Conversion of Transition-Metal Complexes with Stannyl and Phosphenium Ligands into Those with Stannylene and Phosphine Ligands by Alkyl Migration from Sn to P

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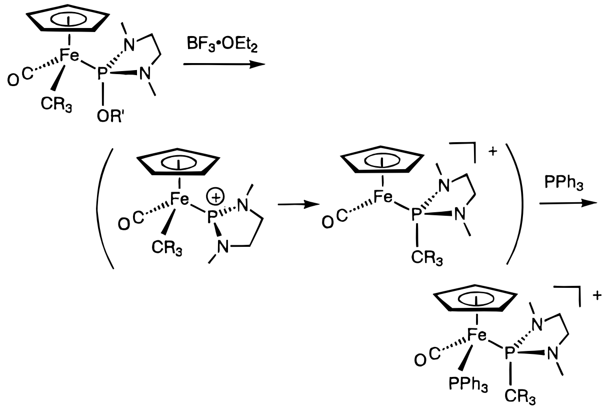
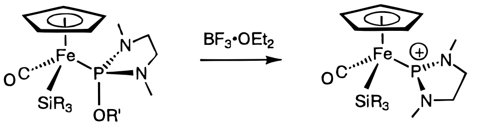
*Summary: Treatment of Cp(CO)(SnMe$_3$)Fe{PN(Me)CH$_2$CH$_2$NMe(OR)} (R = Me, Et) with Me$_3$SiOSO$_2$CF$_3$ (TMSOTf) yields [Cp(CO)(SnMe$_2$)Fe{PN(Me)CH$_2$CH$_2$NMe(Me)}]OTf (**2**), showing that P−OR bond cleavage and Me migration from Sn to P take place. The X-ray analysis of **2** reveals that this is a stannylene complex of iron stabilized by both an OTf$^-$ anion and an N atom in the phosphorus ligand. In solution, **2** is in equilibrium with an OTf-dissociated species.*

The preparations, structures, and reactivities of compounds with a multiple bond between a transition metal and a main-group element are subjects of growing interest. Cationic transition-metal phosphenium complexes[1] have been considered to have a double-bond character between a transition metal and a phosphorus. We recently found an unprecedented reaction relating to a cationic iron phosphenium complex: a phosphenium ligand undergoes a migratory insertion into an iron−alkyl bond (eq 1; simply designated as a migration of an alkyl ligand to a phosphenium ligand or as a 1,2-rearrangement), whereas a silyl group does not migrate to a phosphenium ligand (eq 2).[2] Herein we report the reaction of an iron−stannyl complex, [Cp(CO)(SnR$_3$)Fe{PN(Me)CH$_2$CH$_2$NMe(OR)}], with a Lewis acid, in which not a stannyl group but an alkyl group on a stannyl ligand migrates to a phosphenium ligand to give a stannylene complex.



(1)



(2)

Treatment of [Cp(CO)(SnMe$_3$)Fe{PN(Me)CH$_2$CH$_2$NMe(OMe)}] (**1a**)[3] with an excess of Me$_3$SiOSO$_2$CF$_3$ (TMSOTf) at −78 °C yields a reaction mixture from which yellow crystals can be isolated in 36% yield. Elemental analysis and IR and ^{1}H, ^{13}C, ^{31}P, and ^{119}Sn NMR spectra established the formation of a stannylene complex formulated as [Cp(CO)(SnMe$_2$)Fe{PN(Me)CH$_2$CH$_2$NMe(Me)}]OTf (**2**)[4] (Scheme 1). Exactly the same complex was produced in the reaction of [Cp(CO)(SnMe$_3$)Fe{PN(Me)CH$_2$CH$_2$NMe(OEt)}] (**1b**)[3] with TMSOTf, indicating that the methyl group directly bonded to the coordinating P in **2** comes from a SnMe$_3$ group in **1a** or **1b**.

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(3) Complexes **1a**,**b** were prepared from Cp(CO)$_2$Fe(SnMe$_3$) and PN(Me)CH$_2$CH$_2$NMe(OR) (R = Me, Et) in benzene by photolysis followed by purification with column chromatography. Yield: 72% (**1a**) and 79% (**1b**).

(4) Elemental analysis and spectroscopic data are as follows. 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. IR (ν(CO), in CH$_2$Cl$_2$): 1942 cm^{-1}. ^{1}H NMR (δ, in CD$_2$Cl$_2$): 0.71 (s with Sn satellites, $J_{\mathrm{H}-^{119}\mathrm{Sn}} = J_{\mathrm{H}-^{117}\mathrm{Sn}} = 36.3$ Hz, 6H, SnCH$_3$), 1.28 (d, $J_{\mathrm{H-P}} = 5.9$ Hz, 3H, PCH$_3$), 2.45 (d, $J_{\mathrm{H-P}} = 13.5$ Hz, 3H, NCH$_3$), 2.62 (d, $J_{\mathrm{H-P}} = 11.9$ Hz, 3H, NCH$_3$), 2.78 (m, 1H, NCH$_2$), 3.04 (m, 3H, NCH$_2$), 4.65 (d, $J_{\mathrm{H-P}} = 1.3$ Hz, 5H, C$_5$H$_5$). ^{13}C NMR (δ, in CD$_2$Cl$_2$): 6.32 (d with Sn satellites, $J_{\mathrm{C-P}} = 3.6$ Hz, $J_{\mathrm{C}-^{119}\mathrm{Sn}} = J_{\mathrm{C}-^{117}\mathrm{Sn}} = 144.2$ Hz, SnCH$_3$), 21.69 (d, $J_{\mathrm{C-P}} = 4.9$ Hz, PCH$_3$), 33.79 (d, $J_{\mathrm{C-P}} = 8.5$ Hz, NCH$_3$), 34.56 (d, $J_{\mathrm{C-P}} = 4.9$ Hz, NCH$_3$), 51.16 (s, NCH$_2$), 51.90 (d, $J_{\mathrm{C-P}} = 4.9$ Hz, NCH$_2$), 80.48 (s, C$_5$H$_5$), 120.86 (q, $J_{\mathrm{C-F}} = 317.3$ Hz, OSO$_2$CF$_3$), 216.74 (d with Sn satellites, $J_{\mathrm{C-P}} = 29.3$ Hz, $J_{\mathrm{C}-^{119}\mathrm{Sn}} = 225.9$ Hz, $J_{\mathrm{C}-^{117}\mathrm{Sn}} = 219.8$ Hz, CO). ^{31}P NMR (δ, in CD$_2$Cl$_2$): 174.33 (s, with Sn satellites, $J_{\mathrm{P}-^{119}\mathrm{Sn}} = 547.9$ Hz, $J_{\mathrm{P}-^{117}\mathrm{Sn}} = 522.1$ Hz). ^{119}Sn NMR (δ, in CD$_2$Cl$_2$/CH$_2$Cl$_2$): 495.8 (d, $J_{^{119}\mathrm{Sn-P}} = 600.2$ Hz).

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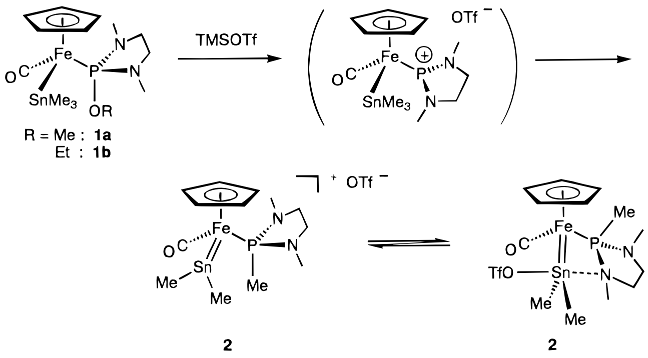
Scheme 1



A single-crystal X-ray diffraction study confirmed that **2** was a doubly base-stabilized stannylene complex of iron (Figure 1).[5] The tin atom is five-coordinate with a geometry that is best described as trigonal bipyramidal, with one oxygen (O2) and one nitrogen (N2) occupying the axial sites: the FeSnC1C2 unit is nearly planar (the sum of angles around Sn amounts to 359.1°), and the O2−Sn−N2 angle is 173.8°. In comparison with structures of O or N base-stabilized stannylene complexes reported previously,[6,7] the Sn−O2 bond length (2.343 Å) is reasonable, whereas the Sn−N2 bond is slightly longer (2.695 Å) but significantly shorter than the sum of the van der Waals radii (3.72 Å). The Fe−Sn bond is not shortened in comparison with various $Cp(CO)_2Fe(SnR_3)$ compounds, where Fe−Sn bond lengths between 2.46 and 2.56 Å have been measured.[7]

In solution, there may be an equilibrium for **2** between a base-stabilized stannylene form, as shown in the solid state, and a base-free one. The molar conductivity (Λ_M) of **2** in nitromethane was 76.1 Ω^{-1} cm^2 mol^{-1}, which is a reasonable value for a 1:1 electrolyte.[8] This indicates that **2** is 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 **2** in CH_2Cl_2, the chemical shift (495.8 ppm) and $J_{^{119}Sn-P}$ value (600.2 Hz)[9] show that **2** is present as a base-free stannylene form to a considerable extent. The ^{1}H and ^{13}C NMR spectra of **2** in CD_2Cl_2 at room temperature show that the two Me groups 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 the Fe−Sn bond. Low-temperature ^{1}H NMR measurement revealed that two $SnMe_2$ resonances were present at 178 K, and they coalesced at 188 K. Application of the coalescence formula[10] gave a $\Delta G^‡$(188 K) value of 9.0 kcal mol^{-1} for the methyl group exchange.[11]

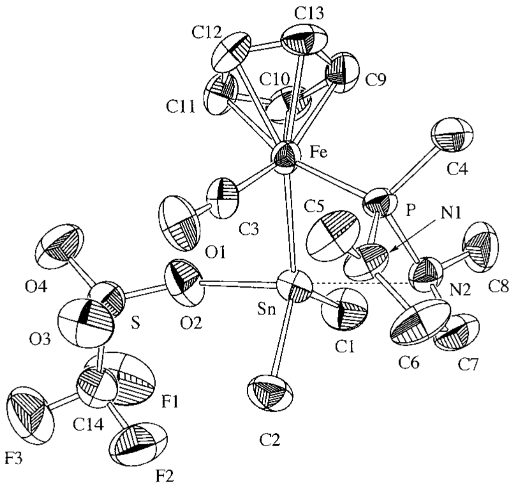


Figure 1. ORTEP view of **2** showing the atom-numbering scheme. Selected bond lengths (Å) and angles (deg): Fe−Sn, 2.488(1); Fe−P, 2.140(2); Fe−C3, 1.738(5); Sn−Cl, 2.136(5); Sn−C2, 2.145(5); Sn−O2, 2.343(4); Sn−N2, 2.695(4); C3−Fe−Sn, 88.0(2); C3−Fe−P, 94.2(2); Sn−Fe−P, 81.0(1); Fe−Sn−C1, 126.4(2); Fe−Sn−C2, 123.2(2); C1−Sn−C2, 109.5(3); Fe−Sn−O2, 99.0(1); Fe−Sn−N2, 77.0(1).

Many experimental results have accumulated about transition-metal stannylene complexes, and they have been nicely reviewed by Petz,[7] Herrmann,[12] Nelson,[13] and Lappert.[14] However, to our knowledge, only three examples are known where a stannylene complex is prepared by Sn−C bond cleavage.[6a,15] Out 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 coordinating carbon monoxide in an Os cluster, forming an Os stannylene complex.[15a] We believe that our finding is the first example of the migration of an alkyl group on a tin ligand to a coordinating phosphorus atom to give a stannylene complex. Moreover, it should be noted that the results reported here present an interesting contrast to the previous findings: for iron phosphenium complexes formulated as $[Cp(CO)(ER_3)Fe\{PN(Me)CH_2CH_2NMe\}]^+$, an alkyl ligand (E = C) migrates to the phosphorus, a silyl ligand (E = Si) does not migrate, keeping the phosphenium ligand intact, and in the case of the stannyl complex (E = Sn), an alkyl group on the tin rather than a stannyl group itself migrates to the phosphorus to give a stannylene complex.

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[5] Crystal data: monoclinic, space group $P2_1/c$, a = 16.010 (2) Å, b = 7.852 (2) Å, c = 18.420 (3) Å, β = 110.35(1)°, V = 2171.1(7) Å^3, Z = 4, R = 0.043, R_w = 0.040 for 3666 reflections with $I > 3\sigma(I)$.

[6] For example: (a) Almeida, J. F.; Dixon, K. R.; Eaborn, C.; Hitchcock, P. B.; Pidcock, A.; Vinaixa, S. *J. Chem. Soc., Chem. Commun.* **1982**, 1315. (b) Scheidsteger, O.; Huttner, G.; Dehnicke, K.; Pebler, J. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 428. (c) Balch, A. L.; Oram, D. E. *Organometallics* **1988**, *7*, 155.

[7] Petz, W. *Chem. Rev.* **1986**, *86*, 1019.

[8] The Λ_M of $[Cp(CO)(PPh_3)Fe\{PN(Me)CH_2CH_2NMe(Me)\}]BF_4$ was measured in nitromethane as a typical 1:1 electrolyte and a complex structurally related to **2**, and a similar value (Λ_M = 82.4 Ω^{-1} cm^2 mol^{-1}) was obtained. For a variety of Λ_M values, see for example: Geary, W. J. *Coord. Chem. Rev* **1971**, *7*, 81.

[9] For the starting complex $[Cp(CO)(SnMe_3)Fe\{PN(Me)CH_2CH_2N(Me)(OMe)\}]$ (**1a**): ^{119}Sn NMR (δ, in $CDCl_3$) 99.1 (d, $J_{^{119}Sn-P}$ = 455.4 Hz).

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

[11] Gladysz reported the $\Delta G^‡$ values for methyl group exchange. $\Delta G^‡$(307 K) > 14.8 kcal mol^{-1} for $[CpRe(NO)(PPh_3)({=}SiMe_2)]OTf$ (Lee, K. E.; Arif, A. M.; Gladysz, J. A. *Chem. Ber.* **1991**, *124*, 309) and $\Delta G^‡$(211 K) = 9.6 kcal mol^{-1} for $[CpRe(NO)(PPh_3)({=}GeMe_2)]OTf$ (Lee, K. E.; Gladysz, J. A. *Phosphorus, Sulfur Silicon Relat. Elem.* **1994**, *87*, 113).

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

[15] (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.

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Supporting Information Available: Text giving experimental details and spectroscopic and analytical data for **1a**,**b** and tables of crystal data, bond distances and angles, atomic coordinates, and anisotropic thermal parameters for **2** (12 pages). Ordering information is given on any current masthead page.

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