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Review

The chemistry of transition metal complexes containing a phosphenium ligand

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Abstract

A molybdenum complex containing diamino-substituted phosphite, *fac*-$[(\mathrm{bpy})(\mathrm{CO})_3\mathrm{Mo}\{\mathrm{PNN(OMe)}\}]$ (PNN stands for $\overline{\mathrm{PN(Me)CH_2CH_2N}}\mathrm{Me}$) reacts with a Lewis acid such as $\mathrm{BF_3{\cdot}OEt_2}$ to give a cationic phosphenium complex *fac*-$[(\mathrm{bpy})(\mathrm{CO})_3\mathrm{Mo}\{\mathrm{PNN}\}]^+$, where an OMe on a phosphorus is abstracted as an anion. The facial isomer spontaneously isomerizes into its meridional form. Group 6 transition metal complexes, *fac*-$[(\mathrm{bpy})(\mathrm{CO})_3\mathrm{M}\{\mathrm{PXY(OMe)}\}]$ ($\mathrm{M = Cr, Mo, W}$; $\mathrm{XY = (NEt_2)_2}$, $\mathrm{N(Me)CH_2CH_2O}$, $\mathrm{(NEt_2)(OMe)}$ and $\mathrm{OCMe_2CMe_2O}$, $\mathrm{(OMe)_2}$) have been subjected to reaction with $\mathrm{BF_3{\cdot}OEt_2}$. These reactions reveal that the stability of cationic phosphenium complexes increases with: (i) going to a heavier congener; (ii) increasing the number of amino substituents on the phosphenium phosphorus; and (iii) adding an ethylene bridge between X and Y when at least one of X and Y is an amino substituent. The cationic phosphenium complex reacts with a nucleophile ($\mathrm{Nu = OEt^-, Me^-}$) at the phosphenium phosphorus to give *fac*-$[(\mathrm{bpy})(\mathrm{CO})_3\mathrm{M}\{\mathrm{PXY(Nu)}\}]$, and also reacts with a tertiary phosphorus compound (L) to give $[(\mathrm{bpy})(\mathrm{CO})_2\mathrm{LM}\{\mathrm{PXY}\}]^+$. The reaction of a cationic monoaminomonoalkoxy phosphenium complex of Mo, *mer*-$[(\mathrm{bpy})(\mathrm{CO})_3\mathrm{Mo}\{\mathrm{PNO}\}]^+$ (PNO stands for $\overline{\mathrm{PN(Me)CH_2CH_2O}}$) with a diamino-substituted phosphorus compound, PNN(Y) ($\mathrm{Y = OMe, OEt, SEt, N(CH_2)_3CH_2}$) proceeds with substitution for CO and then with the Y group migration to the coordinating phosphenium phosphorus to give $[(\mathrm{bpy})(\mathrm{CO})_2\{\mathrm{PNO(Y)}\}\mathrm{Mo}\{\mathrm{PNN}\}]^+$. The reaction is irreversible. Reactions of iron complexes containing a Group 14 element ligand ($\mathrm{ER_3}$; $\mathrm{E = C, Si, Ge, Sn}$) and diamino-substituted phosphite, $\mathrm{Cp(CO)(ER_3)Fe\{PNN(OMe)\}}$ with a Lewis acid have been examined. The reaction product depends on E. In any case, an OMe anion abstraction by a Lewis acid uniformly takes place at the first stage of the reaction to give a cationic phosphenium iron complex containing an $\mathrm{ER_3}$ ligand. The subsequent reaction is strongly dependent on E. When E is C, migratory insertion of the phosphenium ligand into the Fe–C bond or more simply an alkyl migration from Fe to phosphenium phosphorus occurs. When E is Si or Ge, the cationic phosphenium complex is stable and Fe–Si and Fe–Ge bonds remain intact. In contrast, when E is Sn, one alkyl group on the Sn, and not $\mathrm{SnR_3}$, migrates to the phosphenium phosphorus to give a stannylene complex. The corresponding Ru complexes show similar reactions. X-ray structures of cationic phosphenium complexes of Mo and Fe have been employed and reveal that there is considerable double bond character between a transition metal and the phosphenium phosphorus. ^{31}P- and ^{95}Mo-NMR spectroscopic data also support the double bond character. Activation parameters concerning phosphenium ligand rotation along the P–Fe axis could be estimated from VT-NMR studies. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Cationic phosphenium complexes; $\mathrm{OR^-}$ abstraction; Migratory insertion; π-Back donation; Double bond; Rotational barrier

1. Introduction

A cationic phosphenium species described as $[\mathrm{PR_2}]^+$ has both lone pair electrons and a vacant p orbital in addition to two substituents on a phosphorus atom. It can be considered to be a member of an isoelectronic series consisting of silicenium, phosphenium, sulfenium, and chloronium irons (Chart 1) It is also, except for a high cationic charge accumulated at the phosphorus atom, parallel to a singlet carbene and the higher homologues (silylene, germylene, stannylene, and plumbylene) (Chart 2). From such points of view, the coordination chemistry of a phosphenium cation, as

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well as its own chemistry, has received considerable attention.

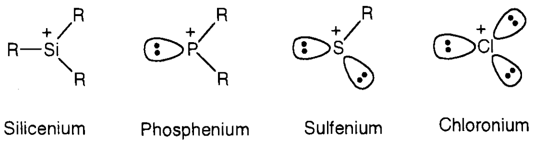


Chart 1.

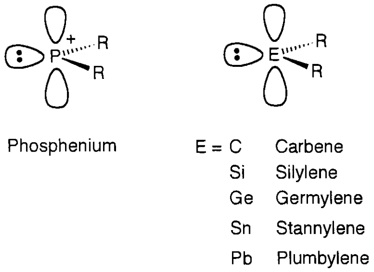


Chart 2.

The chemistry of transition metal complexes containing a cationic phosphenium ligand dates back to the synthesis and characterization of $[(CO)_4Fe\{P(NR_2)_2\}][PF_6]$ by Parry in 1978 [1]. Since then, many cationic phosphenium complexes have been prepared and a few review articles have appeared [2–5]. $[L_nM(PR_2)]$, being an electrically neutral transition metal complex, is sometimes treated as a phosphenium complex because it can be considered to consist of L_nM^- and $^+PR_2$ [6]. In this article, the focus is on electrically cationic transition metal complexes described as $[L_nM(PR_2)]^+$. I have been engaged in the study of cationic phosphenium complexes for about 10 years. This article reviews mainly my results of synthesis, structures, properties, and reactivities of transition metal complexes containing phosphenium. Through this article, PNN and PNO stand for $\overline{\text{PNMeCH}_2\text{CH}_2\text{N}}\text{Me}$ and $\overline{\text{PNMeCH}_2\text{CH}_2\text{O}}$, respectively.

2. Synthetic routes

Methods of preparation for cationic phosphenium complexes can be classified into the following: (i) halogen abstraction from a precursor halophosphine complex by $AlCl_3$ or PF_5 (Eq. (1)) [1,7]; (ii) hydride abstraction from a precursor phosphine complex by BR_3 (Eq. (2)) [8]; (iii) electrophilic attack of a phosphenium cation on a metal carbonyl complex (Eq. (3)) [1]; (iv) protic attack toward a phosphite complex (Eq. (4)) [9].

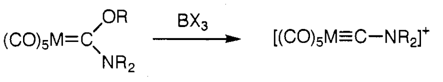
$$(CO)_4Fe\{PXR^1R^2\} + AlCl_3(PF_5)$$
$$\rightarrow [(CO)_4Fe\{PR^1R^2\}]^+ + AlCl_4^-(PF_6^-) \quad (1)$$

$$Ni(CO)_3\{PH(NR_2)_2\} + B^iBu_3$$
$$\rightarrow [Ni(CO)_3\{P(NR_2)_2\}]^+ + HB^iBu_3^- \quad (2)$$

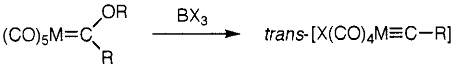
$$Fe(CO)_5 + \overline{PN(Me)CH_2CH_2N}Me^+$$
$$\rightarrow (CO)_4Fe\{\overline{PN(Me)CH_2CH_2N}ME\}]^+ + CO \quad (3)$$

$$[Mo\{P(OMe)_3\}_6] + H^+$$
$$\rightarrow [Mo\{P(OMe)_3\}_5\{P(OMe)_2\}]^+ + HOMe \quad (4)$$

Reactivity of boron trihalides which abstract an OR group or halogen on a carbon atom has been applied to the preparation of transition metal carbyne complexes from Fischer-type carbene complexes and to the halogen exchange to transition metal perfluoroalkyl carbonyl complexes. In Eq. (5), an OR group on the carbene carbon is abstracted as an OR^- anion by BX_3, resulting in the increase in the bond order from 2 to 3 between the transition metal and the carbon atom [10]. In Eq. (6), the reaction involves simultaneous removal of the OR group and the CO ligand *trans* to the carbene carbon and the introduction of a halogen into the complex [10]. In Eq. (7), the halogen exchange reaction takes place [11].



$$(CO)_5M{=}C(OR)(NR_2) \xrightarrow{BX_3} [(CO)_5M{\equiv}C{-}NR_2]^+ \quad (5)$$



$$(CO)_5M{=}C(OR)(R) \xrightarrow{BX_3} trans\text{-}[X(CO)_4M{\equiv}C{-}R] \quad (6)$$

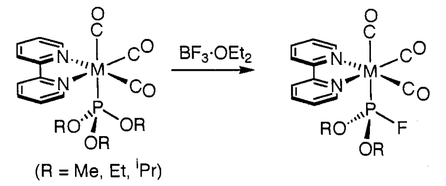
$$L_nM{-}CF_3 \xrightarrow{BX_3} L_nM{-}CX_3 \quad (7)$$

BX_3 is also effective for P–OR bond fission. Free phosphites, $P(OR)_3$, react with BX_3 to give $P(OR)_2X$, $P(OR)X_2$, or PX_3, depending upon the reaction conditions such as molar ratio of reactants, the type of phosphites and boron trihalides used, and the temperature (Eq. (8)) [12].

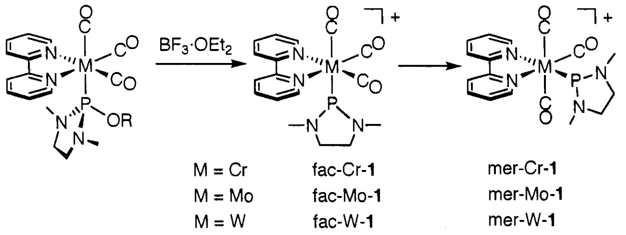
$$P(OR)_3 \xrightarrow{BX_3} P(OR)_2X \xrightarrow{BX_3} P(OR)X_2 \xrightarrow{BX_3} PX_3 \quad (8)$$

However, the reaction of phosphite coordinated to a transition metal with BX_3 had not been reported when I started my project. If a reaction similar to Eq. (1) takes place in this case, a transition metal complex containing a dicoordinate phosphorus cation as a ligand, i.e. a phosphenium transition metal complex, would be generated. Many reactions of phosphite-coordinated transition metal complexes with boron trihalides have been examined in the hope of preparing a cationic phosphenium complex.

Reaction of an Mo complex containing phosphite, *fac*-$[(bpy)(CO)_3Mo\{P(OR)_3\}]$ (R = Me, Et, ^{i}Pr), with $BF_3{\cdot}OEt_2$ yields *fac*-$[(bpy)(CO)_3Mo\{P(OR)_2F\}]$ (Scheme 1), where OR/F substitution reaction takes place [13]. Although a phosphenium complex $[(bpy)(CO)_3Mo\{P(OR)_2\}]^+$ could be postulated, spectroscopic evidence could not be obtained. In contrast, an Mo complex with diamino-substituted phosphite (PNN(OR)) reacts with $BF_3{\cdot}OEt_2$ to give a cationic

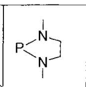
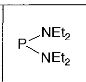
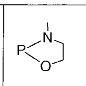
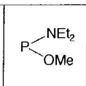
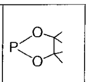
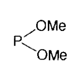


Scheme 1.



Scheme 2.

Table 1
Stability of cationic phosphenium complexes formulated as $[(bpy)(CO)_3M\{PXY\}]^+$

PXY / M						
Cr	⊚	○	○	$\boxed{\text{F}}$	$\boxed{\text{F}}$	$\boxed{\text{F}}$
Mo	⊚	◎	◎	○	$\boxed{\text{F}}$	$\boxed{\text{F}}$
W	⊚	◎	◎	○	$\boxed{\text{F}}$	$\boxed{\text{F}}$

⊚ Stable, both the *fac* and *mer* isomers are observed and the *fac* form gradually isomerizes to the *mer* isomer.
◎ Stable, but only the *mer* isomer is observed (the isomerization is too fast to detect the *fac* isomer).
○ A phosphenium complex is observed with some other by-products.
$\boxed{\text{F}}$ A phosphenium complex in not detected but a fluorinated complex, $[(bpy)(CO)_3M\{PXYF\}]$, is formed.

phosphenium complex (Scheme 2) [14,15]. The phosphenium complex has a facial geometry, which then gradually isomerizes to the meridional isomer. Therefore, the facial isomer is a kinetic product and the meridional isomer is a thermodynamic product.

3. Influence of substituents of the phosphenium phosphorus on the stability of the complexes

The stability of transition metal phosphenium complexes is appreciably affected by the nature of substituents on the phosphenium phosphorus: a transition metal and two organic substituents. In order to elucidate the influence of these substituents on the stability of the complexes, 18 phosphite complexes formulated as $(bpy)(CO)_3M\{PXY(OMe)\}$ were systematically selected, and they were subjected to reaction with $BF_3·OEt_2$ and the stability of the phosphenium complexes thus formed was compared.

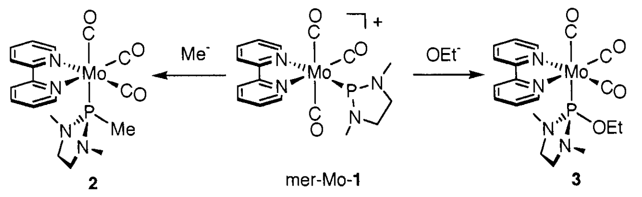
The results show a tendency which is somewhat qualitative, shown in Table 1 [16]. Bridged diamino phosphenium complexes of a Group 6 triad are very stable and both *fac* and *mer* isomers are observed. For non-bridged diamino phosphenium complexes, the Mo and W complexes are stable though only the *mer* isomer is observed due to the fast *fac–mer* isomerization. The corresponding Cr complex is less stable than Mo and W complexes. The stability of bridged monoaminomonoalkoxy phosphenium complexes is similar to that of non-bridged diamino phosphenium complexes. Non-bridged monoaminomonoalkoxy phosphenium complexes of Mo and W are observed with some by-products, whereas that of Cr is not detected but the F-introduced complex is formed. Bridged and non-bridged dialkoxy phosphenium complexes are not detected for any Group 6 congener. Only the F-introduced products are obtained. Therefore, it can generally be said as follows: (i) cationic phosphenium complexes of Mo and W are more stable than that of Cr, but there is no apparent difference in stability between the Mo and W complexes. (ii) Increasing the number of amino substituents on the phosphenium phosphorus increases the stability. (iii) The ethylene bridge between an amino group and an alkoxy or an amino group stabilizes cationic phosphenium complexes. (iv) In addition, the ethylene bridge between an amino and an alkoxy substituent contributes to the stabilization of a cationic phosphenium complex roughly to the same extent as the substitution of one OMe group by an NEt_2 group.

The stability difference based on the Group 6 congeners may be related to the extent of π-back donation from a filled d orbital of a transition metal to an empty p orbital of a phosphenium phosphorus. The extent of the π-back donation from Mo and W may be greater than that from Cr.

4. Reactivity of cationic phosphenium complexes of *mer*-$[(bpy)(CO)_3Mo(PNN)]^+$

4.1. Reactivity with R^- and OR^-

The molybdenum phosphenium complex, *mer*-Mo-**1**, reacts with Me^- and OEt^- to give diaminomethylphosphine complex (**2**) and diaminoethylphosphite complex (**3**) with a facial geometry, respectively (Scheme 3) [14]. The reaction of $[(bpy)(CO)_3Mo\{PNN(OMe)\}]$ with Me^- or OEt^- gives neither **2** nor **3**, which indicates that a cationic phosphenium complex is susceptible to nucleophilic attack at the phosphorus atom. It is



Scheme 3.

known that cationic carbonyl complexes react with OR^- to give alkoxy carbonyl complexes [17]. The complex *mer*-Mo-**1** can be regarded as a cationic carbonyl complex. In this case, nonetheless, OR^- and R^- selectively attack the phosphorus atom but not the carbonyl carbon.

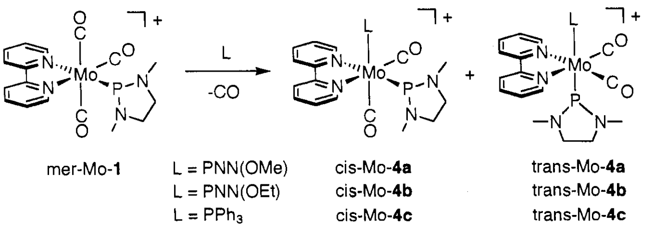
4.2. Reactivity with a tertiary phosphorus compound

As mentioned above, phosphenium is isoelectronic to carbene or silylene. It is known that a carbene carbon and a silylene silicon in transition metal complexes are very electrophilic and these complexes are stabilized by adduct formation with Lewis bases. Therefore, the reactivity of phosphenium complexes with a trivalent phosphorus compound acting as a Lewis base is of interest.

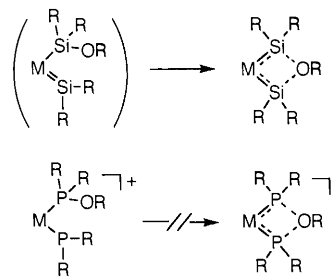
The reaction of *mer*-Mo-**1** with L (phosphite or phosphine) proceeds with substitution of L for CO to give two phosphenium complexes (*cis*-Mo-**4** and *trans*-Mo-**4** isomers) (Scheme 4) [18]. Reactions of phosphenium complexes of Cr and W show basically similar results, i.e. the phosphenium ligand remains intact and the CO/L exchange reaction takes place.

Recently, Tobita, Ogino and their co-workers reported the preparative methods and the X-ray structures of donor-stabilized bis(silylene)complexes [19]. They proposed that these complexes are formed from an alkoxy-substituted-silyl(silylene)complex, which is not detected because of the coordination of the alkoxy oxygen to the silylene silicon. In contrast, a phosphite(phosphenium)complex shown in this article is detected and the cyclization product (which may be referred to as a bis(phosphenium)complex) is not observed (Scheme 5).

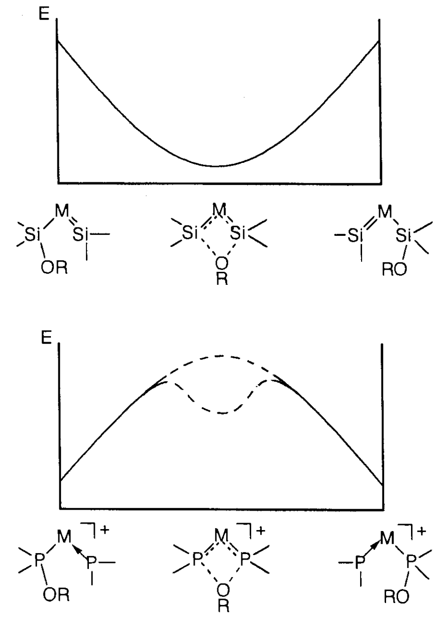
Muetterties also reported the X-ray structure of $[Mo\{P(OMe)_3\}_5\{P(OMe)_2\}]PF_6$, which does not take a cyclization form but has a discrete phosphenium ligand [9c]. Therefore, a phosphenium ligand seems to have an inherently lesser tendency to take a base stabilized form, unlike the silylene ligand, even though phosphenium and silylene ligands are isoelectronic. In other words, as shown in Scheme 6, the middle point between the two silicon ligands for alkoxy-substituted-silyl(silylene)complexes is the energy minimum position for the OR group, whereas the middle point between the two phosphorus ligands for phosphite(phosphenium)complexes is not.



Scheme 4.



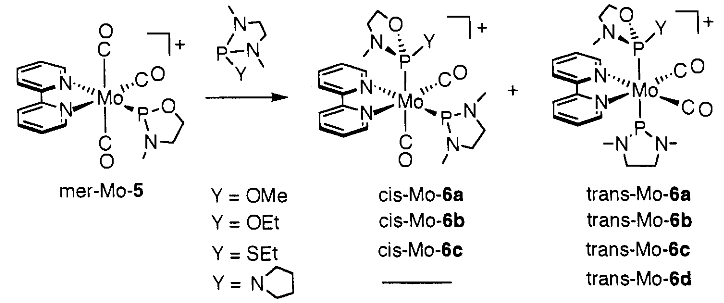
Scheme 5.



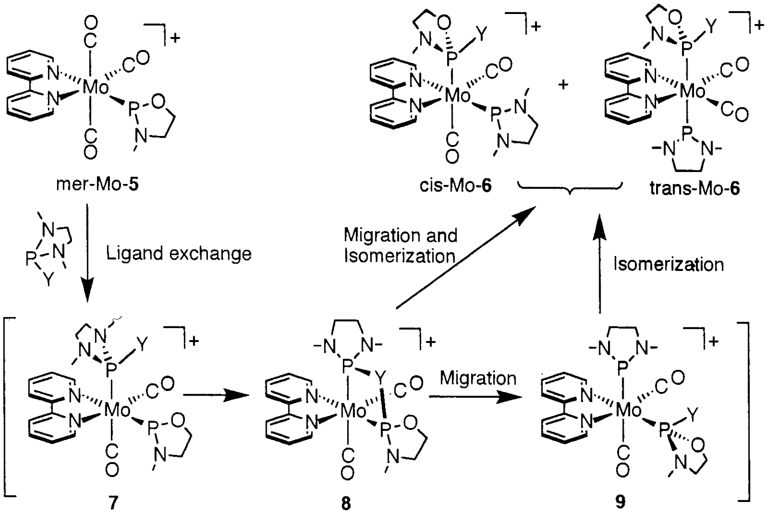
Scheme 6.

4.3. Migration of OR, SR, and NR_2 on a tertiary phosphorus compound to a phosphenium ligand

Complex *mer*-Mo-**5**, which is a monoaminomonoalkoxy phosphenium complex, reacts with PNN(OMe) to give *cis*-Mo-**6a** and *trans*-Mo-**6a** [20]. In this reaction, in addition to CO/PNN(OMe) substitution, an OMe group migration from a phosphite P to a phosphenium phosphorus takes place. Similarly, OEt, SEt, and $N(CH_2)_3CH_2$ groups migrate from a tertiary phosphorus compound to the phosphenium phosphorus in a coordination sphere (Scheme 7). In contrast, Me and Ph groups do not show this type of migration.



Scheme 7.



Scheme 8.

The proposed reaction pathway is shown in Scheme 8. First, the CO/PNNY exchange reaction takes place to give **7**, where the phosphenium and the phosphite are mutually *cis*. Then, the Y group donates its lone pair electrons to the vacant p orbital of the phosphenium phosphorus to give **8**. Subsequent cleavage of the original P–Y bond with concomitant formation of the new P–Y σ bond results in the migration of Y to give **9**. Intermediate **9** isomerizes to more stable geometrical isomers (*cis*-Mo-**6** and *trans*-Mo-**6**). An alternative pathway from **8** is possible: Y migration is accomplished with the accompanying rearrangement around the Mo without the formation of **9**. In any case, Y with lone pair electrons can migrate, suggesting that migration is achieved via a Y-bridged intermediate like **8**.

A diamino phosphenium complex is more stable than a monoaminomonoalkoxy phosphenium complex, which is more stable than a dialkoxy phosphenium complex. Therefore, the driving force of the migration is considered to form a more stable phosphenium ligand. The fact that Mo complexes with diamino phosphenium and monoamino phosphite are not converted into complexes with aminoalkoxy phosphenium and diamino phosphite, is reasonable because in this case the starting phosphenium complex is more stable than the phosphenium complex expected to be produced by migration.

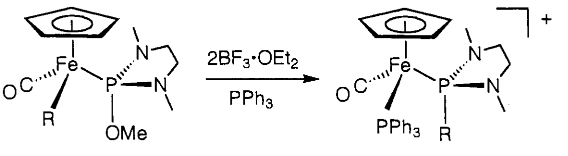
After the first discovery of OMe migration with P–O bond cleavage and formation [9], no examples concerning the migration of a substituent on a tertiary phosphorus ligand to a cationic phosphenium ligand have been reported for about two decades. It has now been revealed that not only OR but also SR and NR_2 groups migrate to a coordinating phosphenium phosphorus with P–S and P–N bond cleavage and formation, that lone pair electrons seem indispensable for a migrating group, and that the driving force of the migration is to make a more stable phosphenium ligand. In other words, these migrations are irreversible.

5. Reactivity of cationic phosphenium complexes possessing a Group 14 element ligand

5.1. Reactivity of phosphenium complexes possessing an alkyl ligand

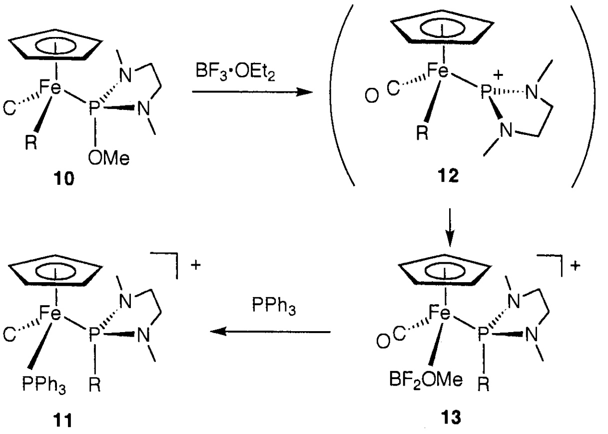
An iron complex **10** containing an alkyl and PNN-(OMe) ligand reacts with $BF_3 \cdot OEt_2$ and then PPh_3 to give complex **11** (Scheme 9) [21]. The results show that an OMe group on the phosphorus is eliminated and an alkyl group on the iron migrates to the phosphorus.

The reaction sequences are proposed in Scheme 10. In the reaction of **10** with $BF_3{\cdot}OEt_2$, an OMe group on a phosphorus atom is abstracted by BF_3 as an anion to give a cationic phosphenium complex **12**. The complex itself could not be detected presumably due to its high reactivity. Migratory insertion of the phosphenium ligand into the iron–alkyl bond, or more simply, alkyl migration from Fe to the phosphenium phosphorus then takes place to give the 16 electron species **13**, which is stabilized presumably by the coordination of BF_2OMe via oxygen present in the solution. Such a species is observed in the ^{31}P-NMR spectrum, but several attempts to isolate it were unsuccessful due to its instability. The BF_2OMe in **13** is readily replaced by a stronger base such as PPh_3 to give a stable complex **11**.

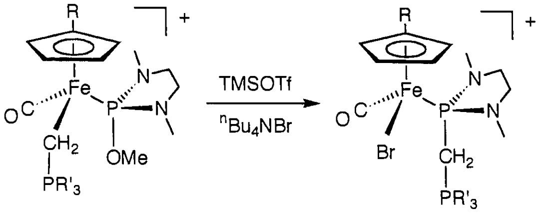


10a	R = Me	**11a**
10b	R = CH₂Ph	**11b**

Scheme 9.

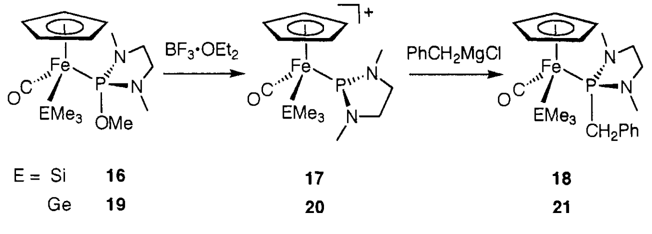


Scheme 10.



R = H,	R' = Me :	**14a**	**15a**
R = H,	R' = Et :	**14b**	**15b**
R = H,	R' = Ph :	**14c**	**15c**
R = Me,	R' = Me :	**14d**	**15d**
R = Me,	R' = Et :	**14e**	**15e**

Scheme 11.



E = Si	**16**	**17**	**18**
Ge	**19**	**20**	**21**

Scheme 12.

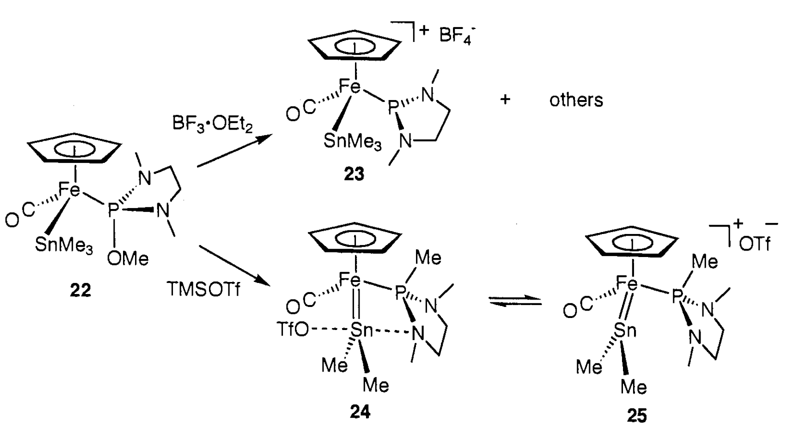
Alkyl migration to a CO ligand to give an acyl ligand on a transition metal is well known [22]. Complex **12** has a terminal carbonyl ligand in addition to a phosphenium ligand. It is thus notable that an alkyl group migrates exclusively to a phosphenium ligand in the present reaction. Similar results were obtained for the corresponding alkyl ruthenium complexes [23] and also for the corresponding alkyl molybdenum complexes [24].

Some examples [25] and theoretical studies [26] have been reported for the migration of an alkyl (or aryl) group from a coordinating phosphorus ligand to the transition metal to which it is coordinating. The findings mentioned above correspond to the reversed movement of an alkyl group (from a transition metal to a coordinating phosphorus), which is unprecedented.

Complex **14** is a phosphorus ylide complex of iron. The phosphorus ylide ligand is a sort of an alkyl ligand but has a positive charge on the phosphorus. Complex **14** reacts with a Lewis acid ($Me_3SiOSO_2CF_3$, TMSOTf) and then ^{n}Bu$_4$NBr to give **15** (Scheme 11) [27]. The reaction may proceed basically according to the mechanism shown in Scheme 10. This reaction should be noted for two points: (i) TMSOTf from a coordinating phosphite is capable of abstracting an OMe anion even in a cationic complex; and (ii) a cationic phosphorus ylide ligand can migrate to a cationic phosphenium ligand. Crossover experiments of phosphorus ylide migration revealed that the migration takes place intramolecularly.

5.2. Reactivity of phosphenium complexes possessing a silyl or a germyl ligand

The reactions of silyl and germyl iron complexes corresponding to the alkyl complex **10** with $BF_3{\cdot}OEt_2$ showed informative results from a mechanistic point of view (Scheme 12). The reaction of a silyl complex **16** with $BF_3{\cdot}OEt_2$ gives a phosphenium complex **17** [21,28]. Treatment of **17** with PPh_3 causes no reaction. No silyl migration to the phosphenium phosphorus may be due to a stronger transition metal–silyl bond than metal–alkyl bond. The phosphenium complex (**17**) reacts with $PhCH_2MgCl$ to give **18** and Cp(CO)(CH$_2$Ph)Fe-{PNN(SiMe$_3$)} is not formed, indicating that **17** does



Scheme 13.

not undergo silyl migration from Fe to the phosphenium phosphorus. The crystal structure of **17** as a BPh_4^- salt was obtained.

A germyl complex **19** shows the same results as those of the corresponding silyl complex [28]. That is, **19** reacts with $BF_3·OEt_2$ to give a cationic phosphenium complex, **20**, germyl migration from Fe to P was not observed, and **20** reacts with $PhCH_2MgCl$ to give **21**.

The same results were obtained for the corresponding silyl and germyl ruthenium complexes [23].

5.3. Reactivity of phosphenium complexes possessing a stannyl ligand

The reaction of a trimethyl stannyl complex of iron (**22**) with $BF_3·OEt_2$ causes the formation of several kinds of complexes involving a phosphenium complex (**23**). This indicates that $BF_3·OEt_2$ is not an adequate Lewis acid for a stannyl complex.

When TMSOTf is used as a Lewis acid, the reaction proceeds cleanly, and a stannylene complex (**24**) is isolated (Scheme 13) [28,29]. The X-ray structure (Fig. 1) shows that the tin atom is apparently five-coordinate, which is best described as trigonal bipyramidal. The FeSnC1C2 unit forms a trigonal plane. Two apical bonds (Sn–O2 and Sn–N2) are slightly longer than the normal covalent bonds but significantly shorter than the sum of the van der Waals radii. Therefore, **24** can be regarded as a doubly base-stabilized stannylene complex. In solution, **24** is considered to be present to a considerable extent in the base-free stannylene form (**25**) because of the molar conductivity ($\Lambda_M = 76.1\ \Omega^{-1}\ cm^2\ mol^{-1}$ in nitromethane), the very low chemical shift (495.8 ppm) and the large $J_{^{119}Sn\text{–}P}$ value (600.2 Hz) in the ^{119}Sn-NMR spectrum.

The interesting point in the reaction of the stannyl complex **22** with TMSOTf is that an alkyl group on a tin atom, and not a stannyl, migrates to a coordinating phosphorus atom to give a stannylene complex. The reaction seems to proceed via a phosphenium complex.

The reaction of a Sn^nBu_3 complex **26** with a Lewis acid is very informative from a mechanistic point of view (Scheme 14). In the reaction of **26** with $BF_3·OEt_2$, a cationic phosphenium complex **27** is formed, which can be converted into **28** by the reaction with $PhCH_2MgCl$.

In the reaction of **26** with TMSOTf, a phosphenium complex (**27′**) is first observed spectroscopically, and it is then converted into a stannylene complex (**29**) with time. It has been reported that an Sn–Me bond is more reactive than an Sn–Bu bond in electrophilic cleavage reactions [30]. The relatively strong Sn–Bu bond retards the Bu migration from Sn to P to the extent that a cationic phosphenium complex is detected.

Complex **27** prepared from **26** and $BF_3·OEt_2$ gradually decomposes and is not converted into the stannylene complex **29**, whereas **27′** prepared from **26** and TMSOTf changes quantitatively to **29**. Addition of NaOTf to the solution of **27** gives **29**, indicating that an

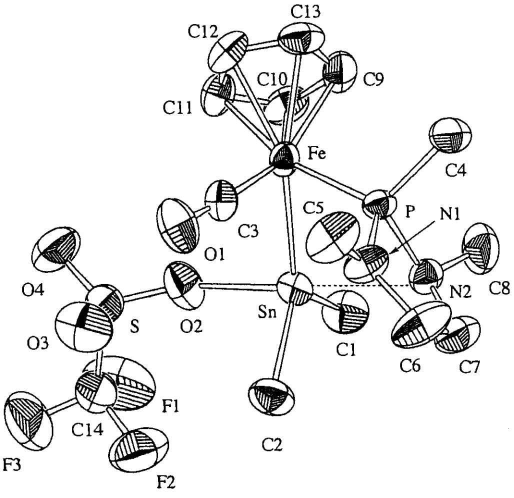
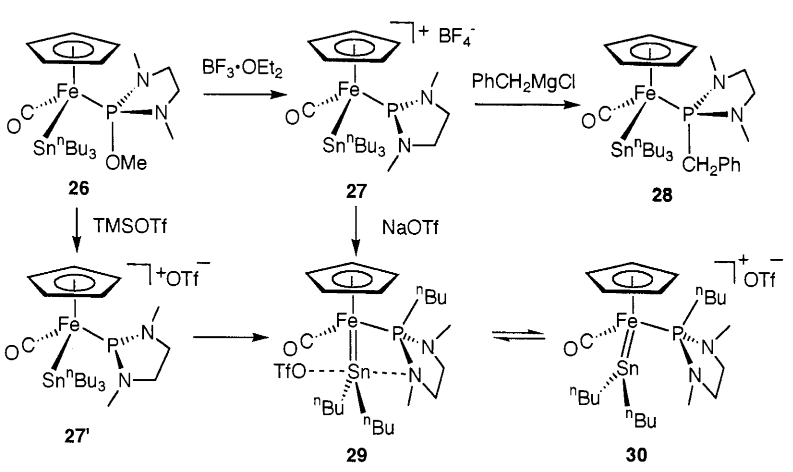


Fig. 1. ORTEP drawing of **24** showing the atom-numbering scheme. Selected bond lengths (Å) and angles (°): Fe–Sn, 2.488(1); Fe–P, 2.140(2); Sn–C1, 2.136(5); Sn–C2, 2.145(5); Sn–O2, 2.343(4); Sn–N2, 2.695(4); Sn–Fe–P, 81.0(1); Fe–Sn–C1, 126.4(2); Fe–Sn–C2, 123.2(2); C1–Sn–C2, 109.5(3); Fe–Sn–O2, 99.0(1); Fe–Sn–N2, 77.0(1).



Scheme 14.

OTf$^-$ anion promotes an alkyl migration from Sn to P in a phosphenium complex, presumably by coordination of the oxygen in OTf$^-$ to the Sn. Similar results were obtained for the corresponding stannyl ruthenium complexes [23].

Many experimental results relating to transition metal stannylene complexes have been accumulated, and they have been reviewed by Petz [31], Herrmann [32], Nelson [33], and Lappert [34]. However, only three examples are known in which a stannylene complex is prepared by Sn–C bond cleavage [35,36]. Of these three, only one example shows alkyl migration from a stannyl group on a transition metal: alkyl group migration from tin to the carbon of a coordinated carbon monoxide ligand in an Os cluster, forming an Os stannylene complex [36a]. The finding mentioned above is the first example of the migration of an alkyl group on a tin ligand to a coordinating heteroatom (in this case, phosphorus) to give a stannylene complex.

5.4. Activation parameters concerning phosphenium ligand rotation along the P–Fe axis

Since cationic phosphenium complexes of iron containing trimethylsilyl, trimethylgermyl, and tri-*n*-butylstannyl groups are stable, the solution structures and dynamics can be studied by variable-temperature NMR experiments. The ^{1}H-NMR signals of the methyl protons on the amino groups for **17** are temperature-dependent. While the spectrum shows a doublet above 268 K, at lower temperatures the signals broaden and coalesce at 248 K. As the temperature is lowered further, the broad resonance splits and eventually sharpens into two doublets. This spectral behavior is explained on the basis of phosphenium ligand rotation along the P–Fe axis: it rotates freely at room temperature, and the rotation is frozen or slower than the NMR time scale at 228 K. Similar spectral changes can be observed for **20** and **27**: coalescence temperature is 221 K for **20** and 223 K for **27**. Line-shape analysis affords activation parameters (Table 2) [28].

The small positive entropies of activation in all cases imply no participation of solvent, which is consistent with phosphenium ligand rotation. The comparable values of $\Delta H^\ddagger$ have been observed for **17**, **20**, and **27**. It is well known in organosilicon chemistry that carbonium ion formation or development at a position β to a silicon atom (Si–C–C$^+$) is favored [37]. The so-called β-effect has been ascribed to overlap between the vacant p orbital on the β carbon atom and the σ orbital between the silicon atom and the α-carbon atom (σ–π conjugation). Recently, the β-effect was reported for germyl and stannyl groups and the magnitude has been predicted to increase in the order C < Si < Ge < Sn [38]. The stability of **17**, **20**, and **27** can be ascribed to the β-effect of silyl, germyl, and stannyl groups, respectively, because the positive phosphenium phosphorus is located at the β position to the Group 14 elements (E–Fe–P$^+$). However, the $\Delta H^\ddagger$ values obtained are almost identical. Therefore, the β-effect of a Group 14 element on the stability of a phosphenium complex seems to be lower.

The observation of barriers to rotation about a transition metal–phosphorus bond in cationic phosphenium complexes $[L_nM{-}PR_2]^+$ is unprecedented. However, some barriers have been reported for three electron-donor terminal phosphide complexes, $[L_nM=PR_2]$,

Table 2
Activation parameters $\Delta H^\ddagger$, $\Delta S^\ddagger$, and $\Delta G^\ddagger$ for **17**, **20**, and **27**

	17	**20**	**27**
$\Delta H^\ddagger$ (kcal mol^{-1})	15.6 ± 0.46	14.3 ± 1.10	12.7 ± 0.53
$\Delta S^\ddagger$ (cal mol^{-1} K^{-1})	11.7 ± 1.85	14.3 ± 5.18	8.60 ± 2.49
$\Delta G^\ddagger$ (kcal mol^{-1})	12.7 ± 0.9 (248 K)	11.0 ± 2.2 (221 K)	10.8 ± 1.1 (223 K)

Table 3
Selected crystal structural data of cationic phosphenium complexes

Complex	Angles (°) around P	Bond distance (Å)				References
		M–P (PX_2)	M–P (PX_3)	P–X (PX_2)	P–X (PX_3)	
$[Mo\{(P(OMe)_3\}_5\{P(OMe)_2\}]^+$	358.7	2.229	2.428 [a]	1.573 [a]	1.586 [a]	[9c]
trans-Mo-**4**	359.9	2.254	2.496	1.642 1.644	1.648 1.662	[18]
trans-Mo-**31**	359.2	2.238	2.529	1.65	1.63	[18]
$[Fe(CO)_4\{P(NEt_2)_2\}]^+$	[b]	2.10		1.61 1.62		[42]
17	359.9	2.018		1.621 1.601		[28]
$Ni(CO)_4\{P(NSiMe_3)_2GaCl_2\}$	360.0	2.123		1.604 1.611		[43]

[a] Average value.

[b] Described just as 'planar'.

which can be considered as phosphenium complexes if one thinks that they consist of L_nM^- and $^+PR_2$: $\Delta G^\ddagger < 10$ kcal mol^{-1} for $Cp^*HfCl_2\{P(CMe_3)_2\}$ and $Cp^*HfCl\{P(CMe_3)_2\}_2$ [39], $\Delta G^\ddagger = 8.4$–9.9 kcal mol^{-1} for 1,2-$M_2(PR_2)_2(NMe_2)_4$ (M = Mo, W) [40], and $\Delta G^\ddagger = 11.6$ kcal mol^{-1} for $Cp^*Ta(C_2H_4)Me(PPh_2)$ [41]. Therefore, the comparison of these data reveals that barriers to rotation about an M–PR_2 bond do not differ considerably whether these complexes are electrically cationic or neutral.

6. X-ray structures of cationic phosphenium complexes

The first X-ray structure of a cationic phosphenium complex was reported in 1978 [9a,c]. To date, however, only six X-ray structures have been obtained; three Mo complexes [9a,c,18], two iron complexes [28,42] and one nickel complex [43] (Chart 3 and Table 3). In all cases, the phosphenium phosphorus has a planar geometry. The ORTEP drawings of *trans*-Mo-**4a**, *trans*-Mo-**31**, and **17** are displayed in Figs. 2–4, respectively.

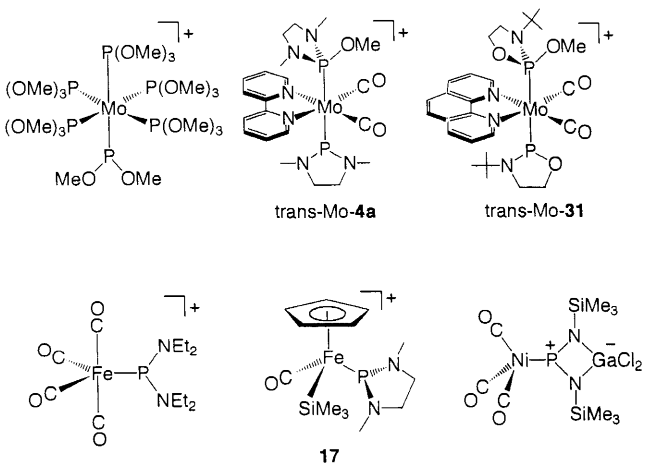


Chart 3.

The complexes $[Mo\{P(OMe)_3\}_5\{P(OMe)_2\}]^+$, *trans*-Mo-**4a**, and *trans*-Mo-**31** all have both a phosphenium ligand and corresponding phosphite ligand(s) in one molecule, which allows us to directly compare the two types of M–P bond distances. The Mo–P(phosphenium) bond is about 10% shorter than the Mo–P dative bond. The Fe–P(phosphenium) bond distances for $[Fe(CO)_4\{P(NEt_2)_2\}]^+$ and **17** are significantly shorter

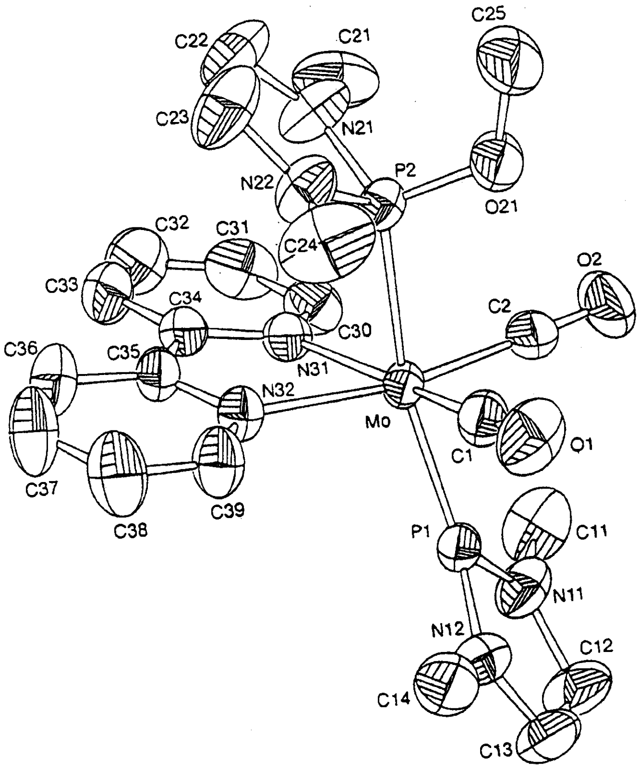


Fig. 2. ORTEP drawing of *trans*-Mo-**4** showing the atom-numbering scheme. Selected bond lengths (Å) and angles (°): Mo–P1, 2.254(1); Mo–P2, 2.495(1); Mo–P1–N11, 132.7(2); Mo–P1–N12, 132.7(2); N11–P1–N12, 92.6(2).

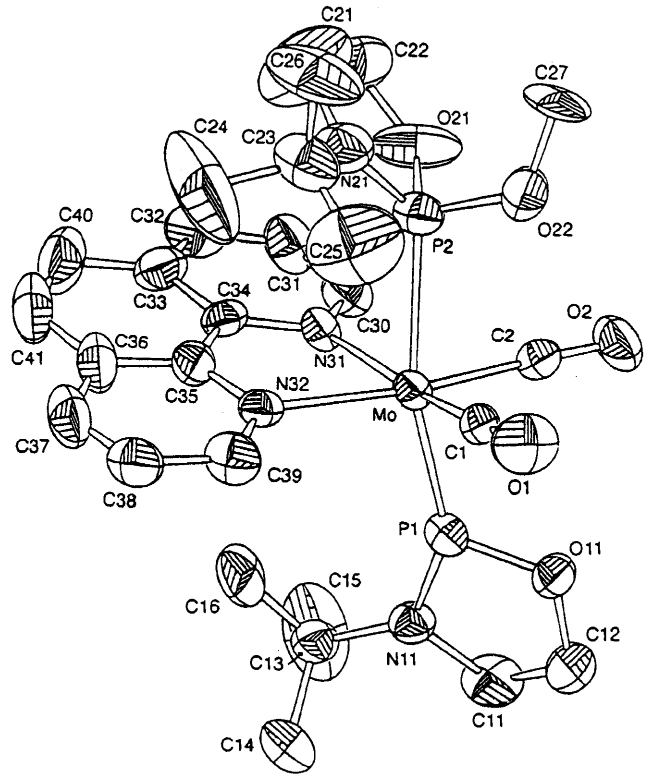


Fig. 3. ORTEP drawing of *trans*-Mo-**31** showing the atom-numbering scheme. Selected bond lengths (Å) and angles (°): Mo–P1, 2.238(4); Mo–P2, 2.529(4); Mo–P1–N11, 146.9(3); Mo–P1–O11, 118.8(3); N11–P1–O11, 93.4(4).

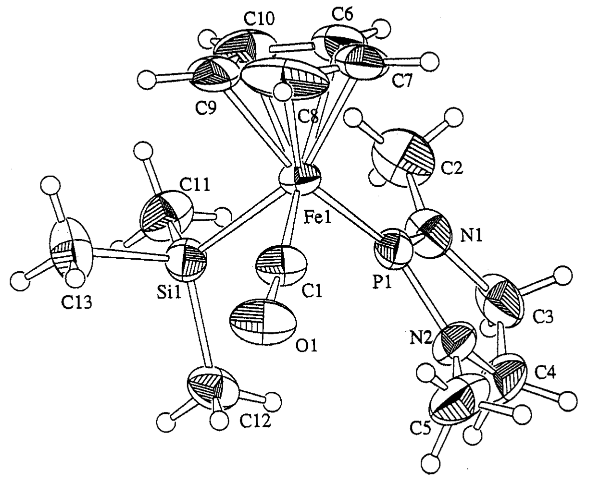


Fig. 4. ORTEP drawing of **17** showing the atom-numbering scheme. Selected bond lengths (Å) and angles (°): Fe1–P1, 2.018(2); Fe1–Si1, 2.364(3); Fe1–P1–N1, 132.0(3); Fe1–P1–N2, 133.1(3); N1–P1–N1, 94.8(4).

than Fe–P dative bond distances reported. The Fe–P bond distance (2.018 Å) in **17** is the shortest bond among phosphorus–iron complexes reported to date. These observations indicate that an M–P(phosphenium) bond has considerable double bond character.

Another structural feature of interest is concerned with the P–N bond distances. For both *trans*-Mo-**4a** and *trans*-Mo-**31**, the P–N bond distances in phosphenium and in phosphite ligands are almost equal. A similar tendency has been observed in the P–O bond distances for $[Mo\{P(OMe)_3\}_5\{P(OMe)_2\}]^+$.

7. Double-bond character between a transition metal and a phosphenium phosphorus

A cationic phosphenium complex can be described in the resonance forms shown in Chart 4. **R2** corresponds to a transition metal phosphenium complex where a plus charge is located on the phosphorus and a phosphenium cation coordinates to a transition metal through its lone pair. The bond between M and P in **R2** can be seen as a dative bond. If sufficient electron density flows from the filled d orbital of a transition metal into the vacant p orbital on the phosphorus, the plus charge would be located on a transition metal and the M–P bond would become a double bond (**R1**). The π-electron donation to the empty p orbital of the phosphorus may occur not only from M but also from the two other substituents on the phosphorus (X and Y). These features are depicted in **R3** and **R4**.

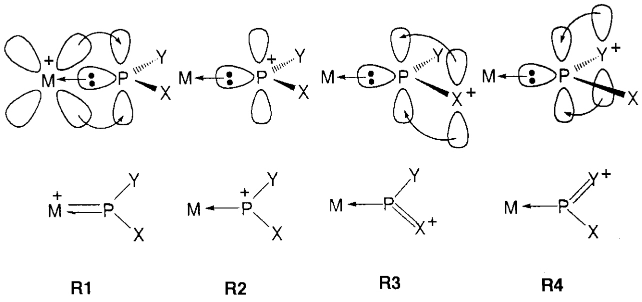


Chart 4.

As is shown above, the bond lengths of M–P(phosphenium) are clearly shorter than those of M–P(phosphite), indicating that an M–P(phosphenium) bond bears a significant double bond character, in other words, the contribution of **R1** is significant. An amino nitrogen bonding to a phosphorus has generally a trigonal planar geometry, i.e. sp^2 hybridization. Therefore, the nitrogen has lone pair electrons in its p orbital, which can potentially be donated to the empty p orbital of a phosphenium phosphorus. The P–N bond lengths are, however, almost equal whether the bond exists in a phosphenium or in a phosphite, indicating no significant π-donation from an amino N to a phosphenium phosphorus, that is, the contribution of **R3** and **R4** is not important if any. The role of an amino substituent on a phosphenium phosphorus for stabilizing the phosphenium complex may be to protect the approach of a nucleophile to a phosphenium phosphorus by high pπ lone pair density flanking the phosphenium center [18]. A similar role of amino lone pair density has been proposed by Arduengo for imidazol-2-ylidene (carbene) [44]. This may be the reason for the tendency mentioned above: diamino phosphenium complexes are more stable than monoaminomonoalkoxy phosphenium complexes, which are more stable than dialkoxy phosphenium complexes. The ethylene bridge between an amino substituent and an amino or an alkoxy substituent makes the lone pair p orbital of N parallel to the empty p orbital of phosphenium phosphorus. This orientation exerts the most effective inhibitory action of the amino lone pair electrons on nucleophilic attack toward a phosphenium phosphorus. Presuming that $[(bpy)(CO)_3M\{P(NEt_2)_2\}]^+$ has one amino lone pair parallel to and the other perpendicular to the empty p orbital of phosphenium phosphorus, it is reasonably understood that the stability of $[(bpy)(CO)_3M\{P(NEt_2)_2\}]^+$ and $[(bpy)(CO)_3M\{PNO\}]^+$ are similar, and the stability of $[(bpy)(CO)_3M\{PNN\}]^+$ is greater than that of $[(bpy)(CO)_3M\{P(NEt_2)_2\}]^+$. These features are schematically shown in Fig. 5 [16]. An alkoxy substituent may not effectively protect a nucleophilic attack to a phosphenium phosphorus. Therefore, a dialkoxy phosphenium complex is not detected but an F-introduced complex is obtained.

8. NMR spectroscopic studies

8.1. ^{31}P-NMR spectra

^{31}P-NMR spectroscopy is nowadays indispensable in the investigation of phosphenium chemistry. Table 4 shows ^{31}P-NMR data for cationic phosphenium complexes, together with those for the corresponding phosphite complexes. As expected from the low coordination number and the presence of some positive charge at phosphenium phosphorus, the ^{31}P-NMR chemical shifts are rather desielded and are observed in the range 230–310 ppm. In any case, a cationic phosphenium complex is roughly at more than 100 ppm lower magnetic field than the corresponding phosphite complex. In addition, for W complexes the ^{31}P–^{183}W coupling constant is diagnostic of the W–P double-bond properties, and it is more than 100 Hz greater for a phosphenium complex than for the corresponding phosphite complex.

Table 4
^{31}P-NMR data [a] for a cationic phosphenium complex, $[L_nM\{PNN\}]^+$, and for the corresponding phosphite complex, $L_nM\{PNN(OMe)\}$

L_nM	$[L_nM\{PNN\}]^+$	$L_nM\{PNN(OMe)\}$
(bpy)(CO)$_3$M		
M = Cr (*fac*)	263.8 (*fac*-Cr-**1**)	153.9
M = Cr (*mer*)	277.3 (*mer*-Cr-**1**)	
M = Mo (*fac*)	252.5 (*fac*-Mo-**1**)	138.0
M = Mo (*mer*)	268.2 (*mer*-Mo-**1**)	
M = W (*fac*)	233.7 (J_{PW} = 441.7 Hz) (*fac*-W-**1**)	129.8 (J_{PW} = 334.6 Hz)
M = W (*mer*)	242.6 (J_{PW} = 561.1 Hz) (*mer*-W-**1**)	
Cp(CO)(ER$_3$)Fe		
$ER_3 = SiMe_3$	305.1 (**17**)	176.6
$ER_3 = GeMe_3$	311.1 (**20**)	176.6
$ER_3 = SnMe_3$	307.5 (**23**)	177.2
$ER_3 = Sn^nBu_3$	307.9 (**27**)	177.8
Cp(CO)(ER$_3$)Ru		
$ER_3 = SiMe_3$	286.6	153.6 [b]
$ER_3 = SiMe_2SiMe_3$	286.1	151.3 [b]
$ER_3 = GeMe_3$	289.1	153.3 [b]
$ER_3 = SnMe_3$	286.2	151.9 [b]
$ER_3 = Sn^nBu_3$	287.6	154.8 [b]

[a] In CH_2Cl_2

[b] In $CDCl_3$.

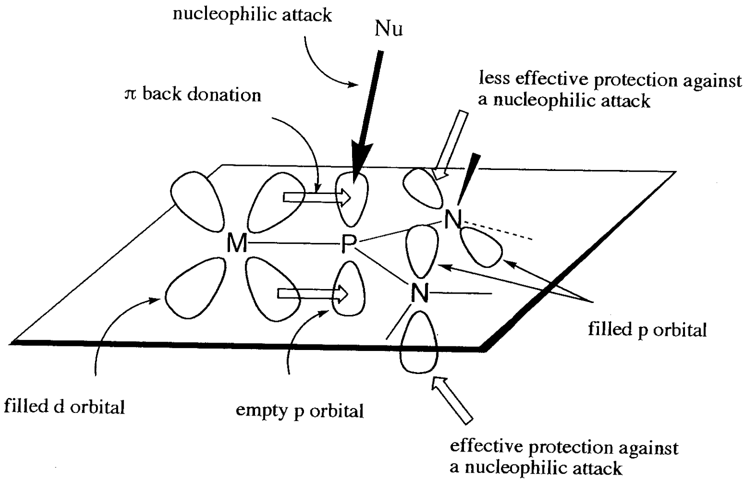


Fig. 5. Bonding feature of a cationic phosphenium complex with two amino substituents on a phosphenium phosphorus.

8.2. ^{95}Mo-NMR spectra

Transition metal NMR spectroscopy has been developed well and is becoming a good direct probe of the transition metal environment [45]. However, no example of a transition metal NMR study on cationic phosphenium complexes has been reported. Recently, a ^{95}Mo-NMR study was reported for [(bpy)(CO)$_3$Mo{PNN}]$^+$ and [(bpy)(CO)$_3$Mo{PNO}]$^+$ [46].

The chemical shifts (δ), coupling constants (*J*) between Mo and P, and the line widths ($W_{1/2}$) are listed in Table 5. Going from [(bpy)(CO)$_3$Mo{PNN(OMe)}] to *fac*-Mo-**1** to *mer*-Mo-**1** causes deshielding of the chemical shift, increasing the Mo–P coupling constant, and increasing the linewidth. [(bpy)(CO)$_3$Mo{PNO(OMe)}] and *mer*-Mo-**7** show the same trend.

For a theoretical understanding of chemical shifts, the Ramsey equation ($\sigma = \sigma^d + \sigma^p$) is generally used [47], where the shielding, σ, is separated into a diamagnetic (σ^d) term and a paramagnetic (σ^p) term. The paramagnetic term is the dominant factor in heavy nuclei such as ^{95}Mo [48], and is represented in Eq. (9), where ΔE is the average excitation energy, $\langle r^{-3} \rangle$ is related to the nephelauxetic effect, and B corresponds to the imbalance of electron density at the nucleus [47d].

$$\sigma^p = -B\langle r^{-3} \rangle / \Delta E \tag{9}$$

The variations in the ^{95}Mo chemical shifts, as well as the coupling constants and the linewidths can be discussed in terms of the imbalance of electron density at Mo rather than ΔE and $\langle r^{-3} \rangle$. The reason seems to come from a significant double bond character between a Mo and a phosphenium phosphorus.

Table 5
^{95}Mo-NMR data for cationic phosphenium complexes, [(bpy)(CO)$_3$Mo{PNN}]$^+$ and [(bpy)(CO)$_3$Mo{PNO}]$^+$ and for the corresponding phosphite complexes, [(bpy)(CO)$_3$Mo{PNN(OMe)}] and [(bpy)(CO)$_3$Mo{PNO(OMe)}].

Complex	δ (ppm) [a]	$^1J_{\text{Mo–P}}$ (Hz)	$W_{1/2}$ (Hz)
(bpy)(CO)$_3$Mo{PNN(OMe)}	−1081 (d)	193	35
fac-[(bpy)(CO)$_3$Mo{PNN}]$^+$ (*fac*-Mo-**1**)	−1049 (d)	264	90
mer-[(bpy)(CO)$_3$Mo{PNN}]$^+$ (*mer*-Mo-**1**)	−1015 (d)	337	300
(bpy)(CO)$_3$Mo{PNO(OMe)}	−1098 (d)	209	37
mer-[(bpy)(CO)$_3$Mo{PNO}]$^+$ (*mer*-Mo-**7**)	−986 (d)	343	445

[a] The chemical shifts are referenced to 1 M Na_2MoO_4 in D_2O (pD 11) as the external standard.

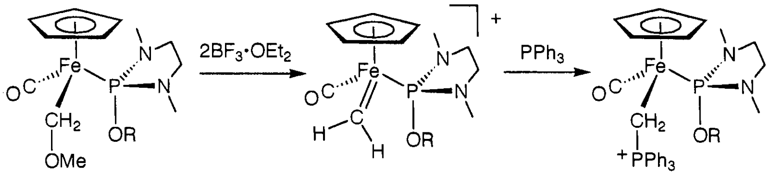
9. Selectivity of OR group abstraction

9.1. Preferential formation of a carbene complex over a phosphenium complex

As is mentioned above, an OR group on a phosphorus coordinating to a transition metal is abstracted as an anion by a Lewis acid such as $BF_3 \cdot OEt_2$ to give a cationic phosphenium complex. It has been reported that an OR group in $(C_5X_5)L_2Fe(CY_2OR)$ (X = H, Me; L = CO, tertiary phosphine; Y = H, alkyl; R = alkyl, silyl) is abstracted as an anion to give cationic iron carbene complexes [49].

Complex **32** has two OR groups; one is on a coordinating phosphorus and the other is on a coordinating carbon. The treatment of **32** with $BF_3 \cdot OEt_2$ seems interesting. If OR is abstracted from the carbon, a methylidene complex would be formed, whereas if abstraction from the phosphorus takes place, a phosphenium complex would be formed.

The reaction of **32** with $BF_3 \cdot OEt_2$ and then PPh_3 leads to isolation of **34** as an orange complex (Scheme 15) [21]. The complex **34b** was identified by an X-ray crystallographic study. It is concluded that an OR group is abstracted selectively from the carbon but not from the phosphorus. The reaction may proceed as follows: the OMe abstraction on the carbon atom by BF_3 takes place to give a methylidene complex (**33**), which is then trapped by PPh_3 to give an ylide complex. The reason for the selectivity may come from the difference in bond energy between C–O and P–O, or may come from the difference in overall stability between a methylidene complex and a phosphenium complex.



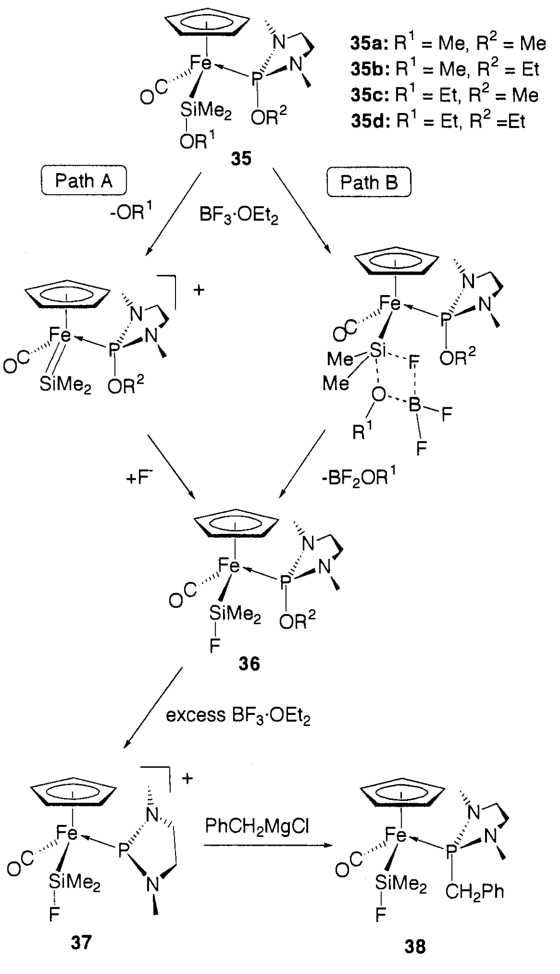
R = Me : **32a** **33a** **34a**
Et : **32b** **33b** **34b**

Scheme 15.

9.2. Preferential formation of a silylene complex over a phosphenium complex

Complex **35** has two OR groups; one is on a coordinating silicon and the other is on a coordinating phosphorus. It is expected in the reaction of **35** with a Lewis acid that a silylene complex would be obtained if an OR group on Si is abstracted, while a phosphenium complex would be obtained if an OR group on P is abstracted.

The reaction of **35** with one equivelent of $BF_3{\cdot}OEt_2$ yields **36** (Scheme 16) [50]. This result implies that an OR group on the Si is selectively abstracted. Two plausible reaction pathways are proposed. An OR group on Si, but not on P, is first abstracted by $BF_3{\cdot}OEt_2$ to give a silylene complex, which is, however, too reactive to be isolated or to be detected spectroscopically, and thus reacts further with F^- present in the reaction mixture to yield **36** (path A). An alternative reaction pathway (path B) is also probable as judged from the general reactivity of main group elements. In this pathway the reaction proceeds via a five-coordinate silicon intermediate. There is, at present, no evidence to show which pathway is more plausible.

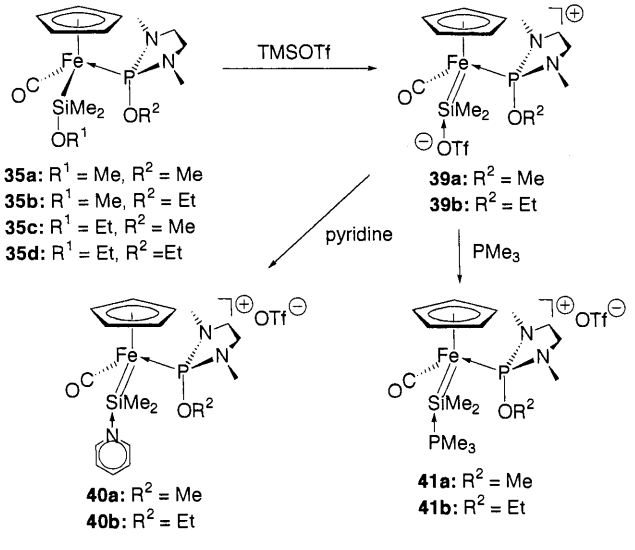


Scheme 16.

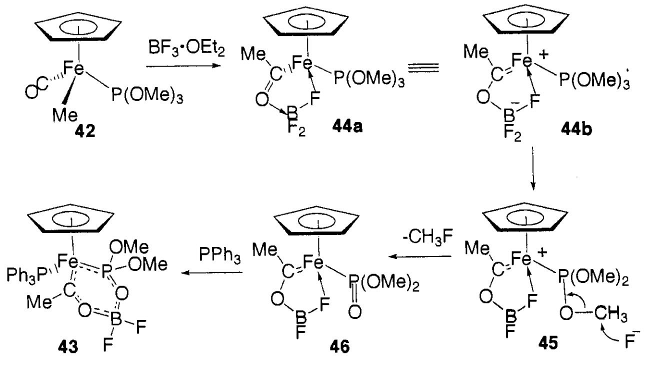
In the reaction of **35** or **36** with excess $BF_3{\cdot}OEt_2$, the complex **37**, which has no OR groups on Si or P but instead has an F substituent on the Si atom, is obtained as a main product. Although complex **37** has not been isolated due to its instability, it can be converted, by the reaction with $PhCH_2MgCl$, into an isolable complex, **38**.

In the reaction shown in Scheme 16, an OR group is selectively abstracted from Si. Although the silylene complex might have been formed transiently, it can not be detected even spectroscopically. In the reaction of **35** with $BF_3{\cdot}OEt_2$, a fluorine atom is introduced into the Si atom right after OR abstraction. TMSOTf is an alternative Lewis acid because it has no replaceable fluorine atom but serves similarly as a Lewis acid. The reaction of **35** with TMSOTf yields a silylene complex (**39**), where the silylene is stabilized by adduct formation with OTf^- (Scheme 17). Although **39** can be detected spectroscopically, it cannot be isolated. However, it is converted into the fully base-stabilized silylene complexes **40** and **41** with a strong Lewis base such as pyridine or PMe_3. The structure of **41b** was established by X-ray analysis.

These reactions clearly show that an OR group on Si is selectively abstracted by TMSOTf. Although it is not easy to say where the selectivity comes from, it should be noted that the selectivity is opposite to the trend simply expected from a comparison between Si–O bond energy (452 kJ mol^{-1}) and P–O bond energy (335 kJ mol^{-1}) [51]. As far as the thermodynamic aspects are concerned, a difference in the O atom basicity between the Si–OR and P–OR groups, and/or a thermodynamic stability difference between the resulting silylene and phosphenium complexes are probably responsible for the interesting selectivity.



Scheme 17.



Scheme 18.

9.3. Preferential formation of a metallacycle complex

As is shown in Scheme 9, in the reaction of an alkyl complex (**10**) having diaminophosphite with $BF_3{\cdot}OEt_2$, an OR group is abstracted to give a cationic phosphenium complex, then the alkyl migrates from Fe to the phosphenium phosphorus. In contrast, an alkyl iron complex containing trimethylphosphite (**42**) shows a different reactivity.

Complex **42** reacts with $BF_3{\cdot}OEt_2$ and then PPh_3 to give a six-membered metallacycle (**43**) consisting of Fe, C, P, B, and two O atoms (Scheme 18) [52]. The product was isolated, characterized spectroscopically and confirmed by X-ray analysis.

A plausible reaction mechanism is also shown in Scheme 18. In the reaction, BF_3 induces a migratory insertion of a CO ligand into an Fe–Me bond rather than OMe abstraction from the coordinating $P(OMe)_3$. The acyl complex (**44a**) thus produced, also described as a cationic carbene complex (**44b**), releases F^- to give **45**. Since **45** is a cationic complex containing $P(OMe)_3$ ligand, it is reasonably expected to undergo the Arbuzov-like dealkylation with F^- to give a phosphonate complex (**46**) [53,54], which is converted, by PPh_3 addition, into **43**, forming a bond between the phosphoryl oxygen and the boron. This reaction is the first example of migratory insertion of CO into an M–C bond over OR abstraction from coordinating phosphite by BF_3.

The interesting point is that, in the reaction of Cp(CO)MeFe{PXY(OMe)} with $BF_3{\cdot}OEt_2$, OMe abstraction from phosphorus takes place when X and/or Y is an amino group, whereas migratory insertion of CO into Fe–Me occurs when $X = Y = OMe$. The reason for the different reactivity may come from the basicity of an OMe group on the phosphorus: the OMe group in the former complex may be enough basic to attract BF_3 due to electron donating ability of an amino group to a phosphorus causing the increasing OR basicity, whereas the OMe group in the latter one would be less attractive than the carbonyl oxygen toward BF_3.

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