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^{95}Mo NMR Studies on Cationic Phosphenium Complexes of Molybdenum

Hiroshi Nakazawa,*,† Yoshitaka Yamaguchi,† Katsuhiko Miyoshi,‡ and
Akira Nagasawa*,§

*Coordination Chemistry Laboratories, Institute for Molecular Science, Myodaiji,
Okazaki 444, Japan, Department of Chemistry, Faculty of Science, Hiroshima University,
Higashi-Hiroshima 739, Japan, and Department of Chemistry, Faculty of Science,
Saitama University, Urawa, Saitama 338, Japan*

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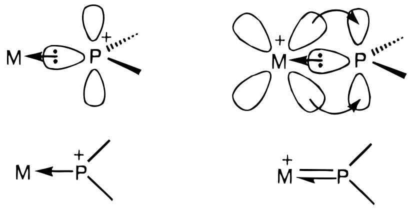
The ^{95}Mo NMR spectra of cationic molybdenum phosphenium complexes have been measured. Going from *fac*-[(bpy)(CO)$_3$Mo{$\overline{\mathrm{PN(Me)CH_2CH_2N}}$Me(OMe)}] (**1a**) to *fac*-[(bpy)(CO)$_3$Mo{$\overline{\mathrm{PN(Me)CH_2CH_2N}}$Me}]$^+$ (*fac*-**1b**) to *mer*-[(bpy)(CO)$_3$Mo{$\overline{\mathrm{PN(Me)CH_2CH_2N}}$Me}]$^+$ (*mer*-**1b**) causes deshielding of the ^{95}Mo doublet resonance (δ −1081 (**1a**), −1049 (*fac*-**1b**), −1015 (*mer*-**1b**)), an increase in the Mo−P coupling constant (193 Hz (**1a**), 264 Hz (*fac*-**1b**), 337 Hz (*mer*-**1b**)), and an increase in the line width (35 Hz (**1a**), 90 Hz (*fac*-**1b**), 300 Hz (*mer*-**1b**)). The conversion of *fac*-[(bpy)(CO)$_3$Mo{$\overline{\mathrm{PN(Me)CH_2CH_2O}}$(OMe)}] (*fac*-**2a**) into *mer*-[(bpy)(CO)$_3$Mo{$\overline{\mathrm{PN(Me)CH_2CH_2O}}$}]$^+$ (*mer*-**2b**) showed a similar trend in ^{95}Mo NMR data, though *fac*-[(bpy)(CO)$_3$Mo{$\overline{\mathrm{PN(Me)CH_2CH_2O}}$}]$^+$ was not detected in this case. *mer*-**2b** exhibits the largest Mo−P coupling constant (343 Hz) among those reported so far. These changes can be reasonably attributed to a dominant contribution from the imbalance of electron density at the Mo in the Ramsey equation due to a significant double-bond character between the molybdenum and the phosphenium phosphorus. Comparison of coupling constants between M and a phosphenium P in [(bpy)(CO)$_3$M{$\overline{\mathrm{PN(Me)CH_2CH_2N}}$Me}]$^+$ (M = Mo, W) revealed that the ratio $^1J_{\mathrm{W-P}}/^1J_{\mathrm{Mo-P}}$ is 1.67, which is very close to the ratio (1.76) reported for many series of M−phosphine (or phosphite) complexes (M = Mo, W). The ^{95}Mo NMR spectra of *cis*- and *trans*-[(bpy)(CO)$_2$Mo{$\overline{\mathrm{PN(Me)CH_2CH_2X}}$(OMe)}{$\overline{\mathrm{PN(Me)CH_2CH_2X}}$}]$^+$ (X = NMe, *cis*-**1c**, *trans*-**1c**; X = O, *cis*-**2c**, *trans*-**2c**) have also been measured; the chemical shifts are understood similarly in terms of the imbalance of electron density at Mo.

Introduction

A phosphenium cation, described as [PR$_2$$^+$], has lone-pair electrons and a vacant p orbital on phosphorus, which make it an interesting ligand toward transition metals. A bond between a transition metal and a phosphenium ligand is simply described as a resonance form of the two extreme descriptions.



A **B**

Form **A** expresses a situation in which a plus charge is located on phosphorus and the phosphenium cation coordinates to the transition metal through its lone pair, where the bond between M and P can be seen as a dative bond. Form **B** shows the state where donating a sufficient electron density from a filled d orbital of M into a vacant p orbital on P results in localization of the plus charge on M, and thus the M-P bond becomes a double bond. Cationic transition-metal phosphenium complexes^1 have been reported for several kinds of transition metals,$^{2-6}$ and it has been established that the bond between a transition metal and a phosphenium phosphorus has a significant double-bond character.

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† Institute for Molecular Science.
‡ Hiroshima University.
§ Saitama University.
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(1) Electrically neutral transition-metal complexes, described as [L$_n$MPR$_2$], can be considered as phosphenium complexes if they are thought to consist of L$_n$M$^-$ and $^+$PR$_2$. However, in this paper we focus on electrically cationic transition-metal complexes, described as [L$_n$MPR$_2$]$^+$.

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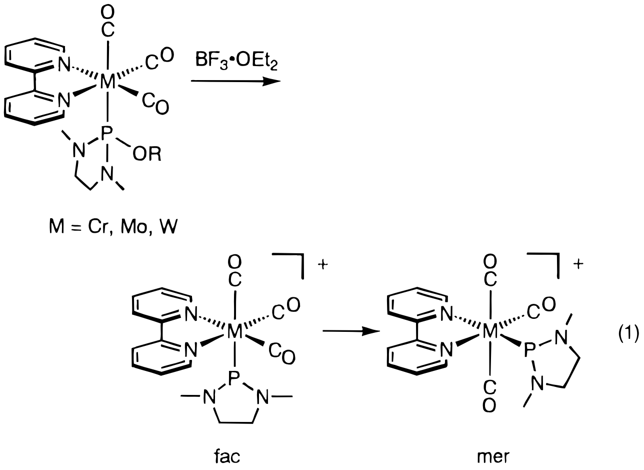
We have been studying cationic phosphenium complexes of group 6 transition metals[6a–d,f] and have reported the new preparative method shown in eq 1, where an OR group on a coordinating phosphite is abstracted as an anion by Lewis acid such as BF_3. In the reaction, ^{31}P NMR data have been very informative and diagnostic of the M-P double-bond property: the product shows a singlet at δ 230–265, which is more than 100 ppm lower in magnetic field than that for the starting complex (δ 130–150).[6c]

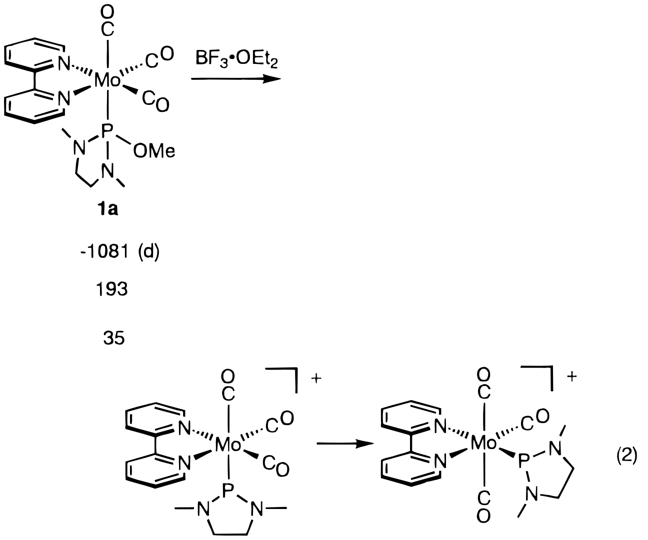


NMR chemical shifts and coupling constants have been widely employed to study metal-ligand bonding properties. Especially the development of transition-metal NMR spectroscopy has recently provided a direct probe of the metal environment[7] and enabled observation of chemical shifts and, for example, metal–phosphorus coupling constants, which are difficult to observe via ^{31}P NMR spectroscopy. Among metal NMR spectroscopies, ^{95}Mo NMR spectroscopy is well-established as a sensitive probe of the molybdenum complexes.[8]

We here report ^{95}Mo NMR data for cationic phosphenium complexes of molybdenum and consider the effect of a Mo–P double-bond character on the ^{95}Mo NMR chemical shifts, the ^{95}Mo–^{31}P coupling constants, and the line widths. This work represents the first example of a transition-metal NMR study on cationic phosphenium complexes.

Results

We already have reported that the reaction of *fac*-[(bpy)(CO)$_3$Mo{PN(Me)CH$_2$CH$_2$NMe(OMe)}] (**1a**; bpy = 2,2′-bipyridine) with BF_3·OEt_2 in CH_2Cl_2 yields a cationic phosphenium complex with a facial geometry, *fac*-[(bpy)(CO)$_3$Mo{PN(Me)CH$_2$CH$_2$NMe}]$^+$ (*fac*-**1b**), which then isomerizes gradually at room temperature to give the meridional form, *mer*-[(bpy)(CO)$_3$Mo{PN(Me)CH$_2$CH$_2$NMe}]$^+$ (*mer*-**1b**) (eq 2).[6b,c,9] The isomerization is completed within several hours, and the resulting *mer*-**1b** is stable for several days at room temperature under an inert atmosphere.



^{95}Mo NMR Data	1a	fac-1b	mer-1b
δ (ppm)	-1081 (d)	-1049 (d)	-1015 (d)
$^1J_{Mo-P}$ (Hz)	193	264	337
$W_{1/2}$ (Hz)	35	90	300

The ^{95}Mo NMR spectra have been measured for **1a** and the reaction mixture of **1a** with BF_3·OEt_2. The spectrum of **1a**, shown in Figure 1a, exhibits a doublet at δ −1081 with $^1J_{Mo-P}$ = 193 Hz. The spectrum shown in Figure 1b was obtained by Fourier transformation of FID accumulated for 6 h at 300 K just after the reaction started. Therefore, the solution subjected to the ^{95}Mo NMR measurement can be considered to contain *fac*-**1b** and *mer*-**1b**. The spectrum exhibits a doublet at δ −1049 with $^1J_{Mo-P}$ = 264 Hz and a broad singlet at about δ −1015. The spectrum shown in Figure 1c was obtained by Fourier transformation of FID accumulated for 12 h after 6 h had passed from the start of the reaction. The solution subjected to the ^{95}Mo NMR measurement which has been confirmed to have only the *mer*-**1b** species shows a doublet, though with a broad line width, at δ −1015 with $^1J_{Mo-P}$ = 337 Hz. Therefore, doublets at δ −1049 and −1015 are reasonably assigned to *fac*-**1b** and *mer*-**1b**, respectively. The ^{95}Mo NMR data (chemical shift, coupling constant, and line width) for these complexes are shown in eq 2.

Information about the lowest energy electronic transition is helpful for the discussion of ^{95}Mo NMR chemical shifts. The UV–vis spectra were thus measured for the

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[9] The counteranions of the cationic phosphenium complexes discussed in this paper may be $BF_3(OR)^-$ or BF_4^- (BF_4^- would be produced from $BF_3(OR)^-$ and BF_3 remaining unreacted). Since the ^{31}P NMR data of cationic phosphenium complexes are known to be independent of the counteranion, it seems that also ^{95}Mo NMR data would be independent of the counteranion. In this paper, a cationic phosphenium complex is described without its counteranion.

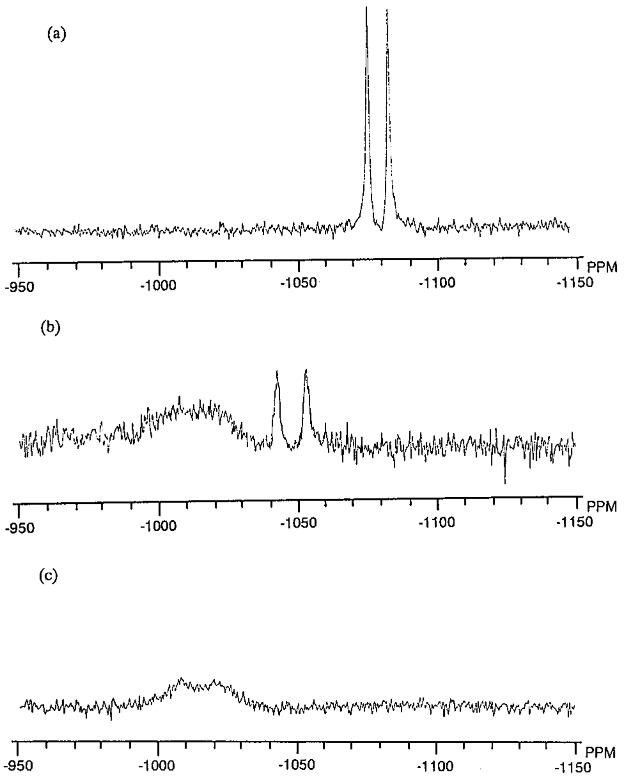
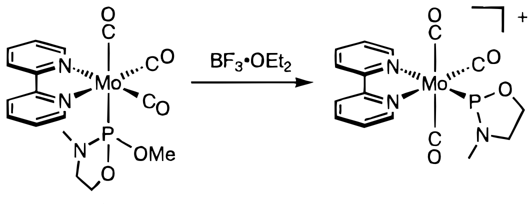


Figure 1. ^{95}Mo NMR spectra: (a) obtained for **1a**; (b) obtained by Fourier transformation of FID accumulated for 6 h just after the reaction of **1a** with $BF_3{\cdot}OEt_2$; (c) obtained by Fourier transformation of FID accumulated for 12 h after 6 h had passed from the start of the reaction.

reaction of eq 2. The lowest energy absorption band for **1a** was observed at $\lambda = 540$ nm (molar extinction coefficient $\epsilon = 1541$ L mol^{-1} cm^{-1}). Continuing the reaction shown in eq 2 caused a shift of the band to shorter wavelength and a decrease in ϵ, and finally the solution showed $\lambda = 412$ nm ($\epsilon = 245$ L mol^{-1} cm^{-1}). Therefore, it can be said that the HOMO-LUMO gap moves to higher energy on going from **1a** to *fac*-**1b** and then to *mer*-**1b**.

The reaction of *fac*-[(bpy)(CO)$_3$Mo{$\overline{\text{PN(Me)CH}_2\text{CH}_2\text{O}}$(OMe)}] (**2a**) with $BF_3{\cdot}OEt_2$ is shown in eq 3. The ^{31}P NMR measurement has already proven that in this reaction a cationic phosphenium complex with the meridional form (*mer*-**2b**) is generated, but the facial isomer is not detected even immediately after the reaction.[6f] The ^{95}Mo NMR data obtained here are shown in eq 3.



^{95}Mo NMR Data	2a	mer-2b
δ (ppm)	-1098 (d)	-986(d)
$^1J_{\text{Mo-P}}$ (Hz)	209	343
$W_{1/2}$ (Hz)	37	445

(3)

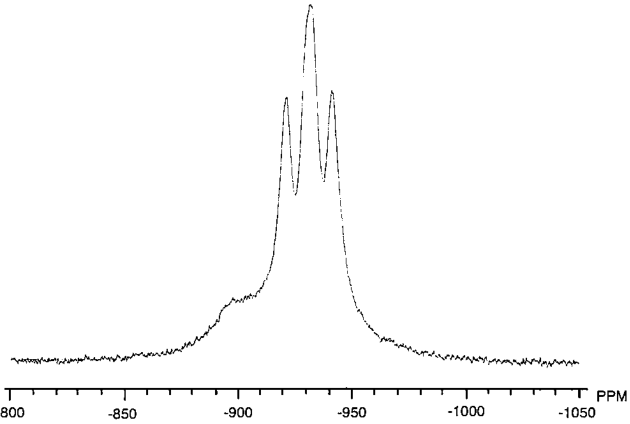
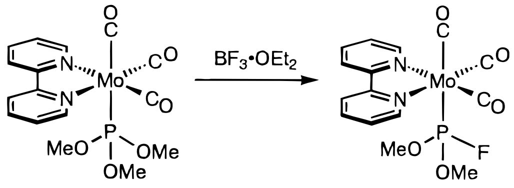


Figure 2. ^{95}Mo NMR spectrum of the reaction mixture of *mer*-**1b** with $\overline{\text{PN(Me)CH}_2\text{CH}_2\text{N}}$Me(OMe).

The reaction of *fac*-[(bpy)(CO)$_3$Mo{P(OMe)$_3$}] (**3a**) with $BF_3{\cdot}OEt_2$ does not give a cationic phosphenium complex such as [(bpy)(CO)$_3$Mo{P(OMe)$_2$}]$^+$ but yields an OMe/F exchange product, *fac*-[(bpy)(CO)$_3$Mo-{P(OMe)$_2$F}] (**3z**).[6a,b] The reaction together with the ^{95}Mo NMR data is shown in eq 4.



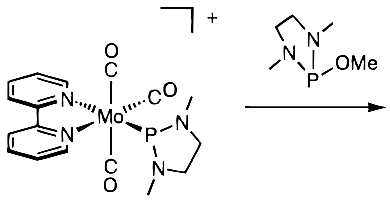
^{95}Mo NMR Data	3a	3z
δ (ppm)	-1103 (d)	-1118 (d)
$^1J_{\text{Mo-P}}$ (Hz)	209	235
$W_{1/2}$ (Hz)	24	40

(4)

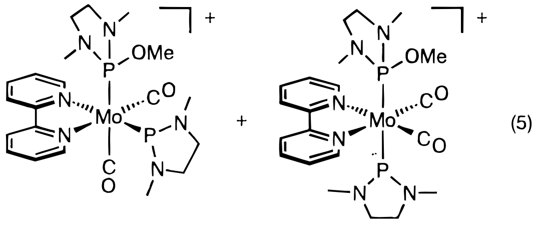
Recently we found that *mer*-[(bpy)(CO)$_3$Mo(phosphenium)]$^+$ reacts with phosphite to give [(bpy)(CO)$_2$Mo(phosphite)(phosphenium)]$^+$ by the CO/phosphite exchange reaction.[6d] Therefore, some [(bpy)(CO)$_2$Mo(phosphite)(phosphenium)]$^+$ complexes were subjected to the ^{95}Mo NMR measurements. The NMR spectrum obtained in the reaction of *mer*-**1b** with $\overline{\text{PN(Me)CH}_2\text{CH}_2\text{N}}$Me(OMe) is shown in Figure 2, which consists of a triplet at δ −931 with $J = 266$ Hz and a broad singlet at δ −897. Since it is known that *cis*-**1c** and *trans*-**1c** are in equilibrium and the ratio is 24:76,[6d] we assigned the triplet to *trans*-**1c** and the broad singlet to *cis*-**1c** (eq 5). Similar results were obtained in the reaction of *mer*-**2b** with $\overline{\text{PN(Me)CH}_2\text{CH}_2\text{O}}$(OMe) (eq 6).

Discussion

[(bpy)(CO)$_3$Mo(phosphite)] Derivatives. Many ^{95}Mo NMR data have been reported for Mo complexes with a phosphine or phosphite as a ligand.[8] The ^{95}Mo data for **1a**, **2a**, **3a**, and **3z** are reasonable compared with those reported so far. Increasing the number of N substituents on the phosphorus causes deshielding of the ^{95}Mo resonance in the order **3a** (δ −1103) < **2a** (−1098) < **1a** (−1081). Although this behavior is the opposite of what might be expected on the basis of

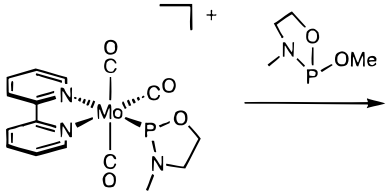


mer-1b

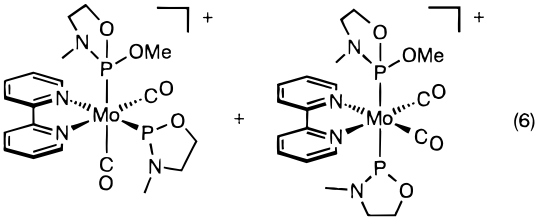


(5)

^{95}Mo NMR Data	mer-1b	cis-1c	trans-1c
δ (ppm)	-1015 (d)	-897 (s)	-931 (t)
$^1J_{Mo-P}$ (Hz)	337	——	266
$W_{1/2}$ (Hz)	300	579	294



mer-2b



(6)

^{95}Mo NMR Data	mer-2b	cis-2c	trans-2c
δ (ppm)	-986 (d)	-893 (s)	-926 (t)
$^1J_{Mo-P}$ (Hz)	343	——	280
$W_{1/2}$ (Hz)	445	700	285

electronegativity arguments, it has been found in the previous studies on a wide variety of molybdenum complexes.[8a,10–12] The Mo−P coupling constant of **2a** (209 Hz) is larger than that of **1a** (193 Hz), and that of **3z** (235 Hz) is larger than that of **3a** (209 Hz). This tendency is consistent with the earlier observation that the magnitude of $^1J_{Mo-P}$ appears to increase with increasing electronegativity of a substituent on a phosphorus.[12b,13] Coupling constants between Mo and P have been reported for a series of $Mo(CO)_{6-n}(PF_3)_n$ (n = 1−6).[14] The values are in a small range (279−290 Hz; average 285 Hz) irrespective of the number of PF_3 groups and the geometrical structures. The difference in $^1J_{Mo-P}$ between $Mo(CO)_{6-n}(PF_3)_n$ and $Mo(CO)_5\{P(OMe)_3\}$ is 66 Hz. It is interesting to note that the difference in $^1J_{Mo-P}$ between **3a** and **3z** is 26 Hz, which corresponds approximately to one-third of 66 Hz. It seems that a replacement of one OMe group on a phosphorus coordinating to Mo by one F increases $^1J_{Mo-P}$ by 22−26 Hz.

[(bpy)(CO)$_3$Mo(phosphenium)]$^+$ Derivatives. A comparison of the ^{95}Mo NMR data of the complexes shown in eq 2 revealed that going from **1a** to *fac*-**1b** to *mer*-**1b** causes deshielding of the chemical shift, an increase in the coupling constant between Mo and P, and an increase in the line width.

For a theoretical understanding of chemical shifts, the Ramsey equation ($\sigma = \sigma^d + \sigma^p$) is generally used,[15] 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[16] and is represented by the equation[15b]

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

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.

The ΔE term can often be related to the HOMO−LUMO gap, e.g., to the wavelength of the lowest frequency UV−vis transition (or absorption) λ, and a good correlation has been observed between the chemical shifts of the ^{95}Mo resonances and λ value of a series of Mo complexes.[12b,17−21] Conversion of **1a** into *fac*-**1b** and then into *mer*-**1b** accompanies a lower wavelength shift of λ, corresponding to an increase in ΔE in this order. This suggests that ΔE does not contribute dominantly to σ^p, because if so, an increase in ΔE should result in shielding of ^{95}Mo resonances.

Since a phosphenium ligand serves as a strong π-acceptor, in other words, since a bond between a transition metal and phosphenium phosphorus has a considerable double-bond character, cationic phosphe-

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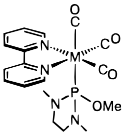
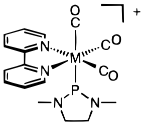
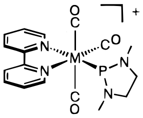
Table 1. Coupling Constants of W−P and Mo−P

M = Mo and W		 fac	 mer
$^1J_{\text{Mo-P}}$	193	264	337
$^1J_{\text{W-P}}$	335	442	561
$^1J_{\text{W-P}}/^1J_{\text{Mo-P}}$	1.74	1.67	1.66

nium Mo complexes *fac*-**1b** and *mer*-**1b**, are expected to have Mo atoms which are more electronically imbalanced than a Mo atom in **1a**. Between the two cationic phosphenium complexes, *mer*-**1b** is expected to have a greater double-bond character than *fac*-**1b** because the phosphenium ligand is *trans* to bpy in the *mer* isomer, whereas in the *fac* isomer it is *trans* to the CO ligand, also requiring strong π-back-donation. This means that the extent of the imbalance at Mo is greater for *mer*-**1b** than for *fac*-**1b**. Increasing of the double-bond character in the order **1a** < *fac*-**1b** < *mer*-**1b** causes an increase in the amount of s character in the Mo−P bond in this order. Actually, the Mo−P coupling constant increases in the order **1a** (193 Hz) < *fac*-**1b** (264 Hz) < *mer*-**1b** (337 Hz). The greater the double-bond character, i.e., the greater the imbalance in electron density at the metal nucleus, the greater the deshielding.

Although it is hard to determine quantitatively changes in the $\langle r^{-3}\rangle$ term on going from **1a** to *fac*-**1b** and *mer*-**1b**, the following is a rought estimate. Conversion of **1a** into *fac*-**1b**, corresponding to a change from a neutral to a positive complex, may cause a decrease in r, i.e. an increased $\langle r^{-3}\rangle$ term. Therefore, the deshielding in the ^{95}Mo NMR chemical shift is expected. However, conversion of *fac*-**1b** into *mer*-**1b** may result in less change in the $\langle r^{-3}\rangle$ term because of the geometrical isomerization. Therefore, it may be said with cationic phosphenium complexes that a change in the imbalance of Mo electron density rather than ΔE and $\langle r^{-3}\rangle$ terms is mainly responsible for the change in ^{95}Mo chemical shift. Only a few examples have been reported in which the delocalization of electrons from the metal atom to its ligand is the major contributor to the change in deshielding.[22−24]

Unless ligand-exchange processes are included, the line width would be related to an effective symmetry at the molybdenum nucleus. The order of electron imbalance is consistent with the order of increasing line width: **1a** (35 Hz) < *fac*-**1b** (90 Hz) < *mer*-**1b** (300 Hz).

Concerning a coupling constant between Mo and P, it should be noted that $J = 337$ Hz for *mer*-**1b** and $J = 343$ Hz for *mer*-**2b** are greater than $J = 290$ Hz for Mo(CO)$_3$(PF$_3$)$_3$,[14] which had been recognized, to our knowledge, as the largest Mo−P coupling constant reported so far.

Observation of the Mo−P coupling constants of *fac*- and *mer*-[(bpy)(CO)$_3$Mo{$\overline{\text{PN(Me)CH}_2\text{CH}_2\text{N}}$Me}]$^+$ allows us to compare $^1J_{\text{Mo−P}}$ with $^1J_{\text{W−P}}$ of the corresponding W−phosphenium complexes which have been determined from the ^{31}P NMR measurements.[6c] These values are listed in Table 1. A comprehensive study of a series of Mo(0)− and W(0)−phosphorus complexes indicates that $^1J_{\text{Mo−P}}$ and $^1J_{\text{W−P}}$ are quite related; the experimental ratio $^1J_{\text{W−P}}/^1J_{\text{Mo−P}}$ is 1.76.[11,25] The ratio for the present cationic phosphenium complexes are 1.67 for the *fac* isomer and 1.66 for the *mer* isomer, which are slightly smaller than but very close to the value of 1.76. The correlation seems to hold for the cationic phosphenium complexes as well.

[(bpy)(CO)$_2$Mo(phosphite)(phosphenium)]$^+$ Derivatives. The ^{95}Mo NMR spectra of [(bpy)(CO)$_2$Mo(phosphite)(phosphenium)]$^+$ could be obtained (eqs 5 and 6). In principle the ^{95}Mo NMR spectrum of *trans*-**1c** should exhibit a doublet of doublets, because the ^{31}P NMR spectrum shows two doublets (130.15 ppm ($^2J_{\text{PP}} = 174.7$ Hz), due to $\overline{\text{PN(Me)CH}_2\text{CH}_2\text{N}}$Me(OMe), and 242.18 ppm ($^2J_{\text{PP}} = 274.7$ Hz), due to $\overline{\text{PN(Me)CH}_2\text{CH}_2\text{N}}$Me).[6d] However, the ^{95}Mo NMR signal was observed apparently as a triplet. Although the two coupling constants were not determined accurately, both values are estimated to be in the range 220−310 Hz. Since ^{95}Mo NMR data have not been reported for Mo complexes possessing two different phosphorus-donating ligands, these are the first examples.[26] The Mo nucleus in the *cis* isomer is more deshielded than that in the *trans* isomer. This tendency is reasonably understood if the ^{95}Mo NMR chemical shifts of cationic phosphenium complexes are dominantly due to the imbalance of electron density at Mo: the *cis* isomer has lower symmetry than the *trans* isomer. The lower symmetry of the *cis* isomer is also apparent from the line width. The resonance of the *cis* isomer is about twice as broad as that of the *trans* isomer: $W_{1/2}$ (Hz) = 579 (*cis*-**1c**) vs 294 (*trans*-**1c**), 700 (*cis*-**2c**) vs 285 (*trans*-**2c**).

Conclusion

Cationic phosphenium complexes of molybdenum were studied by ^{95}Mo NMR. Going from **1a** to *fac*-**1b** to *mer*-**1b** causes deshielding of the chemical shift, an increase in the Mo−P coupling constant, and an increase in the line width. The variations in the ^{95}Mo chemical shifts, as well as the coupling constants and the line widths can be discussed in terms of the imbalance of electron density at Mo rather than of the HOMO−LUMO energy gap, employed for many Mo complexes. This imbalance seems to be due to a significant double-bond character between Mo and phosphenium phosphorus.

The changing of ^{95}Mo chemical shifts from *mer*-**1b** to *cis*-**1c** and then to *trans*-**1c** is also understood in terms of the imbalance of electron density at Mo; an increase in the imbalance from *mer*-**1b** to *cis*-**1c** causes the deshielding and a decrease in the imbalance from *cis*-**1c** to *trans*-**1c** results in the shielding.

Experimental Section

All reactions were carried out under an atmosphere of dry argon by using Schlenk tube techniques. The starting electri-

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cally neutral complexes and cationic phosphenium complexes of molybdenum in this paper were prepared according to the literature methods.[6b-d,f] A solution of CH_2Cl_2/CD_2Cl_2 (ca. 3/1) containing the desired complex(es) (0.08 mol L^{-1}) was transferred to an NMR sample tube (10 mm in diameter) under an Ar atmosphere. After the tube was capped by a septum, the solution was subjected to ^{95}Mo NMR measurement. The NMR spectra were recorded at 25 °C on Bruker ARX400 and AM400 instruments and referenced to 1 M Na_2MoO_4 in D_2O (pD 11) as the external standard. The pulse parameters were as follows: transmitter frequency 26.10 MHz, sweep width 83 333.34 Hz (=3192.85 ppm), pulse width 18.5 μs (=90° pulse), acquisition time 0.098324 s, pulse delay 0.001 s, 16 384 data points). The electronic spectra were recorded on a Hewlett-Packard 8452A instrument.

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