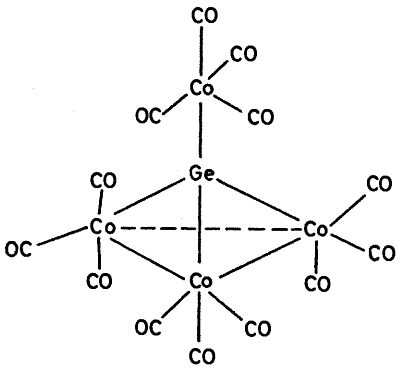
Germanium Analogue of the well known Methylidyne Cobalt Clusters: *X*-Ray Crystal Structure of $(CO)_9Co_3Ge{-}Co(CO)_4$†

By Roland Boese and Günter Schmid*
(*Fachbereich Chemie, The University, Universitätsstrasse* 5-7, D-4300 *Essen* 1, *Germany*)

Summary The molecular structure of the germylidynenonacarbonyltricobalt cluster compound $(CO)_9Co_3Ge{-}Co(CO)_4$ has been established by *X*-ray crystallographic analysis and is compared with the analogous methylidyne and silylidyne cluster molecules.

After the first report of a probable germylidyne-cluster in 1970[1] we recently succeeded in preparing the μ_3-(tetracarbonylcobaltogermylidyne)*cyclo*-tris(tricarbonylcobalt) (*3Co–Co*) by reaction of $NaCo(CO)_4$ with $GeBr_4$.[2] Our interest in the structural behaviour of tetrahedral heteronuclear cobalt cluster systems prompted us to establish the molecular structure of $(CO)_9Co_3Ge{-}Co(CO)_4$, to compare it with the methylidyne, and especially with the corresponding silylidyne cluster $(CO)_9Co_3{-}Si{-}Co(CO)_4$.[3]



Crystal data: $C_{13}Co_4GeO_{13}$, M 672·46, triclinic, $a = 15\cdot853(9)$, $b = 8\cdot855(5)$, $c = 8\cdot096(3)$ Å, $\alpha = 110\cdot45(3)$, $\beta = 104\cdot77(4)$, $\gamma = 80\cdot64(5)^\circ$, $U = 1026\cdot3(9)$ Å^3, $Z = 2$, $D_c = 2\cdot18$ g cm^{-3}, $F(000) = 644$, Mo-K_α radiation ($\lambda = 0\cdot71069$ Å), μ (Mo-K_α) = 48·8 cm^{-1}, space group $P1$, empirical absorption correction based on five reflexions within the 2θ-range.‡

---

† For Part 16 of the series Heteronuclear Cluster Systems, see R. Boese and G. Schmid, *Chem. Ber.*, in the press.

‡ The atomic co-ordinates for this work are available on request from Prof. Dr. G. Bergerhoff, Institut für Anorganische Chemie, Universität, Gerhard-Domagk-Str. 1, D-5300 Bonn 1, W. Germany. Any request should be accompanied by the full literature citation for this communication. The structure factor table is available as supplementary publication no. Sup 22530 (38 pp.) from the British Library, Lending Division. For details of obtaining this material see Notice to Authors No. 7, *J.C.S. Dalton* or *Perkin I* and *II*, Index Issues.

The structure was solved by taking the positions of the cobalt atoms of the isostructural silicon compound[3] as starting parameters. They were refined by least squares to $R = 0{\cdot}234$. The difference Fourier revealed the positions of all other atoms of the molecule in the asymmetric part in the unit cell. All atoms were anisotropically refined to $R = 0{\cdot}036$ for 1817 observed and 100 unobserved reflexions ($F_{\mathrm{obs}} > 3{\cdot}9 \times \sigma_F$). The 2θ range was 40° on a SYNTEX R3 diffractometer, calculated with the SYNTEX XTL-program system on a NOVA 3/12 computer.

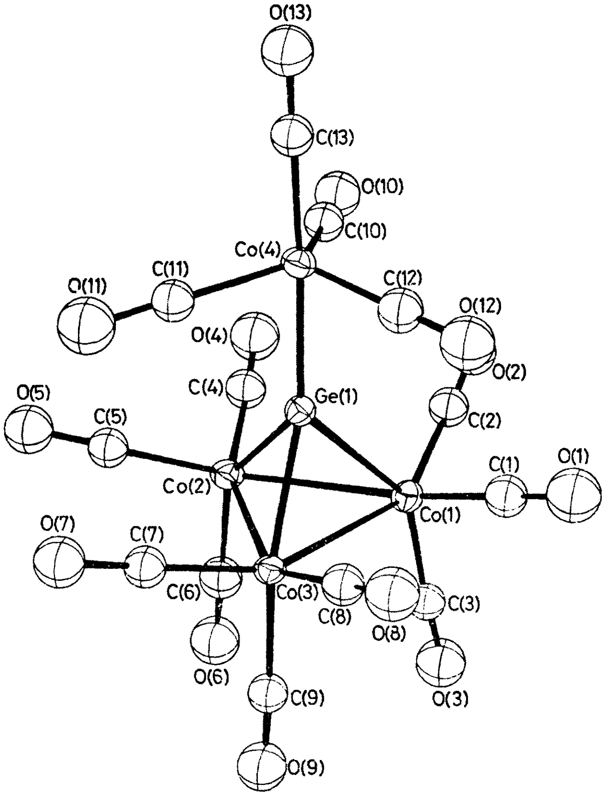


FIGURE. The molecular structure of $(CO)_9Co_3Ge–Co(CO)_4$. Thermal ellipsoids are drawn at the 50% probability level. Significant bond lengths and angles are: Ge(1)–Co(1), **2·281**(1); Ge(1)–Co(2), **2·284**(1); Ge(1)–Co(3), **2·277**(1); Ge(1)–Co(4), **2·349**(1); Co(1)–Co(2), **2·613**(1); Co(1)–Co(3), **2·625**(1); and Co(2)–Co(3), **2·601**(1) Å; ∠Co(1)–Ge(1)–Co(2), **69·82**(4); Co(1)–Ge(1)–Co(3), **70·33**(4); Co(2)–Ge(1)–Co(3), **69·53**(4); Co–Co–Co, 60(av.); Co(1)–Ge(1)–Co(4), **137·83**; Co(2)– Ge(1)–Co(4), **139·96**; Co(3)–Ge(1)–Co(4), **137·98**; Ge(1)–Co(4)–C(10), **82·0**(3); Ge(1)–Co(4)–C(11), **83·8**(3); and Ge(1)–Co(4)–C(12), **86·5**(3)°.

The essential part of the structure of $(CO)_9Co_3Go–Co(CO)_4$ consists of a Co_3Ge tetrahedron. The structure shows 3 pseudo-mirror planes through the linear arrangement Ge(1)–Co(4)–C(13)–O(13). Plane 1: O(3),C(3), Co(1),Ge(1),-Co(4), C(13), C(11), O(11); plane 2: O(6), C(6), Co(2), Ge(1), Co(4),C(13),O(13),C(12),O(12); plane 3: O(9),C(9),Co(3), Ge(1),Co(4),C(13),O(13),C(10),O(10). The Co(1)–Co(2)–Co(3) plane lies almost parallel to the equatorial plane of the $Co(CO)_4$ group whose equatorial CO ligands are tilted towards the Co_3Ge tetrahedron as can be seen by the small Ge–Co(4)–C angles (82·0—86·5°). They are in a staggered position relative to the equatorial CO group of the $(CO)_9Co_3$ unit.

The cobalt atoms of the tetrahedral framework are electronically and co-ordinatively saturated by 3 terminal CO groups and 3 bonds to the other tetrahedron atoms. The tetrahedron is based on an isosceles triangle of the cobalt atoms Co(1), Co(2), and Co(3). The Co–Co distances (average 2·61 Å) correspond to single bonds and may be compared with those in the corresponding silicon cluster (2·60 Å)[3] or in $(CO)_9Co_3S$[4] (2·64 Å) and $(CO)_9Co_3Se$[5] (2·62 Å). Only the methylidyne clusters of type $(CO)_9Co_3CR$ show significantly smaller angles with an average Co–Co distance of 2·5 Å.

There are two different Co–Ge bond lengths: the distances between Ge and the Co atoms of the tetrahedron are significantly shorter (average 2·281 Å) than the bond length Ge–Co(4) (2·349 Å), although all correspond to single bonds. As a consequence of the increasing covalent radii of the elements C, Si, and Ge, the tetrahedral environment of the hetero-atoms is distorted increasingly: ∠Co–C–Co 80,[6] Co–Si–Co 71·9 [3] and Co–Ge–Co 69·89° (all average values) because the Co_3 triangle is difficult to deform. As shown previously, the unsuccessful synthesis of tin and lead containing tetrahedrons[7] clearly demonstrates that these elements avoid cluster formation, yielding instead the open complexes $Sn[Co(CO)_4]_4$ and $Pb[Co(CO)_4]_4$. These results can be compared with those of investigations with the group 5A elements P, As, and Bi. Phosphorus and arsenic may be incorporated into the tetrahedral cluster core while bismuth forms the open complex $Bi[Co(CO)_4]_3$.

We thank Mr. H. Rippstein (Scintag) for his help.

(*Received*, *27th November* 1978; *Com.* 1268.)

---

[1] R. Ball, M. J. Bennet, E. H. Brooks, W. A. G. Graham, J. Hoyano, and S. M. Illingworth, *Chem. Comm.*, 1970, 592.
[2] G. Schmid and G. Etzrodt, *J. Organometallic Chem.*, 1977, **137**, 367.
[3] G. Schmid, V. Bätzel, and G. Etzrodt, *J. Organometallic Chem.*, 1976, **112**, 345.
[4] Ch. Wei and L. F. Dahl, *Inorg. Chem.*, 1967, **6**, 1229.
[5] C. E. Strouse and L. F. Dahl, *J. Amer. Chem. Soc.*, 1971, **93**, 6032.
[6] P. W. Sutton and L. F. Dahl, *J. Amer. Chem. Soc.*, 1967, **89**, 261.
[7] G. Schmid and G. Etzrodt, *J. Organometallic Chem.*, 1977, **131**, 477.