Crystal Structure of a Five-membered Cobalt–Germanium–Iron Heterocycle, $\{(\pi\text{-}C_5H_5)Co(CO)\}_2(GeCl_2)_2Fe(CO)_4$

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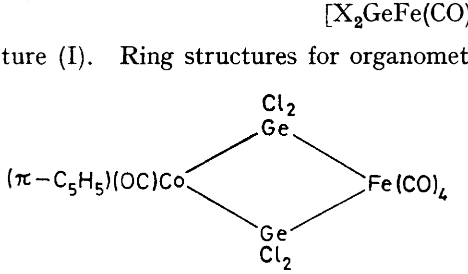
The title compound has been shown by single-crystal X-ray analysis to contain a five-membered Co–Ge–Fe–Ge–Co ring, which is planar within error limits and exhibits the bond distances Fe–Ge 2·438(4), Ge–Co 2·341(9), and Co–Co 2·439(5) Å. The crystals are orthorhombic, space-group $P2_12_12_1$, with a = 39·26(2), b = 12·16(1), and c = 9·82(1) Å, and Z = 8. 3032 above-background reflections were collected by counter methods and refined to 7·0%. For least-squares refinement purposes the cyclopentadienyl rings were treated as rigid groups undergoing hindered rotation.

CRYSTAL structure analysis of $\{(\pi\text{-}C_5H_5)Co(CO)\}_2(GeCl_2)_2Fe(CO)_4$ was undertaken in order to establish its molecular structure. A preliminary report of this work has been published previously.[1] The compound was isolated from the reaction products of $Fe(CO)_5$ and $(\pi\text{-}C_5H_5)(OC)Co(GeCl_3)_2$, and the molecular formula was determined by mass spectrometry.[1] By analogy with reaction (1),[2] the reaction should have yielded a product of

$$Fe(CO)_5 + cis\text{-}(GeX_3)_2Fe(CO)_4 \longrightarrow [X_2GeFe(CO)_4]_2 \tag{1}$$

structure (I). Ring structures for organometallic com-



(I)

pounds such as this have been established for $[R_2SnFe(CO)_4]_2$ (four-membered ring)[3] and $Ph_2GeFe_2(CO)_8$ (three-membered ring).[4] The present structure is the first five-membered ring of this type whose structure has been confirmed.

EXPERIMENTAL

Crystal Data.—$C_{16}H_{10}Cl_4Co_2FeGe_2O_6$, M = 758·9, Orthorhombic, a = 39·26(2), b = 12·161(8), c = 9·82(1) Å, U = 4688 Å^3, D_m = 2·17 (by flotation), Z = 8, D_c = 2·15, $F(000)$ = 2928. Space-group $P2_12_12_1$ from systematic extinctions. Cu-K_α radiation, λ = 1·5418 Å; μ(Cu-K_α) = 254 cm^{-1}.

Small black crystals suitable for X-ray work were obtained according to the method of ref. 1, and were stable both in air and when exposed to X-rays. Unit-cell parameters were obtained with a crystal mounted about the c axis. The dimensions a and b were derived from least-squares fits of measurements made with a PAILRED diffractometer by a previously described method.[5] The third dimension was obtained from a precession photograph corrected for film shrinkage.

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[4] E. H. Brooks, M. Elder, W. A. G. Graham, and D. Hall, *J. Amer. Chem. Soc.*, 1968, **90**, 3587.

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Intensity data were collected on a PAILRED fully automated diffractometer equipped with a scintillation counter, by use of Cu-K_α radiation monochromatized by a graphite single crystal (002 reflection). A single crystal of regular dimensions $0{\cdot}12 \times 0{\cdot}14 \times 0{\cdot}16$ mm mounted on a glass fibre with the *c* axis coincident with the machine rotation axis was used for data collection. A moving-crystal stationary-counter (ω-scan) technique was employed. The scan range of 3·0° ($\theta \leqslant 15°$) and 2·0° ($\theta > 15°$) used for μ 0° was increased regularly to 4·4 and 2·8° respectively at μ 39° to accommodate the increasing peakwidth at higher levels. The scan speed was 2·5° min^{-1}. Each reflection was measured until the raw count at the end of a scan exceeded 4000 or until the reflection had been scanned three times. This method enhances the significance of reflections with intensity close to background and allows a faster scan speed than usual to be employed. Background was measured for 20 s at the end of each scan. A counter aperture of 1·5° was used with the pulse-height analyser centred on the K_α peak and set to accept 90% of the peak. Counter linearity for the peaks of highest intensity was confirmed by re-scanning on reduced voltages. Data within $\theta < 50°$ were collected from levels *hk*0—8. Four well spaced zero-level reflections, measured as standards after each level, had a maximum variation of 4% from the mean. There was no systematic trend to indicate crystal instability.

The intensities were corrected for background and standard errors estimated according to $I = T - tB$ and $\sigma^2(I) = T + t^2B + (kI)^2$ where T is the raw count, B the total background, and t a scale factor to bring T and B to the same time scale. A value of 0·06 was used for k. A significance criterion $I > 2{\cdot}5\sigma(I)$ yielded 3042 above background reflections after combination of data for which k or l were zero. Data of the form *hkl* and $\bar{h}kl$ were not combined in view of the large anomalous scattering of Cu-K_α radiation by iron and cobalt atoms. Lorentz and polarization corrections were applied together with absorption corrections computed by integration over a 512 point grid.*

Structure Analysis.—The three-dimensional Patterson function sharpened to point atoms at rest was computed, and used to locate the metal atoms. Consideration of the Patterson maxima within 4·5 Å of the origin indicated that the heavy atoms of the two independent molecules were approximately planar, and that the planes were perpendicular, respectively, to the x and y axes. A vector search method applied to these near-origin regions yielded trial orientations for two slightly distorted pentagons. Consideration of the Harker sections, together with the implication maps of the two models, produced trial orientations of the two molecules in the unit cell. The remaining non-hydrogen atoms were located from Fourier electron density maps. The structure was refined by full-matrix least-squares techniques, minimizing the function $\Sigma w(|F_o| - |F_c|)^2$ where $w = 1/\sigma^2(F)$. Scattering factors for neutral atoms were taken from ref. 6 together with anomalous dispersion corrections for chlorine ($\Delta f' = 0{\cdot}33$, $\Delta f'' = 0{\cdot}72$), iron ($\Delta f' = -1{\cdot}13$, $\Delta f'' = 3{\cdot}45$), cobalt ($\Delta f' = -2{\cdot}51$, $\Delta f'' = 3{\cdot}95$), and germanium ($\Delta f' = -1{\cdot}31$, $\Delta f'' = 1{\cdot}04$).[7] The alternate refinement of the parameters of each molecule, with all atoms given isotropic temperature factors yielded R 0·082 and R' 0·085 (where $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$). On the evidence of an electron difference map the metal and chlorine atoms and the carbon atoms of the rings were given anisotropic temperature factors and refinement continued to R 0·071 and R' 0·074. At this point the cyclopentadienyl rings were treated as rigid groups of D_{5h} symmetry undergoing hindered rotation, following the method of ref. 8. For each ring the usual six parameters define the centre of gravity (fractional co-ordinates x_c, y_c, and z_c) and the orientation (angles D, E, and F).[9] The remaining parameters are R, the ring radius, B, which allows for out-of-plane oscillations and motion of the centre of gravity of the ring,[10] and Bd which measures the oscillation about the metal–ring axis. The mathematical method for handling the least-squares equations has been described in detail,[12] but is summarized here. The calculation assumes the rigid group is undergoing oscillations in the plane of the ring. These oscillations are governed by a potential which is a sinusoidal function of the angle in the ring. The scattering from the group is given [8,10] by (2) where h is the reciprocal lattice vector,

$$F_h = f_j \exp\,[B_j \sin^2\theta/\lambda^2]\,\exp\,[2\pi i h\,.\,k_j]M_n{}^F(a_j,Bd_j) \qquad (2)$$

k_j the vector from the origin to the centre of ring j, and $M_n{}^F(a_j,Bd_j)$ is a slightly modified form of the Lipscomb–King M function.[8] The parameter a_j describes the orientation and size of the ring. All parameters were refined by full-matrix least-squares techniques. The reduction in variable parameters achieved by this method (9 parameters for a rigid rotor as against 45 for five anisotropic atoms) allowed all parameters to be varied simultaneously in the final refinement cycles. The hydrogen atoms were included in positions calculated by taking C–H = 1·0 Å, with the same parameters as the carbon rings. These parameters were not refined but were adjusted after each cycle. The hydrogen scattering curve was taken from ref. 11. The final agreement ratios were R 0·070 and R' 0·071, which represents an appreciable decrease in view of the smaller number of variable parameters. This indicates that in the present case it is less physically reasonable to assign anisotropic thermal ellipsoids to the ring carbon atom than to allow motion of the atoms along the arc of a circle. An attempt to refine the atoms of the carbonyl groups anisotropically resulted in physically unreal values for some of these parameters, indicating that the data were not of sufficient accuracy to support such a refinement.

There was no evidence of the need for an extinction correction. The correctness of the arbitrary assignment of all-positive indices to one quadrant of data was indicated by comparison of the calculated structure factors for reflections where the forms *hkl* and $\bar{h}kl$ exhibited appreciable differences in observed structure factors. This was confirmed by an R factor ratio test [13] on the agreement factors obtained by refinement with the signs of the h indices reversed. The final difference map showed no anomalous regions of electron density, with a maximum residual of

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TABLE 1

Positional and thermal parameters, molecule (1)

Atom	x/a	y/b	z/c	$B/\text{Å}^2$
Fe(1)	0·1995(1)	0·6158(3)	1·0225(4)	
Co(1)	0·1791(1)	0·8939(3)	0·7816(4)	
Co(2)	0·1778(1)	0·9560(3)	1·0172(4)	
Ge(1)	0·1930(1)	0·7065(3)	0·8025(3)	
Ge(2)	0·1886(1)	0·7917(3)	1·1323(3)	
Cl(1)	0·1563(2)	0·6082(8)	0·6837(9)	
Cl(2)	0·2397(2)	0·6725(7)	0·6803(8)	
Cl(3)	0·1461(2)	0·7605(7)	1·2774(7)	
Cl(4)	0·2315(2)	0·8168(6)	1·2780(6)	
C(1)	0·1545(7)	0·593(2)	1·013(3)	4·5(7)
O(1)	0·1255(4)	0·585(2)	1·009(2)	4·9(4)
C(2)	0·2439(6)	0·652(2)	1·012(2)	2·5(5)
O(2)	0·2716(4)	0·677(2)	1·015(2)	5·5(5)
C(3)	0·2065(8)	0·489(3)	0·931(4)	6·2(9)
O(3)	0·2108(6)	0·411(2)	0·875(3)	8·4(7)
C(4)	0·2045(8)	0·559(3)	1·192(4)	6·2(8)
O(4)	0·2030(6)	0·525(2)	1·301(3)	8·2(7)
C(5)	0·1464(7)	0·876(2)	0·915(3)	4·1(7)
O(5)	0·1183(4)	0·837(2)	0·926(2)	4·0(4)
C(6)	0·2152(6)	0·921(2)	0·907(2)	3·0(6)
O(6)	0·2451(4)	0·918(1)	0·909(2)	3·5(4)

Atom	β_{11} *	β_{22}	β_{33}	β_{12}	β_{13}	β_{23} ($\times 10^4$)
Fe(1)	7·1(3)	46(3)	81(5)	−1(1)	−5(1)	−4(4)
Co(1)	4·7(3)	52(4)	74(5)	2(1)	−2(1)	−3(4)
Co(2)	5·2(3)	42(3)	86(5)	0(1)	−1(1)	−26(4)
Ge(1)	6·0(2)	47(3)	67(3)	0(1)	−1(1)	−11(3)
Ge(2)	5·1(2)	61(3)	59(3)	0(1)	−1(1)	−3(3)
Cl(1)	15·1(8)	103(9)	165(12)	−18(2)	−19(3)	2(9)
Cl(2)	11·4(7)	97(8)	165(11)	13(2)	19(2)	21(9)
Cl(3)	8·2(9)	117(8)	87(8)	−7(2)	6(2)	−3(7)
Cl(4)	7·4(5)	84(7)	110(8)	1(2)	−9(2)	−34(9)

* The expression for the anisotropic thermal ellipsoid is $T = \exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$

1·15 eÅ^{-3} near the metal atoms. The validity of the experimental weights and the constant k 0·06 in the expression for $\sigma^2(I)$ was confirmed by the near constancy of $\Sigma w(|F_o| - |F_c|)^2$ for reflections grouped both by $\sin\theta/\lambda$ and by F_o values. The final structure factor listing may be obtained as a supplementary publication, No. SUP 20251 (5 pp., 1 microfiche).* The final atomic parameters are listed in Tables 1 and 2, together with their standard deviations obtained from the last cycle of refinement in which all parameters were refined and none changed by more than 0·1σ. The parameters for groups undergoing hindered rotation are given in Table 3.

TABLE 2

Positional and thermal parameters, molecule (2)

Atom	x/a	y/b	z_4c	$B/\text{Å}^2$
Fe(2)	0·0982(1)	0·3196(4)	0·4524(4)	
Co(3)	−0·0065(1)	0·3132(3)	0·3762(3)	
Co(4)	0·0006(1)	0·3030(4)	0·6231(3)	
Ge(3)	0·0499(1)	0·3207(2)	0·2996(2)	
Ge(4)	0·0598(1)	0·3044(3)	0·6451(3)	
Cl(5)	0·0582(2)	0·1906(6)	0·1454(7)	
Cl(6)	0·0572(2)	0·4615(6)	0·1657(8)	
Cl(7)	0·0756(2)	0·1562(6)	0·7631(7)	
Cl(8)	0·0757(2)	0·4311(6)	0·7927(9)	
C(7)	0·0962(7)	0·173(3)	0·440(3)	5·5(7)
O(7)	0·0946(5)	0·080(2)	0·428(2)	4·8(5)
C(8)	0·0926(8)	0·473(3)	0·463(4)	6·8(9)
O(8)	0·0888(5)	0·560(2)	0·479(2)	6·7(6)
C(9)	0·1253(8)	0·339(3)	0·297(4)	7·3(9)
O(9)	0·1429(5)	0·340(2)	0·207(2)	7·5(6)
C(10)	0·1323(8)	0·318(3)	0·567(3)	6·4(8)
O(10)	0·1533(5)	0·308(2)	0·653(2)	6·6(5)
C(11)	0·0060(6)	0·198(2)	0·487(2)	3·1(5)
O(11)	0·0141(4)	0·100(2)	0·478(2)	3·9(4)
C(12)	0·0044(7)	0·424(2)	0·500(3)	4·1(6)
O(12)	0·0108(4)	0·521(2)	0·503(2)	4·1(4)

Atom	β_{11} *	β_{22}	β_{33}	β_{12}	β_{13}	β_{23} ($\times 10^4$)
Fe(2)	5·6(3)	48(4)	106(5)	0(1)	−1(1)	−11(4)
Co(3)	5·3(3)	30(3)	55(4)	2(1)	0(1)	0(3)
Co(4)	6·7(3)	32(3)	56(4)	2(1)	1(1)	1(4)
Ge(3)	5·3(2)	30(2)	57(3)	1(1)	3(1)	−4(3)
Ge(4)	6·1(2)	42(2)	63(3)	3(1)	−2(1)	−10(3)
Cl(5)	8·6(6)	59(6)	94(8)	7(2)	3(2)	3(8)
Cl(6)	10·0(6)	52(6)	141(11)	−1(2)	4(2)	35(7)
Cl(7)	10·3(6)	78(7)	119(10)	12(2)	0(2)	37(7)
Cl(8)	14·0(8)	94(8)	138(11)	0(2)	−11(3)	−67(9)

* See footnote to Table 1.

TABLE 3

Cyclopentadienyl parameters

Ring	x_c *	y_c	z_c	B	Bd	R	D	E	F
(2)	0·1732(4)	0·949(1)	0·622(1)	3·4(5)	0·8(2)	1·22(1)	3·52(1)	0·12(1)	5·11(3)
(3)	0·1706(4)	1·077(1)	1·103(2)	3·2(5)	0·5(1)	1·22(1)	4·11(1)	2·84(2)	4·39(4)
(4)	−0·0394(3)	0·321(1)	0·261(1)	2·9(4)	2·0(4)	1·20(1)	3·20(2)	0·81(1)	2·38(2)
(5)	−0·0256(3)	0·295(1)	0·764(1)	3·1(4)	1·4(2)	1·21(1)	6·23(2)	2·54(1)	5·88(2)

Derived positional co-ordinates for ring carbon atoms

Atom	x/a	y/b	z/c	Atom	x/a	y/b	z/c
C(21)	0·1863(9)	1·035(2)	0·658(2)	C(41)	−0·0554(4)	0·254(2)	0·321(2)
C(22)	0·2039(4)	0·941(3)	0·603(2)	C(42)	−0·0573(4)	0·368(2)	0·340(1)
C(23)	0·1790(9)	0·858(2)	0·574(2)	C(43)	−0·0345(5)	0·418(1)	0·249(2)
C(24)	0·1462(6)	0·900(3)	0·611(2)	C(44)	−0·0184(5)	0·335(2)	0·174(1)
C(25)	0·1507(7)	1·009(2)	0·663(2)	C(45)	−0·0313(5)	0·233(1)	0·219(2)
C(31)	0·1872(12)	1·131(2)	1·022(2)	C(51)	−0·0486(4)	0·255(2)	0·698(1)
C(32)	0·1513(11)	1·111(2)	1·015(5)	C(52)	−0·0430(5)	0·369(2)	0·722(2)
C(33)	0·1421(7)	1·045(2)	1·130(3)	C(53)	−0·0134(5)	0·380(2)	0·804(2)
C(34)	0·1723(14)	1·024(2)	1·207(3)	C(54)	−0·0006(3)	0·273(2)	0·830(1)
C(35)	0·2001(6)	1·077(3)	1·141(5)	C(55)	−0·0223(6)	0·196(1)	0·765(2)

* See text.

All computing was carried out on an IBM360 67 computer. Programs used were: FORDAP, a Fourier summation program by A. Zalkin; SFLS5, full-matrix least-squares, by C. T. Prewitt, modified for group refinement by M. J. Bennett and B. Foxman, and for hindered-rotor

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refinement by W. L. Hutcheon; GNABS, absorption corrections, D. P. Shoemaker; ORTEP, plotter program. C. K. Johnson; and ORFFE2, the molecular geometry program by W. R. Busing and H. A. Levy, modified by R. J. Doedens, and by us to accommodate hindered rotor parameters.

RESULTS

The molecular structure of $(\pi\text{-}C_5H_5CoCO)_2(GeCl_2)_2Fe(CO)_4$ is shown in the Figure. The thermal ellipsoids of the anisotropic atoms are scaled to include 50% probability. The hydrogen atoms are not shown. The molecular geometry is tabulated in Tables 4 and 5. Cell parameter errors were taken into account in the calculation of the standard errors. The intermolecular distances are normal with no non-bonded contacts being appreciably shorter than the sum of the appropriate van der Waals radii.

TABLE 4

Intramolecular distances (Å)

(*a*) Bonding

Fe(1)–Ge(1)	2·439(5)	Fe(2)–Ge(3)	2·437(5)
Fe(1)–Ge(2)	2·433(5)	Fe(2)–Ge(4)	2·444(5)
Ge(1)–Co(1)	2·352(5)	Ge(3)–Co(3)	2·344(4)
Ge(2)–Co(2)	2·334(5)	Ge(4)–Co(4)	2·334(5)
Co(1)–Co(2)	2·434(6)	Co(3)–Co(4)	2·444(5)
Ge(1)–Cl(1)	2·206(8)	Ge(3)–Cl(3)	2·177(8)
Ge(1)–Cl(2)	2·230(7)	Ge(3)–Cl(4)	2·214(8)
Ge(2)–Cl(3)	2·231(7)	Ge(4)–Cl(5)	2·231(8)
Ge(2)–Cl(4)	2·227(7)	Ge(4)–Cl(6)	2·206(8)
Co(1)–C(5)	1·85(3)	Co(3)–C(11)	1·84(3)
Co(1)–C(6)	1·91(3)	Co(3)–C(12)	1·86(3)
Co(2)–C(5)	1·86(3)	Co(4)–C(11)	1·86(3)
Co(2)–C(6)	1·87(3)	Co(4)–C(12)	1·91(3)
C(5)–O(5)	1·21(3)	C(11)–O(11)	1·24(3)
C(6)–O(6)	1·17(3)	C(12)–O(12)	1·21(3)
Fe(1)–C(1)	1·79(4)	Fe(2)–C(7)	1·79(4)
Fe(1)–C(2)	1·80(2)	Fe(2)–C(8)	1·89(4)
Fe(1)–C(3)	1·80(4)	Fe(2)–C(9)	1·85(4)
Fe(1)–C(4)	1·81(4)	Fe(2)–C(10)	1·73(3)
C(1)–O(1)	1·14(4)	C(7)–O(7)	1·14(3)
C(2)–O(2)	1·13(3)	C(8)–O(8)	1·08(4)
C(3)–O(3)	1·11(3)	C(9)–O(9)	1·13(3)
C(4)–O(4)	1·15(3)	C(10)–O(10)	1·19(3)
Co(1)–C(21)	2·12(4)	Co(3)–C(41)	2·12(4)
Co(1)–C(22)	2·08(4)	Co(3)–C(42)	2·13(3)
Co(1)–C(23)	2·08(4)	Co(3)–C(43)	2·09(4)
Co(1)–C(24)	2·12(4)	Co(3)–C(44)	2·06(4)
Co(1)–C(25)	2·14(4)	Co(3)–C(45)	2·07(4)
C(21)–C(22)	1·44(1)	C(41)–C(42)	1·41(1)
Co(2)–C(31)	2·16(4)	Co(4)–C(51)	2·14(4)
Co(2)–C(32)	2·15(4)	Co(4)–C(52)	2·12(4)
Co(2)–C(33)	2·09(4)	Co(4)–C(53)	2·08(4)
Co(2)–C(34)	2·05(4)	Co(4)–C(54)	2·07(4)
Co(2)–C(35)	2·10(5)	Co(4)–C(55)	2·11(5)
C(31)–C(32)	1·43(1)	C(51)–C(52)	1·42(1)

(*b*) Non-bonding

C(1) · · · C(3)	2·53(5)	C(7) · · · C(9)	2·71(5)
C(1) · · · C(4)	2·66(5)	C(7) · · · C(10)	2·59(5)
C(2) · · · C(3)	2·59(5)	C(8) · · · C(9)	2·64(5)
C(2) · · · C(4)	2·61(5)	C(8) · · · C(10)	2·66(5)
C(3) · · · C(4)	2·70(5)	C(9) · · · C(10)	2·68(5)
Cl(1) · · · Cl(2)	3·37(1)	Cl(5) · · · Cl(6)	3·30(1)
Cl(3) · · · Cl(4)	3·42(1)	Cl(7) · · · Cl(8)	3·36(1)

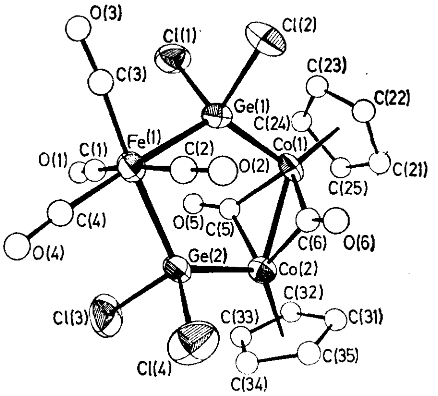
DISCUSSION

The structure of $\{(\pi\text{-}C_5H_5)CoCO\}_2(GeCl_2)_2Fe(CO)_4$ is based upon a planar five-membered ring of metal atoms. The two independent molecules of the asymmetric unit exhibit no significant differences. In Table 6 the mean

TABLE 5

Bond angles (deg.)

Ge(1)–Fe(1)–Ge(2)	88·7(2)	Ge(3)–Fe(2)–Ge(4)	89·0(2)
Co(1)–Ge(1)–Fe(1)	122·7(2)	Co(3)–Ge(3)–Fe(2)	123·2(2)
Co(2)–Ge(2)–Fe(1)	124·7(2)	Co(4)–Ge(4)–Fe(2)	123·7(2)
Co(1)–Co(2)–Ge(2)	101·0(2)	Co(3)–Co(4)–Ge(4)	101·8(2)
Co(2)–Co(1)–Ge(1)	102·9(2)	Co(4)–Co(3)–Ge(3)	102·3(2)
Co(1)–C(5)–Co(2)	82·0(1)	Co(3)–C(11)–Co(4)	83·0(1)
Co(1)–C(6)–Co(2)	80·0(1)	Co(3)–C(12)–Co(4)	82·0(1)
Cl(1)–Ge(1)–Cl(2)	98·7(4)	Cl(5)–Ge(3)–Cl(6)	97·5(3)
Cl(3)–Ge(2)–Cl(4)	100·3(3)	Cl(7)–Ge(4)–Cl(8)	98·3(3)
C(5)–Co(1)–C(6)	94·0(1)	C(11)–Co(3)–C(12)	96·0(1)
C(5)–Co(2)–C(6)	95·0(1)	C(11)–Co(4)–C(12)	94·0(1)
Ge(1)–Co(1)–C(5)	89·1(8)	Ge(3)–Co(3)–C(11)	88·1(7)
Ge(1)–Co(1)–C(6)	86·6(7)	Ge(3)–Co(3)–C(12)	87·9(8)
Ge(2)–Co(2)–C(5)	86·2(8)	Ge(4)–Co(4)–C(11)	87·6(7)
Ge(2)–Co(2)–C(6)	86·7(8)	Ge(4)–Co(4)–C(12)	88·6(8)
Ge(1)–Fe(1)–C(1)	86·0(1)	Ge(3)–Fe(2)–C(7)	85·0(1)
Ge(1)–Fe(1)–C(2)	86·0(1)	Ge(3)–Fe(2)–C(8)	86·0(1)
Ge(1)–Fe(1)–C(3)	88·0(1)	Ge(3)–Fe(2)–C(9)	86·0(1)
Ge(1)–Fe(1)–C(4)	175·0(1)	Ge(3)–Fe(2)–C(10)	177·0(1)
Ge(2)–Fe(1)–C(1)	89·0(1)	Ge(4)–Fe(2)–C(7)	86·0(1)
Ge(2)–Fe(1)–C(2)	89·0(1)	Ge(4)–Fe(2)–C(8)	88·0(1)
Ge(2)–Fe(1)–C(3)	176·0(1)	Ge(4)–Fe(2)–C(9)	174·0(1)
Ge(2)–Fe(1)–C(4)	87·0(1)	Ge(4)–Fe(2)–C(10)	87·0(1)
C(1)–Fe(1)–C(2)	172·0(1)	C(7)–Fe(2)–C(8)	169·0(1)
C(1)–Fe(1)–C(3)	89·0(2)	C(7)–Fe(2)–C(9)	96·0(2)
C(1)–Fe(1)–C(4)	95·0(2)	C(7)–Fe(2)–C(10)	94·0(2)
C(2)–Fe(1)–C(3)	92·0(2)	C(8)–Fe(2)–C(9)	90·0(2)
C(2)–Fe(1)–C(4)	92·0(2)	C(8)–Fe(2)–C(10)	94·0(2)
C(3)–Fe(1)–C(4)	97·0(2)	C(9)–Fe(2)–C(10)	96·0(1)
Fe(1)–C(1)–O(1)	175·0(4)	Fe(2)–C(7)–O(7)	178·0(3)
Fe(1)–C(2)–O(2)	175·0(3)	Fe(2)–C(8)–O(8)	175·0(4)
Fe(1)–C(3)–O(3)	180·0(3)	Fe(2)–C(9)–O(9)	172·0(3)
Fe(1)–C(4)–O(4)	171·0(3)	Fe(2)–C(10)–O(10)	173·0(3)
Co(1)–C(5)–O(5)	138·0(2)	Co(3)–C(11)–O(11)	139·0(2)
Co(2)–C(5)–O(5)	140·0(2)	Co(4)–C(11)–O(11)	141·0(3)
Co(1)–C(6)–O(6)	138·0(3)	Co(3)–C(12)–O(12)	138·0(2)
Co(2)–C(6)–O(6)	141·0(2)	Co(4)–C(12)–O(12)	138·0(3)



The molecular structure of $(\pi\text{-}C_5H_5)Co(CO)\}_2(GeCl_2)_2Fe(CO)_4$

TABLE 6

Mean bond distances (Å) and angles (deg.)

(*a*) Bonds

Fe–Ge	2·438(4) *	Co–C(CO)	1·87(3)
Ge–Co	2·341(9)	Co–C(π-C_5H_5)	2·10(3)
Co–Co	2·439(5)	C–C	1·42(1)
Fe–C	1·81(4)	O–C(term.)	1·13(3)
Ge–Cl	2·22(2)	O–C(br.)	1·21(3)

(*b*) Angles

Ge–Fe–Ge	88·2(2)	Ge–Fe–C	87(1)
Fe–Ge–Co	123·6(8)	Cl–Ge–Cl	98·7(12)
Ge–Co–Co	102·0(8)	Ge–Co–C	87·6(10)
C–Fe–C	93(3)	Co–C–Co	95(1)

* The errors quoted are computed according to $[\sum_n (x - \bar{x})^2/(n - 1)]^{\frac{1}{2}}$.

bond lengths and angles are grouped for convenience. Averaging has been carried out over all equivalent values in both molecules and the errors quoted are standard deviations from the mean. The molecule exhibits approximate non-crystallographic C_{2v}-mm symmetry if the individual atoms of the cyclopentadienyl rings are ignored: one mirror plane passes through the five metal atoms whilst the second contains the iron atom, two terminal carbonyl groups, and the bridging carbonyl groups. The deviations from these planes, listed in Table 7, indicate how closely the symmetry is maintained.

TABLE 7

Equations of best least-squares planes in the form $Ax + By + Cz + D = 0$ where x, y, and z are co-ordinates in Å, with deviations (Å) of atoms from the plane given in square brackets

Atoms	A	B	C	D	χ^2 *
Plane (1)					
Fe(1), Ge(1), Ge(2), Co(1), Co(2)	0·9778	−0·2080	0·0246	−9·0231	151
[Fe(1) −0·009, Ge(1) −0·024, Ge(2) 0·009, Co(1) 0·026, Co(2) −0·020]					
Plane (2)					
Fe(2), Ge(3), Ge(4), Co(3), Co(4)	0·0256	0·9979	0·0588	4·0265	54
[Fe(2) −0·016, Ge(3) 0·010, Ge(4) 0·018, Co(3) 0·000, Co(4) −0·012]					
Plane (3)					
Fe(1), C(1), C(2), C(5), C(6)	0·0450	0·2817	0·9584	11·3331	9·8
[Fe(1) −0·047, C(1) 0·039, C(2) 0·009, C(5) −0·020, C(6) 0·018]					
Plane (4)					
Fe(2), C(7), C(8), C(11), C(12)	−0·1149	−0·0511	0·9921	4·6454	1·4
[Fe(2) −0·019, C(7) 0·019, C(8) 0·001, C(11) −0·013, C(12) 0·012]					

* χ^2 is defined by $\sum_i d_i^2/\sigma_i^2$ where d_i is the deviation of an atom from the plane and σ_i is the atom's positional standard deviation.

It is evident from a consideration of the molecular geometry that ring closure has been achieved with very little strain. The bond angles about the metal atoms closely parallel those in similar structures where there are no constraints imposed by the requirements of bridging. The Ge–Fe–Ge angle is 88·8(2)°, slightly less than octahedral, as are the C–Fe–Ge angles, mean 87(1)°. The C–Fe–C angles are correspondingly slightly larger at 93(3)°. The Fe–Ge distance is 2·438(5) Å, somewhat longer than the distances 2·357(4) in $(Cl_2Ge)[(\pi$-$C_5H_5)Fe(CO)_2]_2$ (ref. 14) and 2·28(1) Å in $(\pi$-$C_5H_5)(\pi$-$C_4H_6)Fe(GeCl_2Me)$.[15] It is postulated that in the latter compound, which contains the shortest Fe–Ge distance yet observed, strong $d_\pi(Fe) \rightarrow d_\pi(Ge)$ back-donation is enhanced by the weak π-acceptor properties of the ligands π-C_5H_5 and π-C_4H_6 attached to the iron atom. It is certainly reasonable that the three molecules, with respectively four, two, and zero carbonyl groups, which are relatively strong π-acceptors, should exhibit a progressively decreasing Fe–Ge distance. Two other Fe–Ge distances where there are only carbonyl groups on the iron atom, 2·398(4) in $(Me_2Ge)_3Fe_2(CO)_6$ (ref. 16) and 2·422(3) Å in $(GePh_2)Fe_2(CO)_7$ (ref. 17) are also at the long end of this range, although they must also be affected by the germanium atoms bridging short Fe–Fe distances. An even longer distance, 2·492 Å, occurs in the four-membered ring $[Fe(CO)_4(GeEt_2)]_2$,[18] where, although the Fe–Ge–Fe angle is acute, there is no Fe–Fe bond, and electron-acceptor ability of the $GeEt_2$ entity is less than that of a $GeCl_2$ group.

The co-ordination around the germanium atoms is very similar to that in $(Cl_2Ge)[(\pi$-$C_5H_5)Fe(CO)_2]_2$ (ref. 14) where the two Fe–Ge bonds are free to adopt any orientation. The Fe–Ge–Fe and Cl–Ge–Cl angles are respectively 128·4(2) and 96·1(2) in the latter compound and 123·6(9) (for Fe–Ge–Co) and 98·7(13)° in the present molecule. The mean Ge–Cl distance is an unexceptional 2·22(2) Å.

The geometry of the $Co_2(CO)_2(\pi$-$C_5H_5)_2$ portion of the molecule is based upon the $Co_2(CO)_8$ structure.[19] The cyclopentadienyl groups can be regarded as replacing the terminal carbonyl ligands *trans* to the bridging groups, whilst the two remaining terminal carbonyl groups are replaced by germanium atoms. Thus the π-cyclopentadienyl groups are dichoric in King's terminology,[20] replacing two carbonyl groups whilst providing the five electrons needed to satisfy the inert-gas rule for the cobalt atoms. The Ge–Co distances average 2·341(9) Å, shorter than the values 2·383(3) Å for Ge bridging a $Co_2(CO)_7$ entity and 2·456(3) Å for Ge–Co(CO)$_4$ observed in $(PhGe)Co_3(CO)_{11}$.[21] The argument of Adrianov *et. al.*[15] applied to these Ge–Co bonds would indeed predict a shorter Ge–Co length when carbonyl groups are replaced by a π-cyclopentadienyl ligand. The same reasoning may apply to the Co–Co distance which is 2·439(5) Å, appreciably shorter than the 2·52 Å in $Co_2(CO)_8$,[16] although the Co–C distances and the Co–C–O angles are the same in both structures. Sutton and Dahl[22] list a range of Co–Co distances of 2·43—2·64 which makes the 2·44 Å in this molecule one of the shortest yet observed. It does not seem possible that the shortening is due to ring closure constraints since a longer distance could be accommodated by either twisting the cobalt atoms out of the plane of the remaining three metal atoms or by increasing the Fe–Ge–Co angle toward the comparable value in the unconstrained $(Cl_2Ge)[(\pi$-$C_5H_5)Fe(CO)_2]_2$.

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The mean Co–C distance for the cyclopentadienyl rings is 2·10(3) Å, and the mean C–C(ring) distance is 1·42(1) Å. Both these values agree with those given in Wheatley's review,[23] 2·069 and 1·42(2) Å. The hindered-rotor model moves the atoms along the arc of a circle and so no ' riding ' correction is necessary. Thus the bond lengths obtained from the hindered-rotor refinement should be compared with the thermally corrected values given by Wheatley.

The value of parameter *Bd* is an indication of the amount of rotation the group undergoes. A value of infinity would give no rotation while one of zero would result in free rotation. Intermediate values are directly related to the root mean square angular displacement of the group. Root-mean-square angular displacement values for the four cyclopentadienyl rings are given in Table 8.

TABLE 8

Root-mean-square angular displacements for ring carbon atoms

Ring	*Bd*	Displacement (deg.)	B_{iso} *
(2)	0·8(2)	15(1)	6·3
(3)	0·5(1)	17(1)	6·9
(4)	2·0(4)	10(1)	4·1
(5)	1·4(2)	12(1)	4·9

* B_{iso} is an equivalent isotropic temperature factor calculated according to $B_{iso} = B + 8/3\pi^2R^2\bar{u}^2$.

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