

Polynuclear Carbonylcobalt Derivatives of Silicon and Germanium: X-Ray Structure of $C_6H_5GeCo_3(CO)_{11}$

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Summary The X-ray structure of $PhGeCo_3(CO)_{11}$, prepared from $PhGeH_3$ and $Co_2(CO)_8$, has been determined; the compound may be converted into $PhGeCo_3(CO)_9$ or into unstable $PhGeCo_3(CO)_{12}$.

non-zero unique reflections was collected on a PAILRED diffractometer and absorption corrections applied. The structure was solved by conventional heavy-atom methods, and least-squares refinement with only the heavy atoms

HYDRIDES of silicon and germanium are valuable reagents for the synthesis of polynuclear compounds such as $(Me_2Ge)_3Fe_2(CO)_6$,¹ $Ph_2GeFe_2(CO)_8$,¹ $(Ph_2Ge)_2Fe_2(CO)_7$,² and $Ph_2SiH_2Re_2(CO)_8$.³ We now report the use of these reagents in the preparation of new cobalt carbonyl derivatives, the structures of which demonstrate an important trend among metal-metal bonded compounds of elements of the fourth main group.

The reaction of $PhGeH_3$ with $Co_2(CO)_8$ (n-hexane, room temp.) gave $PhGeCo_3(CO)_{11}$, m.p. 77–78° (decomp.), characterized by analysis and mass spectrometry (all ions of the series $[PhGeCo_3(CO)_n]^+$, $n = 0–11$, were observed). Carbonyl stretching bands were observed in the i.r. spectrum (cyclohexane) at 2104w, 2082s, 2056s, 2044w, 2036s, 2025m, 2014m, 1998w, and 1850w cm^{-1} . In addition, a weak, broad band at 1835 cm^{-1} was observed as a shoulder on the 1850 cm^{-1} band.

The orange crystals of $PhGeCo_3(CO)_{11}$ are monoclinic, space group $P2_1/c$; $a = 9.17$, $b = 13.20$, $c = 18.98$ Å, $\beta = 105^\circ$, $Z = 4$. Using Mo- K_α radiation, a set of 1457

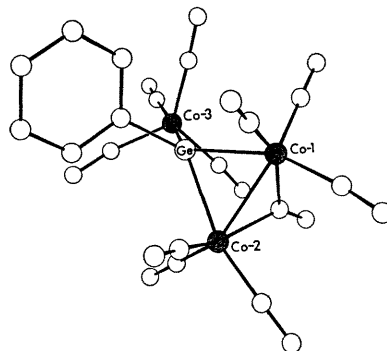


FIGURE. The molecular structure of $PhGeCo_3(CO)_{11}$. Bond lengths (Å) and angles ($^\circ$), with estimated standard deviations in parentheses, are: Ge-Co-3, 2.456(3); Ge-Co-1, 2.375(3); Ge-Co-2, 2.392(3); Co-1-Co-2, 2.546(3); Ge- C_6H_5 , 1.967(8); Co-CO (terminal), 1.75(2) (average value); Co-1-Ge-Co-2, 64.6(1); Co-2-Ge-Co-3, 124.3(1); Co-1-Ge-Co-3, 121.9(1); C_6H_5 -Ge-Co-3, 117.0(3); C_6H_5 -Ge-Co-2, 117.5(3); C_6H_5 -Ge-Co-3, 107.0(3).

anisotropic has given the current R index of 0.073. Examination of the Figure shows that the molecule may be regarded as a derivative of dicobalt octacarbonyl, in which a bridging carbonyl group has been replaced by the $\text{PhGeCo}(\text{CO})_4$ moiety. A comparison of the Co-Co bond length in the $\text{Co}_2(\text{CO})_7$ portion of the structure with that in dicobalt octacarbonyl⁴ (2.52 Å) shows a small but significant increase for the germanium-bridged compound; a similar trend is more marked in related germanium-iron compounds.^{1,2} If the terminal $\text{Co}(\text{CO})_4$ group were replaced by a phenyl group, one would obtain $\text{Ph}_2\text{GeCo}_2(\text{CO})_7$.^{5,6}

An interesting structural feature is the dihedral angle of 95° between the Co-1-Co-2-Ge plane and the bridging carbonyl plane. The appearance of a second bridging carbonyl absorption may be attributed to a second isomer, in which the bridging carbonyl group lies on the phenyl side of the Co-1-Co-2-Ge plane.

When $\text{PhGeCo}_3(\text{CO})_{11}$ is refluxed in *n*-hexane for several hours, it is transformed with loss of CO to black, crystalline $\text{PhGeCo}_3(\text{CO})_9$, also characterized by analysis and mass spectrometry: the i.r. band pattern strongly resembles that of $\text{PhCCo}_3(\text{CO})_9$,⁷ with a shift of about 10 cm^{-1} to lower frequencies in the germanium compound. There is little doubt that $\text{PhGeCo}_3(\text{CO})_9$ has a cluster structure similar to that established⁸ for the carbon analogues. Its

thermal and oxidative stability, however, is much less than that of the unusually stable carbon compounds. Treatment of $\text{PhGeCo}_3(\text{CO})_{11}$ with carbon monoxide at 300 atm afforded $\text{PhGe}[\text{Co}(\text{CO})_4]_3$, recognized by the similarity of its i.r. spectrum to that of $\text{PhSn}[\text{Co}(\text{CO})_4]_3$.⁹ The dodecacarbonyl germanium derivative could not be isolated owing to its rapid loss of carbon monoxide to reform the undecacarbonyl.

Silanes give similar compounds, up to a point. Thus Ph_2SiH_2 gives $\text{Ph}_2\text{SiCo}_2(\text{CO})_7$ (considerably more air-sensitive than its germanium analogue) and PhSiH_3 gives $\text{PhSiCo}_3(\text{CO})_{11}$. So far, attempts to convert the latter into $\text{PhSiCo}_3(\text{CO})_9$ have led only to decomposition; indeed, our attempts to form such nonacarbonyltricobalt derivatives of silicon by the reactions earlier reported to produce them¹⁰ have been unsuccessful.

Tin-cobalt compounds $\text{RSn}[\text{Co}(\text{CO})_4]_3$ do not undergo loss of carbon monoxide to form an isolable analogue of the carbon-cobalt derivatives $\text{RCCo}_3(\text{CO})_9$.⁹ Germanium, perhaps on account of its favourable size, forms compounds of both these categories, as well as an intermediate, partially condensed, type.

We thank the National Research Council of Canada for financial support.

(Received, March 24th, 1970; Com. 424.)

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