]$ in tetrahydrofuran (thf) with Na_4K alloy [10] and converted into $[NEt_4][Co(CO)_4]$ by metathesis with NEt_4Br.

Preparation of $[NEt_4][Ge\{Co_5(CO)_{16}\}]$ (4).—A solution of $[Ge\{Co_2(CO)_7\}_2]$ (0.14 g, 0.2 mmol) and $[NEt_4][Co(CO)_4]$ (0.13 g, 0.4 mmol) in CH_2Cl_2 (20 cm³) was refluxed gently for 2.5 h. Ionic products were precipitated by the addition of hexane (20 cm³). An Et_2O extract of the solids was filtered and evaporated to give the crude product which was recrystallised from CH_2Cl_2–hexane to give deep red-black *crystals* of (4) (0.12 g, 64%); ν(CO) (CH_2Cl_2) 2 078w, 2 053m, 2 025vs, 2 004(sh), 1 970w, 1 825w; ν(CO) (Nujol) 2 080w, 2 050m, 2 020vs,br, 1 828w, and 1 810w cm⁻¹.

An identical product was obtained starting from $[Ge\{Co(CO)_4\}_4]$ or $[(OC)_4CoGeCo_3(CO)_9]$ using a similar procedure. The $N(PPh_3)_2^+$, K^+, Na^+, and NMe_4^+ salts of $[Co(CO)_4]^-$ also provide the same complex anion (by i.r. spectroscopy) but are less suitable for the isolation of a crystalline product.



(1)



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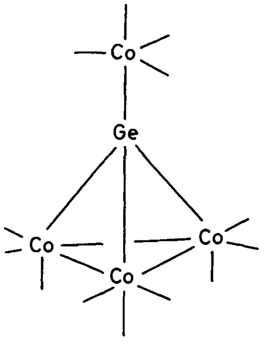

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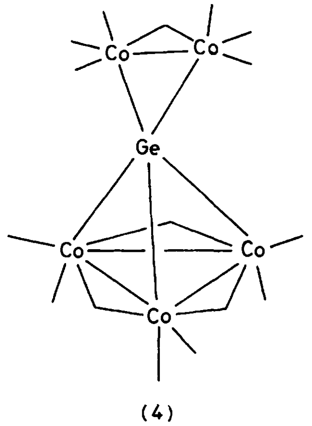

(4)

X-*Ray Structure of* $[NEt_4][Ge\{Co_5(CO)_{16}\}]$ (4).—A deep red-black needle of dimensions 0.7 × 0.1 × 0.07 mm from CH_2Cl_2–hexane (1 : 1) was sealed in a thin-walled glass capillary.

[†] Part 1 is regarded as ref. 15.

[‡] Tetraethylammonium [μ-carbonyl-bis(tricarbonylcobaltio)-(*Co–Co*)](tri-μ-carbonyl-hexacarbonyl-*triangulo*-tricobaltio)-germanate(5 *Co–Ge*).

Crystal data. $C_{24}H_{20}Co_5GeNO_{16}$, $M = 945.68$, Orthorhombic, space group $Pn2_1a$ [a non-standard setting of $Pna2_1$ (no. 33)],* $a = 12.014(1)$, $b = 36.938(4)$, $c = 15.249(2)$, $U = 6\,767$ Å^3, D_m not measured, $Z = 8$, $D_c = 1.86$ g cm^{-3}, $F(000) = 3\,728$, μ(Mo-K_α) = 32 cm^{-1}, $\lambda = 0.7107$ Å, 23 °C. Preliminary precession photography indicated either $Pnma$ or $Pn2_1a$ from systematic absences ($0kl$, $k + l$ odd; $hk0$, h odd), the latter eventually proving correct. Unit-cell dimensions were obtained from the setting angles of 12 high-angle reflections. A total of 4 227 unique reflections, $2\theta < 44°$, was collected using the θ—2θ scan technique on a Hilger and Watts four-circle diffractometer. Three standard reflections, monitored at regular intervals, showed no crystal decomposition.

The raw data were corrected for background, Lorentz, and polarisation effects and for absorption. Of the 4 227 reflections, 1 590 had $F^2 > 2\sigma(F^2)$ and these were used for refinement.

Attempts to solve the structure in space group $Pnma$ were unsuccessful. On changing to $Pn2_1a$, direct methods gave the positions of the two germanium and ten cobalt atoms in the asymmetric unit. Subsequent least-squares refinements and difference maps ultimately revealed all other non-hydrogen atoms, although with some difficulty. This arose because of pseudo-symmetry; the heavy-metal positions of the two independent molecules are approximately centrosymmetric but the carbonyl groups and the NEt_4^+ cation are not. The final cycle of full-matrix refinement, with anisotropic thermal parameters for the metal atoms, isotropic thermal parameters for the other atoms, and with the N–C and the C–C bonds of the NEt_4^+ constrained to common values, gave $R = 0.088$ and $R' = 0.081$ for 1 590 reflections with $F^2 > 2\sigma(F^2)$. Some bond lengths and angles involving the carbonyl groups refined to unrealistic values, presumably due to the pseudo-symmetry problem; no way of overcoming this could be found. However, the overall structure is unambiguous and parameters involving only the metal atoms are apparently reliable. Computation was carried out on a VAX 11/780 computer using HILGOUT and ABSORB for data processing, SHELX-76 for solution and refinement, and PLUTO for diagrams.[9,11]

TABLE 1

Final positional parameters (× 10^4) for $[NEt_4][Ge\{Co_5(CO)_{16}\}]$ (4)

	Molecule 1			Molecule 2		
Atom	X/a	Y/b	Z/c	X/a	Y/b	Z/c
Ge(1)	5 557(6)	2 297(1)	−178(5)	−104(7)	9 856(2)	5 105(5)
Co(1)	4 859(8)	2 858(4)	490(7)	−329(10)	9 829(4)	3 487(8)
Co(2)	6 766(8)	2 601(3)	783(7)	−535(8)	9 294(3)	4 491(7)
Co(3)	5 047(9)	2 291(4)	1 419(9)	1 358(8)	9 568(4)	4 236(8)
Co(4)	5 639(8)	1 704(3)	−863(7)	367(10)	10 011(4)	6 643(8)
Co(5)	5 623(10)	2 271(4)	−1 796(7)	−1 206(10)	10 325(4)	5 837(8)
C(B12)	6 437(72)	3 125(23)	126(60)	−1 675(63)	9 562(19)	3 757(49)
C(B13)	3 751(44)	2 568(13)	889(37)	1 187(69)	9 945(21)	3 456(62)
C(B23)	6 567(71)	2 222(25)	1 586(62)	984(62)	9 120(19)	4 819(55)
C(11)	4 853(55)	3 217(19)	1 345(50)	−285(43)	9 651(14)	2 289(41)
C(12)	4 218(63)	2 986(20)	−452(57)	9 277(79)	10 249(26)	3 385(64)
C(21)	7 389(76)	2 885(25)	1 479(68)	−611(57)	8 977(20)	3 816(50)
C(22)	7 925(77)	2 421(27)	217(63)	−1 133(61)	9 180(19)	5 249(56)
C(31)	5 086(80)	2 439(29)	2 304(72)	1 938(59)	9 282(21)	3 317(55)
C(32)	4 535(50)	1 869(16)	1 426(41)	2 383(66)	9 708(19)	4 845(57)
C(41)	4 332(60)	1 622(18)	−617(49)	1 370(64)	10 319(20)	6 331(50)
C(42)	6 420(45)	1 512(14)	−11(38)	928(74)	9 525(27)	6 829(62)
C(43)	5 730(106)	1 349(29)	−1 515(87)	568(86)	10 295(27)	7 673(76)
C(51)	4 201(64)	2 358(22)	−1 756(51)	−356(82)	1 646(25)	5 211(70)
C(52)	6 225(64)	2 637(21)	−1 919(49)	−2 392(55)	10 200(16)	5 315(46)
C(53)	5 428(76)	2 114(23)	−2 754(69)	−1 517(66)	10 611(21)	6 525(55)
C(B45)	6 673(56)	1 991(17)	−1 680(45)	−1 319(66)	9 983(21)	6 658(60)
O(B12)	6 838(43)	3 343(14)	−122(37)	−2 668(41)	9 568(12)	3 679(31)
O(B13)	2 767(39)	2 506(14)	1 074(34)	1 882(49)	10 172(16)	3 110(42)
O(B23)	7 122(35)	2 004(13)	1 967(32)	1 303(36)	8 898(13)	5 267(32)
O(11)	4 641(40)	3 424(12)	1 798(35)	−0 362(54)	9 547(17)	1 658(49)
O(12)	3 707(55)	3 153(18)	−940(49)	−1 425(49)	10 495(15)	3 309(41)
O(21)	7 551(46)	3 005(16)	2 141(42)	−0 751(40)	8 717(13)	3 185(35)
O(22)	8 668(49)	2 731(18)	−178(41)	−1 709(44)	9 062(14)	5 980(40)
O(31)	4 852(39)	2 591(12)	3 165(37)	2 392(41)	9 048(13)	3 046(33)
O(32)	4 031(46)	1 587(15)	1 599(39)	3 186(45)	9 764(15)	5 345(43)
O(41)	3 294(46)	1 588(14)	−542(38)	2 147(47)	10 466(14)	6 095(39)
O(42)	7 001(57)	1 428(17)	602(52)	1 010(49)	9 257(17)	6 981(40)
O(43)	5 655(52)	1 125(20)	2 141(39)	268(49)	10 305(17)	8 481(46)
O(51)	3 260(50)	2 394(18)	−1 642(41)	65(71)	10 831(18)	4 763(52)
O(52)	6 856(50)	2 916(18)	−1 970(42)	−3 241(56)	10 107(16)	5 002(41)
O(53)	5 674(52)	2 051(16)	−3 569(47)	−1 954(48)	10 888(15)	7 033(38)
O(B45)	7 716(42)	1 895(13)	−1 763(34)	−1 775(47)	9 778(15)	7 199(41)
N(1)	5 256(37)	1 141(12)	4 111(28)	4 833(37)	8 583(12)	5 153(31)
C(1)	5 442(57)	1 072(20)	5 161(33)	4 868(51)	8 816(15)	4 238(38)
C(2)	5 069(52)	1 560(14)	3 875(45)	5 193(49)	8 152(14)	5 184(43)
C(3)	4 201(47)	896(14)	3 819(46)	5 774(49)	8 778(14)	5 742(41)
C(4)	6 415(48)	1 030(17)	3 656(40)	3 761(46)	8 811(15)	5 444(43)
C(5)	4 309(60)	1 175(21)	5 685(47)	5 960(59)	8 640(20)	3 712(53)
C(6)	5 987(57)	1 849(18)	4 135(55)	4 096(55)	7 974(19)	4 741(50)
C(7)	4 477(64)	467(16)	3 946(56)	5 409(64)	9 198(16)	5 774(54)
C(8)	6 443(62)	1 110(22)	2 618(43)	3 564(65)	8 500(18)	6 187(51)

* Equivalent positions are: x, y, z; $-x, \frac{1}{2} + y, -z$; $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} + z$; $\frac{1}{2} + x, y, \frac{1}{2} - z$.

TABLE 2

Selected * bond lengths (Å) and angles (°) for $[Ge\{Co_5(CO)_{16}\}]^-$ (4)

Bond lengths

	A	B		A	B
Ge–Co(1)	2.46(1)	2.48(1)	Co(1)–Co(2)	2.52(1)	2.51(1)
Ge–Co(2)	2.35(1)	2.33(1)	Co(1)–Co(3)	2.54(1)	2.52(1)
Ge–Co(3)	2.51(1)	2.44(1)	Co(2)–Co(3)	2.55(1)	2.52(1)
Ge–Co(4)	2.43(1)	2.48(1)	Co(4)–Co(5)	2.53(1)	2.54(1)
Ge–Co(5)	2.47(1)	2.45(1)			

Co–C (terminal)	1.54—2.03	C–O (terminal)	1.01—1.37
Co–C (bridge)	1.63—2.04	C–O (bridge)	1.06—1.29

Bond angles

	A	B		A	B
Co(1)–Ge–Co(2)	63	63	Co(2)–Co(3)–Co(1)	59	60
Co(1)–Ge–Co(3)	62	62	Co(3)–Co(1)–Co(2)	61	60
Co(2)–Ge–Co(3)	63	64			
Co(4)–Ge–Co(5)	62	62	Ge–Co(4)–Co(5)	60	59
Co(1)–Co(2)–Co(3)	60	60	Ge–Co(5)–Co(4)	58	60

Non-bonded distances

Co(1) · · · Co(5)	4.20
Co(3) · · · Co(4)	4.17
Co(2) · · · Co(4)	4.39
Co(2) · · · Co(5)	4.36

Dihedral angles

	A	B
Ge–Co(4)–Co(5)/Co(1)–Co(2)–Co(3)	85	84
Ge–Co(4)–Co(5)/Co(1)–Co(3) vector	7	6

* Only parameters relating to the heavy-metal skeleton are given in detail since those involving carbonyl groups are unreliable because of refinement difficulties (see Experimental section). A and B are the independent anions in the asymmetric unit.

The final atomic positional parameters are listed in Table 1 and selected bond lengths and angles in Table 2. Observed and calculated structure factors and thermal parameters have been deposited as Supplementary Publication No. SUP 23257 (23 pp).*

RESULTS AND DISCUSSION

Preparation of $[NEt_4][Ge\{Co_5(CO)_{16}\}]$ (4).—Addition of $[Co(CO)_4]^-$ to $[Ge\{Co_2(CO)_7\}_2]$ occurs under mild conditions to give the pentacobalt anion (4) in good yields [see equation (i)]. Other germanium tetracobalt

$$[Ge\{Co_2(CO)_7\}_2] + [Co(CO)_4]^- \xrightarrow[40\ °C]{CH_2Cl_2} [Ge\{Co_5(CO)_{16}\}]^- + 2\ CO \quad (i)$$

species, (1) or (3), can also be used. Indeed all preparations probably involve addition to (3) since both (1) and (2) are converted into (3) under the conditions necessary for reaction. There is i.r. evidence that an as yet uncharacterised anion [ν(CO) (CH_2Cl_2) 2 080w, 2 047m, 2 022vs, 1 997m, and 1 825w cm^{-1}] is initially formed and that this rearranges to the final product, (4), which can be isolated as pure crystals with NEt_4^+ as counter ion. The solid can be safely handled briefly in air but solutions are air-sensitive, giving $[Co(CO)_4]^-$ and $[Co_4(CO)_{12}]$ among other decomposition products.

The i.r. spectrum of $[Ge\{Co_5(CO)_{16}\}]^-$ in CH_2Cl_2 is relatively simple (see Experimental section) with only a very weak bridging carbonyl band. A Nujol spectrum is also rather featureless although two reasonably intense bridging modes are apparent. The solid-state structure of the anion (see below) has three bridging carbonyl groups around the base of the $GeCo_3$ tetrahedron which contrasts with the all-terminal structure found[3] for $[(OC)_4CoGeCo_3(CO)_9]$. It has been suggested[2,12] that carbonyl bridging in these and related species is favoured by (i) increased negative charge since bridging CO groups are stronger π acceptors and (ii) increased steric demands by the apical group ML_n of $[ML_n\{Co_3(CO)_9\}]$. Both effects are operating for (4) but too much significance should not be attached to the bridged solid-state structure since the solution i.r. spectrum indicates a non-bridged isomer predominates, so the observed bridging may well be due to crystal-packing forces.

Structure of $[NEt_4][Ge\{Co_5(CO)_{16}\}]$.—The crystal consists of discrete NEt_4^+ and $[Ge\{Co_5(CO)_{16}\}]^-$ ions. The two crystallographically independent species in the asymmetric unit show no chemically significant differences. A perspective view of the anion showing the atom-numbering scheme is presented in Figure 1 while the stereoview given in Figure 2, looking along the main axis of the anion, shows the relative orientations of the two halves of the complex. The metal core of $[Ge\{Co_5(CO)_{16}\}]^-$ consists of a $GeCo_3$ tetrahedron and a $GeCo_2$ triangle sharing a common apex, the germanium atom, which is thus involved in five Ge–Co bonds. Five-co-ordinate germanium species are known[13] (*e.g.* GeF_5^-) but this is the first example involving five metallic substituents. The two cobalt atoms of the $GeCo_2$ fragment are each bonded to three terminal CO

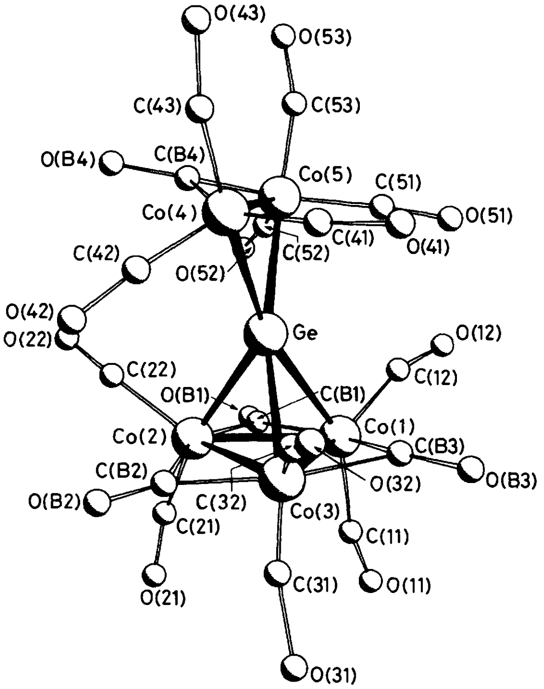

FIGURE 1 A perspective view of the $[Ge\{Co_5(CO)_{16}\}]^-$ anion showing the atom-labelling scheme

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* For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

groups, with one CO group bridging the bond between them. The cobalt atoms of the $GeCo_3$ unit each have two terminal CO groups, with an additional bridging CO ligand along each edge of the Co_3 triangle.

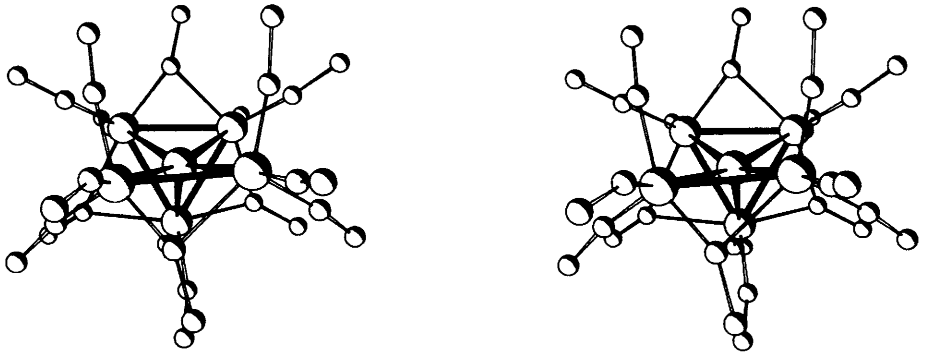
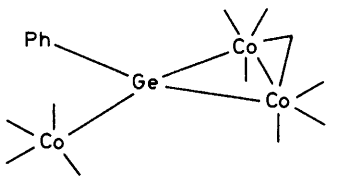


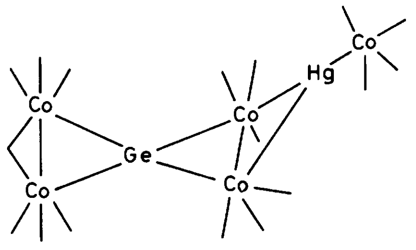
FIGURE 2 A stereoview of $[Ge\{Co_5(CO)_{16}\}]^-$ perpendicular to the base of the $GeCo_3$ unit showing the relative orientation of the $GeCo_2$ and $GeCo_3$ fragments

The orientation of the $GeCo_2$ triangle is perpendicular to the Co_3 base of the tetrahedron and almost parallel to the Co(1)–Co(3) sides (see Figure 2), which appears to be the least sterically crowded arrangement rather than one determined by electronic constraints. The co-ordination about the germanium atom can be regarded as a very distorted square pyramid with Co(1), Co(3), Co(4), and Co(5) forming the base and Co(2) the apex.

Several structures incorporating a $GeCo_2(CO)_7$ unit are known,[9,14,15] namely $[Ge\{Co_2(CO)_7\}_2]$ (2), $[GePh\{Co(CO)_4\}\{Co_2(CO)_7\}]$ (5), and $[HgGeCo_5(CO)_{17}]^-$ (6) while a non-bridged form of the $GeCo_3(CO)_9$ unit has been described[3] for (3). Comparisons can therefore be made to assess the effect of five-co-ordination at germanium on structural features.



(5)



(6)

Considering the $GeCo_2(CO)_7$ unit first, the Co(4)–Co(5) bond (2.54 Å) is similar to the Co–Co bonds found in (2), (5), and (6), lying between values found for $[Co_2(CO)_8]$ (2.52 Å, two CO bridges)[16] and for $[Co_2(CO)_6(PBu^n_3)_2]$ (2.66 Å, no bridges).[17] However, the Ge–Co bonds in the $GeCo_2(CO)_7$ unit of (4) are significantly longer (mean 2.46 Å) than those involving four-co-ordinate germanium (typically 2.36 Å). This is the expected effect of increased co-ordination numbers, on both steric and electronic grounds, and is also observed in the $GeCo_3$ unit of (4) where the Ge–Co bond lengths range from 2.33 to 2.51 Å, compared with an average value of 2.28 Å in $[(OC)_4CoGeCo_3(CO)_9]$. The individual variations in the Ge–Co bonds of the $GeCo_3$ group presumably arise through non-bonded interactions with the $Co_2(CO)_7$ moiety in the other half of the anion, the Co(1) · · · Co(5) and Co(3) · · · Co(4) distances (4.20 and 4.17 Å respectively) being significantly shorter than the Co(2) · · · Co(5) (4.36 Å) or Co(2) · · · Co(4) distances (4.39 Å).

The Co–Co bonds in the $GeCo_3$ group of (4) are shorter (mean 2.53 Å) than in $[(OC)_4CoGeCo_3(CO)_9]$ (2.61 Å). This may be due to the bridging CO groups in (4) but not in (3), although it may also be related in part to weaker Ge–Co bonding in (4) since it has previously been noted[15] that there is an inverse relationship between Ge–Co and Co–Co bond lengths in $GeCo_2$ triangles.

CONCLUSIONS

The preparation and structural characterisation of $[Ge\{Co_5(CO)_{16}\}]^-$ demonstrates the feasibility of the rational synthesis of metal clusters about a main-group atom by addition of metal carbonyl anions to neutral Group 4 derivatives. An obvious extension is towards mixed-metal clusters by the appropriate choice of starting species, although substitution rather than addition was observed[18] for the reaction of $[Mn(CO)_5]^-$ with (2) or (3) [see equation (ii)].

$$[Mn(CO)_5]^- + [Ge\{Co_2(CO)_7\}_2] \longrightarrow [(OC)_5MnGeCo_3(CO)_9] + [Co(CO)_4]^- + CO \quad (ii)$$

It is interesting to speculate on the structure of the as yet hypothetical $[Ge\{Co_6(CO)_n\}]^{2-}$ which would result on addition of a further $[Co(CO)_4]^-$ to (4) followed by CO loss and rearrangement. The interstitial hole within a Co_6 octahedron is too small to allow a Ge analogue of the closed CCo_6 clusters,[19] making a 'semi-interstitial' structure similar to that[20] of the isoelectronic $[P\{Co_6(CO)_{16}\}]^-$ more likely. However, the $GeCo_3(CO)_9$ unit is apparently very stable[21] suggesting a structure based on two $GeCo_3$ tetrahedra with a common apex might also be found.

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