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Photochemistry of bridged disilyldiiron complexes $(SiMe_2)[(\eta^5\text{-}C_5H_4)Fe(CO)_2SiMe_2SiMe_2R]_2$, R = Me, Ph

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Abstract

Photochemical irradiation of the new bimetallic disilyliron complexes $(SiMe_2)[(\eta^5\text{-}C_5H_4)Fe(CO)_2SiMe_2SiMe_2R]_2$, R = Me, Ph, results in silylene elimination chemistry, as observed for the mono-metallic analogs, resulting in the formation of complexes $(SiMe_2)[(\eta^5\text{-}C_5H_4)Fe(CO)_2SiMe_2R]_2$. The intermediate silyl(silylene) complexes can be intercepted with HMPA. Apart from a very reactive minor product that we have been unable to identify at this time, the proximity of the two transition metal centers has little impact upon the observed chemistry. © 2001 Published by Elsevier Science B.V.

Keywords: Photochemistry; Iron carbonyl complexes; Silyl(silylene)iron intermediates; Silylene elimination

1. Introduction

Photochemical irradiation of $(\eta^5\text{-}C_5H_5)Fe(CO)_2$-substituted oligosilanes results, subsequent to CO expulsion, in formation of silyl(silylene) intermediates $(\eta^5\text{-}C_5H_5)Fe(CO)(=SiR_2)(SiR_3)$ via an α-elimination process. These intermediates lead to either silylene eliminations, Eq. (1), or rearrangements, Eq. (2) [1]. Both may be effected catalytically under appropriate conditions [2–13].

$$Fp\text{–}SiMe_2SiMe_3 \rightarrow Fp\text{–}SiMe_3 + [SiMe_2] \quad (1)$$

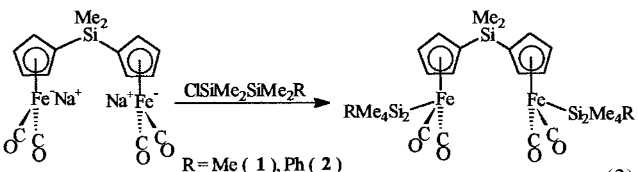
$$Fp\text{–}SiMe_2SiMe_2SiMe_2SiMe_3 \rightarrow Fp\text{–}Si(SiMe_3)_3 \quad (2)$$

The proposed silyl(silylene) intermediates have been observed spectroscopically by low-temperature matrix isolation [14], and isolated, and structurally characterized, as intramolecularly base- and metal-stabilized species and observed as intermolecularly HMPA-stabilized complexes [15–18].

The photochemistry of oligosilyl complexes containing two metal centers produces distinctive results. Irradiation of $FpSiMe_2SiMe_2Fp$ resulted in no silylene expulsion; mono- and bis-bridging silylene diiron complexes were formed sequentially [19–22]. Our recent observation that photochemical treatment of $FpCH_2SiR_2SiR_2CH_2Fp$ resulted in the unprecedented stereospecific formation of 1,3-disilacyclobutanes reinforces the idea that binuclear systems offer a fertile region for chemical investigation [23]. We report the synthesis and photochemical irradiation of the monosilyl-bridged diiron complexes $(SiMe_2)[(\eta^5\text{-}C_5H_4)Fe(CO)_2SiMe_2SiMe_2R]_2$, R = Me (**1**), Ph (**2**). The two metal centers are held together via a dimethylsilylene unit bridging two cyclopentadienyl ligands, thus the inherent closeness of the two reaction centers might produce new chemistry.

2. Results and discussion

The reaction between the chlorodisilanes $ClSiMe_2SiMe_2R$ (R = Me, Ph) and $[(\eta^5, \eta^5\text{-}C_5H_4Me_2SiC_5H_4)Fe_2(CO)_4]^{2-}\ 2Na^+$ yielded moderate to good yields of the corresponding (disilyl)iron complexes $(SiMe_2)[(\eta^5\text{-}C_5H_4)Fe(CO)_2SiMe_2SiMe_2R]_2$ (R = Me (**1**), Ph (**2**)) (Eq. (3)). The spectroscopic data for **1** and **2** are in accord with the proposed structures [4,24].



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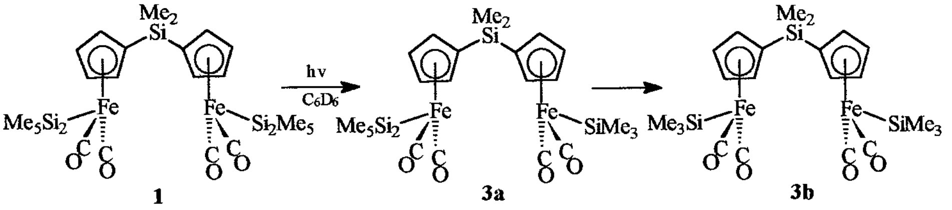
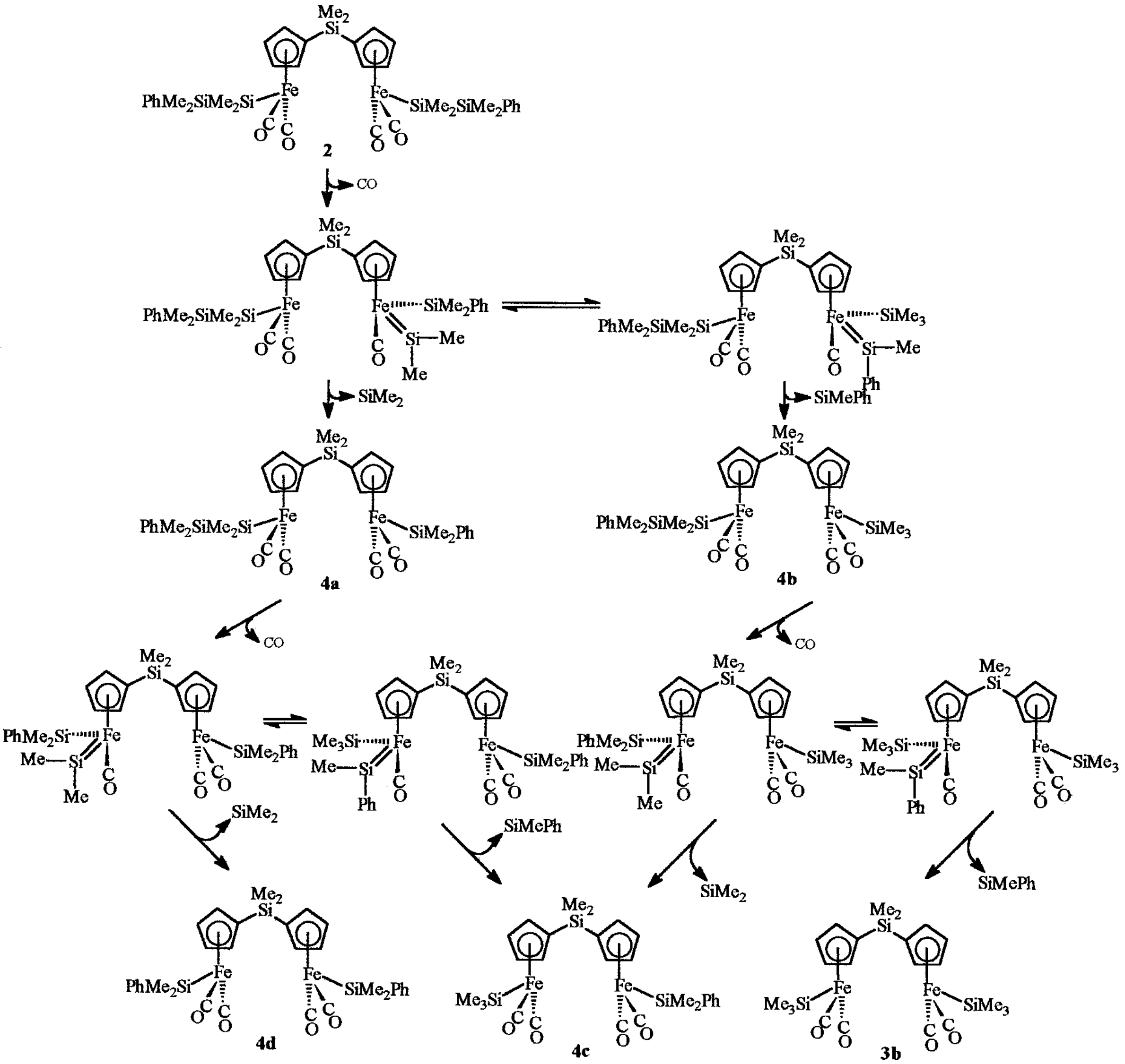
Photolysis of **1** in C_6D_6 resulted in the formation of $(SiMe_2)[(\eta^5\text{-}C_5H_4)Fe(CO)_2SiMe_3]_2$ (**3b**) after 25 h. NMR monitoring indicated the intermediacy of $[Me_3Si(CO)_2Fe(\eta^5\text{-}C_5H_4)(SiMe_2)(\eta^5\text{-}C_5H_4)Fe(CO)_2\text{-}SiMe_2SiMe_3]$ (**3a**), indicating the photo-reaction is stepwise (Eq. (4)). Along with **3a**, irradiation of **1** resulted in the formation of a minor product (20%) exhibiting ^{29}Si-NMR signals at 31.3 and −8.9 ppm.



(4)

The photolysis of **2** was both more rapid and complex, Scheme 1. Initially formed were $[PhMe_2Si\text{-}(CO)_2Fe(\eta^5\text{-}C_5H_4)(SiMe_2)(\eta^5\text{-}C_5H_4)Fe(CO)_2SiMe_2\text{-}SiMe_2Ph]$ (**4a**) and $[Me_3Si(CO)_2Fe(\eta^5\text{-}C_5H_4)(SiMe_2)(\eta^5\text{-}C_5H_4)Fe(CO)_2SiMe_2SiMe_2Ph]$ (**4b**), with the former dominant over the course of the photolysis. Continued irradiation led to the complete disappearance of **2**, **4a** and **4b** and the formation of the monosilyl iron complexes $[Me_3Si(CO)_2Fe(\eta^5\text{-}C_5H_4)(SiMe_2)(\eta^5\text{-}C_5H_4)\text{-}Fe(CO)_2SiMe_2Ph]$ (**4c**), $[Me_2PhSi(CO)_2Fe(\eta^5\text{-}C_5H_4)\text{-}(SiMe_2)(\eta^5\text{-}C_5H_4)Fe(CO)_2SiMe_2Ph]$ (**4d**) and **3b**, 1:8:1.



Scheme 1.

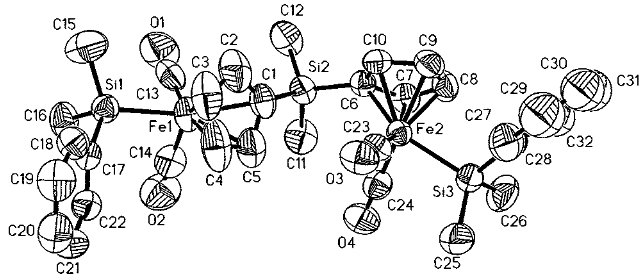


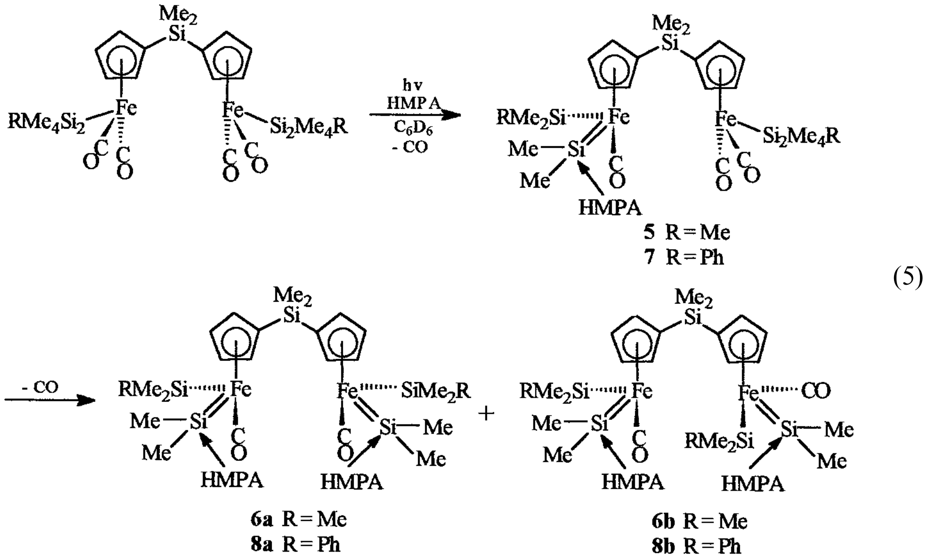
Fig. 1. Molecular structure of **4d**. Hydrogen atoms are omitted for clarity.

Overall, the photolysis of **1** and **2** led to similar results to those of their non-bridged analogs Fp–$SiMe_2SiMe_2R$, (R = Me, Ph) involving silylene elimination, and the predominant formation of $FeSiMe_2Ph$ compounds where possible. Although it seems that the proximity of the two Fe centers has little impact upon the chemistry at each center, the unknown and highly labile species formed along with **3** during the irradiation of **1** suggests a minor new pathway. With the ^{29}Si-NMR chemical shifts of 31.3 and − 8.85 ppm this may well be a disilyl bridged diiron complex derived from the association of two silylene transients. At present we have been unable to further study this material; however, changing the various groups associated with the Fe atoms may be useful to tease out this new chemistry and we are pursuing this aspect of the project.

The ORTEP drawing of **4d** is shown in Fig. 1. The molecule consists of two $(\eta^5-C_5H_4)Fe(CO)_2SiMe_2Ph$ groups linked a $SiMe_2$ bridge. The Fe–Si bond lengths (mean 2.330 Å) are well within the range of 2.312–2.378 Å [25–29] for such bonds, Table 2. The Ph group is *trans* to two CO groups possibly to reduce steric repulsion and the two Cp rings are almost perpendicular to each other with a dihedral angle of 82.2°.

The presence of HMPA $[(Me_2N)_3PO]$ during photolysis of Fp–disilanes is an effective route for stabilizing the iron–silylene intermediates [18]. After 10 h irradiation a C_6D_6 solution of **1** and 2.5 equivalents of HMPA showed the complete disappearance of **1** and the formation of HMPA-coordinated silyl(silylene) complexes **5** and **6**, Eq. (5). Further irradiation for 15 h resulted in the complete disappearance of **5** and almost quantitative formation of **6** further supporting the stepwise nature of the reaction, Scheme 1. The ^{29}Si-NMR spectrum of **6** exhibited six resonances at − 9.23, − 9.13, 31.09, 31.17, 116.66 and 116.70 ppm which are assigned to two isomers **6a** and **6b** (*meso* and *rac* relative peak ratios of 10:8). In the ^{13}C-NMR spectrum of **6**, bridged silicon methyl groups exhibited three resonances. Two resonances of equal intensity observed at − 0.95 and 1.71 ppm are assigned to the *meso* isomer with a mirror symmetry about the $SiMe_2$ bridge, and the remaining resonance observed at 0.56 ppm is assigned to the *rac* isomer with a C_2 axis about the $SiMe_2$ bridge.

Similar irradiation of **2** as a C_6D_6 solution containing HMPA resulted in the ultimate formation of a single HMPA-coordinated silyl(silylene) complex **8** via the transient formation of **7**, Eq. (5). All spectroscopic data are in accord with the proposed structures. For example, the ^{29}Si-NMR spectrum of **8** exhibited six resonances at − 9.20, − 9.24, 29.44, 29.57, 115.70 and 115.80 ppm which are assigned to two isomers **8a** and **8b** (*meso*/*rac* = 10/8.5). Two ^{13}C resonances of equal intensity observed at − 1.08 and 1.11 ppm for bridged silicon methyl groups were similarly assigned to the *meso* isomer **8a**, while the third resonance at − 0.11 ppm for bridged silicon methyl groups was assigned to the *rac* isomer **8b**.



5 R = Me
7 R = Ph

6a R = Me
8a R = Ph

6b R = Me
8b R = Ph

(5)

During irradiation of **2** we did not observe the formation of the other possible HMPA-coordinated silyl(silylene) complexes containing the (Fe = SiMePh·HMPA) fragments despite the fact that photolysis with-out HMPA resulted in two transient intermediate products **4a** and **4b**. This result indicates that the silyl(silylene)iron intermediates, once formed, are immediately coordinated by HMPA before they have time to participate in 1,3-aryl migrations. This result contrasts the behavior of $Cp^{*}(OC)Fe(=SiMe_2{\cdot}HMPA)SiMe_3$ where exchange between the diastereotopic methyl groups in the $Fe(=SiMe_2{\cdot}HMPA)$ unit was observed [18], but is in line with the chemistry of $Cp(OC)_2W(SiMe_3)(=SiMe_2{\cdot}HMPA)$ [30].

3. Experimental

3.1. General data

All manipulations were carried out under an argon atmosphere or in vacuo. THF was distilled under nitrogen from sodium benzophenone ketyl prior to use. The following reagents were used as received, silica gel (grade 950, 60–200 mesh) MCB; $PhMe_2SiCl$, $Me_3SiSiMe_3$, Gelest; HMPA $[(Me_2N)_3PO]$, Aldrich. Other reagents were synthesized by literature procedures: $PhMe_2SiSiMe_2Cl$ [31], $Me_3SiSiMe_2Cl$ [32], $(SiMe_2)[(\eta^5\text{-}C_5H_4)Fe(CO)_2]_2$ [33]. NMR spectra were recorded on a Bruker ARX-300 FT spectrometer in C_6D_6; IR spectra were obtained on a Perkin–Elmer 1600 series FT-IR spectrometer in hexane. Elemental analyses were performed by Galbraith Laboratories.

3.2. Synthesis of $(SiMe_2)[(\eta^5\text{-}C_5H_4)Fe(CO)_2Si_2Me_5]_2$ (1)

To 50 ml of a THF solution of $[(\eta^5,\eta^5\text{-}C_5H_4Me_2SiC_5H_4)Fe_2(CO)_4]^{2-}2Na^+$ (prepared from 1.50 g (3.66 mmol) of $(SiMe_2)[(\eta^5\text{-}C_5H_4)Fe(CO)_2]_2$ and an excess of Na–Hg amalgam in THF) 1.22 g (7.32 mmol) of $ClMe_2SiSiMe_3$ was added at 0 °C. The solution was stirred at 0 °C for 30 min and then permitted to warm to room temperature (r.t.) and stirred overnight. The solvent was removed under vacuum and the residue was extracted with methylene chloride. The solution was filtered through a short silica gel column and concentrated to 5 ml and placed upon a 2.5 × 30 cm silica gel column. Elution with a mixture of hexane/methylene chloride (10:1) developed a yellow band which was collected and subsequent to solvent removal afforded a yellow oil. The oil was put in the refrigerator for several days and slowly solidified to form **1** as a brown yellow crystalline solid (0.92 g, 1.37 mmol, 37%), m.p. 38–40 °C. Anal. Calc. (Found) C, 46.42 (46.45); H, 6.59 (6.92)%; ^{1}H-NMR δ 0.21 (s, 18H, $SiMe_3$), 0.44 (s, 6H, bridged-$SiMe_2$), 0.53 (s, 12H, $SiMe_2$), 4.34, 4.43 (s, s, 4H, 4H, Cp); ^{13}C-NMR δ −1.06 (bridged-$SiMe_2$), −0.33 ($SiMe_3$), 3.68 ($SiMe_2$), 86,54, 88.53, 89.83 (Cp), 215.94 (CO); ^{29}Si-NMR δ −11.47 ($SiMe_3$), −10.04 (bridged-$SiMe_2$), 17.05 ($SiMe_2$); IR ν(CO) 1994 (s), 1943 (s).

Using the same procedure as above, $(SiMe_2)[(\eta^5\text{-}C_5H_4)Fe(CO)_2SiMe_2SiMe_2Ph]_2$ (**2**, oil) and $(SiMe_2)[(\eta^5\text{-}C_5H_4)Fe(CO)_2SiMe_2Ph]_2$ (**4d**, m.p. 78–80 °C) were prepared in 37 and 67% yields, respectively. **2**: Anal. Calc. (Found) C, 54.26 (54.21); H, 6.07(5.85)%; ^{1}H-NMR δ 0.38 (s, 6H, bridged-$SiMe_2$), 0.47 (s, 12H, $SiMe_2Ph$), 0.56 (s, 12H, Fe–$SiMe_2$), 4.12, 4.23 (s, s, 4H, 4H, Cp), 7.21 (m, 6H, Ph), 7.51(m, 4H, Ph); ^{13}C-NMR δ −2.31 ($SiMe_2Ph$), −1.06 (bridged-$SiMe_2$), 4.00 (Fe–$SiMe_2$), 86,49, 88.56, 89.91 (Cp), 128.41, 128.92, 134.31, 141.45 (Ph), 215.93 (CO); ^{29}Si-NMR δ −15.10 ($SiMe_2Ph$), −10.07 (bridged-$SiMe_2$), 17.09 (Fe–$SiMe_2$); IR ν(CO) 1993 (s), 1943 (s). **4d**: Anal. Calc. (Found) C, 56.47 (56.81); H, 5.33 (5.41)%; ^{1}H-NMR δ 0.23 (s, 6H, bridged-$SiMe_2$), 0.64 (s, 12H, $SiMe_2Ph$), 3.89, 4.11 (s, s, 4H, 4H, Cp), 7.06–7.18 (m, 6H, Ph), 7.53–7.56 (m, 4H, Ph); ^{13}C-NMR δ −1.19 (bridged-$SiMe_2$), 5.84 (Fe–$SiMe_2Ph$), 88.65, 88.26 (Cp), 127.88, 128.52, 133.04, 147.60 (Ph), 216.18 (CO); ^{29}Si-NMR δ −10.04 (bridged-$SiMe_2$), 35.62 (Fe–$SiMe_2Ph$); IR ν(CO) 1994 (s), 1943 (s).

3.3. Photolysis of 1: formation of $(SiMe_2)[(\eta^5\text{-}C_5H_4)Fe(CO)_2SiMe_3]_2$ (3b)

A 5 mm Pyrex NMR tube was charged 0.15 g (0.22 mmol) of **1** and 0.8 ml of C_6D_6. After three freeze–pump–thaw cycles it was sealed under vacuum and irradiated with 450 W medium-pressure Hg lamp at a distance of 2 cm. After 3 h, NMR monitoring showed the formation of a major product **3a**, along with traces of **3b**. Further irradiation for 22 h resulted in the complete disappearance of **1** and **3a** and the formation of **3b**, along with a minor product with two ^{29}Si-NMR resonances (31.33, −8.85 ppm), which we have not yet to identify. The reaction mixture was placed upon a 1.0 × 20 cm silica gel column. Elution with hexanes developed a light yellow band which was collected and subsequent to solvent removal afforded a yellow oil which after several days in a refrigerator formed **3b** as a brown yellow crystalline solid (50 mg, 0.09 mmol, 41%), m.p. 68–70 °C.

3a: ^{1}H-NMR δ 0.20 (s, 9H, $SiMe_2\mathit{SiMe_3}$), 0.41 (s, 6H, bridged-$SiMe_2$), 0.47 (s, 9H, Fe–$SiMe_3$), 0.52 (s, 6H, $\mathit{SiMe_2}SiMe_3$), 4.17, 4.34, 4.42 (s, s, s, 2H, 4H, 2H, Cp); ^{13}C-NMR δ −1.04 (bridged-$SiMe_2$), −0.31 ($SiMe_2Si\mathit{Me_3}$), 3.69 ($Si\mathit{Me_2}SiMe_3$), 7.98 (Fe–$SiMe_3$), 86.50, 87.26, 88.52, 88.76, 89.43, 89.92 (Cp), 215.91, 216.05 (CO); ^{29}Si-NMR δ −11.49 ($SiMe_2\mathit{Si}Me_3$), −10.08 (bridged-$SiMe_2$), 17.00 ($\mathit{Si}Me_2SiMe_3$), 41.28 (Fe–$SiMe_3$).

3b: Anal. Calc. (Found) C, 47.49 (47.68); H, 4.80 (3.98)%; ^{1}H-NMR δ 0.42 (s, 6H, bridged-$SiMe_2$), 0.51 (s, 18H, $SiMe_3$), 4.14, 4.34 (s, s, 4H, 4H, Cp); ^{13}C-NMR

δ −0.98 (bridged-$SiMe_2$), 7.95 ($SiMe_3$), 3.68 ($SiMe_2$), 87.26, 88.80, 89.44 (Cp), 216.16 (CO); ^{29}Si-NMR δ −10.13 (bridged-$SiMe_2$), 41.28 ($SiMe_2$); IR ν(CO) 1995 (s), 1943 (s).

3.4. Photolysis of **2**

As described above, 0.30 g (0.38 mmol) of **2** in 1 ml of C_6D_6 was irradiated and the reaction monitored by NMR spectroscopy. The formation of a major product **4a**, along with traces of 4b was observed after 2 h. Further irradiation for 12 h resulted in the complete disappearance of **2**, **4a** and **4b** and the formation of three products **4c**, **4d** and **3b** (1:8:1) along with traces of unidentified products. Complexes **3b** and **4d** were identified by comparison with the spectroscopic data of authentic samples.

[$PhMe_2Si(CO)_2Fe(\eta^5$ - $C_5H_4)(SiMe_2)(\eta^5$ - $C_5H_4)Fe(CO)_2SiMe_2SiMe_2Ph$], **4a**: ^{13}C-NMR δ −2.34 (Fe–$SiMe_2Si\mathit{Me}_2Ph$), −1.14 (bridged-$SiMe_2$), 3.97 (Fe–$Si\mathit{Me}_2SiMe_2Ph$), 5.83 (Fe–$SiMe_2Ph$), 88.45, 88.52, 88.61, 89.21, 89.87 (Cp), 128.18, 128.36, 128.46, 128.88, 132.98, 134.25, 141.40, 147.53 (Ph), 215.87, 216.10 (CO); ^{29}Si-NMR δ −15.10 ($SiMe_2\mathit{Si}Me_2Ph$), −10.10 (bridged-$SiMe_2$), 17.02 (Fe–$\mathit{Si}Me_2SiMe_2Ph$), 35.58 (Fe–$SiMe_2Ph$).

[$Me_3Si(CO)_2Fe(\eta^5$ - $C_5H_4)(SiMe_2)(\eta^5$ - $C_5H_4)Fe(CO)_2SiMe_2SiMe_2Ph$], **4b**: ^{29}Si-NMR δ −15.10 ($SiMe_2\mathit{Si}Me_2Ph$), −10.11 (bridged-$SiMe_2$), 17.04 (Fe–$\mathit{Si}Me_2SiMe_2Ph$), 41.27 (Fe–$SiMe_3$). [$Me_3Si(CO)_2Fe(\eta^5$-$C_5H_4)(SiMe_2)(\eta^5$-$C_5H_4)Fe(CO)_2SiMe_2Ph$], **4c**: ^{29}Si-NMR δ −10.10 (bridged-$SiMe_2$), 35.58 (Fe–$SiMe_2Ph$), 41.26 (Fe–$SiMe_3$)

3.5. Photolysis of **1** in the presence of HMPA

In a sealed 5 mm NMR tube a mixture of **1** (0.1g, 0.15 mmol) and HMPA (54 mg, 0.3 mmol) was irradiated and monitored by NMR spectroscopy. After 3 h the transient $Me_3SiMe_2Si(CO)_2Fe(\eta^5$-$C_5H_4)(SiMe_2)(\eta^5$-$C_5H_4)Fe(CO)(SiMe_3)({=}SiMe_2{\cdot}HMPA)$, **5** was formed (^{29}Si-NMR δ −11.69 ($SiMe_2\mathit{Si}Me_3$), −9.56 (bridged-$SiMe_2$), 16.44 ($\mathit{Si}Me_2SiMe_3$), 31.00 (Fe–$SiMe_3$), 116.26 (d, $^2J_{P-Si}$ = 28.8 Hz, Fe=$SiMe_2{\cdot}$HMPA)) along with traces of di-HMPA coordinated silyl(silylene) complex **6**, existing as a mixture of *meso* (**6a**) and *trans* (**6b**). Further irradiation, 22 h, resulted in the complete disappearance of **1** and **5** and almost quantitative formation of **6a** and **6b** (**6a**/**6b** = 10/8). $SiMe_2[(\eta^5$-$C_5H_4)Fe(CO)(SiMe_3)({=}SiMe_2{\cdot}HMPA]_2$ **6a** and **6b**: ^{1}H-NMR δ 0.72, 0.75 (s, 6H, bridged-$SiMe_2$), 0.58, 0.60 (s, 18H, $SiMe_3$), 0.63, 0.80 (s, 12H, Fe=$SiMe_2{\cdot}$HMPA), 2.24 (d, 36H, $^2J_{P-H}$ = 9.9 Hz, HMPA), 4.23–4.28, 4.46, 4.51, 4.67, 4.72 (m, 8H, Cp); ^{13}C-NMR δ −0.95, 0.56, 1.71 (bridged-$SiMe_2$), 11.30, 11.36 ($SiMe_3$), 13.47, 13.51 (Fe=$SiMe_2{\cdot}$HMPA), 36.65, 36.68 (d, d, $^2J_{P-C}$ = 5.1 Hz, $^2J_{P-C}$ = 5.1 Hz, HMPA), 80.04, 80.51, 80,76, 81.01, 85.47, 85.52, 86.51, 87.52, 87.44, 87.58 (Cp), 220.80, 220.89 (CO); ^{29}Si-NMR δ **6a**: −9.23 (bridged-$SiMe_2$), 31.09 ($SiMe_3$), 116.66 (d, $^2J_{P-Si}$ = 27.3 Hz, Fe=$SiMe_2{\cdot}$HMPA); **6b**: −9.13 (bridged-$SiMe_2$), 31.17 ($SiMe_3$), 116.70 (d, $^2J_{P-Si}$ = 28.5 Hz, Fe=$SiMe_2{\cdot}$HMPA).

When hexane was utilized as the solvent instead of C_6D_6, brown–yellow crystals of **6** was formed directly in the NMR tube over the course of irradiation. We did not isolate this compound due to its extreme sensitivity toward air and moisture.

3.6. Photolysis of **2** in the presence of HMPA

As above a solution of **2** (0.18 g, 0.23 mmol) and HMPA (112 mg, 0.63 mmol) was irradiated and the reaction monitored by NMR spectroscopy. After 3 h formation of [$PhMe_2SiMe_2Si(CO)_2Fe(\eta^5$-$C_5H_4)(SiMe_2)(\eta^5$-$C_5H_4)Fe(CO)(SiMe_2Ph)({=}SiMe_2{\cdot}HMPA)$] **7** was observed along with traces of di-HMPA coordinated silyl(silylene) complex **8**, existing as a mixture of *meso* (**8a**) and *trans* (**8b**) isomers. Further irradiation, 22 h resulted in the complete disappearance of **2** and **7** and almost quantitative formation of **8a** and **8b** (**8a**/**8b** = 10/8.5).

7: ^{13}C-NMR δ −2.28 ($SiMe_2Si\mathit{Me}_2Ph$), 0.51 (bridged-$SiMe_2$), 3.88 ($Si\mathit{Me}_2SiMe_2Ph$), 8.50 (Fe–$SiMe_2Ph$), 13.24, 13.28 (Fe=$SiMe_2{\cdot}$HMPA) 36.77 (d, $^2J_{P-C}$ = 4.4 Hz, HMPA), 79.08, 82.20, 83.98, 85.74, 86.25, 86.32, 88.66, 88.82, 89.70, 94.31 (Cp) 125.87, 127.21, 128.32, 128.87, 133.73, 134.23, 141.58, 156.40 (Ph), 216.57, 216.66, 220.75 (CO); ^{29}Si-NMR δ −15.4 ($SiMe_2\mathit{Si}Me_2Ph$), −9.57 (bridged-$SiMe_2$), 16.4 ($SiMe_2\mathit{Si}Me_2Ph$), 29.03 (Fe–$SiMe_2Ph$), 115.10 (d, $^2J_{P-Si}$ = 30.0 Hz, Fe=$SiMe_2{\cdot}$HMPA). $SiMe_2[(\eta^5$-$C_5H_4)Fe(CO)(SiMe_2Ph)({=}SiMe_2{\cdot}HMPA)]_2$ **8a** and **8b**: ^{13}C-NMR δ −1.08, −0.11, 1.11 (bridged-$SiMe_2$), 8.75, 8.90, 8.94, 8.97, 10.20, 10.42 ($SiMe_2Ph$), 13.33, 13.36, 13.42, 13.46 (Fe=$SiMe_2{\cdot}$HMPA) 36.61, 36.65 (d, d, $^2J_{P-C}$ = 5.1 Hz, $^2J_{P-C}$ = 4.9 Hz, HMPA), 79.78, 80.29, 81.04, 81.97, 85.61, 85.70, 87.70, 88.24, 88.40 (Cp), 125.70, 125.73, 127.10, 133.85, 133.96, 156.69 (Ph), 220.97, 221.11 (CO); ^{29}Si-NMR δ **8a**: −9.24 (bridged-$SiMe_2$), 29.44 ($SiMe_2Ph$), 115.70 (d, $^2J_{P-Si}$ = 28.2 Hz, Fe=$SiMe_2{\cdot}$HMPA); **8b**: −9.20 (bridged-$SiMe_2$), 29.57 ($SiMe_2Ph$), 115.80 (d, $^2J_{P-Si}$ = 28.2 Hz, Fe=$SiMe_2{\cdot}$HMPA).

3.7. X-ray crystal structure determination of ***4d***

Crystals suitable for X-ray diffraction analysis were obtained from a hexane solution. Intensity data were collected on a Nicolet–Siemens R3m/V four-circle diffractometer at room temperature, using graphite-monochromated Mo–K_α radiation (λ = 0.71073 Å). The ω-scan technique was applied in the 2θ range $3.5 \leq$

Table 1
Summary of X-ray diffraction data

	4d
Formula	$C_{32}H_{36}Fe_2O_4Si_3$
Formula weight	680.59
Space group	$P2_1/c$
Crystal system	Monoclinic
Z	4
Unit cell dimensions	
a (Å)	18.527(5)
b (Å)	11.582(3)
c (Å)	16.815(5)
α (°)	90
β (°)	109.76(2)
γ (°)	90
V (Å^3)	3395.7(16)
D_{calc} (g cm^{-1})	1.331
μ (cm^{-1})	9.89
F(000)	146
Crystal size (mm^3)	$0.20\times0.20\times0.30$
No. of reflections collected	4639
No. of independent reflections	4454
R_{int}	0.025
No. of observed data [$F>4.0\sigma(F)$]	3304
R_{obs}	0.0545
R_{w}	0.071
R_{tot}	0.0728
Goodness-of-fit	1.57
Largest difference peak and hole (e Å^{-3})	0.79 and -0.55

Table 2
Selected bond lengths (Å) and bond angles (°) for **4d**

Bond lengths			
Fe(1)–Si(1)	2.329(2)	Fe(2)–Si(3)	2.331(2)
Fe(1)–C(13)	1.730(10)	Fe(1)–C(14)	1.728(8)
Fe(2)–C(23)	1.738(6)	Fe(2)–C(24)	1.732(7)
C(13)–O(1)	1.162(8)	C(14)–O(2)	1.148(8)
C(23)–O(3)	1.150(6)	C(24)–O(4)	1.154(7)
Bond angles			
C(13)–Fe(1)–C(14)	94.6(3)	C(23)–Fe(2)–C(24)	92.3(3)
Si(1)–Fe(1)–C(13)	83.5(2)	Si(1)–Fe(1)–C(14)	86.8(2)
Si(3)–Fe(2)–C(23)	86.8(2)	Si(3)–Fe(2)–C(24)	84.7(2)
Fe(1)–Si(1)–C(17)	109.9(2)	Fe(2)–Si(3)–C(27)	109.5(2)
C(1)–Si(2)–C(6)	106.0(2)	C(11)–Si(2)–C(12)	110.7(4)

$2\theta \leq 45.0°$ with variable scan speeds. The structures were refined by anisotropic, full-matrix least-squares. Hydrogen atomic positions were generated from the assumed geometry. Crystallographic data are summarized in Table 1, and selected bond distances and angles in Table 2.

4. Supplementary material

Crystallographic data (excluding structure factors) for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 166567 for **4d**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1233-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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