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Reactivity of Alkoxy-bridged Bis(silylene)iron Complexes

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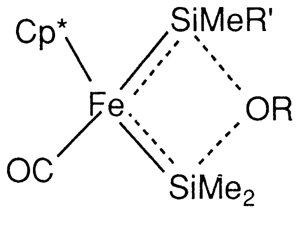
Alkoxy-bridged bis(silylene)iron complexes $Cp^*Fe(CO)\{SiMe_2\cdots O(Me)\cdots SiMe_2\}$ ($Cp^* = Cp, Cp'$; $Cp = \eta\text{-}C_5H_5$; $Cp' = \eta\text{-}C_5Me_5$) are unreactive toward $PhC{\equiv}CPh$, Et_2MeSiH, and $H_2C{=}C(Me)C(Me){=}CH_2$. With methanol, however, addition occurs across the Fe=Si double bond to give, hydridobis(methoxysilyl)iron complexes $Cp^*(OC)FeH(SiMe_2OMe)_2$ quantitatively.

Recently several donor-stabilized and donor-free silylene complexes have been isolated and characterized.1-7) This achievement has made it possible for chemists to investigate the reactivity of silylene complexes, which have been regarded as reactive intermediates in many transition-metal catalyzed reactions of silicon-containing compounds.8) To date, some reactivity studies have been reported using isolated silylene complexes including thermal decomposition,1b, 2d, 2e) donor-substitution on the silylene ligand of donor-stabilized silylene complexes,5) reduction of cationic silylene complexes by $LiAlH_4$,1a, 1b) hydrolysis, alcoholysis, or oxidation followed by loss of a silicon-containing ligand,1b, 1f, 4) hydrolysis to form a zwitter-ionic silyl complex,2i) substitution of a silylene ligand by a phosphine,2d) reaction with acids or ketones,1f, 2e) and silylene transfer reactions from the metal to another reagent.2e, 4b) However, investigation of the reactivity of silylene transition-metal complexes is still in the early stages of development since the stable coordination compounds with silylene ligands are still rare. We have recently reported the preparation and characterization of alkoxy-bridged bis(silylene)iron complexes $Cp^*Fe(CO)\{SiMe_2\cdots O(R)\cdots SiMeR'\}$ (**1**).3a, 3b) The spectroscopic and structural data of the complexes **1** revealed that the iron-silicon bonds in the complexes have significant double bond character despite the donor-coordination of the alkoxy groups to the silylene ligands. Thus the complexes **1** are quite appropriate as materials for examining reactivity of silylene complexes. Here we report a study of the reactivity of the bis(silylene)iron complexes **1**, which includes the first isolation of a methanol addition product.



1 $Cp^* = Cp, Cp'$
$R = Me, Bu^t$
$R' = Me, OMe, OBu^t$

The bis(silylene)iron complexes **1**, $Cp^*Fe(CO)\{SiMe_2\cdots O(Me)\cdots SiMe_2\}$ (**1a** : $Cp^* = Cp$; **1b** : $Cp^* = Cp'$), prepared using procedures described previously,3b) were found to be unreactive toward conventional silylene trapping agents, 2,3-dimethylbutadiene (**2**),9) Et_2MeSiH (**3**),9) and $PhC{\equiv}CPh$ (**4**),10) even when the reaction mixture was heated up to 80 °C or irradiated using a medium pressure Hg arc lamp. In contrast to our

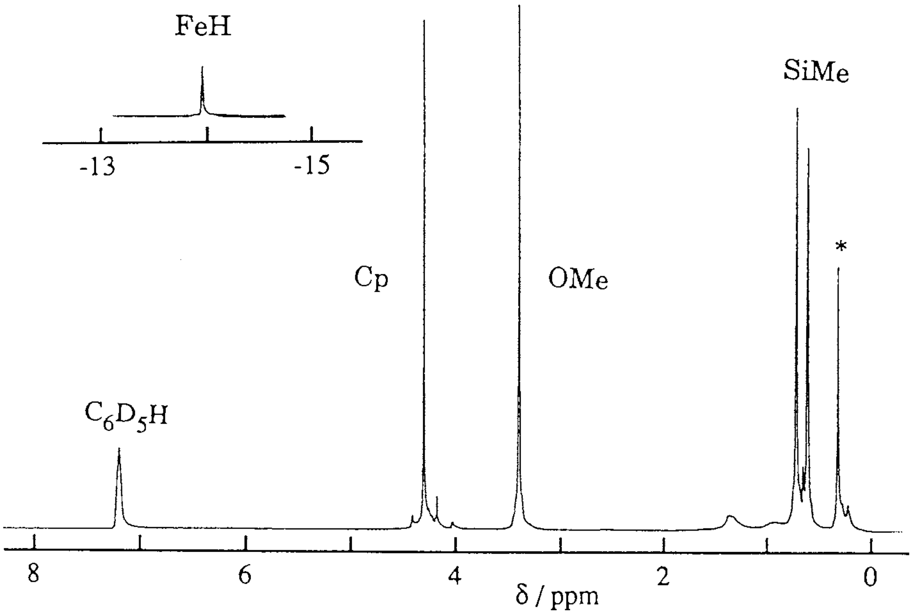
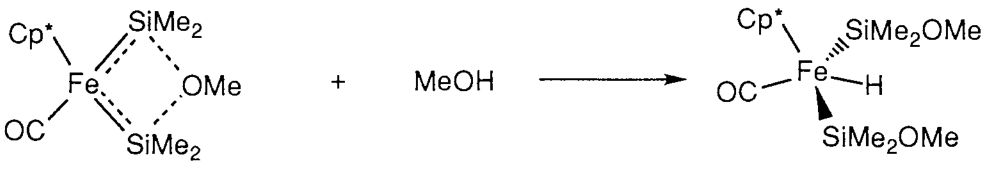


Fig. 1. ^{1}H NMR spectrum of $Cp(OC)FeH(SiMe_2OMe)_2$ (**5a**) in benzene-d_6. * impurity.

result, Zybill[2e] and Corriu[4b] reported that the donor-coordinated silylene complexes $(OC)_4Fe{=}SiR_2$(donor) reacted with the silylene trapping agent **2** upon irradiation to form the silylene-trapped product, 1,1,3,4-tetramethyl-1-silacyclopent-3-ene. The poor reactivity of the bis(silylene)iron complexes **1** toward the silylene trapping agents is attributable to the structure of the bis(silylene)iron complex: The silylene ligands in the bis(silylene)iron complexes are strongly stabilized by intramolecular coordination of the alkoxy group to form a 4-membered chelate ring. The stable chelate ring prevents the generation of a donor-free Fe=Si bond which would be essential for the silylene transfer reaction.

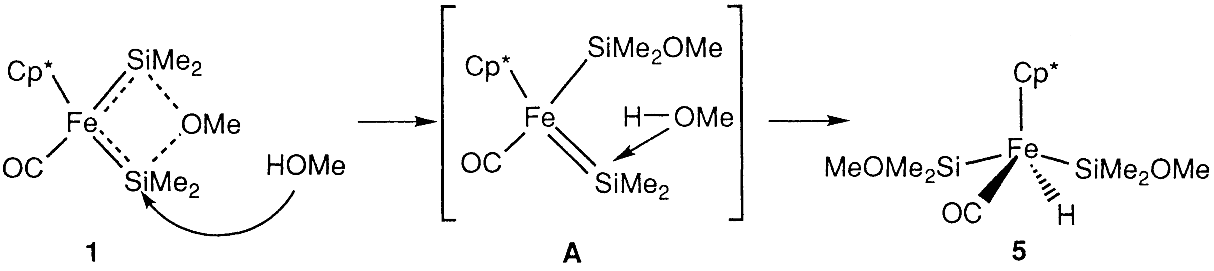
In contrast with the poor reactivity of **1** toward **2**, **3**, and **4**, the bis(silylene)iron complexes **1** react with methanol very easily and quantitatively: Addition of a slight excess of methanol to a benzene solution of **1a** or **1b** gave the hydridobis(methoxysilyl)iron complex $Cp^*(OC)FeH(SiMe_2OMe)_2$ **5a** (Cp* = Cp) and **5b** (Cp* =



1 **5** (1)

Cp') (Eq. 1), respectively, which was isolated in both cases as an orange oil after evaporation of solvent. Complex **5b** was much less stable than complex **5a**. The ^{1}H NMR spectrum of **5a** in benzene-d_6 shows a resonance at -13.99 ppm which is assignable to the hydride ligand bonded to iron (Fig. 1). The configuration of the complex **5a** is *trans* since ^{29}Si NMR spectrum of **5a** showed only one signal. Furthermore Fig. 1 shows two singlets at 0.69 and 0.58 ppm. These are assignable to SiMe groups in the $SiMe_2OMe$ ligands because these groups constitute a diastereotopic pair. The complexes **5** can be regarded as the 1,2-methanol addition products across an iron-silicon double bond in the bis(silylene)iron complex **1**. The complex **5b** is also characterized as the *trans* isomer by NMR.

Formation of **5** by the reaction of **1** with methanol suggests that the iron-silicon bonds in the complexes are polarized in the sense $Fe^{\delta-}-Si^{\delta+}$. This is consistent with the result of the ab initio MO calculation for $(OC)_5Cr{=}SiH(OH)$:[13)] Nakatsuji et al. predicted that the silylene complex undergoes a nucleophilic attack on the Si atom. Thus the first step of the reaction would be a nucleophilic attack of methanol oxygen to the electron-deficient silylene ligand to give an intermediate A (Scheme 1). Then hydrogen migration occurs from the coordinated MeOH to the iron center to give the final product **5**.



Scheme 1.

The hydrido complexes **5** obtained in this study are the first isolated compounds produced by alcohol addition across the metal-silicon double bond of silylene complexes. Recently Tilley et al. reported that the base-stabilized silylene ruthenium complex $[Cp'(PMe_3)_2RuSiPh_2{\cdot}NCMe]BPh_4$ reacts with alcohols ROH (R = Me, Et, and Bu^t) to produce the ruthenium acetonitrile complex $[Cp'(Me_3P)_2RuNCMe]BPh_4$ and the corresponding alkoxysilanes $HSiPh_2OR$.[1f)] They observed an ethanol-addition intermediate, *cis*-$[Cp'(Me_3P)_2Ru(H)SiPh_2OEt]BPh_4$ or $[Cp'(Me_3P)_2Ru(\eta^2\text{-}HSiPh_2OEt)]BPh_4$, during the reaction but no stable addition product was isolated.

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11) Cp(OC)FeH(SiMe$_2$OMe)$_2$ (**5a**): ^{1}H NMR (C_6D_6) δ 4.27 (s, 5H, Cp), 3.37 (s, 6H, OMe), 0.69 (s, 6H, SiMe), 0.58 (s, 6H, SiMe), -13.99 (s, 1H, FeH); ^{13}C NMR (C_6D_6) δ 213.3 (CO), 83.9 (Cp), 50.6 (OMe), 9.7, 9.3 (SiMe); ^{29}Si NMR (C_6D_6) δ 60.3; IR(C_6D_6, ν, cm^{-1}) 1990 (FeH), 1930 (CO), 1080, 1060(Si-O, C-O); MS m/z 328 (M$^+$, 0.1), 239 (5.9), 238 (52.1), 210 (100); Anal. Found: C, 43.82; H, 7.08 %. Calcd for $C_{12}H_{24}FeO_3Si_2$: C, 43.90; H, 7.37%.

12) Cp'(OC)FeH(SiMe$_2$OMe)$_2$ (**5b**): ^{1}H NMR (C_6D_6) δ 3.40 (s, 6H, OMe), 1.64 (s, 15H, Cp'), 0.74 (s, 6H, SiMe), 0.60 (s, 6H, SiMe), -13.26 (s, 1H, FeH).

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