Phosphorus Ylide Migration from Fe to a Phosphenium Phosphorus

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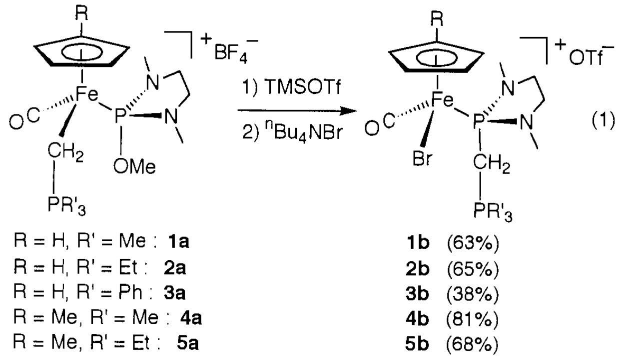
The reaction of a phosphorus ylide complex $[(C_5H_4R)(CO)(CH_2PR'_3)Fe\{PNN(OMe)\}]BF_4$ (R = H, Me; R' = Me, Et, Ph; PNN = $PN(Me)CH_2CH_2NMe$) with TMSOTf and then $^nBu_4NBr$ gave $[(C_5H_4R)(CO)BrFe\{PNN(CH_2PR'_3)\}]OTf$ through intramolecular migration of a cationic phosphorus ylide ligand from Fe to a cationic phosphenium phosphorus.

A phosphenium cation (PR_2^+) is of interest as a ligand in a field of transition metal chemistry, because it has both lone pair electrons and an empty p orbital on the phosphorus atom.[1] Cationic phosphenium complexes have been reported for several kinds of transition metals.[2] However, information concerning their reactivity is much more sparse. We recently reported the unprecedented example of a migratory insertion reaction of the phosphenium ligand into a transition metal-carbon bond, or more simply, alkyl migration from a transition metal to a phosphenium phosphorus.[3] In this paper, we report migration of a phosphorus ylide ligand ($-CH_2P^+R_3$) from a transition metal to a phosphenium phosphorus in the reaction with a Lewis acid of $[Cp(CO)(CH_2PR_3)Fe\{PNN(OMe)\}]^+$ and their derivatives, where PNN(OMe) stands for $PN(Me)CH_2CH_2NMe(OMe)$. This is the first example of a cationic ligand migration to a cationic phosphenium phosphorus. We also report that the migration takes place in an intramolecular pathway.

$[Cp(CO)(CH_2PMe_3)Fe\{PNN(OMe)\}]BF_4$ (**1a**)[4] was treated with two equivalents of TMSOTf ($Me_3SiOSO_2CF_3$) at room temperature in CH_2Cl_2 and the reaction mixture was stirred for 2 h. Then $^nBu_4NBr$ was added to give a dark green solution. Removal of the solvent followed by purification with a silica gel column afforded $[Cp(CO)BrFe\{PNN(CH_2PMe_3)\}]$ OTf (**1b**)[5] in 63% yield as a dark green powder (eq 1).



The product **1b** shows no signal assigned to POMe in either ^1H or ^{13}C NMR spectra. Instead, it shows a multiplet at 2.63-2.80 ppm in the ^1H NMR spectrum and a doublet of doublets at 31.75 ppm in the ^{13}C NMR spectrum, which are assignable to PCH_2P. In the ^{31}P NMR spectrum, two doublets at 22.61 and 166.12 ppm with the same coupling constant are observed. The ν_{CO} value (1964 cm^{-1}) in the IR spectrum indicates that the product is a cationic complex having one terminal carbonyl ligand. Considering these spectroscopic data and elemental analysis data, we concluded that the product is a CH_2PMe_3 migrated complex from Fe to the PNN fragment. Similar reactions of **2a**-**5a** with TMSOTf and then $^nBu_4NBr$ gave the corresponding phosphorus ylide-migrated complexes **2b**-**5b** (eq 1). The molecular structure of **3b** determined by X-ray crystallography[6] is depicted in Figure 1, which clearly shows that **3b** is a migration product of a CH_2PPh_3 fragment from Fe to the PNN moiety.

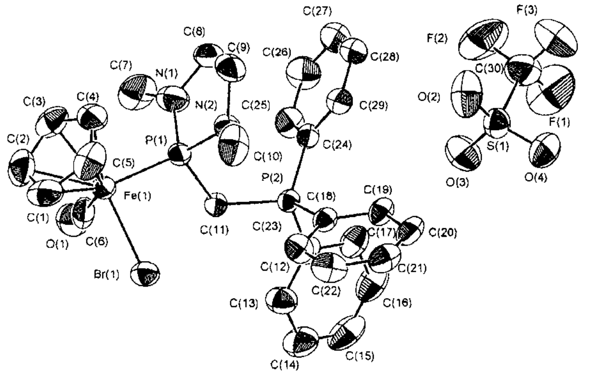
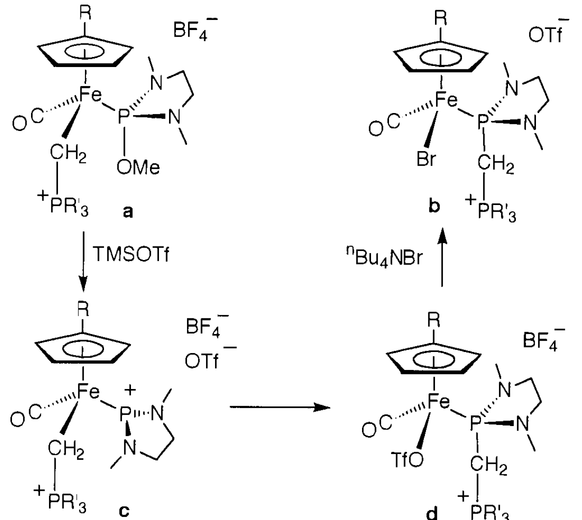


Figure 1. An ORTEP drawing of **3b**. Selected bond distances (Å) and angles (deg); Fe(1)-P(1) 2.179(1), Fe(1)-Br(1) 2.437(1), P(1)-C(11) 1.878(4), C(11)-P(2) 1.803(3); Br(1)-Fe(1)-P(1) 94.5(1), Fe(1)-P(1)-C(11) 110.3(1), P(1)-C(11)-P(2) 120.5(2).

We next examined the reaction of **1a** with TMSOTf in the absence of $^nBu_4NBr$. Although the isolation was unsuccessful, the product could be inferred from the ^{31}P NMR data of the reaction mixture. It showed two doublets at 21.64 and 164.01 ppm with J_{PP} = 29.2 Hz, indicating the formation of $[Cp(CO)(OTf)Fe\{PNN(CH_2PMe_3)\}]^+$.

Based on the results mentioned above together with the knowledge obtained already in our previous studies,[3] a plausible reaction mechanism shown in Scheme 1 is proposed. The first step of the reaction would be an abstraction of an OMe^- anion from the phosphorus in **a** in the reaction with the added Lewis acid to give a dicationic phosphenium complex **c**. Subsequent $-CH_2P^+R_3$ migration from Fe to the phosphenium P followed by coordination of OTf^- to the Fe takes place to afford **d**. Addition of Br^- resulted in the OTf^-/Br^- substitution at the Fe to give an isolable complex **b**. Two points should be noted here: (i) an OMe^- anion is able to be abstracted by TMSOTf from a coordinated diamino-substituted phosphite even in a cationic complex, and (ii) a cationic phosphorus ylide ligand can migrate to a cationic phosphenium ligand.



Scheme 1.

In order to elucidate whether intra- or inter-molecular migration occurs, we examined the reaction of a mixture of **1a** and **5a** with TMSOTf and then $^{n}Bu_4NBr$ because the migration rates for **1a** and **5a** are qualitatively the same. The reaction mixture was subjected to the ^{31}P NMR measurement, and it was found that the products were **1b** and **5b**, and neither **2b** nor **4b** corresponding to the cross-migration products were detected at all. Therefore, we concluded that the phosphorus ylide migration from Fe to P takes place only within a molecule.

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4 Complex **1a** was prepared via the reaction of [Cp(CO)MeFe{PNN(OMe)}] in CH_2Cl_2 with Ph_3CBF_4 (-78 ˚C, 1.5 h) and then PMe_3 (-78 ˚C, 1h; 25 ˚C, 20 h). Removal of the solvent followed by purification with a silica gel column gave pure **1a** as an orange powder (74 % yield). IR (in CH_2Cl_2, cm^{-1}) ν_{CO} 1923. ^1H NMR (acetone-d_6) δ 0.30 (ddd, J = 15.6, 12.8, 10.6 Hz, 1H, $FeCH_2$), 1.33 (t, J_{PH} = 13.2 Hz, 1H, $FeCH_2$), 1.75 (d, J_{PH} = 13.4 Hz, 9H, PMe_3), 2.78 (d, J_{PH} = 10.6 Hz, 3H, NMe), 2.84 (d, J_{PH} = 10.3 Hz, 3H, NMe), 3.23-3.42 (m, 2H, NCH_2), 3.32 (d, J_{PH} = 11.2 Hz, 3H, POMe), 3.46-3.58 (m, 2H, NCH_2), 4.77 (d, J_{PH} = 1.3 Hz, 5H, Cp); ^{13}C NMR (acetone-d_6) δ –20.15 (dd, J_{PC} = 35.2, 30.9 Hz, $FeCH_2$), 13.01 (d, J_{PC} = 55.5 Hz, PMe_3), 32.91 (d, J_{PC} = 10.7 Hz, NMe), 33.27 (d, J_{PC} = 11.7 Hz, NMe), 52.20 (d, J_{PC} = 2.1 Hz, NCH_2), 52.37 (d, J_{PC} = 12.8 Hz, POMe), 52.39 (d, J_{PC} = 4.3 Hz, NCH_2), 84.12 (s, Cp), 223.45 (dd, J_{PC} = 48.0, 6.4 Hz, CO); ^{31}P NMR (CH_2Cl_2) δ 37.98 (s, PMe_3), 166.00 (s, PNN(OMe)). Anal. Found: C, 37.67; H, 5.95; N, 5.68%. Calcd for $C_{15}H_{29}BF_4FeN_2O_2P_2$: C, 38.01; H, 6.17; N, 5.91%. Complexes **2a**-**5a** were obtained in the similar manner.

5 **1b**: IR (in CH_2Cl_2, cm^{-1}) ν_{CO} 1964. ^1H NMR ($CDCl_3$) δ 1.92 (d, J_{PH} = 13.9 Hz, 9H, PMe_3), 2.63-2.80 (m, 1H, PCH_2P), 2.73 (d, J_{PH} = 12.8 Hz, 3H, NMe), 3.10 (d, J_{PH} = 12.7 Hz, 3H, NMe), 3.15-3.50 (m, 4H, NCH_2), 3.15-3.50 (m, 1H, PCH_2P), 4.68 (d, J_{PH} = 0.9 Hz, 5H, Cp); ^{13}C NMR ($CDCl_3$) δ 10.88 (d, J_{PC} = 56.6 Hz, PMe_3), 31.75 (dd, J_{PC} = 43.7, 12.8 Hz, PCH_2P), 33.26 (d, J_{PC} = 7.5 Hz, NMe), 37.46 (d, J_{PC} = 9.6 Hz, NMe), 51.22 (d, J_{PC} = 3.2 Hz, NCH_2), 53.39 (s, NCH_2), 82.73 (s, Cp), 120.60 (q, J_{FC} = 320.1 Hz, OTf), 218.85 (d, J_{PC} = 35.2 Hz, CO); ^{31}P NMR (CH_2Cl_2) δ 22.61 (d, J_{PP} = 26.7 Hz, PMe_3), 166.12 (d, J_{PP} = 29.2 Hz, $PNNCH_2$). Anal. Found: C, 30.83; H, 4.31; N, 4.72%. Calcd for $C_{15}H_{26}BrF_3FeN_2O_4P_2S$: C, 30.79; H, 4.48; N, 4.79%.

6 Crystal data for **3b**: $C_{30}H_{32}BrF_3FeN_2O_4P_2S$, M = 771.35, monoclinic, space group $P2_1/a$, a = 11.514, b = 26.024, c = 11.436 Å, b = 107.75 °, V = 3263.3 $Å^3$, Z = 4, Dc = 1.570, $g\cdot cm^{-3}$, μ = 18.827 mm^{-1}, R = 0.048, R_w = 0.065. The structure was solved and refined with teXsan program package.