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Formation of Iron−Fluorophosphorane Complexes $(\eta^5\text{-}C_5H_5)(CO)LFe\{P(OPh)_nF_{4-n}\}$ (L = CO, $P(OPh)_3$; *n* = 0, 1) and $(\eta^5\text{-}C_5H_5)(CO)_2Fe\{\overline{P(OC_6H_4N}Me)F_2\}$. Nucleophilic Attack of F⁻ toward a Trivalent Phosphorus Atom Coordinated to a Transition Metal

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The reaction of a phosphite complex, $[Cp(CO)_2Fe\{P(OPh)_3\}]PF_6$, with Et_4NF in CH_2Cl_2 at room temperature yielded a mixture of metallafluorophosphoranes, $Cp(CO)_2Fe(PF_4)$ (**1**) and $Cp(CO)_2Fe\{P(OPh)F_3\}$ (**2**). Similar phosphite complexes $[Cp(CO)Fe\{P(OPh)_3\}_2]PF_6$ and $[Cp(CO)_2Fe\{\overline{P(OC_6H_4N}Me)(OC_6H_4NMeH)\}]PF_6$ also reacted with F^- to form $Cp(CO)\{P(OPh)_3\}$-$Fe(PF_4)$ (**3**) and $Cp(CO)_2Fe\{\overline{P(OC_6H_4N}Me)F_2\}$ (**4**), respectively. The ^{31}P and ^{19}F NMR studies of these metallafluorophosphoranes revealed that pseudorotation around the hypervalent phosphorus center takes place readily in **1** and **3**, whereas it marginally occurs at room temperature in **4**, but not in **2** even at elevated temperature. The difference in the energy barrier of the rotation process was interpreted in terms of the apicophilicity of the substituents on the phosphorane phosphorus.

Introduction

During the past few decades, much attention has been focused on the syntheses, structures, and properties of pentacoordinate phosphorus compounds, phosphoranes, partly because they have many attractive properties arising from their unusual valency.[1] However, studies on the transition-metal derivatives have been started in relatively recent years, and a few synthetic approaches to metallaphosphoranes have been reported to date.[2] They are based roughly on two strategies. One is based on reactions of a transition-metal complex with an organic phosphorane or a phosphoranide (a tetracoordinate anionic phosphorus compound).[3−8] Most of metallaphosphoranes reported so far have been prepared with recourse to this simple strategy. The other approach involves valence expansion of a lower-coordinate phosphorus ligand such as a phosphide or a phosphite ligand, coordinated to a transition metal, into a pentacoordinate phosphorus species by oxidative or nucleophilic addition of some inorganic or organic reagents to the phosphorus atom. For example, Ebsworth et al. reported the oxidative addition of halogens (Cl_2 or XeF_2) to a phosphide phosphorus coordinated to an iridium center (eq 1),[9] and we recently reported a new synthetic method for metallaphosphoranes, in which a trivalent phosphorus compound coordinated to a cationic transition-metal center is nucleophilically attacked by organic Lewis bases to expand its formal valence (eq 2).[10]

As an extension of our above-mentioned preparative method, we herein report the synthesis of metallafluo-

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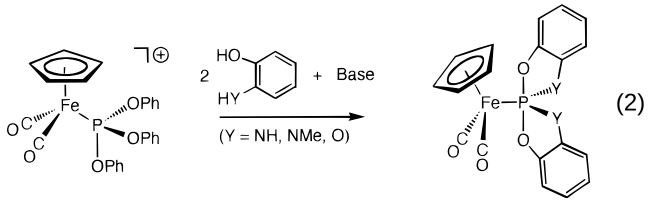
$$\mathrm{Ir(CO)Cl_2(PEt_3)_2PX_2} \xrightarrow[\text{(X = Cl or F)}]{\mathrm{X_2\ or\ XeX_2}} \mathrm{Ir(CO)Cl_2(PEt_3)_2PX_4} \quad (1)$$

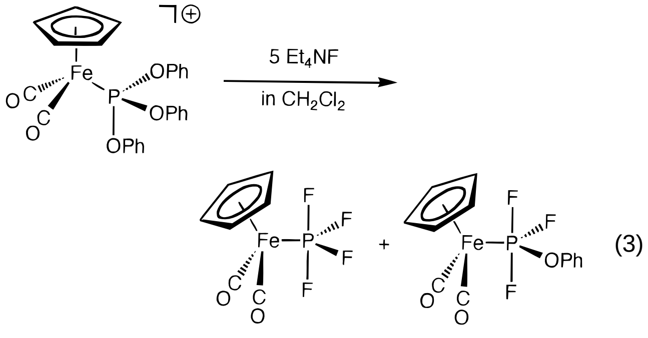


rophosphoranes by the reactions of cationic iron complexes having a phosphite ligand with a fluoride anion as a nucleophile. Also reported is dynamic behavior of the resulting metallaphosphoranes, i.e., pseudorotation around the hypervalent phosphorus.

Results and Discussion

Reaction of [Cp(CO)LFe{P(OPh)$_3$}]PF$_6$ (L = CO, P(OPh)$_3$) with F$^-$. In any case, products obtained were extremely moisture-sensitive, and several attempts to isolate them were unsuccessful (vide infra). The IR data of the products were somewhat unreliable because of their high instability. Therefore, the products were characterized by the NMR measurements of the reaction mixture alone. Their ^{31}P NMR and ^{19}F NMR data are given in Table 1.

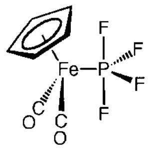
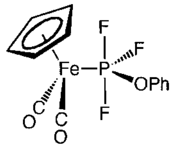
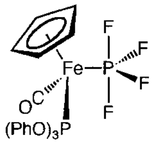
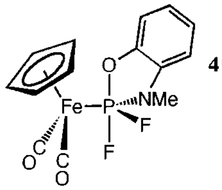
A cationic iron complex with a triphenyl phosphite ligand [Cp(CO)$_2$Fe{P(OPh)$_3$}]PF$_6$ (Cp stands for η^5-C$_5$H$_5$) was treated with 5 equiv of Et$_4$NF in CH$_2$Cl$_2$ at room temperature. The ^{31}P NMR monitoring of the mixture revealed that the signal assignable to the starting complex disappeared in a few minutes, and new signals appeared around 35 ppm. On the basis of the following discussions, we concluded that the main products in the reaction were two iron–phosphorane complexes, Cp(CO)$_2$Fe(PF$_4$) (**1**) and Cp(CO)$_2$Fe{P(OPh)F$_3$} (**2**) (eq 3).



1 **2**

The ^{31}P NMR spectrum of the reaction mixture exhibits three main signals; a septet at −142.87 ppm (J = 710 Hz), a quintet at 45.26 ppm (J = 1127 Hz), and a doublet of triplets at 31.23 ppm (J = 1168 and 1032 Hz) (Figure 1). The septet is unambiguously assigned to PF$_6^-$. The chemical shifts of the quintet and the doublet of triplets are at a higher field by ca. 120 ppm than that of the starting complex, indicating that the valence of the phosphorus atoms is expanded. The large coupling constants (greater than 1000 Hz) indicate that these products have direct P−F bond(s). These observations suggest that the quintet arises from complex **1** if a pseudorotation process around the pentacoordinate phosphorus is taking place fast on the NMR time scale and that the doublet of triplets arises from complex **2** if the corresponding pseudorotation does not occur or is very slow on the NMR time scale.

Table 1. ^{31}P and ^{19}F NMR Data[a]

Complex	^{31}P NMR (δ; ppm)	^{19}F NMR (δ; ppm)
 **1**[b]	45.26 (qui, J_{PF} = 1127 Hz)	20.71 (d, J_{PF} = 1128 Hz)
 **2**[b]	31.23 (d t, J_{PF} = 1168, 1032 Hz)	-34.01 (d t, J_{PF} = 1173 Hz, J_{FF} = 92 Hz, equatorial F) 76.44 (d d, J_{PF} = 1033 Hz, J_{FF} = 92 Hz, apical F)
 **3**[b]	49.07 (qui d, J_{PF} = 1108, J_{PP} = 191 Hz, PF$_4$) 170.02 (d, J_{PP} = 190 Hz, P(OPh)$_3$)	20.35 (d, J_{PF} = 1108 Hz)
 **4**[c]	39.98 (d d, J_{PF} = 1205, 1010 Hz)	-21.20 (d d, J_{PF} = 1205 Hz, J_{FF} = 107 Hz, equatorial F) 63.13 (d d, J_{PF} = 1009 Hz, J_{FF} = 105 Hz, apical F)

[a] In CH$_2$Cl$_2$. [b] At room temperature. [c] At −80 °C.

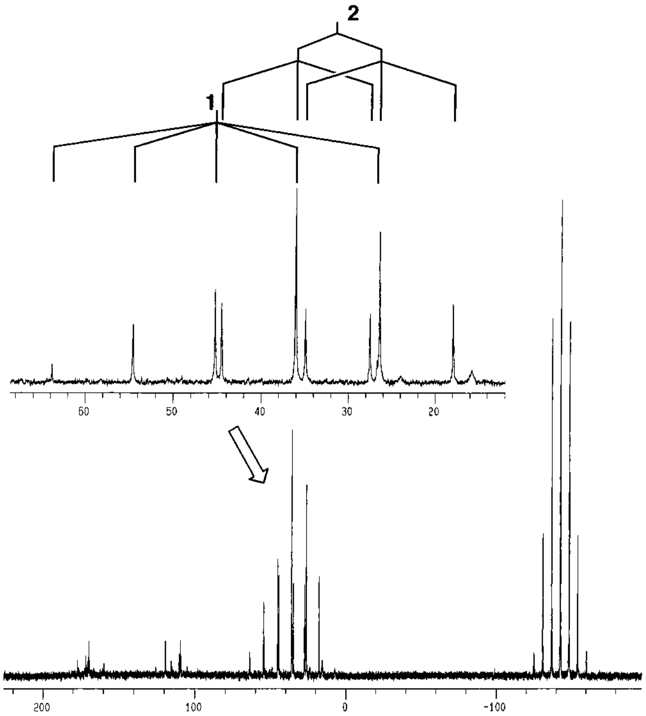


Figure 1. ^{31}P NMR spectrum of the reaction mixture of [Cp(CO)$_2$Fe{P(OPh)$_3$}]PF$_6$ with 5 equiv of Et$_4$NF in CH$_2$Cl$_2$ at room temperature.

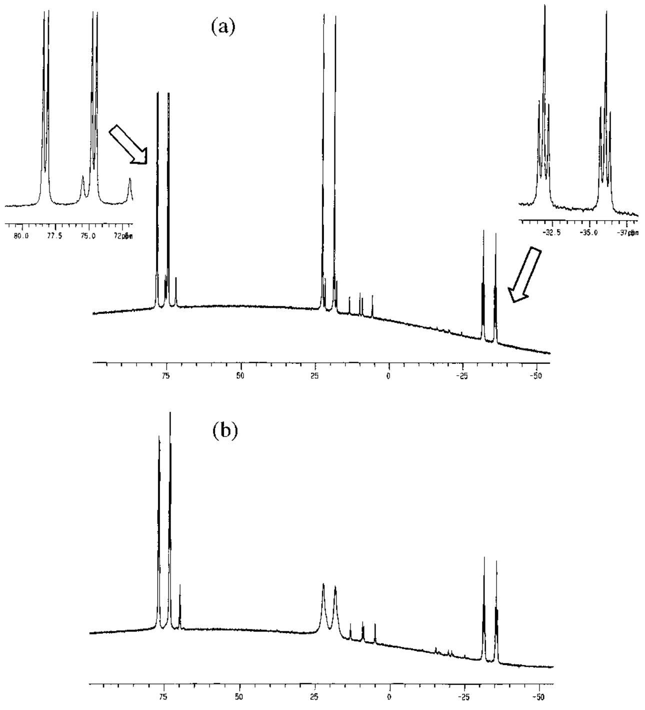


Figure 2. ^{19}F NMR spectrum of the reaction mixture of [Cp(CO)$_2$Fe{P(OPh)$_3$}]PF$_6$ with 5 equiv of Et$_4$NF in CH$_2$Cl$_2$. A doublet assignable to PF$_6^-$ is omitted for simplicity. (a) At room temperature. (b) At −50 °C.

The ^{19}F NMR spectrum of the reaction mixture shown in Figure 2a exhibits three main signals, together with some other weak ones. For the doublet at 20.71 ppm, the coupling constant (1128 Hz) is the same as that (1127 Hz) of a quintet at 45.26 ppm in the ^{31}P NMR spectrum within experimental error. The doublet is thus assigned to **1**, in which a facile pseudorotation around the phosphorus is taking place. The other two strong signals, a doublet of triplets at −34.01 ppm (J = 1173 and 92 Hz) and a doublet of doublets at 76.44 ppm (J = 1033 and 92 Hz), can be thought to arise from **2**, in which a pseudorotation does not take place. Considering the great equatophilicity of an OPh and a Cp(CO)$_2$Fe group (vide infra), it is reasonably concluded that the doublet of triplets is due to the equatorial F which couples with P with a coupling constant of 1173 Hz, corresponding to 1168 Hz observed in the ^{31}P NMR spectrum, and also with the two apical F's with a coupling constant of 92 Hz, and the doublet of doublets is due to the two apical F's which couple with P with a coupling constant of 1033 Hz, corresponding to 1032 Hz observed in the ^{31}P NMR spectrum, and also with the equatorial F with a coupling constant of 92 Hz.

On the basis of the ^{31}P and ^{19}F NMR spectra examined above, it is reasonably proposed that **1** and **2** have PF$_4$ and P(OPh)F$_3$ fragments, respectively. However, it is still not clear whether they have a Cp(CO)$_2$Fe fragment or not. Thus, ^{13}C NMR and ^{1}H NMR spectra of [Cp(CO)$_2$Fe{P(OPh)$_3$}]PF$_6$ treated with Et$_4$NF in CD$_2$Cl$_2$ in a sealed NMR tube were measured. The ^{13}C NMR spectrum showed two broad doublets at 210.19 ppm (J_{CP} = 50.9 Hz) and 211.27 ppm (J_{CP} = 52.2 Hz). They are assignable to the terminal carbonyl carbons in the Cp(CO)$_2$Fe fragment in **1** and **2**, respectively, which couple with a P atom (and probably with F atoms as well). These P−C coupling constants strongly suggest that the phosphorus atom is directly bonded to the Cp(CO)$_2$Fe fragment both in **1** and in **2**. In addition, the ^{13}C NMR spectrum exhibited two signals at 86.30 and 86.17 ppm due to Cp carbons for **1** and **2**, respectively. The ^{1}H NMR spectrum also showed two intense signals in a Cp-proton region at 5.24 and 5.20 ppm, which are assignable to **1** and **2**, respectively, together with a few small signals. However, in the ^{13}C NMR and ^{1}H NMR spectra, the signals due to the OPh group in **2** were not assignable because of overlap with the signals due to free PhO$^-$.

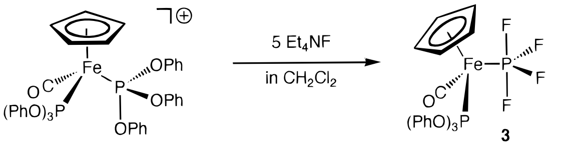
The metallafluorophosphoranes thus formed decompose slowly even under a nitrogen atmosphere at room temperature, and they are extremely moisture-sensitive. During the continued stirring of the solution for several days, the color changed from pale yellow to reddish yellow, and the Cp-proton signal assignable to a reduced iron complex, [Cp(CO)$_2$Fe]$_2$, appeared in the ^{1}H NMR spectrum of the reaction mixture. When the reaction mixture was exposed to air, the signals due to **1** and **2** disappeared rapidly, while small signals around 115 ppm, which had been also observed before exposure to air, increased in intensity in the ^{31}P NMR spectrum, indicating the hydrolysis of the products occurring. Unfortunately, any effort to isolate the metallafluorophosphoranes from the mixture was in vain. Therefore, we attempted to estimate the yields of the products directly from the integrated intensity of the signals in the NMR spectra. The reaction mixture was homogeneous and seemed to have no insoluble material. However, the signals in the ^{1}H NMR spectrum were not well resolved, and we could not estimate the exact yields. Thus, the yields were obtained roughly from the ^{31}P NMR and ^{13}C NMR spectra. The ^{31}P NMR spectrum revealed that **1** and **2** were generated approximately in 86% total yield, and their formation ratio was about 2:7.

Similarly, the Cp-carbon signals in the ^{13}C NMR spectrum suggested ca. 80% total yield for them on the basis of all Cp-containing species. These observations suggest that **1** and **2** had formed quantitatively with the accompanying decomposition of the products.

Complexes **1** and **2** were formed from [Cp(CO)$_2$Fe{P(OPh)$_3$}]PF$_6$ and F$^-$ presumably by several cycles of nucleophilic attack of F$^-$ at the P atom coordinated to Fe and a sequential elimination of OPh$^-$ from the P. Complex **2** can be thought as an intermediate complex formed during the course of the formation of **1**. Indeed, the treatment of [Cp(CO)$_2$Fe{P(OPh)$_3$}]PF$_6$ with a greater excess amount of Et$_4$NF and a longer reaction time led to almost exclusive formation of **1**. It should be noted that complex **2** is the first example of a phosphorane with three different monodentate substituents including a metal fragment.

Recently, Verkade et al. reported fluoride-catalyzed reduction of Pd(II) to Pd(0)–phosphine complexes, in which a phosphine ligand coordinated to the Pd center is oxidized to R$_3$PF$_2$, which is finally converted to O=PR$_3$.[11] In this reaction, a metallafluorophosphorane intermediate was proposed, although it has not been detected. Our present results seem to be consistent with their proposal.

The reaction with Et$_4$NF of [Cp(CO)Fe{P(OPh)$_3$}$_2$]PF$_6$ having two phosphite ligands on the iron center was also examined under conditions similar to those in the reaction of [Cp(CO)$_2$Fe{P(OPh)$_3$}]PF$_6$ (eq 4). Although the reaction mixture contained a considerable amount of the starting materials even after overnight stirring, the formation of Cp(CO){P(OPh)$_3$}Fe(PF$_4$) (**3**) was verified by the following observations (ca. 30% yield): The ^{31}P NMR spectrum displayed a doublet at 170.02 ppm (J_{PP} = 190 Hz) assignable to a P(OPh)$_3$ ligand and a quintet of doublets at 49.07 ppm (J_{PF} = 1108 Hz, J_{PP} = 191 Hz) assignable to a PF$_4$ ligand. The coupling constant of J_{PP} = 191 Hz strongly suggests that P(OPh)$_3$ and PF$_4$ ligands are coordinated to the same iron center. Namely, one of the two P(OPh)$_3$ ligands was converted into the PF$_4$ group, while the other remained intact. This observation can be rationally explained as follows: The nucleophilic substitution of an F atom for an OPh group may be promoted on a phosphorus atom, if it has been already substituted by F because of the accompanying increase in positive charge on the phosphorus. Therefore, the subsequent substitution may be more incident to that phosphorus atom on which the first nucleophilic attack of the F$^-$ had occurred, eventually to form **3**. However, F$^-$ may not be so nucleophilic to attack the remaining P(OPh)$_3$ phosphorus in electrically neutral **3**. When the reaction mixture was subjected to prolonged stirring, a decomposition reaction proceeded with some starting materials remaining.



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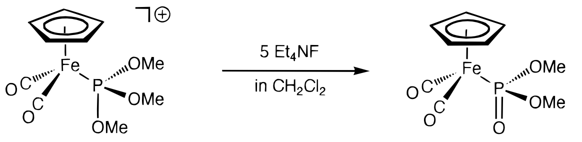
Next we attempted the reaction of [Cp(CO)$_2$Fe{P(OMe)$_3$}]PF$_6$, having P(OMe)$_3$ in place of P(OPh)$_3$, with F$^-$ (eq 5). In this reaction, the formation of a phosphonate complex, Cp(CO)$_2$Fe{P(O)(OMe)$_2$}, was confirmed by comparison of its spectroscopic data with those of the authentic sample, and there was no evidence that the phosphorus atom was directly attacked by F$^-$ to give a pentacoordinate phosphorus species. In general, a transition-metal complex L$_n$MX (X = halogen) reacts with trialkyl phosphite P(OR)$_3$ to give a cationic phosphite complex, [L$_n$M{P(OR)$_3$}]X, as an intermediate. Then, X$^-$ readily attacks an α-carbon in the OR group on the phosphorus atom to form a phosphonate complex L$_n$M{P(O)(OR)$_2$} and RX (the Arbuzov-like dealkylation reaction).[12] Therefore, in the reaction of [Cp(CO)$_2$Fe{P(OMe)$_3$}]PF$_6$ with F$^-$, F$^-$ attacks not a phosphorus atom of the P(OMe)$_3$ ligand but its methyl carbon, yielding the phosphonate complex. This reaction seems in general to be an energetically more favorable process because of greater stability of the resulting phosphonate complex. However, in the reaction of [Cp(CO)$_2$Fe{P(OPh)$_3$}]PF$_6$, the formation of Cp(CO)$_2$Fe{P(O)(OPh)$_2$} is kinetically prevented by a reluctance of the sp^2 ipso-carbon in the Ph group to be nucleophilically attacked by F$^-$. Instead, F$^-$ directly attacks the phosphorus center to form a pentavalent species.



(5)

Reaction of [Cp(CO)$_2$Fe{P(OC$_6$H$_4$NMe)(OC$_6$H$_4$NMeH)}]PF$_6$ with F$^-$. We recently reported the syntheses of metallaphosphoranes with two chelate substituents on the phosphorane phosphorus (eq 2). In contrast, metallaphosphoranes discussed above have only monodentate substituents on the phosphorus. Then, we attempted to obtain a metallaphosphorane having one chelate and two monodentate substituents in addition to a transition-metal fragment on the phosphorus center. For this purpose, a readily available phosphite complex, [Cp(CO)$_2$Fe{P(OC$_6$H$_4$NMe)(OC$_6$H$_4$NMeH)}]PF$_6$, which has one O–N chelate on the phosphorus atom, was chosen as a starting material and treated with F$^-$ (eq 6). The reaction mixture at room temperature displayed broad signals in the NMR spectra, which sharpened at low temperature, because of dynamic behavior of the product (vide infra). Therefore, the NMR data were collected at −80 °C. The ^{31}P NMR spectrum of the mixture showed a doublet of doublets at 39.98 ppm (J_{PF} = 1205, 1010 Hz) as a unique product. Signals due to the inert PF$_6$$^-$ were also observed. In the ^{13}C NMR spectrum, a broad doublet at 212.56 ppm (J_{CP} = 50.4 Hz) and a broad multiplet at 211.61 ppm were observed, both of which are assignable to diastereotopic carbonyl carbons in the Cp(CO)$_2$Fe fragment. The signals assignable to the carbons in NMe (32.73 ppm, d, J_{CP} = 14.3 Hz), Cp (85.96 ppm, s) and aromatic ring

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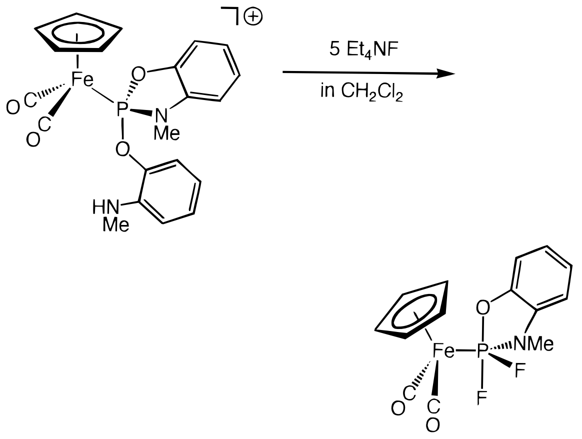
[11] (a) Mason, M. R.; Verkade, J. G. *Organometallics* **1992**, *11*, 2212. (b) McLaughlin, P. A.; Verkade, J. G. *Organometallics* **1999**, *17*, 5937.

[12] (a) Brill, T. B.; Landon, S. J. *Chem. Rev.* **1984**, *84*, 577, and references therein. (b) Nakazawa, H.; Fujita, T.; Kubo, K.; Miyoshi, K. *J. Organomet. Chem.* **1994**, *473*, 243, and references therein.



(6)

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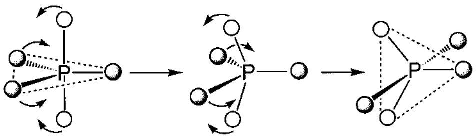
(107.46 ppm, s; 108.66 ppm, d, J_{CP} = 9.4 Hz; 119.02 ppm, s; 119.43 ppm, s; 134.65 ppm, d, J_{CP} = 18.1 Hz; 149.52 ppm, d, J_{CP} = 11.8 Hz) were also observed. In the ^{1}H NMR spectrum, a signal assignable to protons in Cp (5.08 ppm, s) was also observed, although the signals due to aromatic ring and NMe protons could not be identified because of overlap with free $[OC_6H_4NHMe]^-$ and intense NEt_4^+ signals, respectively. In the ^{19}F NMR spectrum, two doublets of doublets at −21.20 ppm (J_{PF} = 1205 Hz, J_{FF} = 107 Hz) and at 63.13 ppm (J_{PF} = 1009 Hz, J_{FF} = 105 Hz) were observed in equal intensity, together with a doublet assignable to PF_6^-. We assigned the former to an equatorial F atom and the latter to an apical F atom on the basis of the similarity in chemical shifts to those of **2**. In this way, the formation of the metallaphosphorane Cp(CO)$_2$Fe-$\{\overline{P(OC_6H_4N}Me)F_2\}$ (**4**) is indicated in which one F atom is in an apical position and the other F atom is in an equatorial position. The yield of **4** was estimated as 97% from the ^{31}P NMR spectrum.

Trends for the Metallafluorophosphoranes in ^{31}P NMR Spectra. The ^{31}P NMR chemical shifts of the metallafluorophosphoranes reported here are reasonable when compared with those of the reported metallaphosphoranes having a Cp(CO)LFe fragment (L = CO, P(OPh)$_3$, P(OMe)$_3$, PMe$_3$).[8,10] In **2** and **4**, an apical P−F bond displays a smaller coupling constant than an equatorial P−F bond. The same trend is also observed in non-transition-metalated fluorophosphoranes and can be explained by the intrinsic difference in bond nature between apical and equatorial bonds. It has been well-known that the apical bond in a trigonal bipyramidal structure is weaker and longer than an equatorial bond. This reflects the difference in the overlap populations between the two, which has been ascribed to the smaller 3s orbital character in the apical bond than that in the equatorial bond.[13] Therefore, this smaller s character in the apical bond should give rise to a smaller P−F coupling constant in the NMR spectra. In this way, the electronic structure of the transition-metalated phosphoranes is understood similarly to that of organic ones.

Scheme 1. Berry's Pseudorotation Mechanism



In complex **3**, the iron center has a P(OPh)$_3$ ligand, which is a more efficient electron donor than CO. Therefore, **3** should have a greater electron density on the iron center than **1**, which renders the transition-metal fragment in **3** a stronger π donor than in **1**. Recently, we have reported that greater π donacity of a transition-metal fragment gives a lower magnetic field shift to a phosphorane phosphorus in the ^{31}P NMR spectrum.[10b] The chemical shift of the PF$_4$ group in **3** is, as expected, in a lower magnetic field than that of **1**, suggesting that this trend is general for metallaphosphoranes.

Pseudorotation Process and Apicophilicity. Rearrangement of substituents around the central atom is one of the unique properties exhibited by pentacoordinate hypervalent compounds. It is widely accepted that this process proceeds via the Berry's pseudorotation mechanism (Scheme 1).[14] For complex **1**, a very fast pseudorotation is observed at room temperature, and thus four F atoms look equivalent on the ^{31}P and ^{19}F NMR time scale. When a CH$_2$Cl$_2$ solution of **1** is cooled to −50 °C, broadening of its signal is observed in the ^{19}F NMR spectrum, indicating that the rotation becomes slower (Figure 2b). For **2**, in contrast, the rearrangement does not take place or is very slow on the NMR time scale at room temperature. When a toluene solution of **2** was heated to 100 °C, slight broadening of its signals was observed in both the ^{31}P and ^{19}F NMR spectra with some decrease in their intensity due to the accompanying decomposition of **2**. Thus, a quantitative estimate of the energy barrier for the pseudorotation could not be performed. Previous NMR studies on the MePF$_4$ and Me$_2$PF$_3$ have revealed that the fast rotation takes place for MePF$_4$, whereas no evidence for such a rotation is obtained for Me$_2$PF$_3$.[15] Such contrasting dynamic behavior has been examined theoretically by Wasada et al. and has been interpreted in terms of site preference of the substituents on the pentacoordinate phosphorus as follows:[16e] an electronegative group prefers an apical position (apicophilicity), and a less electronegative group, a group forming a strong covalent bond to phosphorus, and/or a good π donor group prefer an equatorial position.[16] In the pseudorotation process of Me$_2$PF$_3$, at least one relatively equatophilic Me group has to occupy an apical position, which would lead to the phosphorane to a high-energy state. Therefore, its rotation process may be hindered. In contrast, a low-energy barrier is expected for MePF$_4$ because the Me group can keep a pivotal position during the pseudorotation process and apical and equatorial F atoms can

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(16) For recent theoretical considerations on apicophilicity and equatophilicity or equatoriphilicity, see: (a) Deiters, J. A.; Holmes, R. R.; Holmes, J. M. *J. Am. Chem. Soc.* **1988**, *110*, 7672. (b) Mathiew, S.; Morokuma, K.; Dorigo, A. E. *The 1989 International Chemical Congress of Pacific Basin Societies*; Chemical Society of Japan: Tokyo, 1989; Phys590. (c) Mathiew, S.; Morokuma, K. *Annu. Rev. Inst. Mol. Sci.* **1990**, 18. (d) Wang, P.; Zhang, Y.; Glaser, R.; Reed, A. E.; Schleyer, P. v. R.; Streitwieser, A. *J. Am. Chem. Soc.* **1991**, *113*, 55. (e) Wasada, H.; Hirao, K. *J. Am. Chem. Soc.* **1992**, *114*, 16. (f) Wang, P.; Zhang, Y.; Glaser, R.; Streitwieser, A.; Schleyer, P. v. R. *J. Comput. Chem.* **1993**, *14*, 522.

exchange their positions readily. The same argument could be applied to the difference in rotation energy barriers between **1** and **2**. That is, a transition-metal fragment acts as a good π donor toward a hypervalent phosphorus center and thus prefers an equatorial position, as Martin[8a] and we[10b] have revealed. In addition, Akiba et al. found the high pseudorotation barrier in some hypervalent antimony species, which was attributed to the great electron donacity and bulkiness of transition-metal substituents.[17] Thus, both Cp(CO)$_2$Fe and OPh groups, which are more equatophilic groups than an F atom, are expected to keep equatorial positions, leading to a high rotation energy barrier in **2**. To date, the pseudorotation process of metalated hypervalent compounds has been examined only for the species bearing chelate substituents.[2a,10b,17] The chelate would introduce some steric rigidity around the phosphorus center and make the rotation energy barrier higher. Therefore, metallaphosphoranes having no chelate substituent on the phosphorus center could be better probes to estimate the relative apicophilicity of substituents.

Additional information about the pseudorotation process was derived from the NMR study of the metallaphosphorane **4**. A five-memberd ring generally prefers to occupy an apical–equatorial position rather than an equatorial–equatorial position on steric grounds.[18] Therefore, the *o*-OC$_6$H$_4$NMe chelate preferentially takes an apical–equatorial position, in which a more equatophilic nitrogen atom may occupy an equatorial position. The strong π donor Cp(CO)$_2$Fe group then should be in an equatorial site. **4** is thus expected to have a high rotational energy barrier because the two equatophilic substituents are in equatorial positions as in **2**. However, a CH$_2$Cl$_2$ solution of **4** at room temperature displays a broad doublet of doublets in the ^{31}P NMR spectrum, which sharpens at −80 °C. This observation indicates that the pseudorotation is almost beginning even at room temperature. The reason for a relatively low energy barrier for **4** could arise from the F atom being in an equatorial position; although an F atom is generally highly apicophilic, one F atom has to take an equatorial position in **4** because the *o*-OC$_6$H$_4$NMe chelate occupies an apical–equatorial position on steric demand. This electronically unfavorable situation probably makes the energy barrier lower.

Experimental Section

All reactions were carried out under an atmosphere of dry nitrogen by using Schlenk tube techniques or in a sealed NMR tube. CH$_2$Cl$_2$ was purified by distillation from P$_2$O$_5$, and toluene was distilled from sodium benzophenone ketyl, and they were stored under a nitrogen atmosphere. Et$_4$NF was obtained from a common commercial source and dried by azeotropic distillation with CHCl$_3$ three times before use. [Cp(CO)$_2$Fe(THF)]PF$_6$,[19] [Cp(CO)$_2$Fe{P(OPh)$_3$}]PF$_6$,[10a] [Cp(CO)$_2$Fe{P(OMe)$_3$}]PF$_6$,[20] and [Cp(CO)$_2$Fe{$\overline{\mathrm{P(OC_6H_4N}}$Me)(OC$_6H_4$NMeH)}]PF$_6$[10b] were prepared according to the literature.

A JEOL LA-300 spectrometer was used to obtain ^{1}H NMR, ^{13}C NMR, ^{31}P NMR, and ^{19}F NMR spectra. ^{1}H NMR and ^{13}C NMR data were referred to SiMe$_4$, as an internal standard. ^{31}P NMR and ^{19}F NMR data were referred to 85% H$_3$PO$_4$ and CFCl$_3$, respectively, as external standards.

Preparation of [Cp(CO)Fe{P(OPh)$_3$}$_2$]PF$_6$. P(OPh)$_3$ (0.60 mL, 2.3 mmol) was added to a solution of [Cp(CO)$_2$Fe(THF)]PF$_6$ (450 mg, 1.14 mmol) in CH$_2$Cl$_2$ (6 mL), and the mixture was refluxed for 14 h. After the volatile components were removed under reduced pressure, the resulting residue was dissolved in a small amount of CH$_2$Cl$_2$. Then the CH$_2$Cl$_2$ solution was loaded on a silica gel column and eluted with CH$_2$Cl$_2$ and then with acetone. A pale yellow band, which contained Cp$_2$Fe, was first eluted with CH$_2$Cl$_2$. The second yellow band that eluted with CH$_2$Cl$_2$/acetone (1:1) was collected, and the effluent was concentrated to ca. 0.5 mL in vacuo. Addition of ether resulted in the formation of a pale yellow precipitate, which was washed with ether several times and dried under reduced pressure to give a pale yellow powder of [Cp(CO)Fe{P(OPh)$_3$}$_2$]PF$_6$ (767 mg, 0.84 mmol, 73% yield). Anal. Calcd for C$_{42}$H$_{35}$F$_6$FeO$_7$P$_3$: C, 55.16; H, 3.86. Found: C, 54.92; H, 3.85. IR (ν_{CO}, in CH$_2$Cl$_2$): 2016. ^{31}P NMR (δ, in acetone-d_6): 158.55. ^{1}H NMR (δ, in acetone-d_6): 4.91 (s, 5H, C$_5$H$_5$), 7.32–7.50 (m, 30H, OPh). ^{13}C NMR (δ, in acetone-d_6): 86.51 (s, C$_5$H$_5$), 122.36 (s, OPh), 127.63 (s, OPh), 131.80 (s, OPh), 152.15 (t, J_{CP} = 5.58 Hz, OPh), 212.65 (t, J_{CP} = 37.54 Hz, CO).

Reactions of Iron–Phosphite Complexes with NEt$_4$F. Since reactions of iron–phosphite cationic complexes with F$^-$ are basically similar in all cases, the reaction of [Cp(CO)$_2$Fe{P(OPh)$_3$}]PF$_6$ with NEt$_4$F is shown as a typical example. A CH$_2$Cl$_2$ solution (0.83 mL) containing [Cp(CO)$_2$Fe{P(OPh)$_3$}]PF$_6$ (106 mg, 0.17 mmol) and NEt$_4$F (124 mg, 0.83 mmol) was stirred at room temperature for a few minutes. Then, the resulting reaction mixture was subjected to ^{31}P and ^{19}F NMR measurements at room temperature and at −50 °C. After removal of volatile components under reduced pressure from the CH$_2$Cl$_2$ solution, the products were extracted with toluene and the toluene solution was subjected to NMR measurements at 100 °C.

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