An Unprecedented Synthetic Route for a Metallaphosphorane Complex. Nucleophilic Attack of Lewis Base on a Trivalent Phosphorus Atom Coordinating to a Transition Metal

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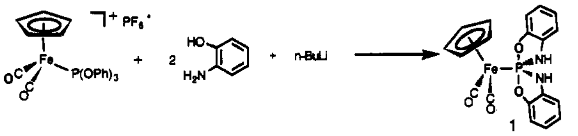
Metalated derivatives of pentacoordinate phosphorus compounds, metallaphosphoranes, have recently received considerable attention because they have a hypervalent 3-center, 4-electron bond. Metallaphosphoranes were first synthesized by Riess[1] in 1981 with deprotonation at a nitrogen in polycyclic species with phosphine– and amine–metal bonds. During the decade after that, a few preparative methods were reported: oxidative addition to metalated trivalent phosphines by Ebsworth[2] (Sb and As analogues by Malisch[3]), nucleophilic substitution at phosphorane phosphorus atoms by transition-metal carbonyl anions by Lattman,[4] and nucleophilic substitution at a transition metal by phosphoranides by Martin.[5] In addition, reactions of cyclenephosphoranes with transition-metal complexes were shown by Lattman[6] to yield metallaphosphoranes involving transannular interaction[7] and three-fragment oxidative addition.[8] There are some reports in which metallaphosphorane is proposed as a reaction intermediate.[9,10] We here report an unprecedented preparative method for a metallaphosphorane involving nucleophilic attack of an organic Lewis base on a phosphorus atom in a phosphite coordinating to a transition metal. This work exemplifies a new type of reaction pattern in the reaction of transition-metal complexes possessing phosphorus compounds with nucleophiles.

$[Cp(CO)_2Fe\{P(OPh)_3\}]PF_6$[11] (Cp stands for η^5-C_5H_5) was added to a reaction mixture of 2 equiv of *o*-$HOC_6H_4NH_2$ and 1 equiv of *n*-BuLi in THF cooled at −78 °C to give a yellow powder.[12] For the following reasons, we concluded that the product is the metallaphosphorane $[Cp(CO)_2Fe\{\overline{P(o\text{-}OC_6H_4N}H)_2\}]$ (**1**) (eq 1). (i) Two IR absorption bands due to ν_{CO} were observed in a terminal carbonyl region of electrically neutral complexes. (ii) In the ^{31}P NMR spectrum, one resonance was observed at 24.18 ppm, which is 136 ppm higher in magnetic field than that of the starting complex, as a singlet with proton irradiation and as a triplet with J = 19.9 Hz without proton irradiation, indicating the existence of a pentavalent pentacoordinate phosphorus with two NHR groups directly bonded to the phosphorus. (iii) In the ^1H NMR spectrum, in addition to a doublet assigned to Cp protons and an apparent singlet due to phenyl protons, a broad doublet due to NH protons was observed at 5.20 ppm with J = 20.0 Hz.



(1)

Among metallaphosphoranes reported thus far, the phosphorane ligands containing nitrogens usually act as a bidentate ligand toward the transition metal through the P and the apical N atoms. In the complex isolated in this work, the phosphorane ligand is bonded to the Fe as a monodentate ligand though it has two nitrogen atoms. The phosphorus may have a trigonal-bipyramidal geometry with two oxygen atoms in the apical positions. The ^{13}C NMR spectrum of this complex showed two doublets due to the carbonyl carbons at 212.62 and 210.96 ppm with J_{CP} = 44.1 and 42.3 Hz, respectively, which indicates that the two carbonyls are diastereotopic. Therefore, it can be concluded that pseudorotation on the hypervalent phosphorus atom does not take place on the NMR time scale. The $Cp(CO)_2Fe$ fragment is considered to supply some electron density on the filled d-orbitals or p-orbitals of the metal for the vacant antibonding molecular orbital on the 3-center, 4-electron hypervalent bond.[5] The equatophilicity of the $Cp(CO)_2Fe$ due to this interaction, coupled with the apicophilicity of the oxygen atoms, would make the rotation barrier higher, which may be one of the reasons for the exclusive formation of the metallaphosphorane in which the phosphorane ligand is acting as a monodentate ligand.

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(11) Although $[Cp(CO)_2Fe\{P(OPh)_3\}]^+$ has been prepared in the literatures (Haines, R. J.; DuPreez, A. L. *Inorg. Chem.* **1969**, *8*, 1459. Haines, R. J.; DuPreez, A. L.; Marais, I. L. *J. Organomet. Chem.* **1971**, *28*, 405. Reimainn, R. H.; Singleton, E. *J. Organomet. Chem.* **1971**, *32*, C44), preparative descriptions and spectroscopic data have been reported insufficiently. Therefore, we obtained the complex as a PF_6^- salt from $[Cp(CO)_2Fe(THF)]PF_6$ and $P(OPh)_3$ in CH_2Cl_2 at room temperature, yield 70%. IR (ν_{CO}, in THF): 2072, 2030. ^{31}P NMR (δ, in THF): 160.61 (s, $P(OPh)_3$), −142.90 (sept, J_{PF} = 711.1 Hz, PF_6^-). ^1H NMR (δ, in acetone-d_6): 7.60–6.96 (m, 15H, Ph), 5.56 (s, 5H, Cp).

(12) A solution of *o*-$HOC_6H_4NH_2$ (343 mg, 3.15 mmol) in THF (5 mL) was cooled at −78 °C, and then *n*-BuLi (1 mL of 1.6 mol/L hexane solution, 1.6 mmol) was added. After the cooling bath was removed and the solution was stirred for 20 min, the solution was cooled again to −78 °C and $[Cp(CO)_2Fe\{P(OPh)_3\}]PF_6$ (976 mg, 1.54 mmol) was added. The heterogeneous reaction mixture was allowed to warm to room temperature and stirred overnight, becoming a homogeneous solution as indicated by the color change from yellow to reddish yellow. After the solvents were removed under reduced pressure, soluble compounds were extracted with ether (60 mL). The ether solution was concentrated to 2 mL, and hexane (2 mL) was added to give a yellow powder. After the solvents were removed by filtration, the residual powder was washed with 5 × 4-mL portions of toluene/hexane (1/1) to give **1** (452 mg, 1.07 mmol, 69% yield), mp 193–195 °C. Anal. Calcd for $C_{19}H_{15}FeN_2O_4P$: C, 54.05; H, 3.58; N, 6.64. Found: C, 53.84; H, 3.38; N, 6.44. IR (ν_{CO}, in THF): 2026, 1977. ^{31}P NMR (δ, in THF): 24.18 (t, J_{PH} = 19.9 Hz). ^1H NMR (δ, in $CDCl_3$): 6.67 (s, 8H, Ph), 5.20 (d, J_{PH} = 20.0 Hz, 2H, NH), 4.97 (d, J_{PH} = 0.8 Hz, 5H, Cp). ^{13}C NMR (δ, in $CDCl_3$): 212.62 (d, J_{PC} = 44.1 Hz, CO), 210.96 (d, J_{PC} = 42.3 Hz, CO), 149.55 (d, J_{PC} = 5.5 Hz, Ph), 132.46 (d, J_{PC} = 11.0 Hz, Ph), 119.27 (s, Ph), 118.73 (s, Ph), 108.69 (s, Ph), 108.55 (d, J_{PC} = 12.9 Hz, Ph), 85.31 (s, Cp).

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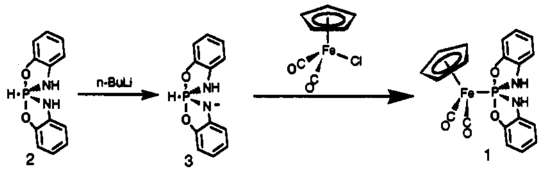
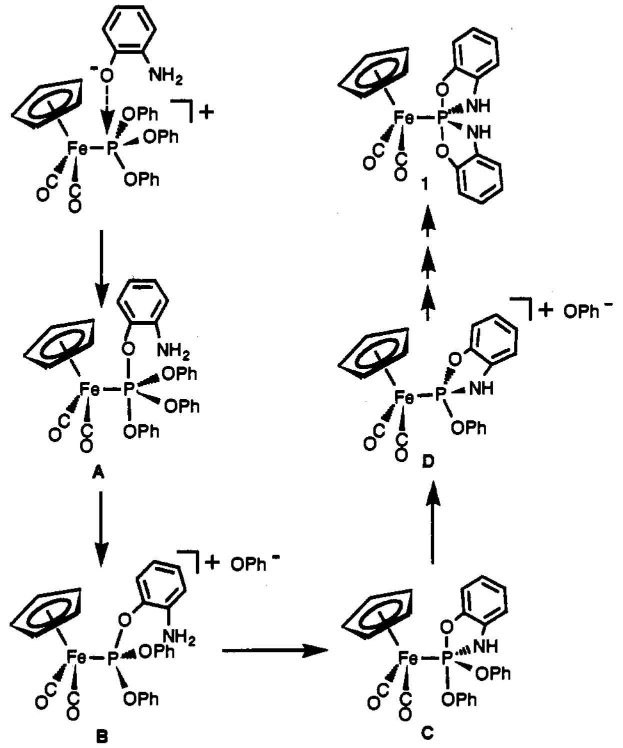
We attempted the preparation of **1** by nucleophilic attack of a phosphoranide anion on a transition metal. In the reaction of a hydridophosphorane (**2**) with *n*-BuLi in THF, a hydrogen on the N, but not one on the P, was abstracted to give an amide (**3**),[13] which then reacted with $Cp(CO)_2FeCl$ to give **1**[14] (eq 2). In the reaction, a complex containing an Fe–N bond, which was expected to form by the direct nucleophilic attack of the amide group to Fe, was not detected at all. Therefore, the reaction seems to proceed with H transfer from P to N. To our knowledge, this is the first example of ligand transfer (H transfer in this case) on a hypervalent phosphorus atom. The detailed mechanism of this reaction and reactions of **3** with other Lewis acids or other transition-metal complexes are now under investigation.



(2)

The reaction mechanism to form the metallaphosphorane in eq 1 is proposed in Scheme I. $[o\text{-}OC_6H_4NH_2]^-$, produced from $o\text{-}HOC_6H_4NH_2$ and *n*-BuLi, nucleophilically attacks the phosphorus atom of $[Cp(CO)_2Fe\{P(OPh)_3\}]^+$ to give a metallaphosphorane (**A**), followed by release of OPh^- to yield a cationic iron complex (**B**). The released OPh^- abstracts the NH proton of **B** to yield the NH^- group, which then attacks nucleophilically the P atom to give **C**, followed by release of OPh^- to obtain **D**. This OPh^- reacts with $o\text{-}HOC_6H_4NH_2$ remaining unreacted to give $[o\text{-}OC_6H_4NH_2]^-$, which undergoes similar reactions leading finally to the formation of **1**. In the reaction shown in eq 1, 2 equiv of $o\text{-}HOC_6H_4NH_2$ was necessary, but 1 equiv of *n*-BuLi based on the cationic iron complex was sufficient, which is consistent with the mechanism.

Scheme I



In eq 1, the coordinating phosphite can be converted into a metalated phosphorane by using organic nucleophiles, which is an unprecedented preparative method for metallaphosphoranes. Complex **1** is the first example in which a hypervalent phosphorus atom has one transition metal, two oxygen atoms, and two nitrogen atoms as its ligand atoms. It is known that cationic carbonyl complexes react with OR^- or NR_2^- to give alkoxy carbonyl or carbamoyl complexes.[15] In our reaction, such complexes were not isolated at all. Nucleophilic attack of F^- or H^- on a coordinating phosphine phosphorus to give a metallaphosphorane has been proposed,[9,10] but it has not been clarified. This work points to the possibility of such a reaction. Further studies on reactions with Lewis bases of transition-metal complexes containing a trivalent phosphorus compound as a ligand are in progress.

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(13) The formation of **3** was deduced from the ^{31}P NMR spectrum showing a singlet at −29.27 ppm which became a doublet with J_{PH} = 723.3 Hz without proton irradiation.

(14) A solution of **2** (1.667 g, 6.77 mmol) in THF (15 mL) was cooled at −78 °C, and then *n*-BuLi (4.3 mL of 1.6 mol/L hexane solution, 6.88 mmol) was added. After the cooling bath was removed and the solution was stirred for 20 min, the solution was cooled again to −78 °C, and a solution of $Cp(CO)_2FeCl$ (1.460 g, 6.87 mmol) in THF (10 mL) was added dropwise. The solution was allowed to warm to room temperature and stirred for 3 h. After the solvents were removed under reduced pressure, soluble compounds were extracted with ether (130 mL). The ether solution was concentrated to 3 mL, and hexane (6 mL) was added to give a yellow powder, which was then washed with hexane (4 × 10 mL) to give **1** (2.206 g, 5.23 mmol, 76% yield).

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