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Reactivity of Cationic Phosphenium Complexes of Molybdenum: Migration of OR, SR, and NR$_2$ on a Tertiary Phosphorus Compound to a Phosphenium Ligand

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The reaction of a cationic monoaminomonoalkoxy phosphenium complex of Mo, *mer*-$[(\mathrm{bpy})(\mathrm{CO})_3\mathrm{Mo}\{\overline{\mathrm{PN(Me)CH_2CH_2O}}\}]^+$ (**1a**), with a diamino-substituted phosphorus compound, $\overline{\mathrm{PN(Me)CH_2CH_2N}}\mathrm{Me(Y)}$ (Y = OMe, OEt, SEt, $\overline{\mathrm{N(CH_2)_3C}}\mathrm{H_2}$), proceeds with substitution for CO and then with the Y group migration to the coordinating phosphenium phosphorus to give $[(\mathrm{bpy})(\mathrm{CO})_2\{\overline{\mathrm{PN(Me)CH_2CH_2O}}(\mathrm{Y})\}\mathrm{Mo}\{\overline{\mathrm{PN(Me)CH_2CH_2N}}\mathrm{Me}\}]^+$ (**2**), which is also prepared from a cationic diamino phosphenium complex of Mo, *mer*-$[(\mathrm{bpy})(\mathrm{CO})_3\mathrm{Mo}\{\overline{\mathrm{PN(Me)CH_2CH_2N}}\mathrm{Me}\}]^+$ (**1b**), and a monoamino-substituted phosphorus compound, $\overline{\mathrm{PN(Me)CH_2CH_2O}}(\mathrm{Y})$, by a simple CO/$\overline{\mathrm{PN(Me)CH_2CH_2O}}(\mathrm{Y})$ substitution. This migration reaction is irreversible. The migration mechanism is also discussed.

Introduction

Since a cationic phosphenium ($^+\mathrm{PR_2}$) can be considered to have the same electronic configuration as a carbene (sp^2 hybridization with a vacant p orbital and lone pair electrons), considerable attention has been focused on the coordination chemistry of a cationic phosphenium,[1] and many cationic transition-metal phosphenium complexes[2] have been prepared for several kinds of transition metals.[3−6] Nevertheless, the reactivity of these complexes is much less investigated than that of carbene complexes.[6d,7]

We have been engaged in the study of the preparation, structures, properties, and reactivities of cationic phosphenium complexes of group 6[6] and 8[7] transition metals and recently reported that *mer*-$[(\mathrm{bpy})(\mathrm{CO})_3\mathrm{M}\{\overline{\mathrm{PN(Me)CH_2CH_2X}}\}]^+$ (bpy = 2,2′-bipyridine; M = Cr, Mo, W; X = NMe, O) reacts with $\overline{\mathrm{PN(Me)CH_2CH_2X}}(\mathrm{OR})$ to give $[(\mathrm{bpy})(\mathrm{CO})_2\{\overline{\mathrm{PN(Me)CH_2CH_2X}}(\mathrm{OR})\}\mathrm{M}\{\overline{\mathrm{PN(Me)CH_2CH_2X}}\}]^+$ where CO/$\overline{\mathrm{PN(Me)CH_2CH_2X}}(\mathrm{OR})$ substitution takes place and the phosphenium ligand remains intact (Scheme 1).[6d]

Concerning the reactivity of a coordinating phosphenium phosphorus, some noticeable migration reactions have been reported: facile methoxy group migration for $[\mathrm{M}\{\mathrm{P(OMe)_3}\}_5\{\mathrm{P(OMe)_2}\}]^+$ (M = Mo, W) based on its stereochemical nonrigidity,[4] an alkyl migration from iron to a coordinating phosphenium phosphorus for $[\mathrm{Cp(CO)RFe}\{\overline{\mathrm{PN(Me)CH_2CH_2N}}\mathrm{Me}\}]^+$,[7a] and an alkyl migration from tin to phosphenium phosphorus for $[\mathrm{Cp(CO)(SnR_3)Fe}\{\overline{\mathrm{PN(Me)CH_2CH_2N}}\mathrm{Me}\}]^+$ resulting in the

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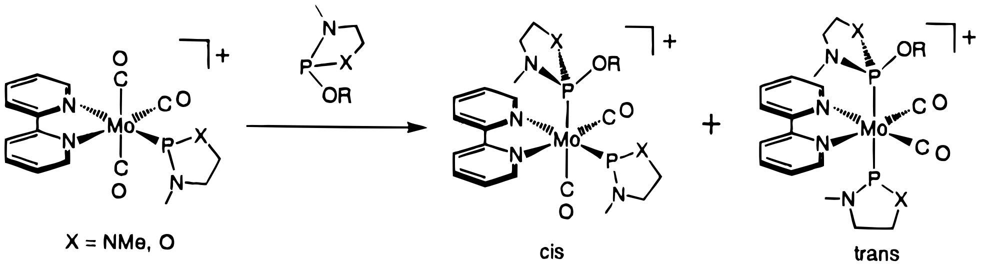
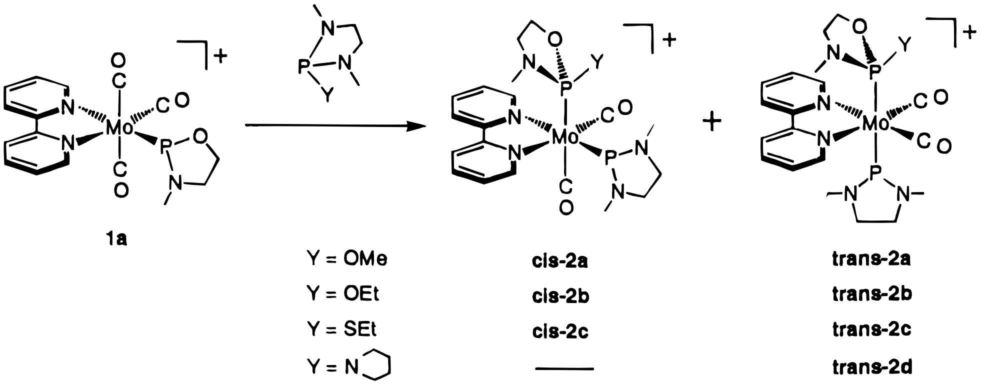
Scheme 1



Scheme 2



formation of a stannylene complex.[7b] These results seem to imply the possibility of OR migration to a phosphenium phosphorus for the above-mentioned $[(bpy)(CO)_2\{\overline{PN(Me)CH_2CH_2X}(OR)\}M\{\overline{PN(Me)CH_2CH_2X}\}]^+$. However, this is not a suitable complex to investigate whether the OR migration takes place or not, because the complexes before and after the migration would be the same. Reported herein are the reactions of $[(bpy)(CO)_3M\{\overline{PN(Me)CH_2CH_2O}\}]^+$ with $\overline{PN(Me)CH_2CH_2NMe}(Y)$, revealing that, after the CO/$\overline{PN(Me)CH_2CH_2NMe}(Y)$ substitution, Y (OR, SR, NR_2) migrates to the phosphenium phosphorus and that the migration is irreversible in our system.

Results and Discussion

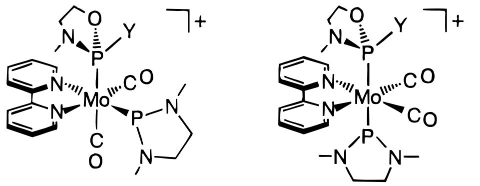
It has been reported that *fac*-$[(bpy)(CO)_3Mo\{\overline{PN(Me)CH_2CH_2O}(OMe)\}]$ reacts cleanly with $BF_3{\cdot}OEt_2$ to produce *mer*-$[(bpy)(CO)_3Mo\{\overline{PN(Me)CH_2CH_2O}\}]^+$ (**1a**) by the abstraction of the OMe group from the phosphorus as an anion.[6c,f] The cationic phosphenium complex produced is stable in solution unless exposed to air, though it has not been isolated as a solid due to the high reactivity. It has also been reported that reaction of **1a** with $\overline{PN(Me)CH_2CH_2O}(OMe)$ proceeds with CO/$\overline{PN(Me)CH_2CH_2O}(OMe)$ substitution to give $[(bpy)(CO)_2\{\overline{PN(Me)CH_2CH_2O}(OMe)\}Mo\{\overline{PN(Me)CH_2CH_2O}\}]^+$.[6d] Therefore, we first examined the reaction of **1a** prepared from *fac*-$[(bpy)(CO)_3Mo\{\overline{PN(Me)CH_2CH_2O}(OMe)\}]$ and $BF_3{\cdot}OEt_2$, with a variety of $\overline{PN(Me)CH_2CH_2NMe}(Y)$ in hope of a simple CO/$\overline{PN(Me)CH_2CH_2NMe}(Y)$ substitution reaction. However, the reactions were complicated: the ^{31}P NMR spectrum of the reaction mixture showed the formation of several kinds of Mo complexes. In order to obtain a clean reaction system, we examined many reactions and finally found that the reaction of **1a** with $\overline{PN(Me)CH_2CH_2NMe}(Y)$ proceeds cleanly when **1a** is produced from *fac*-$[(bpy)(CO)_3Mo\{\overline{PN(Me)CH_2CH_2O}(NEt_2)\}]$ and HOTf ($HOSO_2CF_3$) by NEt_2 abstraction as an anion. $HNEt_2$ produced in this system may not disturb the successive reaction, while $BF_2(OMe)$ produced in the reaction of *fac*-$[(bpy)(CO)_3Mo\{\overline{PN(Me)CH_2CH_2O}(OMe)\}]$ with $BF_3{\cdot}OEt_2$ may be involved in the successive reaction, which is probably responsible for the above complicated reaction.

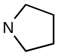
A CH_2Cl_2 solution containing a cationic complex (**1a**) thus prepared was cooled to −78 °C, an equimolar amount of $\overline{PN(Me)CH_2CH_2NMe}(Y)$ (Y = OMe, OEt, SEt, $\overline{N(CH_2)_3CH_2}$) was added, and then the solution was warmed to room temperature. From the following discussion, we concluded that the reaction shown in (Scheme 2) takes place.

The ^1H and ^{13}C NMR spectra of the reaction mixture were too complicated to estimate what the products are and what geometrical structures they have. In contrast, the ^{31}P NMR spectra of the reaction mixture are very informative to identify the products. The ^{31}P NMR data of the products in Scheme 2 are summarized in Table 1.

First, let us consider the reaction of **1a** with $\overline{PN(Me)CH_2CH_2NMe}(OMe)$. The reaction mixture showed two absorption bands at 1915 and 1839 cm^{-1} in the ν_{CO} region in the IR spectrum, indicating that the added

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



Y = OMe	*cis*-**2a**	*trans*-**2a**
	150.20 (42.7)	146.36 (289.9)
	151.48 (48.8)	246.53 (289.9)
	259.10 (42.7)	
	260.77 (48.8)	
Y = OEt	*cis*-**2b**	*trans*-**2b**
	147.08 (48.8)	143.55 (289.9)
	148.71 (45.7)	246.25 (289.9)
	258.50 (48.8)	
	259.86 (45.7)	
Y = SEt	*cis*-**2c**	*trans*-**2c**
	181.03 (36.6)	179.30 (277.7)
	182.82 (36.6)	250.87 (277.7)
	259.31 (36.6)	
	259.99 (36.6)	
Y = 		*trans*-**2d**
		136.87 (262.5)
		243.44 (262.5)

[a] In CH_2Cl_2. Assignment: d; numbers in parentheses are $^2J_{PP}$ in hertz.

phosphorus compound is substituted for a CO ligand. The ^{31}P NMR spectrum showed three doublets in the region of coordinating trivalent phosphorus compounds ($\delta = 146.36$ ($J = 289.9$ Hz), 150.20 ($J = 42.7$ Hz), 151.48 ($J = 48.8$ Hz)) and three doublets in the region of coordinating phosphenium ligands ($\delta = 246.53$ ($J = 289.9$ Hz), 259.10 ($J = 42.7$ Hz), 260.77 ($J = 48.8$ Hz)), and three kinds of coupling constants ($J = 289.9$, 48.8, 42.7 Hz) were observed in both regions. Comparison of these ^{31}P NMR data with those of $[\mathrm{(bpy)(CO)_2(phosphite)Mo(phosphenium)}]^+$ complexes reported previously[6d] suggests strongly that two doublets with a relatively large coupling constant at 146.36 and 246.53 ppm are due to the *trans* type (*trans*-**2a**) and the rest four doublets are due to the *cis* type (*cis*-**2a**) of $[\mathrm{(bpy)(CO)_2(phosphite)Mo(phosphenium)}]^+$ complex.

The relevant reactions already been reported are shown in Schemes 3 and 4 together with their ^{31}P NMR data.[6d] The products in Scheme 3 (*cis*-**3a** and *trans*-**3a**) have a monoamino-substituted phosphenium and a monoamino-substituted phosphite, and the products in Scheme 4 (*cis*-**3b** and *trans*-**3b**) have a diamino-substituted phosphenium and a diamino-substituted phosphite. *cis*-**3a** shows four doublets in the ^{31}P NMR spectrum because of a pair of diastereomers resulting from two chiral centers at Mo and P in $\overline{\mathrm{PN(Me)CH_2CH_2O}}\mathrm{(OMe)}$.

Comparison of ^{31}P NMR data of the products in Scheme 2 with those in Schemes 3 and 4 revealed the following: (i) A doublet at 146.36 ppm of *trans*-**2a** is closer to a doublet (144.28 ppm) of *trans*-**3a** than to that (130.15 ppm) of *trans*-**3b**, indicating that *trans*-**2a** has a monoamino-substituted phosphite. (ii) A doublet at 246.53 ppm of *trans*-**2a** is closer to a doublet (242.18 ppm) of *trans*-**3b** than to that (235.57 ppm) of *trans*-**3a**, indicating that *trans*-**2a** has a diamino-substituted phosphenium. (iii) The ^{31}P NMR pattern of *cis*-**2a** is similar to that of *cis*-**3a**, indicating that *cis*-**2a** has a chiral phosphite. (iv) Doublets at 150.20 and 151.48 ppm of *cis*-**2a** are closer to doublets (149.61 and 149.73 ppm) of *cis*-**3a** than that (135.00 ppm) of *cis*-**3b**, indicating that *cis*-**2a** has a monoamino-substituted phosphite. (v) Doublets at 259.10 and 260.77 ppm of *cis*-**2a** are closer to that (257.71 ppm) of *cis*-**3b** than to those (241.94 and 242.36 ppm) of *cis*-**3a,** indicating that *cis*-**2a** has a diamino-substituted phosphenium. Therefore, it is strongly suggested that the products in Scheme 2 are *cis* and *trans* isomers of $[\mathrm{(bpy)(CO)_2\{\overline{PN(Me)CH_2CH_2O}(OMe)\}Mo\{\overline{PN(Me)CH_2CH_2NMe}\}}]^+$.

In order to confirm the products, the reaction of **1b** possessing a diamino-substituted phosphenium with $\overline{\mathrm{PN(Me)CH_2CH_2O}}\mathrm{(OMe)}$ being a monoamino-substituted phosphite was examined (Scheme 5). In this reaction, $[\mathrm{(bpy)(CO)_2\{\overline{PN(Me)CH_2CH_2O}(OMe)\}Mo\{\overline{PN(Me)CH_2CH_2NMe}\}}]^+$ is reasonably expected to be formed. The reaction mixture showed, in the ^{31}P NMR spectrum, exactly the same resonances as those observed in the reaction of **1a** with $\overline{\mathrm{PN(Me)CH_2CH_2N}}\mathrm{Me(OMe)}$.

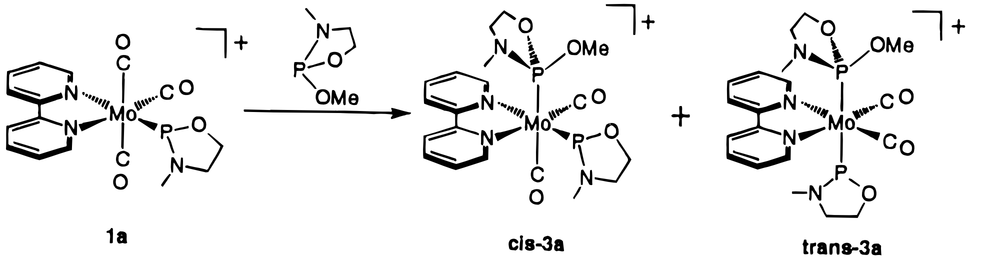
Considerable difficulty was encountered in our attempts to isolate the products in Scheme 2 as a solid due to the high reactivity. Finally, two complexes, *trans*-**2a** and *trans*-**2b**, were isolated as dark red powders, which enabled us to obtain the ^{1}H and ^{31}P NMR data reasonable for *trans*-**2a** and *trans*-**2b**. However, satisfactory ^{13}C NMR and elemental analysis data could not be obtained due to the decomposition during the measurements.

From the results mentioned above, we concluded that the products in the reaction of **1a** with $\overline{\mathrm{PN(Me)CH_2CH_2N}}\mathrm{Me(OMe)}$ are *cis*- and *trans*-$[\mathrm{(bpy)(CO)_2\{\overline{PN(Me)CH_2CH_2O}(OMe)\}Mo\{\overline{PN(Me)CH_2CH_2NMe}\}}]^+$. Therefore, it was found that an OMe group migrates from a phosphite P to a phosphenium P, and the migration is irreversible.

In order to grasp the scope of a migration to a coordinating phosphenium phosphorus, we next examined the reaction of **1a** with some $\overline{\mathrm{PN(Me)CH_2CH_2N}}\mathrm{Me(Y)}$ (Y = OEt, SEt, $\overline{\mathrm{N(CH_2)_3CH_2}}$, Me, Ph). Similar experiments and considerations made for the reaction with $\overline{\mathrm{PN(Me)CH_2CH_2N}}\mathrm{Me(OMe)}$ concluded that OEt, SEt, and $\overline{\mathrm{N(CH_2)_3CH_2}}$ migrate to the phosphenium phosphorus to give *cis*- and *trans*-$[\mathrm{(bpy)(CO)_2\{\overline{PN(Me)CH_2CH_2O}(Y)\}Mo\{\overline{PN(Me)CH_2CH_2NMe}\}}]^+$, though, when Y = $\overline{\mathrm{N(CH_2)_3CH_2}}$, only the *trans* isomer is observed, presumably due to steric reasons. In contrast, when Y = Me and Ph, the ^{31}P NMR spectra showed that complicated reactions took place and the products were not identified. However, there were no resonances expected for phosphenium complexes produced by Me or Ph migration. Therefore, it can be said that Y in $\overline{\mathrm{PN(Me)CH_2CH_2N}}\mathrm{Me(Y)}$ migrates to the coordinating $\overline{\mathrm{PN(Me)CH_2CH_2O}}$ ligand only when Y is a heteroatom substituent, in other words, Y has lone pair electrons.

Let us consider the reaction pathway of Scheme 2.

Scheme 3

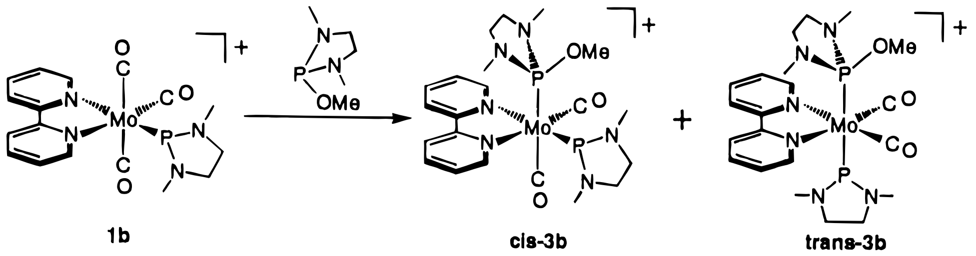


^{31}P NMR data

cis-3a:
149.61 (d, $^2J_{PP}$ = 54.9 Hz)
149.73 (d, $^2J_{PP}$ = 54.9 Hz)
241.94 (d, $^2J_{PP}$ = 54.9 Hz)
242.36 (d, $^2J_{PP}$ = 54.9 Hz)

trans-3a:
144.28 (d, $^2J_{PP}$ = 326.6 Hz)
235.57 (d, $^2J_{PP}$ = 326.6 Hz)

Scheme 4

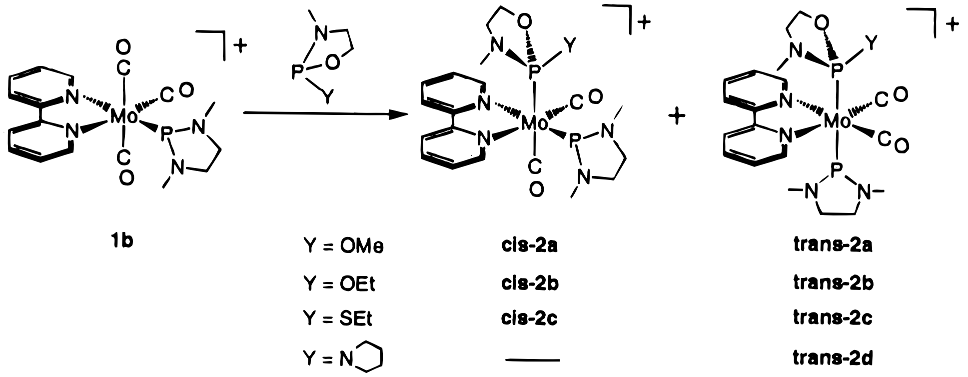


^{31}P NMR data

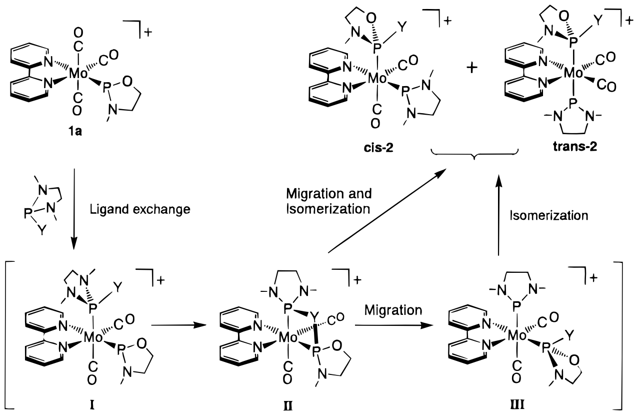
cis-3b:
135.00 (d, $^2J_{PP}$ = 42.7 Hz)
257.71 (d, $^2J_{PP}$ = 42.7Hz)

trans-3b:
130.15 (d, $^2J_{PP}$ = 274.7 Hz)
242.18 (d, $^2J_{PP}$ = 274.7 Hz)

Scheme 5



Scheme 6



Scheme 6 shows our proposed pathway. It is highly likely that **1a** reacts with $\overline{\text{PN(Me)CH}_2\text{CH}_2\text{N}}\text{Me(Y)}$ to give **I**, because CO ligands in **1a** are activated by a strong π-accepting phosphenium ligand, and such type of reaction has been demonstrated for several kinds of Mo complexes.[6d] Since the phosphenium and the phosphite in the intermediate **I** are mutually *cis*, the Y group may donate its lone pair electrons to the vacant p orbital of the phosphenium phosphorus to give **II**. Then the cleavage of the original P—Y bond with the concomitant formation of the new P—Y σ bond results in Y migration to give **III**. Intermediate **III** thus formed isomerizes to more stable geometrical isomers to give the final products *cis*-**2** and *trans*-**2**. An alternative pathway from **II** is possible: Y migration is accomplished with the accompanying rearrangement around the Mo without the formation of **III**. In any case, the finding that Y with lone pair electrons can migrate suggests that the migration is achieved via a Y-bridged intermediate like **II**.

It has been established that a diamino phosphenium complex is more stable than a monoaminomonoalkoxy phosphenium complex, which is more stable than a dialkoxy phosphenium complex for Cr, Mo, and W.[6f]

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 (Scheme 5) is reasonable because in this case the starting phosphenium complex is more stable than the phosphenium complex expected to be produced by migration. *cis*-**3a** and *cis*-**3b** do not show OMe migration to the phosphenium ligand within the ^{31}P NMR time scale, though complexes before and after the migration have the same formulas. The reason may be as follows. If the OMe group in *cis*-**3a** and *cis*-**3b** migrates to the phosphenium with the ligand positions kept intact around the Mo, newly created phosphenium is located *trans* to CO. The complex is unstable compared with the starting phosphenium complex (*cis*-**3**) because a strong π-accepting phosphenium ligand is *trans* to CO, which is also a good π acceptor. $[\mathrm{M\{P(OMe)_3\}_5\{P(OMe)_2\}}]^+$ (M = Mo, W) shows, at room temperature, apparently rapid migration of OMe groups about all phosphorus atoms in the coordination sphere.[4] This may be due to exactly the same stability between before and after the migration.

After the first discovery of OMe migration with P−O bond cleavage and formation 18 years ago, no examples have been reported concerning migration of a substituent on a tertiary phosphorus ligand to a cationic phosphenium ligand. In this paper, we exemplified not only OR migration but also new migration of SR and $\mathrm{NR_2}$ to a coordinating phosphenium phosphorus with P−S and P−N bond cleavage and formation and pointed out 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.

Experimental Section

General Remarks. All reactions were carried out under an atmosphere of dry nitrogen by using standard Schlenk tube techniques. All solvents were purified by distillation: $\mathrm{CH_2Cl_2}$ was distilled from $\mathrm{P_2O_5}$, and ether, THF, and hexane were distilled from sodium/benzophenone. Those were stored under an $\mathrm{N_2}$ atmosphere. TMSOTf was distilled prior to use. All other reagents were used without further purification.

IR spectra were recorded on a Shimadzu FTIR-4000 spectrometer. ^{1}H NMR and ^{31}P NMR spectra were measured on JEOL EX-270 and EX-400 spectrometers. ^{1}H NMR data were referred to $\mathrm{Si(CH_3)_4}$ as an internal standard. ^{31}P NMR data were referred to 85% $\mathrm{H_3PO_4}$ as an external standard.

Phosphorus(III) compounds, $\mathrm{PN(Me)CH_2CH_2O(X)}$ (X = OMe,[8a] OEt,[6b] Cl[8b]) and $\mathrm{PN(Me)CH_2CH_2NMe(X)}$ (X = OMe,[8c] $\mathrm{N(CH_2)_3CH_2}$,[8c] Me,[8d] Ph,[8d] Cl[8c]) were prepared according to the literature method. Molybdenum complexes *fac*-$[\mathrm{(bpy)(CO)_3MoL}]$ (L = $\mathrm{PN(Me)CH_2CH_2O(OMe)}$,[6d,f] $\mathrm{PN(Me)CH_2CH_2O(NEt_2)}$[6f]) and *mer*-$[\mathrm{(bpy)(CO)_3Mo\{PN(Me)CH_2CH_2NMe\}}]^+$ (**1b**)[6b,c] were prepared by literature methods.

Preparation of Tertiary Phosphorus Compounds. $\mathrm{PN(Me)CH_2CH_2O(OEt)}$ (bp 40−44 °C (5.5 mmHg)) was prepared in a manner similar to that of $\mathrm{PN(Me)CH_2CH_2O(OMe)}$ from $\mathrm{PN(Me)CH_2CH_2O(Cl)}$ and HOEt in the presence of an equimolar amount of $\mathrm{NEt_3}$ in ether. ^{1}H NMR (δ, neat): 1.09 (t, $^3J_{\mathrm{HH}}$ = 6.3 Hz, 3H, $\mathrm{CH_2CH_3}$), 2.59 (d, $^3J_{\mathrm{PH}}$ = 10.8 Hz, 3H, $\mathrm{NCH_3}$), 2.79−3.16 (m, 2H, $\mathrm{NCH_2}$), 3.33−4.38 (m, 4H, $\mathrm{OCH_2CH_3}$ + $\mathrm{OCH_2CH_2N}$). ^{31}P NMR (δ, neat): 134.81 (s).

$\mathrm{PN(Me)CH_2CH_2O\{N(CH_2)_3CH_2\}}$ (bp 83−87 °C (6 mmHg)) was prepared in a manner similar to that of $\mathrm{PN(Me)CH_2CH_2NMe(N(CH_2)_3CH_2)}$ from $\mathrm{PN(Me)CH_2CH_2O(Cl)}$ and 2 equiv of $\mathrm{HN(CH_2)_3CH_2}$ in ether. ^{1}H NMR (δ, neat): 1.48−1.83 (m, 4H, $\mathrm{NCH_2CH_2}$), 2.55 (d, $^3J_{\mathrm{PH}}$ = 11.0 Hz, 3H, $\mathrm{NCH_3}$), 2.75−3.33 (m, 6H, $\mathrm{NCH_2}$), 3.62−4.37 (m, 2H, $\mathrm{OCH_2}$). ^{31}P NMR (δ, in $\mathrm{CH_2Cl_2}$): 123.67 (s).

$\mathrm{PN(Me)CH_2CH_2O(SEt)}$ (bp 65−67 °C (2 mmHg)) was prepared in a manner similar to that of $\mathrm{PN(Me)CH_2CH_2O(OMe)}$ from $\mathrm{PN(Me)CH_2CH_2O(Cl)}$ and HSEt in the presence of an equimolar amount of $\mathrm{NEt_3}$ in ether. ^{1}H NMR (δ, neat): 1.24 (t, $^3J_{\mathrm{HH}}$ = 7.1 Hz, 3H, $\mathrm{CH_2CH_3}$), 2.57 (d, $^3J_{\mathrm{PH}}$ = 11.0 Hz, 3H, $\mathrm{NCH_3}$), 2.40−3.28 (m, 4H, $\mathrm{NCH_2}$ + $\mathrm{SCH_2}$), 3.72−4.45 (m, 2H, $\mathrm{OCH_2}$). ^{31}P NMR (δ, in $\mathrm{CH_2Cl_2}$): 184.63 (s).

According to a procedure analogous to that mentioned above, $\mathrm{PN(Me)CH_2CH_2NMe(SEt)}$ (bp 79−82 °C (5 mmHg)) was prepared from $\mathrm{PN(Me)CH_2CH_2NMe(Cl)}$. ^{1}H NMR ($\delta$, neat): 1.23 (t, $^3J_{\mathrm{HH}}$ = 7.4 Hz, 3H, $\mathrm{CH_2CH_3}$), 2.34−3.18 (m, 6H, $\mathrm{NCH_2}$ + $\mathrm{SCH_2}$), 2.53 (d, $^3J_{\mathrm{PH}}$ = 14.6 Hz, 6H, $\mathrm{NCH_3}$). ^{31}P NMR (δ, in $\mathrm{CH_2Cl_2}$): 159.02 (s).

Preparation of Cationic Phosphenium Complex (1a). A solution of the complex *fac*-$[\mathrm{(bpy)(CO)_3Mo\{PN(Me)CH_2CH_2O(NEt_2)\}}]$ (ca. 0.4 mmol) in $\mathrm{CH_2Cl_2}$ (10 mL) was cooled to −78 °C, and an equimolar amount of HOTf was added. Stirring the solution for 1 h at −78 °C caused the color of the solution to change from reddish purple to reddish orange. The formation of a cationic phosphenium complex, **1a**, was confirmed by the ^{31}P NMR measurement (δ, in $\mathrm{CH_2Cl_2}$, 254.08 (s)). The resulting solution was used for the reaction with a phosphite or a phosphine without isolation.

Reaction of 1 with a Tertiary Phosphorus Compound. A solution of a cationic phosphenium complex **1** in $\mathrm{CH_2Cl_2}$ (10 mL) was cooled to −78 °C, and an equimolar amount of a tertiary phosphorus compound was added. The reaction mixture was then warmed to room temperature. The resulting solution was subjected to spectroscopic measurements. IR (ν_{CO}, in $\mathrm{CH_2Cl_2}$, cm^{-1})): 1915, 1839 for **2a**; 1913, 1838 for **2b**; 1918, 1831 for **2c**; 1910, 1834 for **2d**.

Preparation of *trans*-[(bpy)(CO)₂{PN(Me)CH₂CH₂NMe(OMe)}Mo[PN(Me)CH₂CH₂NMe}]OTf (*trans*-2a·OTf). $\mathrm{PN(Me)CH_2CH_2NMe(OMe)}$ (0.99 mmol) was added a solution of **1a** (0.99 mmol) in $\mathrm{CH_2Cl_2}$ (11 mL) at −78 °C, and then the solution was warmed to room temperature. After some insoluble materials formed were removed by filtration, the filtrate was concentrated under reduced pressure. A dark red powder thus formed was collected by filtration and washed with hexane several times to give *trans*-**2a**·OTf (663 mg, 0.93 mmol, 94%). ^{1}H NMR (δ, in $\mathrm{CDCl_3}$): 2.42 (d, $^3J_{\mathrm{PH}}$ = 10.3 Hz, 3H, $\mathrm{PN(CH_3)CH_2CH_2O(OMe)}$), 2.66 (d, $^3J_{\mathrm{PH}}$ = 11.0 Hz, 6H, $\mathrm{PN(CH_3)CH_2CH_2N(CH_3)}$), 2.76 (m, 1H, $\mathrm{PN(Me)CH_2CH_2O(OMe)}$), 2.94 (m, 1H, $\mathrm{PN(Me)CH_2CH_2O(OMe)}$), 3.07 (d, $^3J_{\mathrm{PH}}$ = 10.8 Hz, 3H, $\mathrm{PN(Me)CH_2CH_2O(OCH_3)}$), 3.42 (d, $^3J_{\mathrm{PH}}$ = 5.1 Hz, 4H, $\mathrm{PN(Me)CH_2CH_2NMe}$), 3.53 (m, 1H, $\mathrm{PN(Me)CH_2CH_2O(OMe)}$), 3.99 (m, 1H, $\mathrm{PN(Me)CH_2CH_2O(OMe)}$), 7.33 (s, 2H, bpy), 7.95 (t, $^3J_{\mathrm{HH}}$

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= 7.3 Hz, 2H, bpy), 8.34 (d, $^3J_{HH}$ = 5.9 Hz, 2H, bpy), 8.85 (d, $^3J_{HH}$ = 4.8 Hz, 2H, bpy).

Preparation of *trans*-[(bpy)(CO)$_2${PN(Me)CH$_2$CH$_2$NMe(OEt)}Mo[PN(Me)CH$_2$CH$_2$NMe}]OTf (*trans*-2b·OTf). Complex *trans*-**2b**·OTf was prepared from **1a** and PN(Me)CH$_2$CH$_2$NMe(OEt) in the same manner as that for *trans*-**2a**·OTf (yield 90%). ^{1}H NMR (δ, in CDCl$_3$): 0.71 (t, $^3J_{HH}$ = 7.0 Hz, 3H, OCH$_2$C*H*$_3$), 2.43 (d, $^3J_{PH}$ = 10.3 Hz, 3H, PN(C*H*$_3$)CH$_2$CH$_2$O(OEt)), 2.67 (d, $^3J_{PH}$ = 10.8 Hz, 6H, PN(C*H*$_3$)CH$_2$CH$_2$N(C*H*$_3$)), 2.86 (m, 1H, PN(Me)C*H*$_2$CH$_2$O(OEt)), 3.03 (m, 2H, OC*H*$_2$CH$_3$), 3.36 (m, 1H, PN(Me)C*H*$_2$CH$_2$O(OEt)), 3.42 (d, $^3J_{PH}$ = 5.1 Hz, 4H, PN(Me)C*H*$_2$C*H*$_2$NMe), 3.60 (m, 1H, PN(Me)CH$_2$C*H*$_2$O(OEt)), 4.02 (m, 1H, PN(Me)CH$_2$C*H*$_2$O(OEt)), 7.35 (t, $^3J_{HH}$ = 8.3 Hz, 2H, bpy), 7.95 (t, $^3J_{HH}$ = 7.5 Hz, 2H, bpy), 8.34 (d, $^3J_{HH}$ = 7.7 Hz, 2H, bpy), 8.86 (s, 2H, bpy).

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