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A COBALT–GERMANIUM BOND: THE STRUCTURE OF $Co[Ge(C_6H_5)_3](CO)_3[P(C_6H_5)_3]$

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SUMMARY

The structure of $Co[Ge(C_6H_5)_3](CO)_3[P(C_6H_5)_3]$ has been determined from X-ray data collected by counter methods. The material crystallizes with eight molecules in space group $C_{2h}^6 = I2/a$ in a cell of dimensions $a = 18.703(6)$, $b = 15.469(6)$, $c = 24.013(8)$ Å, $\beta = 105°42(1)'$. The final conventional R factor for the 1345 reflections above background is 0.092. The coordination about Co is that of a trigonal bipyramid, with equatorial carbonyl groups and partially disordered $Ge(C_6H_5)_3$ and $P(C_6H_5)_3$ axial groups. The Co–Ge bond length of 2.34(2) Å is consistent with a degree of Co–Ge multiple bonding.

Complexes with metal–metal bonds between transition metals and the group IVB metals, silicon, germanium, tin, and lead, have been the subject of much interest[1]. Particular emphasis has been placed on the relative importance of σ- and π-bonding in these complexes; Brown *et al.*[2] in a ^{59}Co nuclear quadrupole resonance study of compounds of the type $Co(MX_3)(CO)_4$ (M = a group IV element and X = halide or organic group) have found evidence for Co–Ge and Co–Sn π-bonding. Such π-bonding had previously been postulated[3] for Co–Si bonding in $Co(SiCl_3)(CO)_4$.

Curtis[4] has prepared the series of complexes $Co[M(C_6H_5)_3](CO)_3[P(C_6H_5)_3]$ for M = Si, Ge, and Sn. The infrared spectra of these compounds exhibit two bands in the carbonyl stretching region, suggesting a C_{3v} trigonal-bipyramidal configuration similar to that found[5] for $Co(SiCl_3)(CO)_4$. The determination of the structure of (triphenylgermyl)tricarbonyl(triphenylphosphine)cobalt(I), $Co[Ge(C_6H_5)_3](CO)_3[P(C_6H_5)_3]$, reported here was undertaken to provide the first determination of the Co–Ge bond distance, with possible concomitant evidence on π-bonding.

EXPERIMENTAL

Colorless crystals of $Co[Ge(C_6H_5)_3](CO)_3[P(C_6H_5)_3]$ were kindly supplied by Professor M. D. Curtis. Small, thin needles were obtained by recrystallization from a benzene/ethanol solution. A long needle of approximate dimensions 0.04 × 0.07 × 0.72 mm was attached to the end of a glass fiber and mounted on a eucentric goniometer head. Weissenberg and precession photographs exhibited monoclinic symmetry, with the *b*-axis parallel to the needle axis. Systematic absences were observed for hkl, $h+k+l \neq 2n$, and $h0l$, $h \neq 2n$, indicating space groups C_s^4–Ia or C_{2h}^6–$I2/a$. The cell parameters as determined from diffractometer measurements using Cu $K\alpha$ radiation ($\lambda = 1.54056$ Å) are $a = 18.703(6)$, $b = 15.469(6)$, $c = 24.013(8)$ Å; $\beta = 105°\ 42(1)'$ (temp. 22°). The calculated density for eight molecules per cell is 1.41 g/cm^3, which agrees fairly well with the observed value of 1.36 ± 0.04 g/cm^3 obtained by flotation in CF_2ClCCl_2F/ethanol solution.

A unique data set was collected to $2\theta = 36°$ using Mo $K\alpha$ radiation and techniques as previously described[6]. The data were processed to correct for background, and standard deviations were assigned using a value of 0.04 for p. Of the 2326 data collected, 1891 were above background $[F_o^2 > \sigma(F_o^2)]$, but only the 1345 reflections for which $F_o^2 \geqslant 3\sigma(F_o^2)$ were used in the solution and refinement of the structure. No correction for absorption was applied, as test calculations indicated less than a 2% difference between minimum and maximum transmission coefficients.

A three-dimensional Patterson function was computed, and this readily yielded the positions of the Co, Ge, and P atoms, assuming the centric space group $I2/a$. {The equipoints of $I2/a$ are $(000, \frac{1}{2}\frac{1}{2}\frac{1}{2}) + [\pm(x,y,z), \pm(\frac{1}{2}-x,y,\bar{z})]$.} Three cycles of least-squares refinement resulted in discrepancy factors $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$ and $R_2 = \{\Sigma[w\cdot(|F_o|-F_c|)^2]/\Sigma(w\cdot F_o^2)\}^{\frac{1}{2}}$ of 0.366 and 0.464, respectively. Throughout the refinement process the function minimized was $\Sigma[w\cdot(|F_o|-|F_c|)^2]$, with the weights w taken as $4F_o^2/\sigma^2(F_o^2)$. The atomic scattering factors for Co, Ge, P, C, and O were those tabulated by Ibers[7], and the values of Cromer[8] for $\Delta f'$ and $\Delta f''$ were used for the anomalous scattering contribution to F_c by Co, Ge, and P[9]. Two difference Fourier maps interspersed with a least-squares refinement led to the positions of all remaining nonhydrogen atoms. The six phenyl rings were treated as rigid groups[10,11] of known geometry and dimensions (C–C = 1.392 Å) with a single group temperature factor, and three cycles of least-squares refinement resulted in values of $R_1 = 0.119$ and $R_2 = 0.149$. This refinement, however, exhibited some disturbing features: the temperature factor for Ring 3 was very high ($B = 12$ Å^2), and the temperature factor for P was negative ($B = -0.7$ Å^2) while that for Ge was rather large ($B = 5.9$ Å^2) compared with the value of 3.5 Å^2 for Co. It is possible that Ring 3 is simply disordered slightly because of packing forces, but there is also the possibility of disorder of the $P(C_6H_5)_3$ and $Ge(C_6H_5)_3$ groups. To test this hypothesis, a refinement was carried out assuming an average scattering for Ge and P, such that $f(\text{"Ge"}) = \alpha\cdot f(\text{Ge}) + (1-\alpha)\cdot f(\text{P})$ and $f(\text{"P"}) = \alpha\cdot f(\text{P}) + (1-\alpha)\cdot f(\text{Ge})$. One cycle of least-squares refinement, ignoring the anomalous dispersion of Ge and P, led to a value of 0.65 for α, gave reasonable temperature factors for "Ge" and "P" of 3.4 and 3.3 Å^2, respectively, and lowered the discrepancy factors to $R_1 = 0.092$ and $R_2 = 0.108$. The positions of the Co, Ge, and P atoms did not change. The final parameters* then correspond to those for an average structure with 65% of the molecules in one orientation Ge–Co–P and 35% in the reversed orientation, P–Co–Ge. The atomic and group parameters are listed in Table 1. The highest peak on a final difference Fourier map was 1.9 e/Å^3, compared with an average value of 3.6 e/Å^3 for a carbon atom; most peaks were in the vicinity of Ring 3.

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* Refinement of an ordered arrangement of two independent molecules in the asymmetric unit of space group Ia did not reduce the value of R_2 significantly nor did it lead to reasonable values for the isotropic thermal parameters of the P and Ge atoms. For these reasons we adopt the disordered arrangement of molecules in $I2/a$ as the description of the structure.

TABLE 1

ATOMIC AND GROUP PARAMETERS FOR $Co[Ge(C_6H_5)_3](CO)_3[P(C_6H_5)_3]$

Atom[a]	x	y	z	B (Å^2)
Co	0.0331(2)	0.1769(2)	0.2536(1)	3.8(1)
Ge	0.0173(2)	0.1685(2)	0.3470(1)	3.4(1)
P	0.0626(2)	0.1823(3)	0.1680(2)	3.3(1)
C_1	−0.021(1)	0.268(2)	0.240(1)	4.3(6)
O_1	−0.062(1)	0.327(1)	0.229(1)	7.0(5)
C_2	−0.006(2)	0.079(2)	0.238(1)	5.3(7)
O_2	−0.039(1)	0.013(1)	0.228(1)	7.0(5)
C_3	0.124(2)	0.183(2)	0.287(1)	7.1(8)
O_3	0.189(1)	0.193(1)	0.311(1)	7.5(5)

Group[b]	x_c	y_c	z_c	δ	ε	η	B
Ring 1	−0.1591(6)	0.1836(6)	0.3492(5)	−0.84(2)	−1.99(1)	−0.81(2)	4.9(3)
Ring 2	0.1029(5)	0.3265(7)	0.4309(5)	0.65(1)	2.57(1)	−2.53(1)	5.0(3)
Ring 3	0.0908(10)	−0.0080(12)	0.4170(7)	−1.34(3)	2.69(2)	−2.66(2)	13.2(6)
Ring 4	−0.0763(6)	0.1420(6)	0.0534(5)	1.13(1)	−2.39(1)	1.05(1)	4.6(3)
Ring 5	0.1337(6)	0.3665(8)	0.1430(5)	2.72(1)	−2.31(1)	−1.52(1)	5.8(3)
Ring 6	0.1835(7)	0.0369(8)	0.1576(4)	−0.73(1)	2.88(1)	2.88(1)	6.1(3)

[a] x, y, and z are in fractional coordinates. B is the isotropic thermal parameter in Å^2. The standard deviations of the least significant figures are given in parentheses. [b] x_c, y_c, and z_c are the fractional coordinates of the group centers. The angles δ, ε, and η (in radians) which bring about alignment (except for translation) of an internal coordinate system within the ring with a fixed external coordinate system are those previously described[10,11].

DISCUSSION

The molecular configuration is illustrated in Fig. 1; it can be seen that, except for interchanging Ge and P, the molecule very nearly possesses a two-fold rotation axis passing through the Co, C_3, and O_3 atoms. The geometry of the molecule is trigonal-bipyramidal, with the three carbonyls in the equatorial plane; the six phenyl rings are eclipsed, and are staggered with respect to the three carbonyl groups. It is probable that the existence of the *pseudo*-two-fold axis permits the disorder, as the phenyl rings, which ordinarily determine the packing of molecules in a structure of this type, must be related by a symmetry operation if disordering is to occur.

A few selected bond distances and angles are presented in Table 2. The standard deviation in the Co–Ge distance, as estimated from the inverse matrix, is 0.004 Å. The uncertainty in this distance resulting from the partial disorder of the Ge and P atoms has been estimated in the following way. Examination of superimposed theoretical electron density distributions for Ge and P suggests that the center of the 65% Ge density distribution is displaced less than 0.01 Å by the presence of a 35% P density distribution assumed to lie 0.08 Å away. Thus we believe that a realistic estimated standard deviation for the Co–Ge distance is 0.02 Å. The Co–Ge bond of 2.34 Å is 0.08 Å longer than the Co–P bond, as would be expected on the basis of covalent radii assuming equivalent π-bonding in the Co–Ge and Co–P bonds. If the covalent radius

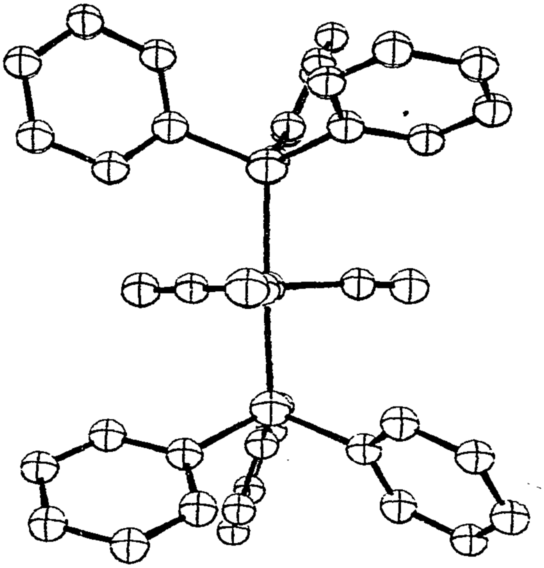

Fig. 1. Perspective view of $Co[Ge(C_6H_5)_3](CO)_3[P(C_6H_5)_3]$. View is looking down the $Co-C_3-O_3$ two-fold axis.

TABLE 2

SELECTED INTERATOMIC DISTANCES (Å) AND BOND ANGLES (DEGREES)

Atoms	Distance	Atoms	Angle
Co–Ge	2.34(2[a])	Ge–Co–P	173
Co–P	2.26	C_1–Co–C_2	118(1)
Co–C_1	1.69(3)	C_1–Co–C_3	122(1)
Co–C_2	1.71(3)	C_2–Co–C_3	120(1)
Co–C_3	1.70(3)	Co–C_1–O_1	178(2)
C_1–O_1	1.19(3)	Co–C_2–O_2	175(3)
C_2–O_2	1.15(4)	Co–C_3–O_3	175(3)
C_3–O_3	1.16(4)		
Ge–Ring C	1.93(3[b])		
P–Ring C	1.87(2[b])		

[a] See text for a discussion of this error estimate. [b] Standard deviation of a single observation estimated from the three individual distances.

of Co is taken as 1.34 Å* and that of Ge as 1.22 Å[14], then a single Co–Ge bond length should be approximately 2.56 Å. The observed shortening of 0.22 Å is consistent with a degree of Co–Ge multiple bonding, but does not provide sufficient evidence to eliminate alternative explanations for the lengths of metal–Group IVb bonds. (See, for example, the discussion of Fe–Sn bond lengths in ref. 15.) Contractions of this order have been noted in a number of M–Si bonds[16] and in an Fe–Ge bond[17].

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* This covalent radius is derived from the Co–Co bond distance in $[(CH_3CN)_5Co]_2^{4+}$ (see ref. 12) and $Co_2(CO)_6[P(C_4H_9)_3]_2$ (see ref. 13).

The determination of the structures of the remaining two complexes in this series, $Co[Si(C_6H_5)_3](CO)_3[P(C_6H_5)_3]$ and $Co[Sn(C_6H_5)_3](CO)_3[P(C_6H_5)_3]$, was not attempted because of this disorder observed for the germanium complex.

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