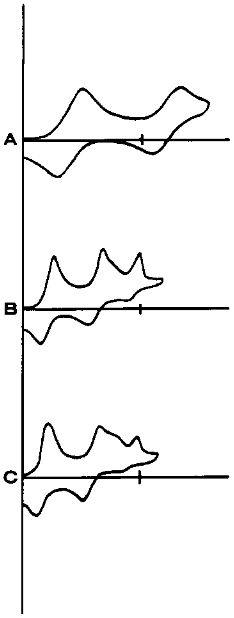

Figure 5. Oscilloscope tracings of first scan cyclic voltammograms of II under the conditions of Figure 4: A, x = 0.10 V cm^{-1}, y = 100 μA cm^{-1}, scan rate 20 V s^{-1}; B, same as A except x = 0.20 V cm^{-1}; C, x = 0.20 V cm^{-1}, y = 200 μA cm^{-1}, scan rate 100 V s^{-1}. The first and second waves only were scanned in A; all waves were scanned in B and C.

resonances begin to coalesce to an average signal at 210.3 ppm (8). This process probably involves intermediates with bridging carbonyls between iron and cobalt. Further warming to 45 °C produces a sharper average signal at 209.3 ppm, and subsequent cooling shows that all the observed processes are thermally reversible.

The ^{31}P NMR spectrum of II in THF-d_8 solution at −55 °C consisted of two doublets, J(PP) = 88 Hz, at 206 and 233 ppm, with respect to external H_3PO_4. On being warmed to 45 °C, these resonances began to broaden. In toluene solution, it was possible to observe the reversible coalescence of these signals at 75 ± 10 °C. This observation allowed an approximate calculation of $\Delta F^{\ddagger}$ = 14.4 ± 0.5 kcal mol^{-1} at this temperature for the carbonyl-exchange process that generates a C_2 axis through the molecule.

Electrochemistry. Three one-electron reduction waves were observed for II in acetonitrile solution at −1.01, −1.45, and −1.75 V vs. a Ag (0.10 N $AgNO_3$) reference electrode.[17] In cyclic voltammograms of II, taken at a scan rate of 50 to 500 mV s^{-1} (Figure 4), the first and third waves appear to be reversible and the second irreversible. After the scan rate was increased to 20 V s^{-1}, the second wave appeared to be reversible (Figure 5). Oscilloscope tracing A is of the first two waves only with x = 0.10 V cm^{-1}. Tracing B is of all three waves with x = 0.20 V cm^{-1}.[18] At a scan rate of 100 V s^{-1}, tracing C, a small new wave began to appear at −1.6 V between the second and third waves. We interpret these data as follows: II is most probably reduced to a radical anion reversibly at −1.01 V; at −1.45 V, the radical anion is reduced to a dianion capable of undergoing a reaction that is fast on the 50–500 mV s^{-1} time scale. This reaction may be a structural rearrangement such as the breaking of a M–M bond or a simple protonation by traces of water in the solvent. At this time we cannot say what species undergo reduction in either the third reversible wave at −1.75 V or the small wave observed at −1.6 V at fast scan rates. Attempted oxidation of II in acetonitrile produced only one irreversible wave at +0.4 V vs. a Ag (0.10 N $AgNO_3$) reference electrode.

Reduction of II in THF with sodium amalgam was followed by infrared spectroscopy (see Experimental Section). The changes in the metal carbonyl region indicated one or more intermediates were formed before the final limiting spectrum was obtained. It was possible to isolate a new, brown product from these solutions. Treatment of this material with H_3PO_4 produced II in high yield, thus indicating a high degree of chemical reversibility. We are continuing to investigate the nature of these anions.

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Registry No. I, 41383-38-4; II, 77462-26-1; $Co_2(CO)_8$, 10210-68-1.

Supplementary Material Available: Complete structure determination data, including tables of general temperature factor expressions, root-mean-square amplitudes of thermal vibration, bond distances and bond angles, least-squares planes, and intensity data (37 pages). Ordering information is given on any current masthead page.

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(17) These potentials were observed at −0.68, −1.20, and −1.45 V vs. a saturated calomel reference electrode in acetonitrile.

(18) The second and third waves appeared smaller than the previous wave in Figure 5B,C due to diffusion limiting effects. With rapid multiple scans, the first and second waves collapsed, while the third grew in size as expected.

(19) $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$; $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$. Scattering factors were taken from: Cromer, D. T.; Waber, J. T. "International Tables for X-Ray Crystallography"; Kynoch Press: Birmingham, England, 1975; Vol. IV. Anomalous dispersion effects were included in F_c; the values of $\Delta f'$ and $\Delta f''$ were those of: Cromer, D. T.; Liberman, D. *J. Chem. Phys.* **53**, 1891 (1970).

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(η^2-Vinylsilane)tetracarbonyliron Complexes

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The relatively stable title complexes [$(CH_2{=}CHSiMe_2Z)Fe(CO)_4$ (Z = Me, Me_3Si, OEt, OPh, OH, Cl, F, N_3)] have been prepared by reaction of the corresponding vinylsilanes with $Fe_2(CO)_9$ and/or by nucleophilic substitution of the chloride complex (Z = Cl). Spectroscopic characterization is provided. Reactions of these complexes designed to prepare elusive (η^3-1-silapropenyl)tetra- or tricarbonyliron species are described.

Introduction

Although (η^4-diene)tricarbonyliron complexes are quite prevalent, stable (η^2-monoene)tetracarbonyliron complexes are relatively rare. As a general rule, stability is accorded to only those η^2-olefin–$Fe(CO)_4$ complexes in which the coordinated double bond either (a) bears highly electronegative substitu-

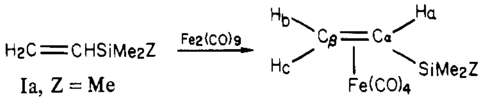
Table I. Selected IR Data for Substituted (η^2-Vinyldimethylsilane)tetracarbonyliron Complexes II (cm^{-1})[a]

Me	SiMe$_3$	OEt	OSiMe$_2$C$_2$H$_3$[b]	OPh[b]	OH[b]	F	Cl	N$_3$[b]
2085 m	2083 m	2088 m	2088 m	2085 s	2082 s	2091 m	2090 m	2085 m, 2140 s
2040 s, sh	2030 s, sh	2040 s, sh	2010 s, sh	2010 s, sh	2005 s, sh	...	...	...
2000 vs	1997 vs	2000 vs	1990 vs	1980 vs	1990 vs	2012	2000 vs	2000 vs
1971 vs	1973 vs	1975 vs	1968 vs	1900 vs	1970 vs	1974 vs	1980 vs	1970 vs
				1597 m				
1404 w	~1400 w	1390 w	1400 w	1490 s	1400 w	1400 w	1407 w	1405 w
1320 m	1317 m	1325 m	1316 m	1317 m	1319 m	1315 m	1316 m	1317 m
1259 m	1245 s	1253 s	1256 s	1253 s	1252 s	1255 s	1254 s	1260 s
1249 s								
1201 m	1200 m	1197 m	1195 m	1198 m	1195 m	1196 m	1195 m	1196 m
		1104 s						
		1070 s	1032 s	1025 m	1030 m	1039 m	1042 m	1037 m
853 s	835 s	838 s	830 s	910 s	830 s	864 s	844 s	839 s
837 s						841 s	812 s	815 s
	800 s	792 s	784 s		774 s	795 s	790 s	790 s
635 s	637 s	637 vs				638 s	695 s	
616 m	617 w	618 s	627 vs		624 s	624 m	615 m	625 s
592 s	595 m	598 s				598 s	594 m	

[a] Thin films (5-10 mm) at 90 K, unless otherwise indicated. Spectra recorded at room temperature were only slightly different. [b] Thin films at room temperature.

tents, (b) is in conjugation with other multiple bonds, or (c) is part of a highly strained ring.[1] (η^2-Ethylene)tetracarbonyliron, for example, is purported to decompose slowly above −40 °C,[2] whereas the η^2-tetracarbonyliron complexes of dimethyl maleate, 1,3-butadiene, and cyclobutene species are relatively stable at room temperature.[3]

We now report the preparation of stable tetracarbonyliron complexes of vinylsilanes by the reaction of the silanes Ia–e with $Fe_2(CO)_9$ at room temperature (eq 1)[4] and by nucleophilic substitution of the chloride complex IId (eq 2).



(1)

Ia, Z = Me
b, Z = Me$_3$Si
c, Z = OEt
d, Z = Cl
e, Z = F

IIa, Z = Me
b, Z = Me$_3$Si
c, Z = OEt
d, Z = Cl
e, Z = F

$$\text{IId} \xrightarrow{Z^-} \text{IIe–h} \quad (\text{Z: e, F; f, OH; g, OPh; h, N}_3) \qquad (2)$$

Additionally, in view of the demonstrated ability of transition metals to stabilize a variety of highly reactive species such as cyclobutadiene and trimethylenemethane,[5] efforts were made to transform the η^2-vinylsilane complexes IIc and IId into either (η^3-1-silapropenyl)tetracarbonyl- or tricarbonyliron species. Such species would formally represent the stabilization of multiply bonded silicon species, whose reactivity has been notorious.[6]

Table II. ^{1}H NMR Data for Substituted (η^2-Vinyldimethylsilane)tetracarbonyliron Complexes II[a]

Z	H$_a$	H$_b$	H$_c$	Me	J_{ab}	J_{bc}
Me	2.14 dd	3.04 d	2.58 d	0.18	10.7	14.6
SiMe$_3$[b]	2.15 dd	3.03 d	2.53 d	0.23, 0.00	10.5	14.8
OEt	1.90 dd	2.90 d	2.56 d	0.22, 0.20	11.0	14.5
OPh	1.99 dd	2.95 d	2.66 d	0.35, 0.34	10.9	14.3
OH	1.96 dd	2.92 d	2.56 d	0.26, 0.23	10.7	14.4
						2.35(OH)
F[c]	1.81 qd	2.88 dd	2.52 d	0.34, 0.31	10.4	14.4
Cl	2.08 dd	2.95 d	2.56 d	0.54, 0.47	10.5	13.9
N$_3$	1.92 dd	2.94 d	2.59 d	0.40, 0.34	11.2	14.3

[a] σ relative to Me_4Si; CS_2 as solvent. Chemical shifts in ppm; coupling constants in Hz. [b] Our values differed uniformly by ~0.15 ppm from those reported.[4] [c] ^{19}F coupling data given in text.

Experimental Section

All reactions were performed under nitrogen or argon. All solvents were degassed immediately prior to use by purging with inert gas for 10–15 min. Tetrahydrofuran was dried by distillation under nitrogen from sodium benzophenone ketyl. Anhydrous ether was taken from a previously unopened can and degassed by purging. Dichlorodifluoromethane (Freon 12) and sulfur dioxide were dried by passage through a column packed with 4A molecular sieves. Vinylpentamethyldisilane and vinyldimethylfluorosilane were prepared according to published procedures.[7,8] All other vinylsilanes were obtained from Petrarch Systems and used without further purification.

All complexes gave satisfactory elemental analyses.

Spectroscopic Data. The infrared spectra were obtained from thin films with use of a Beckman IR 8 spectrometer at room temperature or a Digilab FTS-20C IR spectrometer at 90 K.

Mass spectra were obtained on a CEC 21-110B mass spectrometer at 70 eV with an ambient inlet temperature and an ion-source temperature of 100–110 °C. The samples were introduced directly into the ionization chamber through a molecular leak. At higher temperatures the parent mass peaks are either very weak or absent.

Preparation of Complexes from Vinylsilanes and $Fe_2(CO)_9$. The following general procedure was used for the preparation of the complexes IIa–e. A mixture of the vinyldimethylsilane (~8 mmol), enneacarbonyldiiron (~12 mmol), and degassed, anhydrous ether (70 mL) was stirred at room temperature under argon until the suspended $Fe_2(CO)_9$ had disappeared (4–5 h). The reaction mixture

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(1) In all three cases the energy of the π* orbital of the double bond is lowered relative to that for ethylene, leading to greater back-donation by the iron and hence greater stability relative to the ethylene complex or its alkyl-substituted derivatives.

(2) Murdoch, H. D; Weiss, E. *Helv. Chim. Acta* **1963**, *46*, 1558.

(3) Murdoch, H. D.; Weiss, E. *Helv. Chim. Acta* **1962**, *45*, 1156.

(4) Two (η^2-vinylsilane)tetracarbonyliron complexes have been prevously prepared; however, they were incorrectly identified as (η^3-1-silapropenyl)tricarbonyliron complexes (Sakurai, H.; Kamiyama, Y.; Nakadaira, Y. *J. Am. Chem. Soc.* **1976**, *98*, 7453). A correction of this work and preliminary communciation of the ability to prepare the tetracarbonyliron complexes has been published (Radnia, P.; McKennis, J. S. *J. Am. Chem. Soc.* **1980**, *102*, 6349). Professor Sakurai has recently obtained ^{29}Si NMR data consistent with the η^2-tetracarbonyliron structure (private communication).

(5) See, e.g.: Emerson, G. F.; Watts, L.; Pettit, R. *J. Am. Chem. Soc.* **1965**, *87*, 131. Pettit, R. *J. Organomet. Chem.* **1975**, *100*, 205. Emerson, G. F.; Ehrlich, K.; Giering, W. P.; Lauterbur, P. C. *J. Am. Chem. Soc.* **1966**, *88*, 3172.

(6) For a recent review, see: Gusel'nikov, L. E.; Nametkin, N. S. *Chem. Rev.* **1979**, *79*, 529.

(7) Sakurai, H.; Tominaga, K.; Kumada, M. *Bull. Chem. Soc. Jpn.* **1966**, *39*, 1279.

(8) Svoboda, P.; Vaisaroua', V.; Chvalovsky, V. *Collect. Czech. Chem. Commun.* **1972**, *37*, 2258.

(9) This compound was prepared in 27% yield from the reaction of Id with sodium azide in tetrahydrofuran; bp 56–57 °C (31 mm).

was filtered though Celite and the resulting filtrate was concentrated in vacuo with the use of a rotary evaporator to yield a dark green, viscous oil. Vacuum distillation (0.250–0.005 mm) afforded the tetracarbonyliron complexes in yields ranging from 25 to 68%. In some cases, a second distillation was necessary in order to obtain the pure, pale yellow complexes.

In the cases of the complexes IIb ($Z = Me_3Si$) and IIc ($Z = OEt$), the green oils were chromatographed on short columns of silica gel and alumina, respectively. Elution of the yellow bands with pentane and removal of the solvent in vacuo gave yellow oils. Vacuum distillation of the oils gave the pure complexes.

Tables I and II list the IR and ^1H NMR data for the complexes. Characteristic ^{13}C NMR data for the series have been published.[4] Representative yields, boiling points, and mass spectral data for the complexes are given below.

(η^2-Vinyltrimethylsilane)tetracarbonyliron (IIa): 25%; bp 25–27 °C (0.25 mm); MS *m/e* (relative intensity) [assignment] 268 (9.1) [P], 253 (3.0) [P – Me], 240 (6.1) [P – CO], 212 (14) [P – 2CO], 184 (33) [P – 3CO], 156 (69) [P – 4CO], 100 (19) [P – $Fe(CO)_4$], 85 (100) [P – $Fe(CO)_4$, Me].

(η^2-Vinylpentamethyldisilane)tetracarbonyliron (IIb): 60%; bp 45 °C (0.005 mm) [lit.[4] bp 45 °C (0.005 mm)]; MS *m/e* 326 (12.8), 311 (3.5), 298 (9.9), 270 (36.1), 242 (48.9), 214 (73.0), 158 (30.5), 143 (39.7), 85 (87.2), 73 (100) [Me_3Si].

(η^2-Vinyldimethylethoxysilane)tetracarbonyliron (IIc): 68%; bp 37–38 °C (0.005 mm); MS m/e 298 (8.1), 283 (8.8), 270 (30.9), 253 (6.6) [P – OEt], 242 (50), 214 (27.9), 186 (100), 184 (44.9), 115 (74.3) [P – $Fe(CO)_4$, Me].

(η^2-Vinyldimethylchlorosilane)tetracarbonyliron (IId): 44%; bp 28–30 °C (0.005 mm); MS *m/e* 288 (2), 273 (1.5), 260 (17), 253 (4) [P – Cl], 232 (36), 204 (74), 176 (79), 120 (100).

(η^2-Vinyldimethylfluorosilane)tetracarbonyliron (IIe): 35%; bp 24 °C (0.03 mm); MS *m/e* 272 (8.3), 244 (8.3), 216 (14.6), 188 (29.2), 160 (100), 104 (8.3).

Preparation of Complexes from the Chloride Complex IId and Nucleophiles. (η^2-Vinyldimethylfluorosilane)tetracarbonyliron (IIe). This complex was prepared in 80% yield by reaction of IId and anhydrous NaF (2 equiv) in anhydrous acetone at room temperature. It was identical in all respects to the material obtained above.

(η^2-Vinyldimethylsilanol)tetracarbonyliron (IIf). This complex was most conveniently prepared, albeit in low yield, by hydrolysis of the chloride (or fluoride) complex by passage through an acid-washed alumina column. Elution of the column with pentane yielded (η^2-divinyltetramethyldisiloxane)tetracarbonyliron (85%) and a small amount of the starting complex. Elution with dichloromethane then yielded the silanol complex IIF as a viscous, pale yellow oil (~3%), which could be recrystallized from pentane to give an off-white solid, mp 42–43 °C.

(η^2-Vinyldimethylphenoxysilane)tetracarbonyliron (IIg). A mixture of the chloride complex IId (0.1 g, 3.5 mmol) and potassium phenoxide (freshly prepared from phenol and potassium hydride) (0.46 g, 3.5 mmol) in ca. 25 mL of the THF was stirred at room temperature for 40 h. The reaction mixture was then filtered through Celite, and the solvent was removed from the filtrate in vacuo. The resulting oil was extracted several times with pentane, and the combined extracts were concentrated under reduced pressure to give a yellow oil. The oil was then chromatographed over acid-washed alumina. Elution with pentane gave (η^2-divinyltetramethyldisiloxane)tetracarbonyliron. Elution with pentane–benzene (1:1) afforded the phenoxysilane complex IIg contaminated with a small amount of phenol. A second chromatography yielded the pure complex as a viscous, air-sensitive oil (37 mg, 3%).

(η^2-Vinyldimethylazidosilane)tetracarbonyliron (IIh). A mixture of the chloride complex IId (1.6 g, 5.5 mmol) and anhydrous sodium azide (dried under vacuum at 80 °C for 24 h) (0.37 g, 5.7 mmol) in 50 mL of freshly distilled THF was stirred at room temperature for 95 h. The reaction mixture was filtered, and the solvent was removed from the filtrate in vacuo. The resulting yellow oil was extracted repeatedly with pentane. The pentane extracts were combined, and the pentane was removed in vacuo. Distillation of the residue afforded the azidosilane complex IIh as a yellow liquid (1.2 g, 72%), bp 45 °C (0.005 mm).

Reaction of (η^2-Vinyldimethylchlorosilane)tetracarbonyliron (IId) with Antimony Pentachloride. To a stirred solution of the chloride complex IId (0.3 g, 1.04 mmol) in dichloromethane (~40 mL) at –78 °C was added dropwise a solution of antimony pentachloride (0.13 mL, 1.02 mmol) in dichloromethane (4 mL). During the addition the reaction mixture became orange. After an additional stirring for 15 min, anhydrous ether (~15 mL) was added. With the reaction mixture still at –78 °C, stirring was continued for an additional 1 h, during which time a yellow solid precipitated. Cooling was discontinued, and the reaction mixture was permitted to come to room temperature. Filtration under argon yielded 150 mg (68%) of yellow dichlorotetracarbonyliron, dec pt ~85 °C. Its IR spectrum (C_2Cl_4) agreed well with that reported for the authentic material.[10] The IR spectrum of the filtrate was devoid of metal–carbonyl absorption.

Reaction of (η^2-Vinyldimethylethoxysilane)tetracarbonyliron (IIc) with Antimony Pentachloride. A procedure analogous to that used in the chloride reaction above was followed. The ethoxy complex IIc (0.5 g, 1.68 mmol) and antimony pentachloride (0.2 mL, 1.57 mmol) yielded 89 mg (25%) of dichlorotetracarbonyliron, identical in all respects with the material obtained in the chloride reaction.

Reaction of (η^2-Vinyldimethylchlorosilane)tetracarbonyliron (IId) with Silver Tetrafluoroborate. The chloride complex IId (0.6 g, 2.08 mmol) was added to an ice-cooled, stirred suspension of silver tetrafluoroborate (0.9 g, 4.6 mmol) in tetrahydrofuran (~35 mL). The reaction mixture was stirred for 30 min at 0 °C and then for 15 min at room temperature. Filtration followed by solvent removal from the filtrate yielded 89 mg (16%) of the yellow oil, (η^2-vinyldimethylfluorosilane) tetracarbonyliron, identical in all respects with the material obtained from the fluorovinylsilane and $Fe_2(CO)_9$.

Reaction of (η^2-Vinyldimethylethoxysilane)tetracarbonyliron (IIc) with Triphenylmethyl Tetrafluoroborate. A solution of triphenylmethyl tetrafluoroborate[11] (1.3 g, 3.2 mmol) and the ethoxy complex IIc (1.0 g, 3.4 mmol) in dichloromethane (~40 mL) was stirred at room temperature for 5 h. An IR spectrum of the reaction mixture gave no evidence for the generation of a cationic complex. The reaction mixture was then filtered and the solvent removed in vacuo. A small quantity of methanol was added to the oily residue, and the insoluble trityl ethyl ether was removed by filtration. Removal of the solvent from the filtrate yielded 0.25 g (28%) of (η^2-vinyldimethylfluorosilane)tetracarbonyliron, which was identified by comparison of its spectral data with those for the authentic complex.

Reaction of (η^2-Vinyldimethylethoxysilane)tetracarbonyliron (IIc) with Hexafluorophosphoric Acid. To an ice-cooled, stirred solution of the ethoxy complex IIc (2.0 g, 6.7 mmol) in 70 mL of anhydrous ether was added dropwise 1.5 g (6.7 mmol) of hexafluorophosphoric acid–diethyl ether. After the addition was complete (ca. 10 min), the reaction mixture was allowed to assume room temperature and then stirred for an additional 3 h. The two layers were separated, and the ether layer was concentrated in vacuo to give a yellow oil. The oil was taken up in pentane, and the resulting solution was treated with a small quantity of solid sodium bicarbonate. After the evolution of carbon dioxide had subsided, the mixture was filtered. Removal of solvent in vacuo from the filtrate afforded 1.4 g (75%) of bright yellow (η^2-vinyldimethylfluorosilane)tetracarbonyliron (IIe). The boiling point and spectral data agreed with those for the complex prepared from Ie and $Fe_2(CO)_9$.

Results and Discussion

All the substituted vinyldimethylsilane complexes (IIa–h) were pale yellow liquids at or near room temperature. They were relatively air sensitive but in the absence of air were reasonably stable at temperatures up to ca. 50 °C. Their thermal stability varied considerably and appeared to be roughly correlated with the electronegativity of the substituent Z, the more electronegative substituents leading to greater stability. Not unexpectedly however, the complexes with more electronegative substituents (especially $Z = Cl$) were more sensitive to moisture.

With regard to the enhanced stability of the silane complexes compared to the ethylene or hydrocarbon analogues, inductively the silicon, being more electropositive than either carbon or hydrogen, would be expected to raise both the π and π^* orbitals and lead to destabilization rather than stabilization. The "resonance effect", on the other hand, should lower both

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[10] Hieber, W.; Bader, G. *Ber. Dtsch. Chem. Ges.* **1928**, *61*, 1717.

[11] Dauben, H. J., Jr.; Honnen, L. R.; Harmon, K. M. *J. Org. Chem.* **1960**, *25*, 1442.

orbitals, the π^* orbital more so than the π orbital, owing to the expected greater perturbation interaction of the former with a d orbital on silicon.[12] With a lowering of the π^* orbital (relative to that for ethylene), back-donation by the iron would be enhanced, the net effect being stabilization of the complex. With the introduction of more electronegative substituents Z on silicon, the silicon atom becomes less electropositive and, hence, inductively becomes less destabilizing. Increased electronegativity of the substituents should also contract and lower the energy of the d orbitals, thereby bringing the d orbitals and the vinyl π^* orbital closer in energy. The enhanced perturbation interaction of these orbitals effectively lowers the π^* orbital and, consequently, would lead to stabilization by virtue of greater back-donation from the iron.

Spectroscopic Characterization. The IR and NMR data are both consistent with the assigned η^2-tetracarbonyliron structure. The data are given in Tables I and II.

IR Data. The infrared spectra (Table I) of the complexes possess three prominent metal–carbonyl stretching bonds at room temperature, indicative of either a tri- or tetracarbonyliron species. At low temperature (90 K), however, in keeping with a tetracarbonyl species, a fourth band can usually be clearly observed as a shoulder at 2010–2040 cm^{-1}.

The azide and halide complexes (IIh,d,e) exhibit IR absorption bands characteristic of Si–X′ stretching vibrations, consistent with preservation of the integrity of the substituted vinylsilane upon coordination. Correlation of the Si–X′ absorptions for the complexed and free ligand is excellent: cf. ν_{Si-N_3} 2140 and 2143 cm^{-1}, ν_{Si-Cl} 470 and 470 cm^{-1},[13] and ν_{Si-F} 864 and 878, 895 cm^{-1},[13] respectively.

The infrared spectra of all the vinylsilane complexes possess absorption of medium to weak intensity at 1317–1325 cm^{-1}. Such absorption is not present in the spectra of the free ligands and is tentatively assigned to a CH_2 deformation. Weak absorption at 1317 cm^{-1} has also been reported in the solid-state (thin film) IR spectrum of (ethylene)tetracarbonyliron.[14]

NMR Data. Consistent with the (η^2-vinylsilane)tetracarbonyliron structure, the ^{1}H and ^{13}C NMR spectra of the complexes exhibit the expected upfield shifts for the protons and carbons of a double bond coordinated to iron. Additionally, two distinct absorptions (relative intensity 1:1) expected for the diastereotopic methyl groups on the silicon atom were observed for the complexes IIb–IIh.[15] The ^{13}C chemical shifts for C_α and C_β of the vinyl group linearly correlate well with those for the analogous carbons in the free ligand. Not surprisingly, in view of neighbor anisotropy effects from the adjacent silicon atom and its substituents, the correlation of shift for C_α is poorer than that for C_β. In addition to being consistent with the preservation of the vinylsilane structure upon coordination, the reasonably linear correlation suggests similar transmission of electronic effects in the complexed and free ligand.

The upfield shift of the C_α absorption upon coordination for the series Ia–h is remarkably constant, being ~95 ppm. For the C_β absorption, however, the induced upfield shifts range from ~88 to 97 ppm.

NMR Data for Fluoride Complex IIe. The ^{1}H, ^{13}C, and ^{19}F NMR spectra of the fluoride complex IIe are consistent with the η^2-vinylsilane structure, indicating long-range ^{19}F coupling through the silicon atom. The ^{19}F–^{1}H coupling constants $^3J_{F-Si-CH_3} = 7.0$ Hz, $^3J_{F-Si-CH_a} = 8.6$ Hz, $^4J_{F-Si-C-CH_b} = 1.4$ Hz, and $^4J_{F-Si-C-CH_c} \approx 0$, agree reasonably well with analogous values for related, but noncoordinated silanes. For example, for the free ligand $^3J_{F-Si-CH_3}$ is 7.3 Hz and reported values for the same coupling in Me_3SiF range from 7.0 to 7.5 Hz.[16] The observed greater four-bond coupling of fluorine with $H_{b(trans)}$ compared to that with $H_{c(cis)}$ in IIe is similarly observed in related systems, e.g., in 3-fluoropropene,[17] 2-(trifluoromethyl)propene,[18] and vinyltrifluorosilane.[19]

The complexity of the absorption in the vinyl region in the ^{1}H NMR spectrum of the free ligand did not permit simple extraction of the constants for the coupling of fluorine with the vinylic protons of the free ligand. As a consequence, no comparison with the values obtained for the complex has beeen made.

Interestingly, whereas in the ^{13}C NMR spectrum of the free ligand Ie, coupling of fluorine with the vinyl carbons, C_α and C_β, is substantial ($J_{F-Si-C_\alpha} = 17.4$ Hz;[20] $J_{F-Si-C_\beta} = 4.2$ Hz), only F–Si–C_β coupling (3.3 Hz) is observed in the case of the complex IIe. For the free ligand the ^{13}C absorption for the silicon methyl carbons appears as a doublet, owing to coupling with fluorine ($J_{F-Si-CH_3} = 15.5$ Hz).[20] On the other hand, in the ^{13}C NMR spectrum of the complex, the situation is more complicated, owing to the diastereotopic nature of the silicon methyl groups. Interestingly we observe slightly different coupling of fluorine with the two diastereotopic methyl carbons ($J_{F-Si-(CH_3)_a} = 16.9$ Hz; $J_{F-Si-(CH_3)_b} = 15.5$ Hz). The two carbons exhibit only slightly different chemical shifts ($\sigma_{(CH_3)_a} = -0.11$ ppm; $\sigma_{(CH_3)_b} = -0.17$ ppm, vs. Me_4Si).

The ^{19}F chemical shift of the fluorine in the complex [$\sigma_{CDCl_3} = 152.8$ ppm vs. CCl_3F)] is similar to that observed for the fluorines in the free ligand ($\sigma_{CDCl_3} = 162.2$ ppm) and in Me_3SiF ($\sigma_{CDCl_3} = 158$ ppm).[21]

Reactions. In view of the known stabilities of the (η^3-propenyl)tetracarbonyliron cation[22] and its halide derivatives,[23] attempts have been made to prepare the analogous (η^3-1-silapropenyl)tricarbonyliron species III and IV or the tetracarbonyl analogue V. The cations IV or V were of special interest since they embody the features of both a coordinated silicenium ion and doubly bonded silicon species. The report[4] from the Sakurai group that the reaction of vinylpentamethyldisilane (Ib) with $Fe_2(CO)_9$ afforded the (η^3-1-silapropenyl)tricarbonyliron complex III, X = Me_3Si, provided initial encouragement that the related species III, X = Cl, IV, or V could indeed be isolated. Unfortunately, however, during the course of our investigations of the reactions of vinylsilanes with $Fe_2(CO)_9$ it became clear that the structural assignment of the complex obtained by Sakurai was in error, the complex being in fact the η^2-tetracarbonyliron complex of the starting silane, viz., IIb.[4]

Attempts to thermally rearrange the η^2-chloride IId to the η^3-chloride complex III, X = Cl, in either refluxing ether, hexane, or benzene were unsuccessful, giving rise to small quantities of the free ligand, the starting complex, and decomposition products. With the hope of preparing the cationic complex V by halide abstraction, IId was treated with several

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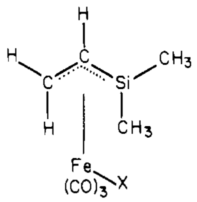
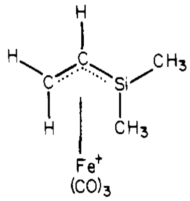
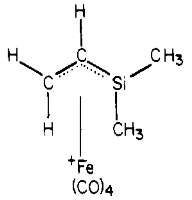


III



IV



V

halide-abstracting agents. Reaction of IId with $SbCl_5$ in CH_2Cl_2 at −78 °C followed by workup at room temperature yielded $(CO)_4FeCl_2$ (68%) as the only characterizable organometallic product.[24] The same reaction performed at −100 °C in SO_2 in the probe of an NMR spectrometer gave no ^1H NMR evidence for the possible generation of the desired cation. Gradual degradation, as evidence by the concomitant appearance of free, uncoordinated vinyl absorption and the disappearance of the coordinated vinyl absorption, occured over the temperature range −100 to −20 °C. With the exception of a single absorption for the free ligand, no new absorption was observed in the upfield methylsilicon region. Reaction of the ethoxy complex IIc with $SbCl_5$ gave similar results.

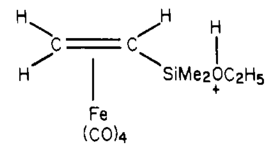
Reaction of IId with $AgBF_4$ yielded the fluoride complex IIe in 16% yield. Although the cation V could be an intermediate, the formation of the Si–F bond in concert with the cleavage of the Si–Cl is certainly reasonable. The affinity of silicon for fluorine ($\Delta H_{Si-F} \approx 135$ kcal/mol) is well-known, and abstraction of fluoride ion from BF_4^- by silicon has been reported previously.[25] Similarly, the fluoride complex was produced by treatment of the ethoxy complex IIc with either hexafluorophosphoric acid or triphenylmethyl tetrafluoroborate.

Reaction of the chloride complex with the nitrates of either silver or thallium led to partial oxidative decomposition with the formation of silver or thallium mirrors. Infrared spectral examination of the reaction solution gave no new metal–carbonyl absorption bands characteristic of a cationic complex. After workup a mixture of the silanol IIf and (η^2-divinyltetramethyldisiloxane)tetracarbonyliron was obtained, presumably owing to rapid hydrolysis of the expected silyl nitrate complex, since during workup no stringent efforts were made to exclude atmospheric moisture.

With hope of preparing cation V or complex III (X = sulfate, acetate or trifluoroacetate) by protonation of the ethoxy complex IIc with subsequent loss of ethanol, the reactions of IIc with sulfuric, acetic, and trifluoroacetic acids were examined. Unfortunately, sulfuric acid rapidly degraded the complex even at −80 °C. Acetic acid, on the other hand, failed to react with the complex even for extended periods at room temperature. Trifluoroacetic acid readily degraded the complex at room temperature, but relatively clean reaction could be observed at low temperatures by ^1H NMR. At −100 °C in either Freon 12 (CCl_2F_2) or sulfur dioxide, the addition of trifluoroacetic acid (2 equiv) to IIc resulted in the disappearance of the closely spaced doublet ($\Delta\sigma$ = 0.04 and 0.14 ppm in CCl_2F_2 and SO_2, respectively for the diastereotopic methyl protons in IIc and the appearance of a larger spaced doublet ($\Delta\sigma \approx 0.25$ ppm) centered at 0.31 ppm and slightly downfield (by 0.04 ppm) from the center of the doublet for IIc. As the temperature was gradually raised, the doublet was reduced in intensity at the expense of the development of a new, more closely spaced doublet ($\Delta\sigma \approx 0.11$ ppm) centered at 0.52 ppm. In CCl_2F_2, at −35 °C, the transformation was complete, with the absence of the initial doublet. In SO_2 the transformation was more rapid at low temperature and was accompanied by extensive degradation even at −70 °C.

The conversion of the initially formed complex to the final complex could be easily detected in CCl_2F_2 by the appearance of coordinated vinyl absorption slightly downfield from that of the initial complex. Although the final complex was not isolated and characterized, owing to its extreme sensitivity toward moisture, we believe it most likely is the trifluoroacetate complex II, Z = O_2CCF_3, since its spectrum matches with that obtained for the complex prepared from IId and sodium trifluoroacetate.

The question arises as to the structure of the complex initially formed at low temperature. Three possible complexes need to be considered: (1) the η^3-silapropenyl cationic complex V, (2) the η^3-silapropenyl complex III, X = O_2CCF_3, and (3) the protonated ethoxy complex VI. The formation of either V or III, X = O_2CCF_3, necessitates the liberation of ethanol whiich could then be protonated or react further with trifluoroacetic acid (TFA). Comparison of the ^1H NMR absorptions for the ethoxy groups in the initial complex in CCl_2F_2 at −100 and −80 °C with those obtained for the ethoxy group for solutions of ethanol and ethanol–TFA in CCl_2F_2 at −100 or 80 °C indicates, however, that ethanol has not been liberated at these temperatures. Additionally, if the initial complex were V or III, X = O_2CCF_3, there should be little if any change in the absorption of the ethoxy group in the conversion of either of these species to the trifluoroacetate II, Z = O_2CCF_3. However, as the conversion proceeds, a new triplet for a newly formed ethoxy species grows in intensity with concomitant reduction in the triplet for the ethoxy group of the initial complex. A broad featureless absorption suggestive of the production of ethanol also develops with concomitant reduction in the sharp ethoxy methylene triplet of the initial complex. These observations as well as the fact that the vinyl proton absorptions for the ethoxy complex are only slightly shifted upon the addition of acid at −100 °C suggest that the complex intially formed at −100 °C is most likely the protonated ethoxy complex VI and not the desired cation V.



VI

Acknowledgment. The technical assistance of Dr. J. Paul Devlin and Mr. Norman Perriera is acknowledged with our thanks.

Registry No. IIa, 75361-63-6; IIb, 75361-62-5; IIc, 75374-48-0; IId, 75901-33-6; IIe, 77080-83-2; IIf, 77080-84-3; IIg, 77080-85-4; IIh, 77080-86-5; $(CH_2{=}CHSiMe_2OSiMe_2CH{=}CH_2)Fe(CO)_4$, 77080-87-6; $Fe_2(CO)_9$, 15321-51-4; $SbCl_5$, 7647-18-9; $AgBF_4$, 14104-20-2; $(CO)_4FeCl_2$, 21475-90-1; triphenylmethyl tetrafluoroborate, 341-02-6; hexafluorophosphoric acid, 16940-81-1.

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(24) Presumably the dichlorotetracarbonyliron is formed by disproportionation of the intermediate (antimony pentachloride)tetracarbonyliron to the dichloride and antimony trichloride (Hieber, W.; Wirsching, A. *Z. Anorg. Allg. Chem.* **1940**, *245*, 35).

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