Selective Abstraction of an OR Group in the Reaction of (C5H5)(CO)Fe{SiMe2(OR1)}{PN(Me)CH2CH2NMe(OR2)} with a Lewis Acid: Preferential Formation of a Silylene Complex over a Phosphenium Complex

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The reactions of Cp(CO)Fe{SiMe2(OR1)}{PN(Me)CH2CH2NMe(OR2)} (R1 = Me, Et, R2 = Me, Et) (**1**) with a Lewis acid (BF3·OEt2 or Me3SiOSO2CF3 (TMSOTf)) have been examined. In the reaction with an excess of BF3·OEt2, not only is an OR group on Si replaced by fluoride but also an OR group attached to the phosphorus is abstracted, to give the cationic phosphenium complex Cp(CO)Fe(SiMe2F){PN(Me)CH2CH2NMe}+BF4− (**3**). The reaction with an equimolar amount of BF3·OEt2 leads only to fluorination of the silyl group and isolation of Cp(CO)Fe{SiMe2F}{PN(Me)CH2CH2NMe(OR)} (R = R1 or R2) (**2**), indicating that BF3·OEt2 reacts preferably with the OR group on Si rather than with that on P. In the reaction with equimolar or excess TMSOTf, an OR1 group on Si is abstracted selectively to give the corresponding silylene complex Cp(CO){PN(Me)CH2CH2NMe(OR2)}Fe=SiMe2·OTf (**5**). Complex **5** was characterized by spectroscopic data and by its further reaction with a Lewis base such as pyridine or PMe3, leading to the corresponding base-stabilized silylene complex. The structure of the PMe3-stabilized silylene complex [Cp(CO){PN(Me)CH2CH2NMe(OEt)}-Fe=SiMe2·PMe3]OTf (**7b**) has been determined by single-crystal X-ray diffraction.

Introduction

The chemistry of transition-metal compounds having a multiple bond with a main-group element is a subject of current interest. For example, carbene complexes, which have a double bond between a transition metal and a carbon atom, have been widely investigated regarding their preparations, structures, and reactivities.[1] Since cationic phosphenium salts and silylenes assume sp² hybridization and are thus regarded as isolobal with singlet carbenes (Chart 1),[2] they are also expected to coordinate to a transition metal via both σ-donor and π-acceptor orbitals to give the corresponding carbene-like complexes. For these reasons the coordination chemistry of phosphenium cations and silylenes, and their own chemistry as well, has received considerable attention, and many cationic phosphenium[3−10] and silylene complexes[11,12] have been prepared.

Chart 1

Phosphenium Cation   Carbene   Silylene
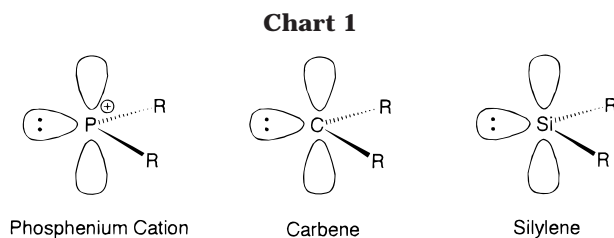
We have recently developed a new method for the preparation of cationic-phosphenium transition-metal

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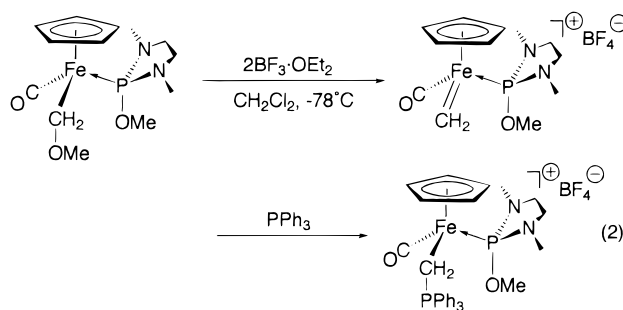
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complexes of Cr,[6] Mo,[6−8] W,[6,8] Fe,[9] and Ru.[10] In the reaction of Cp(CO)Fe(SiMe₃){PN(Me)CH₂CH₂NMe(OMe)} with BF₃·OEt₂, for example, an OMe group on the phosphorus is abstracted as an anion to afford the cationic phosphenium complex Cp(CO)Fe(SiMe₃){PN-(Me)CH₂CH₂NMe}⁺BF₄⁻, which has some double bond character between P and Fe (eq 1).[9a,b] A similar reaction

$$\text{(1)}$$
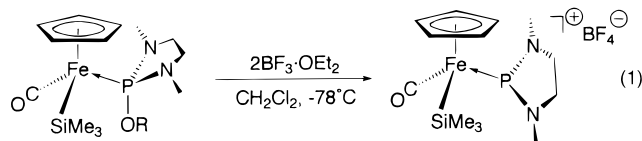
of iron complexes having an alkyl, germyl, or stannyl group in place of a silyl group gave the corresponding cationic phosphenium complexes at least in the initial step.[9a−c]

Interestingly, we also found that the reaction with BF₃·OEt₂ of a methoxymethyl−iron complex, Cp(CO)-Fe(CH₂OMe){PN(Me)CH₂CH₂N(Me)(OMe)}, which has an OMe group on both C and P, gave the cationic carbene complex (eq 2).[9a] In this reaction, the OMe

$$\text{(2)}$$

group on C was selectively abstracted, but no phosphe-

nium complexes (which would be formed by abstraction of an OMe group from P) were observed.

As an extension of our study, we examine here reactions of alkoxysilyl−iron complexes having both Si−OR and P−OR groups with a Lewis acid such as BF₃·OEt₂ or Me₃SiOSO₂CF₃ (TMSOTf). It is expected that a silylene complex would be obtained if an OR group on Si is abstracted, while a phosphenium complex would be obtained if an OR group on P is abstracted. In any case, the formation of the iron complexes with a multiple bond to a main-group element would be obtained in these reactions.

Experimental Section

General Remarks. All reactions were carried out under an atmosphere of dry nitrogen by using standard Schlenk tube techniques. All solvents were purified by distillation: ether, THF, and benzene were distilled from sodium/benzophenone, heptane, hexane, and pentane were distilled from sodium metal, and CH₂Cl₂ was distilled from P₂O₅. All solvents were stored under a nitrogen atmosphere. BF₃·OEt₂ and TMSOTf were distilled prior to use. PN(Me)CH₂CH₂NMe(OMe) (abbreviated to PNN(OMe) in this paper),[13] PNN(OEt),[13] ClSiMe₂-(OMe),[14] and ClSiMe₂(OEt)[14] were prepared according to the respective literature methods. Cp(CO)₂FeSiMe₂(OMe)[15] and Cp(CO)₂FeSiMe₂(OEt) were prepared from [Cp(CO)₂Fe]K and ClSiMe₂(OMe) or ClSiMe₂(OEt), respectively. Other reagents employed in this study were used as received. Column chromatography was carried out quickly in air on Merck aluminum oxide 90 (No. 1.01097).

IR spectra were recorded on a Shimadzu FTIR-8100A spectrometer. A JEOL LA-300 multinuclear spectrometer was used to obtain ¹H, ¹³C, ¹⁹F, ²⁹Si, and ³¹P NMR spectra. The reference was as follows: for ¹H and ¹³C NMR data, Si(CH₃)₄ as an internal standard; for ¹⁹F NMR data, CFCl₃ as an external standard; for ²⁹Si NMR data, Si(CH₃)₄ as an external standard; for ³¹P NMR data, 85% H₃PO₄ as an external standard. Elemental analyses were performed on a Perkin-Elmer 2400CHN elemental analyzer.

Preparation of Cp(CO){SiMe₂(OMe)}Fe{PNN(OMe)}, 1a. Cp(CO)₂FeSiMe₂(OMe) (1550 mg, 5.82 mmol), benzene (90 mL), and PNN(OMe) (1.00 mL, 6.82 mmol) were put in a Pyrex Schlenk tube, and the solution was irradiated with a 400 W medium-pressure mercury arc lamp at 0 °C for 15 h. After removal of the solvent, the resulting residue was loaded on an alumina column and eluted with CH₂Cl₂. The yellow band which developed was collected and was reloaded on an alumina column. The yellow band eluted with CH₂Cl₂/hexane (1/4) was collected, and the solvents were removed in vacuo to give a yellow powder of **1a** (1877 mg, 4.84 mmol, 83%). Anal. Calcd for C₁₄H₂₇FeN₂O₃PSi: C, 43.53; H, 7.05; N, 7.25. Found: C, 43.51; H, 7.30; N, 7.00.

Preparation of Cp(CO){SiMe₂(OMe)}Fe{PNN(OEt)}, 1b. Complex **1b** was prepared from Cp(CO)₂FeSiMe₂(OMe) and PNN(OEt) in the same manner as was **1a**. Yield: 71%. Anal. Calcd for C₁₅H₂₉FeN₂O₃PSi: C, 45.01; H, 7.30; N, 7.00. Found: C, 44.78; H, 7.54; N, 6.98.

Preparation of Cp(CO){SiMe₂(OEt)}Fe{PNN(OMe)}, 1c. Complex **1c** was prepared from Cp(CO)₂FeSiMe₂(OEt) and PNN(OMe) in the same manner as was **1a**. Yield: 85%. Anal. Calcd for C₁₅H₂₉FeN₂O₃PSi: C, 45.01; H, 7.30; N, 7.00. Found: C, 45.18; H, 7.10; N, 6.89.

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Preparation of Cp(CO){SiMe₂(OEt)}Fe{PNN(OEt)}, **1d.** Complex **1d** was prepared from Cp(CO)₂FeSiMe₂(OEt) and PNN(OEt) in the same manner as was **1a**. Yield: 90%. Anal. Calcd for $C_{16}H_{31}FeN_2O_3PSi$: C, 46.38; H, 7.54; N, 6.76. Found: C, 46.55; H, 7.16; N, 6.71.

Preparation of Cp(CO)(SiMe₂F)Fe{PNN(OMe)}, **2a.** A solution of **1a** (95 mg, 0.25 mmol) in CH_2Cl_2 (3 mL) was cooled to −78 °C, and then $BF_3 \cdot OEt_2$ (0.035 mL, 0.25 mmol) was added. After being warmed to room temperature, the reaction mixture was charged on an alumina column. The yellow band eluted with CH_2Cl_2 was collected, and the solvent was removed under reduced pressure to give **2a** as a lemon-yellow powder (42 mg, 0.11 mmol, 46%). Anal. Calcd for $C_{13}H_{24}FFeN_2O_2PSi$: C, 41.72; H, 6.46; N, 7.49. Found: C, 41.86; H, 6.35; N, 7.31.

Preparation of Cp(CO)(SiMe₂F)Fe{PNN(OEt)}, **2b.** Complex **2b** was prepared from **1d** and $BF_3 \cdot OEt_2$ in the same manner as was **2a**. Yield: 56%. Anal. Calcd for $C_{14}H_{26}FFeN_2O_2PSi$: C, 43.31; H, 6.75; N, 7.21. Found: C, 43.40; H, 6.62; N, 7.05.

Preparation of Cp(CO)(SiMe₂F)Fe(PNN)⁺BF₄⁻, **3.** A solution of **1a** (147 mg, 0.38 mmol) in CH_2Cl_2 (1.5 mL) was cooled to −78 °C, and then $BF_3 \cdot OEt_2$ (0.28 mL, 2.30 mmol) was added. After the solution was warmed to room temperature, it was directly subjected to spectroscopic measurements, which confirmed the formation of **3**.

Preparation of Cp(CO)(SiMe₂F)Fe{PNN(CH₂Ph)}, **4.** A solution of **1a** (267 mg, 0.69 mmol) in CH_2Cl_2 (5 mL) was cooled to −78 °C, and then $BF_3 \cdot OEt_2$ (0.18 mL, 1.43 mmol) was added. After the reaction mixture had been stirred at −78 °C for 1 h, it was treated with PhCH₂MgCl (0.35 mL of 2.0 M THF solution, 0.70 mmol), warmed to room temperature, and then stirred for 2 h to complete the reaction. The solvent was removed under reduced pressure, and the residue was loaded on an alumina column. The yellow band eluted with CH_2Cl_2 was reloaded on a silica gel column. The yellow band eluted with CH_2Cl_2/hexane (1/1) was collected, and the solvents were removed in vacuo to give a lemon-yellow powder of **4** (95 mg, 0.22 mmol, 32%). Anal. Calcd for $C_{19}H_{28}FFeN_2OPSi$: C, 52.54; H, 6.50; N, 6.45. Found: C, 52.29; H, 6.30; N, 6.54.

Preparation of Cp(CO)(SiMe₂)Fe{PNN(OMe)}⁺OTf⁻, **5a.** A solution of **1a** (130 mg, 0.34 mmol) in CD_2Cl_2 (1 mL) was cooled to −78 °C, and then TMSOTf (0.061 mL, 0.34 mmol) was added. After the solution was stirred for 15 min, it was subjected to spectroscopic measurements, which confirmed the formation of **5a**.

Preparation of Cp(CO)(SiMe₂)Fe{PNN(OEt)}⁺OTf⁻, 5b. A solution of **1d** (130 mg, 0.34 mmol) in CD_2Cl_2 (1 mL) was cooled to −78 °C, and then TMSOTf (0.061 mL, 0.34 mmol) was added. After the solution was stirred for 15 min, it was subjected to spectroscopic measurements, which suggested the formation of **5b**.

Preparation of Cp(CO){SiMe₂(NC₆H₅)}Fe{PNN(OMe)}⁺OTf⁻, 6a. TMSOTf (0.082 mL, 0.45 mmol) was added to a solution of **1a** (175 mg, 0.45 mmol) in CH_2Cl_2 cooled to −78 °C. After the reaction mixture had been stirred at −78 °C for 1 h, it was treated with pyridine (0.037 mL, 0.45 mmol), stirred for 30 min, and then concentrated to ca. 2 mL under reduced pressure. After addition of ether (5 mL) at −78 °C, the solution was kept for crystallization at −78 °C for 2 days to give yellow microcrystals, which were collected by filtration, washed with ether and pentane, and dried in vacuo, yielding **6a** (210 mg, 0.39 mmol, 86%). The complex was so hygroscopic that correct elemental analysis data could not be obtained, though satisfactory spectroscopic data were obtained.

Preparation of Cp(CO){SiMe₂(NC₆H₅)}Fe{PNN(OEt)}⁺OTf⁻, 6b. Complex **6b** was prepared from **1d**, TMSOTf, and pyridine in the same manner as that for **6a**. Yield: 84%. The complex was so hygroscopic that correct elemental analysis data could not be obtained, though satisfactory spectroscopic data were obtained.

Preparation of Cp(CO){SiMe₂(PMe₃)}Fe{PNN(OMe)}⁺OTf⁻, 7a. Complex **7a** was prepared from **1a**, TMSOTf, and PMe₃ in the same manner as that for **6a**. The isolated yellow powder consisted mainly of **7a**, but it contained some unremovable impurities, which prevented us from obtaining ¹H and ¹³C NMR data and elemental analysis data for **7a**, though its IR data and ²⁹Si and ³¹P NMR data were obtained. IR ($ν_{CO}$, in CH_2Cl_2, cm⁻¹): 1928. ²⁹Si NMR (δ, in CH_2Cl_2): 60.83 (dd, J_{PSi} = 31.6, 54.8 Hz). ³¹P NMR (δ, in CH_2Cl_2): −16.72 (s, PMe₃), 170.25 (s, PNN(OMe)).

Preparation of Cp(CO){SiMe₂(PMe₃)}Fe{PNN(OEt)}⁺OTf⁻, 7b. Complex **7b** was prepared from **1d**, TMSOTf, and PMe₃ in the same manner as that for **6a**. The isolated yellow powder consisted mainly of **7b**, but it contained some unremovable impurities such as **7a**, and only its IR data and ²⁹Si and ³¹P NMR data were obtained. In this case, a small amount of pure single crystals of **7b** was obtained, which was subjected to the X-ray analysis. IR ($ν_{CO}$, in CH_2Cl_2, cm⁻¹): 1928. ²⁹Si NMR (δ, in CH_2Cl_2): 58.20 (dd, J_{PSi} = 35.2, 56.6 Hz). ³¹P NMR (δ, in CH_2Cl_2): −16.86 (s, PMe₃), 166.86 (s, PNN(OEt)).

X-ray Structure Determination for 7b. Crystallographic and experimental details of X-ray crystal structure analysis for **7b** are given in Table 2. A single crystal of **7b** was mounted on a glass fiber. All measurements were made on a MacScience DIP2030 imaging plate area detector with graphite-monochromated Mo Kα radiation ($λ$ = 0.710 69 Å). Indexing was performed from one still which was exposed for 6.0 min. The crystal-to-detector distance was 100 mm with the detector at the zero swing position. Readout was performed in the 0.050 mm pixel mode. Cell constants and an orientation matrix for data collection corresponded to a primitive monoclinic cell with dimensions of a = 27.530(1) Å, b = 14.6560(3) Å, c = 15.5390-(5) Å, $β$ = 93.796(1)°, Z = 8, and V = 5450.7(3) Å³. $C2/c$ was selected as the space group, which led to successful refinements. The data were collected at a temperature of 200 ± 1 K to a maximum 2θ value of 50.0°.

The structure was solved by heavy-atom Patterson methods[16] and expanded using Fourier techniques.[17] The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included, but their positions were not refined; isotropic B values were refined. The final cycle of full-matrix least-squares refinement was calculated on the basis of 4044 observed reflections ($I > 3σ(I)$) and 334 variable parameters and converged (the largest parameter shift was less than 0.01 times its esd) with unweighted and weighted agreement factors R = 0.044 and R_w = 0.050. All calculations were performed on an SGI Indy O₂ computer using the program system teXsan[18] with neutral atom scattering factors from Cromer and Waber.[19]

Results and Discussion

Iron complexes having an alkoxysilyl group, SiMe₂-(OR¹) (R¹ = Me, Et), and diamino-substituted phosphite, PNN(OR²) (R² = Me, Et) standing for $\overline{PN(Me)CH_2CH_2}$-NMe(OR²), were prepared from Cp(CO)₂FeSiMe₂(OR¹) and PNN(OR²) by photoreaction (Experimental Section). The complexes were characterized by IR, ¹H, ¹³C, ²⁹Si, and ³¹P NMR spectra as well as elemental analysis.

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Table 1. Spectroscopic Data

complex	^{1}H NMR δ (ppm)^a	^{13}C NMR δ (ppm)^a	^{31}P NMR δ (ppm)^a	^{29}Si and ^{19}F NMR δ (ppm)^a	IR (ν_{CO}) (cm^{-1})^b
1a	0.32 (s, 3H, SiCH$_3$) 0.41 (s, 3H, SiCH$_3$) 2.72 (d, J_{PH} = 10.6 Hz, 3H, NCH$_3$) 2.74 (d, J_{PH} = 10.6 Hz, 3H, NCH$_3$) 3.09 (m, 2H, NCH$_2$) 3.15 (d, J_{PH} = 11.4 Hz, 3H, POCH$_3$) 3.29 (m, 2H, NCH$_2$) 3.39 (s, 3H, SiOCH$_3$) 4.41 (s, 5H, C$_5$H$_5$)	7.49 (s, SiCH$_3$) 8.44 (s, SiCH$_3$) 33.07 (d, J_{PC} = 11.2 Hz, NCH$_3$) 33.32 (d, J_{PC} = 11.8 Hz, NCH$_3$) 50.34 (s, SiOCH$_3$) 50.92 (d, J_{PC} = 13.1 Hz, POCH$_3$) 51.17 (d, J_{PC} = 1.9 Hz, NCH$_2$) 51.62 (d, J_{PC} = 3.7 Hz, NCH$_2$) 81.06 (d, J_{PC} = 1.2 Hz, C$_5$H$_5$) 218.97 (d, J_{PC} = 41.0 Hz, CO)	176.71 (s)	75.08 (d, J_{PSi} = 48.0 Hz)	1905
1b	0.35 (s, 3H, SiCH$_3$) 0.46 (s, 3H, SiCH$_3$) 1.10 (t, J_{HH} = 7.0 Hz, 3H, CH$_2$CH_3) 2.74 (d, J_{PH} = 10.6 Hz, 6H, NCH$_3$) 3.08 (m, 2H, NCH$_2$) 3.26 (m, 2H, NCH$_2$) 3.40 (s, 3H, OCH$_3$) 3.50 (m, 2H, CH_2CH$_3$) 4.42 (s, 5H, C$_5$H$_5$)	7.48 (s, SiCH$_3$) 8.64 (s, SiCH$_3$) 16.01 (d, J_{PC} = 5.6 Hz, CH$_2$CH$_3$) 33.07 (d, J_{PC} = 11.2 Hz, NCH$_3$) 33.43 (d, J_{PC} = 11.2 Hz, NCH$_3$) 50.35 (s, OCH$_3$) 51.12 (d, J_{PC} = 1.2 Hz, NCH$_2$) 51.54 (d, J_{PC} = 3.7 Hz, NCH$_2$) 59.72 (d, J_{PC} = 13.1 Hz, CH$_2$CH$_3$) 81.10 (s, C$_5$H$_5$) 218.52 (d, J_{PC} = 41.5 Hz, CO)	173.16 (s)	74.93 (d, J_{PSi} = 48.0 Hz)	1905
1c	0.33 (s, 3H, SiCH$_3$) 0.40 (s, 3H, SiCH$_3$) 1.15 (t, J_{HH} = 6.4 Hz, 3H, CH$_2$CH_3) 2.73 (d, J_{PH} = 11.7 Hz, 3H, NCH$_3$) 2.77 (d, J_{PH} = 11.4 Hz, 3H, NCH$_3$) 3.09 (m, 2H, NCH$_2$) 3.16 (d, J_{PH} = 11.2 Hz, 3H, OCH$_3$) 3.31 (m, 2H, NCH$_2$) 3.64 (q, J_{HH} = 6.6 Hz, 2H, CH_2CH$_3$) 4.41 (s, 5H, C$_5$H$_5$)	8.14 (s, SiCH$_3$) 8.60 (s, SiCH$_3$) 18.77 (s, CH$_2$$CH_3$) 33.15 (d, J_{PC} = 11.2 Hz, NCH$_3$) 33.39 (d, J_{PC} = 11.8 Hz, NCH$_3$) 50.91 (d, J_{PC} = 13.1 Hz, OCH$_3$) 51.21 (d, J_{PC} = 2.5 Hz, NCH$_2$) 51.66 (d, J_{PC} = 3.1 Hz, NCH$_2$) 57.78 (s, CH$_2$CH$_3$) 81.17 (d, J_{PC} = 1.2 Hz, C$_5$H$_5$) 219.05 (d, J_{PC} = 41.0 Hz, CO)	175.85 (s)	71.63 (d, J_{PSi} = 47.2 Hz)	1904
1d	0.34 (s, 3H, SiCH$_3$) 0.43 (s, 3H, SiCH$_3$) 1.08 (t, J_{HH} = 7.2 Hz, 3H, POCH$_2$CH_3) 1.15 (t, J_{HH} = 6.4 Hz, 3H, SiOCH$_2$CH_3) 2.72 (d, J_{PH} = 10.6 Hz, 3H, NCH$_3$) 2.75 (d, J_{PH} = 10.6 Hz, 3H, NCH$_3$) 3.06 (m, 2H, NCH$_2$) 3.25 (m, 2H, NCH$_2$) 3.50 (m, 2H, POCH_2CH$_3$) 3.64 (q, J_{HH} = 7.2 Hz, 2H, SiOCH_2CH$_3$) 4.40 (s, 5H, C$_5$H$_5$)	8.13 (s, SiCH$_3$) 8.78 (s, SiCH$_3$) 16.02 (d, J_{PC} = 5.6 Hz, POCH$_2$$CH_3$) 18.76 (s, SiOCH$_2$$CH_3$) 33.10 (d, J_{PC} = 11.2 Hz, NCH$_3$) 33.45 (d, J_{PC} = 11.8 Hz, NCH$_3$) 51.13 (d, J_{PC} = 1.9 Hz, NCH$_2$) 51.54 (d, J_{PC} = 3.7 Hz, NCH$_2$) 57.74 (s, SiOCH$_2$CH$_3$) 59.65 (d, J_{PC} = 13.1 Hz, POCH$_2$CH$_3$) 81.16 (s, C$_5$H$_5$) 219.02 (d, J_{PC} = 41.0 Hz, CO)	173.36 (s)	72.31 (d, J_{PSi} = 47.7 Hz)	1905
2a	0.45 (d, J_{FH} = 3.9 Hz, 3H, SiCH$_3$) 0.47 (d, J_{FH} = 3.7 Hz, 3H, SiCH$_3$) 2.76 (d, J_{PH} = 10.6 Hz, 6H, NCH$_3$) 3.11 (m, 2H, NCH$_2$) 3.21 (d, J_{PH} = 11.4 Hz, 3H, OCH$_3$) 3.35 (m, 2H, NCH$_2$) 4.47 (d, J_{PH} = 1.3 Hz, 5H, C$_5$H$_5$)	10.01 (d, J_{FC} = 13.7 Hz, SiCH$_3$) 10.66 (d, J_{FC} = 14.3 Hz, SiCH$_3$) 33.17 (d, J_{PC} = 11.2 Hz, NCH$_3$) 33.28 (d, J_{PC} = 11.2 Hz, NCH$_3$) 51.03 (d, J_{PC} = 5.6 Hz, OCH$_3$) 51.23 (d, J_{PC} = 1.9 Hz, NCH$_2$) 51.68 (d, J_{PC} = 2.1 Hz, NCH$_2$) 81.20 (s, C$_5$H$_5$) 217.91 (d, J_{PC} = 39.8 Hz, CO)	175.54 (s)	96.77 (dd, J_{FSi} = 335.7 Hz, J_{PSi} = 51.6 Hz) ^{19}F NMR −126.45 (s, with Si satellites, J_{SiF} = 336.4 Hz)	1913
2b	0.46 (d, J_{FH} = 6.1 Hz, 3H, SiCH$_3$) 0.49 (d, J_{FH} = 6.2 Hz, 3H, SiCH$_3$) 1.11 (t, J_{PH} = 7.0 Hz, 3H, POCH$_2$CH_3) 2.73 (d, J_{PH} = 10.8 Hz, 3H, NCH$_3$) 2.75 (d, J_{PH} = 10.6 Hz, 3H, NCH$_3$) 3.09 (m, 2H, NCH$_2$) 3.30 (m, 2H, NCH$_2$) 3.53 (m, 2H, POCH_2CH$_3$) 4.45 (s, 5H, C$_5$H$_5$)	10.21 (d, J_{FC} = 13.7 Hz, SiCH$_3$) 10.60 (d, J_{FC} = 14.3 Hz, SiCH$_3$) 16.06 (d, J_{PC} = 5.6 Hz, POCH$_2$$CH_3$) 33.03 (d, J_{PC} = 13.1 Hz, NCH$_3$) 33.30 (d, J_{PC} = 11.8 Hz, NCH$_3$) 51.10 (d, J_{PC} = 1.9 Hz, NCH$_2$) 51.50 (d, J_{PC} = 3.1 Hz, NCH$_2$) 59.90 (d, J_{PC} = 13.1 Hz, POCH$_2$CH$_3$) 81.13 (s, C$_5$H$_5$) 217.91 (d, J_{PC} = 40.4 Hz, CO)	172.94 (s) J_{PSi} = 50.9 Hz)	96.34 (dd, J_{FSi} = 335.0 Hz, ^{19}F NMR −126.15 (s, with Si satellites, J_{SiF} = 334.2 Hz)	1913
3	0.56 (d, J_{FH} = 7.3 Hz, 3H, SiCH$_3$)^{b,c,d} 0.58 (d, J_{FH} = 7.2 Hz, 3H, SiCH$_3$) 2.97 (d, J_{PH} = 12.5 Hz, 6H, NCH$_3$) 5.11 (s, 5H, C$_5$H$_5$)	10.72 (d, J_{FC} = 12.4 Hz, SiCH$_3$)^{b,c} 10.75 (d, J_{FC} = 11.8 Hz, SiCH$_3$) 34.16 (d, J_{PC} = 11.8 Hz, NCH$_3$) 52.35 (s, NCH$_2$) 84.76 (s, C$_5$H$_5$) 212.43 (d, J_{PC} = 42.3 Hz, CO)	311.07 (s)^{b,c}	86.02 (dd, J_{FSi} = 329.9 Hz, J_{PSi} = 45.1 Hz)^{b,c} ^{19}F NMR −121.26 (s, with Si satellites, J_{SiF} = 327.2 Hz)^{b,c}	1955^b

Table 1 (Continued)

complex	^{1}H NMR δ (ppm)^a	^{13}C NMR δ (ppm)^a	^{31}P NMR δ (ppm)^a	^{29}Si and ^{19}F NMR δ (ppm)^a	IR (ν_{CO}) (cm^{-1})^b
4	0.60 (d, J_{FH} = 8.3 Hz, 3H, SiCH$_3$) 0.71 (d, J_{FH} = 8.1 Hz, 3H, SiCH$_3$) 2.34 (m, 2H, NCH$_2$) 2.77 (m, 2H, NCH$_2$) 2.80 (d, J_{PH} = 10.5 Hz, 3H, NCH$_3$) 2.82 (d, J_{PH} = 9.9 Hz, 3H, NCH$_3$) 3.03 (d, J_{PH} = 14.7 Hz, 1H, PCH$_2$) 3.38 (d, J_{PH} = 14.7 Hz, 1H, PCH$_2$) 4.42 (s, 5H, C$_5$H$_5$) 7.00~7.21 (m, 5H, C$_6$H$_5$)	11.19 (d, J_{FC} = 14.9 Hz, SiCH$_3$) 11.38 (d, J_{FC} = 13.7 Hz, SiCH$_3$) 33.76 (d, J_{PC} = 10.6 Hz, NCH$_3$) 33.85 (d, J_{PC} = 10.6 Hz, NCH$_3$) 48.88 (dd, J_{PC} = 9.3 Hz, J_{FC} = 4.3 Hz, PCH$_2$) 50.92 (d, J_{PC} = 1.2 Hz, NCH$_2$) 51.38 (d, J_{PC} = 1.9 Hz, NCH$_2$) 81.72 (s, C$_5$H$_5$) 125.53 (d, J_{PC} = 2.5 Hz, *p*-C$_6$H$_5$) 127.68 (d, J_{PC} = 1.9 Hz, *m*-C$_6$H$_5$) 130.00 (d, J_{PC} = 3.1 Hz, *o*-C$_6$H$_5$) 137.00 (d, J_{PC} = 9.9 Hz, ϵ-C$_6$H$_5$) 218.57 (d, J_{PC} = 32.3 Hz, CO)	179.09 (s)	91.26 (dd, J_{FSi} = 332.1 Hz, J_{PSi} = 43.6 Hz) ^{19}F NMR −128.76 (s, with Si satellites, J_{SiF} = 330.9 Hz)	1906
5a	0.58 (s, 3H, SiCH$_3$)^{c,e} 0.76 (s, 3H, SiCH$_3$) 2.61 (d, J_{PH} = 10.0 Hz, 3H, NCH$_3$) 2.68 (d, J_{PH} = 11.2 Hz, 3H, NCH$_3$) 3.05 (m, 2H, NCH$_2$) 3.16 (d, J_{PH} = 11.7 Hz, 3H, OCH$_3$) 3.30 (m, 2H, NCH$_2$) 4.49 (s, 5H, C$_5$H$_5$)	10.01 (s, SiCH$_3$)^{c,e} 11.63 (s, SiCH$_3$) 32.67 (d, J_{PC} = 11.2 Hz, NCH$_3$) 33.31 (d, J_{PC} = 11.2 Hz, NCH$_3$) 51.23 (s, NCH$_2$) 51.49 (d, J_{PC} = 3.1 Hz, NCH$_2$) 51.50 (d, J_{PC} = 11.2 Hz, OCH$_3$) 82.00 (s, C$_5$H$_5$) 118.58 (q, J_{FC} = 317.6 Hz, CF$_3$) 217.01 (d, J_{PC} = 39.8 Hz, CO)	171.95 (s)^{c,e}	128.13 (d, J_{PSi} = 55.9 Hz)^{c,e}	1938
5b	0.58 (s, 3H, SiCH$_3$)^{c,e} 0.78 (s, 3H, SiCH$_3$) 1.08 (t, J_{HH} = 7.1 Hz, 3H, OCH$_2$CH_3) 2.58 (d, J_{PH} = 11.0 Hz, 3H, NCH$_3$) 2.66 (d, J_{PH} = 11.2 Hz, 3H, NCH$_3$) 3.06 (m, 2H, NCH$_2$) 3.24 (m, 2H, NCH$_2$) 3.46 (m, 2H, OCH_2CH$_3$) 4.48 (s, 5H, C$_5$H$_5$)	10.01 (s, SiCH$_3$)^{c,e} 11.62 (s, SiCH$_3$) 15.75 (d, J_{PC} = 5.6 Hz, CH$_2$CH_3) 32.59 (d, J_{PC} = 10.6 Hz, NCH$_3$) 33.24 (d, J_{PC} = 11.2 Hz, NCH$_3$) 51.07 (s, NCH$_2$) 51.33 (s, NCH$_2$) 60.50 (d, J_{PC} = 12.4 Hz, CH$_2$CH$_3$) 81.92 (s, C$_5$H$_5$) 117.01 (q, J_{FC} = 317.6 Hz, CF$_3$) 216.93 (d, J_{PC} = 39.2 Hz, CO)	170.05 (s)^{c,e}	127.99 (d, J_{PSi} = 55.9 Hz)^{c,e}	1933
6a	0.80 (s, 3H, SiCH$_3$) 0.98 (s, 3H, SiCH$_3$) 2.66 (d, J_{PH} = 11.0 Hz, 3H, NCH$_3$) 2.70 (d, J_{PH} = 11.4 Hz, 3H, NCH$_3$) 3.06 (d, J_{PH} = 11.7 Hz, 3H, OCH$_3$) 3.13 (m, 2H, NCH$_2$) 3.34 (m, 2H, NCH$_2$) 4.39 (s, 5H, C$_5$H$_5$) 7.96 (t, J_{HH} = 5.8 Hz, 2H, NC$_5$H$_5$) 8.29 (t, J_{HH} = 6.6 Hz, 1H, NC$_5$H$_5$) 8.80 (d, J_{HH} = 4.4 Hz, 2H, NC$_5$H$_5$)	9.19 (s, SiCH$_3$)^f 10.49 (s, SiCH$_3$) 32.96 (d, J_{PC} = 9.3 Hz, NCH$_3$) 33.09 (d, J_{PC} = 9.9 Hz, NCH$_3$) 51.29 (s, NCH$_2$) 51.51 (s, NCH$_2$) 51.73 (d, J_{PC} = 12.4 Hz, OCH$_3$) 82.14 (s, C$_5$H$_5$) 127.04 (s, NC$_5$H$_5$) 143.47 (s, NC$_5$H$_5$) 145.49 (s, NC$_5$H$_5$) 217.91 (d, J_{PC} = 40.4 Hz, CO)	169.77 (s)	107.30 (d, J_{PSi} = 54.8 Hz)	1925
6b	0.66 (s, 3H, SiCH$_3$) 0.97 (s, 3H, SiCH$_3$) 0.98 (t, J_{HH} = 7.2 Hz, 3H, OCH$_2$CH_3) 2.57 (d, J_{PH} = 11.0 Hz, 3H, NCH$_3$) 2.65 (d, J_{PH} = 10.8 Hz, 3H, NCH$_3$) 3.06 (m, 2H, NCH$_2$) 3.25 (m, 2H, NCH$_2$) 3.46 (m, 2H, OCH_2CH$_3$) 4.26 (s, 5H, C$_5$H$_5$) 7.93 (t, J_{HH} = 6.6 Hz, 1H, NC$_5$H$_5$) 8.25 (t, J_{HH} = 7.1 Hz, 2H, NC$_5$H$_5$) 8.77 (d, J_{HH} = 5.0 Hz, 2H, NC$_5$H$_5$)	8.76 (s, SiCH$_3$)^f 10.16 (s, SiCH$_3$) 15.76 (d, J_{PC} = 5.6 Hz, OCH$_2$CH_3) 32.67 (d, J_{PC} = 10.6 Hz, NCH$_3$) 32.97 (d, J_{PC} = 11.2 Hz, NCH$_3$) 50.94 (s, NCH$_2$) 51.18 (d, J_{PC} = 1.9 Hz, NCH$_2$) 60.72 (d, J_{PC} = 12.4 Hz, OCH$_2$CH$_3$) 82.06 (s, C$_5$H$_5$) 127.07 (s, NC$_5$H$_5$) 143.33 (s, NC$_5$H$_5$) 145.19 (s, NC$_5$H$_5$) 217.76 (d, J_{PC} = 40.4 Hz, CO)	165.98 (s)	108.00 (d, J_{PSi} = 55.0 Hz)	1926

^{a} In CDCl$_3$. ^{b} In CH$_2$Cl$_2$. ^{c} At −30 °C. ^{d} The NCH$_2$ proton could not be identified due to being superimposed on the CH$_2$ proton resonances of ether. ^{e} In CD$_2$Cl$_2$. ^{f} The CF$_3$ carbon could not be identified.

They were treated with a Lewis acid such as BF$_3$·OEt$_2$ or TMSOTf (Me$_3$SiOSO$_2$CF$_3$). The spectroscopic data of the starting complexes and the reaction products are summarized in Table 1.

Reaction of 1 with an Excess of BF$_3$·OEt$_2$. The reaction of four iron complexes (**1a**−**1d**) having an alkoxysilyl group and a diamino-substituted phosphite with 4 equiv of BF$_3$·OEt$_2$ in CH$_2$Cl$_2$ at −78 °C is shown

in eq 3. In every case, the complex **3**, which has no OR groups on Si or P but instead has an F substituent on the Si atom, was obtained as a main product.

Formation of **3** is evidenced by the spectroscopic data. In the reaction of **1a**, having both Si−OMe and P−OMe groups, for example, the ^{31}P NMR spectrum showed a singlet resonance at 311.1 ppm, which is 134.4 ppm downfield than that of the starting complex. This large

Table 2. Summary of Crystal Data for 7b

formula	$C_{18}H_{35}F_3FeN_2O_5P_2SSi$
fw	594.42
cryst syst	monoclinic
space group	$C2/c$
cell constants	
a, Å	27.530(1)
b, Å	14.6560(3)
c, Å	15.5390(5)
β, deg	93.796(1)
V, Å^3	5450.7(3)
Z	8
D_{calcd}, g cm^{-3}	1.45
μ, cm^{-1}	8.4
cryst size, mm	$0.50 \times 0.37 \times 0.20$
radiation	Mo Kα ($\lambda = 0.710\ 93$ Å)
$2\theta_{max}$, deg	50.0
no. of unique data	6663
no. of unique data with $F_o > 3\sigma(F_o)$	4044
R	0.044
R_w	0.050

downfield shift is very similar in magnitude to the shift obtained in the previous results shown in eq 1[9a] and

1a: R^1 = Me, R^2 = Me
1b: R^1 = Me, R^2 = Et
1c: R^1 = Et, R^2 = Me
**1d:** R^1 = Et, R^2 =Et

(3)
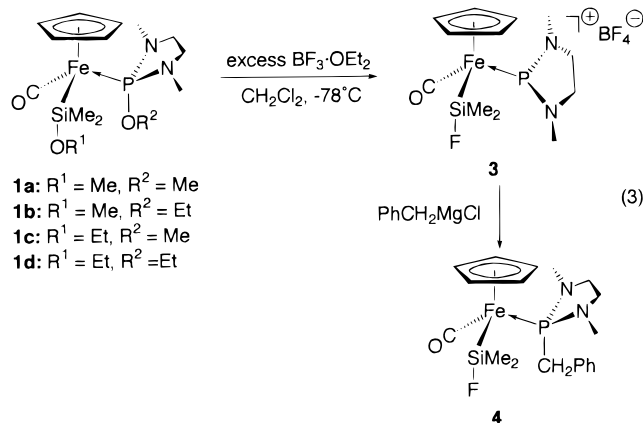
strongly suggests the formation of a cationic phosphenium complex with the OMe group on P eliminated. The ^{13}C NMR spectrum (in CH$_2$Cl$_2$) showed six resonances: 10.72 (d, J_{FC} = 12.4 Hz, SiCH$_3$), 10.75 (d, J_{FC} = 11.8 Hz, SiCH$_3$), 34.16 (d, J_{PC} = 11.8 Hz, NCH$_3$), 52.35 (s, NCH$_2$), 84.76 (s, C$_5$H$_5$), 212.43 (d, J_{PC} = 42.3 Hz, CO). The resonances due to POCH$_3$ and SiOCH$_3$ carbons are not detected; they were observed for the starting complex **1a** at 50.92 ppm with $^2J_{PC}$ = 13.1 Hz and 50.34 ppm, respectively. It should be noted that two NCH$_3$ carbons and two NCH$_2$ carbons in **3** are not diastereotopic, while those in **1a** were diastereotopic. This is consistent with a planar geometry of the phosphorus atom in **3**. Also noted is that the resonances due to the SiCH$_3$ carbons for **3** are observed as a doublet, though those for **1a** were observed as a singlet, suggesting a fluorination on the silyl group (substitution of the OMe group with F). In fact, the formation of the Si−F bond is firmly supported by the following spectroscopic data. The ^{29}Si NMR spectrum shows a doublet of doublets at 86.0 ppm (J_{FSi} = 329.9 Hz, J_{PSi} = 45.1 Hz), and the ^{19}F NMR spectrum shows the appearance of a new singlet resonance at −121.3 ppm.

Several attempts to isolate complex **3** as a solid were unsuccessful due to its instability. However, **3** could be converted, by the reaction with PhCH$_2$MgCl, into an isolable complex, [Cp(CO)(SiMe$_2$F)Fe{PNN(CH$_2$Ph)}] (**4**), which was fully characterized and was shown to
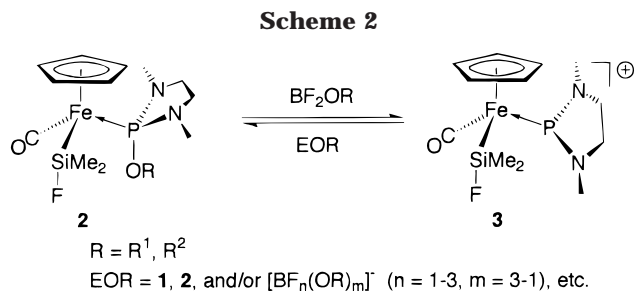
Scheme 1
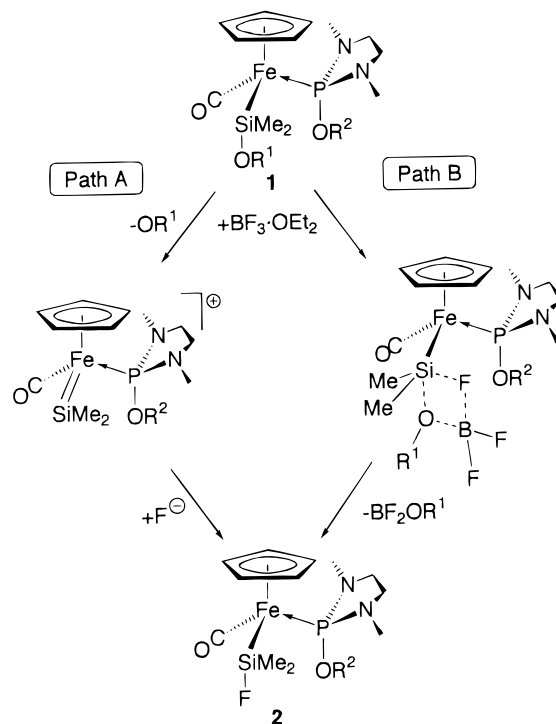
have the PhCH$_2$ group bound to the phosphorus atom (eq 3). This gives further evidence that **3** is a cationic phosphenium complex. These results show that both of the OR groups on Si and P were abstracted in the present reactions with an excess of BF$_3$·OEt$_2$.

Reaction of 1 with an Equimolar Amount of BF$_3$· OEt$_2$. In the above reaction, an excess of BF$_3$·OEt$_2$ was added to effect the abstraction of the OR group on both the Si and P atoms. It is interesting therefore to examine which OR group is abstracted when 1 equiv of BF$_3$·OEt$_2$ is added (eq 4). In the reaction of **1a** under

1a: R^1 = Me, R^2 = Me
1d: R^1 = Et, R^2 =Et

2a: R^2 = Me
2b: R^2 =Et

(4)
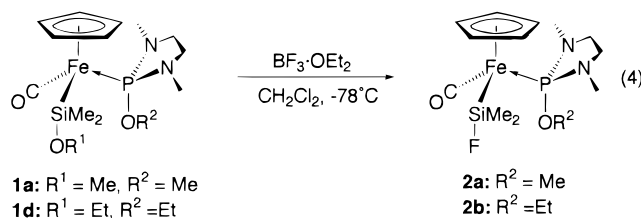
such conditions, the ^{31}P NMR spectrum showed the appearance of a large singlet signal at 175.1 ppm accompanied with some weak signals, including a very small singlet at 311.1 ppm due to a cationic phosphenium complex **3**. The major product with the above chemical shift of 175.1 ppm was isolated by alumina column chromatography as a lemon-yellow powder. The spectroscopic data (including ^{29}Si and ^{19}F NMR) and its elemental analysis established the formation of a neutral complex formulated as [Cp(CO)(SiMe$_2$F)Fe{PNN-(OMe)}] (**2a**). The same result was obtained in the reaction of **1d** to give complex **2b**.

On the basis of these results and the formation of the carbene complex in the reaction of the corresponding methoxymethyl−iron complex (eq 2),[9a] two plausible reaction pathways are proposed as follows (Scheme 1). An OR group on Si, but not on P, is first abstracted by
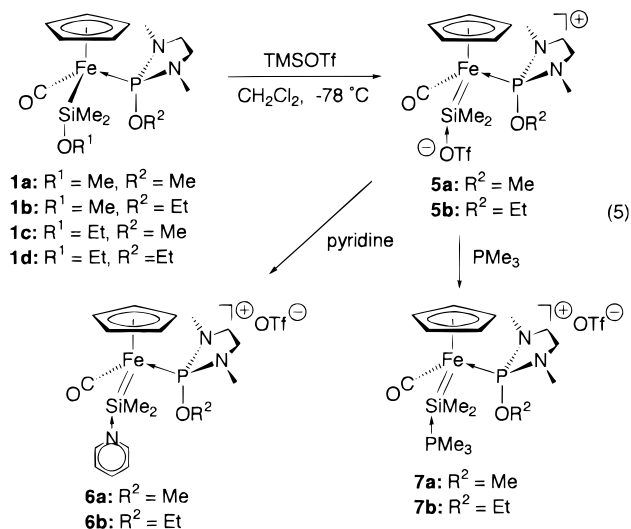
Scheme 2

$$2 \quad \underset{EOR}{\overset{BF_2OR}{\rightleftharpoons}} \quad 3$$

R = R[1], R[2]

EOR = **1**, **2**, and/or [BF$_n$(OR)$_m$]$^-$ (n = 1-3, m = 3-1), etc.

BF$_3$·OEt$_2$ to give a silylene complex, which is, however, too reactive to be isolated or to be detected spectroscopically and thus reacts further with F$^-$ present in the reaction mixture to yield **2** (path A). An alternative reaction pathway (path B) is also probable, as judged from the general reactivity of main-group elements. In this pathway the reaction proceeds via a five-coordination silicon intermediate. There is, at present, no evidence to show which pathway is more plausible.

The reaction pathways in Scheme 1 imply that an OR group on Si is selectively abstracted. However, the following pathway is also conceivable: An OR group on P is first abstracted to give a cationic phosphenium complex, and then an OR group migrates from Si to the phosphenium phosphorus to yield a silylene complex. This is followed by fluorination, resulting in the formation of **2**. To check this possibility, the reaction of **1b** having different OR groups on Si and P with an equimolar amount of BF$_3$·OEt$_2$ was examined. The reaction unexpectedly gave a mixture of **2a** and **2b** in 1/1 ratio. The reaction of **1c** gave the same products. These OR scramblings indicate the existence of some equilibria in these reactions. Presumably, they would involve the formation of a small amount of a cationic phosphenium complex **3**, which also acts as a Lewis acid. The plausible reaction process is shown in Scheme 2. In the reaction of **1** with BF$_3$·OEt$_2$, OR^1/F substitution on Si occurs first to give **2**, accompanied with the formation of BF$_2$OR^1 as a coproduct. If the BF$_2$OR^1 thus formed could react as a Lewis acid with **2**, the cationic phosphenium complex **3** would be produced in the reaction mixture. Then **3** would be converted into **2** again, when **3** itself acts as a Lewis acid to abstract an OR group from complex **2** or from the boron compounds present such as [BF$_3$OR]$^-$, [BF$_2$OR^{1}OR^2]$^-$, etc. Since the OR group scrambling readily occurs, as evidenced in the reaction of **1b** and **1c** with equimolar amounts of BF$_3$·OEt$_2$, selective OR abstraction cannot be affirmed.

Reaction of 1 with Trimethylsilyl Triflate (TMSOTf). It has been reported that a silylene complex of a transition metal is very susceptible to F$^-$/F attack with an Si−F bond readily created.[20] In fact, the reaction of **1** with BF$_3$·OEt$_2$ led eventually to the formation of an Si−F bond, though the silylene complex might have been formed transiently. Therefore, TMSOTf was employed in place of BF$_3$·OEt$_2$, because it has no replacable fluorine atom but serves similarly as a Lewis acid. The results are shown in eq 5.

In a typical reaction, **1a**, having both SiOMe and POMe groups, was treated with an equimolar amount

1a: R^1 = Me, R^2 = Me
1b: R^1 = Me, R^2 = Et
1c: R^1 = Et, R^2 = Me
1d: R^1 = Et, R^2 = Et

5a: R^2 = Me
5b: R^2 = Et

6a: R^2 = Me
6b: R^2 = Et

7a: R^2 = Me
7b: R^2 = Et

(5)

of TMSOTf in CH$_2$Cl$_2$ at −78 °C, and the reaction mixture was stirred for 15 min. From the following reasons, we concluded that the product is best formulated as Cp(CO){PNN(OMe)}Fe=SiMe$_2$·OTf, **5a**: (i) The IR spectrum showed a CO stretching absorption at 1938 cm^{-1}, which is higher by 33 cm^{-1} than that of **1a**, suggesting that the product carries a positive charge. (ii) The ^{31}P NMR spectrum did not exhibit any significant change in the chemical shift, indicating that the phosphite ligand coordinated to Fe remained intact in the reaction, which was also confirmed by the ^{13}C NMR spectrum. (iii) The ^{29}Si NMR spectrum showed a doublet at 128.13 ppm, which is 53 ppm lower than that of **1a**. The downfield shift (53 ppm) is not large compared with those observed when base-free silylene complexes of Pt or Ru are formed.[11f,21] For example, Tilley et al. have reported that the base-free silylene complex of Ru, Cp*-(PMe$_3$)$_2$Ru=Si(S^{p}tol)$_2$BPh$_4$, exhibits a resonance in the ^{29}Si NMR spectrum at 250.6 ppm, which is 177.5 ppm lower than that of the starting OTf$^-$-adduct, Cp*-(PMe$_3$)$_2$RuSi{(S^{p}tol)$_2$(OTf)}.[21] In addition, two SiCH$_3$ carbons appeared as diastereotopic in the ^{13}C NMR spectrum, indicating that the geometry around Si in the product does not have a trigonal planar geometry expected for a base-free silylene complex. Therefore, **5a** can be considered as a weakly OTf$^-$-stabilized silylene complex; it might be in equilibrium with the corresponding base-free silylene complex in solution.

Since this complex is too reactive to be isolated as a solid, it was converted into the fully base-stabilized silylene complex with a strong Lewis base such as pyridine or PMe$_3$ (eq 5). In the reaction of **5** with 1 equiv of pyridine at −78 °C, a pyridine-stabilized silylene complex **6** was quantitatively formed and was isolated as a yellow powder by crystallization from the CH$_2$Cl$_2$/hexane layer in good yield (**6a** 86%, **6b** 84%). Complex **7** was similarly formed via the reaction with PMe$_3$, and the structure of **7b** was established by X-ray analysis (vide infra).

In the reaction with TMSOTf, the OR scrambling reaction observed on treatment with 1 equiv of BF$_3$·OEt$_2$ was not observed at all; that is, **1a** and **1c** gave a common product **5a**, and **1b** and **1d** gave **5b**. Therefore,

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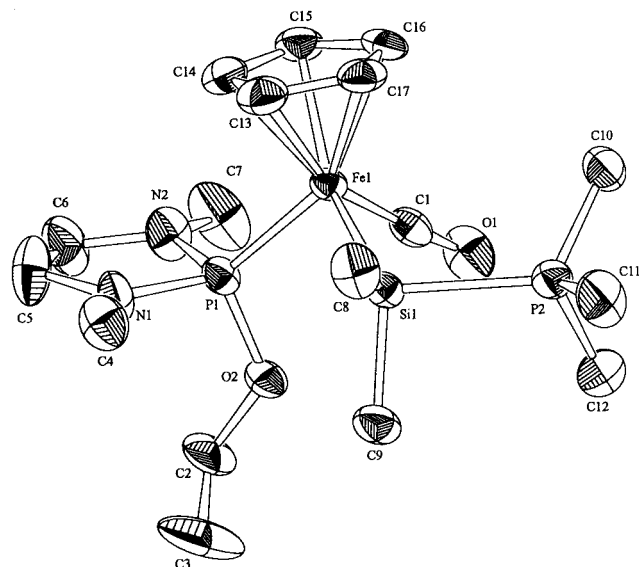
Figure 1. ORTEP drawing of **7b** showing the atom-numbering scheme (the OTf⁻ counterion is omitted for clarity). The thermal ellipsoids are drawn at the 50% probability level.

these reactions clearly show that an OR group on Si is selectively abstracted by TMSOTf. Though it is not easy to say where the selectivity comes from, it should be noted that the selectivity observed here is opposite to the trend simply expected from a comparison between Si−O bond energy (452 kJ mol⁻¹) and P−O bond energy (335 kJ mol⁻¹).[22] As far as the thermodynamic aspects are concerned, a difference in the O atom basicity between the Si−OR and P−OR groups and/or a thermodynamic stability difference between the resulting silylene and phosphenium complexes are probably responsible for the interesting selectivity found here.

The reactions of **5**, **6**, or **7** with an excess of TMSOTf were attempted, but a further reaction, such as the abstraction of the second OR group on P, was not observed at all. This is presumably due to the appreciable drop in the basicity of the OR oxygen on the phosphorus brought about by the positive charge present on these complexes.

Crystal Structure of 7b. X-ray structure analysis of **7b** was undertaken. The ORTEP drawing of **7b** is displayed in Figure 1. The crystal data and the selected bond distances and angles are summarized in Tables 2 and 3.

The X-ray structure of **7b** shows that the iron takes a normal piano stool configuration with a cyclopentadienyl ligand in an η^5 fashion, a terminal CO ligand, a diamino-substituted phosphite ligand, and a silylene group stabilized by a phosphine, SiMe₂PMe₃. The most interesting structural feature is that the Fe1−Si1 (2.272 Å) bond is significantly shorter than those of normal silyl iron complexes (2.32−2.37 Å),[23] suggesting the unsaturated character of the Fe1−Si1 bond, and it falls in the range of those of the usual base-stabilized silylene iron complexes (2.21−2.29 Å).[12] As judged from the P−Si

Table 3. Selected Bond Distances (Å) and Angles (deg) for 2b

Bond Distances			
Fe1−P1	2.1548(9)	Si1−C8	1.888(4)
Fe1−Si1	2.2722(9)	Si1−C9	1.886(4)
Fe1−C1	1.714(4)	O1−C1	1.164(4)
P1−O2	1.615(2)	O2−C2	1.461(4)
P1−N1	1.654(2)	N1−C4	1.452(5)
P1−N2	1.672(2)	N1−C5	1.452(5)
P2−Si1	2.364(1)	N2−C6	1.436(5)
P2−C10	1.807(4)	N2−C7	1.434(5)
P2−C11	1.797(4)	C2−C3	1.444(6)
P2−C12	1.813(4)	C5−C6	1.498(7)

Bond Angles			
P1−Fe1−Si1	97.07(3)	Fe1−Si1−C9	122.8(1)
P1−Fe1−C1	90.1(1)	P2−Si1−C8	100.9(1)
Si1−Fe1−C1	87.3(1)	P2−Si1−C9	96.3(1)
Fe1−P1−O2	110.46(9)	C8−Si1−C9	104.9(2)
Fe1−P1−N1	122.5(1)	P1−O2−C2	121.7(2)
Fe1−P1−N2	125.3(1)	P1−N1−C4	124.5(2)
O2−P1−N1	107.9(1)	P1−N1−C5	115.7(3)
O2−P1−N2	106.6(1)	C4−N1−C5	119.0(3)
N1−P1−N2	92.0(2)	P1−N2−C6	115.2(3)
Si1−P2−C10	116.5(1)	P1−N2−C7	123.2(3)
Si1−P2−C11	113.6(2)	C6−N2−C7	118.5(3)
Si1−P2−C12	109.8(1)	Fe1−C1−O1	177.5(3)
Fe1−Si1−P2	109.20(4)	N1−C5−C6	107.4(3)
Fe1−Si1−C8	118.4(1)	N2−C6−C5	107.7(3)

dative bond distance in H₂Si←PH₃ (2.3272 Å) estimated by ab initio calculations,[24] the P2−Si1 bond (2.364(1) Å) can be considered to be a dative bond. The sum of the bond angles around Si1 (346.1°) in the Fe1Si1C8C9 unit and the P2−Si1 bond distance suggest that the geometry around silicon is rather close to sp³ geometry, and PMe₃ coordinates to the silylene silicon relatively strongly.

Conclusion

The reaction of **1** (a complex containing an OR group on both a silyl ligand and a phosphorus ligand) with excess BF₃·OEt₂ affords the cationic phosphenium complex **3**, where both OR groups, as a result, are abstracted. The reaction with an equimolar amount of BF₃·OEt₂ leads to the fluorination of the silyl group and isolation of **2**, with the concomitant OR scrambling at the P atom. In the reaction with TMSOTf, an OR group on Si is selectively abstracted to give the corresponding silylene complex **5**. It was characterized by spectroscopic data and by the further reaction with a Lewis base such as pyridine or PMe₃, leading to the corresponding base-stabilized silylene complex **6** or **7**, respectively. The selectivity may be derived from a difference in basicity of the oxygen atom between Si−OR and P−OR in the complex and/or from a relative thermodynamic stability between the silylene and phosphenium complexes.

Supporting Information Available: Tables giving positional and thermal parameters for **7b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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