bonding. When compared with distances of ~2.6 and ~2.5 Å for single and double bonds, it suggests the presence of a triple or quadruple bond.

The rotational configuration of the $Mo_2Cl_8^{4-}$ ion is again found to be eclipsed (crystallographic symmetry C_i; virtual symmetry D_{4h}), which requires the presence of a significant δ component in the Mo–Mo bond and thus shows that this bond is quadruple.

In this compound the $Mo_2Cl_8^{4-}$ ion has a very regular square parallelepiped structure, which comes very close to containing a cubic array of eight Cl atoms. The bases of the parallelepiped formed by the sets of Cl atoms bound to each of the Mo atoms are square within the chemical significance of the data. The edges all lie within the range 3.332–3.367 Å and the Cl–Cl–Cl angles run from 89.4 to 90.4°. The vertical edges of the parallelepipid are 3.41 ± 0.01 Å. These vertical

edges are longer than the eight basal edges by 0.06 Å, an amount which is highly significant statistically and undoubtedly this difference is real. Still, the difference is small both relatively (<2%) and in relation to the probable amplitudes of vibration for the Cl atoms, and thus the array of eight Cl atoms is scarcely different from cubic.

It may be noted that there is still no firm evidence that the treatment of $Mo_2(O_2CCH_3)_4$ with mineral acids produces other than dinuclear products.

The dimensions of the $H_3NCH_2CH_2NH_3^{2+}$ ion are normal and require no particular comment. It is interesting to note that the H_2O molecules are held by hydrogen bonding to the $-NH_3^+$ groups but do not engage their own H atoms in any strong hydrogen bonding. This is consistent with the inference from the infrared spectrum as discussed earlier.

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The Crystal and Molecular Structure of μ-Carbonyl-bis-μ-diphenylgermanium-bis(tricarbonyliron), $[Ge(C_6H_5)_2]_2Fe_2(CO)_7$

BY M. ELDER

The structural determination by single-crystal X-ray methods of μ-carbonyl-bis-μ-diphenylgermanium-bis(tricarbonyliron), $[Ge(C_6H_5)_2]_2Fe_2(CO)_7$, is described. The compound crystallizes in the triclinic space group $P\bar{1}$ with a = 10.705 ± 0.004 Å, b = 10.916 ± 0.004 Å, c = 13.702 ± 0.005 Å, α = 103° 19′ ± 4′, β = 96° 39′ ± 4′, and γ = 101° 53′ ± 3′. There are two molecules per unit cell, calculated density 1.68 g cm⁻³. The density measured by flotation is 1.70 ± 0.02 g cm⁻³. A total of 1860 independent observations above background were collected by counter methods using crystal-monochromatized Mo Kα radiation. The structure was refined by least-squares methods to a conventional R factor of 4.9%. Hydrogen atoms were included and the phenyl groups were refined using the rigid-body approximation. The molecule has two tricarbonyliron groups linked by an iron–iron bond of 2.666 (3) Å which is bridged by two diphenylgermanium groups and a carbonyl group. The Fe–Ge distances are in the range 2.402–2.440 Å and the Fe–Fe bond subtends 66.8° at the germanium atoms. There are small deviations in the symmetry of the bridge system. The germanium ligands are slightly closer to one iron atom and the carbonyl group is displaced slightly toward the other.

Introduction

The crystal structure analysis of $[Ge(CH_3)_2]_3Fe_2(CO)_6$ has been described previously.[1] The structure proved to be based upon that of iron enneacarbonyl, with the three bridging carbonyl groups replaced by bridging dimethylgermanium groups. The Fe–Fe distance in the germanium-bridged complex was considerably longer than in the carbonyl, though short enough to imply an Fe–Fe bond. The preparation of a compound with formula $[Ge(C_6H_5)_2]_2Fe_2(CO)_7$, postulated to contain an Fe–Fe bond bridged by two germanium atoms and a carbonyl group,[2] provided an interesting opportunity to obtain more information about the structural details of these germanium-bridged iron carbonyls. In particular, it seemed of interest to determine the effect of the bridging carbonyl group upon the

Fe–Fe distance and the bridging angles of the germanium diphenyl ligands.

Experimental Section

Crystals of $[Ge(C_6H_5)_2]_2Fe_2(CO)_7$ were obtained as small red-black prisms. Preliminary photographs, both Weissenberg with Cu Kα radiation ($hk0$–$hk3$) and precession with Mo Kα radiation ($h0l$ and $0kl$), indicated a triclinic space group. Reciprocal cell parameters were taken from the precession photographs of levels ($h0l$) and ($0kl$), except for the angle γ^* which came from measurements made with the diffractometer, with a crystal mounted about the c axis.[3] Measurement of the precession photographs and the calculation of errors were performed according to Patterson and Love[4] and a sodium chloride (a_{NaCl} = 5.6402 Å) photograph on the same type of film was measured in the same way in order to calibrate the camera and to correct for film shrinkage. Final bond length calculations indicate that the cell parameter errors contribute about 25% of the error in an Fe–Ge distance. Final values for the real lattice parameters (λ 0.71069 Å, Mo Kα, 27°) are: a = 10.705 ± 0.004 Å, b =

(1) M. Elder and D. Hall, *Inorg. Chem.*, **8**, 1424 (1969).
(2) E. H. Brooks and W. A. G. Graham, to be submitted for publication.

(3) M. Elder and D. Hall, *Inorg. Chem.*, **8**, 1273 (1969).
(4) A. L. Patterson and W. E. Love, *Am. Mineralogist*, **45**, 325 (1960).
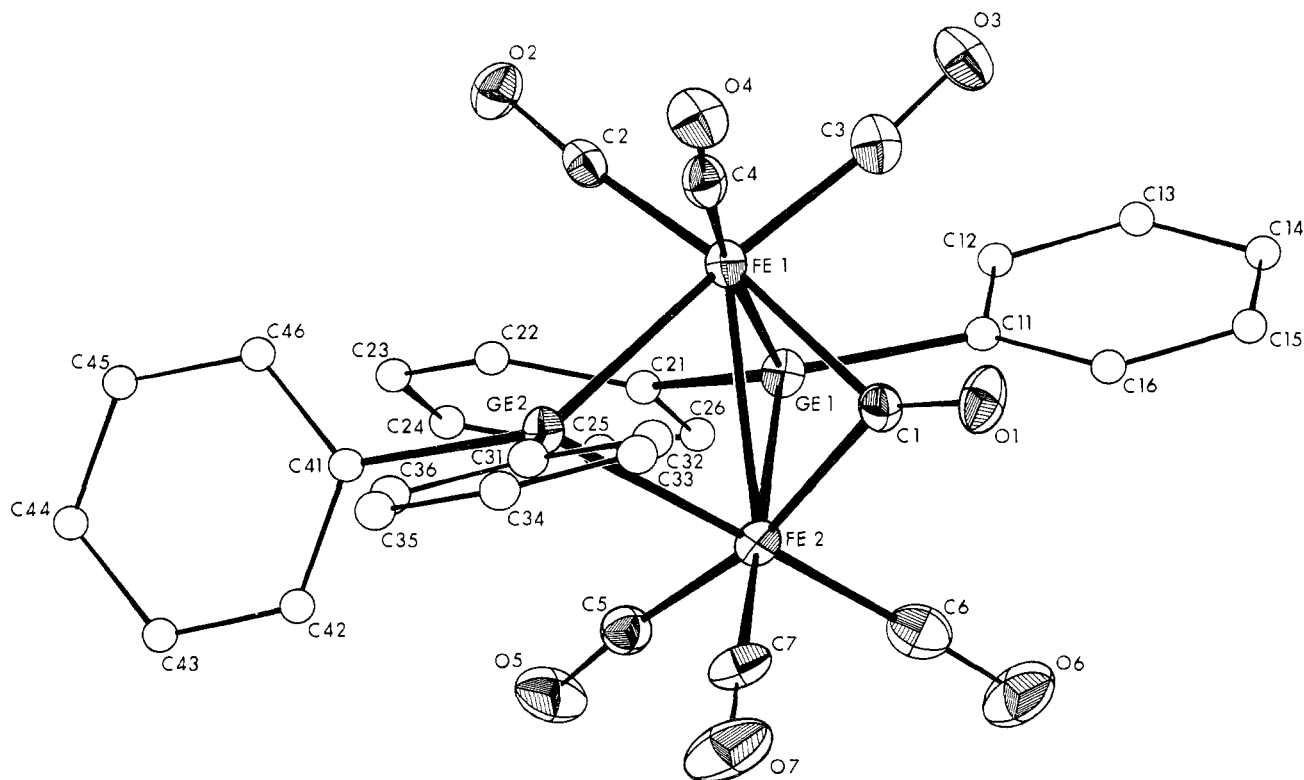
Figure 1.—The molecular structure of [Ge(C$_6$H$_5$)$_2$]$_2$Fe$_2$(CO)$_7$. The thermal ellipsoids are scaled to include 20% probability. The carbon atoms of the phenyl groups have artificial *B* factors of 2.0.

10.916 ± 0.004 Å, *c* = 13.702 ± 0.005 Å, *α* = 103° 19' ± 4', *β* = 96° 39' ± 4', and *γ* = 101° 53' ± 3'. All reflections were indexed with respect to this reduced cell. The space group C$_i^1$-P$\overline{1}$ was assumed, in view of the fact that there were apparently two molecules per unit cell, and confirmed by the appearance of the Patterson map and the successful structure refinement. The calculated density is 1.68 g cm^{-3} for two molecules of formula weight 761.4 per unit cell, volume 1502.2 Å^3. The density measured by flotation in a thallous formate solution was 1.70 ± 0.02 g cm^{-3}, in agreement with the calculated value.

Intensity data were collected on a PAILRED fully automated diffractometer equipped with a scintillation counter, using Mo Kα radiation monochromatized from the [111] face of a silicon crystal. The single crystal used for data collection was fixed inside a thin-walled Lindemann glass capillary and mounted with the *c* axis along the spindle. The data from the 12 reciprocal lattice levels (*hk*0) to (*h,k*,11) were collected out to a maximum *θ* = 22°. For all levels except the zero level the crystal was rotated by 180° about the spindle axis after the first half of each level had been scanned; thus the four forms *hkl*, *h̄kl*, *hk̄l*, and *h̄k̄l* were collected. A scan rate of 1°/min was employed. The scan range was increased regularly from 1.4° for (*hk*0) to 4.0° for (*h,k*,11) to accommodate the increasing peak width with increasing inclination angle. Background was measured for 0.4 min with the crystal stationary at the extremes of the scan range; this time was increased to 1.0 min for levels higher than the sixth in order to lessen the disparity between the total background and the total scan times. A counter aperture of 1.5° was used. Five reflections from well-spaced regions of reciprocal space within the (*hk*0) levels were scanned after each level had been collected as a check of consistency. They indicated no counter or crystal instability throughout the data collection, showing random fluctuation of intensity of less than 2%. The intensity, *I*, and variance estimate, *σ*^{2}(*I*), for each reflection were calculated from *I* = *T* − *tB* and *σ*^{2}(*I*) = *T* + *t*^{2}*B* + (0.01*I*)^2, where *T* is the total count, *B* the sum of the two background counts, and *t* the ratio of time of total count to the total background time. Reflections were treated as above background for *I* ≥ 2.5(*T* +

t^2*B*)$^{1/2}$, resulting in 1860 unique above-background observations. Lorentz and polarization corrections were applied to all data, but no absorption correction was used. The linear absorption coefficient is 31.4 cm^{-1} for Mo Kα radiation. The crystal used for data collection was an irregular chunk of mean radius 0.12 mm. Neglect of absorption corrections is estimated to cause a maximum error in intensity of 11% in a few extreme cases.

Structure Determination and Refinement

The positions of the four heavy atoms were located by inspection of the sharpened Patterson function. Structure factors calculated for these atoms were used to phase a Fourier map which sufficed to locate the remaining nonhydrogen atoms. This trial structure was then refined by least-squares techniques with individual isotropic atomic temperature factors and an over-all scale factor.[5] The weight for each reflection was derived from the previously defined intensity variances according to *w* = 1/*σ*^{2}(*F*) where *σ*(*F*)/*F* = 0.5*σ*(*I*)/*I*. The 1860 independent above-background observations were used. The *R* factors defined by *R$_1$* = Σ||*F$_o$*| − |*F$_c$*||/Σ|*F$_o$*| and *R$_2$* = [Σ*w*(|*F$_o$*| − |*F$_c$*|)^2/Σ*w*|*F$_o$*|^2]$^{1/2}$ were *R$_1$* = 0.067 and *R$_2$* = 0.083 after five cycles of refinement based upon |*F$_o$*|. A difference map was calculated at this stage to confirm the correctness of the structure. There were indications of con-

(5) Programs used in this work were either written for or modified here for an IBM 360/67 computer with 768K storage. The NRC system of F. R. Ahmed, National Research Council, Ottawa, was used, together with W. R. Busing and H. A. Levy's least-squares program ORFLS, C. K. Johnson's thermal ellipsoid plotter program ORTEP, and the molecular geometry program ORFFE2 by Busing and Levy, modified by R. J. Doedens and altered by the present author to handle functions involving atoms of rigid-body groups. Toward the end of refinement C. T. Prewitt's SFLS5, modified by M. J. Bennett and B. Foxman to include a rigid-body routine, became available together with a modified version of A. Zalkin's Fourier program FORDAP.

TABLE I

Observed and Calculated Structure Factor Amplitudes (×10)

siderable anisotropic motion of the metal atoms, so refinement was continued with these atoms given anisotropic temperature factors. R factors of 0.054 and 0.062, respectively, were obtained. A further significant[6] reduction to 0.048 and 0.056 accompanied subsequent refinement with the carbonyl groups allowed to vibrate anisotropically. At this point a second difference electron density map clearly located 18 of the 20 hydrogen atoms and indicated some anisotropic motion of the phenyl carbon atoms. In order to reduce the

number of variable parameters and to prevent undue emphasis being placed upon the relatively unimportant phenyl groups in the refinement the rigid-body refinement routine of program SFLS5 was then employed. Atomic scattering factors for neutral germanium, iron, oxygen, and carbon were taken from the compilation of Ibers,[7] and the correction for anomalous dispersion was included in F_c for the germanium ($\Delta f' = 0.21$ e$^-$, $\Delta f'' = 1.94$ e$^-$) and iron ($\Delta f' = 0.37$ e$^-$, $\Delta f'' = 0.92$ e$^-$)

(6) W. C. Hamilton, "Statistics in Physical Science," Ronald Press Co., New York, N. Y., 1964.

(7) "International Tables for X-Ray Crystallography," Vol. III, Kynoch Press, Birmingham, England, 1962.

curves.[8] The hydrogen form factors were those determined experimentally by Mason and Robertson.[9] Carbon and hydrogen rigid-body parameters were derived from the previous carbon atom coordinates assuming an ideal distance of 1.397 Å from the center of gravity of a ring to the carbon atoms and that the C–H distance was 1.08 Å. Refinement of an over-all scale factor, positional and anisotropic temperature parameters for all atoms except the phenyl groups, and positional and orientation parameters for the four carbon atom rigid bodies, together with individual isotropic temperature factors for these carbon atoms, yielded final agreement factors $R_1 = 0.049$ and $R_2 = 0.060$. The hydrogen atoms were given the isotropic temperature factors of the carbon atoms to which they were attached, and the hydrogen rigid-body parameters were reset in accordance with the carbon atom values after each cycle. There were no shifts greater than one-fifth of the corresponding standard deviation in the last cycle. The standard deviation of an observation of unit weight was 1.35 indicating that the constant 0.06 in the expression for $\sigma^2(I)$ had been reasonably well chosen. A final difference Fourier map showed residual electron density within the range ± 0.55 e$^-$/Å^3. The phenyl carbon atoms ranged in height from 2.1 to 5.3 e$^-$/Å^3 on this scale, and much of the residual density was associated with these atoms in such a way as to suggest vibrational motion of the rings that was not taken into account by the individual isotropic thermal parameters. Final observed and calculated structure factor amplitudes are listed in Table I. The data show no evidence of the need for a secondary extinction correction.

Results

The molecular structure of the compound [Ge(C$_6$H$_5$)$_2$]$_2$Fe$_2$(CO)$_7$ is shown in Figure 1. An indication of the directions and amplitudes associated with the principal axes of thermal vibration of the anisotropic atoms is given in the figure. Table II lists the positional and anisotropic thermal parameters for the metal atoms and the carbonyl groups. The centers of gravity and orientation angles of the phenyl groups are listed in Table III. Details of the rigid-body angle parameters are defined in a paper by Beauchamp, *et al.*[10] The molecular dimensions calculated from the parameters in Tables II and III are given in Table IV (distances and angles). The program ORFFE2[5] was modified to calculate functions and their errors for cases when rigid-body atoms are involved. Thus all bond length and bond angle errors include allowance for correlation between parameters and for errors in the unit cell parameters. There are no intermolecular contacts less than the appropriate van der Waals distances.

(8) D. T. Cromer, *Acta Cryst.*, **18**, 20 (1965).

(9) R. Mason and G. B. Robertson in "Advances in Structure Research by Diffraction Methods," Vol. 2, R. Brill and R. Mason, Ed., Interscience Division, John Wiley & Sons, Inc., New York, N. Y., 1966, p 57.

(10) A. L. Beauchamp, M. J. Bennett, and F. A. Cotton, *J. Am. Chem. Soc.*, **90**, 6675 (1968).

Table II

Final Atomic Parameters[a]

A. Fractional Coordinates and Equivalent Isotropic Temperature Factors

Atom	x	y	z	B_{eq}[b] Å^2
Ge(1)	0.2350 (1)	0.3858 (1)	0.2577 (1)	3.15
Ge(2)	-0.1050 (1)	0.2112 (1)	0.1985 (1)	3.02
Fe(1)	0.0611 (2)	0.3006 (2)	0.1132 (1)	2.78
Fe(2)	0.0279 (2)	0.4229 (2)	0.2971 (1)	3.14
C(1)	0.0087 (12)	0.4736 (12)	0.1676 (9)	3.2
O(1)	-0.0171 (9)	0.5528 (9)	0.1326 (7)	4.9
C(2)	0.1098 (12)	0.1525 (13)	0.0885 (9)	3.2
O(2)	0.1431 (8)	0.0575 (9)	0.0651 (7)	4.4
C(3)	0.1765 (13)	0.3813 (13)	0.0497 (11)	4.0
O(3)	0.2481 (9)	0.4229 (10)	0.0015 (8)	5.3
C(4)	-0.0680 (13)	0.2530 (12)	0.0037 (11)	3.4
O(4)	-0.1403 (9)	0.2245 (9)	-0.0715 (7)	4.6
C(5)	0.0622 (12)	0.3475 (13)	0.3995 (12)	4.0
O(5)	0.0842 (11)	0.3096 (11)	0.4692 (8)	6.7
C(6)	0.1152 (14)	0.5845 (17)	0.3691 (12)	5.0
O(6)	0.1649 (11)	0.6871 (12)	0.4175 (9)	7.4
C(7)	-0.1258 (15)	0.4488 (13)	0.3245 (10)	4.4
O(7)	-0.2215 (11)	0.4667 (11)	0.3470 (9)	7.9

B. Anisotropic Temperature Factors × 10^4

Atom	β_{11}[c]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ge(1)	62 (2)	76 (2)	50 (1)	18 (1)	-5 (1)	19 (1)
Ge(2)	66 (6)	66 (2)	52 (1)	14 (1)	7 (1)	22 (1)
Fe(1)	57 (2)	62 (2)	47 (1)	10 (2)	2 (1)	20 (2)
Fe(2)	65 (2)	71 (2)	49 (1)	18 (2)	2 (1)	10 (1)
C(1)	81 (15)	62 (15)	45 (9)	0 (12)	12 (9)	13 (10)
O(1)	136 (13)	77 (11)	86 (8)	43 (10)	-3 (8)	35 (8)
C(2)	66 (15)	89 (17)	41 (9)	-2 (12)	4 (9)	24 (10)
O(2)	96 (11)	83 (11)	84 (8)	36 (9)	14 (7)	17 (8)
C(3)	76 (16)	102 (17)	65 (11)	15 (14)	-11 (11)	37 (11)
O(3)	98 (12)	159 (15)	76 (8)	8 (10)	7 (8)	53 (9)
C(4)	77 (16)	73 (15)	64 (11)	26 (12)	11 (11)	37 (10)
O(4)	87 (11)	143 (13)	55 (7)	23 (9)	-21 (7)	35 (8)
C(5)	90 (17)	88 (17)	63 (12)	23 (13)	18 (11)	15 (11)
O(5)	207 (18)	200 (17)	42 (7)	43 (13)	8 (8)	42 (9)
C(6)	89 (18)	148 (23)	74 (12)	35 (17)	21 (12)	31 (14)
O(6)	157 (16)	131 (15)	100 (10)	-7 (13)	-1 (9)	-35 (10)
C(7)	103 (19)	105 (18)	53 (10)	32 (15)	5 (11)	-7 (10)
O(7)	109 (14)	193 (17)	131 (11)	57 (13)	18 (10)	-35 (11)

[a] Numbers in parentheses in this and following tables are estimated standard deviations in the last significant figure. [b] B_{eq} is an isotropic temperature factor computed from: $B_{eq} = {}^4/_3(\beta_{11}a^2 + \beta_{22}b^2 + \beta_{33}c^2 - 2\beta_{12}ab - 2\beta_{13}ac - 2\beta_{23}bc)$. [c] The anisotropic ellipsoid has the form: $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$.

Discussion

The molecule has the same basic structure as diironenneacarbonyl, Fe$_2$(CO)$_9$,[11] and the related [Ge(CH$_3$)$_2$]$_3$Fe$_2$(CO)$_6$. Two Fe(CO)$_3$ entities are linked by an Fe–Fe bond which is bridged by three ligands, in this case two germanium diphenyl groups and one carbonyl group. The Fe–Fe distance is long, at 2.666 (3) Å, though not so long as the 2.75 (1) Å found in the tris-(germanium dimethyl) complex. It has been observed previously[12] that in this type of complex bridging sulfur atoms are associated with long Fe–Fe bonds, and bridging carbonyl groups are associated with Fe–Fe bonds rather shorter than those found in nonbridged complexes. The evidence of the two germanium-bridged complexes indicates that long Fe–Fe bonds are also associated with bridging germanium atoms, presumably because of the greater size of germanium compared with carbon or sulfur. The decrease in the Fe–Fe bond length that occurs when a germanium

(11) H. M. Powell and R. V. G. Ewens, *J. Chem. Soc.*, 286 (1937).

(12) M. R. Churchill, *Inorg. Chem.*, **6**, 190 (1967).

TABLE III

RIGID-BODY PARAMETERS

A. Centers of Gravity and Rotation Angles

Ring[a]	Fractional coordinates			Angles, radians		
	x_c	y_c	z_c	D	E	F
1	0.4603 (7)	0.6355 (7)	0.2329 (5)	5.916 (6)	0.252 (7)	3.829 (6)
2	0.3762 (7)	0.2092 (8)	0.3840 (6)	3.489 (7)	2.501 (8)	5.515 (8)
3	−0.4137 (6)	0.1974 (6)	0.1038 (4)	3.803 (6)	2.998 (7)	2.923 (7)
4	−0.1096 (6)	−0.0375 (6)	0.3032 (5)	6.064 (6)	1.316 (6)	0.909 (6)

B. Derived Positional Coordinates and Isotropic Temperature Factors

Atom	x	y	z	B, Å^2
C(11)[b]	0.3666 (9)	0.5351 (8)	0.2481 (6)	3.7 (3)
C(12)	0.4935 (10)	0.5224 (8)	0.2460 (7)	5.8 (4)
C(13)	0.5872 (9)	0.6228 (10)	0.2308 (5)	7.2 (4)
C(14)	0.5540 (10)	0.7359 (8)	0.2177 (6)	6.8 (4)
C(15)	0.4270 (10)	0.7487 (8)	0.2198 (7)	5.8 (4)
C(16)	0.3333 (9)	0.6483 (10)	0.2350 (5)	4.6 (3)
C(21)	0.3173 (11)	0.2809 (12)	0.3286 (8)	3.9 (3)
C(22)	0.2643 (8)	0.1482 (12)	0.3117 (6)	5.2 (3)
C(23)	0.3232 (12)	0.0764 (8)	0.3671 (9)	7.9 (5)
C(24)	0.4351 (11)	0.1374 (12)	0.4394 (8)	9.7 (6)
C(25)	0.4881 (9)	0.2701 (12)	0.4563 (6)	12.7 (7)
C(26)	0.4292 (12)	0.3419 (8)	0.4009 (9)	8.5 (5)
C(31)	−0.2856 (8)	0.2056 (9)	0.1447 (5)	3.5 (3)
C(32)	−0.3144 (9)	0.2978 (7)	0.0955 (5)	4.0 (3)
C(33)	−0.4425 (10)	0.2895 (8)	0.0546 (6)	4.6 (3)
C(34)	−0.5419 (8)	0.1891 (9)	0.0629 (5)	5.6 (3)
C(35)	−0.5131 (9)	0.0970 (7)	0.1122 (5)	6.8 (4)
C(36)	−0.3850 (10)	0.1053 (8)	0.1531 (6)	4.9 (3)
C(41)	−0.1112 (10)	0.0634 (8)	0.2565 (6)	3.5 (3)
C(42)	−0.1489 (10)	0.0720 (8)	0.3516 (8)	6.2 (4)
C(43)	−0.1473 (10)	−0.0289 (9)	0.3983 (5)	7.1 (4)
C(44)	−0.1080 (10)	−0.1384 (8)	0.3499 (6)	6.9 (4)
C(45)	−0.0704 (10)	−0.1470 (8)	0.2584 (8)	6.3 (4)
C(46)	−0.0720 (10)	−0.0461 (9)	0.2081 (5)	4.6 (3)

[a] The coordinates are given for the carbon atom groups, C_{j1}–C_{j6}. The groups H_{j2}–H_{j6} have the same x_c, y_c, z_c, D, and E coordinates, but their F angles are greater by $2\pi/6$ radians. [b] The carbon and hydrogen atoms of the phenyl groups are given two numbers. $C(ji)$ refers to carbon atom i of ring j where $i = 1$ is an atom bonded to germanium and the numbering continues in cyclic order around each ring. The hydrogen atoms have the numbers of the carbon atoms to which they are bonded.

bridge is replaced by a carbonyl could be due to the reduced steric requirements of the resulting bridged system (see below). The Fe–Ge distances are in the range 2.402–2.440 Å, each ±0.003 Å, with mean value 2.422 Å somewhat longer than the corresponding distance of 2.398 (4) Å in [Ge(CH₃)₂]₃Fe₂(CO)₆. Thus the bridging angle of the germanium atoms, 66.8 (1)°, is necessarily more acute than the value of 70.0 (2)° associated with the shorter Fe–Ge bonds and the longer Fe–Fe bond of [Ge(CH₃)₂]₃Fe₂(CO)₆. The bridging carbonyl group subtends 82.1 (5)° at the Fe–Fe bond, with an Fe–C mean distance of 2.03 (5) Å. This distance is appreciably longer than other Fe–C$_{bridge}$ distances in a variety of compounds containing Fe–Fe bonds,[13] although the bridging angle is not unusual. However, the comparison is scarcely valid in view of the considerable variations between the systems. The most closely comparable compound, Fe₂(CO)₉, has a carbonyl bridge angle of 87 (4)° with an Fe–C distance of 1.80 (5) Å. This indicates that in the present compound the carbonyl group is displaced away from

the Fe–Fe bond, lengthening the Fe–C distance and making the bridging angle more acute. This is consistent with the indications of relief of steric strain given by the dihedral angles of Table IV. The angle between the two planes containing germanium atoms is 8.6° greater than 120°, with a concomitant reduction of 4.3° for the other two dihedral angles. Evidently the relatively large germanium diphenyl ligands have moved away from each other and closer to the bridging carbonyl, pushing the carbonyl away from the Fe–Fe bond slightly and relieving some of the steric strain that must be present in the symmetrical [Ge(CH₃)₂]₃-Fe₂(CO)₇ with its 120° dihedral angles. This strain is most readily attributed to the repulsive forces between the germanium atoms. The Ge···Ge distance is 3.655 Å in the present compound, an increase of 0.25 Å from the 3.403 (5) Å in [Ge(CH₃)₂]₃Fe₂(CO)₆. Both values are considerably less than the van der Waals distance, assuming a likely value of 2.00 Å for the germanium van der Waals radius.[14] While it is not unexpected that the distance between two atoms bonded to the same atoms should be less than the van der Waals distance, this interaction seems a more

(13) Distances in the range 1.74–1.97 Å and angles of 78.5–89° have been observed. See Churchill's tabulation[12] and F. A. Cotton and M. D. La-Prade, *J. Am. Chem. Soc.*, **90**, 2026 (1968).

(14) A. Bondi, *J. Phys. Chem.*, **68**, 441 (1964).

TABLE IV
Intramolecular Distances, Å

Bonding		Nonbonding	
Ge(1)–Fe(1)	2.416 (3)	Ge(1)–Ge(2)	3.645 (2)
Ge(1)–Fe(2)	2.432 (3)	Ge(1)–C(1)	3.02 (1)
Ge(2)–Fe(1)	2.402 (3)	Ge(2)–C(1)	3.02 (1)
Ge(2)–Fe(2)	2.440 (3)	C(2)–C(3)	2.64 (2)
Fe(1)–Fe(2)	2.666 (3)	C(3)–C(4)	2.63 (2)
Fe(1)–C(1)	2.08 (1)	C(2)–C(4)	2.67 (2)
Fe(2)–C(1)	1.98 (1)	C(5)–C(6)	2.67 (2)
Fe(1)–C(2)	1.77 (1)	C(6)–C(7)	2.62 (2)
Fe(1)–C(3)	1.79 (2)	C(5)–C(7)	2.70 (2)
Fe(1)–C(4)	1.82 (2)	Ge(1)–C(2)	2.97 (1)
Fe(2)–C(5)	1.82 (2)	Ge(1)–C(3)	2.83 (1)
Fe(2)–C(6)	1.81 (2)	Ge(1)–C(5)	2.87 (1)
Fe(2)–C(7)	1.79 (2)	Ge(1)–C(6)	2.96 (1)
C(1)–O(1)	1.15 (2)	Ge(2)–C(2)	2.99 (1)
C(2)–O(2)	1.15 (2)	Ge(2)–C(4)	2.87 (1)
C(3)–O(3)	1.16 (2)	Ge(2)–C(5)	2.98 (1)
C(4)–O(4)	1.15 (2)	Ge(2)–C(7)	2.83 (1)
C(5)–O(5)	1.14 (2)	C(1)–C(3)	2.74 (2)
C(6)–O(6)	1.14 (2)	C(1)–C(4)	2.79 (2)
C(7)–O(7)	1.15 (2)	C(1)–C(6)	2.75 (2)
Ge(1)–C(11)	1.963 (7)	C(1)–C(7)	2.76 (2)
Ge(1)–C(21)	1.940 (8)	C(11)–C(21)	3.18 (2)
Ge(2)–C(31)	1.971 (7)	C(31)–C(41)	3.14 (2)
Ge(2)–C(41)	1.950 (7)		

Bond Angles, Deg

Fe(1)–Ge(1)–Fe(2)	66.7 (1)	Fe(1)–C(2)–O(2)	174.7 (11)
Fe(1)–Ge(2)–Fe(2)	66.8 (1)	Fe(1)–C(3)–O(3)	173.7 (13)
Fe(1)–C(1)–Fe(2)	82.1 (5)	Fe(1)–C(4)–O(4)	173.1 (11)
		Fe(2)–C(5)–O(5)	174.4 (12)
Fe(1)–C(1)–O(1)	135.2 (10)	Fe(2)–C(6)–O(6)	176.3 (13)
Fe(2)–C(1)–O(1)	142.7 (10)	Fe(2)–C(7)–O(7)	176.4 (13)
C(11)–Ge(1)–C(21)	109.3 (4)	C(31)–Ge(2)–Ge(41)	106.5 (4)
Fe(1)–Ge(1)–C(11)	114.6 (3)	Fe(1)–Ge(2)–C(31)	117.4 (3)
Fe(1)–Ge(1)–C(21)	124.8 (3)	Fe(1)–Ge(2)–C(41)	126.8 (3)
Fe(2)–Ge(1)–C(11)	117.7 (3)	Fe(2)–Ge(2)–C(31)	116.1 (3)
Fe(2)–Ge(1)–C(21)	118.4 (3)	Fe(2)–Ge(2)–C(41)	118.7 (3)
Ge(1)–Fe(1)–Ge(2)	98.3 (1)	Ge(1)–Fe(2)–Ge(2)	96.9 (1)
Ge(1)–Fe(1)–C(1)	84.1 (4)	Ge(1)–Fe(2)–C(1)	85.8 (4)
Ge(2)–Fe(1)–C(1)	84.3 (3)	Ge(2)–Fe(2)–C(1)	85.5 (4)
C(2)–Fe(1)–C(3)	95.8 (6)	C(5)–Fe(2)–C(6)	94.8 (6)
C(3)–Fe(1)–C(4)	93.5 (6)	C(6)–Fe(2)–C(7)	93.5 (6)
C(4)–Fe(1)–C(2)	96.1 (5)	C(7)–Fe(2)–C(5)	96.7 (6)
Ge(1)–Fe(1)–C(2)	88.9 (4)	Ge(1)–Fe(2)–C(5)	83.7 (4)
Ge(1)–Fe(1)–C(3)	83.3 (4)	Ge(1)–Fe(2)–C(6)	87.2 (4)
Ge(1)–Fe(1)–C(4)	174.3 (3)	Ge(1)–Fe(2)–C(7)	179.2 (4)
Ge(2)–Fe(1)–C(2)	90.2 (4)	Ge(2)–Fe(2)–C(5)	87.5 (4)
Ge(2)–Fe(1)–C(3)	173.8 (4)	Ge(2)–Fe(2)–C(6)	175.6 (4)
Ge(2)–Fe(1)–C(4)	84.4 (4)	Ge(2)–Fe(2)–C(7)	82.5 (4)
C(1)–Fe(1)–C(2)	170.4 (4)	C(1)–Fe(2)–C(5)	166.6 (6)
C(1)–Fe(1)–C(3)	89.5 (5)	C(1)–Fe(2)–C(6)	93.0 (6)
C(1)–Fe(1)–C(4)	91.3 (5)	C(1)–Fe(2)–C(7)	93.8 (6)

Dihedral Angles, deg

[Ge(1)–Fe(1)–Fe(2)]–[Ge(2)–Fe(1)–Fe(2)]	128.6 (1)
[Ge(1)–Fe(1)–Fe(2)]–[C(1)–Fe(1)–Fe(2)]	115.7 (4)
[Ge(2)–Fe(1)–Fe(2)]–[C(1)–Fe(1)–Fe(2)]	115.7 (4)

probable source of strain than the interaction between the phenyl groups attached to the germanium atoms. The shortest contact between the two phenyl groups involved is 2.73 Å for C(46)···H(22) while the corresponding van der Waals distance is 2.77 Å.[14] The three bridging groups are all slightly asymmetric. The two germanium atoms are closer to Fe(1), mean distance 2.409 Å, than to Fe(2), mean distance 2.436 Å, while the carbonyl group is closer to Fe(2), 1.98 Å, than to Fe(1), 2.08 Å. It seems likely that this slight asymmetry, acting as it does to increase the Ge···C$_\text{bridge}$ distances, can be attributed to the same forces that influence the dihedral angles. The geometry of the Fe(CO)$_3$ entities is normal. The Fe–C bond distances agree within error, mean value 1.800 (7) Å, which is toward the upper end of the range of such distances.[15] The C–O mean distance is 1.149 (8) Å and the mean Fe–C–O angle is 174.8 (5)°. The Ge–C phenyl distances have a mean value of 1.956 (4) Å which is slightly smaller than the Ge–CH$_3$ distances in [Ge(CH$_3$)$_2$]$_3$Fe$_2$(CO)$_6$. The two diphenylgermanium groups have different orientations. Rings 1 and 2 are inclined at 47.7° and Ge(1) is 0.157 and 0.076 Å, respectively, from the two planes. The corresponding figures for the second ligand are 77.4° and 0.069 and 0.111 Å. These deviations are small but significant and are probably best accounted for by packing requirements. There are no unusually short intermolecular contacts, and the shortest distances between phenyl groups are intramolecular.

(15) P. F. Lindley and P. Woodward, *J. Chem. Soc., A,* 382 (1967), gave a convenient tabulation.