

Contribution from the Department of Chemistry,
Texas A&M University, College Station, Texas 77843**Structural and Dynamical Properties of
 μ -Dimethylgermyl- μ -carbonyl-dicyclopentadienyldicarbonyliron**

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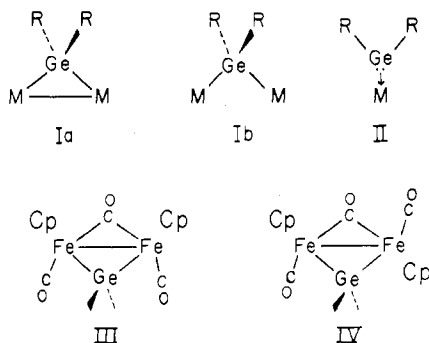
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The molecular structure of $(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_3(\text{GeMe}_2)$ has been determined crystallographically and the structural and dynamical properties of the molecule in solution have been studied by infrared and nuclear (^1H , ^{13}C) spectroscopy. The compound crystallizes in the space group $P2_12_12_1$, with $a = 13.503$ (1) Å, $b = 14.162$ (2) Å, and $c = 8.229$ (1) Å, and with $Z = 4$. From anisotropic refinement of 2141 reflections with intensities greater than their standard deviations the structure was solved and refined to $R_1 = 0.035$ and $R_2 = 0.048$. A number of Friedel pairs were carefully measured and the correct enantiomorph was unequivocally selected. The molecule has a bridging Me_2Ge group and is the cis isomer of $(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_2(\mu\text{-CO})(\mu\text{-Me}_2\text{Ge})$. Each bridging group is symmetrical and the Fe-Fe distance is 2.628 (1) Å. In solution at 25° there is an approximately 8:1 cis-trans mixture, with the isomers interconverting too slowly to influence either ^1H or ^{13}C line shapes. Between 90 and 160° (above which there is decomposition giving rise to paramagnetic impurities) the pmr signals for both CH_3 and $\eta^5\text{-C}_5\text{H}_5$ groups collapse and coalesce. The results are best explained by a process in which concerted opening of the two bridges occurs, leading to a nonbridged intermediate which can undergo internal rotation and then reestablish bridges. This mechanism accounts in detail for all the experimental observations. The high activation energy, ca. 21 kcal mol $^{-1}$, is attributed to the relative instability of the intermediate which contains a terminal dimethylgermylene ligand.

Introduction

It is well known that R_2E groups, where R represents either an alkyl or an aryl and E is one of the group IV elements, Si, Ge, or Sn, can function as bridging units across two metal atoms; this can occur both in the presence (Ia) and in the absence (Ib) of a direct M-M bond. Crystal structures of a



number of such compounds have been determined.¹⁻¹¹

An alternative mode of coordination, in which the R_2M ($\text{M} = \text{Si}, \text{Ge}, \text{Sn}, \text{Pb}$) unit is bonded to a single metal atom, II, is virtually unknown.¹² The instability of this "terminal type" bonding form is surprising since the analogous carbene complexes are relatively stable.¹³

As part of a general program of studying the bonding nature and rearrangement behavior of various functional groups bonded to polynuclear transition metal complexes, we have

investigated the structure and dynamical stereochemistry of $(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_3\text{GeMe}_2$. This molecule was previously prepared¹⁴ and reported to exist in solution as a mixture of cis, III, and trans, IV, isomers each of which has a bridging carbonyl group and a bridging dimethylgermyl group.

Experimental Section

The title compound, $(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_3(\text{GeMe}_2)$, was prepared by photodecarbonylating $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}(\text{CO})_2]\text{GeMe}_2$ according to the procedure of Curtis and Job.¹⁴

Nuclear Magnetic Resonance. Proton magnetic resonance spectra were recorded on a Varian HA-100 spectrometer equipped with a variable-temperature accessory. Temperature measurements were made with a copper-constantan thermocouple inserted into the probe and located just below the sample. The temperatures were recorded on a Leeds and Northrup Numatron Model 615 digital readout thermometer. The thermocouple was calibrated using an ethylene glycol standard. The temperatures are believed to be accurate to within $\pm 2^\circ$. Carbon-13 spectra were recorded on a Jeol PS-100 spectrometer in the FT mode at 25.15 MHz. The samples were enriched to approximately 30% ^{13}C , by direct exchange with ^{13}C , for recording of the carbonyl spectra on 0.1 M solutions in *o*-dichlorobenzene solvent.

Pmr samples were prepared using vacuum-degassed solvents which were added from a syringe to solid samples under nitrogen in serum stopper adapted nmr tubes. The ^{13}C samples were prepared similarly except that these tubes were subsequently evacuated and sealed.

Line shape calculations were performed using the program EXCHSYS.¹⁵ The cis-trans equilibrium parameters were determined by recording pmr spectra over the temperature range 30–90° (slow-exchange region). From the relative intensities the equilibrium constants were determined. A least-squares fit of the data to the equation $\ln k = -(\Delta H/RT) + (\Delta S/R)$ provided the thermodynamic parameters. This equation was then used to calculate the cis:trans ratio at temperatures in the range 90–160° where line shape analyses were conducted. The chemical shifts of the resonances were slightly temperature dependent. Plots of shift values vs. temperature in the slow-exchange region were extrapolated into the exchange region to obtain shift values at the appropriate temperatures.

Crystal Preparation. Dark maroon crystals of $(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_3(\text{GeMe}_2)$ were prepared by recrystallization from toluene at -20° . A well-formed crystal was mounted in a thin-walled Lindemann glass capillary tube.

Crystallographic Data. $\text{GeFe}_2\text{O}_3\text{C}_5\text{H}_{16}$, FW 428.6 is orthorhombic with $a = 13.503$ (1) Å, $b = 14.162$ (2) Å, $c = 8.229$ (1) Å, $V = 1574$ Å 3 , $Z = 4$, $d_{\text{calcd}} = 1.81$ g cm $^{-3}$, and $\mu(\text{Mo K}\alpha) = 38.76$ cm $^{-1}$. The observed extinctions $h00, h = 2n + 1; 0k0, k = 2n + 1; 00l, l =$

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$2n + 1$, uniquely indicate the noncentrosymmetric space group $D_2^4 \cdot P2_1 2_1 2_1$. Unit cell dimensions and their estimated standard deviations were obtained at room temperature ($24 \pm 2^\circ$) with Mo $K\alpha$ radiation (λ 0.7107 Å) using a least-squares procedure and employing 15 strong reflections.

Diffraction data were obtained from a crystal with boundary faces defined by the forms $\{010\}$, $\{101\}$, and $\{10\bar{1}\}$, with dimensions normal to these faces of 0.137, 0.21, and 0.19 mm, respectively. A check of the crystal mosaicity, expressed as width (in degrees) at half-height, of strong low-angle reflections recorded with open-counter ω scans, gave values of 0.17–0.19°.

Data were collected in the range $0 \leq 2\theta \leq 50^\circ$ using Mo $K\alpha$ radiation. The θ - 2θ scan technique was used with a variable-scan rate from 2.0 to 24.0°/min with a symmetric scan range from 2θ (Mo $K\alpha_1$) -1.0° to 2θ (Mo $K\alpha_2$) $+1.0^\circ$. The scan rate used was chosen by sampling the peak intensity. Stationary-crystal, stationary-counter background counts were measured at both ends of the 2θ scan range, with the total background counting time equal to half the scan time. The intensities of three standard reflections were monitored periodically during the course of data collection and no appreciable loss of intensity was observed.

The intensities of 2263 reflections were recorded in this way. Of these, 608 data were nonequivalent Friedel pairs recorded in the range $40 \leq 2\theta \leq 50^\circ$. After Lorentz and polarization corrections were applied to the data, 2141 had intensities greater than their estimated standard deviations, $\sigma(I)$. Here $\sigma(I)$ is calculated from the equation

$$\sigma(I) = [S^2(C + R^2B) + (pI)^2]^{1/2}$$

where S is the scan rate, C is the scan count, R is the ratio of scan time to total background counting time, B is the total background count, and “ p ” is a factor introduced to avoid overweighting strong reflections; a value of 0.06 for “ p ” was used.

An absorption correction was applied to the data using gaussian integration, and transmission factors ranged from 0.464 to 0.541.

Structure Solution and Refinement. The structure was solved using a Patterson synthesis to determine the heavy-atom coordinates and difference Fourier syntheses to locate the rest of the nonhydrogen atoms. The structure was refined using full-matrix least-squares techniques which converged for the isotropic model to discrepancy indices of $R_1 = \Sigma \|F_o\| - |F_c\| / \Sigma F_o = 0.070$ and $R_2 = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma w |F_o|^2]^{1/2} = 0.099$. All structure factor calculations and least-squares refinements were based on F and the quantity minimized was $\Sigma w(|F_o| - |F_c|)^2$. The weights w were taken as $4F_o^2 / \sigma^2(F_o^2)$.

Atomic scattering factors were taken from Cromer and Mann's tabulation¹⁷ and anomalous dispersion corrections¹⁸ were included for Ge and Fe atoms.

Absorption corrections were applied and anisotropic refinements commenced. A difference map after one cycle failed to reveal hydrogen atom positions. The ten cyclopentadienyl hydrogen atoms were therefore introduced at C-H distances of 1.0 Å in the ring planes, with isotropic thermal parameters of 6.0 Å², and their contributions included in subsequent F_c calculations.

Anisotropic refinement converged with $R_1 = 0.035$ and $R_2 = 0.048$. The enantiomorph which had been arbitrarily selected was shown to be correct. The inverse model, obtained by transforming all coordinates through an inversion center, gave significantly higher residuals, namely, $R_1 = 0.042$ and $R_2 = 0.061$.

A final difference Fourier synthesis did not reveal the positions of the methyl hydrogen atoms, and no attempt was made to include these in the model.

Shifts in the last cycle of least-squares refinement were all significantly less than the estimated standard deviations of the corresponding variables. The error in an observation of unit weight is 1.21. A listing of the observed and calculated structure amplitudes for those

(16) The following computer programs written for the IBM 360 were used: DATARED, a data reduction program by Frenz; AGNOST, an absorption correction program by Cahen based on Coppens' DATAP and Tompa analytical subroutines of Cullen's program; JMDAP, a version of Zalkin's FORDAP Fourier program modified by Ibers; NUCLS, a least-squares program by Ibers and Doedens which closely resembles Busing and Levy's ORFLS program; SADIAN, a program for calculating atomic distances and angles by Baur; RSCAN, a structure factor analysis program by Doedens; ORTEP, a plotting program by Johnson; ORFFE, a function and error program by Busing, Martin, and Levy and modified by Brown, Johnson, and Thiessen; LIST, a data listing program by Snyder.

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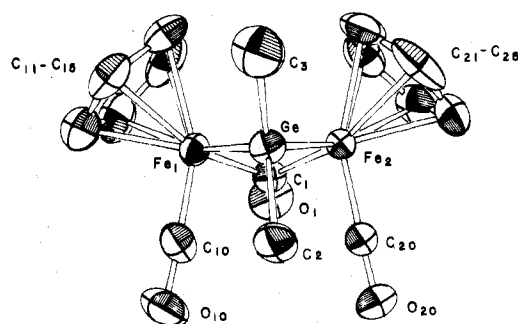


Figure 1. An ORTEP drawing of the molecular structure showing the atom-numbering scheme. Each atom is represented by its thermal vibration ellipsoid drawn to enclose 50% of its electron density.

data used in the refinement is available.¹⁹ The final positional and thermal parameters are listed in Table I, and root-mean-square amplitudes of vibration are given in Table II.

Results

The Crystal Structure. This is straightforward and can be disposed of first. It consists of molecular units, *cis*- $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}(\text{CO})_2(\mu\text{-CO})(\mu\text{-GeMe}_2)]$, as shown in Figure 1, which also gives the atom-numbering scheme, and Figure 2, which gives a stereoscopic representation of the structure. The bond distances and angles are listed in Tables III and IV, respectively.

The molecule is not in any essential structural way dissimilar to the *cis*- $(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_4$ ²⁰ and *cis*- $(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_2(\mu\text{-CO})(\mu\text{-CNCH}_3)$.²¹ There are, naturally, some dimensional differences due to the fact that the bridging germanium atom is considerably larger than a carbon atom. This results in an increased Fe-Fe distance which, in turn, results in a larger angle at the bridging CO carbon atom. Such effects are entirely in accord with previous observations. Thus, while the Fe-Fe distance in $\text{Fe}_2(\text{CO})_9$ is 2.523 (1) Å,²² when two bridging CO groups are replaced by germyl bridges in $[(\text{C}_6\text{H}_5)_2\text{Ge}]_2\text{Fe}_2(\text{CO})_7$,²³ the Fe-Fe distance increases markedly, to 2.67 Å. When all three CO bridges are replaced by Me_2Ge groups,²⁴ the distance increases further to 2.75 Å.

In the present case, both the Me_2Ge and CO bridges are symmetrical, as expected. The two Fe-C bonds are 1.902 (6) and 1.922 (6) Å in length, while the two Fe-Ge bonds are 2.347 (1) and 2.345 (1) Å in length. In this compound the Fe-Ge distances are slightly but significantly shorter than those in the two compounds mentioned above, where distances of 2.40–2.44 Å were found. This is perhaps due to the fact that the electronic requirements of $\text{Fe}(\text{CO})_3$ and $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})\text{Fe}$ are significantly different, in such a way that the latter engages in a little more π donation to the germanium atom than the former. This would be in keeping with the fact that the $\eta^5\text{-C}_5\text{H}_5$ group is less of a π acid than two CO groups. In agreement with this idea, we note that in $\text{Cl}_2\text{Ge}[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2]_2$ the Fe-Ge bond lengths are 2.357 (4) Å.²⁵

Solution Data. We have confirmed the infrared observations of Curtis and Job¹⁴ which show that both *cis* and *trans* isomers are present in solution. This is entirely in keeping

(19) See paragraph at end of paper regarding supplementary material.

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Table I. Positional^a and Thermal^b Parameters

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ge	0.76884 (5)	0.77274 (4)	0.8346 (1)	0.00387 (3)	0.00459 (3)	0.0092 (1)	-0.00025 (3)	-0.00075 (4)	-0.00003 (4)
Fe(1)	0.66619 (5)	0.66357 (5)	0.7107 (1)	0.00374 (4)	0.00299 (4)	0.0090 (1)	0.00015 (3)	0.00034 (5)	-0.00003 (6)
Fe(2)	0.63486 (6)	0.84672 (5)	0.7057 (1)	0.00494 (5)	0.00300 (4)	0.0103 (1)	0.00038 (4)	-0.00019 (6)	0.00052 (6)
O(1)	0.4661 (3)	0.7248 (4)	0.6426 (6)	0.0037 (2)	0.0081 (3)	0.020 (1)	0.0001 (2)	-0.0014 (4)	0.0007 (5)
O(10)	0.5951 (4)	0.6147 (4)	0.0232 (6)	0.0092 (4)	0.0053 (3)	0.016 (1)	-0.0004 (3)	0.0047 (5)	0.0020 (4)
O(20)	0.5535 (5)	0.8757 (5)	0.0249 (7)	0.0107 (5)	0.0082 (4)	0.017 (1)	0.0032 (4)	0.0048 (6)	-0.0014 (5)
C(1)	0.5508 (4)	0.7388 (4)	0.6735 (7)	0.0042 (3)	0.0043 (3)	0.011 (1)	0.0002 (2)	-0.0003 (4)	0.0002 (5)
C(2)	0.7818 (6)	0.7681 (6)	0.0749 (7)	0.0094 (6)	0.0071 (4)	0.008 (1)	0.0003 (5)	-0.0018 (5)	-0.0002 (5)
C(3)	0.9060 (5)	0.8019 (7)	0.762 (1)	0.0044 (4)	0.0103 (6)	0.021 (1)	-0.0018 (4)	-0.0006 (6)	-0.0012 (8)
C(10)	0.6231 (5)	0.6350 (4)	0.8970 (8)	0.0046 (3)	0.0031 (3)	0.013 (1)	0.0005 (2)	0.0017 (5)	0.0004 (4)
C(11)	0.7599 (6)	0.6462 (6)	0.501 (1)	0.0071 (5)	0.0066 (5)	0.019 (1)	-0.0006 (4)	0.0063 (7)	-0.0039 (7)
C(12)	0.6640 (7)	0.6260 (6)	0.456 (1)	0.0095 (6)	0.0063 (4)	0.012 (1)	0.0023 (4)	-0.0012 (7)	-0.0025 (6)
C(13)	0.6317 (7)	0.5513 (6)	0.545 (1)	0.0096 (6)	0.0056 (4)	0.023 (1)	-0.0025 (4)	0.004 (1)	-0.0056 (8)
C(14)	0.707 (1)	0.5255 (5)	0.652 (1)	0.015 (1)	0.0044 (4)	0.020 (1)	0.0039 (5)	0.005 (1)	-0.0002 (6)
C(15)	0.7881 (6)	0.5844 (7)	0.622 (1)	0.0067 (5)	0.0105 (7)	0.022 (2)	0.0045 (5)	-0.0011 (7)	-0.008 (1)
C(20)	0.5870 (5)	0.8622 (5)	0.896 (1)	0.0060 (4)	0.0038 (3)	0.016 (1)	0.0012 (3)	-0.0004 (5)	-0.0009 (5)
C(21)	0.7220 (8)	0.8932 (6)	0.505 (1)	0.0110 (7)	0.0060 (5)	0.015 (1)	-0.0004 (5)	0.0030 (8)	0.0043 (6)
C(22)	0.7223 (7)	0.9621 (6)	0.628 (1)	0.0095 (6)	0.0051 (4)	0.019 (1)	-0.0021 (4)	0.0005 (8)	0.0030 (6)
C(23)	0.6266 (7)	0.9913 (5)	0.660 (1)	0.0102 (6)	0.0033 (3)	0.022 (1)	0.0009 (3)	0.003 (1)	0.0013 (6)
C(24)	0.5632 (6)	0.9429 (6)	0.554 (1)	0.0081 (5)	0.0050 (4)	0.025 (2)	0.0008 (4)	-0.002 (1)	0.0035 (8)
C(25)	0.621 (1)	0.8836 (6)	0.458 (1)	0.017 (1)	0.0051 (4)	0.014 (1)	-0.0006 (6)	-0.004 (1)	0.0041 (7)
H(11)	0.8046	0.6958	0.4507						
H(12)	0.6225	0.6648	0.3775						
H(13)	0.5648	0.5187	0.5303						
H(14)	0.6999	0.4743	0.7387						
H(15)	0.8549	0.5823	0.6788						
H(21)	0.7813	0.8577	0.4573						
H(22)	0.7826	0.9868	0.6862						
H(23)	0.6050	0.0360	0.7485						
H(24)	0.4889	0.9513	0.5391						
H(25)	0.5934	0.8384	0.3719						

^a Figures in parentheses in this and subsequent tables are estimated standard deviations in the least significant figure. ^b The form of the expression for the temperature factors 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 II. Rms Amplitudes (Å)

Atom	Min	Int	Max
Ge	0.170 (1)	0.195 (1)	0.217 (1)
Fe(1)	0.171 (1)	0.176 (1)	0.189 (1)
Fe(2)	0.168 (1)	0.192 (1)	0.216 (1)
O(1)	0.181 (6)	0.263 (6)	0.289 (6)
O(10)	0.180 (8)	0.246 (6)	0.317 (7)
O(20)	0.186 (8)	0.282 (7)	0.357 (8)
C(1)	0.192 (8)	0.202 (7)	0.211 (7)
C(2)	0.165 (9)	0.268 (8)	0.299 (9)
C(3)	0.189 (9)	0.266 (9)	0.33 (1)
C(10)	0.172 (8)	0.188 (9)	0.234 (8)
C(11)	0.16 (1)	0.247 (9)	0.33 (1)
C(12)	0.18 (1)	0.236 (9)	0.32 (1)
C(13)	0.18 (1)	0.25 (1)	0.36 (1)
C(14)	0.17 (1)	0.25 (1)	0.40 (1)
C(15)	0.16 (1)	0.25 (1)	0.40 (1)
C(20)	0.178 (9)	0.229 (8)	0.252 (8)
C(21)	0.16 (1)	0.28 (1)	0.33 (1)
C(22)	0.18 (1)	0.27 (1)	0.31 (1)
C(23)	0.18 (1)	0.26 (1)	0.32 (1)
C(24)	0.19 (1)	0.28 (1)	0.31 (1)
C(25)	0.15 (1)	0.26 (1)	0.41 (1)

Table III. Bond Distances (Å)

Ge-Fe(1)	2.345 (1)	Fe-Fe	2.628 (1)
Ge-Fe(2)	2.347 (1)	Ge-C(2)	1.986 (6)
Fe(1)-C(1)	1.902 (6)	Ge-C(3)	1.990 (7)
Fe(2)-C(1)	1.923 (6)	C(1)-O(1)	1.188 (7)
Fe(1)-C(10)	1.756 (6)	C(10)-O(10)	1.142 (8)
Fe(2)-C(20)	1.706 (7)	C(20)-O(20)	1.172 (9)
Fe(1)-C(11)	2.096 (7)	C(11)-C(12)	1.38 (1)
Fe(1)-C(12)	2.091 (7)	C(12)-C(13)	1.36 (1)
Fe(1)-C(13)	2.100 (8)	C(13)-C(14)	1.39 (1)
Fe(1)-C(14)	2.071 (7)	C(14)-C(15)	1.41 (1)
Fe(1)-C(15)	2.097 (7)	C(15)-C(11)	1.38 (1)
Fe(2)-C(21)	2.130 (8)	C(21)-C(22)	1.40 (1)
Fe(2)-C(22)	2.115 (7)	C(22)-C(23)	1.38 (1)
Fe(2)-C(23)	2.084 (7)	C(23)-C(24)	1.40 (1)
Fe(2)-C(24)	2.086 (8)	C(24)-C(25)	1.40 (1)
Fe(2)-C(25)	2.116 (8)	C(25)-C(21)	1.42 (1)

with observations on related systems such as $(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}_2\text{-}(\text{CO})_4$,^{26,27} $(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_2(\mu\text{-CNCH}_3)_2$,²⁸ and $(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})[(\text{PhO})_3\text{P}](\mu\text{-CO})_2$.^{29,30} However, we have found it more convenient to study both equilibrium and dynamical properties of solutions by nuclear magnetic resonance spectroscopy.

At room temperature the pmr spectrum in *o*-dichlorobenzene solvent shows an 8:1 equilibrium ratio of the cis to

the trans isomer. For the cis form τ values were 5.61 (C_5H_5) and 8.45 and 8.63 (CH_3), while for the trans form the τ values were 5.55 (C_5H_5) and 8.53 (CH_3). The trans \rightarrow cis equilibrium parameters in the same solvent are $\Delta H = -2.14 \pm 0.14$ kcal/mol, $\Delta S = -2.99 \pm 0.7$ cal/deg mol, and $\Delta G_{298} = -1.24 \pm 0.35$ kcal/mol. The ¹³C nmr spectrum of a 30% enriched ¹³CO sample showed two CO resonances at 217.5 and 217.0 ppm (relative to TMS) with relative intensities of approximately 8:1. We assign these resonances accordingly to the terminal carbonyl ligands of the cis and trans isomers, respectively. At 282.2 ppm another small resonance is observed. This we have assigned to an unresolved combination of the bridging carbonyl resonances from the two isomers. The bridging and terminal ¹³CO resonances in $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$ have similar shift values.³¹

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 (28) R. D. Adams and F. A. Cotton, *J. Amer. Chem. Soc.*, **95**, 6589 (1973).
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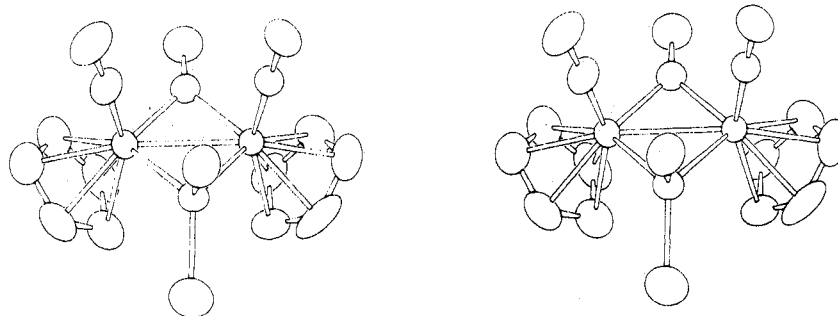


Figure 2. A stereoscopic pair showing the three-dimensional structure of the molecule.

Table IV. Bond Angles (deg)

C(2)-Ge-C(3)	103.0 (4)	C(1)-Fe(1)-Ge	99.9 (2)
C(2)-Ge-Fe(1)	119.6 (3)	C(1)-Fe(2)-Ge	99.4 (2)
C(3)-Ge-Fe(1)	123.1 (3)	O(1)-C(1)-Fe(1)	136.2 (5)
C(2)-Ge-Fe(2)	122.2 (3)	O(1)-C(1)-Fe(2)	136.9 (5)
C(3)-Ge-Fe(2)	119.3 (3)	Fe(1)-C(1)-Fe(2)	86.8 (2)
Fe(1)-Ge-Fe(2)	68.15 (3)	C(11)-C(12)-C(13)	108.6 (8)
Fe(1)-C(10)-O(10)	178.7 (6)	C(12)-C(13)-C(14)	108.3 (8)
Fe(2)-C(20)-O(20)	177.9 (6)	C(13)-C(14)-C(15)	107.5 (8)
C(10)-Fe(1)-Fe(2)	99.4 (2)	C(14)-C(15)-C(11)	106.7 (8)
C(20)-Fe(2)-Fe(1)	101.5 (2)	C(15)-C(11)-C(12)	108.8 (8)
C(10)-Fe(1)-Ge	85.5 (2)	C(21)-C(22)-C(23)	110.2 (8)
C(20)-Fe(2)-Ge	86.3 (2)	C(22)-C(23)-C(24)	107.7 (8)
C(10)-Fe(1)-C(1)	88.2 (3)	C(23)-C(24)-C(25)	107.8 (8)
C(20)-Fe(2)-C(1)	90.3 (3)	C(24)-C(25)-C(21)	108.8 (8)
		C(25)-C(21)-C(22)	105.5 (9)

The intensity ratio of the terminal to bridge resonances is approximately 6:1 and significantly greater than the 2:1 ratio expected. We believe this is largely due to a longer relaxation time of the bridging ^{13}C nucleus and the subsequent partial saturation of the resonance during the course of data collection. This is supported by the observation that in the presence of a relaxation reagent³² this ratio approached very closely to 2:1.

At higher temperatures (above about 90°) the proton nmr spectrum exhibits marked line shape changes indicative of increasingly rapid site-exchange processes. The methyl resonances are shown in Figure 3. They broaden and at about 160° coalesce to a broad single peak. At still higher temperatures there is decomposition which produces paramagnetic impurities. Up to 160° the spectral changes are completely reversible, independent of concentration and, as far as we can tell, not significantly dependent on solvent. The spectral changes were essentially the same in *o*-dichlorobenzene and in diglyme solvents. In this same temperature range the cyclopentadienyl resonances, not illustrated, also broaden and coalesce.

It is evident that the process responsible for the changes in both the methyl and cyclopentadienyl resonances is increasingly rapid cis-trans interconversion. Even at the highest temperatures which could be used prior to the onset of decomposition to paramagnetic impurities, only the coalescence point of the methyl resonances could be reached. The line shape analysis was, therefore, performed in only the slow-to-intermediate exchange rate region. However, there are sufficient data to give accurate activation parameters.

The best fit between observed and calculated spectra occurred for the process in which the single methyl resonance of the trans isomer exchanged with each methyl resonance of the cis isomer, and *vice versa*. Direct exchange between the

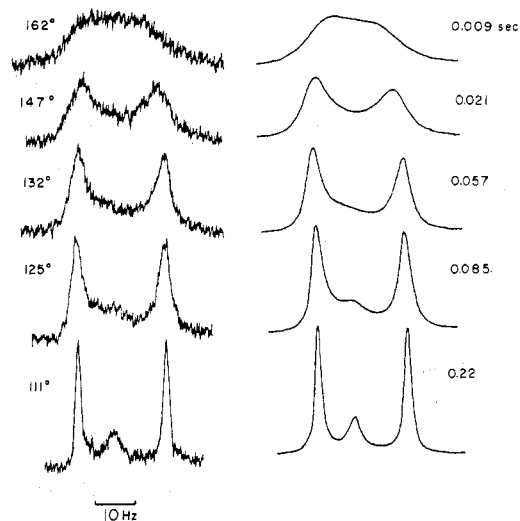


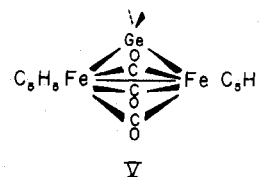
Figure 3. The proton nmr spectra in the CH_3 region at higher temperatures. The observed spectra appear at the left and simulated spectra for various mean residence times at the right. The mechanistic assumptions made in computing spectra are discussed in the text.

two cis methyl resonances was not permitted. A plot of the exchange rates ($1/\tau$) vs. $1/T$ showed that the process obeys the Arrhenius and Eyring equations for unimolecular exchange. The following activation parameters were obtained: $E_a = 20.5 \pm 0.7$, $\log A = 12.2 \pm 1.0$, $\Delta H^\ddagger = 19.7 \pm 0.7$, $\Delta S^\ddagger = -5.0 \pm 2.0$, and $\Delta G^\ddagger_{298} = 21.1 \pm 0.9$.

The ^{13}CO nmr spectra at $+160^\circ$ showed no significant broadening of the resonances.

Discussion

The proton nmr results show that there is a process with an activation energy of about $20.5 \text{ kcal mol}^{-1}$ by which cis and trans isomers, III and IV, are interconverted. We do not believe that a dissociation-recombination mechanism of any sort nor any kind of twisting or deformation of the otherwise intact structure constitutes a credible possibility. Nor do we consider that a pathway traversing the structure V is appeal-



ing either. We therefore turn to a pathway for which there is already abundant evidence in a number of related cases.^{28,30,33,34} This mechanism involves concerted opening

(32) O. A. Gansow, A. R. Burke, and G. N. LaMar, *J. Chem. Soc., Chem. Commun.*, 456 (1972).

(33) F. A. Cotton, Abstracts, 6th International Conference on Organometallic Chemistry, Amherst, Mass., Aug 13, 1973, No. P1.

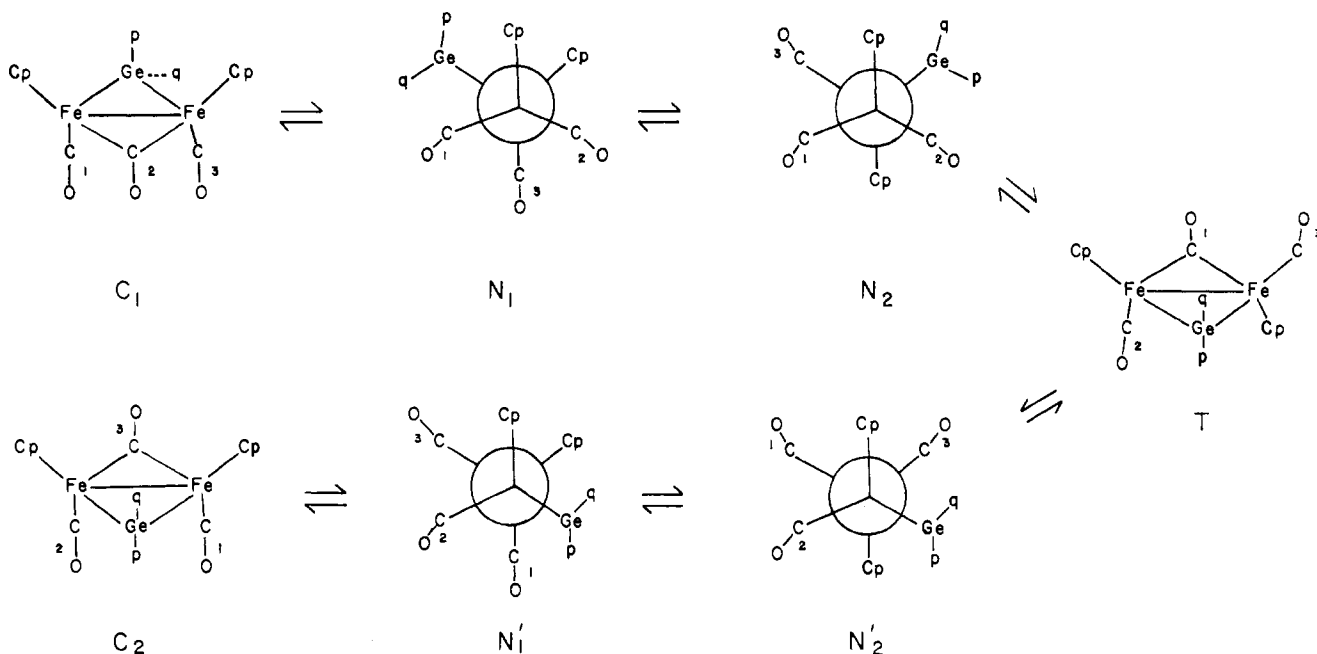
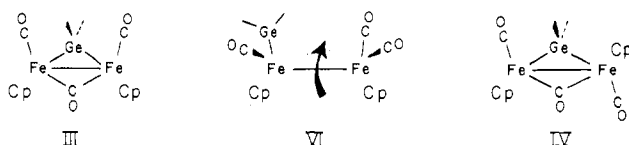


Figure 4. Diagram showing how the cis isomers, C₁ and C₂, are interconverted through the postulated sequence of concerted bridge openings (and closings) and internal rotations. The trans isomer, T, is a necessary intermediate. The overall process C₁ ⇌ C₂ causes site exchange of the methyl groups p and q.

of a pair of bridges, an internal rotation of the nonbridged intermediate, and then concerted reclosing of a pair of bridges. In a simplified form appropriate to the present case it is represented by the sequence III, VI, IV and *vice versa*.



In comparison to systems previously interpreted in terms of such a process, this one is novel in that one of the bridging groups, GeMe₂, opens to give a terminal ligand of a kind which is not yet known in any stable molecule.^{12b} However, in view of the existence of numerous stable metal carbene complexes¹³ the accessibility of the intermediate with a terminal germylene ligand must be considered a reasonable possibility. The expectation that the nonbridged intermediate might be accessible but not very stable would lead to a prediction that the activation energy here would be significantly higher than in cases where two CO groups or a CO group and an isocyano group are the bridging ligands. This is entirely in accord with the experimental facts, since in the present case $E_a \approx 21 \text{ kcal mol}^{-1}$ while for $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_4$, $E_a \approx 12 \text{ kcal mol}^{-1}$.

The proposed mechanism requires that cis-trans isomerization be accompanied by interchange of bridge and terminal CO groups, but this was not actually observed up to 160°, beyond which decomposition to give paramagnetic impurities obscured the spectra. Consideration of the rearrangement rate and its effect on both the proton and ¹³C spectra, however, reveals that these observations are consistent. In the proton spectra the shift differences between the resonances are about 10 Hz and the coalescence point occurs at a rearrangement rate of $\sim 50 \text{ sec}^{-1}$. In the ¹³C spectra, however,

the shift difference between the peaks is about 1600 Hz and coalescence of these peaks would require a rate of about 3500 sec^{-1} . The effect of a rate of 50 sec^{-1} on the ¹³C resonances will, therefore, be only a very slight broadening, as observed.

The line shape analysis of the proton spectra produced the best results when the methyl resonance of the trans isomer was allowed to exchange with each of the methyl resonances of the cis isomer and *vice versa*. However, reasonably adequate spectra were also obtained for the process which allowed random exchange between all three methyl resonances, *i.e.*, exchange of the methyl resonance of the trans isomer with each one from the cis isomer, as well as exchange of the methyl resonances of the cis isomer with each other. We cannot be certain that the apparent difference which favors the nonrandom exchange is real, since small errors in the input of the calculation, such as unrecognized temperature variation in T_2 values or inaccuracies in the temperatures, might be responsible for it. It is worth noting, nevertheless, that such a result is fully consistent with the mechanism we are proposing. To allow discussion of this, the mechanism is presented in detail in Figures 4 and 5.

The cis isomer C₁ has access to the cis isomer C₂ only *via* the trans isomer T. It can reasonably be assumed that rotation about the Fe-Ge bond in the nonbridged isomers is hindered, since the Ge-Fe bond must have considerable π character. If the rotation barrier effectively prevents rotation during the very short time the molecule is in the high-energy states N₁ and N₂, then only by passage through the entire sequence C₁, N₁, N₂, T, N'₂, N'₁, C₂ will there be a net site exchange of the two methyl groups, designated p and q in Figure 4. In this case the rate at which the C₁ ⇌ C₂ interconversion occurs will be half the rate at which C₁ ⇌ T and C₂ ⇌ T interconversions occur, which is in accord with the *prima facie* result of the line shape analysis.

Finally, in connection with the question of the general validity of the process involving concerted, pairwise opening and reclosing of bridges, with intervening rotation, two further observations can be made here. First, if a process ex-

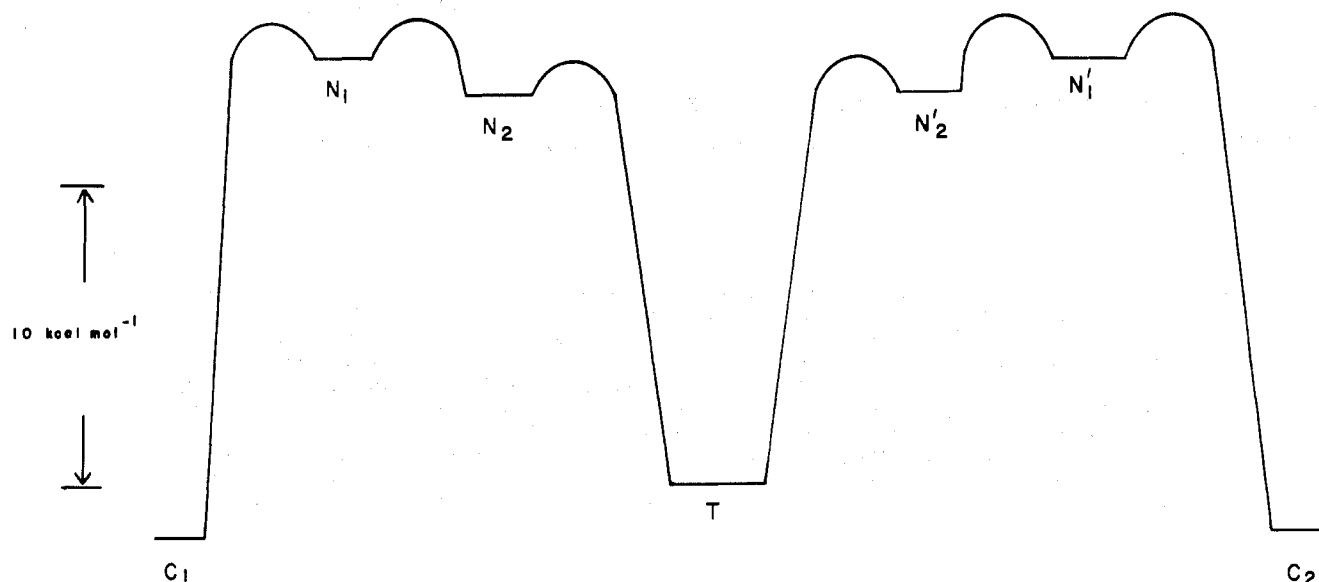
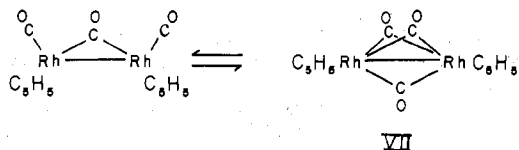


Figure 5. A schematic potential energy diagram corresponding to the rearrangement pathway shown in Figure 4.

changing one terminal and one bridging CO group were facile, we might expect that in $(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_3(\text{GeMe}_2)$ scrambling of bridging and terminal CO groups could occur about as rapidly as in $(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_4$, or in any event more rapidly than cis-trans interconversion, whereas this is not the case. As far as we can tell, bridge-terminal exchange of CO groups is governed by as high an activation energy as the cis-trans interconversion process. Second, we note that there is no case on record in which the postulate of a direct one-for-one exchange of bridge and terminal groups is demanded by experimental data. In the case of $[(\eta^5\text{-C}_5\text{H}_5)\text{-Rh}(\text{CO})]_2(\mu\text{-CO})$ such a process was noted as being consistent with observation,³⁵ as indeed it is. However, the observed bridge-terminal exchange can equally well be explained by traversal of the triply bridged intermediate, VII. The latter



process is of the same concerted, pairwise pattern which occurs in numerous other cases and is also perfectly consistent with all available data.³⁶

(35) J. Evans, B. F. G. Johnson, J. Lewis, and J. R. Norton, *J. Chem. Soc., Chem. Commun.*, 79 (1973).

Registry No. *cis*- $[(\eta\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})]_2(\mu\text{-CO})(\mu\text{-GeMe}_2)$, 50858-99-6.

Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number INORG-74-1080.

(36) Note Added in Proof. Recently it has been stated by R. C. Job and M. D. Curtis, *Inorg. Chem.*, 12, 2114 (1973), that "preliminary results. . . suggest that the methyl group environments are averaged at a faster rate than the rate at which cis-trans isomerization occurs." This, if true, would be inconsistent with the mechanistic analysis we have presented above. We had not previously attempted to carry out a quantitative line shape analysis of the cyclopentadienyl proton signals themselves because we could anticipate that, due to the small separation between them, precise rates and activation parameters would not be obtainable. We had, of course, examined them qualitatively and considered them to be consistent.

However, Mr. Alan J. White has now analyzed the line-shape variation with temperature (75 to 110°) of the cyclopentadienyl signals. Within the relatively large uncertainties arising from the closeness and very unequal intensities of the lines, we find that cis-trans isomerism, as indicated by the coalescence of the cyclopentadienyl signals of the two isomers, is correlated with the site exchange of the methyl groups exactly as required by our proposed mechanism. So far as we can see Job and Curtis's statement is without adequate support either theoretically or experimentally.