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Accounts

Metallaphosphorane Chemistry: Preparations, Structures, and Reactivities

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Transition-metal phosphorane complexes, $[Cp(CO)_2M\{P(OC_6H_4Y)_2\}]$ (M = Fe, Ru; Y = NH, NMe, O) have been prepared from $[Cp(CO)_2M\{P(OPh)_3\}]PF_6$, *o*-$HOC_6H_4YH$, and a Lewis base. With the use of Et_4NF in place of *o*-HOC_6H_4YH, $[Cp(CO)_2Fe(PF_4)]$ and $[Cp(CO)_2Fe\{P(OPh)F_3\}]$ have been prepared. These reactions involve nucleophilic attacks of an organic or an inorganic nucleophile at a trivalent phosphorus coordinated to a transition metal and substitution on the phosphorus. The reaction of phosphorane $HP(OC_6H_4NH)_2$ with a Lewis base leads to NH proton abstraction to give the amide $HP(OC_6H_4NH)(OC_6H_4N^-)$. Subsequent treatment of the anion with EX (MeI, $[Cp(CO)_2FeCl]$) has yielded P-substituted phosphorane $EP(OC_6H_4NH)_2$, whereas that with E′X ($SiMe_3Cl$, $GeMe_3Cl$, $SnMe_3Cl$, $[Cp(CO)CoI_2]$) has yielded N-substituted phosphorane $HP(OC_6H_4NH)(OC_6H_4NE')$. X-ray structure analyses and spectroscopic data for these metallaphosphoranes reveal that the transition metal fragment serves as a strong π donor toward a phosphorane fragment. The activation parameters for Berry pseudorotation around the phosphorus in several metallaphosphoranes have been determined. The reactivity of metallaphosphoranes was also examined. The iron and ruthenium phosphoranes react with a Lewis base to give $Li[\{\eta^5\text{-}C_5H_4P(OC_6H_4Y)_2\}(CO)_2M]$. In this reaction, one of the protons on the Cp ring is abstracted by the Lewis base and then migration of the phosphorane fragment to the Cp ring takes place. This constitutes the first reported migration of a hypervalent element fragment.

Since phosphorus is situated in the group 15 column in the periodic table, it is expected to have trivalent tricoordinate, pentavalent tetracoordinate, and pentavalent pentacoordinate states in electrically neutral molecules. The chemistry of tricoordinate (e.g., phosphine, phosphite) and tetracoordinate phosphorus compounds (e.g., phosphine oxide, phosphine sulfide) has been widely investigated and is well-developed in inorganic and organic fields and also in transition-metal area because they serve as two-electron-donor ancillary ligands. In contrast, the chemistry of pentavalent pentacoordinate phosphorus compounds (phosphoranes) was much less investigated until the 1970's,[1] though one of the typical pentacoordinate inorganic phosphorus compounds (PF_5) has been known since the 19th century and the first pentacoordinate organophosphorus compound (PPh_5) was reported in 1949 by Wittig. However, in the past two decades, there has been increasing interest in phosphoranes.[2] The reasons for the considerable attention paid to phosphoranes may include the fact that some of the interesting facets of phosphorus chemistry are met with in phosphoranes. Phosphoranes are one class of hypervalent compounds that violate the octet rule; they have a trigonal bipyramidal structure with two kinds of bonds (apical and equatorial bonds), and undergo apical-equatorial rearrangement, so-called Berry pseudorotation.

A metallaphosphorane is a phosphorane which has one (or more) transition metal fragment(s) as a substituent on the phosphorus. In contrast to the intense effort in the last two decades in the field of organophosphoranes, metallaphosphorane chemistry still remains in its infancy, especially as to the structures and the reactivity.[3] We have been engaged in the study of metallaphosphoranes. The article reviews mainly our results of syntheses, structures, properties, and reactivities of metallaphosphoranes. Through out this article, the tie lines, for example in $[Cp(CO)_2Fe\{P(OC_6H_4Y)(OC_6H_4Z)\}]$, are omitted for simplicity in favor of $[Cp(CO)_2Fe\{P(OC_6H_4Y)(OC_6H_4Z)\}]$.

Bond Character in Phosphorane

It might be pertinent to summarize briefly the bond charac-

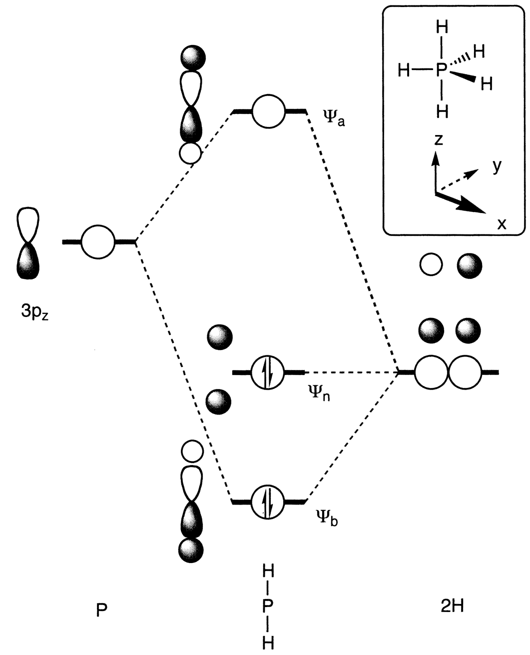


Fig. 1. Molecular orbital (3c–4e) of apical bond of PH_5.

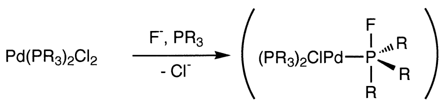
ter in phosphorane before presenting our findings about metallaphosphoranes.

Since phosphorane has 10 electrons beyond the octet within a valence shell, employing only one 3s and three 3p orbitals is not sufficient. Hybridization of dsp^3 using a higher-lying 3d orbital has been proposed to hold these 10 electrons. However, it was shown that the contribution of the 3d orbital is not of fundamental importance because the energy gap between 3s/3p and 3d is too large. Alternatively, a three-center-four-electron (3c–4e) bond has been proposed and is nowadays widely accepted. The 3c–4e bond model is based on the molecular orbital theory. The 3c–4e bond is seen in the apical bond of a pentacoordinate trigonal bipyramidal phosphorus. The apical bond of the molecular orbital of a hypothetical molecule PH_5 is shown in Fig. 1. The bond consists of one $3p_z$ orbital of phosphorus and two 1s orbitals of hydrogen. One set of two 1s orbitals of hydrogen can overlap with $3p_z$ of phosphorus to give a bonding orbital (Ψ_b) and an antibonding orbital (Ψ_a). Another set of two 1s orbitals of hydrogen finds no orbital on P to overlap with, yielding a nonbonding orbital (Ψ_n) which is a HOMO of the molecule. Therefore, the apical bond has 0.5 bond order and the minus charge is mostly localized on the two apical atoms.

Reaction Pathway Involving Metallaphosphorane As an Intermediate

Trivalent tricoordinate phosphorus compounds such as phosphine or phosphite have been widely used as ancillary ligands for transition metals. Two reasons are important. One is that trivalent phosphorus compounds are rich in variety; that is, their electronic and steric factors are finely tunable by changing the substituents. Therefore, desirable electronic and steric circumstances can be attained in a transition metal complex by selecting appropriate trivalent phosphorus ligand(s). The other is that trivalent phosphorus compounds are (believed to be) very stable in a coordination sphere, that is, they do not become reaction sites even under severe reaction conditions.

Recently, a reaction pathway has been proposed involving a nucleophilic attack toward a trivalent phosphorus atom coordinated to a transition metal to give a metallaphosphorane complex. Verkade et al. proposed the formation of $[(PR_3)_2Cl\text{-}Pd\{PFR_3\}]$ in the reaction of $[Pd(PR_3)_2Cl_2]$ with F^- in the presence of PR_3, where nucleophilic attack of fluoride at a coordinated phosphine takes place (Eq. 1).[4] We also proposed the formation of iron-phosphorane by a nucleophilic attack of H^- and OH^- at a coordinated phosphorus. That is, in the reaction of $[Cp(CO)_2Fe(PHPh_2)]$ with $NaBH_4$ to give $[Cp(CO)_2\text{-}FeH]$ and $PHPh_2$, the formation of iron-phosphorane by a nucleophilic attack of H^- has been proposed (Eq. 2).[5] The reaction with KOH of an iron complex having an amino-substituted phosphite yields a deaminated phosphonate complex (Eq. 3). A reaction mechanism is proposed in which an OH^- nucleophilically attacks the coordinating phosphite phosphorus to afford metallaphosphorane.[6] In any case, however, there is no direct evidence for the formation of the metallaphosphorane even as an intermediate.



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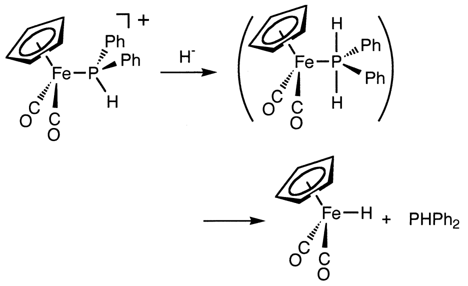

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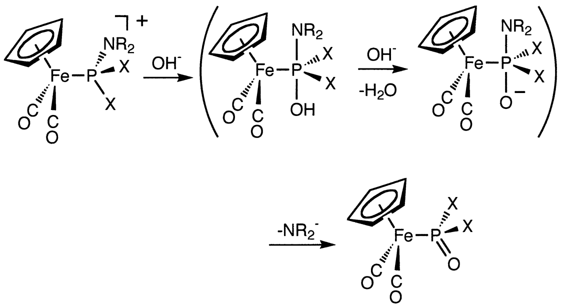
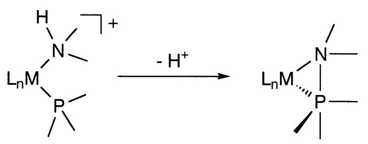


(3)

New Preparative Methods of Metallaphosphoranes

Isolated metallaphosphoranes were first synthesized by Riess[7] in 1981 with deprotonation at a nitrogen in polycyclic species with phosphine- and amine-metal bonds. Since then, several kinds of methods for the preparation of metallaphosphoranes have been reported. They can be roughly classified as follows: deprotonation[7,8] (Eq. 4) and protonation[9] (Eq. 5) at a nitrogen in polycyclic species with phosphine- and/or amine-metal bonds, oxidative addition of halogen to transition-metal phosphide complexes[10] (Sb and As versions[11]) (Eq. 6), nucleophilic substitution at a phosphorane phosphorus atom by a transition-metal anion[12] (Eq. 7), and electrophilic attack of an electron-deficient transition-metal fragment at a phosphoranide[13] (Sb version[14]) (Eq. 8). Some other preparative methods have also been reported.[15]



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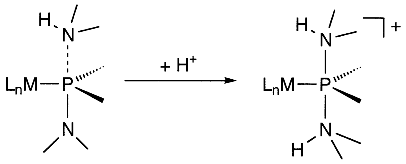

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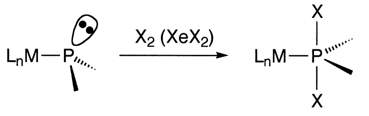

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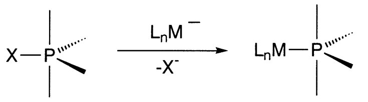

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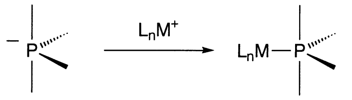

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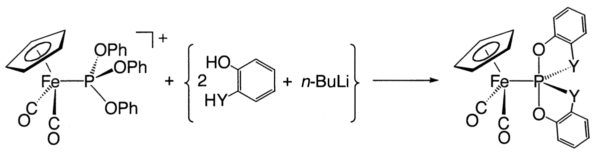
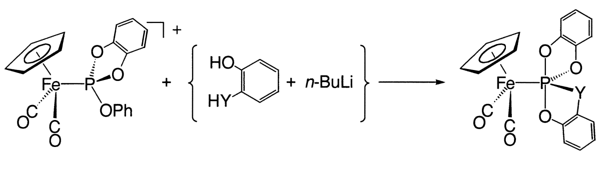
We found an unprecedented synthetic method for metallaphosphoranes, $[Cp(CO)_2Fe\{P(OC_6H_4Y)(OC_6H_4Z)\}]$ (Cp = η^5-C_5H_5; Y, Z = NH, NMe or O), involving the nucleophilic attack of an organic nucleophile at a trivalent phosphorus coordinated to a transition metal.[16,17] $[Cp(CO)_2Fe\{P(OPh)_3\}]PF_6$ was treated with a mixture of 2 molar amounts of *o*-HOC_6H_4NH and an equimolar amount of *n*-BuLi to give a yellow powder of **1a** (Eq. 9). With some modifications, $[Cp(CO)_2Fe\{P(OC_6H_4NMe)_2\}]$ (**1b**) (Eq. 9), $[Cp(CO)_2Fe\{P(OC_6H_4O)(OC_6H_4NR)\}]$ (**2a** and **2b**) (Eq. 10), and $[Cp(CO)_2Fe\{P(OC_6H_4O)_2\}]$ (**3**) (Eq. 11) were similarly prepared.



Y = NH: **1a**, NMe: **1b**

(9)



Y = NH: **2a**, NMe: **2b**

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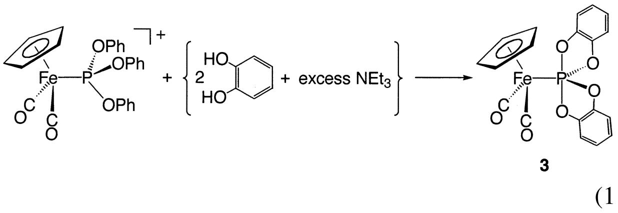

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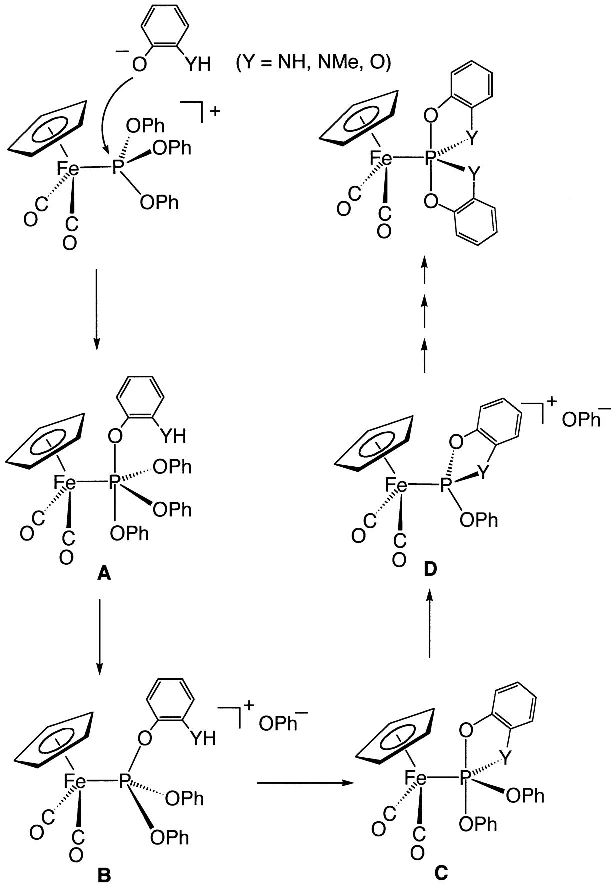
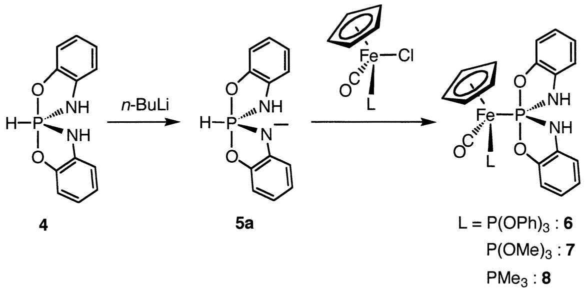


Scheme 1.

It should be noted in these reactions that the valence of the phosphorus is formally expanded from III to V without Fe–P bond cleavage, that is, the nature of the Fe–P bond changes formally from dative to covalent. Corresponding ruthenium phosphorane complexes have been prepared in a similar manner.[18]

The proposed reaction mechanism is shown in Scheme 1. $[o\text{-}OC_6H_4YH]^-$, produced from *o*-HOC_6H_4YH and a base, 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 YH proton of **B** to yield the Y^- group, which then nucleophilically attacks the P atom to give C, followed by release of OPh^- to obtain **D**. This OPh^- reacts with the remaining unreacted *o*-HOC_6H_4YH to give $[o\text{-}OC_6H_4YH]^-$, which undergoes similar reactions leading finally to the formation of $[Cp(CO)_6Fe\{P(OC_6H_4Y)_2\}]$. In Eq. 9, 2 molar amounts of *o*-HOC_6H_4YH were necessary, but an equimolar amount of a base based on the cationic iron complex was sufficient, which is consistent with the mechanism. The proposed intermediates **A**–**D** have not been observed even spectroscopically, presumably due to their high reactivity.

In an attempt to prepare $[Cp(CO)LFe\{P(OC_6H_4NH)_2\}]$ (L = phosphine, phosphite), we encountered interesting findings. The reaction of $[Cp(CO)LFe\{P(OPh)_3\}]PF_6$ with *o*-$HOC_6H_4NH_2$ in the presence of *n*-BuLi did not afford the expected phosphorane $[Cp(CO)LFe\{P(OC_6H_4NH)_2\}]$. Then, the reaction of phosphoranide $^{-}P(OC_6H_4NH)_2$ with [Cp(CO)LFeCl] was next examined. To obtain the phosphoranide, $HP(C_6H_4NH)_2$ (**4**) was treated with *n*-BuLi, and unexpected deprotonation took place to give only an amide $HP(OC_6H_4NH)(OC_6H_4N^-)$ (**5a**). In addition, the reaction of the resulting amide with [Cp(CO)LFeCl] yielded a metallaphosphorane, [Cp(CO)LFe{$P(OC_6H_4NH)_2$}] (Eq. 12), but not an N-metalated $HP(OC_6H_4NH)[OC_6H_4N${FeCp(CO)L}].[17]



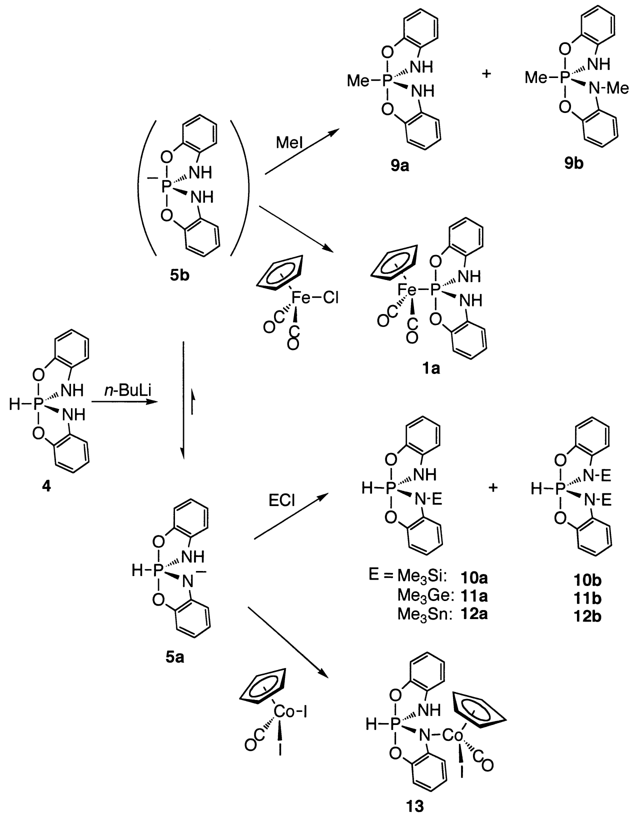
(12)

The reaction of **4** with *n*-BuLi revealed that an amino proton is selectively abstracted to give **5a** and the remaining amino proton is shuttling rapidly between the two N atoms at room temperature, whereas at −80 °C the shuttling does not occur or is very slow on the NMR time scale. There is no evidence for the formation of phosphoranide $[P(OC_6H_4NH)_2]^-$ (**5b**).

Since the amide reacts with [Cp(CO)LFeCl] to give a P-substituted compound, metallaphosphorane, we examined the reaction with a series of group 14 element halides (MeI, Me_3SiCl, Me_3GeCl, Me_3SnCl) and some transition-metal-halide complex ($[Cp(CO)_2FeCl]$ and $[Cp(CO)CoI_2]$) (See Scheme 2).[19] Treatment of the amide with MeI yielded P-methylated phosphoranes (**9a** and **9b**). In contrast, the reaction with ECl (E = $SiMe_3$, $GeMe_3$, $SnMe_3$) led exclusively to N-substituted phosphoranes, $HP(OC_6H_4NH)(OC_6H_4NE)$ (**10a**, **11a**, **12a**) and $HP(OC_6H_4NE)_2$ (**10b**, **11b**, **12b**). In the corresponding reaction with $[Cp(CO)_2FeCl]$, the anion was converted into a P-metalated phosphorane (**1a**), whereas the reaction with $[Cp(CO)CoI_2]$ yielded an N-metalated phosphorane (**13**).

In the reaction with *n*-BuLi of phosphorane **4**, which has one H and two NHR groups in equatorial positions, only an amide **5a** was detected, suggesting that direct NH proton abstraction takes place. The amide **5a** is proposed to be in equilibrium with a phosphoranide **5b**, though the equilibrium is so heavily shifted toward **5a** that **5b** can not be detected spectroscopically. Since it seems often to be the case that a Lewis base converts a hydridophosphorane into an open-form tricoordinate phosphorus compound,[3b] the amide formation reported here is unique in that the phosphorus keeps its pentacoordinate framework. The stability is attributed to the rigid chelate structure of the substituents on the phosphorus atom.

Examination of the reaction patterns of **5** with several halides presented above points to the presence of selectivity. In the reaction with halides of group 14 elements, methyl iodide reacts with **5b** to give a P-substituted phosphorane, whereas trimethyl-silyl, -germyl, and -stannyl chlorides react with **5a** to yield N-substituted phosphoranes.



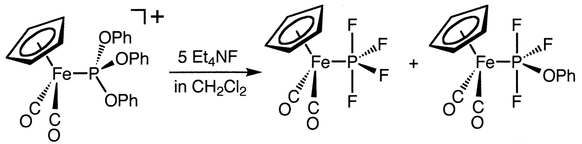
Scheme 2.

Since the P- and N-substituted products prepared in this paper except **13** do not change further, the selectivity mentioned above may be explained by the difference in thermodynamic stability between E–P and E–N bonds. It is well-known that a P–C bond is more stable than P–Si, P–Ge, and P–Sn bonds,[20] so that an alkyl group tends to bond to a phosphorus atom. In contrast, Si, Ge, and Sn fragments would more preferably bond to a nitrogen atom, because the third and subsequent row main group elements can use its empty d and/or σ^* orbital(s) to make a π bond with lone pair electrons on the N atom. These bonding abilities may be responsible for the selectivity mentioned above.

The selectivity in the reaction of **5** with transition-metal–halide complexes can be understood in terms of π donation from a transition metal fragment to a phosphorane phosphorus. It has been demonstrated that a phosphorane fragment accepts π electrons into its empty σ^* orbital of the 3-center-4-electron bond from a filled d orbital of [Cp(CO)LFe] (L = CO, phosphine, phosphite) fragments, making the P–M bond strong.[13a,16,17] In $[Cp(CO)_2FeCl]$, the formal oxidation state of Fe is +II, whereas that of Co in $[Cp(CO)CoI_2]$ is +III. Therefore, the π electron donor ability of the [Cp(CO)CoI] fragment is expected to be poorer than that of the $[Cp(CO)_2Fe]$ fragment. Indeed, in the ^1H NMR spectra, a signal due to the Cp ligand is observed at a lower magnetic field in the cobalt complex (5.96 ppm) than in the iron complex (5.05 ppm). In addition, it is highly likely that σ electron donor ability of the [Cp(CO)CoI] fragment is weaker than that of H. Therefore, the [Cp(CO)CoI] fragment may prefer to make a bond with a nitrogen atom, which does not require π-back donation at all.

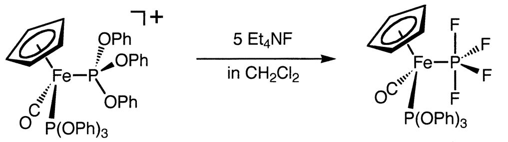
Our new synthetic method for metallaphosphoranes, in which a trivalent phosphorus compound coordinating to a cationic transition-metal center is nucleophilically attacked by

Lewis bases, can be applied to formation of iron fluorophosphorane complexes.[21] A cationic triphenylphosphite complex $[Cp(CO)_2Fe\{P(OPh)_3\}]PF_6$ reacts with 5 molar amounts of NEt_4F to give two iron phosphorane complexes (**14** and **15**) (Eq. 13). These complexes may be formed 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 **15** can be thought of as an intermediate complex formed in the course of the formation of **14**. Indeed, the treatment of $[Cp(CO)_2Fe\{P(OPh)_3\}]PF_6$ with a larger excess amount of Et_4NF for a longer reaction time led to almost exclusive formation of **14**. It should be noted that complex **15** is the first example of a phosphorane with three different monodentate substituents including a metal fragment.



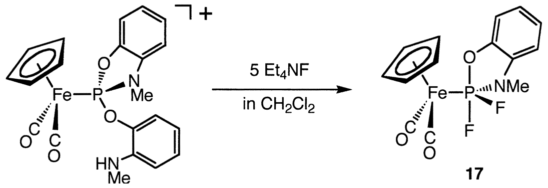
14 **15** (13)

The reaction with Et_4NF of $[Cp(CO)Fe\{P(OPh)_3\}_2]PF_6$, which has two phosphite ligands on the iron center, was also examined under similar conditions, and it was found to form $[Cp(CO)\{P(OPh)_3\}Fe(PF_4)]$ (**16**) (Eq. 14). 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 take place more readily than the former OPh/F substitution, eventually to form **16**. However, F^- may not be so nucleophilic as to attack the remaining $P(OPh)_3$ phosphorus in electrically neutral **16**.



16 (14)

A metallaphosphorane having one chelate and two monodentate substituents in addition to a transition-metal fragment on the phosphorus center has been prepared in the reaction of $[Cp(CO)_2Fe\{P(OC_6H_4NMe)(OC_6H_4NMeH)\}]PF_6$ with F^- (Eq. 15). The product **17** has two F atoms on a phosphorane phosphorus. One is in an apical position and the other in an equatorial one.



17 (15)

Bond Character between a Transition Metal and Phosphorane Phosphorus

For all metallaphosphoranes characterized to date, the five-coordinate phosphorus adopts a trigonal-bipyramidal (tbp) or slightly distorted tbp geometry, and a transition metal fragment is situated in an equatorial position. Therefore, the M–P bond is not a hypervalent bond. However, the character of the bond is still one of the most interesting subjects in metallaphosphoranes. The spectroscopic data (Table 1) suggest that the π back donation from a filled M(dπ) orbital to the σ* orbital of apical P–O bonds (hypervalent bonds) is one of the most important factors to stabilize the M–P bond in the metallaphosphorane complexes.

As one goes from **1** to **2** and **3** (and from **1′** to **3′** for corresponding Ru complexes), the number of amino substituents on the phosphorus decreases. The ν_{CO} values in the IR spectra increase in frequency in this order. This trend is considered to be due to the increase in π-acceptability of a phosphorane fragment in this order.

Comparison of ν_{CO} values of **1**–**3** with those of $[Cp(CO)_2FeX]$ (X = Ph, C(O)Me, $P(O)(OMe)_2$, CF_3) revealed that the acidity of a $P(OC_6H_4Y)(OC_6H_4Z)$ ligand (Y, Z = NH, NMe, O) is greater than that of Ph or C(O)Me, but less than that of CF_3, and is comparable to that of $P(O)(OMe)_2$.[17]

With ^{31}P NMR data, the chemical shift moves upfield on going from **3** to **2** and **1**. This is parallel to the increase in the number of electron-donating amino groups. In a series of $[Cp(CO)LFe\{P(OC_6H_4NH)_2\}]$ where the ligand L on the iron varies, the basicity of L increases from **1a** to **6**, **7**, and **8**, which

Table 1. Comparison of Spectroscopic Data for Fe and Ru Phosphoranes

Complexes	M or L	IR ν_{CO}/cm^{-1} [a]	^{31}P NMR δ/ppm[b]
$[Cp(CO)_2M\{P(OC_6H_4NH)_2\}]$	Fe (**1a**)	2026, 1977	25.67
	Ru (**1a′**)	2037, 1983	0.66
$[Cp(CO)_2M\{P(OC_6H_4NMe)_2\}]$	Fe (**1b**)	2024, 1975	15.95
	Ru (**1b′**)	2036, 1983	−6.93
$[Cp(CO)_2M\{P(OC_6H_4NH)(OC_6H_4O)\}]$	Fe (**2a**)	2034, 1988	48.50[a]
$[Cp(CO)_2M\{P(OC_6H_4NMe)(OC_6H_4O)\}]$	Fe (**2b**)	2033, 1985	45.39[a]
$[Cp(CO)_2M\{P(OC_6H_4O)_2\}]$	Fe (**3**)	2042, 1996	73.43
	Ru (**3′**)	2052, 2001	47.35
$[Cp(CO)LFe\{P(OC_6H_4NH)_2\}]$	$P(OPh)_3$ (**6**)		27.09, 30.00[a,c]
	$P(OMe)_3$ (**7**)		33.89, 35.34[a,c]
	PMe_3 (**8**)		37.78, 38.11[a,c]

a) In THF. b) In $CDCl_3$. c) Phosphorane portion. Two signals are due to diastereomers.

may cause greater π back donation of a [Cp(CO)LFe] fragment to the phosphorus in this order. Thus, an upfield shift in the ^{31}P NMR spectra is expected in this order. However, the opposite tendency was observed. Although factors affecting NMR chemical shifts are sometimes very complicated, one plausible explanation which rationalizes this order is the following. The apical O–P–O hypervalent 3c–4e bond is polarized as $O^{\delta-}$–$P^{\delta+}$–$O^{\delta-}$ intrinsically. Because the electron density on the iron atom flows into the antibonding orbital of the 3c–4e bond, the π donation makes the 3c–4e bond longer, which would cause an increase in the polarization. If so, the π back donation accumulates a positive charge on the phosphorus, leading to the downfield shift in the ^{31}P NMR.

Comparison of ^{31}P and ^{1}H NMR and IR data between corresponding Fe and Ru phosphorane complexes indicates that the Ru–P bond is more polarized as $M^{\sigma+}$–$P^{\delta-}$ than the Fe–P bond.[18] The same tendency has been reported for the related phosphonate complexes [Cp(CO)$_2$M{P(O)R^{1}R^2}] (M = Ru, Fe; R^1 and/or R^2 = OMe, NC$_4$H$_8$),[22] which also have a metal-phosphorus(V) covalent bond. Therefore, the larger $M^{\sigma+}$–$P^{\delta-}$ polarization for Ru than for Fe seems to be general.

Structures of Metallaphosphoranes

X-ray structures of metallaphosphoranes have been reported, to our knowledge, for 23 complexes to date. The structural features for six Pt, four Mo, three Co, one Mn, and one Rh complexes were reviewed by Montgomery in 1993.[3a] With group 8 transition metal phosphoranes, five complexes ([Cp(CO)$_2$Fe{P(OC(CF$_3$)$_2$C$_6$H$_4$)$_2$}],[13a] **1b**, **2b**, **1b′**, and [Cp(CO)$_2$Ru{P(OC$_{10}$H$_6$O)$_2$}][18]) were reported. However, these structures were not cited in the previous review because of the relatively recent reports. This article summarizes their structural features.

In any case, the phosphorus adopts a slightly distorted tbp geometry with two oxygens in the apical positions and with M (Fe or Ru) atom in one equatorial position. The two apical bonds bend away from a transition metal fragment, and the two angles of M–P–(equatorial atom) are slightly greater than the ideal angle (120°), though the sum of the equatorial angles is almost 360°. The distortion may arise from the apical-equatorial five-membered-ring strain and/or a steric demand of a transition metal fragment.

For **1b**, **2b**, and **1b′**, the geometry around nitrogen is planar. The O$_{ap}$–P–O$_{ap}$ bond is in the plane. Therefore, the nitrogen takes sp^2 hybridization and the lone-pair electrons lie on the equatorial plane, implying favorable π donation of the lone-pair electrons to the σ* orbitals of the equatorial bonds on the phosphorus.

It can be considered that the M–P bond in metallaphosphorane consists of σ donation from P to M and π back donation from M to P. The substituents on the phosphorus in **1b** are two amino and two aryloxy groups, whereas those in **2b** are one amino and three aryloxy groups. Therefore, supposing that the σ donation is a dominant factor concerning the Fe–P bond, the bond would be shorter for **1b** than for **2b**, and oppositely, if the π back donation is dominant, the bond would be shorter for **2b** than for **1b**. The X-ray analyses revealed that the Fe–P bond is ca. 0.02 Å shorter for **2b** than for **1b**, indicating that the π back donation is more important in the Fe–P bond. This is also supported by the IR data. The ν_{CO} stretching bands of **2b** (2033 and 1985 cm^{-1}) are at a higher frequency than those of **1b** (2024 and 1975 cm^{-1}). The same comparison can be made between two ruthenium phosphoranes, **1b′** and [Cp(CO)$_2$Ru{P(OC$_{10}$H$_6$O)$_2$}].

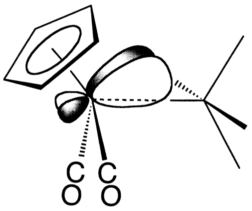


Fig. 2. HOMO of the Cp(CO)$_2$Fe fragment.

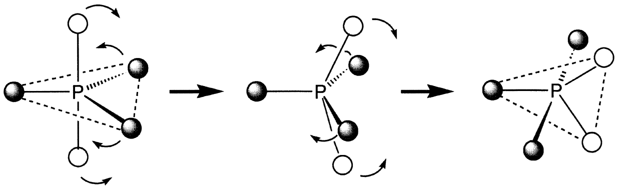
The orientation of Cp(CO)$_2$M fragment also strongly suggests its π donation ability. According to the calculation by Hoffmann,[24] the HOMO of the [Cp(CO)$_2$Fe]$^+$ fragment has π symmetry as illustrated in Fig. 2. If a phosphorane fragment accepts π-electron density into the σ* orbital of the P–O$_{ap}$ bond, the σ* orbital should overlap with the HOMO orbital shown in Fig. 2. This is the case observed in the X-ray structures of the group 8 transition metal phosphoranes.

The π-donor ability of a transition metal fragment on a phosphorane is also deduced from the comparison of the structures of **2b** and of HP(OC$_6$H$_4$O)(OC$_6$H$_4$NMe),[23] which corresponds to the nonmetalated version of **2b**. As we go from the hydridophosphorane to the iron phosphorane (**2b**), a 0.122 Å elongation in the two P–O$_{ap}$ bonds is observed.

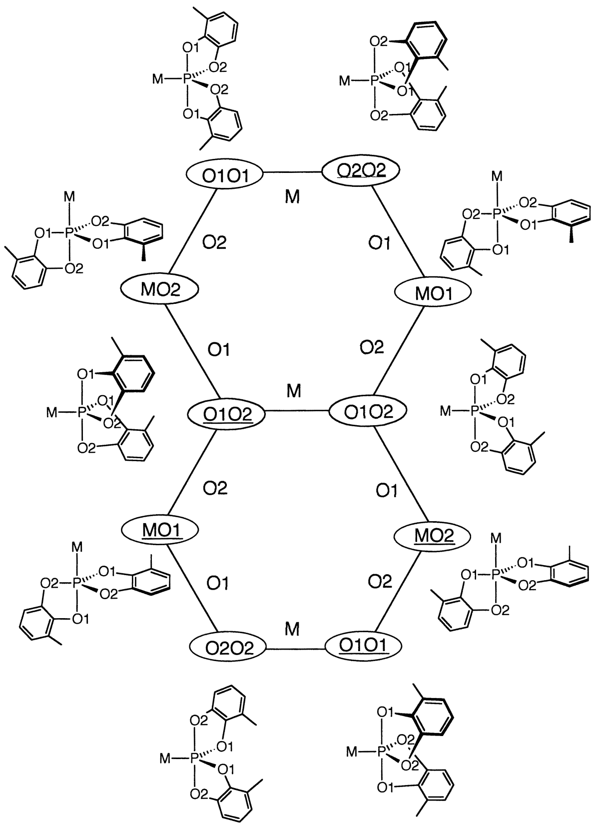
With phosphoranes, a π-electron-donating substituent favors an equatorial position. In an equatorial position, two types of π interaction are conceivable: π donation to the σ* orbital of an equatorial bond (i), and that of an apical bond (ii). Theoretical studies[25] suggest that an amino group energetically favors the type (i) interaction. In addition, in the case of **1b**, **2b**, and **1b′**, the five-membered ring connecting apical and equatorial positions sterically allows the amino substituent to have only type (i) interaction. Therefore, the transition metal fragment is obliged to have type (ii) interaction in the solid state, although a transition metal fragment would basically favor the type (i) interaction. In solution, the free rotation of the M–P bond is deduced from NMR measurements, and the M–P rotation does not cease even at −50 °C. Therefore, the difference between types (i) and (ii) in energy with respect to the transition metal fragment is expected to be small.

Berry Pseudorotation of Metallaphosphorane

Rearrangement of substituents around the central phosphorus is one of the unique properties exhibited by phosphoranes. It is widely accepted that the process proceeds via the Berry pseudorotation mechanism (Scheme 3).[2] Although barriers to



Scheme 3.



Scheme 4.

Berry pseudorotation of several organophosphoranes have been evaluated,[25] those of metallaphosphorane have not been reported. The followings show our results about Berry pseudorotation of metallaphosphoranes.

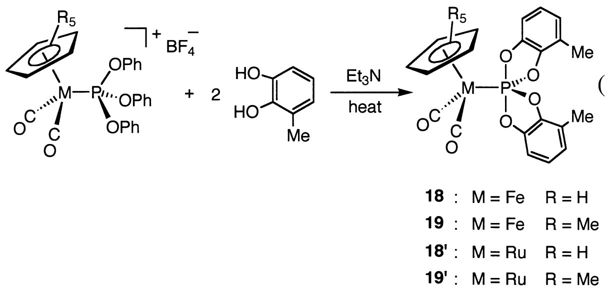
Complex **14** exhibits a very fast pseudorotation at room temperature; the rotation becomes slow at −50 °C but is not frozen. For **15**, in contrast, the rearrangement does not take place or is very slow on the NMR time scale at room temperature. Previous NMR studies on the MePF$_4$ and Me$_2$PF$_3$ have revealed that the fast rotation takes place for MePF$_4$, whereas no evidence for such a rotation is obtained for Me$_2$PF$_3$.[26] 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:[27e] 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.[27] 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 being in 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 exchange their positions readily. The same argument could be applied to the difference in rotation energy barrier between **14** and **15**. That is, a transition-metal fragment acts as a good π donor toward a phosphorane phosphorus, and thus prefers an equatorial position. In addition, Akiba et al. found the high pseudorotation barrier in some hypervalent antimony species, which was attributed to the great electron donating ability and bulkiness of transition-metal substituents.[14a] 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 **15**.

A five-membered ring generally prefers to occupy an apical-equatorial position rather than an equatorial-equatorial position on steric grounds.[28] Therefore, the o-OC$_6$H$_4$NMe chelate in **17** 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 should also be in an equatorial site. **17** is thus expected to have a high rotational energy barrier because the two equatophilic substituents are in equatorial positions as in **15**. However, **17** shows starting of the pseudorotation at room temperature. The reason for a relatively low energy barrier for **17** 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 **17** 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.

In 1999, we found that a metallaphosphorane with two 3-methylcatecholate substituents on a phosphorane phosphorus is suitable to estimate a barrier to Berry pseudorotation from the variable-temperature ^{31}P NMR studies, and we reported the first activation parameters of Berry pseudorotation for a ruthenium phosphorane,[18] and parameters for related iron and cobalt phosphoranes.[29]

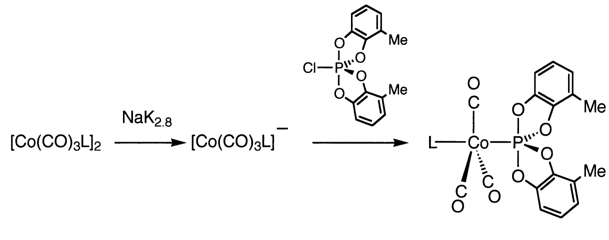
Scheme 4 shows a graph for possible isomers of the metallaphosphorane with two 3-methylcatecholate substituents on a phosphorane phosphorus and the relationship among them through Berry pseudorotation according to the convention.[2a] The phosphorus is surrounded by a transition metal and four oxygens which can be classified into two kinds of oxygens (O1 and O2, which are close to and far from the methyl substituent, respectively). A symbol in an oval is to denote a particular tbp configuration by the apical atoms. An underlined symbol shows the optical isomer of the parent compound. An atom drawn between symbols next to each other shows a pivot atom about which pseudorotation converts one isomer into another. There are 10 possible configurations, which can be linked by 11 Berry pseudorotations.

Six metallaphosphoranes were prepared, all of which have two 3-methylcatecholate substituents on the phosphorus (Eqs. 16 and 17). In each preparation, the product is a mixture of 6 isomers (**O1O1**, **O2O2**, **O1O2**, **O1O2**, **O2O2**, and **O1O1**). Four isomers bearing a transition-metal fragment in an apical position (**MO1**, **MO2**, **MO1**, and **MO2**) are not detected because of equatophilicity of a transition-metal fragment. **O1O1** vs **O2O2**, **O1O2** vs **O1O2**, and **O2O2** vs **O1O1** are interconvertible by one transformation pathway with the transition-metal fragment in an equatorial position as a pivotal group. Therefore, two isomers in each pair are not distinguished in NMR spectra at room temperature. The interconversion between **O1O2** and **O1O2** corresponds to enantiomerization. **O1O1**/**O2O2** is enantiomeric to **O1O1**/**O2O2**, but they are not interconvertible to each other because the inversion requires 4 transformation pathways via two structures which have a transition-metal fragment in an apical position. In the ^{31}P NMR, the two signals are observed, which are attributed to **O1O1/O2O2/O1O1/O2O2** and **O1O2/O1O2**.



(16)

18 : M = Fe R = H
19 : M = Fe R = Me
18' : M = Ru R = H
19' : M = Ru R = Me



20a: L = PPh$_3$
20b: L = PPh$_2$Me

(17)

The ^{31}P NMR signals of these metallaphosphoranes are temperature dependent. The spectral change with temperature is shown in Fig. 3 for **18′**. The spectrum shows two singlets even at 183 K. The two singlets coalesce into one broad resonance at 340 K and then sharpen to one singlet at higher temperature. This means that isomerization between **18′-O1O1/O2O2** and **18′-O1O2/O1O2** (equally between **18′-O1O1/O2O2** and **18′-O1O2/O1O2**) takes place faster than the NMR time scale at temperatures higher than 340 K.

Similar spectral changes were observed for **18**, **19**, **20a**, and **20b**, while the signals for **19′** did not coalesce. Simulation of the VT-NMR spectrum for **18′** is displayed in Fig. 3. The activation parameters obtained are summarized in Table 2. Although the $\Delta H^{\neq}$ for **19′** could not be obtained due to a higher coalescence temperature than the boiling point of the solvent used, the $\Delta H^{\neq}$ could be estimated to be greater than 67.9 kcal mol^{-1} estimated for **19** under the same conditions. Table 2 shows that the $\Delta H^{\neq}$ values for [L(CO)$_3$Co] phosphoranes are the same; these are smaller than those for [Cp(CO)$_2$M] (M = Ru, Fe) complexes (**18**, **18′**), which are smaller than those for [Cp*(CO)$_2$M] derivatives (**19**, **19′**).

The activation parameters evaluated here correspond to the isomerization between **O1O1/O2O2** and **O1O2/O1O2**, and equally to that between **O1O1/O2O2** and **O1O2/O1O2**. In any case, the isomerization takes place via a relatively unstable isomer having a transition metal fragment in an apical position (**MO1**, **MO2**, **MO1**, and **MO2**). Therefore, the activation parameter corresponds to the transition metal movement from an equatorial to an apical position. Since this transformation involves the breaking of π-back donation from M to P in the starting metallaphosphorane, the $\Delta H^{\neq}$ value may roughly correspond to the extent of π-back donation from M to P.

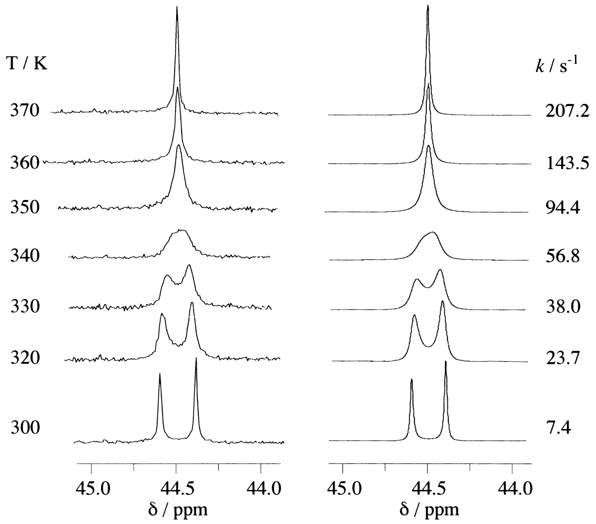
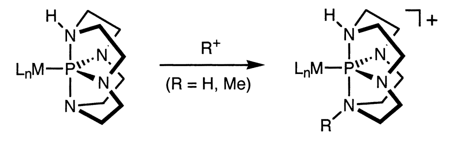


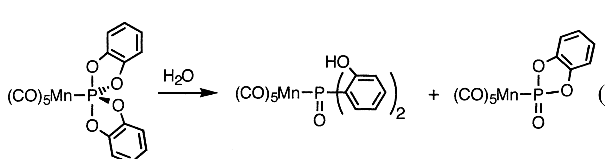
Fig. 3. 121.50 MHz variable-temperature experimental (left) and simulated (right) ^{31}P NMR spectra of **18′**.

Reactivity of Metallaphosphorane

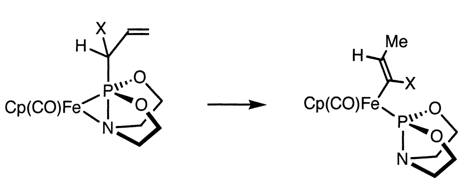
Several methods for the preparation of metallaphosphoranes have been developed during the last two decades. Much spectroscopic and structural data have also been accumulated. However, information on the reactivity of metallaphosphoranes is much more sparse. The following reactivities have been reported to date: (i) protonation (methylation) at apical nitrogen(s) (Eq. 18),[9a,9c,9e,9f] (ii) phosphonate formation by the hydrolysis (Eq. 19),[30] (iii) apical substituent migration to the transition metal (Eq. 20),[8c] and (iv) insertion of substrate into the apical bond (Eq. 21).[8e]



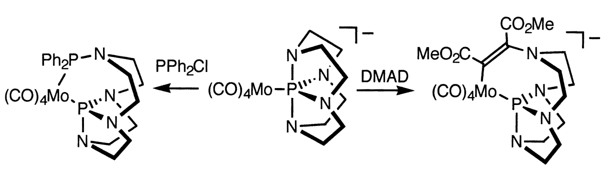
(18)



(19)



(20)



(21)

Recently we found phosphorane fragment migration from a

Table 2. Activation Parameters $\Delta H^{\neq}$, $\Delta S^{\neq}$, and $\Delta G^{\neq}$ for **18**, **19**, **18′**, **19′**, **20a**, and **20b**

Complex	$\Delta H^{\neq}$/kJ mol^{-1}	$\Delta S^{\neq}$/J mol^{-1} K^{-1}	$\Delta G^{\neq}$/kJ mol^{-1}
18	51.4 ± 0.8	−85.7 ± 2.5	84.2 ± 1.3 (383 K)
19	67.9 ± 1.4	−51.8 ± 3.7	89.7 ± 2.1 (420 K)
18′	42.1 ± 0.5	−91.1 ± 1.6	73.1 ± 0.7 (340 K)
19′	> 67.9	—	—
20a	38.6 ± 0.3	−96.5 ± 1.1	67.8 ± 0.5 (303 K)
20b	38.5 ± 0.2	−97.1 ± 0.8	67.9 ± 0.3 (303 K)

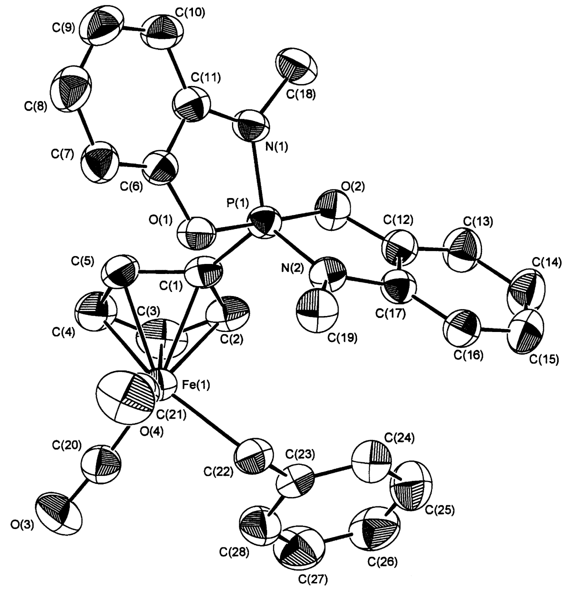
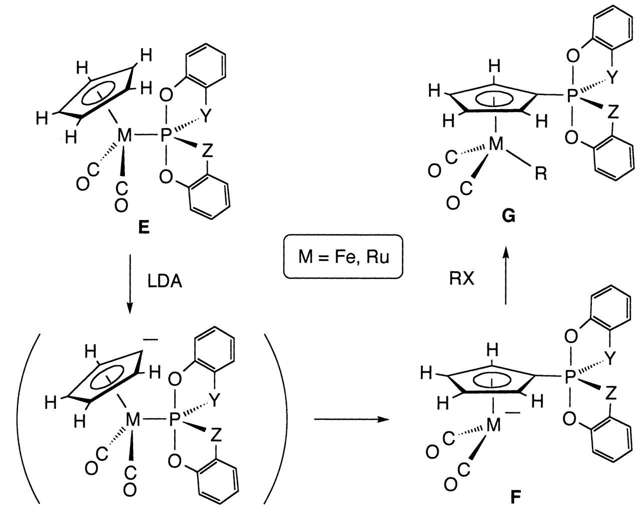
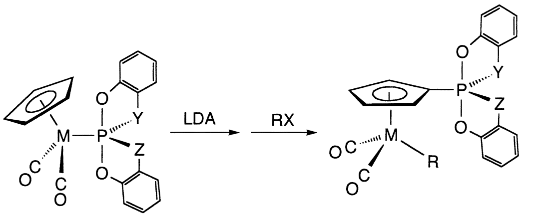


Fig. 4. ORTEP drawing of **22** (50% probability ellipsoids) showing the numbering system. All hydrogen atoms are omitted for clarity.



Scheme 5.

transition metal to the cyclopentadienyl ring.[31] The migration is induced by a Lewis base. The reaction of a phosphorane complex of iron and ruthenium with lithium diisopropylamide (LDA) and then alkyl halide yields a migration product of a phosphorane fragment to a Cp ligand (Eq. 22). The structure of **22** is displayed in Fig. 4. The phosphorane fragment is located on the Cp ring and has a distorted tbp geometry with two oxygens in the apical positions and two nitrogens and one Cp group in the equatorial positions.



1b : M = Fe, Y = Z = NMe

2b : M = Fe, Y = NMe, Z = O
3 : M = Fe, Y = Z = O
1b' : M = Ru, Y = Z = NMe
3' : M = Ru, Y = Z = O

21 : M = Fe, Y = Z = NMe, R = Me
22 : M = Fe, Y = Z = NMe, R = CH_2Ph
23 : M = Fe, Y = NMe, Z = O, R = Me
24 : M = Fe, Y = Z = O, R = Me
21' : M = Ru, Y = Z = NMe, R = Me
24' : M = Ru, Y = Z = O, R = Me

(22)

The migration reaction may proceed as shown in Scheme 5. This reaction is initiated by a proton abstraction on the Cp ring by LDA, followed by migration of the phosphorane fragment to give **F** which is relatively stable in solution and is converted into an isolable complex (**G**) by treatment with alkyl halide.

It has been reported for η^5-Cp containing complexes that one of the ligands undergoes base-induced migration to the Cp ring. The first example of this type of migration reaction was reported by Dean and Graham in 1977 for $[Cp(CO)_3M(GePh_3)]$ (M = Mo, W).[32] Since then, several types of ligand have been found to migrate from a transition metal to the Cp ring: acyl,[33] alkoxycarbonyl,[33c] formyl,[33e,33f] silyl,[34] germyl,[35] stannyl,[35] plumbyl,[35] hydride,[36] and phosphonate[37] migration. These ligands, except hydride, have two common properties. First, the coordinating atom does not have a typical dative bond but has a covalent bond with a transition metal and secondly has an empty orbital such as a π^* or d orbital. Berryhill and Gladysz suggested that the migrating ligand should have a low-lying unoccupied orbital (i.e. π^* or d orbitals) to accept the electron density on the cyclopentadienyl ring carbon.[33e,34c] It is known that a phosphorus atom can accept up to twelve valence electrons forming three hypervalent bonds. In a pentacoordinated phosphorus with a tbp structure, the central phosphorus atom is estimated to have a considerable positive charge due to polarization of apical hypervalent bonds.[27d] This polarization allows the phosphorane phosphorus to act as a Lewis acid to react with nucleophiles yielding anionic hexacoordinate phosphorus species. For example, PF_5 readily reacts with F^- to give a stable hexacoordinated anionic species PF_6^-. In the case of base-induced silyl migration, an intramolecular and concerted reaction has been established.[34c] Therefore, the phosphorane fragment migration would be best described as

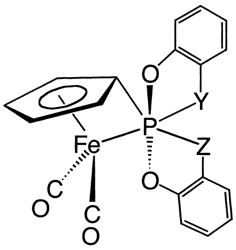
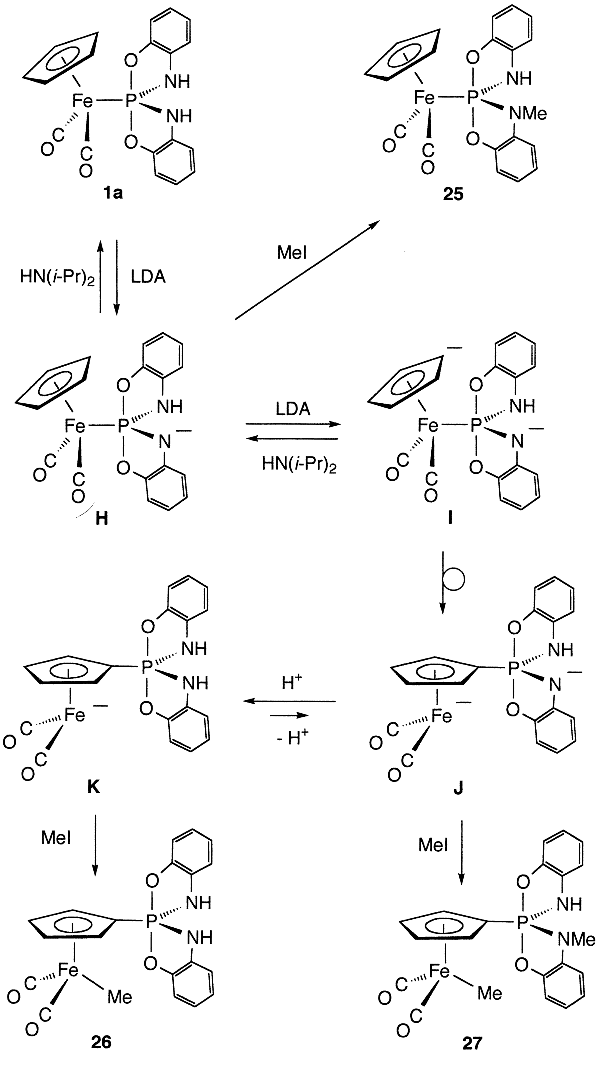


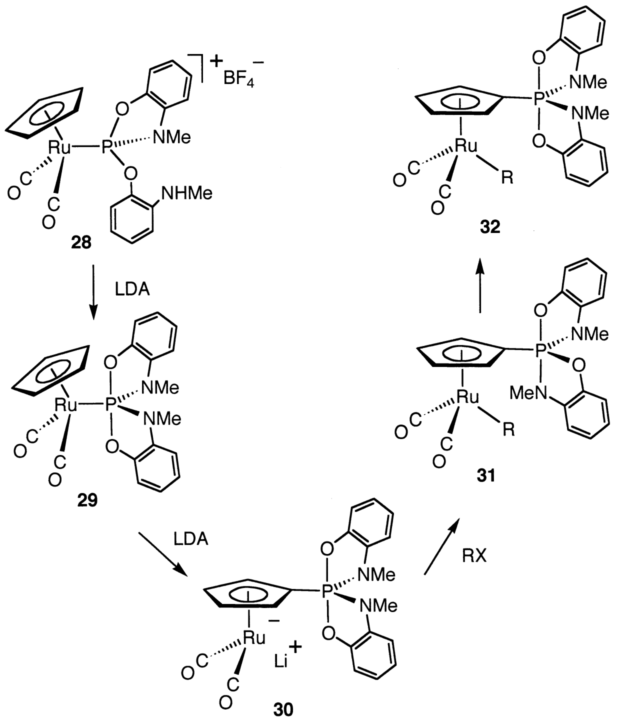
Fig. 5. A metallated hypervalent hexacoordinated phosphorus species.



Scheme 6.

proceeding through a metallated hypervalent hexacoordinated phosphorus species (Fig. 5), and this transition state (or an intermediate in some cases) should make the energy barrier of the migration lower.

Complex **1a** having two amino protons in a phosphorane fragment leads to some interesting results (Scheme 6). The treatment of **1a** with 2 molar amounts of LDA and then MeI gave **25** (main product), **26**, and unreacted **1a**, whereas the treatment with 3 molar amounts of LDA and MeI gave **26** and **27** in the ratio of 4:1.



Scheme 7.

We propose the following reaction pathways. In the reaction of **1a** with 2 molar amounts of LDA, not the Cp proton but the amino proton is abstracted by LDA to give **H**. The basicity of LDA may not be strong enough to abstract completely even one of the amino protons; therefore, **1a** and **H** may be in equilibrium under the present reaction conditions. Complex **H** reacts with MeI at the amido position to give **25**. When 3 molar amounts of LDA are used in the reaction of **1a**, the equilibrium between **1a** and **H** may shift to the latter, and moreover, **H** can react with extra LDA. In this reaction, the Cp proton, not the remaining NH proton, may be abstracted to give **I**, which undergoes an anionic phosphorane fragment migration to yield **J**. If the basicity at the amido group increases on going from **I** to **J**, the amido group in **J** picks up either an amino proton of **1a**, a Cp proton of **H**, or an amino proton of HN(*i*-Pr)$_2$ to give **K**. **J** and **K** are in equilibrium in favor of **K**. MeI reacts with both **J** and **K** to give **27** and **26**, respectively.

It should be noted that, in the reaction of **1a** with 2 molar amounts of LDA and then MeI, **25** is the main product and **26** is a minor one. This indicates that **26** may not be produced by the proton abstraction on the Cp ring in **1a**, followed by the phosphorane migration. **26** and **27** are reasonably assumed to be derived from **K** and **J**, respectively. Therefore, the following two points should be noted: (i) LDA selectively abstracts an amino proton in **1a** and does not abstract the Cp proton, (ii) an anionic phosphorane fragment migrates to the Cp ring; in other words, an anionic phosphorane fragment still can accept a nucleophilic attack.

Since it is generally accepted that a bond between a transition metal and a main group element becomes strong on going down in the periodic table for transition metals in the same group, a phosphorane migration for ruthenium complexes, [Cp(CO)$_2$Ru{P(OC$_6$H$_4$Y)$_2$}] (Y = NMe, O) was examined in the expectation of obtaining or detecting the intermediates proposed for iron complexes. Similar phosphorane migration takes place, but no expected intermediate was detected. However, in the case of a cationic phosphite complex (**28**), an unexpected complex was formed (Scheme 7).[31b] Complex **28** reacts with an equimolar amount of LDA to give ruthenium phosphorane (**29**), which then reacts with another equimolar amount of LDA to give a migration product (**30**). The following addition of RX at −30 °C gives **31**, which contains one O atom and one N atom in apical positions and in equatorial positions as well. The complex gradually isomerizes to a thermally more stable apical oxygen-equatorial nitrogen isomer (**32**). Complex **31** is of interest because an amino group occupies an apical position, though an NR_2 group is reported to have stronger equatophilicity than an OR group. In terms of such an unusual trigonal-bipyramidal isomer, only one example for organophosphorane has been reported.[38] Although the reason for the formation of **31** is not clear now, several experimental results suggest that Li^+ plays an important role when **30** reacts with RX.

Phosphorane fragment migration to the cyclopentadienyl ligand could be demonstrated for Fe and Ru complexes. Nowadays, many hypervalent compounds have been isolated, characterized and structurally determined for several main groups (group 13–17).[3b,39] However, migration of a hypervalent fragment had not been reported for any kind of hypervalent elements. Therefore, our example is the first reported hypervalent fragment migration.

We would like to thank Dr. Tsutomu Mizuta for supporting this research by X-ray studies and for his useful discussions. We also thank all co-workers in our group whose names are cited in the references for their great contributions.

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