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Reactions of Phenylsilanes with Iron Nonacarbonyl

Richard S. Simons and Claire A. Tessier*

Department of Chemistry, University of Akron, Akron, Ohio 44325-3601

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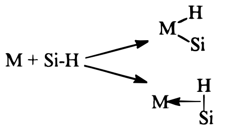
Reaction of equimolar amounts of $Fe_2(CO)_9$ and $SiPhH_3$ yields the triply bridged diiron complex $[(OC)_3Fe]_2(\mu\text{-}SiPhH)_2(\mu\text{-}CO)$ (**1a**). The analogous reaction of $Fe_2(CO)_9$ and $SiPh_2H_2$ provides the singly bridged diiron complex $[(OC)_4Fe{-}Fe(CO)_3(SiHPh_2)](\mu\text{-}\eta^2\text{-}H\text{-}SiPh_2)$ (**4**). When **4** is photolyzed for 12 h, the complex $[(OC)_3Fe]_2(\mu\text{-}\eta^2\text{-}H\text{-}SiPh_2)_2$ (**5**) is obtained. Both **4** and **5** exhibit agostic Fe−H−Si interactions. Reaction of $Fe_2(CO)_9$ or $Fe(CO)_5$ with the disiloxane $Ph_2HSi{-}O{-}SiHPh_2$ gives the singly bridged diiron complex $[(OC)_4Fe]_2(\mu\text{-}\eta^2\text{-}Ph_2Si{-}O{-}SiPh_2)$ (**6**). All compounds have been characterized by ^1H, ^{13}C, and ^{29}Si NMR and IR spectroscopy. Compounds **4**−**6** have been characterized by X-ray crystallography.

Introduction

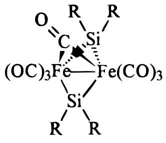
The interaction of a reactive metal center with the Si−H bond of a silane can result in either complete oxidative addition to form M−H and M−Si bonds or a three-center−two-electron agostic interaction (eq 1), and often the latter is regarded as an intermediate to the formation of the former.[1] With the reactions of binary iron carbonyls with silanes, it is usually assumed that simple oxidative addition is the first step in the reaction, though this has only been observed directly with the tertiary silanes $SiHR_3$ (R = Me, Cl, Ph) with $Fe(CO)_5$.[2] The first stable agostic Si−H interaction in iron-silicon chemistry was recently reported after this paper was accepted.[3] Such an interaction also has been suspected in at least two compounds in the solid state and in the gas phase for Fe^+.[1a,4]



(1)

With the binary iron carbonyls, the nature of the reactive iron center which interacts with the silane has not been well-defined. Usually the reactive metal center is believed to be $Fe(CO)_4$. Photolysis of $Fe(CO)_5$ and $Fe_3(CO)_{12}$, heating of $Fe(CO)_5$, and simple dissolution of $Fe_2(CO)_9$ in a solvent have all been suggested as routes to $Fe(CO)_4$.[5] If an understanding of the initial interaction between secondary or primary silanes and $Fe(CO)_4$ is desired, $Fe_2(CO)_9$ would appear to be the reagent of choice. The photolysis or heating required to generate $Fe(CO)_4$ from the other binary iron carbonyls could induce further reactions. However, for $Fe_3(CO)_{12}$, intermediates in which Fe−Fe bonds are retained have also been proposed.[6] Though few kinetic studies of substitution processes of $Fe_2(CO)_9$ have been done due to its low solubility, it appears that $Fe_2(CO)_9$ can also react by way of intermediates which contain Fe−Fe bonds.[5a]

In the reactions of binary iron carbonyls with primary and secondary silanes, reductive elimination of H_2 takes place, presumably after the oxidative addition of the silane. One or more of the three different types of iron-silicon rings **1**−**3** can be obtained from such reactions.



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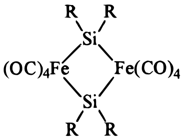

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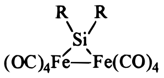

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Corriu, Carré, and co-workers studied the photolysis of $Fe(CO)_5$ with secondary silanes.[7] Iron−silicon rings of the form **1** (R = Ph, Me; $R_2 = Ph_2$) and **2** (R = Ph) were obtained. Kirillova and co-workers also obtained a compound of structure **1** from the reaction of $Fe_2(CO)_9$ and the secondary silane 1,1-dihydro-1-silaphenalene under unspecified conditions.[8] Complexes of structure **2** may be thought of as progenitors of complexes of structure **1** because heating or photolysis of the former has yielded the latter.[7,9] Just recently, Ogino and co-workers reported that the reactions of excess $Fe_2(CO)_9$ with bulky secondary silanes under reflux conditions give the three-membered-ring products **3** (R = Mes, $O(2,6\text{-}i\text{-}Pr_2C_6H_3)$).[10] Complexes of structure **1**−**3** have

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also been obtained by using synthetic routes that involve chlorosilanes, disilanes, or anionic iron complexes.[9,11]

We report herein an investigation of the reactions of $Fe_2(CO)_9$ with phenyl-substituted silanes at room temperature. We find that in addition to structure **1** two new types of iron-silicon rings, both of which contain agostic Si−H interactions, are formed.

Experimental Section

General Procedures. All manipulations were performed using standard Schlenk techniques.[12] All silanes were purchased from Petrarch/Huls America and used without further purification. All solvents were distilled immediately before their use from sodium−benzophenone ketyl. $Fe(CO)_5$ and $Fe_2(CO)_9$ were purchased from Aldrich and used without futher purification. *Caution! Some of the brown-black solids filtered from the reaction mixtures of $Fe_2(CO)_9$ as well as compound **1a** are pyrophoric.*

^1H, ^{13}C, and ^{29}Si NMR were recorded on a Varian 300 spectrometer at variable temperatures using a DEPT pulse sequence for ^{29}Si spectra.[13] Elemental analyses were performed by E & R Microanalytical Laboratories. The photolysis equipment consisted of a Hanovia medium-pressure UV lamp housed in a water-cooled fused-silica jacket.

Synthesis of $[(OC)_3Fe]_2(\mu\text{-}SiPhH)_2(\mu\text{-}CO)$ (1a). $Fe_2(CO)_9$ (1.85 g, 5.1 mmol) was suspended in 60 mL of hexane, and $PhSiH_3$ (0.94 mL, 5.1 mmol) was added by syringe with stirring. After 20 h of stirring, the reaction mixture was filtered and the filtrate was cooled to −30 °C to provide **1a** (0.48 g, 14%) as a yellow pyrophoric powder. Anal. Calcd for $C_{19}H_{12}O_7Si_2Fe_2$: C, 43.87; H, 2.33. Found: C, 43.40; H 2.68. IR: 2129 (w), 2065 (m), 2034 (vs), 1991 (vs), 1835 (s) cm^{-1}. ^1H NMR (300 MHz, C_6D_6): δ 5.8 (s, 2H, Si−H); 7.0, 7.5 (m, 10H, Ar H). ^{13}C NMR (75 MHz, C_6D_6): δ 207.1 (CO); 136.5, 136.0, 135.8, 132.2, 132.0, 128.7, 127.8 (Ar C). ^{29}Si NMR (60 MHz, C_6D_6): δ 161.71, 161.67 (J_{SiH} = 203.3 Hz).

Synthesis of $[(OC)_4Fe-Fe(CO)_3(SiHPh_2)](\mu\text{-}\eta^2\text{-}HSiPh_2)$ (4). $Fe_2(CO)_9$ (1.85 g, 5.1 mmol) was suspended in 60 mL of hexane, and Ph_2SiH_2 (0.94 mL, 5.1 mmol) was added with stirring. After 20 h of stirring, the reaction mixture was filtered and the filtrate was cooled to −30 °C to provide **4** (0.50 g, 37%) as red crystals. Anal. Calcd for $C_{31}H_{22}O_7Si_2Fe_2$: C, 55.21; H, 3.29. Found: C, 55.40; H, 3.43. IR: 2085 (s), 2008 (vs) cm^{-1}. ^1H NMR (300 MHz, C_6D_6): δ −13.2 (s, 1H, Si−H−Fe); 6.3 (s, 1H, Si−H); 7.5, 7.0 (m, 20H, Ar H). ^{13}C NMR (75 MHz, C_6D_6): δ 214.8, 212.7, 211.6, 210.7, 210.2 (CO); 141.1, 139.7, 135.2, 134.1, 130.2, 130.0, 128.8, 128.7 (Ar C). ^{29}Si NMR (60 MHz, C_6D_6): δ 142.1 (μ-$HSiPh_2$, J_{SiH} = 48.3 Hz), 15.2 ($SiHPh_2$, J_{SiH} = 197.7 Hz).

Synthesis of $[(OC)_3Fe]_2(\mu\text{-}HSiPh_2)_2$ (5). Compound **4** (0.30 g, 0.45 mmol) was dissolved in 30 mL of toluene in a Pyrex vessel and the solution photolyzed for 12 h with a medium-pressure mercury lamp. Removing the solvent under vacuum and washing the precipitate with cold hexane provides **5** (0.24 g, 80%) as a yellow powder. Crystals suitable for X-ray crystallography of **5** are obtained by cooling a saturated toluene solution. Anal. Calcd for $C_{30}H_{22}O_6Si_2Fe_2$: C, 55.75; H, 3.43. Found: C, 54.74; H, 3.33. IR: 2044 (s), 2013 (s), 1980 (s) cm^{-1}. ^1H NMR (300 MHz, C_6D_6): δ −14.2 (s, 2H, Si−H−Fe, J_{SiH} = 23.4 Hz); 8.0, 7.7, 7.5, 6.7, 6.5 (m, 20H, ArH). ^{13}C NMR (75 MHz, C_6D_6): δ 210.6 (CO); 134.6, 132.5, 130.2, 126.3 (Ar C). ^{29}Si NMR (60 MHz, C_6D_6): δ 109.2.

Synthesis of $[(OC)_4Fe]_2(\eta{:}\eta\text{-}Ph_2Si-O-SiPh_2)$ (6). A. $Fe_2(CO)_9$ (0.90 g, 2.5 mmol) and $Ph_2HSi-O-SiHPh_2$ (0.5 g, 1.3 mmol) were suspended in 60 mL of hexane. Stirring was continued for 20 h and the mixture filtered. Removal of solvent under vacuum provides **6** (0.10 g, 11%) as red crystals. Anal. Calcd for $C_{32}H_{20}O_9Si_2Fe_2$: C, 53.65; H, 2.81. Found: C, 53.78; H, 2.60. IR: 2094 (s), 2044 (s), 2007 (s) cm^{-1}. ^1H NMR (300 MHz, C_6D_6): δ 7.4 (m, 20H, Ar H). ^{13}C NMR (75 MHz, C_6D_6): δ 212.6, 207.9, 205.3 (CO); 141.9, 135.1, 133.8, 130.1 (Ar C). ^{29}Si NMR (60 MHz, C_6D_6): δ 31.1.

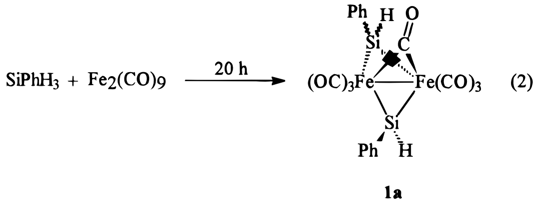
B. $Fe(CO)_5$ (0.67 mL, 5.1 mmol) and $Ph_2HSi-O-SiHPh_2$ (0.97 g, 2.5 mmol) were dissolved in 60 mL of hexane and photolyzed for 16 h. The mixture was filtered and the solvent was removed under vacuum to provide **6** (0.10 g, 5.6%) as red crystals. ^{29}Si NMR and unit cell parameters were identical with those obtained from route A.

X-ray Crystallography. All manipulations were performed on a Syntex $P2_1$ diffractometer with graphite-monochromated Mo Kα (λ = 0.701 73 Å) radiation at −144 °C for **4** and **5** and 18 °C for **6**. Crystal data, data collection, and data reduction parameters are listed in Table 1. The crystals of **4** and **6** were sealed in glass capillaries under argon. The crystal of **5** was coated with vacuum grease under an argon atmosphere and mounted on a glass fiber in air. Unit cell parameters were obtained from the least-squares refinement of the indices and angles of 25 centered reflections with 2θ between 20 and 30°. All intensity data were corrected for Lorentz and polarization effects. An empirical absorption correction was performed by utilizing the method of ψ-scans and applied to the intensity data. The structures of **4** and **6** were solved by direct methods and refined to convergence by a least-squares refinement using anisotropic displacement parameters for all non-hydrogen atoms and isotropic displacement parameters for hydrogen atoms. The structure of **5** was solved similarly, except that anisotropic displacement parameters were used for the iron, silicon, and oxygen atoms and isotropic displacement parameters were used for all carbon and hydrogen atoms. For **4** the positions of agostic and terminal silicon hydrides were determined from a difference map. For **5** the position of the agostic silicon hydride only could be determined in one of the two molecules in the unit cell.

Results and Discussion

A few general comments on the syntheses are appropriate. The reactions involved equimolar quantities of $Fe_2(CO)_9$ and the phenylsilane and were conducted in hexane, a solvent in which $Fe_2(CO)_9$ has little solubility. Reaction mixtures were stirred for about 20 h, at which time no unreacted $Fe_2(CO)_9$ was present. A dark brown-black precipitate, which in some cases was pyrophoric and may have contained elemental iron, was filtered from the hexane solution. Products were isolated from the hexane solution.

The reaction of $Fe_2(CO)_9$ with an equimolar quantity of $PhSiH_3$ in hexane provides $[(OC)_3Fe]_2(\mu\text{-}SiPhH)_2(\mu\text{-}CO)$ (**1a**) in low yield as a yellow pyrophoric powder (eq 2). Complex **1a** was characterized by ^1H, ^{13}C, and ^{29}Si



(2)

1a

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Table 1. Crystal Data, Data Collection and Reduction, and Refinement Details for Compounds 4−6

compd	**4**	**5**	**6**
formula	$C_{31}H_{22}Fe_2O_7Si_2$	$C_{30}H_{22}Fe_2O_6Si_2$	$C_{32}H_{20}Fe_2O_9Si_2$
fw	674.4	626.2	716.4
cryst syst	monoclinic	triclinic	monoclinic
space group	$C2/c$	$P\bar{1}$	$P2_1/c$
a (Å)	29.079(6)	10.018(2)	17.802(4)
b (Å)	9.731(2)	10.436(2)	17.099(3)
c (Å)	21.113(3)	14.881(3)	10.919(2)
α (deg)	90	108.00(3)	90
β (deg)	97.10(3)	91.46(3)	104.50(3)
γ (deg)	90	96.97(3)	90
V (Å^3)	5928(2)	1222.8(4)	3217.8(11)
Z	8	2	4
d(calcd) (Mg/m^3)	1.511	1.419	1.479
μ (Mo Kα) (mm^{-1})	1.102	1.11	1.024
cryst dimens (mm)	0.3 × 0.3 × 0.3	0.15 × 0.15 × 0.2	0.3 × 0.4 × 0.4
scan type	ω	ω	ω
scan range, (deg)	1.20	2.00	1.00
2θ range, (deg)	3.5−50.0	3.5−45.0	3.5−45.0
min, max transmissns	0.3150, 0.7046	0.4796, 0.8390	0.5779, 0.6422
no. of unique data	5254 (R_{int} = 6.84%)	3704 (R_{int} = 2.80%)	4176 (R_{int} = 1.53%)
no. of obsd data ($F_o \geq 4\sigma(F_o)$)	3163	1947	2438
no. of params	379	211	406
GOF	1.14	4.70	2.47
R	5.95	9.15	4.41
R_w	6.62	10.58	4.78

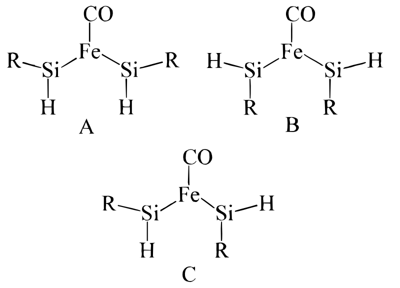


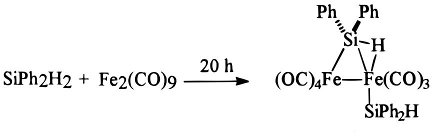
Figure 1. The three possible arrangements of the silyl substituents of **1a**. Each arrangement is drawn as a view down the Fe−Fe bond, and all terminal CO ligands are omitted.

NMR, IR spectroscopy, and elemental analysis. The IR spectrum of **1a** shows bands at 2129, 2065, 2034, 1994, and 1835 cm^{-1}. These have been assigned to the stretching frequencies of Si−H, three terminal C≡O's, and a bridging carbonyl, respectively.

Three isomers of **1a** can be drawn and are represented in Figure 1 as **A**−**C**. Figure 1 is drawn as a view down the Fe−Fe bond; it omits all terminal carbonyl ligands. Each isomer differs from the others by the relationship of their substituents with respect to the bridging carbonyl. In isomers A and B the two bridging silyl ligands are equivalent and, therefore, a single resonance would be observed for each isomer in the ^{1}H and the ^{29}Si{^{1}H} NMR spectra. In isomer C the bridging silyl ligands are chemically inequivalent and a separate resonance should be observed for each. In the Si−H region of the ^{1}H NMR **1a** shows two incompletely resolved singlets of equal intensity centered at about δ 5.8 ppm. In the ^{29}Si{^{1}H} NMR, **1a** shows two resonances of equal intensity centered at about δ 161.7 ppm. This downfield shift for the silicon resonances is consistent with those of other silicon atoms contained in Fe_2Si three-membered rings.[10,11c,14] Barring any accidental equivalence of resonances, the ^{1}H and ^{29}Si{^{1}H} NMR are consistent with only isomer C or a 50:50 mixture of A and B.

The formation of **1a** can be rationalized on the basis of previously observed chemistry. The direct formation of complexes of structure **1** from $SiPhH_3$, $SiPhMeH_2$,[7] and 1,1-dihydro-1-silaphenalene[8] without the observation of the presumed intermediates of structure **2** can be explained by the lower steric hindrance of these silanes. With the bulkier $SiPh_2H_2$ a complex of structure **2** is isolable.[7] We should emphasize that **1a** was obtained in low yield. Other complexes may be present in the reaction mixture because all the $Fe_2(CO)_9$ reacted.

On the basis of previous work and the above results, one would predict a complex of either structure **1** or **2** from the reaction of $Fe_2(CO)_9$ and $SiPh_2H_2$. However, when $Fe_2(CO)_9$ was reacted with an equimolar quantity of $SiPh_2H_2$ in hexane, the complex $[(OC)_4Fe{-}Fe(CO)_3(SiHPh_2)](\mu\text{-}HSiPh_2)$ (**4**) was obtained as red air-sensitive crystals in 37% yield (eq 3).



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(3)

The crystal structure of **4** at −144 °C is shown in Figure 2. Selected bond lengths and angles are listed in Tables 2 and 3, respectively. Complex **4** consists of a diiron moiety singly bridged by a $HSiPh_2$ ligand. The extremely distorted octahedral geometry of Fe(1) is completed by four carbonyl ligands. The octahedral geometry of Fe(2) is completed by three carbonyl ligands, an agostic silicon hydride, and a terminal $SiPh_2H$ ligand trans to the Fe−Fe bond. The Fe(1)−Fe(2) (2.759(1) Å), Fe(1)−Si(1) (2.301(2) Å), and Fe(2)−Si(1) (2.385(2) Å) bond distances are in the range found in other complexes with Fe_2Si three-membered rings.[8,14b,15] A discussion of the agostic Fe−H−Si interaction of **4** will be presented later.

As shown in Scheme 1, compound **4** could be thought

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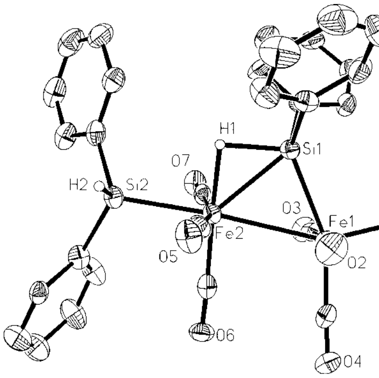


Figure 2. Thermal ellipsoid diagram of $[(OC)_4Fe-Fe(CO)_3(SiPh_2H)](\mu\text{-}HSiPh_2)$ (**4**). The thermal ellipsoids are drawn at the 50% probability level, and hydrogen atoms on phenyl substituents have been omitted for clarity.

Table 2. Selected Bond Lengths (Å) for 4

	Non-Hydrogen Atoms		
Fe(1)−Fe(2)	2.759(1)	Si(1)−C(8)	1.873(7)
Fe(1)−Si(1)	2.301(2)	Si(1)−C(14)	1.887(7)
Fe(1)−C(1)	1.781(8)	Si(2)−C(20)	1.866(8)
Fe(1)−C(2)	1.819(8)	Si(2)−C(26)	1.865(7)
Fe(1)−C(3)	1.798(7)	O(1)−C(1)	1.136(10)
Fe(1)−C(4)	1.813(7)	O(2)−C(2)	1.131(10)
Fe(2)−Si(1)	2.385(2)	O(3)−C(3)	1.134(9)
Fe(2)−Si(2)	2.365(2)	O(4)−C(4)	1.139(9)
Fe(2)−C(5)	1.798(8)	O(5)−C(5)	1.136(9)
Fe(2)−C(6)	1.794(7)	O(6)−C(6)	1.140(8)
Fe(2)−C(7)	1.785(7)	O(7)−C(7)	1.157(9)
	Silicon Hydrides[a]		
Fe(2)−H(1)	1.66	Si(1)−H(1)	1.66
		Si(2)−H(2)	1.43

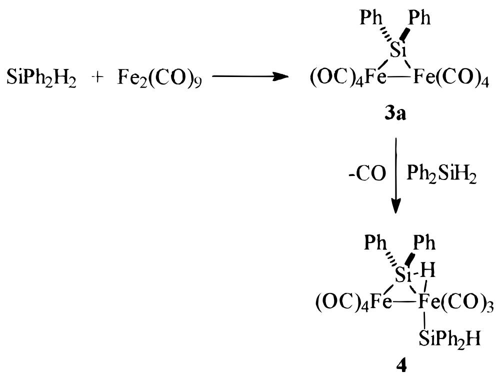
[a] See ref 16.

Table 3. Selected Bond Angles (deg) for 4

	Non-Hydrogen Atoms		
Fe(2)−Fe(1)−Si(1)	55.4(1)	C(2)−Fe(1)−C(4)	92.9(3)
Fe(2)−Fe(1)−C(1)	153.1(2)	C(3)−Fe(1)−C(4)	90.6(3)
Si(1)−Fe(1)−C(1)	97.9(2)	Fe(1)−Fe(2)−Si(1)	52.5(1)
Fe(2)−Fe(1)−C(2)	88.1(2)	Fe(1)−Fe(2)−Si(2)	175.8(1)
Si(1)−Fe(1)−C(2)	86.8(2)	Si(1)−Fe(2)−Si(2)	131.0(1)
C(1)−Fe(1)−C(2)	93.2(3)	Fe(1)−Fe(2)−C(5)	96.0(2)
Fe(2)−Fe(1)−C(3)	82.0(2)	Si(1)−Fe(2)−C(5)	98.5(2)
Si(1)−Fe(1)−C(3)	86.6(2)	Si(2)−Fe(2)−C(5)	81.4(2)
C(1)−Fe(1)−C(3)	95.1(3)	Fe(1)−Fe(2)−C(6)	81.3(2)
C(2)−Fe(1)−C(3)	170.0(3)	Si(1)−Fe(2)−C(6)	133.4(2)
Fe(2)−Fe(1)−C(4)	103.7(2)	Si(2)−Fe(2)−C(6)	95.4(2)
Si(1)−Fe(1)−C(4)	159.1(2)	C(5)−Fe(2)−C(6)	91.8(3)
C(1)−Fe(1)−C(4)	103.0(3)	Fe(1)−Fe(2)−C(7)	102.0(2)
Si(1)−Fe(2)−C(7)	91.0(2)	Fe(2)−Si(1)−C(8)	117.7(2)
Si(2)−Fe(2)−C(7)	80.6(2)	Fe(1)−Si(1)−C(14)	120.1(2)
C(5)−Fe(2)−C(7)	161.8(3)	Fe(2)−Si(1)−C(14)	121.1(2)
C(6)−Fe(2)−C(7)	92.9(3)	C(8)−Si(1)−C(14)	105.4(3)
Fe(1)−Si(1)−Fe(2)	72.1(1)	Fe(2)−Si(2)−C(20)	113.3(2)
Fe(1)−Si(1)−C(8)	118.3(2)	Fe(2)−Si(2)−C(26)	110.1(2)
C(20)−Si(2)−C(26)	109.3(3)	Fe(2)−C(7)−O(7)	177.7(6)
Fe(1)−C(1)−O(1)	177.5(6)	Fe(1)−C(4)−O(4)	176.5(7)
Fe(1)−C(2)−O(2)	177.4(7)	Fe(2)−C(5)−O(5)	178.7(6)
Fe(1)−C(3)−O(3)	177.0(6)	Fe(2)−C(6)−O(6)	177.2(6)
	Agostic Hydride[a]		
Fe(2)−H(1)−Si(1)	92		

[a] See ref 16.

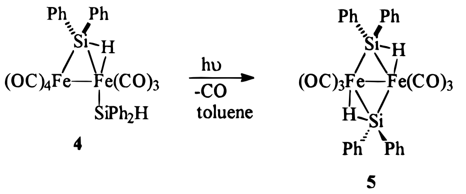
Scheme 1



of as being derived from the reaction of $SiPh_2H_2$ with a complex of structure **3**, which will be referred to as **3a**. The mechanism by which compounds of type **3** form from $Fe_2(CO)_9$ has not been determined.[10] Loss of CO from **3a** followed by reaction with additional $SiPh_2H_2$ would give **4**. In order to test whether Scheme 1 is a reasonable route to **4**, a reaction of 2 molar equiv of $Fe_2(CO)_9$ and 1 molar equiv of Ph_2SiH_2, under otherwise the same conditions as used for **4**, was carried out. The anticipated product **3a** was not isolated. Instead, an oil was obtained whose ^1H NMR showed the presence of **4** and other species which contained terminal Fe−H and Si−H. If **3a** was present, we were unable to detect it. These results suggest either that a mechanism which does not involve **3a** as an intermediate is operative or that **3a** is too reactive to be isolated.

An unresolved question is why complexes of structure **1** or **2** were not obtained as the products from the reaction of $Fe_2(CO)_9$ and $SiPh_2H_2$, as they were from the reaction of $Fe(CO)_5$ and $SiPh_2H_2$. The lack of products of structure **1** or **2** suggests that an intermediate other than $Fe(CO)_4$ was involved in the production of **4** or that UV irradiation used with $Fe(CO)_5$ allows for other processes to take place.

When complex **4** is photolyzed in toluene for 12 h, $[(OC)_3Fe]_2(\mu\text{-}HSiPh_2)_2$ (**5**) is obtained as a yellow air-sensitive powder in high yield (eq 4). (As will be discussed below, resonance forms other than that drawn in eq 4 can be drawn for **5**.) Apparently photolysis of **4** promotes the loss of a carbonyl ligand to provide a 16-electron iron center to which the terminal silyl ligand may coordinate. Mild photolysis conditions (light was filtered by Pyrex) were purposely chosen in order to selectively effect loss of carbon monoxide without also inducing loss of hydrogen.



(4)

The crystal structure of **5** at −144 °C is shown in Figure 3. The unit cell of **5** contains two independent molecules. The bond lengths and angles for each molecule are essentially the same. Selected bond lengths and angles for one of the molecules are listed in Tables 4 and 5, respectively. The structure of **5** consists of a diiron moiety doubly bridged by two silyl ligands, giving a planar four-membered ring. The two Fe−Si bonds are bridged by an agostic hydride (see below). The distorted-octahedral geometry at each iron atom is completed by one equatorial and two apical

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(15) (a) Sheldrick, W. S. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1989; Vol. 1, Chapter 3. (b) Lukevics, E.; Pudova, O.; Struckovich, R. *Molecular Structure of Organosilicon Compounds*; Wiley: New York, 1989.

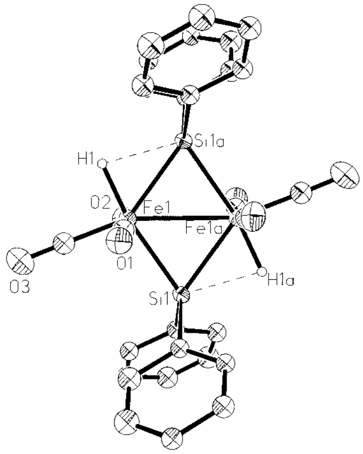

Figure 3. Thermal ellipsoid diagram of one of the two independent molecules of $[(OC)_4Fe]_2(\mu\text{-}SiPh_2H)_2$ (**5**). The thermal ellipsoids are drawn at the 50% probability level, and hydrogen atoms on phenyl substituents have been omitted for clarity.

Table 4. Selected Bond Lengths (Å) for One of the Independent Molecules of 5

	Non-Hydrogen Atoms		
Fe(1)−Si(1)	2.358(6)	Si(1)−C(12)	1.89(2)
Fe(1)−C(1)	1.84(2)	Si(1)−C(18)	1.91(2)
Fe(1)−C(2)	1.82(2)	O(1)−C(1)	1.11(3)
Fe(1)−C(3)	1.73(2)	O(2)−C(2)	1.14(2)
Fe(1)−Fe(1A)	2.759(6)	O(3)−C(3)	1.18(3)
Fe(1)−Si(1A)	2.406(6)		
	Agostic Hydride[a]		
Fe(1)−H(1)	1.57	Si(1)−H(1)	2.10

[a] See ref 16.

Table 5. Selected Bond Angles (deg) for One of the Independent Molecules of 5

	Non-Hydrogen Atoms		
Si(1)−Fe(1)−C(1)	88.3(7)	Fe(1A)−Fe(1)−Si(1A)	53.8(2)
Si(1)−Fe(1)−C(2)	87.1(7)	Fe(1)−Si(1)−C(12)	116.3(5)
C(1)−Fe(1)−C(2)	170.1(9)	Fe(1)−Si(1)−C(18)	116.9(7)
Si(1)−Fe(1)−C(3)	103.8(8)	C(12)−Si(1)−C(18)	108.7(8)
C(1)−Fe(1)−C(3)	84.7(10)	Fe(1)−Si(1)−Fe(1A)	70.8(2)
C(2)−Fe(1)−C(3)	87.9(9)	C(12)−Si(1)−Fe(1A)	118.8(6)
Si(1)−Fe(1)−Fe(1A)	55.4(2)	C(18)−Si(1)−Fe(1A)	121.1(6)
C(1)−Fe(1)−Fe(1A)	92.3(7)	Fe(1)−C(1)−O(1)	175.9(18)
C(2)−Fe(1)−Fe(1A)	92.3(6)	Fe(1)−C(2)−O(2)	176.0(18)
C(3)−Fe(1)−Fe(1A)	159.2(8)	Fe(1)−C(3)−O(3)	178.0(10)
Si(1)−Fe(1)−Si(1A)	109.2(2)	Si(1)−C(12)−C(7)	124.8(13)
C(1)−Fe(1)−Si(1A)	94.3(7)	Si(1)−C(12)−C(11)	118.3(16)
C(2)−Fe(1)−Si(1A)	95.5(6)	Si(1)−C(18)−C(13)	117.8(12)
C(3)−Fe(1)−Si(1A)	146.9(8)	Si(1)−C(18)−C(17)	121.3(15)
	Agostic Hydride[a]		
Fe(1)−H(1)−Si(1A)	81		

[a] See ref 16.

carbonyl ligands. It is interesting that the Fe−Fe bond distance (2.759(6) Å) of **5** is equal, within experimental error, to that found in **4**. Presumably the planarity of the Fe_2Si_2 core alleviates any steric congestion which can be associated with the addition of another bridging ligand.

The M−Si, M−H, and Si−H bond distances combined with the NMR silicon−hydrogen coupling constants are most useful for identifying the agostic hydride interactions. In general, the weakened agostic Si−H interaction is distinguished from a terminal Si−H by an increase in the Si−H bond distance and a decrease in the silicon−hydrogen coupling constant. In addition, the M−Si bond distances increase when bridged by an agostic hydride and M−H distances are longer than those of typical covalent bonds.[1a] Several structural features of **4** and **5** indicate that they both contain agostic hydride interactions.[16] For complex **4**, H(1) was located in the difference map at 1.66 Å from both Fe(2) and Si(1) with an Fe(2)−H(1)−Si(1) angle of 92°. As expected, the agostic Si(1)−H(1) distance of **4** is considerably longer than the terminal Si(2)-H(2) distance of 1.43 Å. In addition, there is a lengthening of the Fe(2)−Si(1) bond distance as compared to the distance of Fe(1)−Si(1). For each molecule of complex **5**, two separate pairs of Fe−Si bond distances exist (2.358(6) and 2.406(6) Å). An agostic hydride was located in the difference map at distances 1.57 and 2.10 Å from the Fe(1) and Si(1a) atoms, respectively, but for only one of the two independent molecules of **5**. The Fe−H−Si angle is 81°.

The crystallographic evidence for agostic Fe−Si−H interactions for **4** and **5** has been corroborated by NMR data. In the ^{1}H NMR for **4**, resonances are observed for the terminal Si−H proton at δ 6.3 and the agostic Fe−H−Si proton at δ −13.2. A signal similar to this latter resonance would be expected for the two equivalent agostic hydrogen atoms of **5**. However, in the ^{1}H NMR of **5** at 23 °C, a broad, barely visible resonance at about −14.2 ppm is observed. The variable-temperature ^{1}H NMR of **5** was investigated from −60 to +60 °C. Compound **5** is fluxional on the ^{1}H NMR time scale down to −40 °C. At −40 °C a single sharp resonance is observed at δ −14.2 ppm with satellite peaks due to weak coupling with ^{29}Si ($J = 23.4$ Hz). The fluxionality of **5** can be explained by the facile complexation-decomplexation of the Si−H bond to the iron center.[17] From the coalescence temperature of the Fe−H−Si resonance, $\Delta G^{\ddagger}$ for this process is calculated to be 22 ± 1 kcal mol^{-1} at both −10 and 23 °C.[18] In contrast to **5**, **4** displays no fluxional behavior at 23 °C.

In the ^{29}Si NMR, the bridging silyl ligand in compound **4** is observed at δ 142.1 ppm, whereas the terminal silyl ligand of **4** is observed at δ 15.2. The Si−H (1.67 Å) bond distance and the silicon−hydrogen coupling constant of 48.3 Hz for the bridging silyl ligand of **4** are parameters expected for "normal" agostic M−H−Si interactions, whereas the Si−H bond distance of 1.44 Å for the nonbridging silyl ligand and the silicon−hydrogen coupling constant of 197.7 Hz are consistent with parameters for terminal silyl hydrides.[15,19] The room-temperature ^{29}Si NMR spectrum for **5** was featureless. However, at −40 °C, the ^{29}Si NMR spectrum of **5** shows a sharp singlet at δ 109.2 ppm with a silicon−hydrogen coupling constant of 23.4 Hz. The silicon−hydrogen coupling constant for **5** is at the lower limit (20−136 Hz[1a,20]) of values reported for other compounds with M−H−Si agostic hydrides. Correspondingly the Si−H distance (2.10 Å) for **5** is at the upper limit of values reported for other compounds with

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(16) The esd values for hydrogen atoms appeared to underestimate their error and have been omitted. Instead, parameters for hydrogen atoms have been truncated by one significant figure.

(17) Wang, W. D.; Eisenberg, R. *J. Am. Chem. Soc.* **1990**, *112*, 1833−1841.

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(19) Kupce, E.; Lukevics, E. In *Isotopes in the Physical and Biomedical Sciences*, Buncel, E., Jones, J. R., Eds.; Elsevier: Amsterdam, 1991; Vol 2, pp 213−295.

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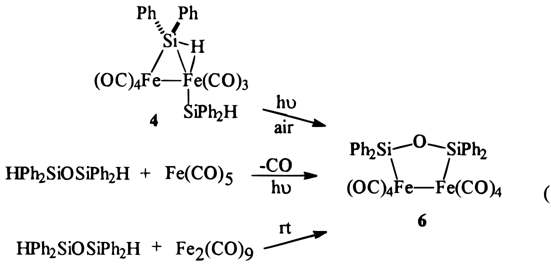
M−H−Si agostic hydrides.[1a] Both NMR and crystallographic data indicate that the agostic Fe−H−Si interactions of **5** are weak. The only other known agostic Fe−H−Si interaction, in the cationic complex $[Cp(CO)(PEt_3)Fe(\eta^2\text{-}H\text{-}SiEt_3)][B(3,5\text{-}(CF_3)_2C_6H_3)_4]$, has been characterized by a silicon-hydrogen coupling constant of 62.4 Hz.[3]

Infrared data have been seldom used to characterize agostic M−H−Si interactions. The position of the broad M−H−Si band has been reported as high as 1890 cm^{-1} for a mononuclear complex and in the range 1790−1650 cm^{-1} for dinuclear complexes, and this band appears to be easier to detect by Raman rather than IR spectroscopy.[21,22] No band in the 1900−1600 cm^{-1} region of the IR spectrum was observed for either **4** or **5**. We assign the strong, sharp band at 2085 cm^{-1} in the spectrum of **4** to the terminal Si−H stretch. Other bands of **4** and all bands of **5** in the 2100−1600 cm^{-1} region are assigned to carbonyl stretching modes.

As shown in eq 5, the complex $[(OC)_4Fe]_2(\eta{:}\eta\text{-}Ph_2Si{-}O{-}SiPh_2)$ (**6**) can be isolated by three different routes.



(5)

Red crystalline complex **6** was first isolated in about 2% yield by conducting the photolysis of **4** without full exclusion of air. In this novel reaction, the product **6** has one more carbonyl ligand than the reagent **4**. Therefore, some of complex **4** serves as a sacrificial source of the extra carbonyl ligand. It seemed reasonable to expect higher yields of **6** from reagents which already have at least four carbonyl ligands per iron. With this in mind, the reaction of $Ph_2HSi{-}O{-}SiHPh_2$ with $Fe(CO)_5$ under photolytic conditions and the room-temperature reaction of $Ph_2HSi{-}O{-}SiHPh_2$ with $Fe_2(CO)_9$ were examined. In both cases the yield of **6** was better than when it was prepared from **4** (5.6% and 11%, respectively), but only marginally. The photolysis of $Fe(CO)_5$ with $HMe_2Si{-}O{-}SiMe_2H$ has been reported to give a 55% yield of the related complex $[(OC)_4Fe]_2(\eta{:}\eta\text{-}Me_2Si{-}O{-}SiMe_2)$.[23] No evidence for a monoiron complex such as $H_2Fe(CO)_3(Ph_2Si{-}O{-}SiPh_2)$ or $HFe(CO)_4(Ph_2Si{-}O{-}SiPh_2H)$ was obtained, even though mononuclear rather than dinuclear complexes are usually obtained when a disiloxane adds to a metal.[24]

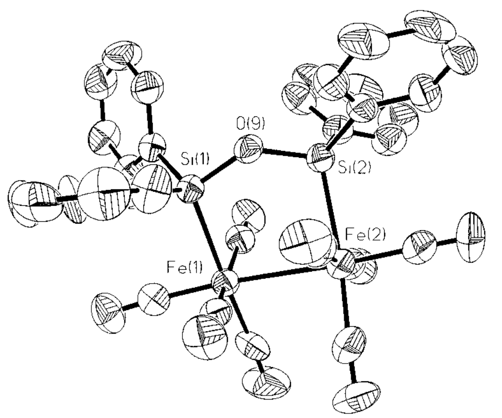


Figure 4. Thermal ellipsoid diagram of $[(OC)_4Fe]_2(\eta{:}\eta\text{-}Ph_2Si{-}O{-}SiPh_2)$ (**6**). The thermal ellipsoids are drawn at the 50% probability level, and hydrogen atoms have been omitted for clarity.

Table 6. Selected Bond Lengths (Å) for 6

Fe(1)−Fe(2)	2.875(2)	Fe(2)−Si(2)	2.426(2)
Fe(1)−Si(1)	2.412(2)	Fe(2)−C(5)	1.807(10)
Fe(1)−C(1)	1.822(9)	Fe(2)−C(6)	1.782(10)
Fe(1)−C(2)	1.804(9)	Fe(2)−C(7)	1.782(11)
Fe(1)−C(3)	1.809(9)	Fe(2)−C(8)	1.793(10)
Fe(1)−C(4)	1.766(10)	O(2)−C(2)	1.134(11)
Si(1)−O(9)	1.638(6)	O(3)−C(3)	1.134(10)
Si(1)−C(9)	1.854(8)	O(4)−C(4)	1.149(12)
Si(1)−C(15)	1.869(7)	O(5)−C(5)	1.155(12)
Si(2)−O(9)	1.641(5)	O(6)−C(6)	1.142(12)
Si(2)−C(21)	1.873(8)	O(7)−C(7)	1.128(14)
Si(2)−C(27)	1.879(9)	O(8)−C(8)	1.147(12)
O(1)−C(1)	1.135(12)		

Table 7. Selected Bond Angles (deg) for 6

Fe(2)−Fe(1)−Si(1)	91.1(1)	Si(2)−Fe(2)−C(8)	79.4(3)
Fe(2)−Fe(1)−C(1)	89.0(3)	C(5)−Fe(2)−C(8)	94.3(4)
Si(1)−Fe(1)−C(1)	173.8(3)	C(6)−Fe(2)−C(8)	166.9(4)
Fe(2)−Fe(1)−C(2)	76.7(3)	C(7)−Fe(2)−C(8)	93.6(5)
Si(1)−Fe(1)−C(2)	87.6(3)	Fe(1)−Si(1)−O(9)	107.5(2)
C(1)−Fe(1)−C(2)	98.5(4)	Fe(1)−Si(1)−C(9)	113.3(3)
Fe(2)−Fe(1)−C(3)	93.9(3)	O(9)−Si(1)−C(9)	108.9(3)
Si(1)−Fe(1)−C(3)	81.1(3)	Fe(1)−Si(1)−C(15)	115.0(2)
C(1)−Fe(1)−C(3)	92.7(4)	O(9)−Si(1)−C(15)	106.7(3)
C(2)−Fe(1)−C(3)	165.2(4)	C(9)−Si(1)−C(15)	105.1(3)
Fe(2)−Fe(1)−C(4)	167.7(3)	Fe(2)−Si(2)−O(9)	106.4(2)
Si(1)−Fe(1)−C(4)	87.9(3)	Fe(2)−Si(2)−C(21)	113.5(3)
C(1)−Fe(1)−C(4)	93.2(4)	O(9)−Si(2)−C(21)	110.0(3)
C(2)−Fe(1)−C(4)	91.0(4)	Fe(2)−Si(2)−C(27)	112.9(2)
C(3)−Fe(1)−C(4)	98.1(4)	O(9)−Si(2)−C(27)	105.6(3)
Fe(1)−Fe(2)−Si(2)	87.9(1)	C(21)−Si(2)−C(27)	108.2(4)
Fe(1)−Fe(2)−C(5)	88.9(3)	Si(1)−O(9)−Si(2)	134.0(3)
Si(2)−Fe(2)−C(5)	172.7(4)	Fe(1)−C(1)−O(1)	174.4(8)
Fe(1)−Fe(2)−C(6)	76.4(3)	Fe(1)−C(2)−O(2)	173.4(9)
Si(2)−Fe(2)−C(6)	89.6(3)	Fe(1)−C(3)−O(3)	176.5(8)
C(5)−Fe(2)−C(6)	96.1(5)	Fe(1)−C(4)−O(4)	176.5(7)
Fe(1)−Fe(2)−C(7)	169.3(3)	Fe(2)−C(5)−O(5)	177.6(9)
Si(2)−Fe(2)−C(7)	89.1(3)	Fe(2)−C(6)−O(6)	174.4(8)
C(5)−Fe(2)−C(7)	95.2(4)	Fe(2)−C(7)−O(7)	176.3(10)
C(6)−Fe(2)−C(7)	93.4(5)	Fe(2)−C(8)−O(8)	176.6(8)
Fe(1)−Fe(2)−C(8)	95.9(3)		

Complex **6** has been characterized by spectroscopy and by X-ray crystallography. The ^{29}Si NMR chemical shift of **6** occurs at δ 31.1 ppm, which is considerably upfield from the chemical shift of silicon atoms contained in the three-membered rings of **4** and **5**. The crystal structure of **6** is shown in Figure 4. Selected bond lengths and angles are listed in Tables 6 and 7, respectively. The structure of **6** consists of a diiron moiety singly bridged by the disiloxane $Ph_2Si{-}O{-}SiPh_2$. The octahedral geometry at each iron atom is completed by four carbonyl ligands. The Fe−Fe (2.875(2) Å) bond distance is long[15] but not unreasonable, considering the steric requirements of the bridging disiloxane. The Fe(1)−Si(1) (2.412(2) Å) and the Fe(2)−Si(2) (2.426(2) Å) bond distances are long but are in the range of other

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(24) Chralovsky, V. In *The Chemistry of Inorganic Homo and Heterocycles*; Haiduc, I., Sowerby, D. B., Eds.; Academic: London, 1987; Vol. 1, Chapter 10.

Fe−Si bond distances.[15] The disiloxane retains typical Si−O (1.638(6) and 1.640(5) Å) bond distances, but the Si−O−Si angle (134.0(3)°) is smaller than in free disiloxanes with similar substituents.[15] The crystal structure of the free ligand $Ph_2HSi{-}O{-}SiHPh_2$ has been found to be disordered. An asymmetric Si−O−Si fragment with Si-O bond distances of 1.56 and 1.69 Å and an apparent Si−O−Si bond angle of 160° were reported.[25] An interesting structural feature is the approximate staggered relationship of the carbonyls on Fe(1) with respect to the carbonyls on Fe(2). Presumably this "twisting" of the Fe−Fe bond is a result of the steric crowding caused by the phenyl substituents on Si(1) and Si(2).

Summary

In conclusion, this study has demonstrated that phenylsilanes oxidatively add to reactive iron carbonyl species to give dinuclear iron−silicon complexes, all of which contain Fe−Fe bonds. With the primary silane $SiPhH_3$, the reductive elimination of the elements of 1 mol of dihydrogen for each of the two silyl ligands provides a complex of structure **1**. As with the primary silane, 2 mol of the secondary silane $SiPh_2H_2$ adds to a diiron fragment. However, with $SiPh_2H_2$, only 1 mol of dihydrogen is lost in the addition of the two ligands, giving the complex **4**. The silyl ligands of **4** each still contain a hydride, one as a terminal ligand and one involved in an agostic interaction. Photolysis of **4** promotes the loss of one carbonyl ligand to give a 16-electron iron center, to which the remaining terminal silyl ligand oxidatively adds to provide **5**. The products obtained from the reaction of $Fe_2(CO)_9$ and $SiPh_2H_2$ and subsequent photolysis are very different from the products of the photolysis of $Fe(CO)_5$ and $SiPh_2H_2$.[7,26] The difference may be partially due to differences in iron to silicon stoichiometry and different conditions for the photolyses: a medium-pressure bulb and a Pyrex apparatus for the former and a high-pressure bulb in a fused-silica apparatus for the latter. With $Fe_3(CO)_{12}$ different chemistries are observed at different wavelengths.[6] The reaction of $Ph_2HSi{-}O{-}SiHPh_2$ with either $Fe_2(CO)_9$ or $Fe(CO)_5$ provides **6**, a diiron complex bridged by a disiloxane. The exact mechanism by which the formation of **1a**, **4**, and **6** from $Fe_2(CO)_9$ and the appropriate phenylsilane proceed is difficult to assess from the experiments described herein, and more than one mechanism could be operating simultaneously. The products **1a**, **4**, and **6** can be rationalized by mechanisms involving either $Fe_2(CO)_n$ and/or $Fe(CO)_4$ as the initial iron carbonyl species.

Acknowledgment. We thank Wiley Youngs and Peter Rinaldi for useful discussions and James Howe (deceased) for library research. This work was supported by the National Science Foundation (Grant No. CHE-9309160) and by the State of Ohio Board of Regents Research Challenge.

Supporting Information Available: Tables of data collection and structure solution details, fractional atomic coordinates and equivalent isotropic displacement parameters, bond distances and angles, and anisotropic and isotropic displacement parameters for the crystal structures of **4**−**6** (24 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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[25] Wojnowski, W.; Peters, K.; Peters, E.-M.; Meyer, T.; von Schnering, H. G. *Z. Anorg. Allg. Chem.* **1986**, *537*, 31−39.

[26] We considered the possibility that $[(OC)_4FeSiPh_2]_2$[7] may have been misidentified because it has a ^{29}Si NMR chemical shift (δ 109 or 111 ppm) which is identical with that of **5** (δ 109 ppm). The lack of fluxionality of $[(OC)_4FeSiPh_2]_2$ and other data (see following references) indicate that $[(OC)_4FeSiPh_2]_2$ and **5** are different compounds: (a) Corriu, R. J. P.; Lanneau, G. F.; Chauhan, B. P. S. *Organometallics* **1993**, *12*, 2001−2003. (b) Chauhan, B. P. S.; Corriu, R. J. P.; Lanneau, G. F.; Priou, C.; Auner, N.; Handwerker, H.; Herdtweck, E. *Organometallics* **1995**, *14*, 1657−1666.