Structural study of disilanes bridging two [(.eta.5-C5Hn)Fe(CO)2] groups (n = 5, 4) via both iron atoms or via both cyclopentadienyl ligands

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Experimental Section

All procedures were performed under an atmosphere of dry N_2 with use of carefully dried solvents saturated with N_2. Column chromatography was performed by using Al_2O_3 (activity grade III). The ^{55}Mn NMR spectra were obtained on a Bruker ASM 360 spectrometer. IR spectra were recorded on a Perkin-Elmer 458 instrument. The electron injection (EI) and field ionization (FI) mass spectra were measured on CH7 MAT and Varian 711 instruments, respectively. $Mn_2(CO)_{10}$ was used as commercially obtained. $K[Mn(CO)_5]$ was prepared from $Mn_2(CO)_{10}$ with excess Na/K alloy in THF solution. Removal of the solvent in vacuo gave a greenish white powder that was used for the reaction.

Reaction of $K[Mn(CO)_5]$ with $Cl_2C=S$ in Pentane. A solution of 1 mL of $SCCl_2$ (excess) in pentane was added to a suspension of $K[Mn(CO)_5]$ (1.80 g, 7.7 mmol) in pentane with rapid stirring at 0 °C for about 10 min.[16] After the mixture was stirred for 30 min at room temperature, the reaction mixture was filtered and the dark brown filtrate evaporated to dryness. Sublimation of the orange yellow residue at 30–40 °C under high vacuum followed by chromatography on Al_2O_3 with pentane gave a yellow crystalline material (300–350 mg, 12–14%) that was shown by spectroscopic methods to be an approximately 9:1 mixture of $Mn_2(CO)_{10}$ and $Mn_2(CO)_9(CS)$.

The dark brown material from the pentane filtrate exhibits IR bands at 2140 m, 2100 sh, 2030 vs, 1960 sh cm^{-1} in the $\nu(CO)$ region and 653 s cm^{-1} in the $\delta(CO)$ region.

Reaction of $[K(18\text{-crown-}6)][Mn(CO)_5]$ with $Cl_2C=S$. To a suspension of $K[Mn(CO)_5]$ (1.76 g, 7.5 mmol) in pentane was added 18-crown-6 (1.98 g, 7.5 mmol) and the mixture stirred for 3 h at room temperature. Excess Cl_2CS was added and the pentane solution worked up in a manner similar to that described above. Only small amounts of $Mn_2(CO)_{10}$ were obtained from the pentane solution, and no CS-containing material could be detected by IR spectroscopy.

Recrystallization of the pentane-insoluble material from THF/pentane gave a yellow-green microcrystalline precipitate of $[K(18\text{-crown-}6)][Mn(CO)_4Cl_2]$. IR (Nujol): $\nu(CO)$ 2095 m, 2005 s, 1980 s, 1932 s cm^{-1}; $\delta(CO)$ 672 m, 644 m, 615 m cm^{-1}. The bands are identical with those of $[C(NMe_2)_3][Mn(CO)_4Cl_2]$ obtained by an independent route.[17] Anal. Calcd for $[K(18\text{-crown-}6)][Mn(CO)_4Cl_2]$: C, 35.50; H, 4.47. Found: C, 34.97; H, 4.41.

Reaction of the $Mn_2(CO)_{10}/Mn_2(CO)_9CS$ Mixture with PPh_3. The mixture of $Mn_2(CO)_{10}$ and $Mn_2(CO)_9CS$ (120 mg) in toluene was stirred with PPh_3 (80 mg) in the presence of $ONMe_3$ (20 mg) for 3 h. The mixture was worked up as described for the preparation of $Mn_2(CO)_9P(C_6H_5)_3$.[14] The IR spectrum of this material showed an additional weak band at 1265 cm^{-1}, which was assigned to a CS-containing complex present in low yields.

Reaction of the $Mn_2(CO)_{10}/Mn_2(CO)_9CS$ Mixture with Br_2. A mixture of $Mn_2(CO)_{10}$ and $Mn_2(CO)_9CS$ (270 mg) in CCl_4 solution was oxidized with Br_2 (120 mg, 0.75 mmol) according to the procedure outlined in ref 18. Evaporation of the solvent and sublimation of the residue gave a mixture of mainly $Mn(CO)_5Br$ and small amounts of $Mn(CO)_4(CS)Br$. IR (Nujol): $\nu(CS)$ 1320 cm^{-1}.

(16) A lower yield of $Mn_2(CO)_9CS$ was observed by addition of stoichiometric amounts of Cl_2CS; the yields also decreased by use of THF as the solvent or by addition of Cl_2CS at −78 °C followed by warming the mixture to room temperature.
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Structural Study of Disilanes Bridging Two [(η^5-C_5H_n)Fe(CO)$_2$] Groups (n = 5, 4) via Both Iron Atoms or via Both Cyclopentadienyl Ligands[1]

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Summary: The structures of two tetramethyldisilyl complexes of the (η^5-C_5H_n)Fe(CO)$_2$ (n = 5, 4) system have been determined by using X-ray diffraction methods, [(η^5-C_5H_5)Fe(CO)$_2$]$_2$Si$_2$Me$_4$ (I) and Si$_2$Me$_4$[(η^5-C_5H_4)Fe-(CO)$_2$CH$_3$]$_2$ (II). The Si–Si bond length in I, where the two silicon atoms are attached to Fe atoms, is significantly longer than that in II, where the two iron-containing moieties are connected via the cyclopentadienyl rings. The two iron centers are conformationally trans with respect to the Si–Si bond in I but gauche in the case of II. ^{29}Si NMR data for the complexes reinforce the structural data indicating that the two metals activate the Si–Si bond in I.

The study of transition-metal–silicon complexes has been an active area of research since Piper, Lemal, and Wilkinson reported the first example, (η^5-C_5H_5)Fe-(CO)$_2$SiMe$_3$, in 1956.[2] Such interest stems in part from the use of transition-metal complexes to catalyze reactions of organosilicon compounds, most notably hydrosilylation.[3,4] However, recently the use of transition-metal complexes to catalyze the formation and cleavage of silicon–silicon bonds has become a topic of considerable interest,[5–7] due to the upsurge in interest in polysilanes as photoresist, preceramic, and photoconducting materials.[8,9]

Oligo- and polysilyl derivatives of the (η^5-C_5H_5)Fe(CO)$_2$ system have been particularly interesting since they have been shown to exhibit a unique range of deoligomerizations,[10,11] molecular rearrangements,[12,13] and group migrations.[10,12] Furthermore, such chemistry is not always duplicated with other metal systems; for example, to date the complexes of Re(CO)$_5$ and (η^5-C_5H_5)Ru(CO)$_2$ have not exhibited a similar rich chemistry.[14]

The particular importance of the (η^5-C_5H_5)Fe(CO)$_2$ systems resulted in various spectroscopic investigations aimed at ascertaining the nature of the Fe–Si bond by such techniques as Mössbauer,[15] IR,[15] and ^{29}Si NMR spectroscopy.[16] From such studies it has been suggested that there is little significant retrodative π-bonding between the metal atom and the silicon atom in complexes of the type (η^5-C_5H_5)Fe(CO)$_2$SiR$_3$.

Structural analyses of such complexes are rare, due in part to the generally noncrystalline nature of the complexes. Drahnak et al. have reported the structures of two (η^5-C_5H_5)Fe(CO)$_2$ derivatives of cyclic silylcyclopentasilane,[17] and we have reported the structural analysis of the single-disilyl complex (η^5-C_5H_5)Fe(CO)$_2$SiMe$_2$SiPh$_3$.[18] This latter study established that the Si–Si bond was elongated with respect to that in Me$_3$SiSiPh$_3$[19] a situation

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paralleled by the related germylsilyl complex $(\eta^5\text{-}C_5H_5)\text{-}$ $Fe(CO)_2SiMe_2GePh_3$.[20]

Since the majority of the studies on oligosilyl compounds and complexes have been performed with permethylated silanes, an analysis of the effects of the transition-metal substituent upon the structures of such permethylated oligosilanes is needed; thus, we have embarked upon a systematic investigation of such complexes.

The photochemical deoligomerizations exhibited by the $(\eta^5\text{-}C_5H_5)Fe(CO)_2$–disilyl complexes are not observed when the disilane is bonded to the complex via the cyclopentadienyl ring;[10] i.e., there is a clear distinction between the disilyl groups in the two positions within the $(\eta^5\text{-}C_5H_n)Fe(CO)_2$ system. It is therefore of particular current interest to investigate the structural aspects of the silicon–silicon bond in these two distinct positions within the same complex coordination sphere. We have therefore investigated the structural features of two crystalline complexes where a tetramethyldisilyl group bridges two Fp units either via the two Fe atoms, $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2Si_2Me_4$ (I), or via the two cyclopentadienyl ligands, $Si_2Me_4[(\eta^5\text{-}C_5H_4)Fe(CO)_2Me]_2$ (II). This note reports the results of this investigation coupled with a ^{29}Si NMR analysis.

Experimental Section

Complex I was synthesized by using the published procedure,[25] and the synthesis of complex II is described below.

Into a 100-mL round-bottomed Schlenk flask was placed 0.23 g (0.49 mmol) of complex I in 30 mL of THF. To this solution at 0 °C was added, via a syringe, 1.1 mmol of freshly prepared lithium diisopropylamide in the same solvent. The solution was stirred for 20 min, after which time infrared monitoring indicated the absence of the starting material, with the concomitant formation of a species exhibiting $\nu(CO)$ stretching frequencies at 1882, 1867, 1812, and 1753 cm^{-1}. To this solution at 0 °C was added an excess (0.5 mL) of methyl iodide. The solution turned green-yellow and was stirred for 30 min, during which time it was

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Table I. Crystal Data, Data Collection, and Least-Squares Parameters

	I	II
Crystal Data		
formula	$C_{18}H_{22}O_4Si_2Fe_2$	$C_{20}H_{26}O_4Si_2Fe_2$
fw	470.2	498.3
a, Å	7.042 (3)	13.509 (5)
b, Å	8.361 (3)	14.839 (5)
c, Å	9.287 (4)	13.157 (5)
α, deg	82.16 (3)	
β, deg	88.09 (3)	114.64 (2)
γ, deg	69.82 (3)	
V, Å³	508.42 (34)	2397.2 (16)
cryst syst	triclinic	monoclinic
space group	$P\bar{1}$	$C2/c$
Z	1	4
D_{exptl}, g cm^{-3}	1.535	1.381
μ(Mo Kα), mm^{-1}	1.56	1.32
$F(000)$	242	1032
approx cryst size, mm	0.1 × 0.03 × 0.1	0.3 × 0.2 × 0.16
cryst color and habit	orange plate	yellow fragment
Data Collection		
temp, K	298	
2θ range, deg	3.5–45	
index ranges	$0 \leq h \leq 7$,	$-1 \leq h \leq 14$,
	$-8 \leq k \leq 8$,	$-5 \leq k \leq 15$,
	$-9 < l \leq 9$	$-14 \leq l \leq 12$
no. of rflns	1547	3654
no. of unique data (R_{int})	1324 (0.008)	1569 (0.009)
no. of obs rflns [$F > 3.0\sigma(F)$]	953	1567
Refinement		
g^a	0.0002	0.0048
R(obs)	0.045	0.055
R_w	0.045	0.076
R(tot.)	0.072	0.057
goodness of fit	1.45	0.82
largest and mean Δ/σ	0.206, −0.012	0.046, 0.000
largest diff peak, e Å^{-3}	0.34	0.72
largest diff hole, e Å^{-3}	−0.44	−0.24

^{a} Weighting scheme: $w^{-1} = \sigma^2(F) + gF^2$.

warmed to room temperature. The solvent was removed in vacuo and the residue extracted with 2 × 50 mL of hexane. The two hexane solutions were combined and filtered, the solvent was removed in vacuo, and the residue, dissolved in 3 mL of hexane, was placed upon a 1 × 15 cm silica gel column. Development of the column with hexane produced a yellow band, which was eluted with a 20:80 methylene chloride–hexane solvent mixture. Subsequent to removal of the solvent, recrystallization from hexane yielded II (0.16 g, 3.2 mmol, 66%). ^{1}H NMR (CDCl$_3$, ppm relative to TMS at 0.0): 0.35 (SiMe); 4.80 (m), 4.50 (m) (C$_5$H$_4$). ^{13}C NMR (CDCl$_3$, ppm): −24.5 (FeMe), −3.5 (SiMe), 92.3, 88.1 (C$_5$H$_4$); 218.1 (CO). ^{29}Si NMR (CDCl$_3$, ppm): −23.2. IR (hexane): ν(CO) 2010, 1956 cm^{-1}. Anal. (Galbraith Laboratories, Knoxville, TN). Calcd (found): C, 48.1 (48.2); H, 5.37 (5.23).

Structure Determination. X-ray data were collected on a Nicolet R3m/V four-circle diffractometer at room temperature, using graphite-monochromated Mo K$\bar{\alpha}$ radiation (λ = 0.071073 Å) and the ω-scan method (variable speed, 3.0–15.0°). Three check reflections were monitored every 1 h, and their intensities remained constant throughout the data collection.

While the structure of I was determined by the heavy-atom method, an initial model of II was obtained by direct methods. The structures were refined by anisotropic full-matrix least squares (the function minimized was $\sum w(F_o - F_c)^2$). Hydrogen atomic positions were calculated from assumed geometries, and they were included in least-squares and structure factor calculations as riding atoms with their U(iso) values fixed at 0.08 Å². Crystal data, data collection, and least-squares parameters are listed in Table I, and the atomic coordinates are recorded in Table II. Absorption corrections were applied to both data sets. The pertinent bond lengths and angles for complexes I and II are recorded in Table III. All calculations were performed on a Micro Vax II minicomputer using the SHELXTL PLUS programs.

Table II. Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Coefficients (Å² × 10³)

	x	y	z	$U(eq)^a$
		Complex I		
Fe	494 (2)	2283 (1)	2672 (1)	35 (1)
Si	−555 (3)	5019 (2)	1230 (2)	34 (1)
O(1)	−2029 (8)	1317 (7)	801 (6)	64 (3)
O(2)	−2814 (8)	3842 (7)	4539 (6)	69 (3)
C(1)	2911 (7)	2259 (6)	3980 (5)	54 (3)
C(2)	2447	740	4402	57 (3)
C(3)	2736	−171	3183	56 (3)
C(4)	3379	786	2007	51 (3)
C(5)	3487	2287	2500	46 (3)
C(6)	−1006 (11)	1715 (9)	1527 (8)	43 (3)
C(7)	−1507 (12)	3254 (9)	3775 (8)	46 (3)
C(8)	−3387 (10)	6027 (9)	1227 (8)	56 (3)
C(9)	335 (12)	6552 (9)	2093 (7)	56 (3)
		Complex II		
Fe(1)	5717 (1)	6828 (1)	133 (1)	61 (1)
Si(1)	5006 (1)	8612 (1)	1613 (1)	56 (1)
C(1)	5585 (4)	7493 (3)	1495 (4)	56 (2)
C(5)	6696 (5)	7299 (4)	1739 (4)	72 (2)
C(2)	5046 (5)	6648 (4)	1301 (5)	76 (3)
C(4)	6811 (6)	6362 (5)	1693 (5)	91 (3)
C(8)	3606 (5)	8722 (5)	505 (5)	86 (3)
C(10)	4180 (6)	6669 (5)	−1084 (6)	111 (4)
C(7)	6186 (5)	6095 (5)	−607 (5)	91 (3)
C(6)	5834 (5)	7762 (5)	−613 (5)	85 (3)
C(3)	5814 (7)	5961 (4)	1424 (6)	95 (4)
C(9)	5907 (5)	9518 (4)	1509 (5)	83 (3)
O(1)	5908 (5)	8402 (4)	−1069 (5)	138 (4)
O(2)	6472 (5)	5614 (4)	−1079 (5)	141 (4)

^{a} Equivalent isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

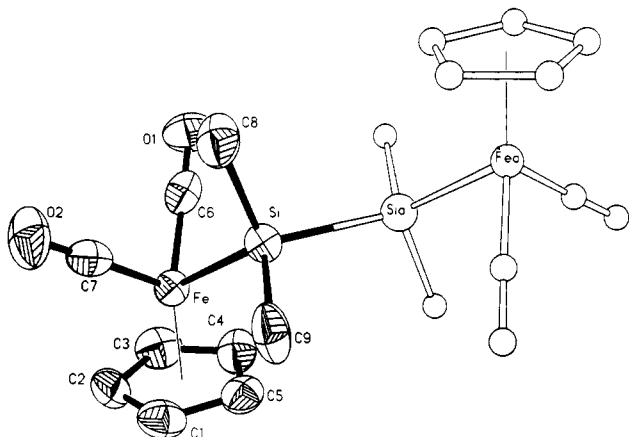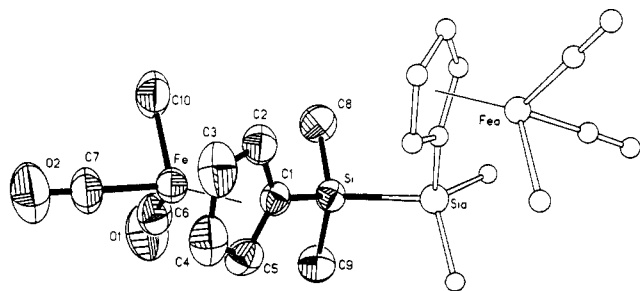**Figure 1.** Structure of complex I.

Figure 2. Structure of complex II.

Results and Discussion

The crystal structures of the two complexes are illustrated in Figures 1 and 2. Both molecules possess molecular symmetries coincident with a crystallographic symmetry operator. An inversion center ($\bar{i}$) sits at the midpoint of the Si–Si bond of I, and the second half of the

Table III. Bond Angles (deg) and Distances (Å)

		(a) Complex I		
Si-Fe-C(1)	105.1 (1)	Si-Fe-C(2)	144.0 (2)	
C(1)-Fe-C(2)	39.2 (1)	Si-Fe-C(3)	148.6 (2)	
C(1)-Fe-C(3)	65.8 (1)	C(2)-Fe-C(3)	39.2 (1)	
Si-Fe-C(4)	109.3 (1)	C(1)-Fe-C(4)	65.9 (1)	
C(2)-Fe-C(4)	65.8 (1)	C(3)-Fe-C(4)	39.3 (1)	
Si-Fe-C(5)	87.9 (1)	C(1)-Fe-C(5)	39.3 (1)	
C(2)-Fe-C(5)	65.8 (1)	C(3)-Fe-C(5)	65.9 (1)	
C(4)-Fe-C(5)	39.3 (1)	Si-Fe-C(6)	86.7 (2)	
C(1)-Fe-C(6)	163.3 (2)	C(2)-Fe-C(6)	129.0 (3)	
C(3)-Fe-C(6)	98.0 (3)	C(4)-Fe-C(6)	99.4 (3)	
C(5)-Fe-C(6)	132.1 (3)	Si-Fe-C(7)	84.2 (2)	
C(1)-Fe-C(7)	98.6 (3)	C(2)-Fe-C(7)	95.6 (3)	
C(3)-Fe-C(7)	126.0 (3)	C(4)-Fe-C(7)	161.2 (3)	
C(5)-Fe-C(7)	132.4 (3)	C(6)-Fe-C(7)	94.2 (4)	
Fe-Si-C(8)	110.3 (2)	Fe-Si-C(9)	110.0 (2)	
C(8)-Si-C(9)	103.6 (3)	Fe-Si-SiA	114.5 (1)	
C(8)-Si-SiA	108.7 (2)	C(9)-Si-SiA	109.1 (3)	
Fe-C(1)-C(2)	70.6 (1)	Fe-C(1)-C(5)	70.1 (1)	
Fe-C(2)-C(1)	70.3 (2)	Fe-C(2)-C(3)	70.2 (1)	
Fe-C(3)-C(2)	70.6 (1)	Fe-C(3)-C(4)	70.1 (1)	
Fe-C(4)-C(3)	70.6 (1)	Fe-C(4)-C(5)	70.3 (2)	
Fe-C(5)-C(1)	70.6 (1)	Fe-C(5)-C(4)	70.3 (1)	
Fe-C(6)-O(1)	178.0 (7)	Fe-C(7)-O(2)	117.5 (6)	
Fe-Si	2.375 (2)	Fe-C(1)	2.117 (6)	
Fe-C(2)	2.121 (4)	Fe-C(3)	2.116 (4)	
Fe-C(4)	2.109 (5)	Fe-C(5)	2.110 (6)	
Fe-C(6)	1.741 (9)	Fe-C(7)	1.742 (7)	
Si-C(8)	1.878 (7)	Si-C(9)	1.883 (9)	
Si-SiA	2.390 (4)	O(1)-C(6)	1.158 (11)	
O(2)-C(7)	1.153 (9)			

		(b) Complex II		
C(1)-Fe(1)-C(5)	39.6 (2)	C(1)-Fe(1)-C(2)	39.3 (2)	
C(5)-Fe(1)-C(2)	65.7 (2)	C(1)-Fe(1)-C(4)	66.2 (3)	
C(5)-Fe(1)-C(4)	39.3 (3)	C(2)-Fe(1)-C(4)	65.4 (3)	
C(1)-Fe(1)-C(10)	107.6 (3)	C(5)-Fe(1)-C(10)	147.2 (3)	
C(2)-Fe(1)-C(10)	87.2 (3)	C(4)-Fen1)-C(10)	143.8 (3)	
C(1)-Fe(1)-C(7)	160.1 (2)	C(5)-Fe(1)-C(7)	123.2 (3)	
C(2)-Fe(1)-C(7)	134.1 (3)	C(4)-Fe(1)-C(7)	93.9 (3)	
C(10)-Fe(1)-C(7)	88.7 (3)	C(1)-Fe(1)-C(6)	99.6 (3)	
C(5)-Fe(1)-C(6)	97.8 (3)	C(2)-Fe(1)-C(6)	133.0 (3)	
C(4)-Fe(1)-C(6)	128.6 (3)	C(10)-Fe(1)-C(6)	87.2 (3)	
C(7)-Fe(1)-C(6)	92.4 (4)	C(1)-Fe(1)-C(3)	66.3 (2)	
C(5)-Fe(1)-C(3)	65.5 (2)	C(2)-Fe(1)-C(3)	39.5 (3)	
C(4)-Fe(1)-C(3)	38.5 (3)	C(10)-Fe(1)-C(3)	105.4 (3)	
C(7)-Fe(1)-C(3)	98.9 (3)	C(6)-Fe(1)-C(3)	163.2 (3)	
C(1)-Si(1)-C(8)	109.8 (2)	C(1)-Si(1)-C(9)	109.1 (3)	
C(8)-Si(1)-C(9)	111.3 (3)	C(1)-Si(1)-Si(1A)	105.0 (2)	
C(8)-Si(1)-Si(1A)	110.8 (3)	Cn9)-Si(1)-Si(1A)	110.5 (2)	
Fe(1)-C(1)-Si(1)	132.0 (2)	Fe(1)-C(1)-C(5)	69.2 (3)	
Si(1)-C(1)-C(5)	126.7 (4)	Fe(1)-C(1)-C(2)	69.7 (4)	
Si(1)-C(1)-C(2)	126.8 (5)	C(5)-C(1)-C(2)	106.0 (5)	
Fe(1)-C(5)-C(1)	71.2 (3)	Fe(1)-C(5)-C(4)	70.1 (3)	
C(1)-C(5)-C(4)	108.3 (5)	Fe(1)-C(2)-C(1)	70.9 (4)	
Fe(1)-C(2)-C(3)	69.9 (5)	C(1)-C(2)-C(3)	108.6 (6)	
Fe(1)-C(4)-C(5)	70.6 (3)	Fe(1)-C(4)-C(3)	70.9 (4)	
C(5)-C(4)-C(3)	109.0 (7)	Fe(1)-C(7)-O(2)	178.6 (7)	
Fe(1)-C(6)-O(1)	177.0 (7)	Fe(1)-C(3)-C(2)	70.7 (4)	
Fe(1)-C(3)-C(4)	70.5 (4)	C(2)-C(3)-C(4)	108.1 (6)	
Fe(1)-C(1)	2.117 (5)	Fe(1)-C(5)	2.091 (5)	
Fe(1)-C(2)	2.101 (8)	Fe(1)-C(4)	2.085 (5)	
Fe(1)-C(10)	2.039 (6)	Fe(1)-C(7)	1.747 (8)	
Fe(1)-C(6)	1.743 (8)	Fe(1)-C(3)	2.090 (7)	
Si(1)-C(1)	1.869 (5)	Si(1)-C(8)	1.851 (5)	
Si(1)-C(9)	1.858 (7)	Si(1)-Si(1A)	2.341 (3)	
C(1)-C(5)	1.427 (8)	C(1)-C(2)	1.419 (7)	
C(5)-C(4)	1.404 (10)	C(2)-C(3)	1.415 (10)	
C(4)-C(3)	1.377 (12)	C(7)-O(2)	1.116 (11)	
C(6)-O(1)	1.150 (10)			

molecule is generated by $\bar{x}$, $1 - y$, $\bar{z}$. Molecule II has a 2-fold axis passing through the Si–Si bond, generating the other half of the molecule by $\bar{x}$, y, $^1/_2 - z$.

There are two features of the disilane group that are important with respect to understanding the nature of complexation of the group to the two distinct portions of
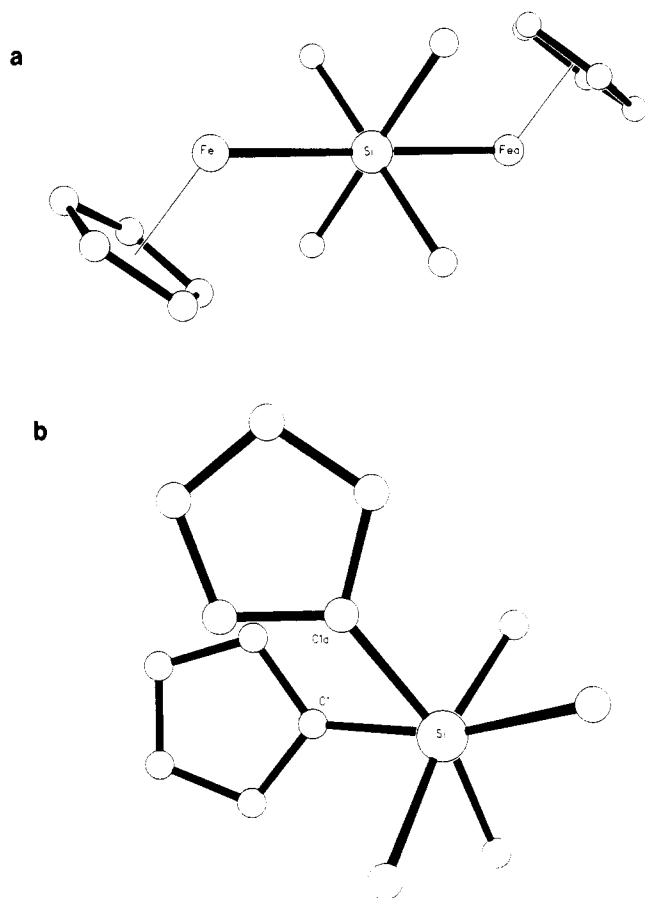
a

b

Figure 3. Newman projections of (a) complex I and (b) complex II viewed along the Si–Si bond.

the $(\eta^5\text{-}C_5H_n)Fe(CO)_2$ system, namely the Si–Si bond length and the conformational arrangement about the Si–Si bond.

The Si–Si bond length in the case of complex I is 2.390 (4) Å, and that in complex II is 2.341 (3) Å. These data represent a significant lengthening of the Si–Si bond when the two Si atoms are bonded directly to the Fe atoms. The value of 2.341 Å obtained for II is well within the normal range of Si–Si bond lengths noted in the literature,[17,19,21,22] and thus the lengthening observed in I is related to the presence of the two Fe atoms. This elongation is not extremely large in comparison to published "long" Si–Si bonds. For example, one of the longest Si–Si bonds was reported for hexa-*tert*-butyldisilane at 2.697 Å,[23] considerably longer than those of I and II.

Examination of the conformation about the Si–Si bond reveals a very distinct difference between the two complexes. As might be expected, the two Fe groups in I are anti to each other, whereas they are gauche to each other in II (Figure 3). Indeed, in II the dihedral angle between the two substituted cyclopentadienyl groups is 46°, considerably less than the 60° expected for a perfectly oriented hexasubstituted disilane. This result suggests that a dipolar interaction may be responsible for the gauche arrangement. Furthermore, it may be observed from Figure 3b that the two cyclopentadienyl groups partially eclipse one another in the gauche arrangement of II, suggesting that π stacking between the two $\eta^5\text{-}C_5H_4$ groups could also

play a minor role in stabilizing this interesting conformation. The distance between the two parallel cyclopentadienyl groups is 5.90 Å, considerably larger than the value of 3.40 Å generally observed for the base stacking in nucleic acids.[24]

In general, the other bond angles and bond lengths of the two structures are well within the normal range for the various portions of the complexes.

Reasons for the elongation of the Si–Si bond in I compared to that in II are clearly not related to steric aspects of the molecules. In I the two $(\eta^5\text{-}C_5H_5)Fe(CO)_2$ groups as noted above are anti to each other, and the two Fe–Si bond lengths at 2.375 (2) Å are *longer* than other reported Fe–Si bonds in the system $(\eta^5\text{-}C_5H_5)Fe(CO)_2$–Si. Thus, $(\eta^5\text{-}C_5H_5)Fe(CO)_2SiMe_2SiPh_3$ (III) and $(\eta^5\text{-}C_5H_5)Fe(CO)_2SiMe_2GePh_3$ (IV) possess Fe–Si bonds of length 2.346 (1) and 2.328 (1) Å, respectively. It is also noteworthy that the longer Fe–Si bond in I occurs with an elongation of the Si–Si bond. We have previously suggested that the shorter Fe–Si bond in IV compared to that in III was due to a greater interaction between the Fe and Si atoms due to enhanced electron donation of the germylsilyl group compared to that of the disilyl group. When this occurs, there is a corresponding weakening of the Ge–Si or Si–Si bond. In the case of III the Si–Si bond length of 2.373 (1) Å was longer by 0.18 Å than that in $Me_3SiSiPh_3$, illustrating this effect. In the present case the increased bond length in the Si–Si bond in I occurs with a longer Fe–Si bond. Such dual elongations of the Fe–Si and Si–Si bonds seem to reflect the problem of electron donation to two Fe atoms. The electron-withdrawing need of the Fe atom on the specific bonded Si atom is hampered because of the other Fe atom in the β-position. The result is that neither Fe atom is as strongly bonded to the Si atoms as in the case of a mono-iron complex, and the electron density in the bonding environment between the two Si atoms is also depleted. Overall it seems that the binding of two $(\eta^5\text{-}C_5H_5)Fe(CO)_2$ groups to the disilane results in weakening of both the Si–Si and Fe–Si bonds in comparison to the case for similar complexes. Related to this observation are the structural data of the 1,3,3,5,5-pentachloro-1,3,5-trisilacyclohexyl and 1,3,5,5-tetrachloro-1,3,5-trisilacyclohexyl derivatives of the $(\eta^5\text{-}C_5H_5)Fe(CO)_2$ system. In these complexes the former has a single $(\eta^5\text{-}C_5H_5)Fe(CO)_2$ group and the latter two such groups, and the Fe–Si bond lengths are 2.264 and 2.279 Å, respectively.[26] These values illustrate an increase in the Fe–Si bonds upon the addition of the second Fe substituent, therefore paralleling the data from our own study.

The ^{29}Si NMR data for the two complexes are of interest. The pair of silicon atoms is equivalent in both complexes, and thus each complex exhibits a single resonance: 29.5 ppm for I and −23.5 ppm for II. These chemical shifts, in C_6D_6, represent $\Delta\delta$ values of 49 and −4 ppm, respectively, when compared to the shift of their methyl-substituted counterpart $Me_3SiSiMe_3$, $\delta = -19.5$ ppm. The two Fe atoms in close proximity to the Si atoms in I clearly have a significant deshielding effect, which appears to be more than additive since, when $(\eta^5\text{-}C_5H_5)Fe(CO)_2SiMe_2SiMe_3$ is compared to $Me_3SiSiMe_3$, the Fe–*Si* atom is deshielded by approximately 36.6 ppm, and Fe–Si–*Si* is deshielded by 8.4 ppm. When the disilyl moiety is bonded via the cyclopentadienyl group, the effect of the

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Fe atoms is smaller and the small shielding effect of the $(\eta^5\text{-}C_5H_4)Fe(CO)_2$ system is more similar to the effect upon the ^{29}Si NMR data of a phenyl group. For example, the chemical shift of Me_3SiPh is at −4.5 ppm relative to Me_4Si, and that of Me_3Si–ferrocenyl is at −3.84 ppm. Given the aromatic nature of the $\eta^5\text{-}C_5H_5$ group, this similarity in behavior is not entirely unexpected. Overall the ^{29}Si NMR data provide further attractive evidence for significant electron withdrawal from silicon by the Fe atoms in such $(\eta^5\text{-}C_5H_5)Fe(CO)_2$–silyl complexes, which is not evidenced when the silyl groups are bonded to the system via the cyclopentadienyl groups.

In summary, the structural and ^{29}Si NMR data indicate that two transition-metal atoms bonded to a disilane moiety in the 1,2-positions have a capacity to weaken the Si–Si bond. We are currently investigating the chemical

and photochemical properties of such complexes in order to demonstrate such activation.

Supplementary Material Available: Structure determination summaries and listings of bond lengths and angles, anisotropic displacement coefficients for non-hydrogen atoms, and positional parameters and isotropic displacement coefficients for hydrogen atoms for I and II (10 pages); listings of observed and calculated structure factors (11 pages). Ordering information is given on any current masthead page.

Communications

Equilibrium between (η^1-Phosphaallyl)- and (η^3-Phosphaallyl)tungsten Complexes

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Summary: The reaction of supermesitylvinylhalophosphine (supermesityl = 2,4,6-tri-*tert*-butylphenyl) with (cyclopentadienyl)tricarbonyltungsten hydride in the presence of Et_3N and UV radiation yields [η^1-supermesitylvinylphosphido](cyclopentadienyl)dicarbonyltungsten with a P=W double bond. This η^1-complex isomerizes upon heating to give the corresponding η^3-phosphaallyltungsten complex. The latter is converted back to the η^1-complex upon irradiation with sunlight in CH_2Cl_2.

In several recent papers,[1-3] we have described a series of new η^3-phosphaallyl complexes (A). Two questions have

A, M = CpFe(CO),[1,2] CpMo(CO)$_2$,[3] CpW(CO)$_2$[3]
M′ = W(CO)$_5$
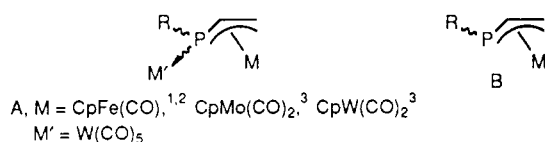
arisen during this work: (a) All these complexes are stabilized via an additional η^1-coordination to a metal center. Is it possible to do without this coordination and to prepare "free" η^3-complexes such as B? (b) All these complexes are obtained as mixtures of readily interconverting isomers. A series of X-ray crystal structure analyses have shown that this isomerism originates at phosphorus with either R in the plane of the η^3-phosphaallyl moiety and M,M′ on

both sides of this plane (C)[3] or M′ in the plane and M,R on both sides (D).[1] The ready C ⇌ D isomerization (eq 1) suggests an equilibrium between these η^3-complexes and
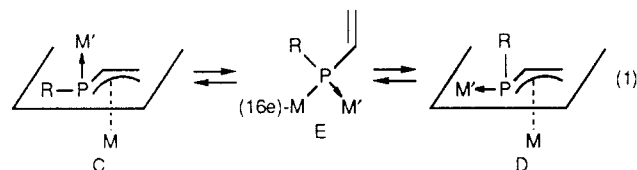
the corresponding 16-electron η^1-complex E with a free C=C double bond. This ready decoordination of the C=C bond could play a crucial role in catalysis. In this work, we describe the first complex of type B and we unambiguously demonstrate the existence of this η^1–η^3 equilibrium (eq 1).

Since stable η^3-1,3-diphosphaallyl complexes without additional η^1-coordination at phosphorus had been prepared by Appel[4] using supermesityl (2,4,6-tri-*tert*-butylphenyl) as the P substituent, we chose to study the reaction of the supermesitylvinylhalophosphine 1[5] with the tungsten hydride 2 (eq 2).

3 (30%)
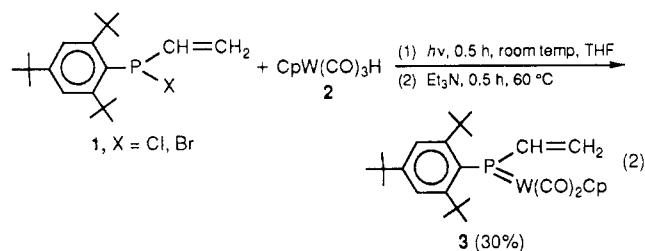
In doing so, we followed a procedure described by Malisch[6] for use in the synthesis of $Cp(CO)_2W{=}PR_2$ complexes, and we were able to obtain such a complex, 3.[7] The presence of the P=W double bond was unambigu-

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