

Isolation of a Dimeric Form of "Bis(trimethylsilyl) iron Tetracarbonyl"

M. A. Nasta,¹ A. G. MacDiarmid,* and F. E. Saalfeld

Contribution from the John Harrison Laboratory of Chemistry and the Laboratory for Research on the Structure of Matter, University of Pennsylvania, Philadelphia, Pennsylvania 19104, and the Naval Research Laboratory, Washington, D. C. 20390. Received June 18, 1971

Abstract: The reaction of $(\text{CH}_3)_3\text{SiI}$ with $\text{Na}_2\text{Fe}(\text{CO})_4$ yields a dimer of empirical formula $[(\text{CH}_3)_3\text{Si}]_2\text{Fe}(\text{CO})_4$. It is believed this species may have a tetrahedral framework consisting of two carbon atoms and two iron atoms which can be represented by the formula $[(\text{CH}_3)_3\text{SiFe}(\text{COSi}(\text{CH}_3)_3)(\text{CO})_3]_2$. It reacts with excess HCl with the liberation of $(\text{CH}_3)_3\text{SiCl}$ to form $[(\text{CH}_3)_3\text{SiFe}(\text{COH})(\text{CO})_3]_2$. This latter compound reacts with $(\text{CH}_3)_3\text{SiCl}$ in the presence of $(\text{CH}_3)_3\text{N}$ to re-form $[(\text{CH}_3)_3\text{SiFe}(\text{COSi}(\text{CH}_3)_3)(\text{CO})_3]_2$. The thermal stability of $[(\text{CH}_3)_3\text{SiFe}(\text{COSi}(\text{CH}_3)_3)(\text{CO})_3]_2$ and also its chemical reactivity toward oxygen, water, methanol, trimethylamine, trimethylphosphine, and tetra-*n*-butylammonium chloride are reported and compared with the reactivity of compounds containing Si-Mn and Si-Co linkages.

A number of compounds of the type $\text{R}_2\text{Fe}(\text{CO})_4$ ($\text{R} = \text{C}_2\text{F}_5$,² C_3F_7 ,² CF_2Br ,³ SiH_3 ,⁴ SiCl_3 ,^{5,6} $\text{Si}(\text{C}_2\text{H}_5)_3$,⁶ GeH_3 ,⁷ $\text{Ge}(\text{C}_2\text{H}_5)_3$,⁶ GeCl_3 ,⁸ GeBr_3 ,⁸ GeI_3 ,⁸ $\text{Sn}(\text{CH}_3)_3$,^{9,10} $\text{Sn}(\text{C}_2\text{H}_5)_2\text{Cl}$,¹⁰ $\text{Sn}(\text{C}_4\text{H}_9)_2\text{Cl}$,¹⁰ $\text{Sn}(\text{C}_6\text{H}_5)_3$,¹¹ SnCl_3 ,⁸ SnBr_3 ,⁸ $\text{Pb}(\text{C}_2\text{H}_5)_3$,⁹ $\text{Pb}(\text{C}_6\text{H}_{11})_3$,¹¹ and $\text{Pb}(\text{C}_6\text{H}_5)_3$,¹¹ and $\text{R}(\text{H})\text{Fe}(\text{CO})_4$ ($\text{R} = \text{H}_3\text{Si}$,⁴ Cl_3Si ,¹² $\text{C}_6\text{H}_5\text{Si}$,¹²) have been described in the literature. These are believed to be monomeric species in which the iron is exhibiting a coordination number of six.

Compounds of the type $\text{R}_2\text{Fe}(\text{CO})_4$ have usually been synthesized by one of three general methods: (1) $\text{RX} + \text{Fe}(\text{CO})_4^{2-}$ (where $\text{R} = \text{C}_2\text{F}_5\text{CO}$ -, H_3Si -, etc.; $\text{X} = \text{halogen}$), (2) $\text{R}_3\text{MX} + \text{Fe}(\text{CO})_5$ (where $\text{R} = \text{alkyl}$, halogen , etc.; $\text{M} = \text{Ge}$, Sn ; $\text{X} = \text{halogen}$), or (3) $\text{R}_3\text{MH} + \text{Fe}_3(\text{CO})_{12}$ (where $\text{R} = \text{alkyl}$, halogen , etc.; $\text{M} = \text{Si}$, Ge). The compounds $\text{R}_3\text{Si}(\text{H})\text{Fe}(\text{CO})_4$ have been formed by the reaction of R_3SiH ($\text{R} = \text{Cl}$, C_6H_5) with $\text{Fe}(\text{CO})_5$, whereas $\text{H}_3\text{Si}(\text{H})\text{Fe}(\text{CO})_4$ has been produced as a by-product in the synthesis of $(\text{H}_3\text{Si})_2\text{Fe}(\text{CO})_4$ and by the reaction of $(\text{H}_3\text{Si})_2\text{Fe}(\text{CO})_4$ with HCl.

Results and Discussion

We have previously reported¹³ that the reaction of $\text{Na}_2\text{Fe}(\text{CO})_4$ with $(\text{CH}_3)_3\text{SiI}$ leads to the formation of a

*Address correspondence to this author at the University of Pennsylvania.

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(2) R. B. King, S. L. Stafford, P. M. Treichel, and F. G. A. Stone, *J. Amer. Chem. Soc.*, **83**, 3604 (1961).

(3) F. Seel and G.-V. Röschenhaler, *Angew. Chem.*, **82**, 182 (1970).

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(7) S. R. Stobart, *Inorg. Nucl. Chem. Lett.*, **7**, 219 (1971).

(8) R. Kummer and W. A. G. Graham, *Inorg. Chem.*, **7**, 1208 (1968).

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(11) F. Hein and W. Jehn, *Justus Liebigs Ann. Chem.*, **684**, 4 (1965); F. Hein and E. Heuser, *Z. Anorg. Allg. Chem.*, **254**, 138 (1947).

(12) W. Jetz and W. A. G. Graham, *J. Amer. Chem. Soc.*, **91**, 3375 (1969); W. Jetz and W. A. G. Graham, *Inorg. Chem.*, **10**, 4 (1971).

compound of empirical composition $[(\text{CH}_3)_3\text{Si}]_2\text{Fe}(\text{CO})_4$. It was surprising to find that molecular weight measurements in cyclohexane and also in chloroform showed that it was a dimer in these solvents. It is not clear whether monomeric $[(\text{CH}_3)_3\text{Si}]_2\text{Fe}(\text{CO})_4$ was formed initially and then spontaneously rearranged to the dimeric species or whether the dimer was formed directly from the reactants in some manner. Some recent observations show that, in certain instances, the reaction of R_3SiCl ($\text{R} = \text{phenyl}$, methyl) with the sodium salt of a transition metal carbonyl in the presence of tetrahydrofuran does not give the corresponding silicon-transition metal product; instead, most of the silicon appears as the disiloxane, $(\text{R}_3\text{Si})_2\text{O}$, and complex transition metal carbonyls are formed.¹⁴⁻¹⁷ Thus when $(\text{CH}_3)_3\text{SiCl}$ and $\text{NaMn}(\text{CO})_5$ underwent reaction in tetrahydrofuran solution only traces of $(\text{CH}_3)_3\text{Si-Mn}(\text{CO})_5$ were formed, but when $(\text{CH}_3)_3\text{SiCl}$ was permitted to react with dry, THF-free $\text{NaMn}(\text{CO})_5$ for 20 min at room temperature, up to 70% yields of $(\text{CH}_3)_3\text{Si-Mn}(\text{CO})_5$ were obtained.^{14,16} In order to ascertain whether tetrahydrofuran could be responsible for the formation of the dimeric " $[(\text{CH}_3)_3\text{Si}]_2\text{Fe}(\text{CO})_4$," a slurry of dry, THF-free $\text{Na}_2\text{Fe}(\text{CO})_4$ in hexane was allowed to react with $(\text{CH}_3)_3\text{SiI}$. The dimer was again produced; it therefore does not seem that tetrahydrofuran is responsible for its formation, although it is always possible that traces of tetrahydrofuran could still have been present in the solid $\text{Na}_2\text{Fe}(\text{CO})_4$.

Structure of Dimeric " $[(\text{CH}_3)_3\text{Si}]_2\text{Fe}(\text{CO})_4$." Four of the most probable structures for this compound, all of which give iron an effective atomic number of krypton, are I-IV. A compound having a somewhat similar structure to those depicted by I and II, which may be considered as containing substituted carbene ligands, has been obtained by Fischer and Kiener,^{18,19} by

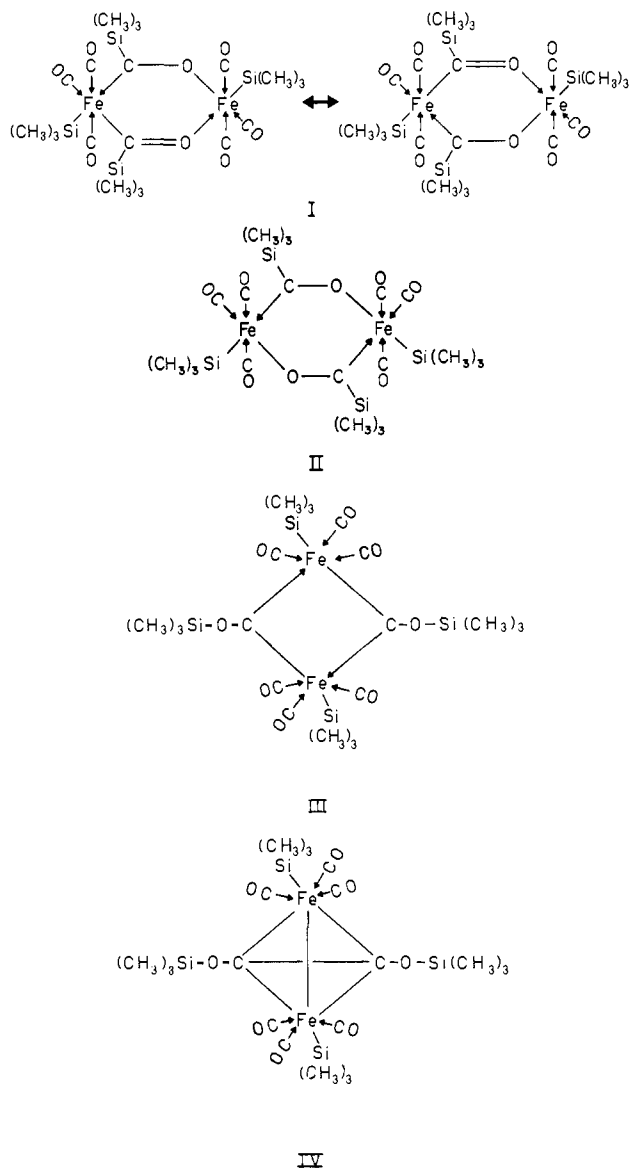
(13) M. A. Nasta and A. G. MacDiarmid, *J. Amer. Chem. Soc.*, **93**, 2813 (1971).

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(16) A. D. Berry and A. G. MacDiarmid, *ibid.*, **5**, 601 (1969).

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treating $\text{Fe}(\text{CO})_5$ with LiR ($\text{R} = \text{CH}_3, \text{C}_6\text{H}_5$) to give $(\text{OC})_4\text{FeC}(\text{R})\text{OLi}$, which, upon reaction with $(\text{C}_6\text{H}_5)_3\text{CCl}$, yielded $(\text{OC})_3\text{FeC}(\text{R})\text{O}_2\text{Fe}(\text{CO})_3$.

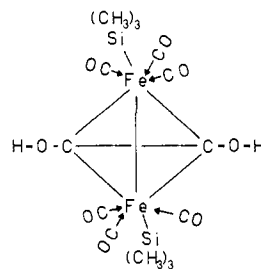
We believe that the most probable configuration of the dimer, $\{[(\text{CH}_3)_3\text{Si}]_2\text{Fe}(\text{CO})_4\}_2$, is $[(\text{CH}_3)_3\text{Si}(\text{COSi}(\text{CH}_3)_3)(\text{CO})_3]_2$, *i.e.*, that given by the closely related structures III or IV.²⁰ As mentioned below, the mass spectrum of the compound favors structure IV somewhat more than structure III, although both structures are consistent with the infrared, proton nmr, and mass spectra of the compound and with its chemical properties. Thus, excess anhydrous hydrogen chloride underwent reaction with a cyclohexane solution of $\{[(\text{CH}_3)_3\text{Si}]_2\text{Fe}(\text{CO})_4\}_2$ to liberate exactly half the $(\text{CH}_3)_3\text{Si}$ groups as $(\text{CH}_3)_3\text{SiCl}$. The other product, a yellow solid, had an empirical composition which would correspond to any one of the three compounds $[(\text{CH}_3)_3\text{SiFe}(\text{COH})(\text{CO})_3]_2$, $(\text{CH}_3)_3\text{Si}(\text{H})\text{Fe}(\text{CO})_4$, or $[(\text{CH}_3)_3\text{SiFe}(\text{CO})_4]_2$. It was not sufficiently soluble in any appropriate solvent to obtain a molecular weight, but

(18) E. O. Fischer and V. Kiener, *J. Organometal. Chem.*, **23**, 215 (1970).

(19) P. F. Lindley and O. S. Mills, *J. Chem. Soc., A*, 1279 (1969).

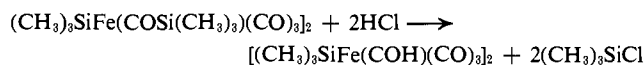
(20) A single-crystal X-ray examination of $\{[(\text{CH}_3)_3\text{Si}]_2\text{Fe}(\text{CO})_4\}_2$ is currently being carried out by Professor Jerry Donohue in this department.

its infrared, proton nmr, and mass spectra favor the configuration $[(\text{CH}_3)_3\text{SiFe}(\text{COH})(\text{CO})_3]_2$, such as that given by structure V. Hence, the reaction with HCl



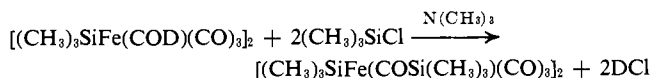
V

may be represented by the equation



This type of reaction with HCl seems reasonable in view of the fact that Si-O-C bonds can be readily cleaved by hydrogen chloride (for example in $n\text{-C}_4\text{H}_9\text{-O-Si}(\text{CH}_3)_3$ ²¹) to give the corresponding alcohol and chlorosilane; no simple process is apparent for obtaining an alcohol and $(\text{CH}_3)_3\text{SiCl}$ by the hydrogen chloride cleavage of the Si-C bonds in structure I or II. The fact that no cleavage of the Si-Fe bond occurred is not necessarily surprising in view of the fact that the Si-Mn bond in $(\text{CH}_3)_3\text{Si-Mn}(\text{CO})_5$ is not cleaved by anhydrous liquid hydrogen chloride (homogeneous solution) during 12 hr at room temperature¹⁴ and that the Si-Co bond in $(\text{CH}_3)_3\text{Si-Co}(\text{CO})_4$ is cleaved only slowly by hydrogen chloride at room temperature.²²

A general reaction of alcohols is that they will react with $(\text{CH}_3)_3\text{SiCl}$ in the presence of a hydrogen chloride scavenger to form the corresponding $\text{>C-O-Si}(\text{CH}_3)_3$ species and hydrogen chloride. It was found that $[(\text{CH}_3)_3\text{SiFe}(\text{COSi}(\text{CH}_3)_3)(\text{CO})_3]_2$ could be regenerated from $[(\text{CH}_3)_3\text{SiFe}(\text{COD})(\text{CO})_3]_2$ by treating it with excess $(\text{CH}_3)_3\text{SiCl}$ and $(\text{CH}_3)_3\text{N}$ at room temperature, *viz.*



Infrared Spectra. The infrared spectrum of $[(\text{CH}_3)_3\text{SiFe}(\text{COSi}(\text{CH}_3)_3)(\text{CO})_3]_2$ (see Table I) in the CO stretching region is not inconsistent with structure IV. The remainder of the spectrum, particularly those bands in the Si-O-C region (1228 (m), 1098 (s), 986 (s) cm^{-1}), support this structure. In this respect it might be noted that $(\text{CH}_3)_3\text{SiOC}(\text{CH}_3)_3$ has bands at 1206 (vs), 1060 (vs), 1029 (vs), and 939 (vs) cm^{-1} ,²³ and that the carbene derivative, $(\text{OC})_5\text{Cr}\leftarrow\text{C}(\text{CH}_3)\text{OSi}(\text{CH}_3)_3$, has bands at 1100 (s) and 975 (m) cm^{-1} .²⁴

No band attributable to an Fe-H stretching vibration was observed in the spectrum of $[(\text{CH}_3)_3\text{SiFe}(\text{COH})(\text{CO})_3]_2$, but well-defined free and hydrogen-bonded OH

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(24) E. Moser and E. O. Fischer, *J. Organometal. Chem.*, **12**, P1 (1968).

Table I. Infrared Absorption Maxima (cm⁻¹)^a

$[(\text{CH}_3)_3\text{SiFe}(\text{COSi}(\text{CH}_3)_3)(\text{CO})_3]_2^b$	$[(\text{CH}_3)_3\text{SiFe}(\text{COH})(\text{CO})_3]_2^c$	Assignment	Ref
	3596 (w)	Free O-H stretch	<i>d</i>
	3578 (w)	Free O-H stretch	<i>d</i>
	3488 (sh)	H-bonded O-H stretch	<i>d</i>
	3382 (m)	H-bonded O-H stretch	<i>d</i>
	2912 (vw)	C-H stretch	<i>e</i>
2066 (s) [2065 (s)]	2064 (s) [2066 (s)]	C-O stretch	
	[2033 (sh)]	C-O stretch	
2022 (vs) [2021 (vs)]	2020 (vs) [2021 (vs)]	C-O stretch	
2000 (vs) [1994 (vs)]	1990 (vs) [1989 (vs)]	C-O stretch	
1976 (vs) [1975 (vs)]	1972 (vs) [1967 (vs)]	C-O stretch	
1962 (sh) [1953 (sh)]	1952 (sh) [1947 (sh)]	¹³ C-O stretch	
1934 (m) [1932 (m)]	1932 (m) [1929 (m)]	¹³ C-O stretch	
	1526 (w)	Unassigned	
1466 (w)		CH ₃ asym def	<i>e</i>
1440 (sh)	1444 (w)	CH ₃ asym def	<i>e</i>
1410 (m)		CH ₃ asym def	<i>e</i>
1354 (w)	1388 (w)	Unassigned	
1266 (w)	1264 (sh)	CH ₃ sym def	<i>e</i>
1256 (m)	1252 (m)	CH ₃ sym def	<i>e</i>
1228 (m)		C-O-Si stretching region	<i>f</i>
	1180 (m)	O-C-C-O stretching region	<i>g</i>
	1168 (sh)	O-C-C-O stretching region	<i>g</i>
1158 (w)		Unassigned	
1098 (s)		C-O-Si stretching region	<i>f, h</i>
	1042 (m)	O-C-C-O stretching region	<i>g</i>
		C-O-Si stretching region	<i>f, h</i>
	956 (m)	O-C-C-O stretching region	<i>g</i>
886 (m)	886 (w)	CH ₃ asym rock	<i>e</i>
852 (s)	850 (m)	CH ₃ asym rock	<i>e</i>
768 (sh)	768 (w)	CH ₃ sym rock	<i>e</i>
760 (w)		CH ₃ sym rock	<i>e</i>
652 (m)	642 (m)	Si-C asym stretch	<i>e</i>
632 (w)	632 (w)	Si-C sym stretch	<i>e</i>
630 (sh)		Si-C sym stretch	<i>e</i>
616 (m)	604 (m)	Fe-C-O vibration	<i>i</i>
600 (sh)		Fe-C-O vibration	<i>i</i>
586 (w)	588 (sh)	Fe-C-O vibration	<i>i</i>
572 (w)	568 (sh)	Fe-C-O vibration	<i>i</i>

^a All spectra were recorded with a Perkin-Elmer Model 521 double-beam grating spectrophotometer. Values in brackets are from the high-resolution spectra in the carbonyl stretching region. ^b Cyclohexane solution in a cell fitted with CsBr windows. ^c Nujol mulls (between KBr plates), with the exception of the peaks at 2912 (vw), 1444 (w), and 1388 (w) cm⁻¹, which were observed using a fluorocarbon mull. ^d R. M. Silverstein and G. C. Bassler, "Spectrometric Identification of Organic Compounds," Wiley, New York, N. Y., 1967, pp 84-85. ^e H. Bürger, *Organometal. Chem. Rev., Sect. A*, **3**, 425 (1968). ^f Assigned on the basis of very strong absorptions in (CH₃)₃SiOC(CH₃)₃ at 1206, 1060, 1029 and 939 cm⁻¹: E. W. Abel, *J. Chem. Soc.*, 4406 (1960). ^g H. A. Szymanski, "Interpreted Infrared Spectra," Vol. II, Plenum Press, New York, N. Y., 1966, pp 23-286. ^h Assigned on the basis of the 1100 (s) and 975 (m) cm⁻¹ absorptions in (OC)₃Cr(CH₃)₃-O-Si(CH₃)₃. ⁱ Reference 6.

Stretching vibrations were present. The infrared spectrum of [(CH₃)₃SiFe(COD)(CO)₃]₂ (prepared from [(CH₃)₃SiFe(COSi(CH₃)₃)(CO)₃]₂ and DCl) showed only very weak OH stretching bands owing to the presence of trace amounts of [(CH₃)₃SiFe(COH)(CO)₃]₂. The OD stretching bands had the same general contours as the OH stretching bands in the analogous compound, [(CH₃)₃SiFe(COH)(CO)₃]₂, and fell at 2654 (sh), 2642 (w), 2578 (w), 2554 (sh), 2502 (m). The (average ν_{OH})/(average ν_{OD}) ratio of the protonated to deuterated compound was 1.35. The ν_{OH}/ν_{OD} ratios in H₂O-D₂O and CH₃OH-CH₃OD are also both 1.35.²⁵ When [(CH₃)₃SiFe(COD)(CO)₃]₂ was treated with gaseous HCl, the infrared spectrum of the product showed that the deuterium was partly replaced by protium.

The rest of the infrared spectrum of [(CH₃)₃SiFe(COH)(CO)₃]₂ is consistent with the proposed structure. The CO stretching region is similar to that of [(CH₃)₃SiFe(COSi(CH₃)₃)(CO)₃]₂, which would seem to indicate that little change has occurred in the metal-carbonyl

framework. The bands attributed to the C-O-Si stretching vibrations in [(CH₃)₃SiFe(COSi(CH₃)₃)(CO)₃]₂ had disappeared and were replaced by a medium band at 1180 cm⁻¹, together with other bands [1042 (m), 956 (m)] which may be associated with the stretching vibrations of the O-C-C-O system.²⁶ With reference to the 1180-cm⁻¹ band, it might be noted that a strong band associated with saturated tertiary alcohols falls in the 1124-1208-cm⁻¹ region.²⁷

Proton Nuclear Magnetic Resonance Spectra. The spectrum of a 5% solution of [(CH₃)₃SiFe(COSi(CH₃)₃)(CO)₃]₂ in cyclohexane consisted of two sharp peaks of exactly equal area in the (CH₃)₃Si region at τ 9.66 and 9.73. At 60 MHz the separation between the peaks was 4.0 Hz; at 100 MHz it was 6.6 Hz, thus indicating that the signals are due to two different types of (CH₃)₃-Si groups rather than to a coupling phenomenon. No change in the shapes or chemical shifts of the peaks was observed when spectra of an 8% solution in decane

(25) G. Herzberg, "Molecular Spectra and Molecular Structure," Vol. II, "Infrared and Raman Spectra of Polyatomic Molecules," Van Nostrand, Princeton, N. J., 1962, p 280-282, 334-335.

(26) H. A. Szymanski, "Interpreted Infrared Spectra," Vol. II, Plenum Press, New York, N. Y., 1966, pp 23-286.

(27) R. M. Silverstein and G. C. Bassler, "Spectrometric Identification of Organic Compounds," Wiley, New York, N. Y., 1967, pp 84-85.

were studied in the 30–110° range. These data are consistent with structure IV; structure I would be expected to give three peaks in the ratio 1:2:1 for each of the three different (CH₃)₃Si environments.

Considerable difficulty was encountered in obtaining a satisfactory proton nmr spectrum of [(CH₃)₃SiFe(COH)(CO)₃]₂ because of its low solubility in common solvents. The (CH₃)₃Si group had a τ value of 9.70 in cyclohexane. No Fe–H signal could be observed. A broad, weak signal was observed in DCCl₃ solution at τ 5.03 using a time-averaging computer. This is consistent with the presence of COH groups, but in view of the experimental difficulties encountered, it should not be considered as definite evidence.

Mass Spectra. Fragmentation patterns obtained at 70 V for [(CH₃)₃SiFe(COSi(CH₃)₃)(CO)₃]₂ and [(CH₃)₃SiFe(COH)(CO)₃]₂, together with their possible assignments, are given in Tables II and III, respectively.

Table II. Mass Spectral Fragmentation Pattern of [(CH₃)₃SiFe(COSi(CH₃)₃)(CO)₃]₂^a

<i>m/e</i>	Rel int	Possible assignments ^b
684	11.3	[(CH ₃) ₃ Si] ₂ Fe ₂ [COSi(CH ₃) ₃] ₂ (CO) ₆ ⁺
656	12.2	[(CH ₃) ₃ Si] ₂ Fe ₂ [COSi(CH ₃) ₃] ₂ (CO) ₇ ⁺
628	8.5	[(CH ₃) ₃ Si] ₂ Fe ₂ [COSi(CH ₃) ₃] ₂ (CO) ₆ ⁺
600	27.7	[(CH ₃) ₃ Si] ₂ Fe ₂ [COSi(CH ₃) ₃] ₂ (CO) ₅ ⁺
572	52.7	[(CH ₃) ₃ Si] ₂ Fe ₂ [COSi(CH ₃) ₃] ₂ (CO) ₄ ⁺
544	13.5	[(CH ₃) ₃ Si] ₂ Fe ₂ [COSi(CH ₃) ₃] ₂ (CO) ₃ ⁺
516	4.8	[(CH ₃) ₃ Si] ₂ Fe ₂ [COSi(CH ₃) ₃] ₂ (CO) ₂ ⁺
300 ^c	7.8	[(CH ₃) ₃ Si] ₂ Fe ₂ [COSi(CH ₃) ₃] ₂ (CO) ₆ ²⁺
286 ^c	3.9	[(CH ₃) ₃ Si] ₂ Fe ₂ [COSi(CH ₃) ₃] ₂ (CO) ₄ ²⁺
272 ^c	7.4	[(CH ₃) ₃ Si] ₂ Fe ₂ [COSi(CH ₃) ₃] ₂ (CO) ₃ ²⁺
258 ^c	34.0	[(CH ₃) ₃ Si] ₂ Fe ₂ [COSi(CH ₃) ₃] ₂ (CO) ₂ ²⁺ , [(CH ₃) ₃ Si] ₂ Fe ₂ ⁺
147	7.8	(CH ₃) ₃ Si–O–Si(CH ₃) ₂ ⁺
145	9.1	(CH ₃) ₃ Si–O–Si(CH ₂) ₂ ⁺
132	7.9	(CH ₃) ₂ Si–O–Si(CH ₃) ₂ ⁺
75	6.5	Isotope peak of <i>m/e</i> 73
74	12.2	Isotope peak of <i>m/e</i> 73
73	100	(CH ₃) ₃ Si ⁺
71	7.4	(CH ₃)(CH ₂) ₂ Si ⁺
44	13.4	SiO ⁺
28	19.4	CO ⁺ , Si ⁺

^a All mass spectra were obtained at 70 V on a modified Bendix time-of-flight instrument using techniques described previously: F. E. Saalfeld and M. V. McDowell, *Inorg. Chem.*, **6**, 96 (1967); F. E. Saalfeld, M. V. McDowell, S. K. Gondal, and A. G. MacDiarmid, *J. Amer. Chem. Soc.*, **90**, 3684 (1968). The compounds were introduced directly into the ion source *via* a heated probe (probe temperature 205°, sample temperature 80°). ^b Only peaks of relative intensity greater than 5% are tabulated, with the exception of the peaks at *m/e* 516 and 286. ^c The doubly charged ion assignments for the group of peaks from *m/e* 258 to 300 are supported by the observation that these peaks first appear at a relatively high electron energy value (~25 V).

Relatively strong parent ion peaks are observed for both [(CH₃)₃SiFe(COSi(CH₃)₃)(CO)₃]₂ and [(CH₃)₃SiFe(COH)(CO)₃]₂. Both spectra exhibit singly and doubly charged fragments where the basic C–C–Fe–Fe framework apparently remains intact. This favors the tetrahedral cage structures of the type given by IV and V rather than the ring-type of structures given by I, II, and III. It seems likely that some thermal decomposition of both compounds may have occurred in the probe, since both spectra showed a relatively strong (CH₃)₃Si–O–Si(CH₃)₂⁺ peak which is the strongest peak in the mass spectrum of [(CH₃)₃Si]₂O.²⁸ This con-

(28) A. G. Sharkey, R. A. Friedel, and S. H. Langer, *Anal. Chem.*, **29**, 770 (1957).

Table III. Mass Spectral Fragmentation Pattern of [(CH₃)₃SiFe(COH)(CO)₃]₂^a

<i>m/e</i>	Rel int	Possible assignments ^b
540	20.3	[(CH ₃) ₃ Si] ₂ Fe ₂ (COH) ₂ (CO) ₆ ⁺
512	6.9	[(CH ₃) ₃ Si] ₂ Fe ₂ (COH) ₂ (CO) ₇ ⁺
484	19.4	[(CH ₃) ₃ Si] ₂ Fe ₂ (COH) ₂ (CO) ₆ ⁺
456	28.9	[(CH ₃) ₃ Si] ₂ Fe ₂ (COH) ₂ (CO) ₅ ⁺
428	44.0	[(CH ₃) ₃ Si] ₂ Fe ₂ (COH) ₂ (CO) ₄ ⁺
400	18.7	[(CH ₃) ₃ Si] ₂ Fe ₂ (COH) ₂ (CO) ₃ ⁺
372	11.3	[(CH ₃) ₃ Si] ₂ Fe ₂ (COH) ₂ (CO) ₂ ⁺
355	9.0	[(CH ₃) ₃ Si][CH ₃ Si]Fe ₂ (CO) ₄ ⁺
327	6.1	[(CH ₃) ₃ Si][CH ₃ Si]Fe ₂ (CO) ₃ ⁺
297	7.4	[(CH ₃) ₃ Si]Fe ₂ (CO) ₄ ⁺
280	5.5	(CO) ₃ Fe–Fe(CO) ₃ ⁺
228 ^c	5.8	[(CH ₃) ₃ Si] ₂ Fe ₂ (COH) ₂ (CO) ₅ ²⁺
226	7.2	[(CH ₃) ₃ Si]Fe ₂ (CO) ₅ ⁺
214 ^c	7.6	[(CH ₃) ₃ Si] ₂ Fe ₂ (COH) ₂ (CO) ₄ ²⁺
212	7.6	(CH ₃) ₃ SiFe(COH)(CO) ₃ ⁺
211	5.0	(CH ₃) ₃ Si(CO)Fe(CO) ₃ ⁺
210	7.1	(CH ₂) ₃ Si(CO)Fe(CO) ₃ ⁺
200 ^{c,d}		[(CH ₃) ₃ Si] ₂ Fe ₂ (COH) ₂ (CO) ₃ ²⁺
186 ^c	5.0	[(CH ₃) ₃ Si] ₂ Fe ₂ (COH) ₂ (CO) ₂ ²⁺
153	7.7	HOC(C)Fe(CO) ₂ ⁺
148	5.3	Isotope peak of <i>m/e</i> 147
147	26.4	(CH ₃) ₃ Si–O–Si(CH ₃) ₂ ⁺
132	7.4	(CH ₃) ₂ Si–O–Si(CH ₃) ₂ ⁺
131	7.7	(CH ₃) ₂ Si–O–Si(CH ₃)(CH ₂) ⁺
112	6.1	Fe(CO) ₂ ⁺
93	6.6	Unidentified
84	16.9	SiFe ⁺ , Fe(CO) ⁺
74	7.7	Isotope peak of <i>m/e</i> 73
73	70.9	(CH ₃) ₃ Si ⁺
56	20.5	Fe ⁺
55	6.8	(CH)(CH ₂) ₂ Si ⁺
45	26.2	SiOH ⁺
44	13.3	SiO ⁺
43	22.1	CH ₃ Si ⁺
42	6.1	CH ₂ Si ⁺
41	12.9	CHSi ⁺
29	12.2	COH ⁺
28	100	CO ⁺ , Si ⁺
27	5.7	Unidentified

^a Probe temperature 275°, sample temperature 117° (see footnote a of Table II). ^b Only peaks of relative intensity greater than 5% are tabulated. ^c The doubly charged ion assignments for the peaks at *m/e* 228, 214, 200, and 186 are supported by the observation that the peaks first appear only at a relatively high electron energy value (~25 V). ^d No intensity is cited because of interference by the mercury isotope at this mass; however, the total intensity observed at *m/e* 200 is greater than that obtained for mercury alone when examined under comparable conditions.

clusion is supported by intense peaks at *m/e* 28 (CO) and 73 ((CH₃)₃Si) in both spectra.

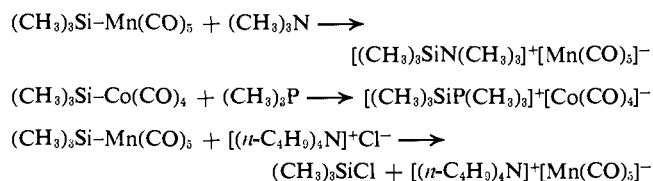
It is interesting to note the presence of (P + 2CO) and (P + CO) peaks in the spectra of both compounds. A similar observation has been noted in the spectrum of C₆H₅SnCl₂Fe(CO)₂(π-C₅H₅), where a (P + 2CO) peak has been reported.²⁹ It is believed that the (P + 2CO) and (P + CO) peaks in the spectra of [(CH₃)₃SiFe(COSi(CH₃)₃)(CO)₃]₂ and [(CH₃)₃SiFe(COH)(CO)₃]₂ may possibly arise from species produced by a gas-phase reaction occurring upon vaporization, in which CO is inserted into the Si–Fe bonds. Such species might be expected to show the consecutive loss of six CO groups (as observed experimentally), the inserted CO groups, being bound to two separate atoms, behaving differently from the six terminal CO groups. Water peaks of variable intensity were present in both spectra and are believed to arise from the desorption of

(29) D. S. Field and M. J. Newlands, *J. Organometal. Chem.*, **27**, 213 (1971).

water from the metal surfaces in the mass spectrometer. This phenomenon is encountered not infrequently in studies of this type involving substances of low volatility.

Attempts are presently being made to synthesize $[(\text{CH}_3)_3\text{Si}]_2\text{Fe}(\text{CO})_4$ by a completely different method (from $(\text{CH}_3)_3\text{SiH}$ and $\text{Fe}_3(\text{CO})_{12}$) in order to ascertain whether the monomeric form might be obtained in this fashion. The properties of certain $(\text{R}_3\text{Si})_2\text{Fe}(\text{CO})_4$ and $\text{R}_3\text{Si}(\text{H})\text{Fe}(\text{CO})_4$ species previously described in the literature are also currently being examined in order to ascertain whether any of them have similar structures to $[(\text{CH}_3)_3\text{SiFe}(\text{COSi}(\text{CH}_3)_3)(\text{CO})_3]_2$ and $[(\text{CH}_3)_3\text{SiFe}(\text{COH})(\text{CO})_3]_2$, respectively.

Chemical Properties of $[(\text{CH}_3)_3\text{SiFe}(\text{COSi}(\text{CH}_3)_3)(\text{CO})_3]_2$. In a previous study,^{30,31} we had examined the thermal stability and chemical properties of another compound containing a Si-Fe bond, *viz.*, $(\text{CH}_3)_3\text{SiFe}(\text{CO})_2(\pi\text{-C}_5\text{H}_5)$, with a variety of reagents. The reactions of $[(\text{CH}_3)_3\text{SiFe}(\text{COSi}(\text{CH}_3)_3)(\text{CO})_3]_2$ with a number of these same reagents under identical experimental conditions (usually 1 hr at room temperature) were studied. Like $(\text{CH}_3)_3\text{Si-Fe}(\text{CO})_2(\pi\text{-C}_5\text{H}_5)$, it showed good thermal stability *in vacuo*. Thus, after 1 hr at 225°, it was recovered essentially unchanged. Similarly to $(\text{CH}_3)_3\text{Si-Fe}(\text{CO})_2(\pi\text{-C}_5\text{H}_5)$, it showed no reaction after 1 hr at room temperature with $(\text{CH}_3)_3\text{N}$, $(\text{CH}_3)_3\text{P}$, or $[(n\text{-C}_4\text{H}_9)_4\text{N}]^+\text{Cl}^-$ in homogeneous solutions. It might be noted that the nonreactivity of the Si-Fe bond toward the reagents differs markedly from that of some other silicon derivatives of the transition metal carbonyls which react instantly with these reagents at room temperature, *viz.*^{14, 16, 32, 33}



After 4 days in the presence of oxygen at somewhat less than atmospheric pressure, $[(\text{CH}_3)_3\text{SiFe}(\text{COSi}(\text{CH}_3)_3)(\text{CO})_3]_2$ was recovered almost quantitatively. Like $(\text{CH}_3)_3\text{Si-Fe}(\text{CO})_2(\pi\text{-C}_5\text{H}_5)$, it did not react with liquid water during 1 day at room temperature, possibly because it was not wet by water. In this respect, these compounds differ greatly from solid $(\text{CH}_3)_3\text{Si-Co}(\text{CO})_4$, which is hydrolyzed rapidly by water to $[(\text{CH}_3)_3\text{Si}]_2\text{O}$.³³ However, $[(\text{CH}_3)_3\text{SiFe}(\text{COSi}(\text{CH}_3)_3)(\text{CO})_3]_2$ differed from $(\text{CH}_3)_3\text{Si-Fe}(\text{CO})_2(\pi\text{-C}_5\text{H}_5)$ in that in ethereal solution it was extensively hydrolyzed to $[(\text{CH}_3)_3\text{Si}]_2\text{O}$ in 1 hr, whereas $(\text{CH}_3)_3\text{Si-Fe}(\text{CO})_2(\pi\text{-C}_5\text{H}_5)$ suffered no hydrolysis under comparable conditions. The Si-Fe bond in it was also more susceptible to cleavage by CH_3OH in homogeneous solution than the Si-Fe bond in $(\text{CH}_3)_3\text{Si-Fe}(\text{CO})_2(\pi\text{-C}_5\text{H}_5)$. In the former compound, nearly 8% of the $(\text{CH}_3)_3\text{Si}$ groups appeared as $(\text{CH}_3)_3\text{SiOCH}_3$ after 1 hr; no $(\text{CH}_3)_3\text{SiOCH}_3$ was formed from the latter compound during a similar period. The greatest difference in properties of the

Si-Fe bond in $[(\text{CH}_3)_3\text{SiFe}(\text{COSi}(\text{CH}_3)_3)(\text{CO})_3]_2$ and $(\text{CH}_3)_3\text{Si-Fe}(\text{CO})_2(\pi\text{-C}_5\text{H}_5)$ was observed in their reactions with anhydrous HCl; no cleavage of this linkage occurred in the former compound, whereas the Si-Fe bond was cleaved extremely rapidly (to give $(\text{CH}_3)_3\text{SiCl}$) in the latter species. In this respect it might be noted that no cleavage of the Si-Mn bond occurs in a homogeneous solution of $(\text{CH}_3)_3\text{Si-Mn}(\text{CO})_5$ in neat, anhydrous HCl during 12 hr at room temperature.¹⁴

From the above data it can be seen that the properties of the $(\text{CH}_3)_3\text{Si}$ -transition metal bond in silicon derivatives of manganese, iron, and cobalt carbonyls differ very greatly indeed with respect to certain reagents, according to the nature of the transition metal.

Experimental Section

Apparatus. All work was carried out in a borosilicate (Pyrex) glass vacuum system. All apparatus and techniques employed were identical with those previously described³⁴ with the exception of the ~6-ml reaction vessels which were constructed from thick-walled Pyrex tubing to which a Teflon stopcock was attached.

Materials. The following commercial reagents were used without further purification: aluminum powder, benzene, deuterium oxide, hexamethyldisiloxane, iodine, mercury, silicon tetrachloride, and sodium. Diethyl ether was dried over P_2O_5 , while hexane, cyclohexane, methanol (mol wt calcd, 32.1; found, 32.6; confirmed by infrared spectrum³⁵), and tetrahydrofuran were dried over 3A molecular sieve. Oxygen was dried by slowly passing it through a column of 5A molecular sieve, then through two traps held at -134° , before it was finally condensed in a trap at -196° ; $[(n\text{-C}_4\text{H}_9)_4\text{N}]\text{Cl}$ was dried for 18 hr by heating at 90° with pumping. HCl (mol wt calcd, 36.5; found, 36.5; confirmed by infrared spectrum³⁵) was distilled through a trap held at -134° . $\text{Fe}(\text{CO})_5$ (confirmed by infrared spectrum^{36,37}) was distilled through a trap held at -45° , in which it condensed. $(\text{CH}_3)_3\text{N}$ (mol wt calcd, 59.1; found, 59.3; confirmed by infrared spectrum³⁵) was distilled through a trap at -96° ; $(\text{CH}_3)_3\text{SiCl}$ (mol wt calcd, 108.7; found, 108.4; confirmed by infrared spectrum³⁸) was distilled through a trap at -45° and another at -134° , in which it condensed. $(\text{CH}_3)_3\text{P}$ (mol wt calcd, 76.1; found, 76.8; confirmed by infrared spectrum³⁹) was distilled through a trap at -78° and another at -96° , in which it condensed. Distilled water was further distilled through a trap at -78° , in which it condensed. $(\text{CH}_3)_3\text{SiI}$ (mol wt calcd, 200.2; found, 201.2; confirmed by infrared spectrum⁴⁰) was prepared according to the method of Voronkov, *et al.*^{41,42} DCl (mol wt calcd, 37.5; found, 37.4; confirmed by infrared spectrum⁴³) was prepared by stirring SiCl_4 with an equal volume of D_2O at room temperature for 15 min, then distilling through a trap at -134° . The DCl, which passed the -134° trap, was dried over 3A molecular sieve.

Synthesis of $[(\text{CH}_3)_3\text{SiFe}(\text{COSi}(\text{CH}_3)_3)(\text{CO})_3]_2$. $\text{Fe}(\text{CO})_5$ (1217.6 mg, 6.2154 mmol) was distilled into a 100-ml vessel containing sodium amalgam (5.5 g of mercury, 296.5 mg of sodium), 20 ml of fresh, dry tetrahydrofuran, and a Teflon-coated magnetic stirring bar. After stirring for 30 min at room temperature and for 2 hr at 60° , excess amalgam was removed in a N_2 -filled glove bag. Approxi-

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(30) M. A. Nasta and A. G. MacDiarmid, *J. Amer. Chem. Soc.*, **18**, P11 (1969).

(31) A. G. MacDiarmid, Y. L. Baay, J. F. Bald, A. D. Berry, S. K. Gondal, A. P. Hagen, M. A. Nasta, F. E. Saalfeld, and M. V. McDowell, *Pure Appl. Chem.*, **19**, 431 (1969).

(32) J. F. Bald and A. G. MacDiarmid, *J. Organometal. Chem.*, **22**, C22 (1970).

(33) Y. L. Baay and A. G. MacDiarmid, *Inorg. Chem.*, **8**, 986 (1969).

mately 14 ml of tetrahydrofuran was then distilled from the mixture and $(\text{CH}_3)_3\text{SiI}$ (3039.8 mg, 15.191 mmol) was distilled into the vessel. The mixture was stirred at room temperature for 30 min, during which time the color changed from light tan to dark brown. After pumping off material volatile at room temperature for 16 hr, the residue was extracted with 5-ml portions of hexane in a N_2 -filled glove bag. The hexane was removed *in vacuo* and the residue was sublimed three times at 80–90° to give a yellow microcrystalline solid (529.5 mg, 0.8423 mmol, 27.1% yield based on $\text{Fe}(\text{CO})_5$ employed), mp 118–120° (sealed capillary tube).

Much smaller yields of the same compound contaminated with $\text{Fe}_3(\text{CO})_{12}$ (identified by infrared spectrum) were obtained when $(\text{CH}_3)_3\text{SiCl}$ was substituted for $(\text{CH}_3)_3\text{SiI}$ or when the $\text{Na}_2\text{Fe}(\text{CO})_4$ was pumped dry and treated with $(\text{CH}_3)_3\text{SiI}$ either without a solvent or in hexane.

Anal. Calcd for $[(\text{CH}_3)_3\text{SiFe}[\text{COSi}(\text{CH}_3)_3](\text{CO})_3]_2$ ($\text{C}_{20}\text{H}_{36}\text{Si}_4\text{Fe}_2\text{O}_8$): C, 38.21; H, 5.78; Fe, 17.77; Si, 17.87; I, 0.00; mol wt, 628.6. Found: C, 38.68,⁴⁴ 37.71,⁴⁵ 38.84,⁴⁶ 38.06;⁴⁵ H, 5.73,⁴⁴ 5.40,⁴⁵ 5.47,⁴⁵ 5.58;⁴⁵ Fe, 17.05,⁴⁴ 17.29,⁴⁵ 17.31;⁴⁵ Si, 17.57;⁴⁶ I, 0.08;⁴⁵ mol wt, 629 (cyclohexane),⁴⁵ 630 (chloroform),⁴⁵ 631 (cyclohexane).⁴⁵ The first two of each of the above sets of data were obtained on the same sample; the third and fourth sets of data were obtained from material from completely different preparations.

Synthesis of $[(\text{CH}_3)_3\text{SiFe}(\text{COH})(\text{CO})_3]_2$. HCl (61.8 mg, 1.70 mmol) was distilled into a solution of $[(\text{CH}_3)_3\text{SiFe}[\text{COSi}(\text{CH}_3)_3](\text{CO})_3]_2$ (98.0 mg, 0.156 mmol) in hexane (152.8 mg) in a reaction vessel and the mixture was stirred at room temperature for 90 min to yield a light yellow precipitate. Noncondensable gas (0.006 mmol) was then removed with a Toepler pump from the reaction mixture held at –196°. Volatile material was then distilled through a trap at –134°. The material passing through the trap was HCl (49.3 mg, 1.35 mmol; mol wt calcd, 36.46; found, 36.2; confirmed by infrared spectrum³⁵). The material which condensed in the –134° trap (187.6 mg) consisted of an inseparable mixture of C_6H_{12} and $(\text{CH}_3)_3\text{SiCl}$ (34.8 mg, 0.320 mmol; identified by infrared³⁸ and nmr spectra, τ lit.⁴⁶ 9.65, found 9.66). The nonvolatile material in the reaction vessel was $[(\text{CH}_3)_3\text{SiFe}(\text{COH})(\text{CO})_3]_2$ (74.8 mg, 0.155 mmol, 99.4% yield). It decomposed above 200° without melting (sealed capillary tube).

Anal.⁴⁵ Calcd for $[(\text{CH}_3)_3\text{SiFe}(\text{COH})(\text{CO})_3]_2$ ($\text{C}_{14}\text{H}_{20}\text{Si}_2\text{Fe}_2\text{O}_8$): C, 34.72; H, 4.17; Fe, 23.07. Calcd for $[(\text{CH}_3)_3\text{SiFe}(\text{CO})_4]_2$ ($\text{C}_{14}\text{H}_{18}\text{Si}_2\text{Fe}_2\text{O}_8$): C, 34.87; H, 3.77; Fe, 23.16. Calcd for $(\text{CH}_3)_3\text{Si}(\text{H})\text{Fe}(\text{CO})_4$ ($\text{C}_4\text{H}_{10}\text{SiFeO}_4$): C, 34.72; H, 4.17; Fe, 23.07. Found: C, 35.11, 34.49; H, 3.15, 4.02; Fe, 22.90, 23.12. The material was insufficiently soluble in CH_2Br_2 , CH_3CN , $\text{C}_2\text{H}_5\text{OH}$, C_6H_6 , H_2O , and methyl ethyl ketone to obtain a value for the molecular weight.⁴⁵

Synthesis of $[(\text{CH}_3)_3\text{SiFe}(\text{COD})(\text{CO})_3]_2$. $[(\text{CH}_3)_3\text{SiFe}[\text{COSi}(\text{CH}_3)_3](\text{CO})_3]_2$ (44.7 mg, 0.0711 mmol) in cyclohexane (82.3 mg) and DCl (45.2 mg, 1.21 mmol) were permitted to react as described for the analogous reaction between $[(\text{CH}_3)_3\text{SiFe}[\text{COSi}(\text{CH}_3)_3](\text{CO})_3]_2$ and HCl. $[(\text{CH}_3)_3\text{SiFe}(\text{COD})(\text{CO})_3]_2$ (30.8 mg, 0.0633 mmol, 89% yield) was obtained.

Reaction of $[(\text{CH}_3)_3\text{SiFe}(\text{COD})(\text{CO})_3]_2$ with HCl. $[(\text{CH}_3)_3\text{SiFe}(\text{COD})(\text{CO})_3]_2$ (61.4 mg, 0.126 mmol) was held with HCl (10.2 mg, 0.280 mmol) in a reaction vessel for 15 min. After removal of the HCl–DCl mixture, the infrared spectrum was recorded in a Nujol mull.

Reaction of $[(\text{CH}_3)_3\text{SiFe}(\text{COD})(\text{CO})_3]_2$ with $(\text{CH}_3)_3\text{SiCl}$. $(\text{CH}_3)_3\text{SiN}$ (16.1 mg, 0.282 mmol) was condensed onto $[(\text{CH}_3)_3\text{SiFe}(\text{COD})(\text{CO})_3]_2$ (30.8 mg, 0.0633 mmol) in a reactor to give an orange, viscous liquid at room temperature. $(\text{CH}_3)_3\text{SiCl}$ (106.8 mg, 0.983 mmol) was distilled into this solution to give a yellow slurry which was stirred at room temperature for 2 hr. Removal of the volatile material, identified by infrared spectrum as a mixture (97.4 mg) of $(\text{CH}_3)_3\text{SiCl}$ ³⁸ and $(\text{CH}_3)_3\text{SiN}$,³⁵ yielded a nonhomogeneous yellow and white solid mixture (55.2 mg). If this had consisted of a 2:1 mixture of $[(\text{CH}_3)_3\text{SiFe}[\text{COSi}(\text{CH}_3)_3](\text{CO})_3]_2$ and $[(\text{CH}_3)_3\text{SiN}]\text{Cl}$, a total of 52.0 mg would be expected. It seems probable that the

additional 3.2 mg was due to extra $[(\text{CH}_3)_3\text{SiNH}]\text{Cl}$, which could have resulted from 0.30 mg of adsorbed water on the walls of the reactor vessel, etc. The infrared and nmr spectra of a cyclohexane extract of this mixture were identical with the spectra of $[(\text{CH}_3)_3\text{SiFe}[\text{COSi}(\text{CH}_3)_3](\text{CO})_3]_2$.

Thermal Stability of $[(\text{CH}_3)_3\text{SiFe}[\text{COSi}(\text{CH}_3)_3](\text{CO})_3]_2$. $[(\text{CH}_3)_3\text{SiFe}[\text{COSi}(\text{CH}_3)_3](\text{CO})_3]_2$ (99.8 mg, 0.159 mmol) was heated *in vacuo* for 1 hr at each of the following temperatures: 80, 110, 135, and 210°. No visual change or evolution of volatile material was noted at any of these temperatures. A trace of $[(\text{CH}_3)_3\text{Si}]_2\text{O}$ was evolved after 1 hr at 225° together with a little noncondensable gas (probably CO). On heating for an additional 18 hr at this temperature, the compound changed to a dark brown oil and then to a black crystalline solid (73.3 mg) which had a strong absorption in the CO stretching region. A noncondensable gas (presumably CO) and $[(\text{CH}_3)_3\text{Si}]_2\text{O}$ (7.4 mg, 0.046 mmol, 14.5% of the $(\text{CH}_3)_3\text{Si}$ groups present in the original material) were obtained.

Reaction of $[(\text{CH}_3)_3\text{SiFe}[\text{COSi}(\text{CH}_3)_3](\text{CO})_3]_2$ with Oxygen. $[(\text{CH}_3)_3\text{SiFe}[\text{COSi}(\text{CH}_3)_3](\text{CO})_3]_2$ (71.1 mg, 0.113 mmol) was dissolved in hexane, which was then evaporated in a 30-ml flask to give a thin film of the solid. Oxygen (638.0 Torr, 40.3 mg, 1.26 mmol) was admitted to the flask, and after 24 hr at room temperature was removed *via* a trap at –196°. The condensable material (2.5 mg) was identified by its infrared spectrum as consisting of $[(\text{CH}_3)_3\text{Si}]_2\text{O}$ ⁴⁷ and $\text{Fe}(\text{CO})_5$.^{36,37} The infrared spectrum of the residue (68.5 mg, 0.109 mmol) was identical with that of the starting material. A second portion of oxygen (591.6 Torr, 39.7 mg, 1.24 mmol) was added to the residue and allowed to stand for 3 days at room temperature. The oxygen was removed as before and the infrared spectrum of this residue (67.9 mg, 0.108 mmol, 95.6% recovery) indicated that it was again essentially unchanged $[(\text{CH}_3)_3\text{SiFe}[\text{COSi}(\text{CH}_3)_3](\text{CO})_3]_2$. An additional 0.7 mg of a mixture of $[(\text{CH}_3)_3\text{Si}]_2\text{O}$ and $\text{Fe}(\text{CO})_5$ was evolved.

Reaction of $[(\text{CH}_3)_3\text{SiFe}[\text{COSi}(\text{CH}_3)_3](\text{CO})_3]_2$ with Water. (a) **In the Absence of Solvent.** Water (48.0 mg, 2.66 mmol) and $[(\text{CH}_3)_3\text{SiFe}[\text{COSi}(\text{CH}_3)_3](\text{CO})_3]_2$ (149.2 mg, 0.2373 mmol) were placed in contact in a reaction vessel for 23 hr at room temperature. Dis-solution did not occur. The water was separated from the solid; both compounds were recovered quantitatively (identified by infrared spectrum) in the pure state.

(b) **In Ethereal Solution.** Water (45.5 mg, 2.53 mmol) was distilled into a solution of $[(\text{CH}_3)_3\text{SiFe}[\text{COSi}(\text{CH}_3)_3](\text{CO})_3]_2$ (144.9 mg, 0.2305 mmol) in $(\text{C}_2\text{H}_5)_2\text{O}$ (118.0 mg) in a reaction vessel. After shaking for 1 hr at room temperature the volatile materials were removed and placed over P_2O_5 for 15 min to remove water. The volatile materials were then distilled through a –64° trap which permitted $(\text{C}_2\text{H}_5)_2\text{O}$ to pass, but which retained $[(\text{CH}_3)_3\text{Si}]_2\text{O}$ (58.4 mg; 0.360 mmol; 78.1% of the $(\text{CH}_3)_3\text{Si}$ groups in original compound; mol wt calcd, 162.42; found, 162.5; confirmed by infrared spectrum⁴⁷).

In another experiment, a solution of water (2.9 mg, 0.16 mmol) in $(\text{C}_2\text{H}_5)_2\text{O}$ (223.5 mg) was employed to dissolve $[(\text{CH}_3)_3\text{SiFe}[\text{COSi}(\text{CH}_3)_3](\text{CO})_3]_2$ (59.8 mg, 0.0951 mmol) in an nmr tube. Spectra were recorded after 15, 25, 45, 60, and 90 min (at 42°) and after 3, 5, 24, and 50 hr (at room temperature). The characteristic peaks of the compound at τ 9.74 and 9.66 slowly decreased in intensity but were still present after 50 hr. The peak characteristic of $[(\text{CH}_3)_3\text{Si}]_2\text{O}$ (τ lit.⁴⁶ 9.98, found 9.98) slowly increased. Two other peaks (τ 9.71, 9.78), presumably due to hydrolysis intermediates, slowly increased and then decreased in intensity. Integration of the peaks showed that 32.8% of the $(\text{CH}_3)_3\text{Si}$ groups originally present in the compound had been converted to $[(\text{CH}_3)_3\text{Si}]_2\text{O}$ after 1 hr.

Reaction of $[(\text{CH}_3)_3\text{SiFe}[\text{COSi}(\text{CH}_3)_3](\text{CO})_3]_2$ with CH_3OH . CH_3OH (10.7 mg, 0.334 mmol) was added to a solution of $[(\text{CH}_3)_3\text{SiFe}[\text{COSi}(\text{CH}_3)_3](\text{CO})_3]_2$ (54.0 mg, 0.0867 mmol) in cyclohexane (240.7 mg) in an nmr tube. Spectra were recorded after 15, 25, 45, and 60 min (at 42°) and after 3, 5, 26, and 48 hr at room temperature. Peaks at τ 9.75 and 9.68 characteristic of the compound slowly decreased but were still strong even after 48 hr. The slow formation of $(\text{CH}_3)_3\text{SiOCH}_3$ was evidenced by the growth of a peak at τ 9.98 (lit.⁴⁸ τ 9.94 for $(\text{CH}_3)_3\text{Si}$ protons of $(\text{CH}_3)_3\text{SiOCH}_3$). Integration showed that after 1 hr 7.4% of the $(\text{CH}_3)_3\text{Si}$ groups present in the original compound had been converted to $(\text{CH}_3)_3\text{SiOCH}_3$.

(44) Analysis was performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

(45) Analyses and molecular weight determinations (vapor pressure osmometry in chloroform or cyclohexane) were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

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Reaction of $[(\text{CH}_3)_3\text{SiFe}[\text{COSi}(\text{CH}_3)_3](\text{CO})_2]$ with $(\text{CH}_3)_3\text{N}$. A dark orange solution of $[(\text{CH}_3)_3\text{SiFe}[\text{COSi}(\text{CH}_3)_3](\text{CO})_2]$ (38.5 mg, 0.0612 mmol) in $(\text{CH}_3)_3\text{N}$ (76.0 mg, 1.29 mmol) was stirred for 1 hr in a reaction vessel at room temperature. The volatile material, $(\text{CH}_3)_3\text{N}$ (75.1 mg; 1.27 mmol; 98.4% recovery; mol wt calcd, 59.13; found, 59.2; confirmed by infrared spectrum³⁵), was distilled from the solid, unchanged $[(\text{CH}_3)_3\text{SiFe}[\text{COSi}(\text{CH}_3)_3](\text{CO})_2]$ (39.0 mg, 0.0620 mmol, 101.3% recovery, identified by infrared spectrum).

Reaction of $[(\text{CH}_3)_3\text{SiFe}[\text{COSi}(\text{CH}_3)_3](\text{CO})_2]$ with $(\text{CH}_3)_3\text{P}$. An orange solution of $[(\text{CH}_3)_3\text{SiFe}[\text{COSi}(\text{CH}_3)_3](\text{CO})_2]$ (175.3 mg, 0.2789 mmol) in $(\text{CH}_3)_3\text{P}$ (83.9 mg, 1.10 mmol) was stirred for 1 hour at room temperature. The volatile material, $(\text{CH}_3)_3\text{P}$ (83.6 mg; 1.10 mmol; 100.0% recovery; mol wt calcd, 76.09; found,

76.5; confirmed by infrared spectrum³⁹) was distilled from the solid, unchanged $[(\text{CH}_3)_3\text{SiFe}[\text{COSi}(\text{CH}_3)_3](\text{CO})_2]$ (174.9 mg, 0.2782 mmol, 99.7% recovery, identified by infrared spectrum).

Reaction of $[(\text{CH}_3)_3\text{SiFe}[\text{COSi}(\text{CH}_3)_3](\text{CO})_2]$ with $[(n\text{-C}_4\text{H}_9)_4\text{N}]\text{Cl}$. A yellow solution of $[(\text{CH}_3)_3\text{SiFe}[\text{COSi}(\text{CH}_3)_3](\text{CO})_2]$ (101.4 mg, 0.1613 mmol) and $[(n\text{-C}_4\text{H}_9)_4\text{N}]\text{Cl}$ (105.8 mg, 0.3806 mmol) in $(\text{C}_2\text{H}_5)_2\text{O}$ (270.7 mg) was stirred for 1 hr at room temperature in a reaction vessel. Some of the $[(n\text{-C}_4\text{H}_9)_4\text{N}]\text{Cl}$ did not dissolve. After distilling off the ether, the residue (207.1 mg, 99.9% recovery) was shown by its infrared spectrum to consist of a mixture of the two starting materials. Pure $[(\text{CH}_3)_3\text{SiFe}[\text{COSi}(\text{CH}_3)_3](\text{CO})_2]$ (77.1 mg, 0.123 mmol, 76.0% recovery, identified by infrared spectrum) was extracted with hexane.

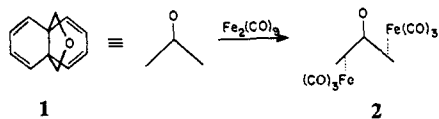
Structure of the Unsymmetrical 12-Oxa[4.4.3]propella-2,4,7,9-tetraene Bis(iron tricarbonyl). An Example of an Oxygen–Diene Interaction through Space

George I. Birnbaum

Contribution from the Biochemistry Laboratory, National Research Council of Canada, Ottawa 2, Ontario, Canada. Received May 18, 1971

Abstract: The three-dimensional structure of the unsymmetrical 12-oxa[4.4.3]propella-2,4,7,9-tetraene-bis(iron tricarbonyl) complex, $(\text{C}_{12}\text{H}_{12}\text{O})\text{Fe}_2(\text{CO})_6$, was determined by X-ray crystallography. The substance crystallizes in the triclinic space group $P\bar{1}$ with two molecules of the complex in a unit cell of dimensions $a = 6.823 \pm 0.006$, $b = 11.480 \pm 0.004$, $c = 11.706 \pm 0.004$ Å; $\alpha = 89.19 \pm 0.04$, $\beta = 94.09 \pm 0.04$, $\gamma = 107.03 \pm 0.04^\circ$. The intensities were measured with a diffractometer and the structure was solved by the heavy-atom method. Refinement by the least-squares method converged at $R = 3.5\%$ for 3288 observed reflections. The positions of all hydrogen atoms were found and refined. Each iron tricarbonyl group is coordinated to a cyclic diene system, one of the systems being perturbed by an interaction with a pair of electrons on the oxygen atom of the propellane. In view of the presence of an internal calibration, the effects of this interaction can be assessed. They include an enhanced back-donation of d_π electrons to the propellane ligand. In both diene systems the central bonds are significantly shorter than the "outer" ones.

Following their studies of the electrocyclic reactions of tetraenic propellanes,¹ Ginsburg and his colleagues turned their attention to an investigation of the behavior upon irradiation of the corresponding bis(iron tricarbonyl) derivatives as well as their thermal behavior.² Three such derivatives were prepared by treating 12-oxa[4.4.3]propella-2,4,7,9-tetraene (**1**) with diiron nonacarbonyl,³ and the structure of one of them was recently reported.⁴ This report deals with the structure of another isomer (**2**), one in which the two iron tricarbonyl groups are complexed unsymmetrically.



The structures of various diene complexes with iron tricarbonyl were recently reviewed.^{5,6} Three such struc-

tures have been reported⁷⁻⁹ in which the diene group was part of a six-membered ring, but only one of them was described in detail.⁸ Although some general features have emerged, the nature of the bond between the iron atom and the diene system is not yet fully understood, partly, at least, because many previous X-ray structure determinations of such complexes have failed to reveal sufficient geometrical details from which theoretical conclusions could be drawn.¹⁰ It was hoped, therefore, that a more accurate X-ray analysis would shed additional light on this subject.

Experimental Section

Crystal Data. 12-Oxa[4.4.3]propella-2,4,7,9-tetraene Bis(iron tricarbonyl), $(\text{C}_{12}\text{H}_{12}\text{O})\text{Fe}_2(\text{CO})_6$; Formula Weight 451.98. The material was one of the products obtained by refluxing a solution of the propellane ligand with $\text{Fe}_2(\text{CO})_9$ in dry benzene for 24 hr in a nitrogen atmosphere.³ It was crystallized from CH_2Cl_2 -petroleum ether (120–160°) to give yellow prisms, mp 135–138°. Precession photographs indicated a triclinic cell. The lattice constants of a centered (nonprimitive) cell were measured at room temperature on a four-circle diffractometer fitted with a Cu target at a 1° takeoff angle with a 0.02° slit. Several reflections were scanned along each

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