Organometallics **1997,** *16,* 4626−4635

Comparison of the Reactivity of Cationic Phosphenium Complexes of Iron Containing a Group 14 Element Ligand

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Received June 9, 1997[⊗]

Reactions of $Cp(CO)(EMe_3)Fe\{\overline{PN(Me)CH_2CH_2N}Me(OMe)\}$ (E = Si (**2a**), Ge (**3a**), and Sn (**4a**)) with a Lewis acid ($BF_3{\cdot}OEt_2$ or $Me_3SiOSO_2CF_3$ (TMSOTf)) have been examined. The silyl complex **2a** reacts with $BF_3{\cdot}OEt_2$ to give a stable cationic phosphenium complex $[Cp(CO)(SiMe_3)Fe\{\overline{PN(Me)CH_2CH_2N}Me\}]BF_4$ by OMe anion abstraction from phosphorus. This reaction is in contrast to that of the corresponding alkyl complex reported earlier showing that the phosphenium complex once formed immediately undergoes migratory insertion of the phosphenium ligand into the Fe−C bond. The X-ray analysis of $[Cp(CO)(SiMe_3)Fe\{\overline{PN(Me)CH_2CH_2N}Me\}]BPh_4$ reveals that there is considerable double-bond character in the Fe−P bond. The rotation barrier around the Fe−P(phosphenium) bond is estimated ($\Delta G^{\ddagger}$ (248 K) = 12.7 kcal/mol) from a variable-temperature ^{1}H NMR study. The germyl complex **3a** exhibits the same reactivity as that of **2a**. In contrast, the stannyl complex **4a** reacts with TMSOTf to give a stannylene complex $[Cp(CO)(SnMe_2)Fe\{\overline{PN(Me)CH_2CH_2N}Me(Me)\}]OTf$ (**4e**). X-ray analysis reveals that **4e** is regarded as a stannylene iron complex doubly-base-stabilized by an oxygen of OTf^- and one nitrogen of the $\overline{PN(Me)CH_2CH_2N}Me(Me)$ ligand. In solution, there is an equilibrium between a base-stabilized and a base-free stannylene form. The activation parameter ($\Delta G^{\ddagger}$ (188 K) = 9.0 kcal/mol) is estimated for the methyl group exchange in the stannylene ligand. The reaction of $Cp(CO)(Sn{}^nBu_3)Fe\{\overline{PN(Me)CH_2CH_2N}Me(OMe)\}$ with TMSOTf verifies that a cationic phosphenium iron complex is formed first and that then an alkyl migration from the Sn to the phosphenium phosphorus takes place.

Introduction

Chart 1

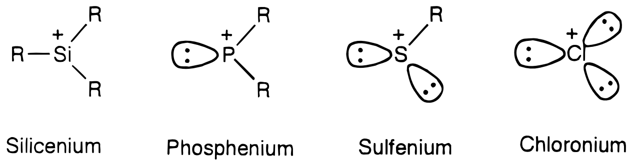
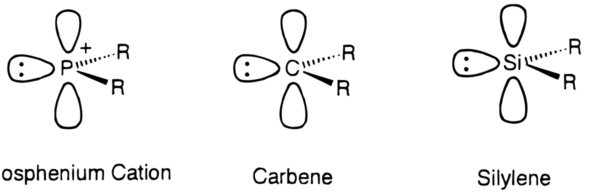


Chart 2



A cationic phosphenium species described as $[PR_2]^+$ can be considered to be a member of an isoelectronic series that extends from silicenium to chloronium ions (Chart 1). A phosphenium cation has lone pair electrons and a vacant p orbital which is, except for a high cationic charge accumulated at the phosphorus atom, parallel to a carbene and a silylene (Chart 2).[1,2] From such points of view, the coordination chemistry of a phosphenium cation, as well as its own chemistry, has received considerable attention, and many cationic transition-metal phosphenium complexes have been prepared.[3−6] Nevertheless, the reactivity of these complexes is much less investigated than that of carbene and silylene complexes.

We have been engaged in the study of the preparation, structures, properties, and reactivities of cationic phosphenium complexes of group 6[6] and 8[7] transition metals.

⊗ Abstract published in *Advance ACS Abstracts,* September 15, 1997.

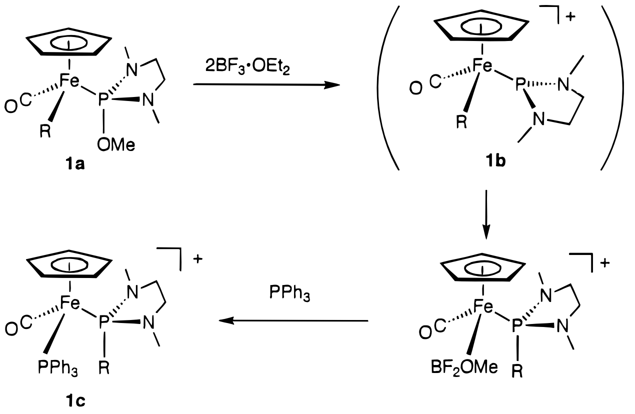
(1) (a) Cowley, A. H.; Kemp, R. A. *Chem. Rev.* **1985**, *85*, 367. (b) Sanchez, M.; Mazieres, M. R.; Lamande, L.; Wolf, R. In *Multiple Bonds and Low Coordination in Phosphorus Chemistry*; Regitz, M., Scherer, O. J., Eds.; Thieme: New York, 1990; Chapter D1.

(2) Electrically neutral tansition-metal complexes described as $[L_nMPR_2]$ can be considered as phosphenium complexes if one thinks that they consist of L_nM^- and $^+PR_2$. (See for example: McNamara, W. F.; Duesler, E. N.; Paine, R. T.; Ortiz, J. V.; Kölle, P.; Nöth, H. *Organometallics* **1986**, *5*, 380. Hutchins, L. D.; Reisachen, H.-U.; Wood, G. L.; Duesler, E. N.; Paine, R. T. *J. Organomet. Chem.* **1987**, *335*, 229. Lang, H.; Leise, M.; Zsolnai, L. *J. Organomet. Chem.* **1990**, *389*, 325. Malisch, W.; Hirth, U.-A.; Bright, T. A.; Köb, H.; Erter, T. S.; Hückmann, S.; Bertagnolli, H. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1525.) In this paper we focus on electrically cationic transition-metal complexes described as $[L_nMPR_2]^+$.

(3) (a) Montemayor, R. G.; Sauer, D. T.; Fleming, S.; Bennett, D. W.; Thomas, M. G.; Parry, R. W. *J. Am. Chem. Soc.* **1978**, *100*, 2231. (b) Bennett, D. W.; Parry, R. W. *J. Am. Chem. Soc.* **1979**, *101*, 755. (c) Snow, S. S.: Jiang, D.-X.; Parry, R. W. *Inorg. Chem.* **1987**, *26*, 1629.

S0276-7333(97)00480-9 CCC: $14.00

Scheme 1



Recently, we reported the interesting reactivity of iron complexes containing phosphenium and alkyl ligands.[7a] In this paper, we report the reactivity of a cationic iron phosphenium complex containing the congeners of an alkyl group, that is, silyl, germyl, and stannyl groups. Part of the results has been communicated.[8]

Results and Discussion

A complex of which the reactivity is examined is formulated as Cp(CO)(EMe$_3$)Fe{PNN(OMe)}, where E is Si, Ge, or Sn and PNN(OMe) stands for PN(Me)CH$_2$CH$_2$NMe(OMe). The spectroscopic data of these starting complexes and the reaction products are summarized in Table 1.

Before describing the results in detail, it is pertinent to discuss the results of the reaction of Cp(CO)(alkyl)Fe{PNN(OMe)} with BF$_3$·OEt$_2$, which are shown in Scheme 1.[7a] In this reaction of **1a**, the OMe group on the phosphorus ligand is abstracted by BF$_3$·OEt$_2$ as an anion to give a cationic phosphenium complex (**1b**), which is too reactive to be detected even spectroscopically. The R group on the iron atom immediately migrates to the phosphenium phosphorus to give the 16-electron species [Cp(CO)Fe{PNN(R)}]$^+$, which is stabilized presumably by the coordination, via oxygen, of the BF$_2$OMe present in the solution. This ligand is readily replaced by a strong Lewis base, such as PPh$_3$, added afterward, leading to an isolable complex **1c**.

Since we have examined, in this study, the reactions of Cp(CO)(EMe$_3$)Fe{PNN(OMe)} (E = Si, Ge, Sn) having an EMe$_3$ substituent, but not EH$_3$, we attempted to prepare Cp(CO)(CMe$_3$)Fe{PNN(OMe)} for direct comparison among group 14 element ligands. However, every trial was unsuccessful, presumably due to steric problems.

Reaction of Cp(CO)(SiMe$_3$)Fe{PNN(OMe)} (2a) with BF$_3$·OEt$_2$. In the previous paper,[7a] we reported that a silyl complex **2a** reacts with BF$_3$·OEt$_2$ to give a cationic phosphenium complex **2b** (Scheme 2). Although the formation of **2b** was evidenced by the spectroscopic data, it had not been isolated. In this paper, we report the preparation of an isolable complex, Cp(CO)(SiMe$_3$)Fe{PNN(CH$_2$Ph)} (**2d**), by the reaction of **2b** with PhCH$_2$MgCl. We also report the isolation of a cationic phosphenium complex as a BPh$_4^-$ salt (**2b′**) and its X-ray structure.

The phosphenium complex **2b** formed in situ from **2a** and BF$_3$·OEt$_2$, was treated with PhCH$_2$MgCl. After work-up, Cp(CO)(SiMe$_3$)Fe{PNN(CH$_2$Ph)} (**2d**) was isolated and characterized by ^{1}H, ^{13}C, ^{31}P, and ^{29}Si NMR and IR spectroscopies as well as by elemental analysis. Monitoring the reaction mixture by ^{31}P NMR spectroscopy proved that the conversion of **2b** into **2d** proceeds cleanly. The low isolated yield of **2d** (15%) is due to losses during the course of the purification procedure. It should be noted that Cp(CO)(CH$_2$Ph)Fe{PNN(SiMe$_3$)} is not detected at all during the reaction. Therefore, it is clear that **2b** does not undergo silyl migration from Fe to the phosphenium phosphorus.

The isolation of a cationic phosphenium complex [Cp(CO)(SiMe$_3$)Fe{PNN}]$^+$ could be accomplished by replacing the counteranion BF$_4^-$ with BPh$_4^-$. The spectroscopic data of the BPh$_4$ salt (**2b′**) (a reddish-brown powder) are similar to those of **2b**. The crystal structure of **2b′** will be described later.

Reaction of Cp(CO)(GeMe$_3$)Fe{PNN(OMe)} (3a) with BF$_3$·OEt$_2$. A germyl complex **3a** was prepared from Cp(CO)$_2$Fe(GeMe$_3$) and PNN(OMe) by photolysis in 85% yield. The reaction of **3a** with BF$_3$·OEt$_2$ in CH$_2$Cl$_2$ gave a homogeneous solution, which showed similar spectroscopic data to those of the silyl complex **2b**: a shift of more than 50 cm^{-1} to higher frequency for ν_{CO} in the IR spectrum compared with that of the starting complex, a singlet at a lower field by more than 300 ppm in the ^{31}P NMR spectrum, and absence of an OMe group and presence of a GeMe$_3$ group signals in the ^{1}H and ^{13}C NMR spectra. Therefore, the product of the reaction was the cationic phosphenium complex, [Cp(CO)(GeMe$_3$)Fe{PNN}]BF$_4$ (**3b**) (Scheme 3).

Scheme 2

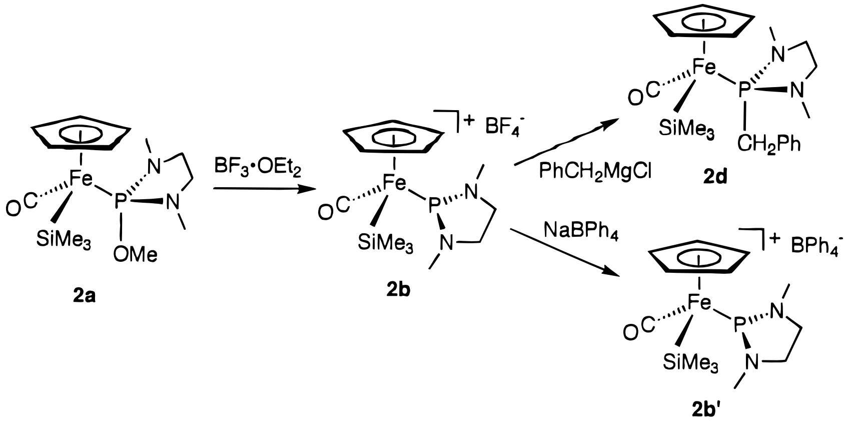
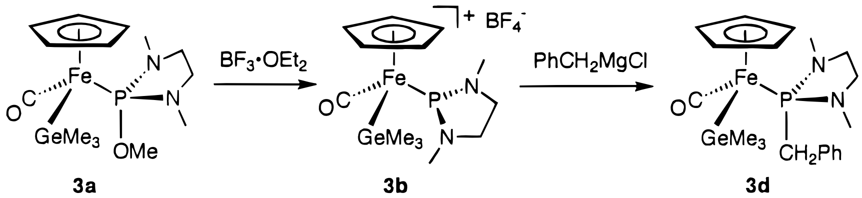


Table 1. Spectroscopic Data

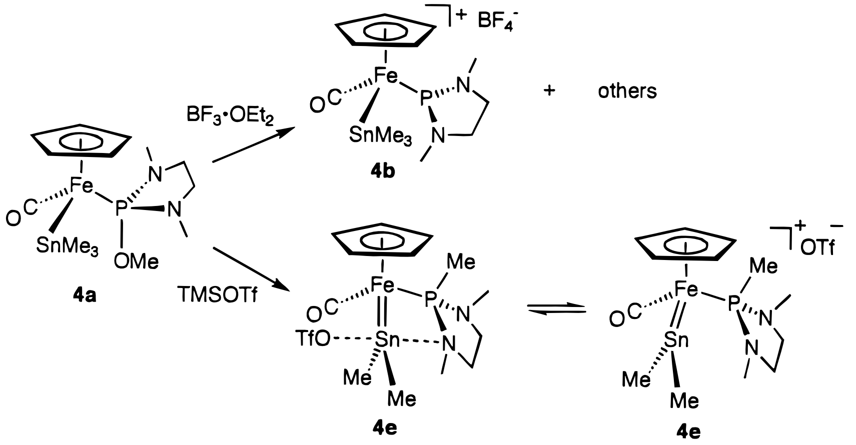
complex	^{1}H NMR δ (ppm)[a]	^{13}C NMR δ (ppm)[a]	^{31}P NMR δ (ppm)[c]	^{29}Si or ^{119}Sn δ NMR (ppm)	IR (ν_{CO}) (cm^{-1})[c]
2a[d]	0.26 (s, 9H, $\mathrm{Si(CH_3)_3}$), 2.72 (d, J_{PH} = 10.6 Hz, 3H, $\mathrm{NCH_3}$), 2.75 (d, J_{PH} = 10.6 Hz, 3H, $\mathrm{NCH_3}$), 3.10 (m, 2H, $\mathrm{NCH_2}$), 3.17 (d, J_{PH} = 11.2 Hz, 3H, $\mathrm{OCH_3}$), 3.32 (m, 2H, $\mathrm{NCH_2}$), 4.35 (d, J_{PH} = 1.3 Hz, 5H, $\mathrm{C_5H_5}$)	8.80 (s, with Si satellites, J_{SiC} = 40.3 Hz, $\mathrm{Si(CH_3)_3}$), 33.50 (d, J_{PC} = 11.0 Hz, $\mathrm{NCH_3}$), 33.58 (d, J_{PC} = 12.2 Hz, $\mathrm{NCH_3}$), 51.04 (d, J_{PC} = 13.4 Hz, $\mathrm{OCH_3}$), 51.37 (d, J_{PC} = 2.4 Hz, $\mathrm{NCH_2}$), 51.71 (d, J_{PC} = 3.7 Hz, $\mathrm{NCH_2}$), 81.13 (s, $\mathrm{C_5H_5}$), 219.39 (d, J_{PC} = 42.7 Hz, CO)	176.64 (s)	37.23 (d, J_{PSi} = 41.7 Hz)[c]	1902
3a	0.32 (s, 9H, $\mathrm{Ge(CH_3)_3}$), 2.70 (d, J_{PH} = 10.6 Hz, 3H, $\mathrm{NCH_3}$), 2.74 (d, J_{PH} = 10.9 Hz, 3H, $\mathrm{NCH_3}$), 3.11 (m, 2H, $\mathrm{NCH_2}$), 3.17 (d, J_{PH} = 11.2 Hz, 3H, $\mathrm{OCH_3}$), 3.33 (m, 2H, $\mathrm{NCH_2}$), 4.33 (d, J_{PH} = 1.3 Hz, 5H, $\mathrm{C_5H_5}$)	7.51 (s, $\mathrm{Ge(CH_3)_3}$), 33.45 (d, J_{PC} = 11.0 Hz, $\mathrm{NCH_3}$), 33.49 (d, J_{PC} = 11.0 Hz, $\mathrm{NCH_3}$), 51.01 (d, J_{PC} = 13.4 Hz, $\mathrm{OCH_3}$), 51.36 (d, J_{PC} = 2.5 Hz, $\mathrm{NCH_2}$), 51.67 (d, J_{PC} = 3.7 Hz, $\mathrm{NCH_2}$), 80.37 (s, $\mathrm{C_5H_5}$), 219.72 (d, J_{PC} = 42.7 Hz, CO)	176.65 (s)		1905
4a	0.15 (s, with Sn satellites, J_{SnH} = 41.6 Hz, 9H, $\mathrm{SnCH_3}$), 2.68 (d, J_{PH} = 10.6 Hz, 3H, $\mathrm{NCH_3}$), 2.77 (d, J_{PH} = 10.9 Hz, 3H, $\mathrm{NCH_3}$), 3.09 (m, 2H, $\mathrm{NCH_2}$), 3.16 (d, J_{PH} = 11.2 Hz, 3H, $\mathrm{OCH_3}$), 3.35 (m, 2H, $\mathrm{NCH_2}$), 4.34 (d, J_{PH} = 1.3 Hz, 5 H, $\mathrm{C_5H_5}$)	−4.06 (s, with Sn satellites, J_{SnC} = 184.4, 175.8 Hz, $\mathrm{SnCH_3}$), 33.55 (d, J_{PC} = 12.3 Hz, $\mathrm{NCH_3}$), 51.23 (d, J_{PC} = 9.8 Hz, $\mathrm{OCH_3}$), 51.28 (d, J_{PC} = 2.4 Hz, $\mathrm{NCH_2}$), 51.68 (d, J_{PC} = 2.5 Hz, $\mathrm{NCH_2}$), 78.83 (s, $\mathrm{C_5H_5}$), 218.94 (d, J_{PC} = 41.5 Hz, CO)	177.21 (s, with Sn satellites, J_{SnP} = 461.4, 441.2 Hz)	99.1 (d, J_{PSn} = 455.4 Hz)[a]	1902
5a	0.99 (t, J_{HH} = 7.3 Hz, 9H, $\mathrm{CH_2CH_2CH_2C}H_3$), 0.90 (m, 6H, $\mathrm{C}H_2\mathrm{CH_2CH_2CH_3}$), 1.32 (sext, J_{HH} = 6.9 Hz, 6H, $\mathrm{CH_2CH_2C}H_2\mathrm{CH_3}$), 1.49 (m, 6H, $\mathrm{CH_2C}H_2\mathrm{CH_2CH_3}$), 2.69 (d, J_{PH} = 10.9 Hz, 3H, $\mathrm{NCH_3}$), 2.78 (d, J_{PH} = 10.9 Hz, 3H, $\mathrm{NCH_3}$), 3.12 (m, 2H, $\mathrm{NCH_2}$), 3.15 (d, J_{PH} = 11.6 Hz, 3H, $\mathrm{OCH_3}$), 3.35 (m, 2H, $\mathrm{NCH_2}$), 4.37 (d, J_{PH} = 1.3 Hz, 5H, $\mathrm{C_5H_5}$)	13.84 (s, $\mathrm{CH_2CH_2CH_2}C\mathrm{H_3}$), 14.20 (s, with Sn satellites, J_{SnC} = 187.9, 181.9 Hz, $C\mathrm{H_2CH_2CH_2CH_3}$), 28.00 (s, with Sn satellites, J_{SnC} = 50.1 Hz, $\mathrm{CH_2CH_2}C\mathrm{H_2CH_3}$), 30.33 (s, with Sn satellites, J_{SnC} = 18.3 Hz, $\mathrm{CH_2}C\mathrm{H_2CH_2CH_3}$), 33.55 (d, J_{PC} = 12.3 Hz, $\mathrm{NCH_3}$), 33.58 (d, J_{PC} = 12.2 Hz, $\mathrm{NCH_3}$), 51.08 (d, J_{PC} = 13.5 Hz, $\mathrm{OCH_3}$), 51.37 (d, J_{PC} = 2.4 Hz, $\mathrm{NCH_2}$), 51.74 (d, J_{PC} = 3.6 Hz, $\mathrm{NCH_2}$), 78.38 (s, $\mathrm{C_5H_5}$), 219.12 (d, J_{PC} = 42.7 Hz, CO)	177.80 (s, with Sn satellites, J_{SnP} = 406.3, 389.7 Hz)	119.94 (d, J_{PSn} = 403.6 Hz)[c]	1898
2b′	0.40 (s, 9H, $\mathrm{Si(CH_3)_3}$),[b] 2.72 (d, J_{PH} = 11.9 Hz, 6H, $\mathrm{NCH_3}$), 3.11 (m, 4H, $\mathrm{NCH_2}$), 4.86 (d, J_{PH} = 1.00 Hz, 5H, $\mathrm{C_5H_5}$), 6.89 (t, J_{HH} = 7.26 Hz, 4H, p-$\mathrm{C_6H_5}$), 7.03 (t, J_{HH} = 7.26 Hz, 8H, m-$\mathrm{C_6H_5}$), 7.36 (m, 8H, o-$\mathrm{C_6H_5}$)	9.34 (s, $\mathrm{Si(CH_3)_3}$,[b] 34.90 (d, J_{PC} = 12.2 Hz, $\mathrm{NCH_3}$), 52.69 (s, $\mathrm{NCH_2}$), 85.10 (s, $\mathrm{C_5H_5}$), 122.39 (s, p-$\mathrm{C_6H_5}$), 126.23 (s, m-$\mathrm{C_6H_5}$), 136.31 (s, o-$\mathrm{C_6H_5}$), 164.43 (qui, J_{BC} = 48.8 Hz, ϵ-$\mathrm{C_6H_5}$), 214.12 (d, J_{PC} = 26.8 Hz, CO)	305.10 (s)[b]	37.03 (d, J_{PSi} = 36.3 Hz)[b]	1953
2d	0.38 (s, 9H, $\mathrm{Si(CH_3)_3}$), 2.33 (m, 2H, $\mathrm{NCH_2}$), 2.72 (m, 2H, $\mathrm{NCH_2}$), 2.74 (d, J_{PH} = 10.6 Hz, 3H, $\mathrm{NCH_3}$), 2.80 (d, J_{PH} = 10.2 Hz, 3H, $\mathrm{NCH_3}$), 2.99 (d, J_{PH} = 14.5 Hz, 1H, $\mathrm{PCH_2}$), 3.15 (d, J_{PH} = 14.5 Hz, 1H, $\mathrm{PCH_2}$), 4.36 (s, 5H, $\mathrm{C_5H_5}$), 6.97−7.25 (m, 5H, $\mathrm{C_6H_5}$)	9.60 (s, $\mathrm{Si(CH_3)_3}$), 33.95 (d, J_{PC} = 11.0 Hz, $\mathrm{NCH_3}$), 34.08 (d, J_{PC} = 11.0 Hz, $\mathrm{NCH_3}$), 49.52 (d, J_{PC} = 4.9 Hz, $\mathrm{PCH_2}$), 51.12 (d, J_{PC} = 2.4 Hz, $\mathrm{NCH_2}$), 51.30 (d, J_{PC} = 2.4 Hz, $\mathrm{NCH_2}$), 82.05 (s, $\mathrm{C_5H_5}$), 125.51 (d, J_{PC} = 2.4 Hz, p-$\mathrm{C_6H_5}$), 127.74 (s, m-$\mathrm{C_6H_5}$), 129.93 (d, J_{PC} = 3.6 Hz, o-$\mathrm{C_6H_5}$), 137.29 (d, J_{PC} = 11.0 Hz, ϵ-$\mathrm{C_6H_5}$), 219.77 (d, J_{PC} = 33.0 Hz, CO)	178.69 (s)[a]	34.54 (d, J_{PSi} = 35.0 Hz)[a]	1894
3b	0.54 (s, 9H, $\mathrm{Ge(CH_3)_3}$),[c] 3.00 (d, J_{PH} = 12.2 Hz, 6H, $\mathrm{NCH_3}$), 3.74 (m, 4H, $\mathrm{NCH_2}$), 5.05 (s, 5H, $\mathrm{C_5H_5}$)	8.30 (s, $\mathrm{Ge(CH_3)_3}$),[c] 34.80 (d, J_{PC} = 13.4 Hz, $\mathrm{NCH_3}$), 52.81 (s, $\mathrm{NCH_2}$), 84.49 (s, $\mathrm{C_5H_5}$), 214.54 (d, J_{PC} = 28.1 Hz, CO)	311.12 (s)		1955
3d	0.44 (s, 9H, $\mathrm{Ge(CH_3)_3}$), 2.32 (m, 2H, $\mathrm{NCH_2}$), 2.71 (m, 2H, $\mathrm{NCH_2}$), 2.73 (d, J_{PH} = 10.6 Hz, 3H, $\mathrm{NCH_3}$), 2.80 (d, J_{PH} = 10.2 Hz, 3H, $\mathrm{NCH_3}$), 2.95 (d, J_{PH} = 14.5 Hz, 1H, $\mathrm{PCH_2}$), 3.08 (dd, J = 14.5, 1.7 Hz, 1H, $\mathrm{PCH_2}$), 4.34 (d, J_{PH} = 1.3 Hz, 5H, $\mathrm{C_5H_5}$), 6.96−7.30 (m, 5H, $\mathrm{C_6H_5}$)	8.27 (s, $\mathrm{Ge(CH_3)_3}$), 33.88 (d, J_{PC} = 11.0 Hz, $\mathrm{NCH_3}$), 34.05 (d, J_{PC} = 12.2 Hz, $\mathrm{NCH_3}$), 49.55 (d, J_{PC} = 6.1 Hz, $\mathrm{PCH_2}$), 51.14 (s, $\mathrm{NCH_2}$), 51.28 (d, J_{PC} = 3.7 Hz, $\mathrm{NCH_2}$), 81.36 (s, $\mathrm{C_5H_5}$), 125.51 (d, J_{PC} = 2.4 Hz, p-$\mathrm{C_6H_5}$), 127.74 (s, m-$\mathrm{C_6H_5}$), 129.86 (d, J_{PC} = 2.4 Hz, o-$\mathrm{C_6H_5}$), 137.17 (d, J_{PC} = 11.0 Hz, ϵ-$\mathrm{C_6H_5}$), 220.34 (d, J_{PC} = 32.9 Hz, CO)	178.64 (s)[a]		1898
4b			307.47 (s)		
4e[e]	0.71 (s, with Sn satellites, J_{SnH} = 36.3 Hz, 6H, $\mathrm{SnCH_3}$),[b] 1.28 (d, J_{PH} = 5.9 Hz, 3H, $\mathrm{PCH_3}$), 2.45 (d, J_{PH} = 13.5 Hz, 3H, $\mathrm{NCH_3}$), 2.62 (d, J_{PH} = 11.9 Hz, 3H, $\mathrm{NCH_3}$), 2.78 (m, 1H, $\mathrm{NCH_2}$), 3.04 (m, 3H, $\mathrm{NCH_2}$), 4.65 (d, J_{PH} = 1.3 Hz, 5H, $\mathrm{C_5H_5}$)	6.32 (d, with Sn satellites, J_{PC} = 3.6 Hz, J_{SnC} = 144.2 Hz, $\mathrm{SnCH_3}$),[b] 21.69 (d, J_{PC} = 4.9 Hz, $\mathrm{PCH_3}$), 33.79 (d, J_{PC} = 8.5 Hz, $\mathrm{NCH_3}$), 34.56 (d, J_{PC} = 4.9 Hz, $\mathrm{NCH_3}$), 51.16 (s, $\mathrm{NCH_2}$), 51.90 (d, J_{PC} = 4.9 Hz, $\mathrm{NCH_2}$), 80.48 (s, $\mathrm{C_5H_5}$), 120.86 (qua, J_{FC} = 317.3 Hz, $\mathrm{SO_3CF_3}$), 216.74 (d, with Sn satellites, J_{PC} = 29.3 Hz, J_{SnC} = 225.9, 219.8 Hz, CO)	174.33 (s, with Sn satellites, J_{SnP} = 547.9, 522.1 Hz)[b]	495.8 (d, J_{PSn} = 600.2 Hz)[b]	1942
5b		13.35 (s, $\mathrm{CH_2CH_2CH_2}C\mathrm{H_3}$),[c] 15.76 (s, with Sn satellites, J_{SnC} = 254.0 Hz, $C\mathrm{H_2CH_2CH_2CH_3}$), 27.35 (s, with Sn satellites, J_{SnC} = 63.5 Hz, $\mathrm{CH_2CH_2}C\mathrm{H_2CH_3}$), 29.94 (s, with Sn satellites, J_{SnC} = 20.7 Hz, $\mathrm{CH_2}C\mathrm{H_2CH_2CH_3}$), 34.47 (d, J_{PC} = 12.2 Hz, $\mathrm{NCH_3}$), 52.40 (s, $\mathrm{NCH_2}$), 82.39 (s, $\mathrm{C_5H_5}$), 213.57 (d, J_{PC} = 28.1 Hz, CO)	307.86 (s, with Sn satellites, J_{SnP} = 301.5, 286.8 Hz)	127.44 (d, J_{PSn} = 300.9 Hz)[c]	1963
5d	0.84 (t, J_{HH} = 7.2 Hz, 9H, $\mathrm{CH_2CH_2CH_2C}H_3$), 0.95 (m, 6H, $\mathrm{C}H_2\mathrm{CH_2CH_2CH_3}$), 1.27 (sext, J_{HH} = 7.3 Hz, 6H, $\mathrm{CH_2CH_2C}H_2\mathrm{CH_3}$), 1.48 (m, 6H, $\mathrm{CH_2C}H_2\mathrm{CH_2CH_3}$), 2.26 (m, 2H, $\mathrm{NCH_2}$), 2.64 (m, 2H, $\mathrm{NCH_2}$), 2.65 (d, J_{PH} = 10.6 Hz, 3H, $\mathrm{NCH_3}$), 2.76 (d, J_{PH} = 10.3 Hz, 3H, $\mathrm{NCH_3}$), 2.89 (d, J_{PH} = 15.2 Hz, 1H, $\mathrm{PCH_2}$), 2.95 (d, J_{PH} = 14.9 Hz, 1H, $\mathrm{PCH_2}$), 4.31 (s, 5H, $\mathrm{C_5H_5}$), 6.90−7.23 (m, 5H, $\mathrm{C_6H_5}$)	13.77 (s, $\mathrm{CH_2CH_2CH_2}C\mathrm{H_3}$), 14.36 (s, with Sn satellites, J_{SnC} = 182.1, 174.0 Hz, $C\mathrm{H_2CH_2CH_2CH_3}$), 27.96 (s, with Sn satellites, J_{SnC} = 50.3 Hz, $\mathrm{CH_2CH_2}C\mathrm{H_2CH_3}$), 30.40 (s, with Sn satellites, J_{SnC} = 18.0 Hz, $\mathrm{CH_2}C\mathrm{H_2CH_2CH_3}$), 33.89 (d, J_{PC} = 11.2 Hz, $\mathrm{NCH_3}$), 34.28 (d, J_{PC} = 11.8 Hz, $\mathrm{NCH_3}$), 51.02 (s, $\mathrm{NCH_2}$), 51.08 (d, J_{PC} = 5.6 Hz, $\mathrm{PCH_2}$), 51.34 (d, J_{PC} = 3.1 Hz, $\mathrm{NCH_2}$), 79.40 (s, $\mathrm{C_5H_5}$), 125.55 (d, J_{PC} = 2.5 Hz, p-$\mathrm{C_6H_5}$), 127.77 (d, J_{PC} = 1.9 Hz, m-$\mathrm{C_6H_5}$), 129.86 (d, J_{PC} = 3.1 Hz, o-$\mathrm{C_6H_5}$), 137.26 (d, J_{PC} = 10.0 Hz, ϵ-$\mathrm{C_6H_5}$), 219.83 (d, J_{PC} = 33.6 Hz, CO)	179.83 (s, with Sn satellites, J_{SnP} = 334.1, 318.5 Hz)	107.76 (d, J_{PSn} = 336.0 Hz)[c]	1892
5e		8.88 (s, with Sn satellites, J_{SnC} = 312.5, 300.3 Hz, $\mathrm{Sn}C\mathrm{H_2CH_2CH_2CH_3}$),[c] 13.64 (s, $\mathrm{PCH_2CH_2CH_2}C\mathrm{H_3}$), 13.72 (s, $\mathrm{SnCH_2CH_2CH_2}C\mathrm{H_3}$), 27.36 (s, $\mathrm{PCH_2CH_2}C\mathrm{H_2CH_3}$), 27.57 (s, with Sn satellites, J_{SnC} = 51.2 Hz, $\mathrm{SnCH_2CH_2}C\mathrm{H_2CH_3}$), 28.40 (s, $\mathrm{PCH_2}C\mathrm{H_2CH_2CH_3}$), 29.42 (s, with Sn satellites, J_{SnC} = 19.6 Hz, $\mathrm{SnCH_2}C\mathrm{H_2CH_2CH_3}$), 33.07 (d, J_{PC} = 9.8 Hz, $\mathrm{NCH_3}$), 33.46 (d, J_{PC} = 12.3 Hz, $\mathrm{NCH_3}$), 51.51 (m, $\mathrm{NCH_2}$), 79.92 (s, $\mathrm{C_5H_5}$), 216.99 (d, J_{PC} = 37.8 Hz, CO)[f]	173.72 (s, with Sn satellites, J_{SnP} = 548.1, 526.6 Hz)	589.06 (d, J_{PSn} = 552.4 Hz)[c]	1934

[a] In $\mathrm{CDCl_3}$. [b] In $\mathrm{CD_2Cl_2}$. [c] In $\mathrm{CH_2Cl_2}$. [d] Nakazawa, H.; Yamaguchi, Y.; Mizuta, T.; Ichimura, S.; Miyoshi, K. *Organometallics* **1995**, *14*, 4635. [e] Nakazawa, H.; Yamaguchi, Y.; Miyoshi, K. *Organometallics* **1996**, *15*, 1337. [f] The $\mathrm{CH_2}$ carbon directly bonded to the P atom could not be identified due to being superimposed on the butyl carbon resonances.

Scheme 3



Scheme 4



Complex **3b** is stable at room temperature in solution and does not undergo germyl migration from Fe to the phosphenium P. The reaction of **3b** with $PhCH_2MgCl$ yielded isolable $[Cp(CO)(GeMe_3)Fe\{PNN(CH_2Ph)\}]$ (**3d**), which was fully characterized.

Reaction of $Cp(CO)(SnMe_3)Fe\{PNN(OMe)\}$ (4a) with a Lewis Acid. A stannyl complex **4a** was prepared from $Cp(CO)_2Fe(SnMe_3)$ and PNN(OMe) by photolysis in 72% yield. The reaction of **4a** with $BF_3{\cdot}OEt_2$ caused the formation of several kinds of complexes, indicating that $BF_3{\cdot}OEt_2$ was not an adequate Lewis acid for a stannyl complex. One of the products was suggested by the ^{31}P NMR spectrum ($\delta = 307.47$) to be a cationic phosphenium complex (**4b**) (Scheme 4), but the other products have not been identified.

When $Me_3SiOSO_2CF_3$ (TMSOTf) was used as a Lewis acid, the reaction proceeded cleanly, as evidenced by the ^{31}P NMR spectrum of the reaction mixture. The product could be isolated as yellow crystals. The spectroscopic data and elemental analysis data established the formation of a stannylene complex formulated as $[Cp(CO)(SnMe_2)Fe\{PNN(Me)\}]OTf$ (**4e**) (Scheme 4). The ^{31}P NMR spectrum shows a singlet at 174.33 ppm with Sn satellites, indicating not phosphenium but PNN(Me) ligand formation. In the ^{119}Sn NMR spectrum, the chemical shift (495.8 ppm) is at considerably lower field than that of **4a** (99.1 ppm), indicating the formation of an $Fe{=}SnMe_2$ fragment. The ^1H and ^{13}C NMR spectra show that there are two Me groups on an Sn and one Me group on a P. Exactly the same complex was produced in the reaction of $Cp(CO)(SnMe_3)Fe\{PNN(OEt)\}$ with TMSOTf, indicating that the methyl group directly bonded to the coordinating P in **4e** comes from an $SnMe_3$ group on **4a**.

The X-ray structure of **4e** confirmed that this was a doubly-base-stabilized stannylene complex in the solid state (vide infra). In solution, there may be an equilibrium for **4e** between a base-stabilized and a base-free stannylene form. The molar conductivity (Λ_M) of **4e** in nitromethane was measured to be 76.1 Ω^{-1} cm^2 mol^{-1}, close to that (82.4 Ω^{-1} cm^2 mol^{-1}) of $[Cp(CO)(PPh_3)Fe\{PNN(Me)\}]BF_4$, which is a typical 1:1 electrolyte and is a complex structurally related to **4e**.[9] Therefore, **4e** seems to be present in nitromethane as a cationic stannylene complex (in which, however, the solvent may coordinate to the tin) and an OTf^- anion. In the ^{119}Sn NMR spectrum of **4e** in CH_2Cl_2, the very low chemical shift (495.8 ppm) and the large $J_{^{119}Sn-P}$ value (600.2 Hz) strongly support that **4e** is present to a considerable extent as a base-free stannylene form.

The interesting point in the reaction of the stannyl complex (**4a**) with TMSOTf is that not a stannyl but an alkyl group on the tin atom migrates to a coordinated

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(4) (a) Muetterties, E. L.; Kirner, J. F.; Evans, W. J.; Watson, P. L.; Abdel-Meguid, S.; Tavanaiepour, I.; Day, V. W. *Proc. Natl. Acad. Sci. U.S.A.* **1978**, *75*, 1056. (b) Day, V. W.; Tavanaiepour, I.; Abdel-Meguid, S. S.; Kirner, J. F.; Goh, L.-Y.; Muetterties, E. L. *Inorg. Chem.* **1982**, *21*, 657. (c) Choi, H. W.; Gavin, R. M.; Muetterties, E. L. *J. Chem. Soc., Chem. Commun.* **1979**, 1085.

(5) (a) Cowley, A. H.; Kemp, R. A.; Wilburn, J. C. *Inorg. Chem.* **1981**, *20*, 4289. (b) Cowley, A. H.; Kemp, R. A.; Ebsworth, E. A. V.; Rankin, D. W. H.; Walkinshaw, M. D. *J. Organomet. Chem.* **1984**, *265*, C19.

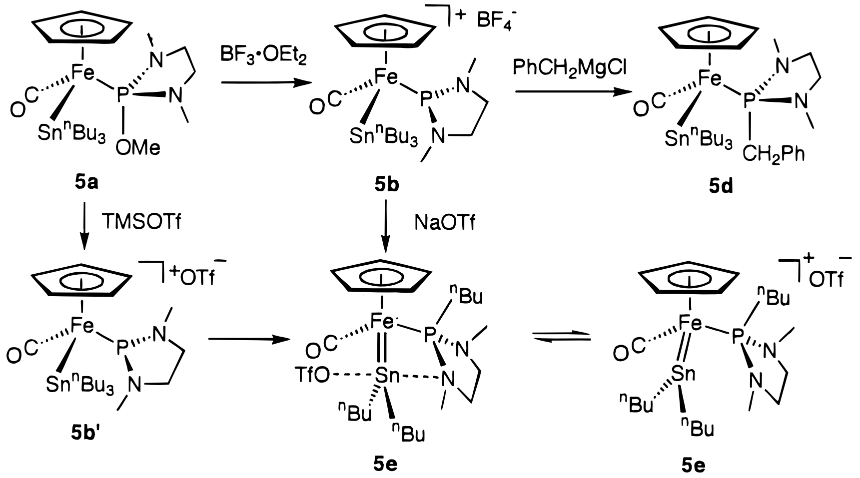
(6) (a) Nakazawa, H.; Ohta, M.; Yoneda, H. *Inorg Chem.* **1988**, *27*, 973. (b) Nakazawa, H.; Ohta, M.; Miyoshi, K.; Yoneda, H. *Organometallics* **1989**, *8*, 638. (c) Nakazawa, H.; Yamaguchi, Y.; Miyoshi, K. *J. Organomet. Chem.* **1994**, *465*, 193. (d) Nakazawa, H.; Yamaguchi, Y.; Mizuta, T.; Miyoshi, K. *Organometallics* **1995**, *14*, 4173 and references cited therein. (e) Nakazawa, H.; Yamaguchi, Y.; Miyoshi, K.; Nagasawa, A. *Organometallics* **1996**, *15*, 2517. (f) Yamaguchi, Y.; Nakazawa, H.; Itoh, T.; Miyoshi, K. *Bull. Chem. Soc. Jpn.* **1996**, *69*, 983. (g) Yamaguchi, Y.; Nakazawa, H.; Kishishita, M.; Miyoshi, K. *Organometallics* **1996**, *15*, 4383. (h) Nakazawa, H.; Kishishita, M.; Yoshinaga, S.; Yamaguchi, Y.; Mizuta, T.; Miyoshi, K. *J. Organomet. Chem.* **1997**, *529*, 423.

(7) (a) Nakazawa, H.; Yamaguchi, Y.; Mizuta, T.; Ichimura, S.; Miyoshi, K. *Organometallics* **1995**, *14*, 4635. (b) Mizuta, T.; Yamasaki, T.; Nakazawa, H.; Miyoshi, K. *Organometallics* **1996**, *15*, 1093. (c) Nakazawa, H.; Yamaguchi, Y.; Miyoshi, K. *Organometallics* **1996**, *15*, 4661.

(8) Nakazawa, H.; Yamaguchi, Y.; Miyoshi, K. *Organometallics* **1996**, *15*, 1337.

(9) For a variety of Λ_M values, see for example: Geary, W. *J. Coord. Chem. Rev.* **1971**, *7*, 81.

Scheme 5



phosphorus atom to give a stannylene complex. The reaction seems to proceed via a phosphenium complex.

Reaction of $Cp(CO)(Sn^nBu_3)Fe\{PNN(OMe)\}$ (5a) with a Lewis Acid. The reaction of an Sn^nBu_3 complex **5a** with a Lewis acid is very informative from a mechanistic point of view (Scheme 5). In the reaction of **5a** with $BF_3{\cdot}OEt_2$, a cationic phosphenium complex **5b** is cleanly formed. Although **5b** could not be isolated, the spectroscopic data confirmed the formation of a cationic phosphenium complex (for example, a singlet at 307.86 ppm in ^{31}P NMR). The treatment of **5b** with $PhCH_2MgCl$ yielded **5d**, which was isolated and fully characterized. This is further evidence that **5b** is a cationic phosphenium complex.

The reaction of **5a** with TMSOTf was monitored by ^{31}P NMR spectroscopy. When **5a** and TMSOTf were mixed, a singlet at 177.80 ppm due to the starting complex disappeared and a new singlet at 307.86 ppm was observed. The chemical shift is characteristic of a cationic phosphenium complex and identical to the resonance for **5b**. Therefore, the product is considered to be $[Cp(CO)(Sn^nBu_3)Fe\{PNN\}]OTf$ (**5b′**). With time, a new resonance at 173.72 ppm appeared at the expense of the resonance at 307.86 ppm, and finally, only the resonance at 173.72 ppm was observed. The complex thus formed is considered to be stannylene complex **5e** because its ^{13}C, ^{31}P, ^{119}Sn NMR and the IR spectra resemble those of **4e**, although the isolation of **5e** was not possible. This observation clearly shows that an OMe group on the phosphorus is first abstracted as an anion to give a phosphenium complex, which then undergoes alkyl migration to give a stannylene complex. It has been reported that an Sn−Me bond is more reactive than an Sn−Bu bond in electrophilic cleavage reactions.[10] The relatively strong Sn−Bu bond retards the Bu migration from Sn to P to the extent that a cationic phosphenium complex is detected spectroscopically.

Complex **5b**, prepared from **5a** and $BF_3{\cdot}OEt_2$, gradually decomposes and is not converted into stannylene complex **5e**, whereas **5b′**, prepared from **5a** and TMSOTf, changes quantitatively to **5e**. The difference between **5b** and **5b′** is in its counteranion. Therefore, we assumed that the Bu migration would be promoted by an OTf^- anion. In order to exemplify this assumption, 1.6 equiv of NaOTf was added to the solution prepared from **5a** and $BF_3{\cdot}OEt_2$, in other words, containing **5b**. After the solution was stirred at room temperature for a few hours, **5b** disappeared and **5e** was formed instead. Therefore, it can be said that an OTf^- anion promotes an alkyl migration from Sn to P in a phosphenium complex, presumably by coordination of the oxygen in OTf^- to the Sn.

Many experimental results have been accumulated about transition-metal stannylene complexes and they have been reviewed by Petz,[11] Herrmann,[12] Nelson,[13] and Lappert.[14] However, to our knowledge, only three examples are known in which a stannylene complex is prepared by Sn−C bond cleavage.[15,16] Of the three, only one example shows alkyl migration from a stannyl group on a transition metal: alkyl group migration from tin to the carbon of a coordinated carbon monoxide ligand in an Os cluster, forming an Os stannylene complex.[16a] We believe that our finding is the first example of the migration of an alkyl group on a tin ligand to a coordinated heteroatom (in this case, phosphorus) to give a stannylene complex.

Crystal Structures of 2b′ and 4e. X-ray structure analyses of **2b′** and **4e** were undertaken. The ORTEP drawings of **2b′** and **4e** are displayed in Figures 1 and 2, respectively. The crystal data and the selected bond distances and angles are summarized in Tables 2−4.

The X-ray structure of **2b′** shows that the iron takes a normal piano-stool configuration with a cyclopentadienyl ligand bonded in an η^5 fashion, a terminal CO ligand, a $SiMe_3$ group, and a diamino-substituted phosphenium ligand. The most interesting structural feature is that the bond distance of Fe1−P1 (2.018(2) Å) is significantly shorter than that of an Fe−P dative bond: for example, $Fe-PPh_3 = 2.237(2)$ Å, $Fe-PNN(Me) = 2.201(2)$ Å for $[Cp(CO)(PPh_3)Fe\{PNN(Me)\}]BF_4$[7a]; $Fe-PNN(OEt) = 2.164(2)$ Å for $[Cp(CO)(CH_2PPh_3)Fe\{PNN$-

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(10) Wardell, J. L. *Chemistry of Tin*; Harrison, P. G., Ed.; Chapman and Hall: New York, 1989; Chapter 5, p 170.

(11) Petz, W. *Chem. Rev.* **1986**, *86*, 1019.

(12) Herrmann, W. A. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 56.

(13) Holt, M. S.; Wilson, W. L.; Nelson, J. H. *Chem. Rev.* **1989**, *89*, 11.

(14) Lappert, M. F.; Rowe, R. S. *Coord. Chem. Rev.* **1990**, *100*, 267.

(15) Almedia, J. F.; Dixon, K. R.; Eaborn, C.; Hitchcock, P. B.; Pidcock, A.; Vinaixa, S. *J. Chem. Soc., Chem. Commun.* **1982**, 1315.

(16) (a) Cardin, C. J.; Cardin, D. J.; Power, J. M.; Hursthouse, M. B. *J. Am. Chem. Soc.* **1985**, *107*, 505. (b) Buil, M. L.; Esteruelas, M. A.; Lahoz, F. J.; Onate, E.; Oro, L. A. *J. Am. Chem. Soc.* **1995**, *117*, 3619.

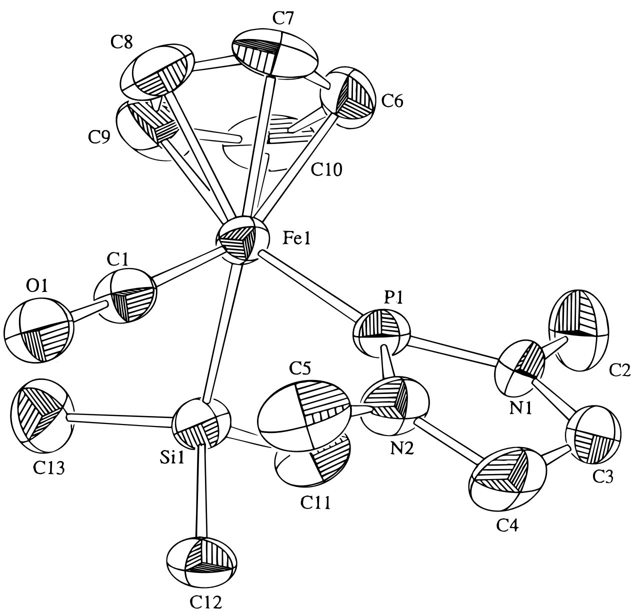

Figure 1. ORTEP drawing of **2b′** showing the atom-numbering scheme (the BPh_4^- counterion is omitted for clarity). The thermal ellipsoids are drawn at the 30% probability level.

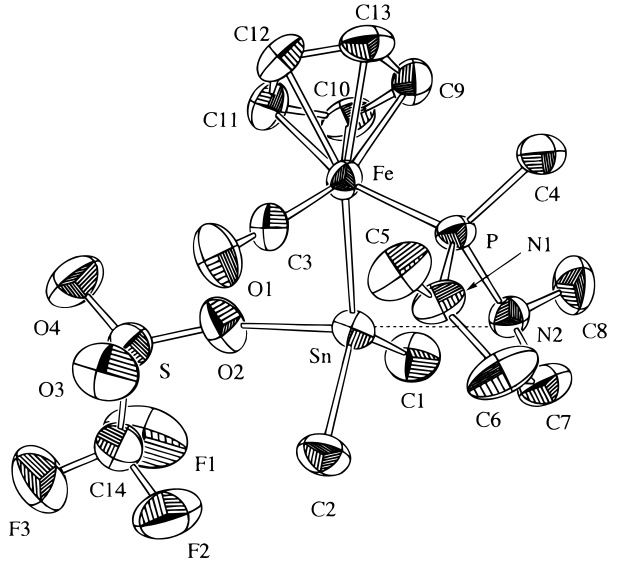

Figure 2. ORTEP drawing of **4e** showing the atom-numbering scheme. The thermal ellipsoids are drawn at the 30% probability level.

Table 2. Summary of Crystal Data for 2b′ and 4e

	2b′	**4e**
formula	$C_{37}H_{44}BFeN_2OPSi$	$C_{14}H_{24}F_3FeN_2O_4P_2SSn$
fw	658.48	578.92
cryst syst	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$
cell constants		
a, Å	14.867(2)	16.010(2)
b, Å	9.833(1)	7.852(2)
c, Å	25.091(4)	18.420(3)
β, deg	105.19(1)	110.35(1)
V, Å^3	3539.7(1)	2171.1(7)
Z	4	4
D_{calcd}, g cm^{-3}	1.24	1.77
μ, cm^{-1}	5.35	20.33
cryst size, mm	0.38 × 0.30 × 0.10	0.32 × 0.25 × 0.13
radiation	Mo Kα (λ = 0.710 93 Å)	Mo Kα (λ = 0.710 93 Å)
scan technique	ω	ω
scan range, deg	$3 > 2\theta < 47.5$	$3 < 2\theta < 60$
scan rate, deg min^{-1}	5.1	5.1
no. of unique data	5838	6726
no of unique data $F_o > 3\sigma(F_o)$	1727	3666
R	0.051	0.043
R_w	0.042	0.040

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

Bond Distances			
Fe1−P1	2.018(2)	Si1−C13	1.857(8)
Fe1−Si1	2.364(3)	C1−O1	1.170(7)
F1−C1	1.718(7)	N1−C2	1.450(10)
Fe1−C6	2.099(7)	N1−C3	1.444(9)
Fe1−C7	2.079(8)	N2−C4	1.463(9)
Fe1−C8	2.063(9)	N2−C5	1.430(10)
Fe1−C9	2.022(9)	C3−C4	1.500(10)
Fe1−C10	2.075(8)	C6−C7	1.380(10)
P1−N1	1.621(6)	C6−C10	1.360(10)
P1−N2	1.601(6)	C7−C8	1.320(10)
Si1−C11	1.860(8)	C8−C9	1.340(10)
Si1−C12	1.867(8)	C9−C10	1.330(10)

Bond Angles			
P1−Fe1−S1	85.73(9)	C4−N2−C5	117.4(7)
P1−Fe1−C1	97.3(3)	Fe1−C1−O1	175.3(7)
Si1−Fe1−C1	81.5(3)	N1−C3−C4	108.0(6)
Fe1−P1−N1	132.0(3)	N2−C4−C3	105.5(7)
Fe1−P1−N2	133.1(3)	Fe1−Si1−C11	113.8(3)
N1−P1−N2	94.8(4)	Fe1−Si1−C12	113.4(3)
P1−N1−C2	127.4(6)	Fe1−Si1−C13	109.5(3)
P1−N1−C3	113.8(6)	C11−Si1−C12	105.8(3)
C2−N1−C3	118.5(6)	C11−Si1−C13	107.9(4)
P1−N2−C4	115.0(6)	C12−Si1−C13	105.9(4)
P1−N2−C5	127.3(6)		

(OEt)}]BF_4.[7a] Cowley et al. reported the X-ray structure of [$(CO)_4Fe\{P(NEt_2)_2\}$]$AlCl_4$, which is, we believe, the only iron phosphenium complex determined by X-ray analysis.[5b] The Fe−P bond distance is 2.10(5) Å, which, to our knowledge, has been the shortest one among phosphorus-bonded iron complexes reported to date. However, the Fe−P bond distance for **2b′** is shorter than that in Cowley's complex. This result strongly suggests double-bond character between the Fe−phosphenium P, which also is supported by the geometry of the phosphenium phosphorus which is trigonal planar: the sum of the angles at the phosphorus is 359.9°.

Two nitrogen atoms on the phosphenium phosphorus have a trigonal planar geometry: the sum of the angles is 359.7° for both nitrogen atoms. The P−N bond distances are 1.621(6) and 1.600(6) Å. For *trans*-[(bpy)$(CO)_2$$\{PNN(OMe)\}Mo\{PNN\}]^+$ and *trans*-[(bpy)$(CO)_2$$\{\overline{PN(^tBu)CH_2CH_2O}(OMe)\}Mo\{\overline{PN(^tBu)CH_2CH_2O}\}]^+$, the P−N bond distances in the phosphenium ligand are 1.642(5) and 1.644(5) Å, respectively, which are almost equal to those of the amino-substituted phosphite ligand in the same complex.[6d] Therefore, we have suggested that the nitrogens on the phosphenium ligand in these Mo complexes do not donate their lone pair electrons to the vacant p orbital on the phosphenium phosphorus. In the case of **2b′**, the P−N bond distances are slightly shorter than those for the Mo complexes mentioned above. Therefore, a small amount of the π-donation from N to P(phosphenium) in the iron phosphenium complex may exist.

Also interesting is the orientation of the phosphenium ligand in a crystal of **2b′**. The Fe1−P1−N1−N2 least-squares mean plane almost holds the Fe−CO axis and is almost perpendicular to the Fe−$SiMe_3$ axis: Torsion angles are 79.1° for Si1−Fe1−P1−N1 and 159.9° for C1−Fe1−P1−N1 (Figure 3). An empty p orbital on the phosphenium phosphorus is perpendicular to the phos-

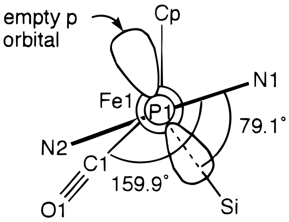

Figure 3. Newman projection along the P1−Fe1 bond for **2b′**.

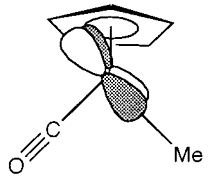

Figure 4. d-Orbital HOMO of the Cp(CO)MeFe fragment.

Table 4. Selected Bond Distances (Å) and Angles (deg) for 4e

Bond Distances			
Sn−Fe	2.488(1)	P−N2	1.722(4)
Sn−O2	2.343(4)	P−C4	1.826(6)
Sn−C1	2.136(5)	F1−C14	1.272(7)
Sn−C2	2.145(5)	F2−C14	1.333(7)
Sn−N2	2.695(4)	F3−C14	1.284(7)
Fe−P	2.140(2)	O1−C3	1.151(6)
Fe−C3	1.738(5)	N1−C5	1.460(7)
S−O2	1.453(4)	N1−C6	1.431(7)
S−O3	1.413(4)	N2−C7	1.484(7)
S−O4	1.415(4)	N2−C8	1.492(7)
S−Cl4	1.814(6)	C6−C7	1.467(9)
P−N1	1.663(4)		

Bond Angles			
Fe−Sn−O2	99.0(1)	Fe−P−N1	118.9(2)
Fe−Sn−N2	77.0(1)	Fe−P−N2	113.2(2)
Fe−Sn−C1	126.4(2)	Fe−P−C4	118.2(2)
Fe−Sn−C2	123.2(2)	N1−P−N2	91.0(2)
O2−Sn−N2	173.8(1)	N1−P−C4	105.8(3)
O2−Sn−C21	84.8(2)	N2−P−C4	105.9(2)
O2−Sn−C2	94.8(2)	Sn−O2−S	139.8(3)
N2−Sn−C1	93.8(2)	P−N1−C5	122.1(4)
N2−Sn−C2	91.4(2)	P−N1−C6	113.5(4)
C1−Sn−C2	109.5(3)	C5−N1−C6	116.7(5)
Sn−Fe−P	81.0(1)	Sn−N2−P	83.0(2)
Sn−Fe−C3	88.0(2)	Sn−N2−C7	125.4(3)
P−Fe−C3	94.2(2)	Sn−N2−C8	105.8(4)
O2−S−O3	114.5(3)	P−N2−C7	110.0(4)
O2−S−O4	112.0(3)	P−N2−C8	115.7(4)
O2−S−C14	101.1(3)	C7−N2−C8	113.7(5)
O3−S−O4	118.0(3)	Fe−C3−O1	177.7(5)
O3−S−C14	105.1(3)	N1−C6−C7	109.1(6)
O4−S−C14	103.7(3)	N2−C7−C6	108.8(5)

phenium ligand plane due to the sp^2 hybridization of the phosphorus. The HOMO of the Cp(CO)FeMe fragment has been reported, as shown in Figure 4.[17] Since a HOMO of its silyl analogue, Cp(CO)Fe(SiR$_3$), would be almost identical, the orientation of the phosphenium ligand revealed by X-ray analysis is optimal for accepting electron density from the HOMO of the Cp(CO)Fe(SiR$_3$) fragment.

The structure of **4e** shows that the iron has a normal piano-stool configuration. The interesting feature of this complex is the geometry of the tin atom. The tin atom is apparently five-coordinate, which is best described as trigonal bipyramidal. The FeSnC1C2 unit forms a trigonal plane (the sum of angles around Sn amounts to 359.1°), and the O2 and N2 atoms occupy the axial sites to make 173.8(1)° of the O2−Sn−N2 angle. In comparison with structures of O or N base-stabilized stannylene complexes reported previously,[11,15,18] the Sn−O2 bond length (2.343(4) Å) can be considered to be a dative bond whereas the Sn−N2 bond is slightly longer (2.695(4) Å) but significantly shorter than the sum of the van der Waals radii (3.72 Å). Therefore, **4e** should be regarded as a doubly-base-stabilized stannylene complex of iron, though the Fe−Sn bond is not shortened in comparison with various Cp(CO)$_2$Fe(SnR$_3$) compounds, where Fe−Sn bond lengths between 2.46 and 2.56 Å have been measured.[11]

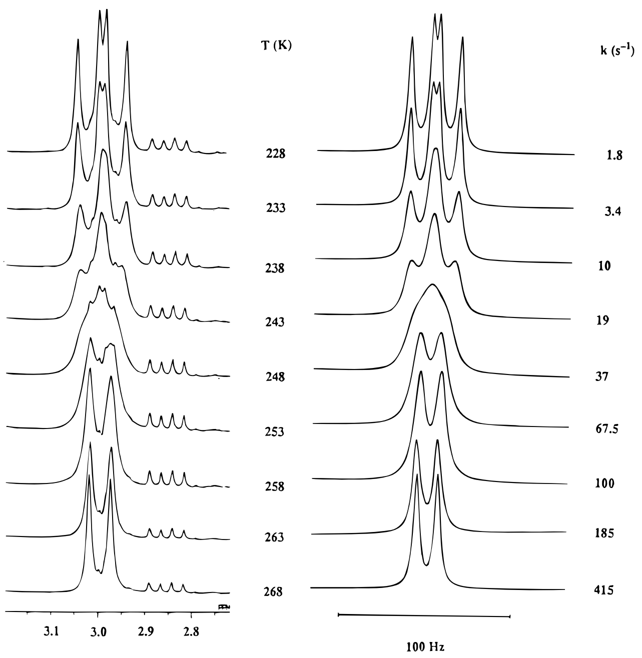

Figure 5. 270 MHz variable-temperature experimental (left) and simulated (right) NMR spectra of the methyl proton region of **2b′** in CD$_2$Cl$_2$. Extra peaks in the higher field region of the experimental spectra are due to impurity.

Variable-Temperature ^{1}H NMR Spectroscopy of 2b, 3b, and 5b. Since cationic phosphenium iron complexes containing trimethylsilyl, trimethylgermyl, and tri-n-butylstannyl groups were found to be stable, the solution structures and dynamics have been investigated by variable-temperature ^{1}H NMR experiments. The ^{1}H NMR signals of the methyl protons on the amino groups for **2b** were temperature dependent, as shown in Figure 5. While the spectrum shows a doublet above 268 K, at lower temperatures the signals broaden and coalesce at 248 K. As the temperature is lowered further, the broad resonance splits and eventually sharpens into two doublets. This spectral behavior is explained on the basis of phosphenium ligand rotation along the P−Fe axis: it rotates freely at room temperature and the rotation is frozen or slower than the NMR time scale at 228 K. Similar spectral changes were observed for **3b** and **5b**: coalescence temperature is 221 K for **3b** and 223 K for **5b**. Line-shape analysis yielded calculated spectra in good agreement with the experimental VT NMR data and afforded activation parameters (Table 5) via an Eyring analysis (Figure 6).[19,20]

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[17] Schilling, B. E. R.; Hoffmann, R.; Faller, J. W. *J. Am. Chem. Soc.* **1979**, *101*, 592.

[18] For example, see: (a) Scheidsteger, O.; Huttner, G.; Dehnicke, K.; Pebler, J. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 428. (b) Balch, A. L.; Oram, D. E.; *Organometallics* **1988**, *7*, 155.

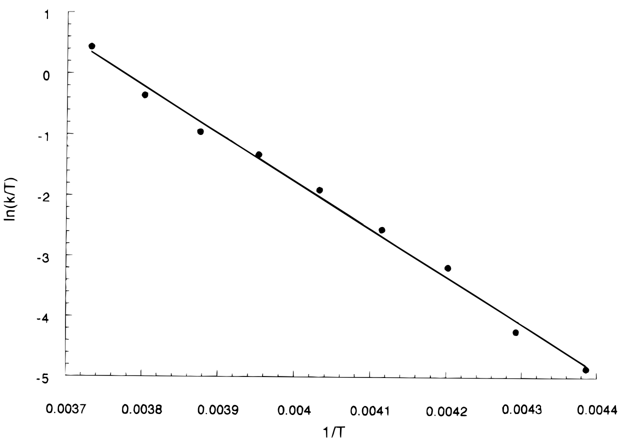

Figure 6. Eyring plot for the rotation of the phosphenium ligand along the Fe−P axis derived from variable-temperature NMR data.

Table 5. Activation Parameters $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$, and $\Delta G^{\ddagger}$ for 2b, 3b, and 5b

	2b	**3b**	**5b**
$\Delta H^{\ddagger}$ (kcal mol^{-1})	15.6 ± 0.46	14.3 ± 1.10	12.7 ± 0.53
$\Delta S^{\ddagger}$ (cal mol^{-1} K^{-1})	11.7 ± 1.85	14.3 ± 5.18	8.60 ± 2.49
$\Delta G^{\ddagger}$ (kcal mol^{-1})	12.7 ± 0.9 (248 K)	11.0 ± 2.2 (221 K)	10.8 ± 1.1 (223 K)

The small positive entropies of activation in all cases imply no participation of solvent, which is consistent with phosphenium ligand rotation. The comparable values of $\Delta H^{\ddagger}$ have been observed for **2b**, **3b**, and **5b**. It is well-known in organosilicon chemistry that carbonium ion formation or development at a position β to a silicon atom ($Si-C-C^+$) is favored.[21] The so-called β-effect has been ascribed to overlap between the vacant p orbital on the β carbon atom and the σ orbital between the silicon atom and the α carbon atom ($\sigma-\pi$ conjugation). Recently, the β-effect was reported for germyl and stannyl groups, and the magnitude has been predicted to increase in the order C < Si < Ge < Sn.[22] The stability of **2b**, **3b**, and **5b** can be considered to be ascribed to the β-effect of the silyl, germyl, and stannyl groups, respectively, because the positive phosphenium phosphorus is located at the β position to the group 14 elements ($E-Fe-P^+$). However, the $\Delta H^{\ddagger}$ values obtained are almost identical for **2b**, **3b**, and **5b**. Therefore, the β-effect of a group 14 element on the stability of a phosphenium complex seems to be small.

Our observation of barriers to rotation about a transition-metal−phosphorus bond in cationic phosphenium complexes $[L_nM-PR_2]^+$ is unprecedented. However, some barriers have been reported for three-electron donor terminal phosphide complexes, $[L_nM{=}PR_2]$, which can be considered as phosphenium complexes if one thinks that they consist of L_nM^- and $^+PR_2$: $\Delta G^{\ddagger} < 10$ kcal/mol for $Cp^*HfCl_2\{P(CMe_3)_2\}$ and $Cp^*HfCl\{P(CMe_3)_2\}_2$,[23] $\Delta G^{\ddagger} = 8.4-9.9$ kcal/mol for 1,2-$M_2(PR_2)_2(NMe_2)_4$ (M = Mo, W),[24] and $\Delta G^{\ddagger} = 11.6$ kcal/mol for $Cp^*Ta(C_2H_4)Me(PPh_2)$.[25] Therefore, the comparison of these data reveals that barriers to rotation about an $M-PR_2$ bond do not differ considerably whether these complexes are electrically cationic or neutral.

Variable-Temperature ^{1}H NMR Spectroscopy of 4e. The ^{1}H and ^{13}C NMR spectra of **4e** in CD_2Cl_2 at room temperature show that the two methyl groups on the Sn atom are magnetically equivalent, indicating that an OTf^- anion and an amino group in the phosphorus ligand dissociate from the Sn, resulting in the rotation of the $SnMe_2$ group along with Fe−Sn bond. The ^{1}H NMR signals of the Me groups in **4e** were found to be temperature dependent. One singlet was observed above 300 K, whereas two resonances were observed at 178 K. As the temperature was raised, the two resonances gradually broadened and finally coalesced to one broad resonance at 188 K. With an increase in temperature, the resonance became to a sharp singlet. Application of the coalescence formula gave a $\Delta G^{\ddagger}$(188 K) value of 9.0 kcal/mol for the methyl group exchange. This value is close to the $\Delta G^{\ddagger}$ values for methyl exchange of $Re{=}EMe_2$ (E = Si and Ge) reported by Gladysz: $\Delta G^{\ddagger}$ (307 K) > 14.8 kcal/mol for $[CpRe(NO)(PPh_3)({=}SiMe_2)]OTf$[26] and $\Delta G^{\ddagger}$ (211 K) = 9.6 kcal/mol for $[CpRe(NO)(PPh_3)({=}GeMe_2)]OTf$.[27]

Conclusion

The reaction product in the reaction of $Cp(CO)(ER_3)Fe\{PNN(OMe)\}$ (**a**) (E = group 14 element) with a Lewis acid such as $BF_3{\cdot}OEt_2$ or TMSOTf depends on E (Scheme 6). In any case, an OMe anion abstraction by a Lewis acid uniformly takes place at the first stage of the reaction to give a cationic phosphenium iron complex containing an ER_3 ligand (**b**). The subsequent reaction is strongly dependent on E. When E is C, migratory insertion of the phosphenium ligand into the Fe−C bond

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[19] Sandström, J. In *Dynamic NMR Spectroscopy*; Academic Press: New York, 1982; Chapter 7.

[20] (a) DNMR5: Stephenson, D. S.; Binch, G. *Program 365, Quantum Chemistry Program Exchange*; Indiana University: Bloomington, IN. (b) DNMR5 (IBM-PC version): LeMaster, C. B.; LeMaster, C. L.; True, N. S. *Program QCMP 059, Quantum Chemistry Program Exchange*; Indiana University: Bloomington, IN.

[21] (a) Colvin, E. W. *Silicon in Organic Synthesis*; Butterworths: London, 1981; p 15. (b) Apeloig, Y. *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; John Wiley & Sons: New York, 1989; Vol. 1, p 196. (c) Bassindale, A. R.; Taylor, P. G. *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds; John Wiley & Sons: New York, 1989; Vol. 2, p 905. (d) Thomas, S. E. *Organic Synthesis, The Roles of Boron and Silicon*; Oxford University Press: Oxford, 1991; p 48.

[22] (a) Dallaire, C.; Brook, M. A. *Organometallics* **1990**, *9*, 2873. (b) Dallaire, C.; Brook, M. A. *Organometallics* **1993**, *12*, 2332. (c) Nguyen, K. A.; Gordon, M. S.; Wang, G.-t.; Lambert, J. B. *Organometallics* **1991**, *10*, 2798.

[23] Roddick, D. M.; Santarsiero, B. D.; Bercaw, J. E. *J. Am. Chem. Soc.* **1985**, *107*, 4670.

[24] Buhro, W. E.; Chisholm, M. H.; Folting, K.; Huffman, J. C.; Martin, J. D.; Streib, W. E. *J. Am. Chem. Soc.* **1992**, *114*, 557.

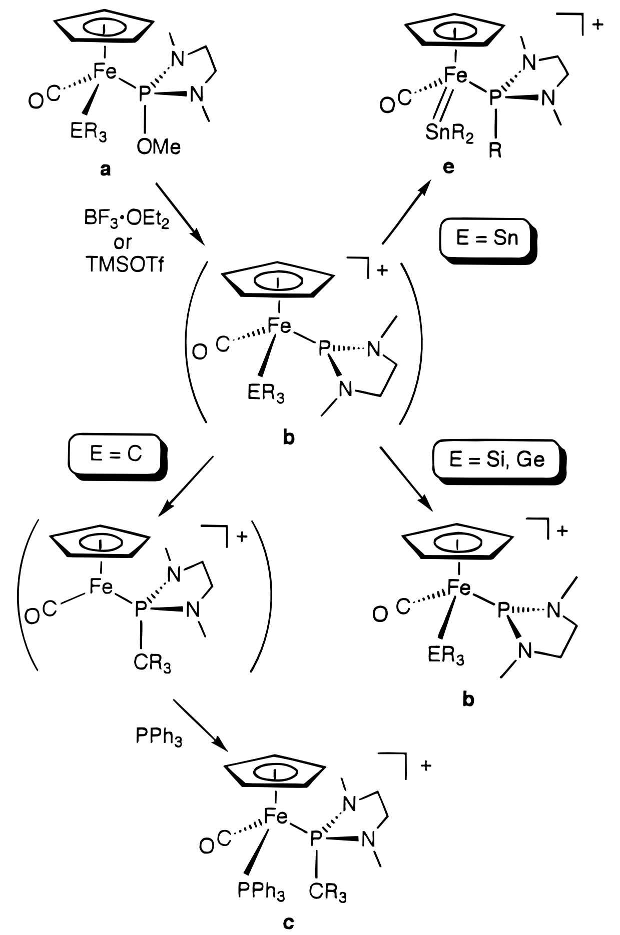
[25] Baker, R. T.; Calabrese, J. C.; Harlow, R. L.; Williams, I. D. *Organometallics* **1993**, *12*, 830.

[26] Lee, K. E.; Arif, A. M.; Gladysz, J. A. *Chem. Ber.* **1991**, *124*, 309.

[27] Lee, K. E.; Gladysz, J. A. *Phosphorus, Sulfur Silicon Relat. Elem.* **1994**, *87*, 113.

[28] (a) Sharma, H. K.; Pannell, K. H. *Chem. Rev.* **1995**, *95*, 1351. (b) Tobita, H.; Ueno, K.; Shimoi, M.; Ogino, H. *J. Am. Chem. Soc.* **1990**, *112*, 3415. (c) Tobita, H.; Wada, H.; Ueno, K.; Ogino, H. *Organometallics* **1994**, *13*, 2545. (d) Okazaki, M.; Tobita, H.; Ogino, H. *Chem. Lett.* **1996**, 477. (e) Ueno, K.; Nakano, K.; Ogino, H. *Chem. Lett.* **1996**, 459. (f) Pannell, K. H.; Brun, M.-C.; Sharma, H.; Jones, K.; Sharma, S. *Organometallics* **1994**, *13*, 1075. (g) Pannell, K. H.; Cervantes, J.; Hernandez, C.; Cassias, J.; Vincenti, S. *Organometallics* **1986**, *5*, 1056. (h) Pestana, D. C.; Koloski, T. S.; Berry, D. H. *Organometallics* **1994**, *13*, 4173. (i) Tanaka, Y.; Yamashita, H.; Tanaka, M. *Organometallics* **1995**, *14*, 530. (j) Tamao, K.; Sun, G.; Kawachi, A. *J. Am. Chem. Soc.* **1995**, *117*, 8043. (k) Mitchell, G. P.; Tilley, T. D.; Yap, G. P. A.; Rheingold, A. L. *Organometallics* **1995**, *14*, 5472. (l) Tatsumi, K.; Sekiguchi, Y.; Nakamura, A. *J. Am. Chem. Soc.* **1986**, *108*, 1358. (m) Pannell, K. H.; Sharma, S. *Organometallics* **1991**, *10*, 1655. (n) Koe, J. R.; Tobita, H.; Suzuki, T.; Ogino, H. *Organometallics* **1992**, *11*, 150. (o) Figge, L. K.; Carroll, P. J.; Berry, D. H. *Organometallics* **1996**, *15*, 209. (p) Sharma, H.; Pannell, K. H. *Organometallics* **1994**, *13*, 4946.

Scheme 6



or more simply an alkyl migration from Fe to phosphenium P occurs. When E is Si or Ge, the cationic phosphenium complex (**b**) is stable and Fe−Si and Fe−Ge bonds remain unreacted. In contrast, when E is Sn, not SnR_3 but one alkyl group on the Sn migrates to the phosphenium P to give a stannylene complex (**e**). The X-ray analysis of the phosphenium complex containing an $SiMe_3$ group reveals that the Fe−P bond has considerable double-bond character. Therefore, the conversion from **b** to **e** corresponds to a double-bond migration from Fe═P to Fe═Sn. Recently 1,2- and 1,3-migration involving a heteroatom as well as a carbon in a coordination sphere of a transition metal has attracted considerable attention.[6g,28] Our phosphenium iron complexes containing a group 14 element ligand are very interesting regarding such migration because the different congeners exhibit different behavior in the iron coordination sphere: 1,2-migration for C, no migration for Si and Ge, and 1,3-migration for Sn.

Experimental Section

General Remarks. All reactions were carried out under an atmosphere of dry nitrogen by using Schlenk-tube techniques. Column chromatography was performed quickly in the air. Benzene, pentane, hexane, and ether were distilled from sodium metal, CH_2Cl_2 was distilled from P_2O_5, and these solvents were stored under nitrogen atmosphere. BF_3·OEt_2 and TMSOTf were distilled prior to use. PNN(OMe) was prepared according to the literature method.[29] Complex **2a** was prepared by the published procedure.[7a]

IR spectra were recorded on a Shimadzu FTIR-8100A spectrometer. JEOL EX-270, EX-400, and LA-300 spectrometers were used to obtain ^{1}H, ^{13}C, ^{29}Si, ^{31}P, and ^{119}Sn NMR spectra. ^{1}H, ^{13}C, and ^{29}Si NMR data were referenced to $(CH_3)_4Si$, ^{31}P NMR data were referenced to 85% H_3PO_4, and ^{119}Sn NMR data were referenced to $(CH_3)_4Sn$. The conductivity measurements were carried out on a HORIBA Conductivity Meter DS-8F. Elemental analyses were performed on a Perkin-Elmer 2400CHN elemental analyzer.

Preparation of 3a. $Cp(CO)_2Fe(GeMe_3)$ (2251 mg, 7.64 mmol), benzene (60 mL), and PNN(OMe) (1.70 mL, 1717 mg, 11.59 mmol) were charged into a Pyrex Schlenk tube, and the solution was irradiated with a 400 W medium-pressure mercury arc lamp at 0 °C for 3 h. After some insoluble materials were removed by filtration, the filtrate was concentrated under reduced pressure and the residue was loaded on an alumina column. The yellow band eluted with CH_2Cl_2 was collected, and the solvent was removed in vacuo. Pentane was added to the residue. After filtration to remove insoluble materials, the solvent was removed in vacuo to give **3a** as a yellow waxy powder (2699 mg, 6.51 mmol, 85%). Anal. Calcd for $C_{14}H_{27}FeGeN_2O_2P$: C, 40.54; H, 6.56; N, 6.75. Found: C, 40.38; H, 6.44; N, 6.69.

Preparation of 4a. $Cp(CO)_2Fe(SnMe_3)$ (2452 mg, 7.20 mmol), benzene (120 mL), and PNN(OMe) (1.58 mL, 1596 mg, 10.77 mmol) were charged into a Pyrex Schlenk tube, and the solution was irradiated with a 400 W medium-pressure mercury arc lamp at 0 °C for 5.5 h. After the solvent was removed, the residue was loaded on an alumina column. The yellow band eluted with CH_2Cl_2 was reloaded on an alumina column. The yellow band eluted with CH_2Cl_2/hexane (1/9) was collected, and the solvents were removed in vacuo to give a yellow powder of **4a** (2394 mg, 5.19 mmol, 72%). Anal. Calcd for $C_{14}H_{27}FeN_2O_2PSn$: C, 36.48; H, 5.90; N, 6.08. Found: C, 36.44; H, 5.62; N, 6.11.

Preparation of 5a. Complex **5a** was prepared from $Cp(CO)_2Fe(SnBu_3)$ and PNN(OMe) in the same manner as that used for **4a**. Yield: 89%. Anal. Calcd for $C_{23}H_{45}FeN_2O_2PSn$: C, 47.05; H, 7.72; N, 4.77. Found: C, 46.85; H, 7.66; N, 4.64.

Preparation of 2b′. A solution of **2a** (232 mg, 0.63 mmol) in CH_2Cl_2 (7.5 mL) was cooled to −78 °C, and then BF_3·OEt_2 (0.16 mL, 180 mg, 1.27 mmol) was added. After the solution was warmed to room temperature, $NaBPh_4$ (241 mg, 0.70 mmol) was added and the mixture was stirred for several hours at room temperature. After filtration to remove $NaBF_4$ salt, the solvent was removed under reduced pressure to give a reddish-brown powder. The crude product was purified by recrystallization from CH_2Cl_2/hexane. The yellowish-orange powder, thus, formed was washed with hexane and ether and dried in vacuo to yield $[Cp(CO)(SiMe_3)Fe\{PNN\}]BPh_4$ (**2b′**) (346 mg, 0.52 mmol, 82%). Anal. Calcd for $C_{37}H_{44}BFeN_2OPSi$: C, 67.49; H, 6.74; N, 4.25. Found: C, 67.12; H, 7.16; N, 4.52.

Preparation of 2d. A solution of **2a** (252 mg, 0.68 mmol) in CH_2Cl_2 (10 mL) was cooled to −78 °C, and then BF_3·OEt_2 (0.20 mL, 226 mg, 1.59 mmol) was added. The reaction mixture was warmed to room temperature and stirred for several hours. The solution was cooled at −78 °C again, and $PhCH_2MgCl$ (1.00 mL of its 1.00 M ether solution, 1.00 mmol) was added. After being warmed to room temperature, this reaction mixture was concentrated to ca. 2 mL and charged on an alumina column. The yellow band eluted with hexane was collected, and the solvent was removed under reduced pressure. Pentane was added to the residue. After filtration to remove insoluble materials, the solvent was removed in vacuo to give **2d** as a yellow powder (43 mg, 0.1 mmol, 15%). Anal. Calcd for $C_{20}H_{31}FeN_2OPSi$: C, 55.82; H, 7.26; N, 6.51. Found: C, 55.69; H, 7.21; N, 6.15.

Preparation of 3b. A solution of **3a** (144 mg, 0.35 mmol) in CH_2Cl_2 (3 mL) was cooled to −78 °C, and then BF_3·OEt_2 (0.087 mL, 98 mg, 0.69 mmol) was added. After the solution was warmed to room temperature, it was concentrated to about

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[29] Ramirez, F.; Patwardham, A. V.; Kugler, H. J.; Smith, C. P. *J. Am. Chem. Soc.* **1967**, *89*, 6276.

1.5 mL under reduced pressure and then subjected to spectroscopic measurements.

Preparation of 3d. Complex **3d** was prepared from **3a**, $BF_3{\cdot}OEt_2$, and $PhCH_2MgCl$ in the same manner as that for **2d**. The crude product was purified by alumina column chromatography. The yellow band eluted with CH_2Cl_2 was collected, and the solvent was removed in vacuo to give a yellow powder of **3d** (yield 45%). Anal. Calcd for $C_{20}H_{31}FeGeN_2OP$: C, 50.58; H, 6.58; N, 5.90. Found: C, 50.98; H, 6.29; N, 5.66.

Preparation of 4b. A solution of **4a** (205 mg, 0.45 mmol) in CH_2Cl_2 (7 mL) was cooled to −78 °C, and then $BF_3{\cdot}OEt_2$ (0.25 mL, 282 mg, 1.99 mmol) was added. After the solution was warmed to room temperature and stirred for 8 h, it was subjected to ^{31}P NMR measurement, which suggested the formation of **4b**.

Preparation of 4e. TMS·OTf (467 mg, 0.38 mL, 2.10 mmol) was added to a solution of **4a** (322 mg, 0.70 mmol) in CH_2Cl_2 (5 mL) cooled at −78 °C. The solution was allowed to warm to room temperature and stirred for 48 h. After addition of pentane (10 mL), the solution was kept in a refrigerator to give yellow crystals, which were collected by filtration, washed with pentane, and dried in vacuo, yielding **4e** (146 mg, 0.25 mmol, 36%). Anal. Calcd for $C_{14}H_{24}F_3FeN_2O_4PSSn$: C, 29.05; H, 4.18; N, 4.84. Found: C, 29.05; H, 4.06; N, 4.87.

Preparation of 5b. A solution of **5a** (307 mg, 0.52 mmol) in CH_2Cl_2 (5 mL) was cooled to −78 °C, and then $BF_3{\cdot}OEt_2$ (0.27 mL, 305 mg, 2.15 mmol) was added. After the solution was warmed to room temperature, it was subjected to spectroscopic measurements, which suggested the formation of **5b**.

Preparation of 5d. A solution of **5a** (371 mg, 0.64 mmol) in CH_2Cl_2 (8 mL) was cooled to −78 °C, and then $BF_3{\cdot}OEt_2$ (0.32 mL, 361 mg, 2.55 mmol) was added. After the solution was stirred for 6 h at room temperature, it was cooled to −78 °C and treated with $PhCH_2Cl$ (0.38 mL of its 2.0 M ether solution, 0.76 mmol). After being stirred for 4 h at room temperature, the solution was concentrated under reduced pressure and then loaded on an alumina column. A yellow band eluted with hexane was collected, and removal of the solvent in vacuo gave a yellow oily product of **5d** (177 mg, 0.27 mmol, 42%). The complex was so hygroscopic that the correct elemental analysis data could not be obtained, though satisfactory spectroscopic data were obtained.

Preparation of 5e. A solution of **5a** (349 mg, 0.59 mmol) in CH_2Cl_2 (7.5 mL) was cooled to −78 °C, and then TMS·OTf (0.35 mL, 431 mg, 1.94 mmol) was added. After the solution had been warmed to room temperature, it was concentrated to about 1 mL under reduced pressure and then subjected to spectroscopic measurements.

X-ray Structure Determination for 2b′ and 4e. Single crystals of **2b′** grown from CH_2Cl_2/pentane at room temperature and **4e** grown from CH_2Cl_2/pentane in a refrigerator were individually sealed under N_2 in a thin-walled glass capillary, mounted on an Enraf-Nonius CAD4 diffractometer, and irradiated with graphite-monochromated Mo Kα radiation ($\lambda = 0.710\,93$ Å). Cell constants and an orientation matrix for data collection, obtained from a least-squares refinement using the setting angles of 15 carefully centered reflections in the range $14° < 2\theta < 21°$, corresponded to a monoclinic cell with dimensions of $a = 14.867(2)$ Å, $b = 9.833(1)$ Å, $c = 25.091(4)$ Å, $\beta = 105.19(1)°$, $Z = 4$, and $V = 3539.7(1)$ Å^3 for **2b′** and those using the setting angles of 25 carefully centered reflections in the range $2° < 2\theta < 60°$ corresponded to a monoclinic cell with dimensions of $a = 9.805(1)$ Å, $b = 18.134(2)$ Å, $c = 30.055(5)$ Å, $\beta = 110.35(1)°$, $Z = 4$, and $V = 2171.1(7)$ Å^3 for **4e**. $P2_1/c$ was selected as a space group for both **2b′** and **4e**, which led to successful refinements. The data were collected at temperature of 20 ± 1 °C using the ω scan technique. The intensities of three representative reflections were measured after every 200 reflections. No decay correction was applied.

The structures were solved by a heavy-atom Patterson method with the SAPI program system.[30] The positions of all hydrogen atoms were calculated by assuming idealized geometries. Absorption and extinction corrections were then applied,[31,32] and several cycles of a full-matrix least-squares refinement with anisotropic temperature factors for non-hydrogen atoms led to final R_w values of 0.042 and 0.040, respectively. All calculations were performed using the program system teXsan.[33]

Acknowledgment. This work was supported by a Grant-in-Aid for Science Research (Grant No. 07404037) and a Grant-in-Aid on Priority Area of Interelement Chemistry (Grant No. 09239235) from the Ministry of Education, Science, Sports and Culture of Japan.

Supporting Information Available: Tables giving positional and thermal parameters for **2b′** and **4e** (22 pages). Ordering information is given on any current masthead page.

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[30] SAPI: Fan, H.-F. *Structure Analysis Programs with Intelligent Control*; Rigaku Corp.: Tokyo, Japan, 1991.

[31] Katayama, C. *Acta Crystallogr.* **1986**, *A42*, 19.

[32] Coppens, P.; Hamilton, W. C. *Acta Crystallogr.* **1970**, *A26*, 71.

[33] teXsan: *Crystal Structure Analysis Package*; Molecular Structure Corp.: The Woodlands, TX, 1985 and 1992.