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α- versus *β*-Elimination Photochemistry of Oligosilyl– and Oligosilylmethyl–Iron Complexes: Photochemistry of $FpSiMe_2SiMe_2CH_2Fp$ ($Fp = (\eta^5\text{-}C_5H_5)Fe(CO)_2$)

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Summary: The bimetallic oligosilylmethyl complex $Fp(SiMe_2)_2CH_2Fp$ (**1**) *has been prepared and characterized. Upon photolytic irradiation* **1** *rearranges, via β-elimination chemistry at the iron–carbon end of the chain, to form* $FpSiMe_2CH_2SiMe_2Fp$ (**2**). *No evidence for α-elimination chemistry at the other iron center was observed. The crystal structures of both* **1** *and* **2** *are presented for complete characterization.*

The activation of the silicon–silicon bond by transition metals is an important area of modern chemistry.[1] Compounds containing such bonds are perhaps best represented by the family of oligosilyl and oligosilylmethyl Fp complexes $Fp(SiMe_2)_nMe$ and $FpCH_2(SiMe_2)_nMe$ ($Fp = (\eta^5\text{-}C_5H_5)Fe(CO)_2$).[2–4] The signature chemistry of these complexes is their photochemically induced rearrangements involving α- and *β*-elimination reactions to form intermediate silylene and silene complexes, respectively (Schemes 1 and 2). There are now many examples of silylene and silene transition-metal complexes and many examples where the intermediacy of such systems are involved in interesting rearrangements.[5]

We have now synthesized a new complex in which either, or both, α- and *β*-elimination chemistry can occur at an Fp center, i.e., $FpSiMe_2SiMe_2CH_2Fp$ (**1**), and report the results of its photochemical irradiation. The

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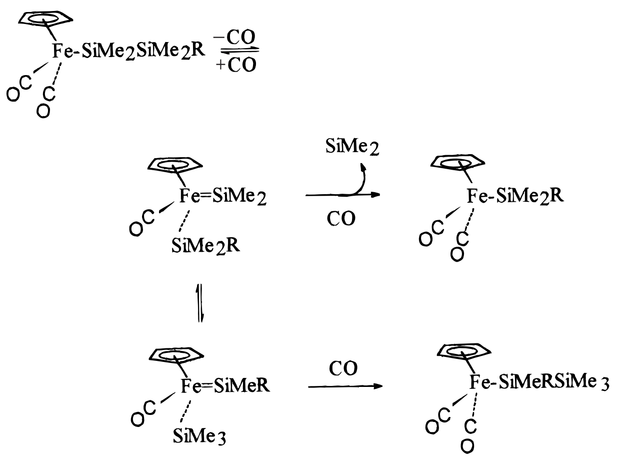
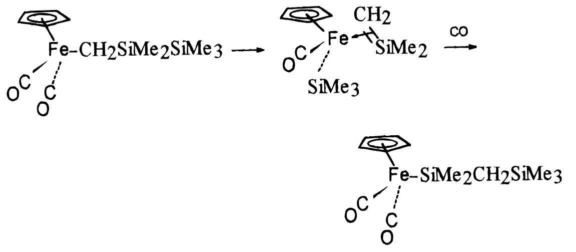
Scheme 1



Scheme 2



complex was readily synthesized by the salt-elimination reactions outlined in eq 1.[6]

$$2[\mathrm{Fp}]^{-}\mathrm{Na}^{+} + \mathrm{Cl(SiMe_2)_2CH_2Cl} \rightarrow \mathrm{Fp(SiMe_2)_2CH_2Fp} + \mathrm{NaCl} \quad (1)$$

The new complex exhibits spectroscopic data in accord with the proposed structure. The ^{29}Si NMR data are useful for structural assignment, and in general silicon atoms attached to the Fe atom are dramatically shifted downfield compared to those of their permethylated analogues; this shift is reduced as the two atoms become separated.[7] The effect is additive; thus, for **1** the two resonances are at 1.98 ppm (Fe−SiMe$_2$*Si*Me$_2$) and 18.4 ppm (Fe−*Si*Me$_2$SiMe$_2$), which can be compared to the resonance at −19.5 ppm for Me$_3$SiSiMe$_3$. The infrared spectrum of **1** is also instructive, since the ν(CO) values for the two distinct Fp groups are evident. The stretching frequencies for the Fp−SiMe$_2$ group (1994 and 1943 cm^{-1}) and the Fp−CH$_2$ group (2010, 1957 cm^{-1}) are typical of Fp−silyl and Fp−alkyl complexes, respectively.[8] These data indicate the greater capacity of the silyl group to increase retrodative bonding between the iron atom and the carbonyl groups, thereby increasing the Fe−C bond order at the silicon-bonded end of the complexes.

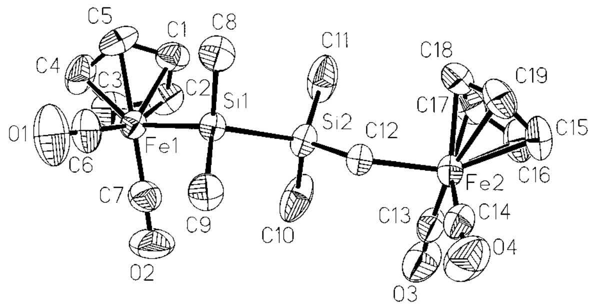


Figure 1. Structure of **1**. Selected bond lengths (Å) and angles (deg): Si1−Si2 = 2.366(1), Fe1−Si = 2.346(1), Fe2−C12 = 2.096(3), Si2−C12 = 1.876(3), Si2−C11 = 1.866(4), C6−O1 = 1.152(5), C13−O3 = 1.144(4); Fe1−C6 = 1.727(4), Fe2−C13 = 1.742(3); Fe1−Si1−Si2 = 116.1(1), Si1−Si2−C12 = 104.0(1), C8−Si1−C9 = 105.0(1), C11−Si2−C10 = 106.3(1).

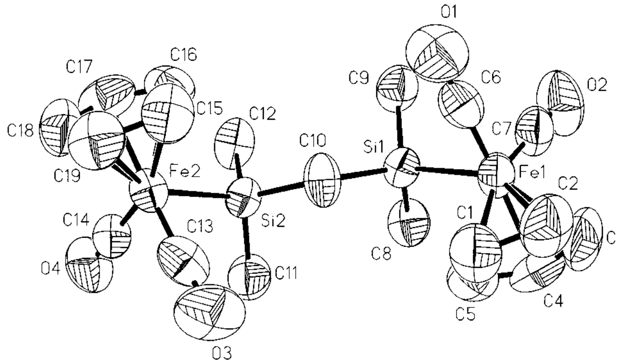
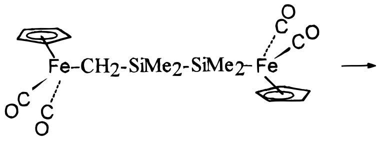


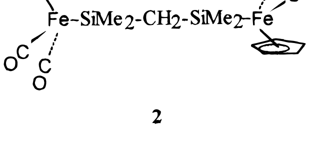
Figure 2. Structure of **2**. Selected bond lengths (Å) and angles (deg): Fe2−Si2 = 2.343(3), Fe1−Si1 = 2.349(3), Si2−C10 = 1.888(8), Si1−C10 = 1.884(8) C−O (average) = 1.167(14); Si2−C10−Si1 = 123.7(4), C10−Si1−Fe1 = 109.1(2).

The single-crystal structure of **1** is illustrated in Figure 1, and crystallographic data are recorded in Table 1. The structure confirms the spectroscopic data analysis, and the data are in accord with expectations. For example, both the Si−Si bond of 2.366(1) Å and the Fe−Si bond of 2.346(1) Å are in line with related Fe−Si−Si data.[9,10]

Photochemical irradiation of **1** provides unambiguous evidence that only β-elimination chemistry occurs to produce FpSiMe$_2$CH$_2$SiMe$_2$Fp (**2**) in good yield.



1



2

When the photochemical reaction was monitored by using ^{29}Si, ^{13}C, and ^{1}H NMR, the reaction appeared

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[6] To 20 mL of a THF solution of [Fp]$^{-}$Na^{+} (prepared from 2.2 g (6.2 mmol) of Fp$_2$ and a Hg/Na amalgam) was added 10 mL of a THF solution of ClCH$_2$SiMe$_2$SiMe$_2$Cl (0.62 g, 3.1 mmol) at ambient temperature. After 2 h of stirring the solvent was removed and the product was extracted into hexane, 100 mL. After removal of the solvent the solid residue was placed on a silica column (30 g) in the minimum amount of hexane and eluted with hexane. The yellow band that developed was collected, and after workup yielded 1.37 g (2.83 mmol, 91%) of **1**. Anal. (Galbraith Laboratories Inc.) Calcd (found): C, 47.13 (47.18); H, 5.00 (4.93). NMR (C$_6$D$_6$, ppm): ^{29}Si, 1.98, 18.4; ^{13}C, −23.2 (CH$_2$), 1.25, 4.14 (SiMe$_2$), 83.3, 85.1 (C$_5$H$_5$), 216.6, 218.3 (CO); ^{1}H, 0.18 (CH$_2$), 0.48, 0.75 (SiMe$_2$), 4.26, 4.35 (C$_5$H$_5$). IR (hexane, cm^{-1}): 2010, 1994, 1957, 1943. Mp: 75.5−76.3 °C.

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Table 1. Crystallographic Data for 1 and 2

	1	**2**
empirical formula	$C_{19}H_{24}Si_2O_4Fe_2$	$C_{19}H_{24}Si_2O_4Fe_2$
color; habit	yellow fragment	yellow fragment
cryst size (mm)	0.20 × 0.40 × 0.80	0.20 × 0.40 × 0.60
cryst syst	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/n$
unit cell dimens		
a (Å)	10.313(2)	7.128(3)
b (Å)	16.050(2)	22.115(13)
c (Å)	13.650(2)	14.405(10)
α (deg)	90.00	90.00
β (deg)	102.31(1)	91.29(5)
γ (deg)	90.00	90.00
V (Å^3)	2207.4(6)	2270(2)
Z	4	4
20 range (deg)	3.5−45	3.5−45
scan type	ω	ω
scan speed (deg/min)	3−15	4−19
scan range (w) (deg)	1.20	1.20
std rflns	3 measd every 197 rflns	3 measd every 197 rflns
index ranges		
h	−2 to +11	−7 to 0
k	0−17	−2 to +23
l	−14 to +14	−15 to +15
no. of rflns collected	3324	3592
no. of indep rflns	2905	2937
no. of obsd rflns	2550 ($F > 3.0\sigma(F)$)	2362 ($F > 3.0\sigma(F)$)
abs cor	semiempirical	semiempirical
min/max transmissn	0.296/0.330	0.125/0.225
final R indices (obsd data) (%)	$R = 2.83$, $R_w = 3.94$	$R = 6.59\%$, $R_w = 9.53$

quantitative: we found no evidence for products that would result from α-elimination, e.g., $FpCH_2SiMe_2Fp$.[11] Complex **2** was isolated in ~80% yield, and the spectral data are as expected. Thus, a single ^{29}Si resonance at 43.0 ppm and two carbonyl stretching frequencies at 1994 and 1942 cm^{-1} are both typical of Fp−silyl complexes. The single-crystal structure of **2** is presented in Figure 2, and crystallographic data are in Table 1. All bond lengths and angles are as expected.

The reason for the specific reactivity at the $Fe-CH_2$ end of the molecule is not clear. We noted above that the IR and structural data suggest that the Fe−CO groups of the carbon-bonded Fp group are longer and possess less Fe−C double-bond character than those of the silicon-bonded Fp group. Thus, it may be simply that initial CO loss is more readily achieved at the former group. However, a detailed photophysical study is needed to pin down the precise reasons for this very clear specificity of reactivity. Also, the relative stabilities of the silene and/or silylene intermediates may be an important consideration.

We are continuing our studies with complexes in which more than two silicon atoms are present, i.e., $FpCH_2(SiMe_2)_nFp$ ($n = 3-6$).

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Supporting Information Available: Complete tables of crystal data, collection and refinement data, atomic coordinates, H atom coordinates, bond distances, bond angles, and anisotropic displacement coefficients for **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM9906161

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(10) From the structural data it is also possible to distinguish the longer C−O, and shorter $Fe-C_{carbonyl}$, bond lengths at the silicon−iron end of the molecule: $C-O_{av}$, 1.152(4) Å vs 1.144(4) Å, $Fe-C_{av}$, 1.730(3) Å vs 1.738(3) Å.

(11) In a 100 mL round-bottomed flask a solution of **1** (0.24 g, 0.49 mmol) in 50 mL of C_6D_6 was irradiated with a Hanovia 450 W medium-pressure lamp for 30 min at a distance of 3 in. The initial yellow solution turned red, and infrared monitoring indicated that all of the starting material had been consumed. The solvent was removed in vacuo and the residue placed upon a silica column (20 g) and eluted with hexane. The yellow band was collected, the solvent was removed, and the solid residue was recrystallized from hexane to yield **2**: 0.19 g (0.38 mmol, 78%). Anal. Calcd (found): C, 47.13 (47.35); H, 5.00 (5.06). NMR (C_6D_6, ppm): ^{29}Si, 43.0; ^{13}C, 8.37 ($SiMe_2$), 21.0 (CH_2), 83.4 (C_5H_5), 216.2 (CO); ^1H, 0.70 ($SiMe_2$), 0.76 (CH_2), 4.13 (C_5H_5). IR (hexane, cm^{-1}): 1994, 1942. Mp: 95.5−96.3 °C.