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Stereochemically Nonrigid Six-Coordinate Metal Carbonyl Complexes. 1. Polytopal Rearrangement and X-Ray Structure of Tetracarbonylbis(trimethylsilyl)iron

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Carbon-13 NMR evidence is presented for the stereochemical nonrigidity of *cis*-$Fe(CO)_4(SiMe_3)_2$ in solution. Preservation of the $^1J(^{13}CO-^{57}Fe)$ and $^2J(^{13}CO-^{29}Si)$ spin–spin couplings in the high-temperature limiting spectrum proves the intramolecular nature of the rearrangement process. The activation parameters for the rearrangement process are $\Delta H^\ddagger = 10.4 \pm 0.6$ kcal mol^{-1} and $\Delta S^\ddagger = -2.3 \pm 2.6$ eu. The crystal and molecular structure of *cis*-$Fe(CO)_4(SiMe_3)_2$ has been determined. This compound is monomeric and crystallizes in the orthorhombic system with space group *Pnma*; $a = 13.358$ (14) Å, $b = 17.591$ (18) Å, $c = 6.635$ (12) Å, and $Z = 4$. The structure was solved by heavy-atom methods and refined to a final R_1 value of 3.0% for 710 independent diffractometer collected data with $I \geq 3.0\sigma(I)$. A disorder in the positions of about 6% of the molecules limits the precision of the model. The structure is best described as a pseudo-bicapped tetrahedron, with four CO groups tetrahedrally arranged around the iron atom and the $SiMe_3$ as capping ligands. The angle between the axial CO groups is 141.2 (1)°.

Introduction

Six-coordinate complexes in solution may undergo isomerization or permutation of ligand positions (that is, exhibit stereochemical nonrigidity) in two conceptually different ways. In the first, there is an intermediate of different coordination number, more commonly lower (achieved through bond breaking) but conceivably higher (through solvent participation or intermolecular interaction). In the second, the coordination number of the metal remains 6 throughout, and such intramolecular non-bond-breaking rearrangements have been termed polytopal rearrangements.[1,2] An operational distinction between the two classes is most unambiguously made on the basis of metal atom–ligand atom or ligand atom–ligand atom spin–spin coupling, or the lack of it, in the high-temperature limiting NMR spectrum.

As yet, the number of established polytopal rearrangements of six-coordinate complexes is small. Most involve tris-chelate derivatives for which trigonal twist mechanisms have been shown to be likely.[3,4] However, molecules exemplified by $Fe[P(OEt)_3]_4H_2$ provided in 1970 the first unequivocal demonstration of a polytopal rearrangement among six-coordinate species[5-7] and led to the suggestion of a "tetrahedral jump" mechanism to account for the low barrier in these highly distorted[8,9] hydrides.

In 1972 we reported on the facile interconversion of cis and trans isomers of $Os(CO)_4(SiMe_3)_2$,[10] and it was suggested that a polytopal rearrangement was involved. Coalescence of the ^1H NMR peaks of the two isomers occurred at 55 °C, a temperature at which no exchange with free ^{13}CO took place. Breaking of the osmium–silicon bond could not be excluded, but it was considered unlikely in view of the long-term thermal stability of the compound and the near-zero value for the activation entropy.

In this initial paper of a comprehensive study of compounds of the $M(CO)_4(ER_3)_2$ type (M = Fe, Ru, Os; E = Si, Ge, Sn, Pb; R = organic group or halogen), we report a spectroscopic and structural study of tetracarbonylbis(trimethylsilyl)iron, $Fe(CO)_4(SiMe_3)_2$. The synthesis of the latter compound has recently been reported.[11]

Experimental Section

Samples of $Fe(CO)_4(SiMe_3)_2$ were kindly supplied by Dr. W. Jetz, and the compound was handled in an argon- or nitrogen-filled glovebag.

A. Spectroscopic Studies in Solution. Hydrocarbon solvents were distilled from $LiAlH_4$ and saturated with argon or nitrogen prior to use; CD_2Cl_2 was dried over Molecular Sieves (Type 4A).

Carbon-13 NMR spectra were recorded in the pulse Fourier transform mode of operation on a Bruker HFX-90-Nicolet 1085 instrument operating at 22.6 MHz. The temperature unit was calibrated with a thermocouple held coaxially in a spinning sample tube partly filled with solvent. Temperature was controlled by means of a thermocouple situated just beneath the probe. The number of pulses was usually one thousand (1K), but as many as 2K pulses were required in spectra where coalescence was occurring. The number of data points (channels) was 8K and the sweep width was 5000 Hz, affording a digital resolution of 0.06 ppm or 1.25 Hz. In the satellite experiment the sweep width was 2500 Hz with 16K data points and digital resolution of 0.3 Hz. The Bruker instrument was equipped with a single coil; a pulse width of 6–8 μs (90° pulse = 27 μs) was used with a dwell time of 100 μs and an acquisition time of 0.8 s. Spectra were recorded using proton broad-band decoupling conditions.

The NMR solvent and lock were CD_2Cl_2 with tetramethylsilane as internal standard. The amount of ^{13}CO-enriched sample used was approximately 10 mg in 2 mL of solvent in a 10-mm (o.d.) tube for variable-temperature experiments. For the satellite experiment, 300 mg of enriched sample was used with the addition of approximately 10 mg of tris(acetylacetonato)chromium(III).

The simulation of the NMR spectrum of $Fe(CO)_4(SiMe_3)_2$ was accomplished by means of a six-site exchange program written and supplied by Professor D. L. Rabenstein of this department. The chemical shift separation was 19.5 Hz and the half-width was taken as 2.6 Hz (see Results). Line shape analysis of seven spectra recorded between −40 and −70 °C led to the following rates: −70 °C, 9.09 s^{-1}; −65 °C, 19.2 s^{-1}; −60 °C, 26.3 s^{-1}; −55 °C, 51.8 s^{-1}; −50 °C, 85.47 s^{-1}; −45 °C, 147.1 s^{-1}; −40 °C, 344.8 s^{-1}. From these results the activation parameters $\Delta H^\ddagger$ and $\Delta S^\ddagger$ were calculated from a least-squares fit to the Eyring equation.

Mass spectra of $Fe(CO)_4(SiMe_3)_2$ were taken with an Associated Electrical Industries MS-9 instrument, with the inlet system at room temperature. Accurate isotope combination patterns were calculated using a program written by R. S. Gay and E. H. Brooks formerly of this department; simulated patterns for varying ^{13}C content were compared with the observed spectrum to estimate the degree of enrichment.

Infrared spectra were recorded in *n*-heptane using a Perkin-Elmer 337 grating spectrometer with scale expansion and calibration with gaseous CO as previously described.[12]

^{13}CO Enrichment of $Fe(CO)_4(SiMe_3)_2$. In view of the very low solubility of the compound below about −40 °C, moderately high degrees of enrichment were required.

Freshly sublimed $Fe(CO)_4(SiMe_3)_2$ (400 mg) and *n*-heptane (10 mL) were placed in a quartz flask (total volume 58 mL) equipped with a Quickfit Teflon valve, a side arm with serum cap, and a magnetic stirrer. The flask was then attached to a vacuum system having a Toepler pump for manipulation of ^{13}CO. After degassing of the solution by several freeze–thaw cycles, the quartz flask was cooled to −78 °C and ^{13}CO (91.0% isotopic purity, Monsanto Research Corp., Miamisburg, Ohio) was pumped in to a pressure of 800 mmHg.

Exchange was performed at room temperature with stirring and was followed by infrared spectra of samples removed through the serum cap. No ^{13}CO exchange was observed in the dark over a 12-h period. Ultraviolet irradiation at a distance of 15 cm from a 140-W lamp

(Engelhart-Hanovia Inc., Newark, N.J., Model 616 A) resulted in exchange. Irradiation was interrupted after 100 min while the atmosphere of ^{13}CO was replaced with fresh 91.0% enriched material. Irradiation was continued for 270 min, and the solution was syringed from the flask. Solvent was removed under vacuum and the product was sublimed onto a water-cooled probe. From mass spectrometry it was estimated that the degree of enrichment was 35–40%.

B. Determination of Crystal and Molecular Structure. X-Ray Data Collection. Pale yellow crystals of *cis*-$Fe(CO)_4(SiMe_3)_2$ suitable for x-ray diffraction analysis were obtained by slow vacuum sublimation at room temperature onto a water-cooled probe. A platelike crystal with approximate dimensions of 0.20 × 0.20 × 0.10 mm in the [201], [110], and [001] directions, respectively, was used to collect intensity data. The crystal was covered with molten wax and affixed to the inner wall of a nitrogen-filled Lindemann glass capillary tube (0.3-mm diameter).

Preliminary oscillation photographs indicated orthorhombic D_{2h}-$2/m\,2/m\,2/m$ Laue symmetry, while Weissenberg photographs exhibited systematic absences of $k + l = 2n + 1$ for $\{0kl\}$ and $h = 2n + 1$ for $\{h0l\}$, consistent with space groups $Pna2_1$ (No. 33) or *Pnam* (a nonstandard setting of *Pnma*, No. 62).[13] The crystal was transferred to an automated Picker four-circle (FACS) diffractometer and 10 general high-angle reflections were carefully centered in ω, 2θ, χ, and ϕ using Mo Kα radiation (λ 0.710 69 Å) monochromated from the 002 plane of a graphite crystal. The angular coordinates were refined by least-squares methods[14] to yield cell parameters of $a = 13.358$ (14) Å, $b = 6.635$ (12) Å, and $c = 17.591$ (18) Å (23 °C). The experimental density of 1.31 g/cm^3 measured by the pycnometer method[15] using water saturated with nitrogen as the filling liquid is in accord with a value of 1.34 g/cm^3 calculated for a unit cell volume of 1559 Å^3 containing four $Fe(CO)_4(SiMe_3)_2$ formula species.

Intensity data were collected *via* the coupled ω–2θ method with a 2θ scan range of 2.0° plus the $\alpha_1\alpha_2$ dispersion and with a 2θ scan speed of 2.0°/min. Stationary-crystal, stationary-counter background measurements were taken for 20 s at both limits of each scan range. Three standard reflections were measured every 2 h to monitor instrument stability as well as crystal alignment and/or decay. The scintillation counter and pulse height analyzer were adjusted to admit 90% of the Mo Kα peak. The Bragg 2θ angle for the highly oriented graphite-crystal monochromator was 12.2° while a takeoff angle of 2.5° was used for the incident x-ray beam.

Intensity data from ca. 2400 reflections were collected for two octants, *hkl* and $hk\bar{l}$, of the orthorhombic reciprocal axis with $2\theta \leq 45°$. Corrections were made for an observed 15% linear decrease in the standard intensities during the data collection period. After correction for background and Lorentz–polarization effects, structure factor amplitudes and corresponding standard deviations were obtained in a manner previously described.[16] This treatment also included the correction of data for absorption effects (based on a μ value of 11.23 cm^{-1} for Mo Kα radiation).[17] Equivalent data from the two octants were merged to yield 1217 independent reflections of which 710 were considered observed with $I \geq 3.0\sigma(I)$.

Solution and Refinement of the Structure. The approximate positions of the iron and silicon atoms were determined by an interpretation of a three-dimensional Patterson map for the space group *Pnam*. An electron density difference map with structure factors phased by the silicon and iron atoms ($R_1 = 25\%$) revealed the positions of the carbonyl ligands. The coordinates for the remaining nonhydrogen atoms were obtained from subsequent Fourier syntheses. Least-squares refinement of the iron, silicon, carbon, and oxygen atoms with anisotropic thermal parameters was carried out until apparent convergence at $R_1 = 7.5\%$.

An electron density difference map afforded the positions of the methyl hydrogen atoms. Also a "ghost" molecule was found in this map with an electron density of 1.8 e/Å^3 at the site of the alternate iron atom. The terms predominant and alternate molecule were adopted for these species.[18] A subsequent electron density map calculated on the basis of 5% occupancy for the alternate orientation had 0.3 e/Å^3 at the site of the alternate iron atom. The occupancy factor for the alternate orientation was therefore set at 6% and was not refined further. The position of the $FeSi_2$ core of the alternate molecule was allowed to vary in further least-squares cycles and *R* fell to 4%. The alternate molecule was related to the predominant molecule by a twofold rotation axis parallel to *y* and passing through −0.1208 and 0.0552 in *x* and *z*, respectively. The geometry of the alternate molecule was assumed to be the same as that of the predominant molecule and the final positional parameters for the alternate molecule were calculated on this basis; thermal parameters were set at the equivalent isotropic value in the predominant molecule and were not refined. For the final stages of refinement all nonhydrogen atoms in the predominant molecule were allowed anisotropic vibration; the hydrogen atoms in this molecule were treated as hindered rotors,[19] and the various parameters for the alternate molecule were used only in structure factor calculations. At this point the data were transformed to the standard space group *Pnma* (No. 62) and all entries in tables are consistent with this space group. The new unit cell becomes $a = 13.358$ (14), $b = 17.591$ (18), and $c = 6.635$ (12) Å.

Table I. ^{13}C NMR Data for *cis*-$Fe(CO)_4(SiMe_3)_2$ and Related Compounds

Compd	^{13}C chem shifts[a]			
	CO_{ax}	CO_{eq}	CH_3	Temp, K
cis-$Fe(CO)_4(SiMe_3)_2$	208.50	207.64	7.50	183[b]
	208.07		7.61	298[b]
	207.96		7.71	301
$Fe(CO)_4SiMe_2CH_2CH_2SiMe_2$[c]	208.89	207.86	8.37	313
cis-$Os(CO)_4(SiMe_3)_2$[d]	181.48	172.58	6.74	303
trans-$Os(CO)_4(SiMe_3)_2$[d]	186.17		8.04	303

[a] On the δ scale, ppm downfield from TMS. Solvent is toluene-d_8 except as noted. Axial and equatorial assignments of carbonyl resonances must be regarded as uncertain; see text. [b] CD_2Cl_2 solvent. [c] Reference 25. [d] Reference 29.

The final discrepancy values were $R_1 = 3.0\%$ and $R_2 = 3.8\%$[20] for 710 observed data with no Δ/σ values greater than 0.5 and with a final goodness of fit value of 1.034. The atomic scattering factors for the hydrogen[21] and nonhydrogen[22] atoms were taken from the literature with corrections applied for real and imaginary anomalous dispersion effects[23] for iron and silicon.

A table of observed and calculated structure factors is available.[24]

Major computer programs used in these analyses are local versions of SFLS5 by C. T. Prewitt, GONO9 by W. C. Hamilton, FORDAP by A. Zalkin, ORFFE by W. A. Busing and H. A. Levy, and ORTEP by C. K. Johnson.

Results

A. Spectroscopic Studies in Solution. At −90 °C, the ^{13}C NMR spectrum showed carbonyl peaks at 208.50 and 207.64 ppm in addition to the methyl resonance at 7.50 ppm. These values are compared with chemical shifts in some related molecules in Table I. In this table, and in subsequent discussion, we define the equatorial plane of the molecule as that containing the iron and both silicon atoms, as is customary with complexes of this type. The assignment of carbonyl resonances as axial or equatorial is made in analogy with the known assignment for $Os(CO)_4H_2$;[25] in view of recent extensive studies of *cis*-$Fe(CO)_4(SnR_3)_2$ complexes,[26] it must be regarded as uncertain.

The pattern of coalescence as the sample was warmed from −90 °C is shown in Figure 1. The low-temperature limiting spectrum was reached at −80 °C. Spectra were completely reversible.

The half-width of the carbonyl signals at −90 °C was 4.0 Hz, larger than the half-width of 2.6 Hz observed at −20 °C. We attribute this to a ^{13}C–^{13}C spin–spin coupling (the sample was 35–40% ^{13}CO enriched because of its low solubility below −40 °C) rather than to a viscosity effect since the half-width of the TMS signal was practically unchanged to −90 °C. In simulation of the spectra, a low-temperature limiting half-width of 2.6 Hz was employed. Line shape analysis of seven spectra recorded between −40 and −70 °C led to the following activation parameters: $\Delta H^{\ddagger} = 10.4 \pm 0.6$ kcal mol^{-1}, $\Delta S^{\ddagger} = -2.3 \pm 2.6$ eu.

The free energy of activation for this rearrangement process can be estimated from the chemical shift separation of the axial and equatorial resonances in the low-temperature limiting spectrum (19.5 Hz) and the coalescence temperature (−55 °C).

Table II

(a) Atomic Coordinates and Thermal Parameters for the Predominant Molecule with Standard Deviations in Parentheses

(1) Positional Parameters for Nonhydrogen Atoms

Atom	x	y	z
Fe	−0.0611 (1)	0.2500[a]	−0.0170 (1)
Si	−0.1488 (1)	0.3656 (1)	0.0920 (2)
C(1)	0.0193 (3)	0.3218 (3)	−0.120 (1)
O(1)	0.0713 (2)	0.3654 (2)	−0.191 (1)
C(3)	−0.1650 (5)	0.2500[a]	−0.179 (1)
O(3)	−0.2333 (4)	0.2500[a]	−0.287 (1)
C(4)	−0.0302 (4)	0.2500[a]	0.243 (1)
O(4)	−0.0119 (4)	0.2500[a]	0.412 (1)
C(5)	−0.1779 (4)	0.4274 (3)	−0.126 (1)
C(6)	−0.0676 (4)	0.4226 (3)	0.263 (1)
C(7)	−0.2699 (3)	0.3478 (3)	0.222 (1)

(2) Hydrogen Coordinates Derived from Hindered Rotors

Atom	x	y	z
H(1)	−0.101	0.474	0.283
H(2)	−0.000	0.432	0.196
H(3)	−0.062	0.394	0.385
H(4)	−0.224	0.401	−0.222
H(5)	−0.113	0.439	−0.202
H(6)	−0.208	0.477	−0.080
H(7)	−0.303	0.396	0.251
H(8)	−0.255	0.319	0.352
H(9)	−0.314	0.314	0.135

(3) Thermal Parameters[b]

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Fe	0.0305	0.0385	0.0565	0.0000	0.0026	0.0000
Si	0.0405	0.0359	0.0808	0.0036	0.0046	0.0004
C(1)	0.0385	0.0575	0.0715	0.0005	0.0079	0.0064
O(1)	0.0615	0.0751	0.1274	−0.0137	0.0297	0.0246
C(3)	0.0572	0.0501	0.0674	0.0000	−0.0016	0.0000
O(3)	0.0767	0.0898	0.1051	0.0000	−0.0457	0.0000
C(4)	0.0380	0.0410	0.0719	0.0000	0.0042	0.0000
O(4)	0.0855	0.0779	0.0582	0.0000	−0.0110	0.0000
C(5)	0.0838	0.0534	0.1378	0.0015	−0.0094	−0.0293
C(6)	0.0753	0.0582	0.1204	0.0126	−0.0015	0.0194
C(7)	0.0629	0.0548	0.1336	0.0099	0.0387	−0.0062

(b) Positional Parameters (Not Refined) for the Alternate Molecule

Atom	x	y	z
Fe	−0.180	0.250	0.128
Si	−0.094	0.136	0.015
C(1)	−0.261	0.178	0.231[c]
O(1)	−0.313	0.135	0.302
C(3)	−0.077	0.250	0.290
O(3)	−0.008	0.250	0.398[c]
C(4)	−0.211	0.250	−0.132
O(4)	−0.229	0.250	−0.301[c]
C(5)	−0.174	0.077	−0.153[c]
C(6)	−0.063	0.073	0.237[c]
C(7)	0.028	0.152	−0.111

[a] Constrained by symmetry considerations. [b] U in the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + \ldots + 2U_{12}hka^*b^* + \ldots)]$. [c] Denotes near coincidence with an atom in the predominant orientation.

The $\Delta G^\ddagger$ value so obtained (10.7 kcal mol^{-1}) is remarkably close to that calculated (10.9 kcal mol^{-1}) from the $\Delta H^\ddagger$ and $\Delta S^\ddagger$ values obtained from complete line shape analysis.

A careful examination of the ^{13}C NMR spectrum above coalescence (28 °C) revealed two satellite pairs of the carbonyl resonance at 208.07 ppm, as shown in Figure 2. The inner pair is assigned as $^2J(^{13}C\text{–}Fe\text{–}^{29}Si)$ = 6 Hz, and the outer pair, as $^1J(^{13}C\text{–}^{57}Fe)$ = 25 Hz. Our $^1J(^{13}C\text{–}^{57}Fe)$ compares favorably with the similar coupling in $Fe(CO)_5$ (23.4 Hz)[27] or (butadiene)$Fe(CO)_3$ (27.9 Hz).[28]

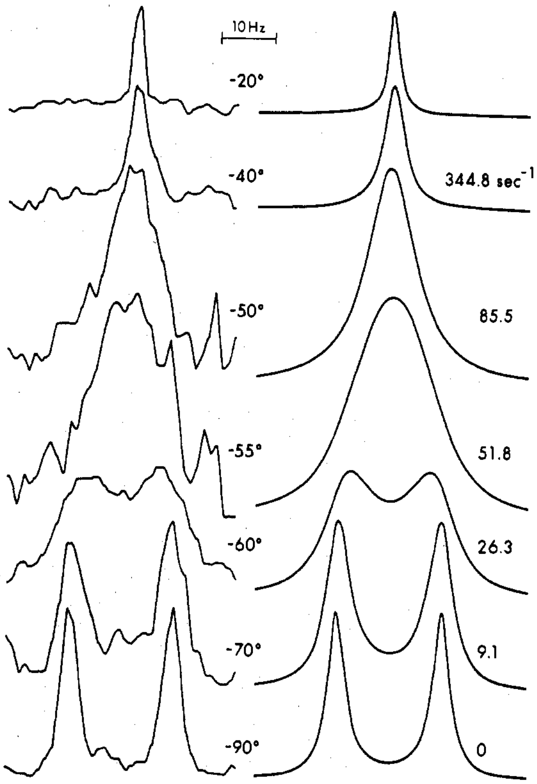

Figure 1. Fourier transform ^{13}C NMR spectrum of the carbonyl region of ^{13}CO-enriched *cis*-$Fe(CO)_4(SiMe_3)_2$ in CD_2Cl_2, observed (left) and calculated (right) for $\Delta H^\ddagger$ = 10.4 kcal mol^{-1} and $\Delta S^\ddagger$ = −2.3 eu.

Table III

(a) Bond Distances (Å) and Their Standard Deviations for the Predominant Molecule

Fe–C(1)	1.793 (5)	Si–C(6)	1.852 (6)
Fe–C(3)	1.756 (7)	Si–C(7)	1.866 (5)
Fe–C(4)	1.775 (7)	C(1)–O(1)	1.137 (6)
Fe–Si	2.456 (2)	C(3)–O(3)	1.160 (9)
Si–C(5)	1.853 (6)	C(4)–O(4)	1.143 (9)

(b) Bond Angles (deg) and Their Standard Deviations for the Predominant Molecule

C(3)–Fe–C(4)	141.2 (1)	Fe–Si–C(6)	110.8 (2)
C(1)–Fe–C(1′)	89.5 (4)	Fe–Si–C(7)	114.4 (2)
C(1)–Fe–C(3)	103.9 (3)	C(5)–Si–C(6)	106.4 (2)
C(1)–Fe–C(4)	103.4 (2)	C(5)–Si–C(7)	108.3 (3)
C(1)–Fe–Si	79.3 (2)	C(6)–Si–C(7)	106.2 (3)
Si–Fe–C(3)	78.7 (2)	Fe–C(1)–O(1)	177.4 (5)
Si–Fe–C(4)	79.9 (2)	Fe–C(3)–O(3)	179.6 (4)
Si–Fe–Si′	111.8 (1)	Fe–C(4)–O(4)	178.8 (4)
Fe–Si–C(5)	110.3 (2)		

(c) Nonbonding Intramolecular Distances (Å)

Si–C(1)	2.759 (7)	C(1)–C(6)	3.310 (7)
Si–C(3)	2.724 (5)	C(3)–C(5)	3.145 (7)
Si–C(4)	2.766 (3)	C(3)–C(7)	3.466 (7)
Si–Si	4.067 (3)	C(4)–C(6)	3.080 (7)
C(1)–C(1′)	2.53 (1)	C(4)–C(7)	3.638 (7)
C(1)–C(3)	2.795 (7)	C(7)–C(7′)	3.437 (7)
C(1)–C(4)	2.797 (7)	H(8)–H(8′)	2.43
C(1)–C(5)	3.224 (7)	H(9)–H(9′)	2.25

Table IV. Deviations of Atoms from the Fe–Si–Si′–C(1)–C(1′) Plane of Equation $0.5268x + 0.8500z + 0.5295 = 0$

Atom	Dev, Å	Atom	Dev, Å
Fe	0.004	C(1)	−0.012
Si	0.002	C(1′)	−0.012
Si′	0.002		

In Figure 3, the infrared spectrum of $Fe(CO)_4(SiMe_3)_2$ is compared with that of the closely related chelate $Fe(CO)_4(SiMe_2CH_2CH_2SiMe_2)$,[25] both spectra in *n*-heptane solution. The infrared spectrum of $Fe(CO)_4(SiMe_3)_2$ has been re-

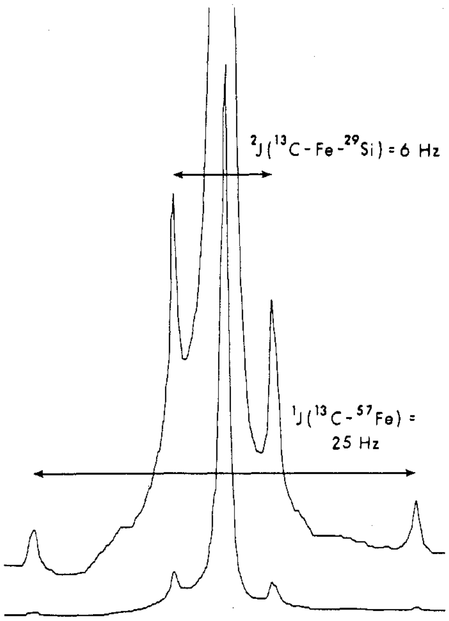

Figure 2. ^{13}C NMR spectrum in CD_2Cl_2 at 28 °C of ^{13}CO-enriched *cis*-$Fe(CO)_4(SiMe_3)_2$ showing spin–spin couplings to ^{57}Fe (2.19% abundant) and ^{29}Si (4.70% abundant).

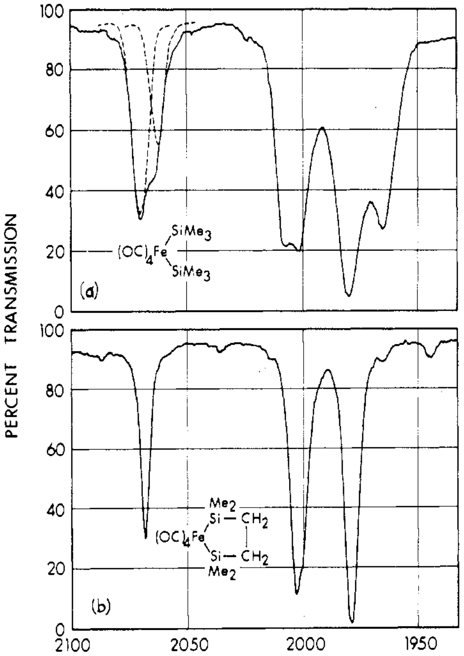

Figure 3. (a) Infrared spectrum in *n*-heptane of *cis*-$Fe(CO)_4(SiMe_3)_2$; precise band positions are 2069, 2062, 2006, 2000, 1979, and 1964 cm^{-1}. First two bands were curve-resolved (dashed line) with a Du Pont 310 curve resolver. (b) Infrared spectrum in *n*-heptane of $Fe(CO)_4SiMe_2CH_2CH_2SiMe_2$; precise band positions are 2068, 2003, 2000, and 1978 cm^{-1}.

produced previously,[11] but a direct comparison with that of the chelate is important in the discussion of the present work.

B. Crystal Structure of *cis*-$Fe(CO)_4(SiMe_3)_2$. The results of the single-crystal x-ray diffraction analysis of *cis*-$Fe(CO)_4(SiMe_3)_2$ are summarized in Tables II–IV. The numbering scheme is defined in Figure 4. The final positional and thermal parameters for the predominant molecule are presented in Table II along with the calculated positional parameters for the alternate molecule. Interatomic distances and bond angles (with standard deviations calculated from the variance–covariance matrix) are listed in Table III. The least-squares plane defined by the equatorial atoms and the perpendicular displacements of individual atoms from this plane are given in Table IV.

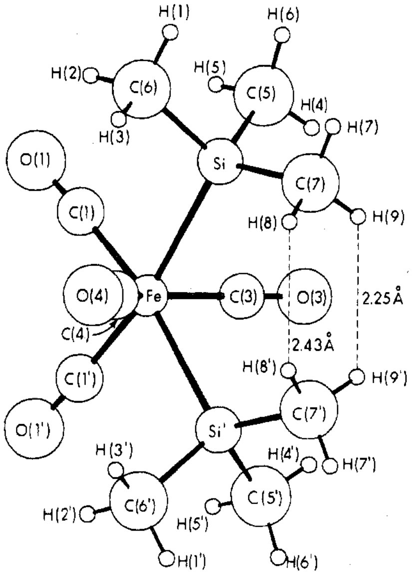

Figure 4. Molecular structure of *cis*-$Fe(CO)_4(SiMe_3)_2$.

Discussion

Two aspects of the investigation of *cis*-$Fe(CO)_4(SiMe_3)_2$ warrant discussion: the process whereby axial and equatorial carbonyl groups of *cis*-$Fe(CO)_4(SiMe_3)_2$ are averaged in solution and the distorted solid-state structure as determined by x-ray crystallography. As is usual with compounds of this geometry, the term equatorial carbonyl refers to the groups trans to the trimethylsilyl substituents.

Axial–Equatorial Carbonyl Averaging. The variable-temperature ^{13}C NMR spectra of Figure 1 show the averaging of signals due to axial and equatorial groups; the high-temperature limiting spectrum of Figure 2, in which both $^{13}CO-^{57}Fe$ and $^{13}CO-^{29}Si$ spin–spin couplings are observed, indicates that the interchange does not involve ligand–metal bond breaking. The failure of *cis*-$Fe(CO)_4(SiMe_3)_2$ to exchange with ^{13}CO in solution without irradiation confirms that the carbonyl ligands do not dissociate; $\Delta S^{\ddagger}$ for the interchange is consistent with a process which is neither dissociative (large positive $\Delta S^{\ddagger}$ expected) nor associative (large negative $\Delta S^{\ddagger}$ expected).

An attractive mechanism for carbonyl averaging in *cis*-$Fe(CO)_4(SiMe_3)_2$ would involve its passage through a trans intermediate (all carbonyl ligands equivalent) followed by its return to the cis form. For the osmium analogue, occurrence of this cis to trans to cis isomerization process was substantiated by the coalescence of ^{13}CO signals observed for cis and trans isomers concurrently with axial–equatorial carbonyl averaging in the cis form.[29] For the iron analogue, our inability to detect any signal due to the trans isomer in the low-temperature limiting ^{13}C NMR spectrum means that no such positive indication is available. It is in no way inconsistent with a trans intermediate, however.[30]

Strong indirect evidence for a trans intermediate in the carbonyl averaging of *cis*-$Fe(CO)_4(SiMe_3)_2$ comes from the variable-temperature ^{13}C NMR study of the closely related chelate derivative $Fe(CO)_4(SiMe_2CH_2CH_2SiMe_2)$.[25] For this compound, the trans form is inaccessible, and the spectra showed stereochemical rigidity on the NMR time scale at 80 °C.

While the present study is consistent with the notion of averaging by the cis to trans to cis process, it affords no insight into the intimate details of ligand motion by which this isomerization is accomplished. The two best known rear-

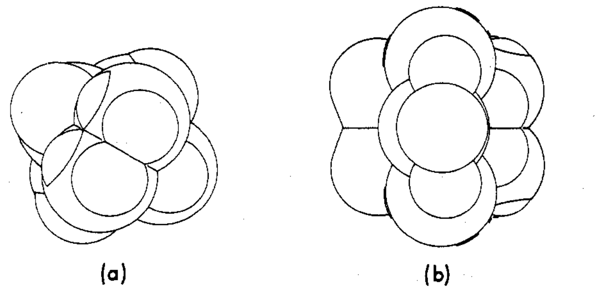

Figure 5. van der Waals surfaces of *cis*-$Fe(CO)_4(SiMe_3)_2$: (a) viewed from the *b* axis; (b) viewed from the direction in the mirror plane perpendicular to the line joining both possible iron atom positions.

rangement pathways are the trigonal twist and the tetrahedral jump. The latter was first proposed to account for the low barriers to polytopal rearrangement in complexes of the type *cis*-$Fe[P(OR)_3]_4H_2$, in which the phosphite ligands were roughly tetrahedrally disposed around iron, with hydride ligands over two faces of the tetrahedron.[5,8] The solid-state geometry of *cis*-$Fe(CO)_4(SiMe_3)_2$ is rather similar, and the rate of ligand averaging is comparable in some cases.[31] However, for the silyliron derivative, the insufficient abundance of ligand nuclei of spin $^1/_2$ precludes the detailed NMR analysis of mechanism that was possible in the FeP_4H_2 system.

Crystal and Molecular Structure. The x-ray diffraction study of crystalline $Fe(CO)_4(SiMe_3)_2$ has revealed a solid-state structure corresponding to the cis isomer (Figure 4). The crystal structure of *cis*-$Fe(CO)_4(SiMe_3)_2$ consists of the packing of four discrete monomeric molecules per orthorhombic unit cell, with each molecule located on a crystallographic mirror plane. Each molecule has crystallographically imposed C_{2v}-$2mm$ symmetry with the mirror plane bisecting the Si–Fe–Si′ angle. The C_{2v} molecular geometry is also exemplified by the planarity of the equatorial ligands (Table IV).

The precision of the model is limited by a disorder in the positions of about 6% of the molecules, with the alternate molecules related to the predominant molecules by a twofold rotation axis. The positional parameters for both the predominant and alternate molecules are listed in Table II. Figure 5 shows the predominant molecule with atoms drawn to their van der Waals radii where (a) and (b) are viewed respectively from the *b* axis and from the direction in the mirror plane perpendicular to the line joining both possible iron atom positions. The van der Waals radii of the predominant molecule (shown) and those of the alternate molecule (obtained by a 180° rotation of the predominant molecule) are very similar.

The molecule exhibits great distortion from regular octahedral geometry such that it may appropriately be described as a pseudo-bicapped tetrahedron with the trimethylsilyl groups as capping ligands. The angle between the axial carbonyl carbons (C(3)–Fe–C(4)) is 141.2 (1)° instead of the expected 180° for a regular octahedron. The angles between the axial and equatorial carbonyl carbons (C(1)–Fe–C(3) and C(1)–Fe–C(4)) are 103.9 (3) and 103.4 (2)°, respectively. Only the angle between the equatorial carbonyl carbons (C(1)–Fe–C(1′)) at 89.5 (4)° is within 1° of its idealized octahedral value.

The orientation of the two $SiMe_3$ groups with respect to each other was initially surprising in that two methyl groups (C(7) and C(7′)) point almost directly at one another (the C(7)–C(7′) distance is 3.437 (7) Å). The deviation of C(7) and C(7′) from the Fe-Si-Si′-C(1)-C(1′) plane is −0.117 Å.

The silicon atom is approximately equidistant from C(1), C(3), and C(4), and all three angles Si–Fe–C(1), –C(3), and –C(4) are less than 90°. This corresponds to a very favorable cis ligand interaction between the whole trimethylsilyl group and the three carbonyl carbons closest to it. The methyl carbons are staggered with respect to the carbonyl carbons such that C(5) is almost bisecting the C(1)–Fe–C(3) angle, C(6) is bisecting the C(1)–Fe–C(4) angle, and C(7) is bisecting the C(3)–Fe–C(4) angle. This "bisecting" geometry dictates the unusual arrangement of methyl groups centered on C(7) and C(7′). The distortion in the present structure relieves the intramolecular repulsions C(4)–C(6) and C(3)–C(5). The Si–Fe–Si′ angle (111.8 (1)°) is consistent with net repulsion between the trimethylsilyl groups.

The trimethylsilyl ligands appear to have a normal geometry. The average silicon–carbon distance of 1.86 Å and average metal–silicon–carbon angle of 112° may be compared with 1.88 Å and 114° for the equivalent parameters in $Ru_2(CO)_6(SiMe_2)_2(SiMe_3)_2$.[32]

The iron–silicon bond length in *cis*-$Fe(CO)_4(SiMe_3)_2$ (2.456 (2) Å) is very close to the value observed in *cis*-$Fe(CO)_4(H)SiPh_3$ (2.415 (3) Å),[33] although it is considerably longer than the distance observed in *trans*-$Fe(CO)_4(SiCl_3)_2$ (2.326 (2) Å).[34] The iron–silicon bond lengths observed in cyclopentadienyliron derivatives ((η-C_5H_5)$Fe(CO)(H)(SiF_2Me)_2$, 2.249 (1) Å;[35] (η-C_5H_5)$Fe(CO)(H)(SiCl_3)_2$, 2.252 (3) Å;[36] (η-C_5H_5)$Fe(CO)(H)(SiMe_2Ph)_2$, 2.336 (3) Å;[33] (η-C_5H_5)$Fe(PMe_2Ph)_2SiMe_2Ph$, 2.339 (2) Å[37]) are all shorter than the present iron–silicon distance.

The average of the three independent iron–carbon distances in *cis*-$Fe(CO)_4(SiMe_3)_2$ is 1.775 Å, which compares favorably with the average value of 1.785 Å in *cis*-$Fe(CO)_4(H)SiPh_3$.[35]

As noted above, the molecule is distorted significantly from ideal octahedral geometry. The angle between the axial carbonyls (C(3)–Fe–C(4)) is 141.2°, although it is less extreme than in $Fe[PPh(OEt)_2]_4H_2$ where the corresponding P–Fe–P angle is 136.7°.[9] The magnitude of this distortion is unprecedented in *cis*-$Fe(CO)_4X_2$ derivatives. Distortions from octahedral geometry to angles of 156 and 165° have been claimed for the two independent molecules of $[Fe(CO)_4SnMe_2]_2$[38] but the reliability of these data is low due to severe disorder problems. Similar distortions were observed in the electron diffraction study of $Fe(CO)_4H_2$[39] or the crystal structures of $[(\sigma\text{-}C_5H_5)_2SnFe(CO)_4]_2$,[40] $Fe(CO)_4(C_{12}H_8O)$,[41] and $Fe(CO)_4(C_8H_6O_6)$[42] where angles of 148.5, 163.5, 164.4, and 166° were observed, respectively. Smaller distortions (less than 10°) were observed in $Fe(CO)_4(HgBr)_2$,[43] $Fe(CO)_4(CF_2CF_2H)_2$,[44] or $[Fe(CO)_4SiCl_2]_2$.[45]

The distortion in *cis*-$Fe(CO)_4(SiMe_3)_2$ undoubtedly has its origin in both steric and electronic grounds. Closing the Si–Fe–Si′ angle to 90° and adopting the most favorable "cogwheel" arrangement of the trimethylsilyl groups reduce the C(7)–C(7′) contact to 3.09 Å, probably an unacceptable value. On the other hand, it has recently been shown by extended Hückel calculations that very good σ donors, such as the trimethylsilyl group, can stabilize the bicapped tetrahedron.[46]

Finally, it is worth contrasting the essentially octahedral geometry of *cis*-$Ru(CO)_4(GeCl_3)_2$, in which OC_{ax}–Ru–CO_{ax} = 173 (1) and 174 (2)°, with Ge–Ru–Ge = 91.5 (2) and 90.5 (1)°.[16] The Fe–Si distance (2.456 (2) Å) and the Ru–Ge distance (from 2.466 (5) to 2.488 (6) Å) differ little, but the $GeCl_3$ ligands, in contrast to the $SiMe_3$ ligands, give rise to no short contacts when arranged at 90° to one another. In our view, the electronic properties of the trichlorogermyl ligand would be quite different from those of a trialkyl-group 4 ligand; we would not regard the $GeCl_3$ ligand as a particularly good σ donor and thus would not expect a distortion toward a bicapped tetrahedral geometry on electronic grounds.

Evidence for *trans*-$Fe(CO)_4(SiMe_3)_2$ in Solution. The appearance of six carbonyl stretching bands in the infrared spectrum of *cis*-$Fe(CO)_4(SiMe_3)_2$ was unexpected, since only four are predicted for the C_{2v} symmetry of the molecule. Four bands were in fact observed in the infrared spectrum of the chelate derivative $Fe(CO)_4(SiMe_2CH_2CH_2SiMe_2)$.[25] When infrared spectra of these two compounds are compared (Figure 3), it is apparent that four of the bands of *cis*-$Fe(CO)_4(SiMe_3)_2$ (those at 2069, 2006, 2000, and 1979 cm^{-1}) are very similar to those of the chelate. The most reasonable explanation is that the remaining two bands of the "cis" isomer (at 2062 and 1964 cm^{-1}) are due in fact to a distorted trans isomer present in equilibrium.[47] No NMR evidence for the trans isomer was found, for the reasons previously outlined.[52]

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Registry No. *cis*-$Fe(CO)_4(SiMe_3)_2$, 53248-31-0; ^{13}C, 14762-74-4.

Supplementary Material Available: Listing of structure factor amplitudes (4 pages). Ordering information is given on any current masthead page.

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(30) Solution infrared spectra discussed below show significant amounts (perhaps 10–20%) of trans isomer in equilibrium with *cis*-$Fe(CO)_4(SiMe_3)_2$ at room temperature. The failure to observe the trans form in the NMR spectrum at −90 °C could be due to a small cis $\rightleftharpoons$ trans equilibrium constant at that temperature; a decrease from 20% trans at 25 °C to 5% trans at −90 °C implies $\Delta H^\circ \simeq 1.5$ kcal mol^{-1}, reasonable in comparison with the measured value of 0.85 kcal mol^{-1} for the osmium analogue.[29] On the other hand, the ^{13}C carbonyl signal observed at 25 °C is precisely the average of the separate carbonyl signals at −90 °C (Table I). This could be rationalized by assuming that the ^{13}CO chemical shift of the trans isomer is equal to the mean of axial and equatorial resonances of the cis isomer. However, the precise agreement of calculated and observed shifts is fortuitously good in view of the digital resolution of 0.06 ppm. Even under the assumption that the chemical shift of the trans isomer is degenerate with that of the axial cis resonance at 208.50 ppm, the calculated average resonance for 20% trans would be 208.16 ppm; the difference between this and the observed 208.07-ppm value is hardly significant. We conclude that there is no discrepancy between the infrared and NMR observations.
(31) Reference 7 gives free energies of activation for a number of H_2FeP_4 complexes: $\Delta G^\ddagger$ values range from 11.5 to 16.2 kcal mol^{-1}; for $H_2Fe[PPh(OEt)_2]_4$, $\Delta G^\ddagger$ at −19 °C is 12.2 kcal mol^{-1}; for *cis*-$Fe(CO)_4(SiMe_3)_2$, $\Delta G^\ddagger$ at −19 °C is calculated to be 11.0 kcal mol^{-1}.
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(52) The situation is entirely opposite to that involving *trans*-$Fe(CO)_4(SiCl_3)_2$ in equilibrium with *cis*-$Fe(CO)_4(SiCl_3)_2$. The presence in solution of the trans form was not suspected from infrared study and was revealed only in the ^{13}C NMR spectrum: ref 29, especially footnote 15.