Organometallics **2006,** *25,* 3969−3973

Photochemical Ring-Contraction of a Tetrasilaferracyclohexane of the (η^5-C_5H_4)Fe(CO)$_2$ System to Trisilaferracyclopentanes

Hemant K. Sharma, Francisco Cervantes-Lee, and Keith H. Pannell*

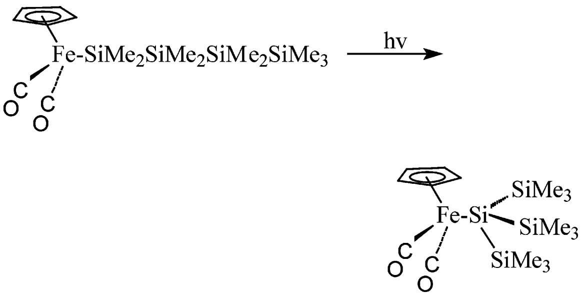
Department of Chemistry, University of Texas at El Paso, El Paso, Texas 79968-0513

Received April 10, 2006

Treatment of (η^5-C_5H_5)Fe(CO)$_2$(SiMe$_2$)$_n$Cl (n = 3, 4) with lithium diisopropylamide leads directly to new trisila- (**1**) and tetrasilaferracycles (**2**) $[(\eta^5\text{-}\overline{\text{C}_5\text{H}_4\text{)Fe(CO)}_2\text{(SiMe}_2}\text{)}_n]$. The trisilaferracycle (**1**) exhibits a degree of ring strain as noted by ^{29}Si NMR spectroscopy and single-crystal X-ray analysis but is stable with respect to limited attempts at ring-opening polymerization and photochemical transformation. In contrast, **2**, with no ring strain, readily transforms via photochemical irradiation by way of iron silyl(silylenes) to a trimethylsilyl-substituted trisilaferracycle **4**, which in turn transforms to **1** upon prolonged irradiation.

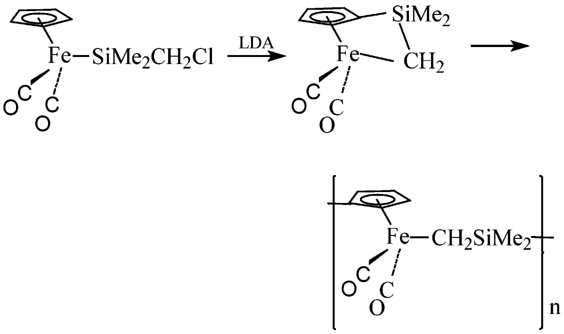
Introduction

We have demonstrated that the linear trisilyl, tetrasilyl, and cyclic polysilyl complexes of iron undergo clean photochemical isomerization to the branched oligosilyl iron complexes via the intermediacy of iron silyl(silylenes),[1−3] e.g., eq 1.



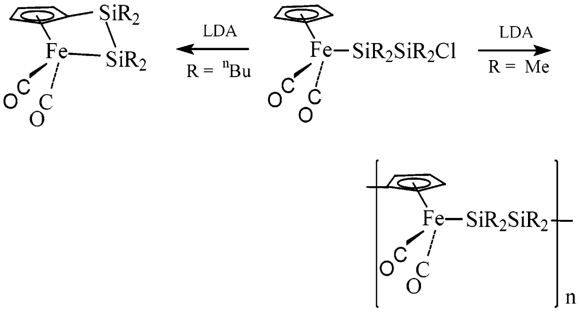
(1)

Recently we also reported the formation of new silaferracycles by base-treatment of (η^5-C_5H_5)Fe(CO)$_2$SiR$_2$CH$_2$Cl, FpSiR$_2$CH$_2$Cl, that could lead to ring-opened polymers,[4] e.g., eq 2.



(2)

Upon treatment with LDA the related 1-Fp-2-chlorotetrabutyldisilane provided a stable disilaferracycle, which does not lead to polymer formation; however, direct polymer formation was obtained when the smaller methyl groups were substituted on the silicon atoms, eq 3. We assume this polymer was formed via an unobserved silaferracycle intermediate.[5]



(3)

We now report the synthesis of the related trisila- and tetrasilaferracycles and the results of ultraviolet irradiation of these new complexes.

Results and Discussion

The reaction between [(η^5-C_5H_5)Fe(CO)$_2$]Na and the permethylated α,ω-dichlorotrisilane and -tetrasilane, Cl(SiMe$_2$)$_n$Cl, n = 3, 4, in THF at low temperature produced Fp(SiMe$_2$)$_n$Cl in 60% (n = 3)[3a,6] and 26% (n = 4) yields, respectively, eq 4.

$$[\mathrm{Fp}]^-\mathrm{Na}^+ + \mathrm{Cl(SiMe_2)}_n\mathrm{Cl} \rightarrow \mathrm{Fp(SiMe_2)}_n\mathrm{Cl} + \mathrm{NaCl} \quad (4)$$

In the case of the reaction with the 1,4-dichlorooctamethyltetrasilane significant amounts of Fp(SiMe$_2$)$_4$Fp were obtained as a yellow crystalline solid.[7] However, its low solubility in hexane permitted ready separation from Fp(SiMe$_2$)$_4$Cl. Treatment of either Fp(SiMe$_2$)$_n$Cl complex with lithium diisopropylamide, LDA, in THF at 0 °C, resulted in formation of the corresponding silaferracycles **1** and **2** in moderate yields, eq 5.

---

(1) (a) Pannell, K. H.; Wang, L.-J.; Rozell, J. M. *Organometallics* **1989**, *8*, 550. (b) Hernandez, C.; Sharma, H. K.; Pannell, K. H. *J. Organomet. Chem.* **1993**, *462*, 259.

(2) (a) Sharma, H. K.; Pannell, K. H. *Chem. Rev.* **1995**, *95*, 1351. (b) Tilley, T. D. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1989; Chapter 24.

(3) (a) Tobita, H.; Kurita, H.; Ogino, H. *Organometallics* **1998**, *17*, 2844. (b) Okazaki, M.; Tobita, H.; Ogino, H. *J. Chem. Soc., Dalton Trans.* **2003**, 493. (c) Tobita, H.; Matsuda, A.; Hashimoto, H.; Ueno, K.; Ogino, H. *Angew. Chem., Int. Ed.* **2004**, *43*, 221. (d) Hashimoto, H.; Matsuda, A.; Tobita. H. *Chem. Lett*. **2005**, 1374.

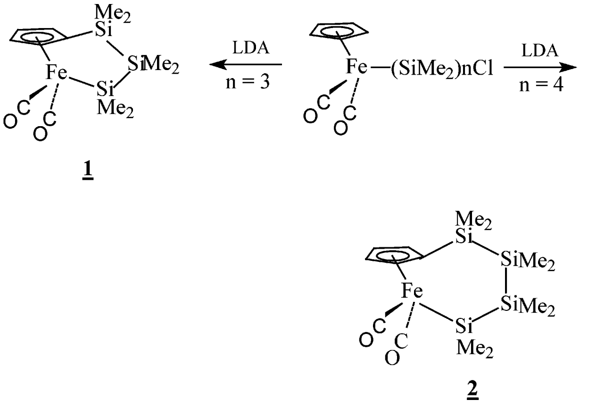
(4) Sharma, H. K.; Cervantes-Lee, F.; Pannell, K. H. *J. Am. Chem. Soc.* **2004**, *126*, 1326.

(5) Sharma, H. K.; Pannell, K. H. *Chem. Commun.* **2004**, 2556.

(6) Sharma, S.; Pannell, K. H. *Organometallics* **2000**, *19*, 1225.

(7) Hengge, E.; Eibl, M.; Stadelmann, B. *Monatsh. Chem.* **1993**, *124*, 523.

10.1021/om060320c CCC: $33.50



(5)

In the reaction used to obtain **1** a significant amount of an insoluble material, possibly polymeric, was formed; however, we have not been able to obtain any useful information via solid-state NMR spectroscopy. The trisilaferracycle **1** was characterized by NMR spectroscopy and single-crystal X-ray diffraction. The ^{29}Si NMR spectrum of **1** exhibited three resonances at 28.4 ppm (Si_α, Fe−*Si*), −9.06 ppm (Si_β, Fe−Si−*Si*), and −21.2 ppm (Si_γ, Fe−Si−Si−*Si*−C_5H_4). An important feature of these data is the significant low-field shift ($\Delta\delta = 27$ ppm) for the β-Si resonance relative to the β-Si resonance of the related linear permethyltrisilane iron complex $FpSiMe_2\mathit{Si}Me_2SiMe_3$[1a,2] presumably due to the ring strain.

Reports concerning disilametallacyclopentanes[8] have appeared in the literature, but there are only two examples of a trisilametallacycle, a trisilairidacyclopentane,[9a] in which the C atom is a methylene carbon, and a trisilazirconacyclopentane[9b] in which the C atom is also part of a fused three-membered ring, N−Zr−C. In both cases the five-membered ring adopts an envelope conformation with dihedral angles of 124.7° and 158°, respectively. The X-ray structure of **1** (Figure 1) exhibits average Si−Si bond lengths of 2.338 Å, typical of the Si−Si bond lengths in Fp-oligosilyl complexes.[2] The five-membered ring composed of Fe, C, and three Si atoms is distorted, with bond angles Fe−C1−Si3 = 126.47(16)°, Fe−Si1−Si2 = 103.82(5)°, C1−Si3−Si2 = 101.78(11)°, Si3−Si2−Si1 = 96.26(6)°, and C1−Fe−Si1 = 90.70(9)°, respectively, illustrating the greater strain at the central silicon atom, as suggested by the ^{29}Si NMR data. The ring is close to an envelope conformation, with C1, Fe, Si2, and Si3 not completely coplanar but showing a dihedral angle of 175.5° between planes (C1−Si3−Si2) and (C1−Si2−Fe) with Si1 at the tip of the envelope, resulting in a 134.5° dihedral angle between planes (C1−Si2−Fe) and (Si2−Fe−Si1).

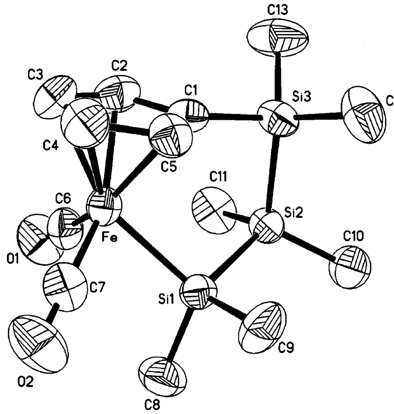


Figure 1. Structure of **1**. Thermal ellipsoids are drawn at 50% probability.

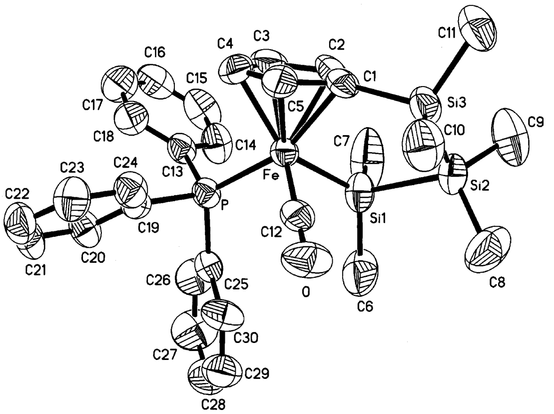
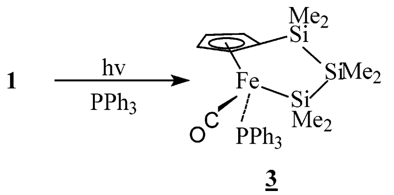


Figure 2. Structure of **3**. Thermal ellipsoids are drawn at 50% probability.

Despite this apparent strain **1** is stable in air and does not undergo ring-opening polymerization, thermally or in the presence of anionic or selected transition-metal catalysts. Furthermore, photochemical treatment of a hexane solution of **1** in a quartz tube for 10 h in the presence of a 2-fold excess of Ph_3P resulted in the formation of red crystalline phosphine-substituted trisilaferracycle **3**, in 24% yield without cleavage of Si−Si bonds or metal-initiated rearrangement[1,2] (eq 6), a distinctive photochemistry compared to that of the related linear Fp-oligosilanes noted in eq 1. Irradiation of **1** alone resulted in no observable chemistry.



(6)

The structure of **3** has also been confirmed by NMR spectroscopy and by single-crystal X-ray crystallography. The ^{13}C NMR spectrum of **3** exhibited different chemical shifts for the Cp carbons and methyl carbon atoms in the molecule due to the chiral metal center. A doublet observed in the ^{29}Si NMR spectrum at 16.8 ppm due to coupling between ^{29}Si and ^{31}P nuclei is assigned to Si_α (Fe−Si) with a large coupling constant, $^2J_{Si-P} = 29.5$ Hz, and a doublet at −12.9 ppm with a smaller coupling constant ($^3J_{Si-P} = 2.4$ Hz) to the Si_β atom. A singlet at −21.2 ppm is assigned to Si_γ (Cp-substituted Si). Substitution of the phosphine ligand for a carbonyl ligand shields the three silicon nuclei about $\Delta\delta = 11.6$ for Si_α, $\Delta\delta = 3.8$ for Si_β, and $\Delta\delta = 0$ ppm for Si_γ in comparison with the Si resonances of ferracycle **1**.[2,10]

The crystal structure of **3** (Figure 2) exhibits a five-membered ring in a twisted conformation with dihedral angles of 145.2° between planes (C1−Si3−Si2) and (C1−Si2−Fe) and 149.1° between (C1−Si2−Fe) and (Si2−Fe−Si1) rather than the

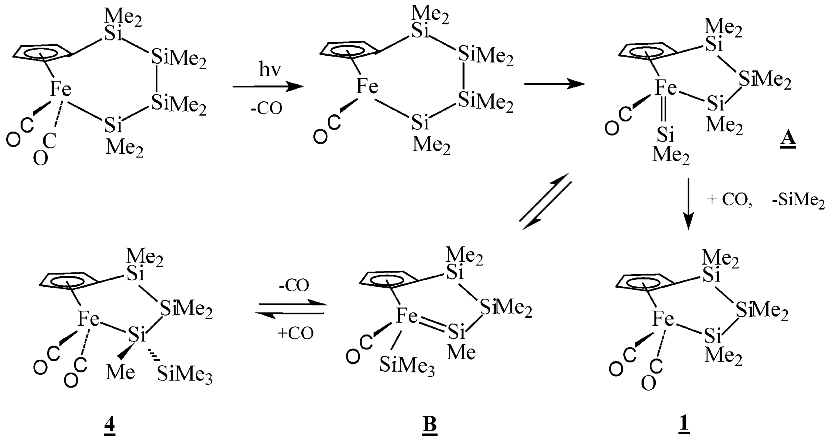
---

[8] (a) Crocco, G. L.; Young, C. S.; Lee, K. E.; Gladysz, J. A. *Organometallics* **1988**, *7*, 2158. (b) Tamao, K.; Yoshida, J.; Okazaki, S.; Kumada, M. *Isr. J. Chem.* **1977**, *15*, 265. (c) Ueno, K.; Ito, S.; Endo, K.; Tobita, H.; Inomata, S.; Ogino, H. *Organometallics* **1994**, *13*, 3309. (d) Tanabe, M.; Yamazawa, H.; Osakada, K. *Organometallics* **2001**, *20*, 4453. (e) Hoffmann, D.; Reinke, H.; Krempner, C. *J. Organomet. Chem.* **2002**, *662*, 1.

[9] (a) Mitchell, G. P.; Tilley, T. D.; Yap, G. P. A.; Rheingold, A. L. *Organometallics* **1995**, *14*, 5472. (b) Fischer, R.; Frank, D.; Gaderbauer, W.; Kayser, C.; Mechtler, C.; Baumgartner, J.; Marschner, C. *Organometallics* **2003**, *22*, 3723.

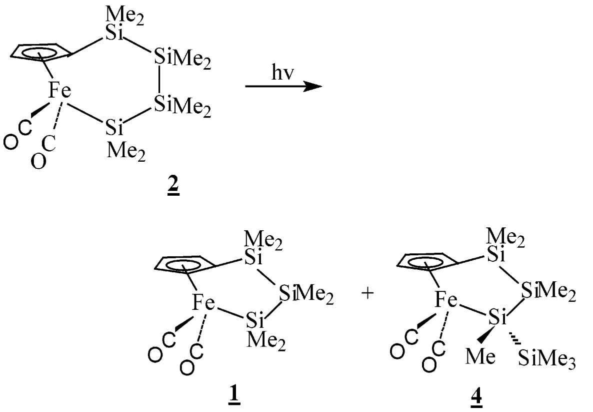
[10] Pannell, K. H.; Bassindale, A. R. *J. Organomet. Chem.* **1982**, *229*, 1.

Scheme 1



envelope conformation present in **1**. The Fe−Si bond and Si−Si bonds are slightly longer than in **1**, the angles in the five-membered ring are greater than the bond angles of **1**, and importantly the Si1−Si2−Si3 angle that was 96.26(6)° in **1** has widened to 102.95(7)° in **3**. The bulky Ph_3P group is oriented away from the trisilaferracyclopentane, presumably to avoid steric interactions.

Tetrasilaferracycle **2** exhibits the expected four ^{29}Si resonances at 19.8 ppm (Si_α), −37.8 ppm (Si_β), −46.2 ppm (Si_δ), and −20.8 ppm (Si_γ) in its ^{29}Si NMR spectrum. These values are within ±5 ppm of the data for $FpSiMe_2SiMe_2SiMe_2SiMe_3$ and suggest, appropriately, the absence of any significant strain within the six-membered ring. However, contrary to the photochemistry of **1** noted above, irradiation of a C_6D_6 solution of **2** in a sealed Pyrex glass NMR tube for 10 h resulted in the transformation of **2** into two ring-contracted trisilaferracyclopentanes, **1** and **4**, in 25% and 75% relative reaction yields, respectively, as determined by GC analysis and NMR spectroscopy, eq 7. Prolonged irradiation of the mixture resulted in the disappearance of **4**, which slowly was transformed to **1**.



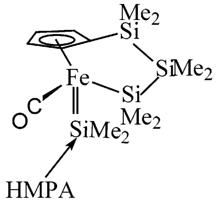
(7)

The ring-contracted ferracyclopentanes **1** and **4** are readily separated by silica gel column chromatography using a 90:10 hexane/methylene chloride mixture as eluent. The formation of **1** and **4** can reasonably be explained through iron silyl(silylene) intermediates **A** and **B**, as illustrated in Scheme 1.

The silyl(silylene) iron complex **A** with an exocyclic silylene ligand undergoes silylene, :$SiMe_2$, substitution by CO to yield the trisilaferracycle **1**. However, intermediate **A** can also undergo a 1,3-methyl shift to produce a dynamic equilibrium with the endocyclic iron silyl(silylene) intermediate **B**. Intermediate **B** does not lose its silylene, but undergoes an isomerization via a 1,2-silyl shift (of the type responsible for the isomerization noted in eq 1), resulting in the formation of the ring-contracted product **4**. The low initial yield of **1** in comparison with **4** indirectly indicates the preference of intermediate **B** over **A** in the initially kinetically driven process. However, prolonged irradiation of **4** does lead to intermediate **B**, which slowly bleeds to **1**, which is the final product of photochemistry. This chemistry contrasts with that noted in eq 1, where no significant silylene elimination has been observed upon prolonged irradiation under the same reaction conditions.

The new silaferracycle **4** was characterized by NMR and mass spectrometry. The ^{29}Si NMR spectrum of **4** exhibits four resonances, which can be assigned as follows: −7.9 ($SiMe_3$), −5.8 (Fe−*Si*), −11.2 (Fe−Si−*Si*), and −19.4 ppm (Fe−Si−Si−*Si*). Due to the Fe−*Si* chiral center, the various diastereotopic methyl groups on silicon give six signals in both the ^{1}H and ^{13}C NMR spectra. As with the other silametallacycles, the cyclopentadienyl ring carbon atoms are inequivalent, which results in five resonances at 84.5, 85.2, 90.5, 91.2, and 95.8 ppm, respectively.

For confirmation of the proposal in Scheme 1, we irradiated ferracycle **2** in the presence of hexamethylphosporamide (HMPA). Monitoring the reaction by NMR spectroscopy we were able to observe the initially formed intermediate **A** as the HMPA-stabilized (silylene) trisilaferracycle,[6,11] **5**.



5

The ^{29}Si NMR spectrum of the silylene **5** exhibited a low-field doublet at 113.5 ppm due to the Fe═Si unit, coupled with the ^{31}P atom of HMPA ($^{2}J_{Si-P} = 28$ Hz), and singlets at 16.1, −12.0, and −21.9 ppm due to α, β, and γ silicons of the trisilaferracycle, respectively. These three signals are comparable to the silicon resonances of **1** at 28.4, −9.1, and −21.2 ppm, respectively, with the Δδ values representing the change of coordination chemistry at the Fe atom. The ^{1}H NMR spectrum showed two doublets at 2.26 and 2.37 ppm for coordinated and free HMPA molecules. The ^{13}C NMR spectrum of **5** exhibited separate resonances due to diastereotopic $SiMe_2$ groups at −6.47, −5.20, −2.29, −0.96, 2.98, and 6.56 and two low-field

---

(11) Ueno, K.; Nakano, K.; Ogino, H. *Chem. Lett.* **1996**, 459.

signals due to coordinated silylene at 10.9 and 13.8 ppm. The C resonance for coordinated and free HMPA appears as doublets at 36.4 and 36.7 ppm, respectively. These data clearly support the formulation of **5** as a base-stabilized silylene complex. Attempts to isolate **5** were unsuccessful due to its extreme air and moisture sensitivity.

Experimental Section

All manipulations were carried out under nitrogen using vacuum line techniques. THF was distilled under nitrogen from benzophenone ketyl prior to use. Other solvents, hexanes and benzene, were dried over sodium metal and distilled before use; HMPA was distilled over CaO; $Cl(SiMe_2)_3Cl$,[12] $Cl(SiMe_2)_4Cl$,[13] and $Fp(SiMe_2)_3Cl$[3a] were synthesized by previously reported procedures. NMR spectra were recorded on a 300 MHz Bruker spectrometer; GC/mass spectra were recorded on a Hewlett-Packard 5890/5971 spectrometer. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN.

Synthesis of Trisilaferracycle 1. A 50 mL round-bottomed Schlenk flask was charged with 1.5 g (3.88 mmol) of $FpSiMe_2SiMe_2SiMe_2Cl$ in 15 mL of THF. To this solution at −25 °C was added 10 mL (3.90 mmol) of freshly prepared LDA in the same solvent via cannula. The color of the solution immediately changed to dark reddish-brown. The solution was stirred overnight at room temperature, and yellow insoluble material precipitated. The supernatant liquid was withdrawn via a syringe, and the THF was evaporated under vacuum. The residue was extracted with 50 mL of hexanes and filtered. The orange sticky residue was dissolved in 5 mL of hexanes and placed upon a 2.5 × 10 cm silica gel column. The yellow band was eluted with hexanes, and upon evaporation of the solvent, a yellow crystalline solid was obtained in 0.2 g (0.58 mmol, 15%) yield, mp 136−142 °C. ^1H NMR (C_6D_6): δ 0.13, 0.29, 0.63 (s, 18H, Me), 4.22 (t, 2H, Cp), 4.43 (t, 2H, Cp). ^{13}C NMR (C_6D_6): δ −4.70, −3.43, 3.36 (Me), 85.2, 90.4, 96.9 (ipso) (C_5H_4), 216.3 (CO). ^{29}Si NMR (C_6D_6): δ 28.4, −9.06, −21.2. IR (ν CO, cm^{-1}) (hexane): 1992, 1940. Anal. Calcd for $C_{13}H_{22}FeO_2Si_3$: C, 44.55; H, 6.33. Found: C, 44.57; H, 6.50. GC/MS: *m/z* 350 $[M]^+$, 9; 322 $[M - CO]^+$, 24; 73 $[SiMe_3]^+$, 100.

Synthesis of $FpSiMe_2SiMe_2SiMe_2SiMe_2Cl$. To a 30 mL THF solution of Fp^-Na^+ (prepared from 1.0 g, 2.82 mmol of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$) was added 1.74 g (5.61 mmol) of $Cl(SiMe_2)_4Cl$ in 10 mL of THF at −25 °C. The solution was stirred at this temperature for 1 h and then warmed to room temperature and stirred overnight. The solvent was removed in vacuo, and the residue was extracted with 60 mL of a 1:1 mixture of hexanes/CH_2Cl_2. The solution was filtered through Celite and the filtrate concentrated to 10 mL. A yellow solid containing 0.35 g of $Fp(SiMe_2)_4Fp$ was precipitated. The solid had poor solubility in hexanes and was readily separated by filtration. The solvent was removed from the filtrate and dissolved in 8 mL of cold hexanes, and traces of an insoluble yellow residue of $Fp(SiMe_2)_4Fp$ were removed by filtration. This process was repeated and the solvent was removed under vacuum, and an orange oily residue containing 0.64 g (26% yield) of >90% pure $FpSiMe_2SiMe_2SiMe_2SiMe_2Cl$ along with traces of $Fp(SiMe_2)_4Fp$ was obtained. ^1H NMR (C_6D_6): δ 0.27, 0.51, 0.86, 1.22 (s, 24H, Me), 4.22 (s, 5H, Cp). ^{13}C NMR (C_6D_6): δ −7.25, −5.52, 2.29, 3.59 (Me), 83.11 (C_5H_5), 215.63 (CO). ^{29}Si NMR (C_6D_6): δ 22.69, 15.09, −40.69, −50.20. IR (ν CO, cm^{-1}) (hexane): 1997, 1947.

Synthesis of Tetrasilaferracycle 2. A 50 mL round-bottomed Schlenk flask was charged with 0.64 g (1.44 mmol) of $FpSiMe_2SiMe_2SiMe_2SiMe_2Cl$ in 10 mL of THF. To this solution at 0 °C was added 6 mL (1.45 mmol) of freshly prepared LDA in the same solvent via cannula. The color of the solution immediately changed to dark reddish-brown. The solution was stirred overnight at room temperature, and the THF was removed in vacuo. The residue was extracted with 50 mL of a 1:1 mixture of hexanes/CH_2Cl_2 and filtered. The orange sticky residue was dissolved in 5 mL of hexanes and placed upon a 2.5 × 10 cm silica gel column, and the yellow band formed was eluted with an 80:20 hexanes/CH_2Cl_2 mixture. Upon evaporation of the solvent, **2** was obtained as a yellow oil (0.14 g, 0.34 mmol, 24% yield). ^1H NMR (C_6D_6): δ 0.19, 0.21, 0.29, 0.58 (s, 24H, Me), 4.22 (t, 2H, Cp), 4.47 (t, 2H, Cp). ^{13}C NMR (C_6D_6): δ −6.06, −4.77, −2.05, 3.69 (Me), 84.5, 87.1 (ipso), 92.1 (C_5H_4), 216.1 (CO). ^{29}Si NMR (C_6D_6): δ 19.8, −20.8, −37.8, −46.2. IR (ν CO, cm^{-1}) (hexane): 1994, 1942. Anal. Calcd for $C_{15}H_{28}FeO_2Si_4$: C, 44.10; H, 6.91. Found: C, 43.49; H, 6.70. GC/MS: *m/z* 408 $[M]^+$, 24; 380 $[M - CO]^+$, 100; 73 $[SiMe_3]^+$, 41.

Photolysis of 2 in C_6D_6. A solution of compound **2** (0.12 g, 0.31 mmol) in 1.0 mL of degassed C_6D_6 was sealed in a Pyrex NMR tube. The NMR tube was placed at a distance of 10 cm from a 450 W medium-pressure mercury lamp and irradiated. The progress of the photoreaction was monitored by ^1H, ^{13}C, and ^{29}Si NMR spectroscopy. The starting material completely disappeared after 10 h of irradiation with the formation of ring-contracted ferracycles **1** and **4** in 1:3 ratio. The solution was placed on a 2.5 × 10 cm silica gel column, and first a yellow band was eluted with hexane. Upon removal of the solvent in vacuo, 0.015 g (0.04 mmol, 13% yield) of **1** along with traces of **4** was obtained. The second yellow band was eluted with a 90:10 hexane/CH_2Cl_2 mixture that after evaporation of the solvent gave 0.028 g (0.068 mmol, 22% yield) of **4**. ^1H NMR (C_6D_6): δ 0.13, 0.17, 0.36, 0.37 (s, 12H, $SiMe_2$), 0.33 (s, 9H, $SiMe_3$), 0.59 (s, 3H, SiMe), 4.20 (t, 1H, Cp), 4.34−4.47 (m, 3H, Cp). ^{13}C NMR (C_6D_6): δ −3.79, −3.68, −3.46, −2.76, 1.07 (Me), 84.5, 85.2, 90.5, 91.2, 95.8 (ipso) (C_5H_4), 216.0, 216.5 (CO). ^{29}Si NMR (C_6D_6): δ −5.88, −7.97, −11.2, −19.4. GC/MS: *m/z* 408 $[M]^+$, 24; 380 $[M - CO]^+$, 35; 307 $[M - CO - SiMe_3]^+$, 19; 73 $[SiMe_3]^+$, 100. HR MS (EI): exact mass found 408.0511, calcd for $C_{15}H_{28}O_2FeSi_4$ 408.0516.

Photolysis of 2 in the Presence of HMPA. A 5 mm Pyrex NMR tube was charged with a mixture of 0.085 g (0.19 mmol) of **2** and 0.14 g of HMPA (0.78 mmol) in 1.0 mL of degassed C_6D_6, and the tube was sealed under vacuum. The sealed NMR tube was irradiated with a 450 W medium-pressure mercury lamp, and the reaction was monitored by ^1H, ^{13}C, and ^{29}Si NMR spectroscopy. After 3 h of irradiation, the starting material had disappeared and spectral data showed the formation of the HMPA-stabilized (silylene)trisilametallacycle, **5**. All attempts to isolate the complex led to its decomposition. ^1H NMR (C_6D_6): δ 0.39, 0.40, 0.45, 0.48, 0.60, 0.64, 0.70 (s, $SiMe_2$), 2.26 (d, $^2J_{P-H} = 10.2$ Hz, coordinated HMPA), 2.37 (d, free HMPA), 4.15−4.19, 4.45−4.54, 4.66, 4.86 (complex m, Cp). ^{13}C NMR (C_6D_6): δ −6.47, −5.20, −2.29, −0.96, 2.98, 6.56 ($SiMe_2$), 10.9 (s), 13.8 (d, $=SiMe_2$), 36.4 (d, $^2J_{P-C} = 5$ Hz, coordinated HMPA), 36.7 (d, free HMPA), 77.0, 84.7, 85.6, 87.3, 90.8 (ipso) (C_5H_4), 219.7 (CO). ^{29}Si NMR (C_6D_6): δ 113.1 (d, $^2J_{Si-P} = 28$ Hz), 16.1, −12.0, −21.9.

Synthesis of Trisilametallacycle 3. To a solution of **1** (0.175 g) (0.5 mmol) in 30 mL of hexane, in a quartz tube, was added 0.30 g (1.14 mmol) of Ph_3P. The solution was irradiated with a Hanovia 450-W medium-pressure mercury lamp at a distance of 4 cm. The progress of the photochemical reaction monitored by infrared spectroscopy indicated that after 10 h the ν(CO) bands of the starting material **1** had been replaced by a single CO stretching frequency at 1920 cm^{-1} and the solution became dark red. The hexane solution was filtered through Celite, and the solvent was evaporated. The red residue was placed upon a silica gel column, and a red band was eluted with a 1:1 hexane/benzene mixture. Upon evaporation of solvent, a red compound was obtained, which was recrystallized from hexanes. Yield: 0.07 g (0.12 mmol, 24%); mp 148−150 °C. ^1H NMR (C_6D_6): δ −0.09, 0.33, 0.42, 0.43, 0.49, 0.74, (s, 18H, Me); 3.43 (m, 1H, $J = 1.5$ Hz, Cp), 4.33 (m, 1H, $J = 1.2$ Hz, Cp), 4.43 (m, 1H, Cp), 5.15 (m, 1H, $J = 1.2$ Hz, Cp), 6.95−7.04, 7.59−7.66 (m, 15H, Ph). ^{13}C NMR (C_6D_6): δ −4.65, −4.36, −2.94, −1.31, 1.05, 6.11 (Me), 83.2, 88.1 (ipso), 89.3, 92.9,

---

[12] Oakley, R. T.; Stanislawski, D. A.; West, R. *J. Organomet. Chem.* **1978**, *157*, 389.

[13] Kumada, M.; Ishikawa, M.; Maeda, S. *J. Organomet. Chem.* **1964**, *2*, 478.

Table 1. Crystallographic and Refinement Data for 1 and 3

	1	**3**
empirical formula	$C_{13}H_{22}FeO_2Si_3$	$C_{30}H_{37}FeOPSi_3$
source	synthesis	synthesis
cryst color	red	orange
cryst habit	irregular fragment	prism
cryst size/mm^3	0.56 × 0.50 × 0.16	0.20 × 0.20 × 0.12
a/Å	13.183(5)	13.363(2)
b/Å	10.707(5)	14.929(3)
c/Å	13.350(5)	31.447(5)
α/deg	90	90
β/deg	106.33(3)	98.188(3)
γ/deg	90	90
volume/Å^3	1808.3(13)	6209.3(18)
cryst syst	monoclinic	monoclinic
space group	$P2(1)/n$	$C2/c$
Z	4	8
D_c/g cm^{-3}	1.287	1.251
μ/mm^{-1}	1.028	0.674
abs corr	semiempirical	Bruker SADABS program
temp/°C	23(2)	23(2)
wavelength	0.71073 Å	0.71073 Å
monochromator	graphite	graphite
diffractometer	Siemens R3m/V	Bruker SMART with Apex CCD
no. of reflns collected	3480	25325
θ range/deg	1.92−25.05 (100% completeness)	2.23−22.48 (99.6% completeness)
no. of ind reflns	3202 [R(int) = 0.0495]	4464 [R(int) = 0.0465]
structure solution technique	direct methods	direct methods
structure solution program	SHELXS-97 (Sheldrick, 1990)	SHELXS-97 (Sheldrick, 1990)
refinement technique	full-matrix least-squares on F^2	full-matrix least-squares on F^2
refinement program	SHELXS-97 (Sheldrick, 1997)	SHELXS-97 (Sheldrick, 1997)
function minimized	$\sum w(F_o^2 - F_c^2)^2$	$\sum w(F_o^2 - F_c^2)^2$
goodness-of-fit on F^2	1.014	1.252
R1,^{a} wR2^b [$I > 2\sigma(I)$]	0.0426, 0.0989	0.0708, 0.01572
R1, wR2 (all data)	0.0633, 0.1103	0.0827, 0.1639

^{a} $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $wR2 = \{\sum[w(F_o^2\text{-}F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

Table 2. Bond Lengths and Angles for $(C_5H_4)Fe(CO)_2(SiMe_2)_3$, 1

Bond Lengths (Å)			
Fe−C7	1.737(4)	Fe−C6	1.740(4)
Fe−C1	2.159(3)	Fe−Si1	2.3437(12)
Si2−Si3	2.3367(15)	Si2−Si1	2.3389(15)
Si3−C1	1.878(4)	O1−C6	1.155(4)
O2−C7	1.152(5)	C1−C5	1.421(5)
Bond Angles (deg)			
C7−Fe−C1	144.52(15)	C6−Fe−C1	118.84(15)
C7−Fe−Si1	82.08(13)	C6−Fe−Si1	86.61(13)
C1−Fe−Si1	90.70(9)	Si3−Si2−Si1	96.26(6)
C9−Si1−Fe	111.36(14)	Si2−Si1−Fe	103.82(5)
C1−Si3−Si2	101.78(11)	C5−C1−Si3	129.7(3)
Si3−C1−Fe	126.47(16)	O1−C6−Fe	177.5(4)
O2−C7−Fe	179.5(4)		

94.1 (C_5H_4), 128.7 (d, J_{P-C} = 6.8 Hz), 129.4 (d) 133.8 (d, J_{P-C} = 9.8 Hz), 139.1 (d, J_{P-C} = 40.2 Hz), 220.2 (d, J_{P-C} = 29.4 Hz, CO). ^{29}Si NMR (C_6D_6): δ 16.8 (d, $^2J_{Si-P}$ = 29.5 Hz), −12.9 (d, $^3J_{Si-P}$ = 2.4 Hz), −20.9 (s). ^{31}P NMR (C_6D_6): δ 81.9. IR (ν CO, cm^{-1}) (hexane): 1905. Anal. Calcd for $C_{30}H_{37}FeOPSi_3$: C, 61.63; H, 6.38. Found: C, 61.74; H, 6.57.

Structure Determinations. A red fragment of $C_{13}H_{22}FeO_2Si_3$ (**1**) of approximate dimensions 0.56 × 0.50 × 0.16 mm was mounted in a random orientation at the tip of a glass fiber for X-ray examination and data collection. All data were collected at 296(2) K using the Siemens/Nicolet P3/V software[14a] on a Siemens R3m/V single-crystal diffractometer with graphite-monochromated Mo Kα radiation, λ(Mo Kα) = 0.71073, and a point detector. The collection was conducted over slightly more than one quadrant of reciprocal space, in the range $-2 \leq h \leq 15$, $0 \leq k \leq 12$, $-15 \leq l \leq 15$. The data were corrected for Lorentz and polarization effects, and a semiempirical absorption correction was also applied.

Table 3. Bond Lengths and Angles for $(C_5H_4)Fe(PPh_3)(CO)(SiMe_2)_3$, 3

Bond Lengths (Å)			
Fe−C12	1.702(5)	Fe−C1	2.118(4)
Fe−P	2.1935(12)	Fe−Si1	2.3491(16)
P−C19	1.845(5)	Si1−Si2	2.371(2)
Si2−Si3	2.350(2)	Si3−C1	1.875(5)
O−C12	1.171(5)		
Bond Angles (deg)			
C12−Fe−P	93.58(15)	C1−Fe−Si1	95.71(15)
P−Fe−Si1	99.91(5)	Fe−Si1−Si2	103.24(7)
Si3−Si2−Si1	102.95(7)	O−C12−Fe	177.0(4)

A red prism of $C_{30}H_{37}FeOPSi_3$ (**3**) of approximately 0.12 mm × 0.20 mm × 0.20 mm was used for the X-ray crystallographic analysis. The X-ray intensity data were measured at 296(2) K on a Bruker SMART APEX diffractometer with a Bruker APEX CCD area detector system equipped with a graphite monochromator and a Mo Kα fine-focus sealed tube. The detector was placed at a distance of 5.953 cm from the crystal. A total of 2400 frames were collected with a scan width of 0.3° in ω and an exposure time of 10 s/frame. The frames were integrated with the Bruker SAINT software package[14b] using a narrow-frame integration algorithm. The structures were solved and refined using the Bruker SHELXTL (Version 6.10)[14c] software package.

Pertinent crystallographic data are given in Table 1, the structures and numbering scheme are shown in Figures 1 and 2, and selected bond lengths and angles are presented in Tables 2 and 3.

Acknowledgment. This research has been supported by the NIH-MARC program. We thank Nebraska Center for Mass Spectrometry, Lincoln, NE, for recording the high-resolution mass spectrum of **4**.

Supporting Information Available: This material is available free of charge via the Internet at http://pubs.acs.org.

OM060320C

---

[14] (a) *Siemens P3/V* data collection program Version 4.11; Siemens Analytical X-ray instruments Inc.: Madison, WI, 1990. (b) *SAINTPLUS* data reduction program Version 5.622; Bruker-AXS: Madison WI, 2001. (c) *SHELXTL* software package Version 6.10; Bruker-AXS: Madison, WI, 2000.