Alkoxyhydrosilanes as Sources of Silylene Ligands: Novel Approaches to Transition Metal–Silylene Complexes

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Irradiation of $Fe(CO)_5$ and $HSiMe_2OR$ (R = alkyl or aryl group) together with hexamethylphosphoric triamide (HMPA) produces $(CO)_4Fe{=}SiMe_2{\cdot}HMPA$ and $SiMe_2(OR)_2$. Even in the absence of HMPA, irradiation of $Fe(CO)_5$ and $HSiMe_2O$-$(2\text{-}C_5H_4N)$ affords $(CO)_3(H)Fe\{SiMe_2{\cdots}O(2\text{-}C_5H_4N){\cdots}SiMe_2\}$. In these reactions, the alkoxyhydrosilanes act as sources of the silylene ligand.

Silylene complexes of the type $L_nM{=}SiR_2$ have attracted much attention as intermediates in transition metal-mediated transformation reactions of organosilicon compounds, such as the dehydrogenative coupling of hydrosilanes and redistribution of substituents on silicon atoms.[1] Our recent interest has focused on the incorporation of alkoxysilanes into the catalytic cycles that supply organosilicon compounds.[2] We report here a novel method to prepare $L_nFe{=}SiMe_2$ complexes using $HSiMe_2OR$ as a starting material of the silylene ligand.

Photoreactions of $Fe(CO)_5$ and 2 equiv. $HSiMe_2OR$ in the presence of hexamethylphosphoric triamide (HMPA) are summarized below.

$$Fe(CO)_5 + \underset{\textbf{1a–1e}}{HSiMe_2OR}\ (2\text{ equiv.}) + HMPA\ (1\text{ equiv.}) \xrightarrow[\substack{-CO,-H_2\\ \text{benzene-}d_6}]{h\nu} \underset{\textbf{2}}{(OC)_4Fe{=}SiMe_2{\cdot}HMPA} + \underset{\textbf{3a–3e}}{SiMe_2(OR)_2} \qquad (1)$$

Table 1. Irradiation of $Fe(CO)_5$ with $HSiMe_2OR$ (**1**) (2 equiv.) for 10 min in the presence of HMPA in benzene-d_6

Silane **1a–e**	Yield/% (NMR)[a]		
	1a–e[b]	**2**	**3a–e**
$HSiMe_2OMe$ (**1a**)	23	19	31
$HSiMe_2OEt$ (**1b**)	38	9	31
$HSiMe_2O^iPr$ (**1c**)	46	3	25
$HSiMe_2O^tBu$ (**1d**)	79	0	9
$HSiMe_2OPh$ (**1e**)	50	6	31

[a] based on the molar amount of Si. [b] unchanged.

Typically, a Pyrex NMR tube was charged with 1,3,5-$^tBu_3C_6H_3$ (ca. 1 mg, internal standard), HMPA (5.4 mg, 0.030 mmol), benzene-d_6 (300 µL), $HSiMe_2OMe$ (**1a**) (5.3 mg, 0.059 mmol), and $Fe(CO)_5$ (6.0 mg, 0.031 mmol) in that order. The tube was flame-sealed under high vacuum, and the sample was irradiated under a 450 W medium-pressure Hg lamp at 10 °C. After irradiation for 10 min, the ^1H NMR spectrum of the reaction mixture showed signals assignable to **1a** (23%), $(CO)_4Fe{=}SiMe_2{\cdot}HMPA$ (**2**) (19%), and $SiMe_2(OMe)_2$ (**3a**) (31%). The yields were based on the molar amount of Si and determined by comparing the relative intensities of the signals between each product and an internal standard 1,3,5-$^tBu_3C_6H_3$.

Identification of **2** was performed by comparison of the NMR data with those in the literature: The synthesis of **2** was first achieved by Zybill et al. by reaction of $Na_2Fe_2(CO)_4$ and Me_2SiCl_2 in the presence of HMPA.[3] Recently, Tessier et al. found that a doubly silylene-bridged diiron complex $Fe_2(\mu\text{-}SiMe_2)_2(CO)_8$ reacted with HMPA to produce **2**.[4] Eq 1 describes the novel pathway to the silylene complexes from alkoxyhydrosilanes via cleavage of the silicon–oxygen bond. Prolonged irradiation, for 120 min in total, caused the complete consumption of **1a**, yet reduced the yield of **2** to 4%. The decrease is attributable to the photo-sensitivity of **2** as reported by Zybill et al.[3] The introduction of bulky OR groups on the silicon atom retarded the reaction to give **2** in only low yields. The rate of reaction and yield of **2** both decrease in the following order: OMe > OEt > $O^iPr \approx OPh \gg O^tBu$.

In order to observe the intermediates of the reactions in Eq 1, we examined the photoreaction of $Fe(CO)_5$ and 1 equiv. $HSiMe_2OR$ in the absence of HMPA. The reactions gave $(CO)_4(H)Fe(SiMe_2OR)$ (**4**) and **3** (Eq 2) in the yields listed in Table 2.[5] The introduction of bulkier substituents on the silicon atom would slow oxidative addition of the hydrosilane, leading to lower yields of **4**. The iron complex corresponding to the formation of **3** was not detected by NMR spectroscopy.

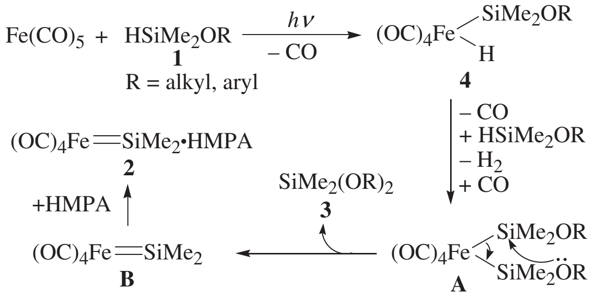
$$Fe(CO)_5 + \underset{\textbf{1a–1e}}{HSiMe_2OR}\ (1\text{ equiv.}) \xrightarrow[\substack{-CO\\ \text{benzene-}d_6}]{h\nu} \underset{\textbf{4a–4e}}{(OC)_4Fe{-}SiMe_2OR} + \underset{\textbf{3a–3e}}{SiMe_2(OR)_2} \qquad (2)$$

Table 2. Irradiation of $Fe(CO)_5$ and $HSiMe_2OR$ (**1**) (1 equiv.) in benzene-d_6 in the absence of HMPA

Silane **1a–e**	Irradiation Time	Yield/% (NMR)[a]		
		1a–e	**4a–e**	**3a–e**
$HSiMe_2OMe$ (**1a**)	10 min	30	49	10
$HSiMe_2OEt$ (**1b**)	30 min	29	45	10
$HSiMe_2O^iPr$ (**1c**)	30 min	35	41	11
$HSiMe_2O^tBu$ (**1d**)	30 min	53	24	12
$HSiMe_2OPh$ (**1e**)	30 min	39	48	4

[a] based on the molar amount of Si.

A possible mechanism for the formation of **2** and **3** is shown in Scheme 1. It is reasonable to consider the initial generation of $(CO)_4(H)Fe(SiMe_2OR)$ (**4**) via dissociation of CO from $Fe(CO)_5$ and subsequent oxidative addition of $HSiMe_2OR$. Further photolysis can induce the dissociation of the second CO, and subsequent oxidative addition of another alkoxyhydrosilane, reductive elimination of H_2, and re-coordination of CO produce $(CO)_4Fe(SiMe_2OR)_2$ (**A**), although we have not observed the NMR signals corresponding to **A**. Pomeroy et al. have already synthesized both $(CO)_4(H)Fe(SiMe_3)$ and $(CO)_4Fe(SiMe_3)_2$ by photoreaction of $Fe(CO)_5$ and $HSiMe_3$.[6] In complex **A**, a nucleophilic OR group in one silyl ligand might quickly attack the silicon atom in the other silyl ligand to yield $SiMe_2(OR)_2$ and $(OC)_4Fe{=}SiMe_2$ (**B**). Coordination of HMPA onto the silylene silicon atom of **B** finally gives **2**. Milstein et al. reported a similar observation, regarding the formation of $SiR'_2(OR)_2$ from a bis(alkoxysilyl) complex, in the thermolysis of *fac*-$(PMe_3)_3(H)Rh\{Si(OMe)_3\}_2$ at 55 °C for 72 h to afford *fac*-$(PMe_3)_3(H)_2Rh\{Si(OMe)_3\}$ (major product), $Si(OMe)_4$ (10%), and $(MeO)_3SiSi(OMe)_3$ (2%).[7] Bergman et al. also reported the formation of $Si(OEt)_4$ and $Cp^*(PMe_3)(H)Ir\{Si(OEt)_2OTf\}$ ($Cp^* = \eta^5\text{-}C_5Me_5$, $OTf = OSO_2CF_3$) in the reaction of $Cp^*(PMe_3)Ir(Me)(OTf)$ and $HSi(OEt)_3$ at 25 °C for 5 min. They proposed a mechanism involving the generation of $[Cp^*(PMe_3)(H)Ir\{Si(OEt)_3\}_2]OTf$ that excludes $Si(OEt)_4$.[8]

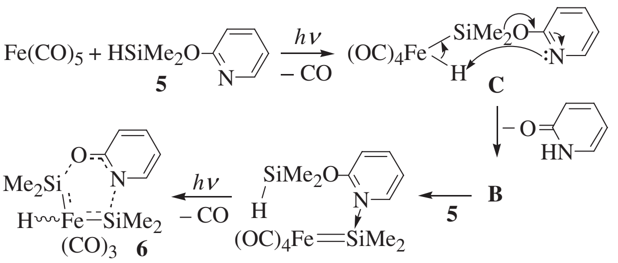


Scheme 1.

A different type of reaction occurred when the OR group was 2-pyridyloxy. Thus, irradiation of $Fe(CO)_5$ and 1 equiv. $HSiMe_2O(2\text{-}C_5H_4N)$ (**5**) for 30 min at 15 °C gave a base-stabilized silyl(silylene) complex, $(CO)_3(H)Fe\{SiMe_2{\cdots}O(2\text{-}C_5H_4N){\cdots}SiMe_2\}$ (**6**) in 41% NMR yield based on Si. The complex **6** was isolated in 16% yield as a yellow powder, which precipitated from hexane at −30 °C.[9] In the ^1H NMR spectrum of **6**, the Fe–H signal was observed at δ −9.95. The ^{29}Si NMR showed two signals at δ 74.9 and 96.0, both of which are in a typical region for the base-stabilized silylene complexes.[1c] We previously reported a similar chelate $Cp^*(CO)Fe\{SiMe_2{\cdots}O(2\text{-}C_5H_4N){\cdots}SiMe_2\}$, for which the silylene character of both silicon atoms was supported by ^{29}Si NMR and X-ray crystal structure analysis.[10]

A plausible formation mechanism for **6** is illustrated in Scheme 2. Similar to Scheme 1, it begins with the generation of hydrido(silyl) complex **C**. In this reaction, the intramolecular nitrogen atom plays a crucial role in abstracting a proton from the iron center. The interaction of FeH with a less basic ether oxygen in **4** or **C** must be negligible. The reaction pathway is similar to that in Schmid's synthesis of the first silyleneiron complex $(CO)_4Fe{=}SiMe_2{\cdot}NHEt_2$ from $Fe(CO)_5$ and $HSiMe_2NEt_2$.[11] The formation of $(CO)_4Fe{\cdot}SiMe_2$ (**B**) is again supported by the experiment in the presence of HMPA giving **2** (46% NMR yield based on Si of **5**). We previously reported that elimination of 2-pyridone from $Cp^*(CO)(H)Fe\{SiMe_2O(2\text{-}C_5H_4N)\}_2$ was induced by $AlEt_3$. In that case, 2-pyridone reacted with $AlEt_3$ to give EtH and $AlEt_2O(2\text{-}C_5H_4N)$.[2] On this occasion, the generated 2-pyridone would be effectively trapped by coordinatively unsaturated iron carbonyls such as $Fe(CO)_4$.[12]

In conclusion, we have developed two novel routes to transition-metal silylene complexes using alkoxyhydrosilanes. As silylene complexes can be involved in the catalytic pathway for metal-catalyzed synthesis of polysilanes,[1] this work demonstrates the potential utility of alkoxyhydrosilanes as good sources of polysilanes.



Scheme 2.

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5 NMR Spectral data of $(CO)_4(H)Fe(SiMe_2OEt)$ (**4b**) in benzene-d_6: ^1H NMR δ −9.45 (s, 1H, FeH), 0.55 (s, 6H, $SiMe_2$), 1.09 (t, 3H, $J = 7.0$ Hz, CMe), 3.50 (q, 2H, $J = 7.0$ Hz, OCH_2). ^{13}C NMR δ 8.8 ($SiMe_2$), 18.6, 58.0 (Et), 206.1, 210.4 (FeCO). ^{29}Si NMR δ 48.4. Complexes **4a**, **4c**, **4d**, and **4e** were also characterized by NMR.

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9 Data of **6**: ^1H NMR (benzene-d_6) δ −9.95 (s, 1H, FeH), 0.60 (s, 6H, $SiMe_2$), 0.82 (s, 6H, $SiMe_2$), 5.85, 6.14, 6.65, 7.20 (1H × 4, C_5H_4N). ^{13}C NMR (benzene-d_6) δ 9.6, 10.8 ($SiMe_2$), 116.5, 118.6, 139.7, 144.3, 163.5 (C_5H_4N), 214.0 (FeCO). ^{29}Si NMR (benzene-d_6) δ 74.9, 96.0. IR (hexane, cm^{-1}) 2050 sh, 2023 vs, 2002 vs, 1969 s. (ν_{CO}, the middle two peaks may be assigned to $Fe(CO)_5$.) Mass (EI, 70 eV) 351 (M^+, 4), 267 (M^+–3CO, 18), 152 ($SiMe_2OC_5H_4N^+$, 100). We were not able to determine the configuration around Fe because **6** showed unidentified fluxional behaviors and decompositions.

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