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Photolysis of $CpFe(CO)_2SiMe_2SiMe_2H$ in the Presence of Methanol. Indirect Evidence for the Transient Formation of a Disileneiron Complex

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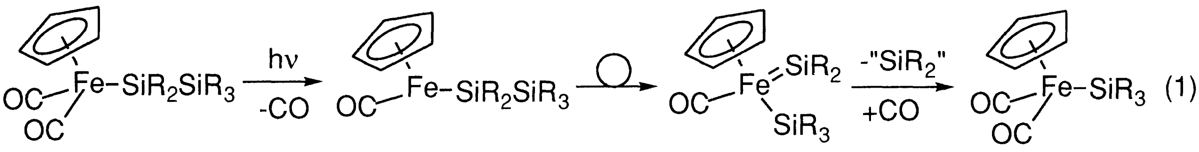
Photolysis of a C_6D_6 solution of a hydrodisilanyliron complex $Cp(OC)_2FeSiMe_2SiMe_2H$ in the presence of MeOH afforded $Cp(OC)FeH(SiMe_2OMe)_2$, $Cp(OC)_2FeSiMe_2OMe$, $[CpFe(CO)_2]_2$, and $MeOSiMe_2H$. A plausible mechanism is proposed for the reaction, in which a disileneiron complex $Cp(OC)FeH(SiMe_2{=}SiMe_2)$ and a methoxy-bridged bis(silylene)iron complex $Cp(OC)Fe\{SiMe_2\cdots O(Me)\cdots SiMe_2\}$ are formed successively as transient intermediates.

It has been shown that the photolysis of a disilanyliron complex $FpSiR_2SiR_3$ ($Fp = CpFe(CO)_2$; R = alkyl, aryl) proceeds through a silyl(silylene)iron intermediate ($Cp(OC)Fe({=}SiR_2)SiR_3$) and gives a monosilyliron complex $FpSiR_3$ as a main product:[1, 2]

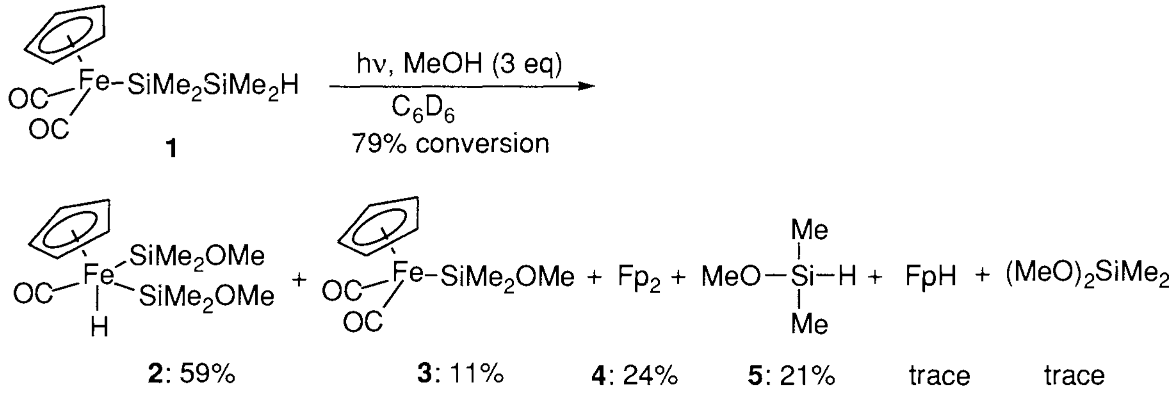


(1)

It has been also shown that rapid R group scrambling on silicon atoms occurs in the silyl(silylene)iron intermediate. If the mechanism given in Eq. 1 is operative in the photolysis of $FpSiMe_2SiMe_2H$ (**1**),[3] the products are expected to be $FpSiMe_3$ and $FpSiMe_2H$. However, this is not the case: The photolysis of **1** in a C_6D_6 solution yielded a mixture of rather complex products *trans*-$[CpFe(CO)]_2(\mu\text{-}SiMe_2)_2$, *cis*-$[CpFe(CO)]_2(\mu\text{-}SiMe_2)_2$, Fp_2, and $[CpFe(CO)]_4$.[4] The approximate yields of the isolated products were 40, 10, 60, and 4%, respectively. This result suggests that the photolysis of **1** proceeds through a different mechanism from Eq. 1, since there is no monosilyliron complex in the products. We carried out the mechanistic investigation of the photolysis of **1** and found that addition of methanol to the reaction system caused complete change of the products. We report here the results for the photolysis of **1** in the presence of methanol and propose a plausible mechanism which explains the observed result.

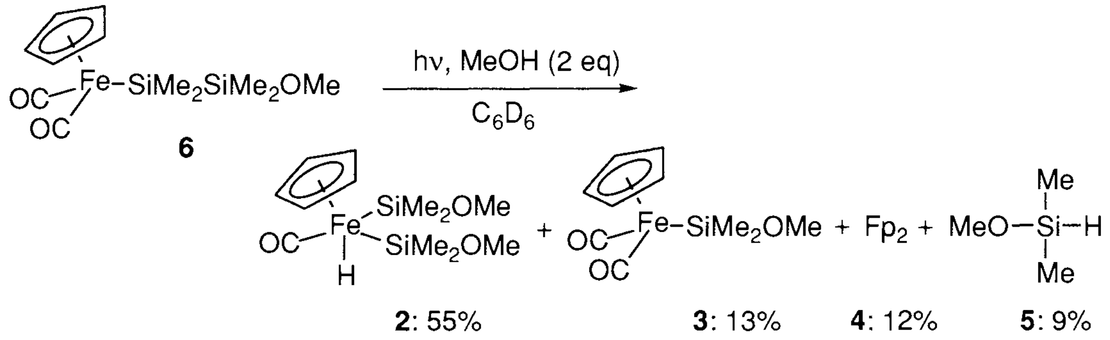
The photolysis of **1** in the presence of methanol gave a mixture containing $Cp(OC)FeH(SiMe_2OMe)_2$ (**2**), $FpSiMe_2OMe$ (**3**), Fp_2 (**4**), and $MeOSiMe_2H$ (**5**). The product ratio depends on the irradiation time since the product **2** also undergoes a slow photoreaction (vide infra). Ten min irradiation of a C_6D_6 solution containing **1** and MeOH (3 eq) showed the product distribution given in Eq. 2. Prolonged irradiation caused decrease of **2**, **3**, and **5** and significant increase of FpH, $(MeO)_2SiMe_2$, and **4**.

To our surprise, the photolysis of $FpSiMe_2SiMe_2OMe$ (**6**) in the presence of methanol showed almost identical product distribution (Eq. 3) with that given in Eq. 2, if the experimental conditions are the same. We

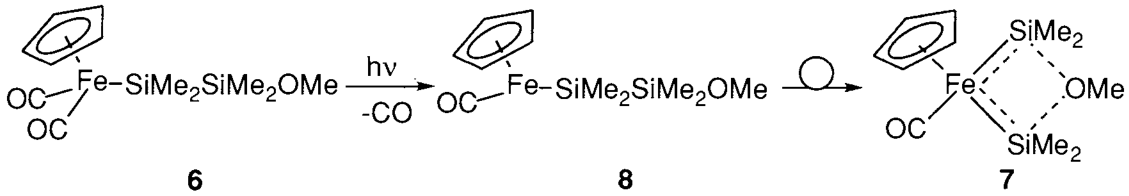


(2)

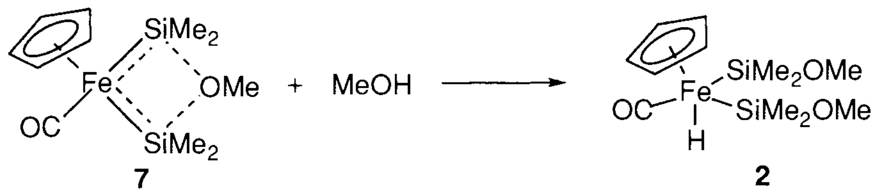
reported recently that the photolysis of **6** affords methoxy-bridged bis(silylene)iron complex **7** almost quantitatively (Eq. 4)[5] and complex **7** reacts with methanol instantaneously to give **2** (Eq. 5).[6] When complex **2** was photolyzed under CO atmosphere, a mixture of **3**, **4**, and **5** was obtained in moderate yields (Eq. 6). Therefore, compounds **3**, **4**, and **5** produced in Eq. 3, and also in Eq. 2, would be the photolytic secondary products derived from **2**. The fact that reactions 2 and 3 gave almost identical product distribution suggests strongly that the photolysis of **1** in the presence of methanol (Eq. 2) proceeds through the formation of



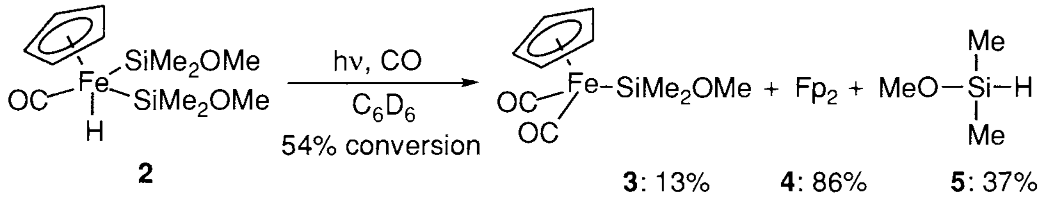
(3)



(4)



(5)



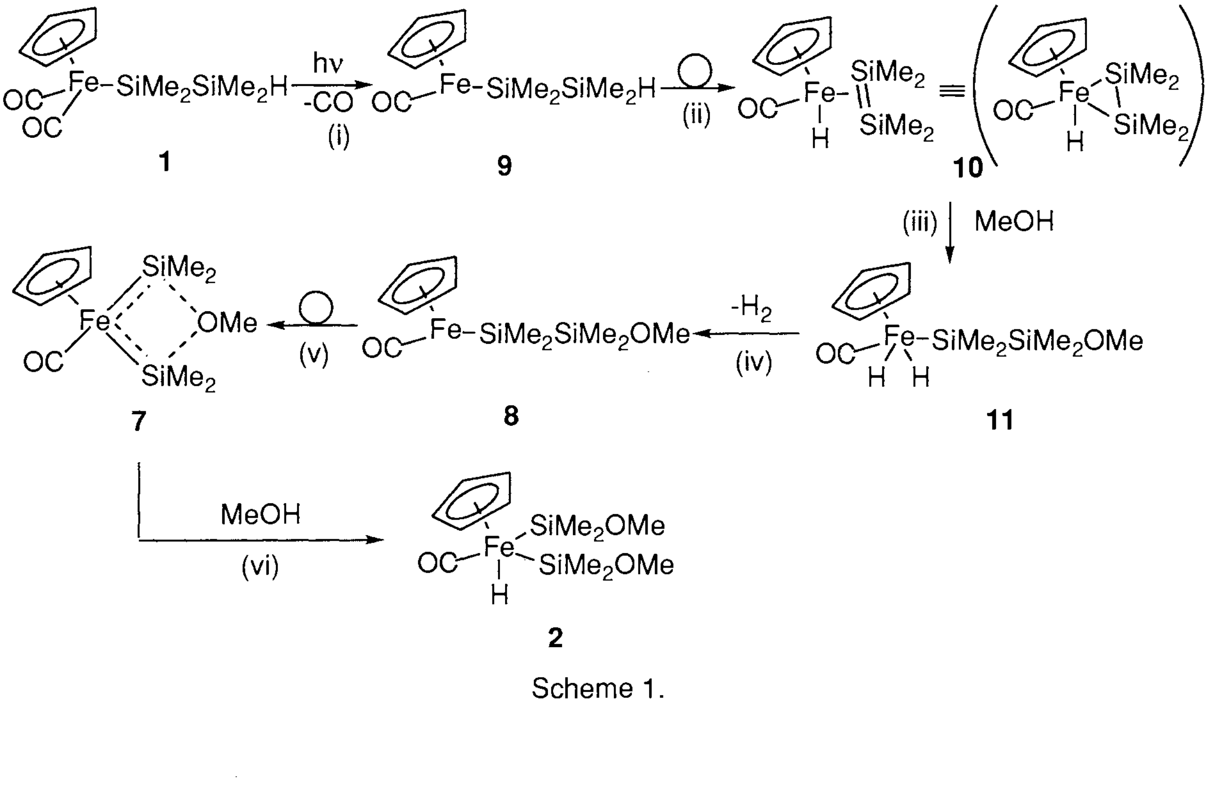
(6)

bis(silylene)iron complex **7**, that is, complex **7** is a common intermediate in Eqs. 2 and 3.

We now propose Scheme 1 as a plausible mechanism for the photolytic reaction of **1** in which bis(silylene)iron complex **7** is formed as a transient intermediate.7) The photolysis of **1** would give a coordinatively unsaturated complex **9** (step (i)) as seen in Eqs. 1 and 4. Then β-hydrogen transfer reaction occurs to give a disilene(hydrido)iron intermediate **10** (step (ii)).8) The β-hydrogen transfer reaction of this type has been postulated in a few systems: The photochemical conversion of $FpCH_2SiMe_2H$ to $FpSiMe_3$ was reported to proceed via a hydrido(silene)iron intermediate $Cp(OC)FeH(\eta^2\text{-}CH_2{=}SiMe_2)$ generated by the β-hydrogen transfer reaction.9, 10) Recently, the first stable silene complexes $(\eta\text{-}C_5Me_5)(R_3P)RuH(\eta^2\text{-}R'_2Si{=}CH_2)$11) and disilene platinum complexes $(R_3P)_2Pt(\eta^2\text{-}R'_2Si{=}SiR'_2)$12) were synthesized by Tilley and West, respectively. Similar type of β-hydrogen transfer reactions were used in these syntheses.

The step (iii) in Scheme 1 is methanolysis of the disilene(hydrido)iron intermediate **10** to form a methoxydisilanyliron intermediate **11**. There are a few reports on the reactions of disilene transition metal complexes with methanol. Berry reported that the methanolysis of a disilenemolybdenum complex, $Cp_2Mo(\eta^2\text{-}Me_2Si{=}SiMe_2)$, affords $CpMo(SiMe_2H)(SiMe_2OMe)$ and $Cp_2Mo(H)(SiMe_2SiMe_2OMe)$ in 80 and 20% yields, respectively.13) West also reported that the reaction of a disileneplatinum complex $(Et_3P)_2Pt(\eta^2\text{-}Mes_2Si{=}SiMes_2)$ (Mes = 2,4,6-trimethylphenyl) with methanol yielded a product $(Et_3P)_2Pt(H)(SiMes_2SiMes_2OMe)$.12c) The cleavage of a metal-silicon bond by methanol to form a methoxydisilanylmetal complex, like the step (iii), is apparently an important route in the reactions of disilenemetal complexes with methanol . Subsequent loss of H_2 from the intermediate **11** results in the formation of a 16 electron intermediate **8** (step (iv)) which is immediately transformed into the methoxy-bridged bis(silylene)iron complex **7** (step (v)) as seen in Eq. 4. Complex **7** reacts with methanol to give **2** (step (vi))6) which then gives the secondary products **3**, **4**, and **5** under the experimental condition (Eq. 6).

According to this mechanism, the hydride ligand bound to the iron in **2** must be supplied exclusively by



Scheme 1.

added methanol. Actually, when **1** was irradiated in the presence of CD_3OD instead of MeOH, $Cp(OC)FeD(SiMe_2OCD_3)_2$ (***2-d***) was obtained along with $FpSiMe_2OCD_3$, **4**, and CD_3OSiMe_2D. Furtheremore, the deuteride in ***2-d*** is supplied from CD_3OD *not after* the formation but upon the formation of this complex, since no thermal hydrogen-deuterium exchange was observed between the Fe-H of complex **2** and CD_3OD.

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3) Complex **1** was prepared by reduction of $FpSiMe_2SiMe_2Cl$ with $LiAlH_4$ in 88% yield. Data for **1**: ^1H NMR (C_6D_6) δ 4.12 (s, 5H, Cp), 4.06 (sept., J = 4.6 Hz, 1H, SiH), 0.27 (s, 6H, Me), 0.25 (d, J = 4.6 Hz, 6H, Me); ^{13}C NMR (C_6D_6) δ 215.6 (CO), 84.3 (Cp), 3.2, -5.2 (Me); ^{29}Si NMR (C_6D_6) δ 16.4 (FeSi), -31.4 (SiH); IR (C_6D_6, ν, cm^{-1}) 1990, 1930 (CO), 2070 (SiH); MS m/z 266 (M^+-CO, 100), 238 (56.4), 235 (79.7), 207 (1.4), 192 (0.9), 179 (1.5), 164 (12.3), 117 (56.7); Anal. Found: C, 44.60; H, 6.17%. Calcd for $C_{11}H_{18}FeO_2Si_2$: C, 44.90; H, 6.17%.

4) Photolyses were carried out in Pyrex NMR tubes and a medium pressure mercury lamp (Ushio UV-450) was used as the light source throughout this work.

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7) A referee pointed out the following possibility for the formation of **7** from **1**: (i) Photolysis of **1** affords a silyl(silylene)iron intermediate $Cp(OC)Fe(=SiMe_2)SiMe_2H$ (**A**), (ii) reaction of **A** with methanol gives a hydridoiron complex $Cp(OC)FeH(SiMe_2H)(SiMe_2OMe)$ (**B**), and (iii) elimination of H_2 from **B** leads to the formation of **7**. However, this possibility can be ruled out, since the photolysis of $FpSiMe_2H$ in the presence of $MeOSiMe_2H$ to give **B** did not afford **7** at all.

8) Professor J. J. Turner (Department of Chemistry, University of Nottingham, England) kindly informed us that he and his colleague observed the formation of disilene(hydrido)iron complex **10** during the photolysis of **1** by IR-spectroscopic method.

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