

## Square Bipyramidal $[\text{Co}_4(\text{CO})_{11}(\text{GeMe})_2]$ ; X-Ray Crystal Structure. A New Structure Type for Group 4-Transition Metal Clusters

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$\text{GeMeH}_3$  reacts with  $[\{\text{Co}_2(\text{CO})_7\}_2\text{Ge}]$  to produce  $[\text{Co}_4(\text{CO})_{11}(\text{GeMe})_2]$ ; X-ray structural analysis shows that this has an irregular square bipyramidal structure containing 5-co-ordinated square pyramidal Ge.

Among the wide variety of compounds with Group 4-transition element bonds, polymetallic closed clusters are rare, with only three types reported. A trigonal bipyramid<sup>1</sup> is formed by the  $\text{Sn}_2\text{M}_3$  units in  $[\text{Fe}_3(\text{CO})_9\{\text{SnFe}(\text{CO})_2(\text{C}_3\text{H}_5)\}_2]$  and  $[\text{Pt}_3(\text{cod})_3(\text{SnCl}_3)_2]$  (cod = cyclo-octa-1,5-diene). The trigonal pyramidal  $\text{M}'\text{M}_3$  group is well-established<sup>2</sup> for  $\text{M}' = \text{Si}, \text{Ge}$ ; *e.g.* in compounds of the type  $[\text{Co}_3(\text{CO})_9\text{M}'\text{R}]$ . Finally, one example of an irregular 5-co-ordination is found<sup>3</sup> at the Ge atom in the  $[\text{Co}_5(\text{CO})_{16}\text{Ge}]^-$  ion. The title compound adds a completely new class of germanium-polymetal structure.

In work reported<sup>4</sup> elsewhere, we found a smooth replacement of bridging CO in  $[\{\text{Co}_2(\text{CO})_7\}_2\text{Ge}]^5$  by dimethylgermane, or related hydrides, to give products with linked  $\text{GeCo}_2$  triangles. However, a 1:1 ratio of monomethylgermane and  $[\{\text{Co}_2(\text{CO})_7\}_2\text{Ge}]$  reacts in hexane, in a sealed tube in the dark, over six months to give an unexpected

rearrangement. A significant yield of the polynuclear species<sup>4</sup>  $[\text{Co}_6(\text{CO})_{20}\text{Ge}_2]$  was recovered, and *ca.* 20% of an orange product which recrystallised as plates from a  $\text{CH}_2\text{Cl}_2\text{-C}_6\text{H}_{14}$  mixture. The only volatile product found was  $[\text{Co}(\text{CO})_4\text{-GeMeH}_2]$  (5%).

The first evidence of an anomaly came from the mass spectrum, which showed a parent ion family at  $m/z = 714\text{--}724$  with an isotope intensity pattern appropriate to 2Ge atoms. This indicates a molecule  $\text{C}_{13}\text{H}_6\text{O}_{11}\text{Co}_4\text{Ge}_2$ , *i.e.*  $\text{Co}_4(\text{CO})_{11}\text{Ge}_2\text{Me}_2$ , implying an unexpected transfer of a methyl group. Fragment ions arising from the loss of 11-CO and of two Me groups reinforced this assignment; all other ions were very weak apart from  $\text{Ge}_2\text{Co}_3^+$  and  $\text{MeGe}_2\text{Co}_3^+$ . The carbonyl stretching frequencies ( $\text{cm}^{-1}$ ): 2034vs, 2016m, 2004sh, and 1853w(br.) showed bridging CO, and a pattern unlike any other previously encountered.

The species was then characterised by X-ray crystallo-

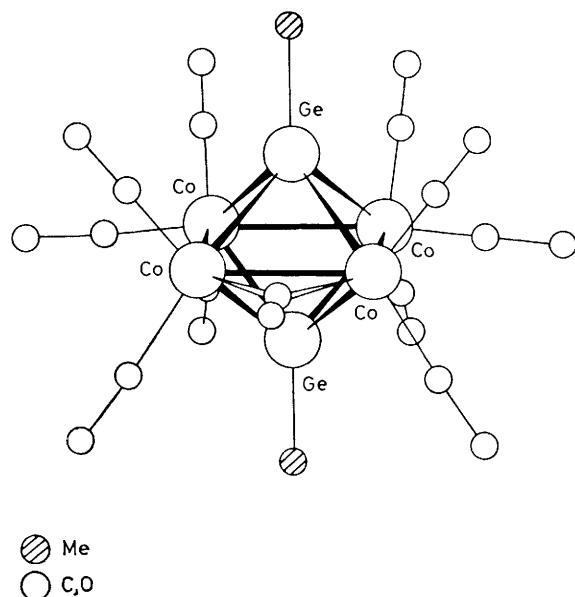


Figure 1

graphy† and found to have the irregular square bipyramidal structure shown in Figure 1. The four Co atoms are co-planar with Co–Co distances (pm) of 258.0 (bridged), two of 269.2 (adjacent to bridge), and 272.1 (opposite). All the Ge–Co distances are very similar, averaging  $239.0 \pm 0.9$  pm, which compares with  $236 \pm 2$  pm<sup>5</sup> in  $[\text{Ge}\{\text{Co}_2(\text{CO})_7\}_2]$ . The Ge...Ge distance of 292.6 pm is only 20% longer than in  $\text{Ge}_2\text{H}_6$ , while the Ge–Me values ( $195 \pm 1$  pm) are normal. The CO bridge is symmetric. It is interesting that there is no

† *Crystal Data*:  $\text{C}_{13}\text{H}_6\text{O}_{11}\text{Co}_4\text{Ge}_2$ ,  $M = 720$ , monoclinic, space group  $C2/m$ ,  $a = 13.755$ ,  $b = 13.94$ ,  $c = 10.88$  Å,  $\beta = 93.19^\circ$ ,  $U = 2082.9$  Å<sup>3</sup>,  $Z = 4$ . The structure was solved from 1214 reflections and refined to  $R = 0.0401$ . The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

asymmetry in the Ge positions, despite the differences in the environments of the cobalt atoms. This is the first example of square pyramidal 5-co-ordination of Ge involving transition metals, although a similar configuration was recently reported<sup>6</sup> in O and S compounds.

Although new for Group 4 elements, this  $\text{E}_2\text{M}_4$  structure type was established<sup>7</sup> a few years ago for the sulphur and phosphorus tetracobalt compounds,  $[\text{Co}_4(\text{CO})_{10}\text{E}_2]$ ,  $\text{E} = \text{S}$  or PPh. Recently Vahrenkamp's<sup>8</sup> group have found the iso-electronic clusters,  $[\text{Fe}_4(\text{CO})_{12}\text{E}_2]$ ,  $\text{E} = \text{PR}$ , and  $[\text{Fe}_2\text{Co}_2(\text{CO})_{11}\text{E}_2]$ ,  $\text{E} = \text{S}$  or PPh. It is noteworthy that all these species contain two skeletal electrons more than the seven pairs expected for a *closo* structure.

Studies of the reaction are proceeding to determine whether it occurs by transfer of a methyl group to the Ge atom in  $[\{\text{Co}_2(\text{CO})_7\}_2\text{Ge}]$ , or whether a more complex sequence of steps occurs with extrusion of this Ge. The observation of  $[\text{Co}_6(\text{CO})_{20}\text{Ge}_2]$  among the reaction products (and the lack of  $\text{GeH}_4$  or  $\text{Ge}_2\text{H}_6$ ) favours the latter interpretation.

Received, 28th June 1982; Com. 751

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