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THE PREPARATION, PROPERTIES AND CRYSTAL STRUCTURE OF BIS[(η^5-CYCLOPENTADIENYLDICARBONYLIRON)DIMETHYLGERMYL]-OXIDE, [(η^5-C_5H_5)$(CO)_2FeGe(CH_3)_2]_2O$*

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Summary

One of the main products of oxidation of $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_3Ge(CH_3)_2$ by air has been shown to be $[(\eta^5\text{-}C_5H_5)(CO)_2FeGe(CH_3)_2]_2O$. The infrared, NMR and mass spectra are consistent with this formula and the detailed structure has been established by X-ray crystallography. In polar solvents the NMR suggests the existence of major and minor conformers interconverting only slowly on the NMR time scale at $\approx 25°$. The X-ray diffraction study has shown the compound to consist of two $(\eta^5\text{-}C_5H_5)(CO)_2FeGe(CH_3)_2$ moieties joined by a bridging oxygen atom. Two rotational isomers are present in the unit cell in a disordered fashion. Some pertinent average distances and angles are: Fe—Ge, 2.372 Å; Ge—O, 1.785 Å; Ge—O—Ge′, 134°. The compound crystallizes in the monoclinic system, space group $P2_1/n$, with a 8.056(2), b 12.506(2), c 22.631(3) Å, β 98.01(1)°, d_{calc} 1.692 g cm^{-3}. Counter data were collected using Mo-K_α radiation. The 1780 reflections above background were used in least-squares refinement which converged at $R_1 = 0.051$ and $R_2 = 0.068$.

Introduction

In the course of our studies [1] of $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_3Ge(CH_3)_2$, a compound earlier reported by Curtis [2], it was observed that decomposition often occurred and that the extent of this was apparently correlated with the extent of exposure of the solution to the atmosphere. In order to determine the identity of one or more of the decomposition products, oxidative degradation was deliberately carried out and one of the products isolated and characterized. The results are reported here.

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Experimental

Preparation

A solution of 0.3 g (0.7 mmole) of $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_3Ge(CH_3)_2$ in toluene (20 ml) was stirred in an open vessel while laboratory air was blown over the surface. The solution became orange-brown in color and a brown precipitate was deposited. The solution was filtered and vacuum evaporated to give an oily residue. This was dissolved in hexane and chromatographed on alumina (5% H_2O). Elution with benzene removed impurities leaving a pale yellow band at the top of the column. This was eluted with 1/1, v/v, CH_2Cl_2/acetone. Vacuum evaporation of this eluate yielded a pale yellow oil which was dissolved in pentane. Off-white crystals were formed when the pentane solution was cooled to —78°. The yield was 110 mg.

Spectral measurements

IR spectra: Perkin—Elmer Model 451 spectrometer calibrated with polystyrene film. Proton NMR spectra: Varian HA-100 spectrometer. Mass spectrum: Consolidated Electrodynamics Co. Model CEC21-110 high resolution spectrometer, operated at 6 kV with a probe temperature of 80° and a source temperature of 300°.

Collection of X-ray data

A thick plate of approximate dimensions 0.2 × 0.2 × 0.07 mm was mounted in a capillary and examined on a Syntex $P\bar{1}$ diffractometer using Mo-K_α radiation monochromatized with a graphite crystal. Preliminary work showed that the crystal belonged to the monoclinic system with cell constants: a 8.056(2), b 12.506(2), c 22.631(3) Å, β 98.01(1)°, V 2257.9(7) Å^3. For $Z = 4$ and F.W. = 575.25, the calculated density is 1.692 g cm^{-3}.

Data were collected at 22 ± 2° using the θ—2θ scan technique with a scan rate varying from 2—24°/min depending on the intensity of the reflection. The scan range extended from 0.85° below the K_{α_1} peak to 0.85° above the K_{α_2} peak. A total of 2986 unique reflections were collected in the range $0° < 2\theta(\text{Mo-}K_\alpha) \leqslant 42.9°$. Four standard reflections were measured periodically. These indicated crystal movement and it was necessary to remount and orient the same crystal several times before data collection was completed.

The data were reduced and standard deviations $\sigma(F^2)$ were calculated for the intensities using a value of 0.07 for the factor p [3]. Owing to the complicated shape of the crystal, an absorption correction [$\mu(\text{Mo-}K_\alpha) = 41.0$ cm^{-1}] was not attempted. An extinction correction was not necessary.

An examination of the data showed systematic absences of $h + l = 2n + 1$ for $h0l$, and $k = 2n + 1$ for $0k0$, corresponding to space group $P2_1/n$. This is a non-standard setting of $P2_1/c$—C_{2h}^5 (No. 14).

*Solution and refinement of the X-ray structure**

All of the top 42 peaks in a three-dimensional, Patterson origin-removed map could be accounted for in terms of the positions of two Fe atoms and two

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* Computer programs used in data reduction and in the solution and refinement of the structure were as follows: DATARED by Frenz was used for data reduction. The program FOURIER by Robinson

Ge atoms. Two cycles of isotropic refinement of these four atoms in full-matrix least-squares resulted in agreement factors $R_1 = \Sigma| |F_o|-|F_c| |/\Sigma|F_o| = 0.253$ and $R_2 = (\Sigma w (|F_o|-|F_c|)^2/\Sigma w \cdot F_o^2)^{1/2} = 0.338$. A subsequent difference Fourier synthesis revealed the positions of 21 additional atoms. Least-squares refinement including these atoms reduced R_1 and R_2 to 0.138 and 0.171, respectively. However, the isotropic thermal parameters for the atom bridging the two Ge atoms refined to an unrealistic value of −2.2. In this refinement carbon scattering factors were assigned to the bridging atom; in subsequent refinements oxygen scattering factors were used and the thermal parameter refined to a reasonable value. A difference Fourier map gave the position of the remaining two atoms. This was followed by least-squares refinement of the atoms with anisotropic thermal parameters. The resulting R factors of 0.089 and 0.106 were abnormally large and $||F_o|-|F_c||/\sigma(F_o)$ was greater than 4.0 for 257 reflections. A difference Fourier map showed one peak at 1.3 Å from Ge(2) and 1.7 Å from the bridging O atom and a second peak at 1.1 Å from Fe(2) and 2.4 Å from the first peak. These two peaks consistently appeared in previous maps at heights slightly greater than those of oxygen atoms; they had been dismissed as chemically unreasonable and it was hoped that they would disappear once the complete structure was refined. However the peaks did not disappear. An examination of their locations in the cell suggested that a second isomer is present in the structure. One-half of the molecule (a $C_5H_5Fe(CO)_2Ge(CH_3)_2O$ fragment) retains the same positions for both isomers; the other half of the molecule differs in the two isomers by a rotation around the Ge(1)—O(br) bond. Since the ratio of isomers is ca. 10/1, only the Ge and Fe atoms of the second isomer have significant heights in the difference Fourier. Subsequent least-squares cycles included anisotropic refinement of the Ge(3) and Fe(3) atoms of the second isomer. In these cycles an occupancy factor α was also refined, where the occupancy for atoms Ge(2) and Fe(2) was α and the occupancy of Ge(3) and Fe(3) was $1-\alpha$. The final refined value for α was 0.882(4). Because of the relatively small percentage of the second isomer present in the cell, the effort required to refine a more complete model that included the remaining "1/9C" atoms and "1/9O" atoms did not seem justified.

Hydrogen atom positions were calculated (C—H 0.95 Å) for the cyclopentadienyl rings. These were included as fixed contributions to the structure factors, using isotropic thermal parameters of 5.0 Å^2. In the last cycle of least-squares refinement none of the 263 variables changed by more than one-third of its e.s.d. The final agreement factors are 0.051 and 0.068, respectively. The error in an observation of unit weight is 1.38.

In refinements only the 1780 reflections with $|F_o|^2 > 3\sigma(F_o^2)$ were used. The function minimized was $\Sigma w(|F_o|-|F_c|)^2$ where the weight w is given by $1/\sigma^2(F_o) = 4F_o^2/\sigma^2(F_o^2)$. Scattering factors and anomalous dispersion factors for Fe and Ge atoms were taken from refs.4 and 5, respectively.

(cont'd.) and Dellaca is a version of Zalkin's FORDAP. The full-matrix least-squares program NUCLS by Ibers and Doedens closely resembles Busing and Levy's ORFLS program. Atomic distances and angles were calculated using a local modification of Baur's SADIAN program and the function and error program ORFFE by Busing, Martin and Levy as modified by Brown, Johnson and Thiessen. PERFACT by Frenz was used for an analysis of structure factors and LIST by Snyder was used for listing the data. ORTEP by Johnson was used for drawing illustrations on a Gerber plotter.

TABLE 1

FINAL POSITIONAL AND ANISOTROPIC THERMAL PARAMETERS AND THEIR RESPECTIVE STANDARD DEVIATIONS[a]

	x	y	z	$10^4\beta_{11}$	$10^4\beta_{22}$	$10^4\beta_{33}$	$10^4\beta_{12}$	$10^4\beta_{13}$	$10^4\beta_{23}$
Ge(1)	0.0434(2)	0.35168(9)	0.10679(5)	204(3)	61.3(9)	22.7(3)	8(1)	1.1(7)	3.4(4)
Ge(2)	−0.0909(2)	0.36612(11)	0.23720(6)	182(4)	66(1)	25.4(4)	15(1)	3.0(8)	−7.0(5)
Ge(3)	0.0622(15)	0.3706(7)	0.2508(5)	166(3)	49(7)	27(3)	2(10)	10(6)	−4(3)
Fe(1)	0.0720(2)	0.18578(12)	0.05800(7)	158(3)	70(1)	22.4(4)	18(2)	6.7(8)	0.4(5)
Fe(2)	−0.0017(4)	0.2721(2)	0.3267(1)	192(5)	79(2)	23.9(5)	−6(2)	19(1)	−2.0(7)
Fe(3)	−0.1203(25)	0.2808(12)	0.3049(7)	135(35)	80(12)	31(4)	8(17)	−11(10)	−4(5)
O(br)	0.034(1)	0.3189(6)	0.1821(3)	249(18)	88(6)	23(2)	40(9)	7(4)	5(3)
O(1,1)	−0.265(1)	0.1438(8)	0.0789(5)	212(20)	120(9)	63(4)	−6(11)	35(7)	−10(5)
O(1,2)	−0.018(1)	0.3001(9)	−0.0524(4)	371(26)	143(10)	30(3)	45(13)	15(6)	12(4)
O(2,1)	0.336(1)	0.3291(10)	0.3065(6)	183(20)	189(13)	66(4)	−27(17)	41(8)	1(6)
O(2,2)	−0.005(2)	0.0842(8)	0.2535(5)	530(34)	81(8)	49(3)	−18(13)	79(9)	−10(4)
C(1,1)	−0.130(2)	0.1619(9)	0.0698(6)	141(23)	83(10)	33(3)	17(13)	7(7)	−7(5)
C(1,2)	0.020(2)	0.2539(10)	−0.0075(6)	209(26)	95(11)	25(3)	11(14)	16(7)	−1(5)
C(1,3)	0.167(2)	0.0303(10)	0.0679(7)	186(26)	78(11)	43(5)	48(14)	−5(9)	−3(6)
C(1,4)	0.184(2)	0.0813(11)	0.1236(6)	233(28)	84(11)	26(3)	41(15)	13(7)	11(5)
C(1,5)	0.289(2)	0.1694(11)	0.1192(7)	215(28)	98(13)	35(4)	45(16)	−29(9)	−5(6)
C(1,6)	0.330(2)	0.1717(13)	0.0605(8)	151(26)	127(15)	44(5)	19(15)	22(9)	15(7)
C(1,7)	0.255(2)	0.0854(14)	0.0305(6)	240(32)	136(15)	29(4)	94(19)	21(9)	0(7)
C(1,8)	−0.161(2)	0.4321(11)	0.0737(6)	295(32)	101(12)	36(4)	83(16)	−8(9)	11(5)
C(1,9)	0.238(2)	0.4498(11)	0.1064(7)	291(33)	101(12)	41(4)	−59(16)	−5(9)	11(6)
C(2,1)	0.205(2)	0.3045(13)	0.3147(6)	325(40)	137(15)	26(4)	28(21)	13(10)	1(6)
C(2,2)	−0.008(2)	0.1593(11)	0.2817(6)	349(36)	89(12)	30(4)	3(17)	42(9)	2(5)
C(2,3)	−0.043(2)	0.3801(14)	0.3896(8)	266(37)	127(16)	39(5)	−73(20)	43(11)	−20(7)
C(2,4)	−0.196(2)	0.3560(14)	0.3617(6)	238(34)	144(17)	33(4)	−18(19)	27(9)	−20(6)
C(2,5)	−0.216(2)	0.2481(17)	0.3683(8)	386(48)	133(18)	43(5)	−129(25)	52(13)	−32(8)
C(2,6)	−0.076(4)	0.2051(16)	0.4031(9)	672(81)	130(18)	40(6)	34(33)	91(17)	26(8)
C(2,7)	0.031(2)	0.2912(22)	0.4161(8)	229(36)	197(23)	47(6)	−36(26)	33(11)	−1(10)
C(2,8)	−0.036(2)	0.5237(9)	0.2436(7)	465(43)	40(9)	47(5)	20(16)	−11(11)	−10(5)
C(2,9)	−0.334(2)	0.3277(12)	0.2058(6)	194(27)	142(15)	39(4)	28(16)	0(8)	−12(6)

[a] The form of the thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

TABLE 3

BOND DISTANCES (Å)

Atoms	Distance	Atoms	Distance
Fe(1)—Ge(1)	2.377(2)	Fe(2)—Ge(2)	2.367(3)
Fe(1)—C(1,1)	1.71(1)	Fe(2)—C(2,1)	1.77(2)
Fe(1)—C(1,2)	1.71(1)	Fe(2)—C(2,2)	1.74(1)
Fe(1)—C(1,3)	2.09(1)	Fe(2)—C(2,3)	2.02(1)
Fe(1)—C(1,4)	2.09(1)	Fe(2)—C(2,4)	2.12(1)
Fe(1)—C(1,5)	2.08(1)	Fe(2)—C(2,5)	2.10(2)
Fe(1)—C(1,6)	2.08(1)	Fe(2)—C(2,6)	2.08(2)
Fe(1)—C(1,7)	2.10(1)	Fe(2)—C(2,7)	2.02(2)
Ge(1)—C(1,8)	1.98(1)	Ge(2)—C(2,8)	2.02(1)
Ge(1)—C(1,9)	1.99(1)	Ge(2)—C(2,9)	2.05(1)
Ge(1)—O(br)	1.765(7)	Ge(2)—O(br)	1.806(8)
C(1,1)—O(1,1)	1.15(1)	C(2,1)—O(2,1)	1.14(2)
C(1,2)—O(1,2)	1.17(1)	C(2,2)—O(2,2)	1.14(1)
C(1,3)—C(1,4)	1.40(2)	C(2,3)—C(2,4)	1.34(2)
C(1,4)—C(1,5)	1.40(2)	C(2,4)—C(2,5)	1.37(2)
C(1,5)—C(1,6)	1.41(2)	C(2,5)—C(2,6)	1.39(2)
C(1,6)—C(1,7)	1.37(2)	C(2,6)—C(2,7)	1.38(3)
C(1,7)—C(1,3)	1.37(2)	C(2,7)—C(2,3)	1.36(2)
Ge(3)—O(br)	1.67(1)	Fe(3)—Ge(3)	2.33(2)

TABLE 4

BOND ANGLES (°)

Atoms[a]	Angle	Atoms	Angle
Ge(1)—Fe(1)—C(1,1)	85.7(4)	Ge(2)—Fe(2)—C(2,1)	86.2(5)
Ge(1)—Fe(1)—C(1,2)	86.6(4)	Ge(2)—Fe(2)—C(2,2)	85.4(5)
Ge(1)—Fe(1)—Ct(1)	119.4	Ge(2)—Fe(2)—Ct(2)	118.7
C(1,1)—Fe(1)—C(1,2)	95.6(6)	C(2,1)—Fe(2)—C(2,2)	92.8(7)
C(1,1)—Fe(1)—Ct(1)	127.0	C(2,1)—Fe(2)—Ct(2)	129.5
C(1,2)—Fe(1)—Ct(1)	129.0	C(2,2)—Fe(2)—Ct(2)	129.6
Fe(1)—Ge(1)—C(1,8)	113.3(4)	Fe(2)—Ge(2)—C(2,8)	112.7(4)
Fe(1)—Ge(1)—C(1,9)	114.1(5)	Fe(2)—Ge(2)—C(2,9)	110.0(4)
Fe(1)—Ge(1)—O(br)	105.4(3)	Fe(2)—Ge(2)—O(br)	107.3(2)
C(1,8)—Ge(1)—C(1,9)	107.4(6)	C(2,8)—Ge(2)—C(2.9)	116.3(6)
C(1,8)—Ge(1)—O(br)	109.7(5)	C(2,8)—Ge(2)—O(br)	103.4(6)
C(1,9)—Ge(1)—O(br)	106.7(5)	C(2,9)—Ge(2)—O(br)	106.4(5)
Fe(1)—C(1,1)—O(1,1)	179(1)	Fe(2)—C(2,1)—O(2,1)	178(2)
Fe(1)—C(1,2)—O(1,2)	179(1)	Fe(2)—C(2,2)—O(2,2)	177(1)
C(1,3)—C(1,4)—C(1,5)	106(1)	C(2,3)—C(2,4)—C(2,5)	107(2)
C(1,4)—C(1,5)—C(1,6)	108(1)	C(2,4)—C(2,5)—C(2,6)	110(2)
C(1,5)—C(1,6)—C(1,7)	108(1)	C(2,5)—C(2,6)—C(2,7)	105(2)
C(1,6)—C(1,7)—C(1,3)	109(1)	C(2,6)—C(2,7)—C(2,3)	109(2)
C(1,7)—C(1,3)—C(1,4)	109(1)	C(2,7)—C(2,3)—C(2,4)	110(1)
Angles associated with Fe(3) and Ge(3):			
Ge(1)—O(br)—Ge(2)	133.9(4)	Ge(1)—O(br)—Ge(3)	142.2(6)
Fe(3)—Ge(3)—C(2,1)	75.6(8)	C(2,1)—Ge(3)—C(2,8)	130.1(8)
Fe(3)—Ge(3)—C(2,8)	103.0(8)	C(2,1)—Ge(3)—O(br)	121.9(7)
Fe(3)—Ge(3)—O(br)	106.7(7)	C(2,8)—Ge(3)—O(br)	106.5(7)
Ge(3)—Fe(3)—C(2,2)	83.1(8)		

[a] Ct( ) designates the centroid of the cyclopentadienyl ring.

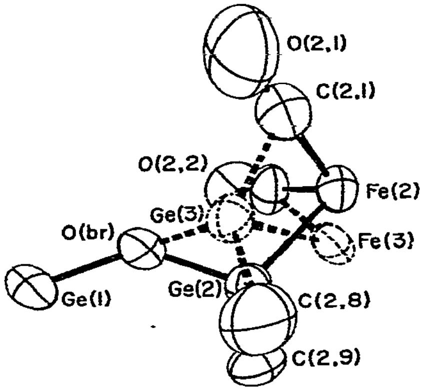

Fig. 2. A portion of the structure showing the rotational disorder around the Ge(1)—O(br) bond. Note that some of the positions refined in the structure can double as substituents for both rotamers.

chain of 4 consecutive bonds, nominally single bonds, about each of which ro tion is possible. This, in fact, leads to the occurrence of two different rotame in the crystal, as described above. It is surprising, however, that in solution th rate of interconversion of the two forms is slow on the NMR time scale. In fa

TABLE 5

ROOT-MEAN-SQUARE AMPLITUDES OF THERMAL VIBRATION (Å)

Atom	Min.	Intermed.	Max.
Ge(1)	0.212(2)	0.240(2)	0.268(2)
Ge(2)	0.212(2)	0.237(3)	0.277(2)
Ge(3)	0.19(2)	0.23(2)	0.26(1)
Fe(1)	0.210(2)	0.239(2)	0.251(2)
Fe(2)	0.227(3)	0.246(3)	0.266(3)
Fe(3)	0.19(3)	0.25(2)	0.30(2)
O(br)	0.22(1)	0.26(1)	0.31(1)
O(1,1)	0.25(1)	0.30(1)	0.40(1)
O(1,2)	0.26(1)	0.32(1)	0.37(1)
O(2,1)	0.22(1)	0.39(1)	0.41(1)
O(2,2)	0.25(1)	0.29(1)	0.45(1)
C(1,1)	0.20(2)	0.25(2)	0.30(2)
C(1,2)	0.24(2)	0.26(2)	0.28(2)
C(1,3)	0.19(2)	0.28(2)	0.35(2)
C(1,4)	0.21(2)	0.26(2)	0.31(2)
C(1,5)	0.20(2)	0.27(2)	0.36(2)
C(1,6)	0.21(2)	0.29(2)	0.36(2)
C(1,7)	0.20(2)	0.28(2)	0.38(2)
C(1,8)	0.19(2)	0.32(2)	0.36(2)
C(1,9)	0.24(2)	0.30(2)	0.37(2)
C(2,1)	0.26(2)	0.30(2)	0.35(2)
C(2,2)	0.25(2)	0.27(2)	0.35(2)
C(2,3)	0.23(2)	0.27(2)	0.39(2)
C(2,4)	0.25(2)	0.28(2)	0.37(2)
C(2,5)	0.22(2)	0.28(2)	0.45(2)
C(2,6)	0.22(2)	0.34(2)	0.49(3)
C(2,7)	0.25(2)	0.35(2)	0.40(2)
C(2,8)	0.17(2)	0.33(2)	0.42(2)
C(2,9)	0.24(2)	0.30(2)	0.36(2)

A comparison of $\Sigma w(|F_o|-|F_c|)^2$ versus λ^{-1} sin θ, $|F_o|$, reflection number, and various classes of indices revealed no unusual trends and suggested that the weighting scheme was satisfactory. A final difference Fourier map showed random electron density throughout the molecule, the highest peak (0.8 e Å^{-3}) lying between Ge(1) and O(br). This is small compared to carbon atoms with height 4.0 e Å^{-3} in previous maps.

Atomic positions and anisotropic thermal parameters are given in Table 1. A table of observed and calculated structure factors in the form $10|F_o|$ and $10|F_c|$ is available*.

Results and discussion

The infrared spectrum in hexane had two strong bands in the CO stretching region at 2000 cm^{-1} and 1951 cm^{-1}.

The proton NMR spectra in non-polar solvents were straightforward. In

TABLE 2

THE MASS SPECTRUM

m/e[a]	Relative intensity	Probable ion
578	0	$[CpFe(CO)_2Ge(CH_3)_2]O$
561	1	
548		$[CpFe(CO)_2GeCH_3]_2O$
520	3	$Cp_2Fe_2(CO)_3Ge_2(CH_3)_2O$
492	1	$[CpFe(CO)Ge(CH_3)]_2O$
477	3	561-3C°
464	15	$Cp_2Fe_2(CO)Ge_2(CH_3)_2O$
448	1	$Cp_2Fe_2(CO)Ge_2(CH_3)_2$
397	64	$CpFe_2(CO)Ge_2(CH_3)_2O$
360	3	$[Fe(CO)Ge(CH_3)]_2O$
343	46	$CpFe(CO)Ge_2(CH_3)_2O$
328	7	$CpFe(CO)Ge_2(CH_3)O$
281	18	$CpFe(CO)_2Ge(CH_3)_2$
257	14	$Cp_2Fe_2(CH_3)$
253	7	$CpFe(CO)Ge(CH_3)_2$
241	15	$CpFeGe(CH_3)_2O$
225	29	$CpFeGe(CH_3)_2$
211	48	CpFeGeO
192	6	$CpFe(CO)_2CH_3$
186	61	Cp_2Fe
161	15	$FeGe(CH_3)O$
139	48	CpGe
121	100	CpFe
119	29	$Ge(CH_3)_3$

[a] For ^{74}Ge; all peaks assigned to Ge-containing species had the appropriate set of satellites for the Ge atom(s) present.

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* The table of structure factors has been deposited as NAPS Document No. 02346. Order from ASIS/NAPS c/o Microfiche Publications, 305 E. 46th St., New York, N.Y. 10017. Remit in advance for each NAPS accession number $1.50 for microfiche or $5.00 for photocopies. Make checks payable to Microfiche Publications.

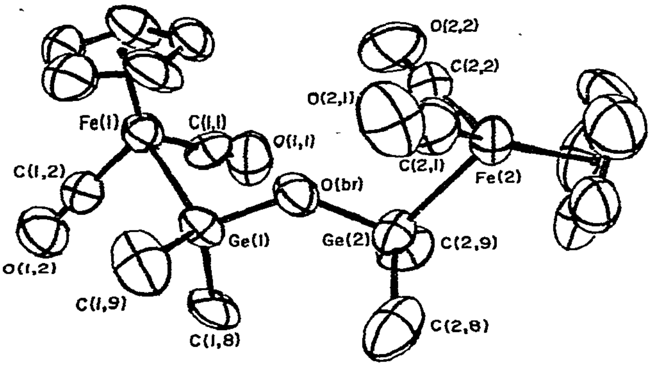

Fig. 1. A view of the $[(C_5H_5)(CO)_2FeGe(CH_3)_2]_2O$ molecule showing the 50% probability ellipsoids and the atomic numbering system used in the text and tables. The hydrogen atoms have been omitted for clarity.

benzene: τ 5.75(5) and 9.11(6) ppm are attributable to the C_5H_5 and CH_3 proto respectively. In polar solvents additional signals were found. In deuteroacetone at ca. 25° the results were: C_5H_5 region: τ 5.10 ($\approx$ 10), 5.03 ($\approx$ 5) ppm; CH_3 region: τ 9.27 ($\approx$ 12), 9.33 ($\approx$ 6) ppm. Apparently there are two species present in a ratio of about 1/2. In CF_2Cl_2 at 25° similar results were obtained, but with a ratio of about 1/3. When the solution in this solvent was cooled the ratio decreased as expected, to $\approx$ 1/10 at $-5°$ and to an extremely small value at $-33°$. Upon rewarming to 25° the original equilibrium ratio was recovered.

The mass spectrum is listed in Table 2. The parent ion peak was not observ

From the X-ray study the compound has been shown to consist of two $(\eta^5\text{-}C_5H_5)(CO)_2FeGe(CH_3)_2$ fragments joined through the Ge atoms by a bridgin oxygen atom, as depicted in Fig. 1. Bond distances and bond angles are given in Tables 3 and 4.

Approximately 88% of the molecules in the crystal have the conformation shown in Fig. 1. The remaining molecules differ from these by a rotation about the Ge(1)—O(br) bond and probably a rotation about the Ge(2)—Fe(2) bond. Interestingly, some of the positions of the substituents on the Ge(2) and Fe(2) atoms probably overlap in the unit cell with positions of substituents on the Ge(3) and Fe(3) atoms. Thus C(2,8) is a methyl carbon for both Ge(2) and Ge(3 while the second methyl carbon for Ge(3) must be close to the (2,1) carbonyl group of Fe(2). Also, the C(2,2) position serves as a carbon atom for both Fe(2) and Fe(3). The remaining ligands on Fe(3) are presumably spread among the other C and O atoms on Fe(2) and in locations of the cell unaccounted for by the refined model. A portion of the disordered molecules is shown in Fig. 2. The disorder in one-half of the molecule accounts for the larger errors calculated for this half relative to the rest of the molecule. This is also evident in the root-mean-square amplitudes of thermal vibration, where the ordered half of the molecule has smaller and more spherical ellipsoids than the corresponding ellipsoids of the disordered half of the molecule (see Table 5).

The structure of this molecule is not in itself surprising. Moreover, the apparent presence of two isomers, presumably conformational isomers, in solutions in polar solvents, is not inherently surprising either, since the molecule has a the crystallographic investigation was undertaken largely because we could not devise a molecular formula and structure which would readily explain this observation. The difficulty of doing so was increased by the fact that no parent ion peak is observed in the mass spectrum, so that even the correct molecular formula was uncertain prior to the X-ray work.

The correct explanation for the NMR results is still not entirely obvious. It would not seem likely that rotational barriers around either the Fe—Ge or Ge—O bonds arising entirely from non-bonded contacts could be large enough to make rotational interconversions slow on the NMR time scale at 25°. It can be estimated that a barrier of at least 15 kcal mol^{-1} would be required. Two other possibilities might be considered, though neither can be substantiated. First, it is possible that Ge—O d_π—p_π bonding is sufficient to impose the necessary barrier to rotation about those bonds. We have not found any data in the literature bearing on the extent of such bonding. The mean Ge—O bond length, 1.785 Å, is about 0.10 Å shorter than the sum of Pauling's single bond radii, thus suggesting some multiple bond character. The other possibility is that polar solvent molecules solvate one (or both) forms of the molecule rather firmly and thus impede the interconversion.

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