Stereospecific Formation of 1,3-Disilacyclobutanes by Photochemical Treatment of Bimetallic Precursors $FpCH_2SiR_2SiR_2CH_2Fp$ ($Fp = (\eta^5\text{-}C_5H_5)Fe(CO)_2$)

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The activation of the silicon−silicon bond by transition metal complexes is an area of chemistry that has implications in catalysis and materials science.[1] Our studies on the chemistry of oligosilyl compounds substituted with the Fp group showed that α-elimination chemistry results in the intermediacy of iron−silylene complexes, $Fp = (\eta^5\text{-}C_5H_5)Fe(CO)_2$). These intermediates lead to either silylene eliminations, eq 1, or rearrangements, eq 2; both may be effected catalytically under appropriate conditions.[2,3]

$$\mathrm{Fp{-}SiMe_2SiMe_3 \rightarrow Fp{-}SiMe_3 + [SiMe_2]} \tag{1}$$

$$\mathrm{Fp{-}SiMe_2SiMe_2SiMe_2SiMe_3 \rightarrow FpSi(SiMe_3)_3} \tag{2}$$

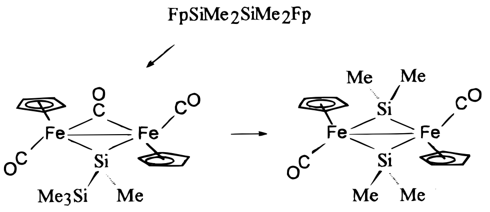
When the metal substituent is attached to the oligosilyl group via a bridging methylene group, *β*-elimination chemistry results in the formation of iron−silene intermediates that lead either to rearrangements, eq 3 ($R = H$, $(SiMe_2)_nSiMe_3$, $GeMe_3$), or silene elimination, eq 4 ($R = GeMe_3$, $Wp = (\eta^5\text{-}C_5H_5)W(CO)_3$).[2a,4]

$$\mathrm{Fp{-}CH_2SiMe_2R \rightarrow Fp{-}SiMe_2CH_2R} \tag{3}$$

$$\mathrm{Wp{-}CH_2SiMe_2R \rightarrow Wp{-}R + Me_2Si{=}CH_2} \tag{4}$$

The silene metal intermediates involved in eq 3 ($R = H$)[4a] have been characterized only by low-temperature matrix-isolation techniques.[5] However, many stable transition metal silene complexes have been isolated and characterized by the research groups of Berry and Tilley.[6]

Scheme 1



The related chemistry of bimetallic systems is less studied. Scheme 1 illustrates the sequential formation of silylene iron complexes by photolysis of $FpSiMe_2SiMe_2Fp$,[7] indicating the significant differences in chemistry that may exist due to the capacity for metal−metal (Fe−Fe) interactions.

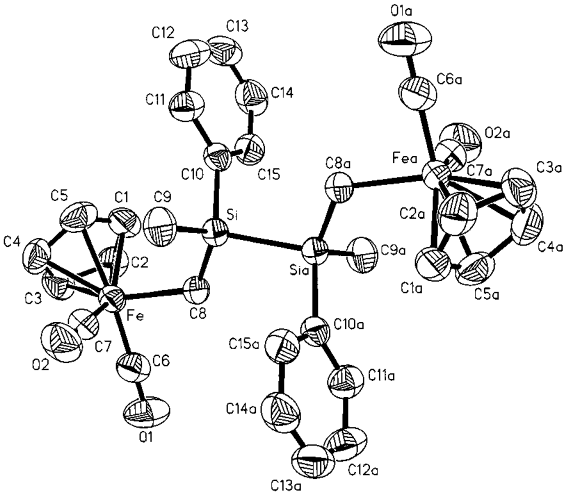


Figure 1. Structure of **2a**.

We have now synthesized the bimetallic complexes $FpCH_2MeRSiSiRMeCH_2Fp$, R = Me (**1**) and Ph (**2**), and report an unprecedented photoreaction leading to the quantitative formation of 1,3-disilacyclobutanes. Complex **1**[8] was prepared in 64% yield from the reaction of $ClCH_2Me_2SiSiMe_2CH_2Cl$[9] with $[Fp]^-Na^+$, while similar treatment of $ClCH_2MePhSiSiMePhCH_2Cl$[10] afforded **2** in 24% yield, eq 5.

$$\mathrm{[Fp]^-Na^+ + [ClCH_2SiMeR]_2 \rightarrow FpCH_2SiMeRSiMeRCH_2Fp} \tag{5}$$

^1H and ^{13}C NMR spectra of **2** indicate a mixture of two isomers, with one isomer dominant (meso/dl = 5:1). Recrystallization of **2** from a mixture of CH_2Cl_2/hexane yielded prisms and the isomers **2a** (meso) and **2b** (dl) could be separated mechanically.[11]

The single-crystal structure of **2a** is illustrated in Figure 1.[12] The molecule consists of two identical $[(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_2\text{-}SiMePh]$ moieties bonded by a Si−Si bond and has C_i symmetry. The Fe−C(8) bond length (2.092(3) Å) is in the range of the normal Fe−C (sp^3) bond distances (2.08−2.16 Å).[13] The Si−Si

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[8] Mp 104−6 °C. Anal. Calcd. for $C_{20}H_{26}Fe_2O_4Si_2$: C, 48.21; H, 5.26. Found: C, 47.76; H, 5.54. ^1H NMR (C_6D_6) δ 0.16 (s, 4H, CH_2), 0.47 (s, 12H, SiMe), 4.27 (s, 8H, Cp). ^{13}C NMR (C_6D_6) δ −23.6 (CH_2), 0.16 (SiMe), 85.0 (Cp), 218.3 (CO). ^{29}Si NMR (C_6D_6) δ −6.03. IR (ν_{CO}, cm^{-1}) 2009(s), 1958(s).

[9] Kobayashi, T.; Pannell, K. H. *Organometallics* **1991**, *10*, 1960.

[10] $ClCH_2MePhSiSiPhMeCH_2Cl$ was similarly synthesized as a mixture of two isomers (1:0.7) in 85% by a literature procedure.[9] ^1H NMR (C_6D_6) δ 0.42 (s, 6H, SiMe), 2.93 (AB, $^2J = 13.6$ Hz, 4H, CH_2), 7.11−7.34 (m, 10H, Ph), 0.43 (s, 6H, SiMe), 2.92 (AB, $^2J = 13.5$ Hz, 4H, CH_2), 7.11−7.34 (m, 10H, Ph). ^{13}C NMR (C_6D_6) δ −6.18, −5.91 (SiMe), 29.5, 29.6 (CH_2), 128.5, 129.9, 134.6, 134.7 (Ph). ^{29}Si NMR (C_6D_6) δ −18.6, −18.5.

[11] For **2a**: Mp 146−8 °C. Anal. Calcd for $C_{30}H_{30}Fe_2O_4Si_2$: C, 57.89; H, 4.86. Found: C, 58.17; H, 4.39. ^1H NMR (C_6D_6) δ 0.02 (d, $^2J = 12.6$ Hz, 2H, CH_2), 0.44 (d, $^2J = 12.6$ Hz, 2H, CH_2), 0.66 (s, 6H, SiMe), 3.97 (s, 8H, Cp), 7.23, 7.55 (m, m, 10H, Ph). ^{13}C NMR (C_6D_6) δ −26.6 (CH_2), −2.42 (SiMe), 84.6 (Cp), 128.0, 128.5, 134.7, 142.4 (Ph), 217.86, 217.93 (CO).^{29}Si NMR (C_6D_6) δ −9.00. IR (ν_{CO}, cm^{-1}) 2011(s), 1959(s). For **2b**: Mp 116−8 °C. Anal. Calcd. for $C_{30}H_{30}Fe_2O_4Si_2$: C, 57.89; H, 4.86. Found: C, 57.10; H, 3.78. ^1H NMR (C_6D_6) δ 0.04 (d, $^2J = 12.6$ Hz, 2H, CH_2), 0.43 (d, $^2J = 12.6$ Hz, 2H, CH_2), 0.64 (s, 6H, SiMe), 4.00 (s, 8H, Cp), 7.22, 7.57 (m, m, 10H, Ph). ^{13}C NMR (C_6D_6) δ −26.8 (CH_2), −2.16 (SiMe), 84.7 (Cp), 128.0, 128.5, 134.7, 142.3 (Ph), 217.9 (CO). ^{29}Si NMR (C_6D_6) δ −9.07. IR (ν_{CO}, cm^{-1}) 2009(s), 1959(s).

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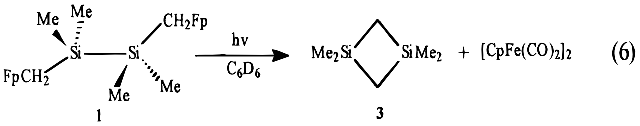
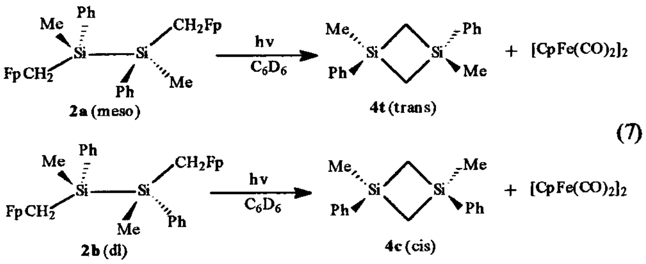
bond length (2.359(1) Å) is equivalent to those in LFeSiMe$_2$SiMe$_3$ (2.361−2.364 Å)[14] and shorter than that of the bimetallic complex FpSiMe$_2$SiMe$_2$Fp (2.390(4) Å).[15]

Irradiation of a C_6D_6 solution of **1** with a medium-pressure Hg lamp in a sealed NMR tube resulted in the quantitative formation of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ and 1,3-tetramethyldisilacyclobutane **3** (eq 6).[16]



(6)

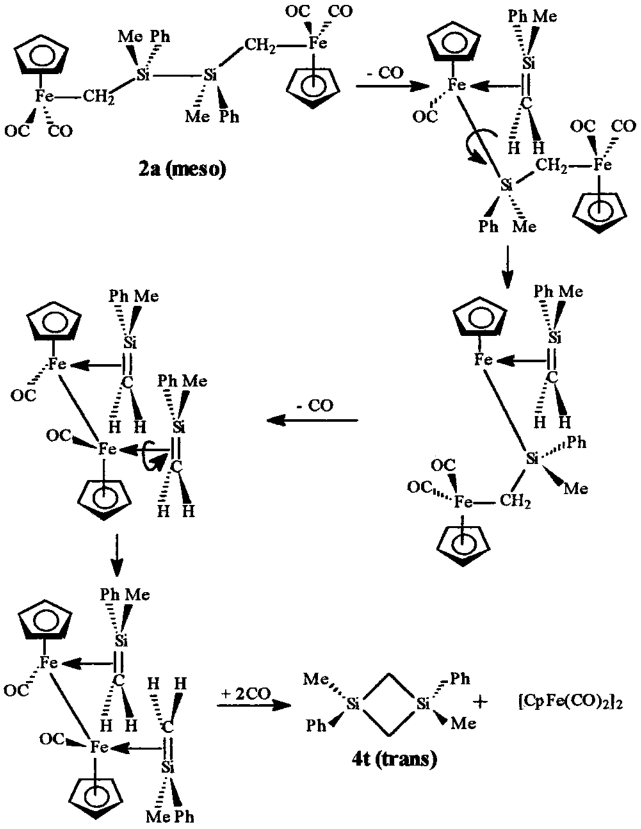
Photolysis of **2a** (meso) for 2 h afforded only the *trans*-1,3-disilacyclobutane **4t**, while similar photolysis of **2b** (dl) afforded only the *cis*-1,3-disilacyclobutane **4c**, eq 7.[17] The photoreactions are stereospecific.



(7)

It is reported that "unstable" silenes carrying small alkyl substituents readily dimerize in a head-to-tail fashion to yield 1,3-disilacyclobutanes,[18] while stable silenes, e.g. $(Me_3Si)_2Si{=}C(OSiMe_3)R$, preferentially yield the head-to-head dimers, 1,2-disilacyclobutanes.[19] Since the photoreactions involving free silene yield a mixture of the cis and trans isomers of 1,3-disilacyclobutanes, it is unlikely that free silene was produced by photolysis of **1** and **2**.[20] Furthermore, the chemistry noted in eq 4 in which silene is liberated never produced silacyclobutanes.[4b] To further prove this point we have photolyzed a mixture of **1** and **2a** and observed no cross-over products; the photoreactions proceed via an intramolecular pathway.

Scheme 2



The stereospecific formation of **4** suggests a special interaction of the complexed silenes upon adjacent metal centers prior to elimination of the product. The mechanism presented in Scheme 2 is our current suggestion. Each step must be stereospecific and the transient formation of iron centers which themselves are potentially enantiomeric may play an important role in the stereochemical outcome of the coupling reaction. It is possible that a direct 1,4-elimination reaction and transient 1,2-disilacyclobutanes are involved, but presently we have no evidence for these species. Finally, as is often the case in the area of organosilicon chemistry, early studies by the Kumada group are relevant. In 1977 they reported that the reaction of XCH$_2$SiMe$_2$SiMe$_2$CH$_2$X (X = Br, I) with Mg resulted in the formation of **3**. Furthermore, 1-metallo-3,4-disilacyclopentanes of Pt and Ni also led to formation of **3** under certain conditions. Bis-silene metal intermediates were suggested.[21]

Overall the new chemistry presents a very unusual and potentially general route to coupling of reagents bonded to adjacent metals and we are continuing our study to flush out the details and generality of the process.

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Supporting Information Available: Listings of crystal data, date collection, solution and refinement, complete atomic coordinates, bond distances and angles, and anisotropic thermal parameters for **2a** and synthetic details (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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[12] Data collected using a Siemens R3m/V diffractometer and Mo Kα radiation. **2a**: triclinic; space group $P\bar{1}$; a = 8.607(2) Å, b = 9.509(2) Å, c = 9.819(2) Å, α = 86.84(2)°, β = 64.95(1)°, γ = 86.58(2)°; Z = 1; R = 4.13; GOF = 1.03. Selected bond distances (Å) and angles (deg): Fe−C(8) 2.092(3), Si−SiA 2.359(1), Fe−C(8)−Si 120.5(1).

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[16] Complex **3** has been characterized by ^{1}H, ^{13}C, and ^{29}Si NMR and GC/MS. ^{1}H NMR (C_6D_6) δ 0.12 (s, 4H, CH$_2$), 0.24 (s, 12H, SiMe$_2$). ^{13}C NMR (C_6D_6) δ 2.56 (SiMe$_2$), 3.99 (CH2).^{29}Si NMR (C_6D_6) δ −2.54. Mass: *m*/*e* 144 (M, 20%), 129 (M − Me, 100%). Kriner, W. A. *J. Org. Chem.* **1964**, *29*, 1601.

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