Reaction of Molybdenum Complexes Containing Phosphite with Boron Trihalides. Formation of Cationic Molybdenum Phosphenium Complexes

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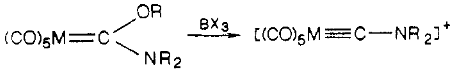
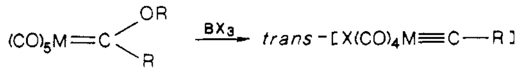
Molybdenum complexes containing a phosphite as a ligand, *fac*-$[Mo(bpy)(CO)_3\{P(OR)_3\}]$ (bpy = 2,2′-bipyridine; R = Me (**1a**), Et (**2a**), or *i*-Pr (**3a**)), react with 2 equiv of $BF_3 \cdot OEt_2$ to afford mono OR/F exchange products, *fac*-$[Mo(bpy)(CO)_3\{P(OR)_2F\}]$. In the reaction of **1a** with 2 equiv of BCl_3, double OR/Cl exchange takes place with the geometry around the Mo atom changed to give *mer*-$[Mo(bpy)(CO)_3\{P(OMe)Cl_2\}]$ (**1c**). Treatment of *fac*-$[Mo(bpy)(CO)_3\{\overline{PN(Me)CH_2CH_2N}Me(OMe)\}]$ (**6**) or *fac*-$[Mo(bpy)(CO)_3\{\overline{PN(Me)CH_2CH_2N}Me(OEt)\}]$ (**7**) with 2 equiv of $BF_3 \cdot OEt_2$ or BCl_3 results in the quantitative formation of a cationic phosphenium complex, $[Mo(bpy)(CO)_3\{\overline{PN(Me)CH_2CH_2N}Me\}]^+$ (**5**). Reaction of **5** with nucleophiles (Nu^- = Me^- or OEt^-) takes place at the phosphorus atom to generate *fac*-$[Mo(bpy)(CO)_3\{\overline{PN(Me)CH_2CH_2N}Me(Nu)\}]$ (Nu = Me (**12**), OEt (**7**)).

Introduction

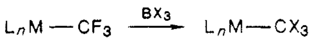
Boron trihalides may abstract an OR group or halogen on a carbon atom.[3] This reactivity has been applied to the preparation of transition-metal carbyne complexes from Fischer-type carbene complexes (eq 1 and 2)[4] and to the halogen exchange of transition-metal perfluoroalkyl carbonyl complexes (eq 3).[5] In eq 1, an OR group on the



$$(CO)_5M{=}C(OR)(NR_2) \xrightarrow{BX_3} [(CO)_5M{\equiv}C{-}NR_2]^+ \quad (1)$$



$$(CO)_5M{=}C(OR)(R) \xrightarrow{BX_3} trans\text{-}[X(CO)_4M{\equiv}C{-}R] \quad (2)$$



$$L_nM{-}CF_3 \xrightarrow{BX_3} L_nM{-}CX_3 \quad (3)$$

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. In eq 2, the reaction involves simultaneous removal of the OR group and the CO ligand trans to the carbene carbon and introduction of halogen into the complex. In eq 3, the halogen exchange reaction takes place.

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, kinds of phosphites and boron trihalides used, and temperature.[6]

$$P(OR)_3 \xrightarrow{BX_3} P(OR)_2X \xrightarrow{BX_3} P(OR)X_2 \xrightarrow{BX_3} PX_3 \quad (4)$$

However, the reaction of phosphite coordinated to a transition metal with BX_3 has not been reported. 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.

Cationic phosphenium transition-metal complexes are of current interest in both transition-metal and phosphorus chemistry.[7] However, the preparative methods of these complexes are limited to the following: (i) halogen abstraction from precursor halophosphine complexes by $AlCl_3$ or PF_5[8,9]

$$(CO)_4FePXR^1R^2 + AlCl_3(PF_5) \rightarrow [(CO)_4FePR^1R^2]^+ + AlCl_4^-(PF_6^-) \quad (5)$$

(ii) electrophilic attack of phosphenium cations on metal carbonyl complexes[9]

$$Fe(CO)_5 + \overline{PN(Me)CH_2CH_2N}Me^+ \rightarrow [(CO)_4Fe\overline{PN(Me)CH_2CH_2N}Me]^+ + CO \quad (6)$$

(iii) protic attack toward phosphite complexes[10]

$$[Mo\{P(OMe)_3\}_6] + H^+ \rightarrow [Mo\{P(OMe)_3\}_5\{P(OMe)_2\}]^+ + HOMe \quad (7)$$

Thus, we have undertaken a study of reactions of phosphite-coordinated transition-metal complexes with boron trihalides in a hope of preparing a cationic phosphenium complex. Herein is described the reactions of *fac*-$[Mo(bpy)(CO)_3(phosphite)]$ (bpy = 2,2′-bipyridine) and related complexes with $BF_3 \cdot OEt_2$ or BCl_3. A part of this work has been previously communicated.[11]

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(3) See, for example: Fieser, L. F.; Fieser, M. In *Reagents for Organic Synthesis*; Wiley: New York: 1967; Vol. 1, p 66; 1969; Vol. 2, p 33; 1974; Vol. 4, p 42.

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Table I. IR and NMR Data[a]

	IR ν(CO),[b] cm^{-1}	^{1}H NMR,[c] ppm	^{31}P{^{1}H} NMR,[d] ppm
fac-[Mo(bpy)(CO)$_3${P(OMe)$_3$}] (**1a**)	1929, 1831, 1795	9.13–7.28 (m, 8 H, bpy) 3.30 (d, J = 10.0 Hz, 9 H, CH$_3$)	153.3 (s)
fac-[Mo(bpy)(CO)$_3${P(OEt)$_3$}] (**2a**)	1925, 1826, 1792	9.10–7.22 (m, 8 H, bpy) 3.67 (m, 6 H, CH$_2$) 0.93 (t, J = 7.0 Hz, 9 H, CH$_3$)	149.1 (s)
fac-[Mo(bpy)(CO)$_3${P(O-*i*-Pr)$_3$}] (**3a**)	1920, 1822, 1790	9.10–7.27 (m, 8 H, bpy) 4.53 (m, 3 H, CH) 0.97 (d, J = 6.0 Hz, 18 H, CH$_3$)	147.8 (s)
fac-[Mo(bpy)(CO)$_3${P(OMe)$_2$F}] (**1b**)	1939, 1844, 1805	9.12–7.32 (m, 8 H, bpy) 3.46 (d, J = 10.0 Hz, 6 H, CH$_3$)	151.9 (d, J = 1171 Hz)
fac-[Mo(bpy)(CO)$_3${P(OEt)$_2$F}] (**2b**)	1937, 1842, 1801	9.12–7.33 (m, 8 H, bpy) 3.88 (m, 4 H, CH$_2$) 1.02 (t, J = 7.0 Hz, 6 H, CH$_3$)	149.8 (d, J = 1169 Hz)
fac-[Mo(bpy)(CO)$_3${P(O-*i*-Pr)$_2$F}] (**3b**)	1934, 1839, 1800	9.10–7.30 (m, 8 H, bpy) 4.60 (m, 2 H, CH) 0.97 (d, J = 6.0 Hz, 12 Hz, CH$_3$)	152.0 (d, J = 1168 Hz)
mer-[Mo(bpy)(CO)$_3${P(OMe)Cl$_2$}] (**1c**)	1960, 1880, 1840	9.23–7.60 (m, 8 H, bpy) 3.85 (d, J = 14.8 Hz, 2 H, CH$_3$) 3.62 (d, J = 12.1 Hz, 1 H, CH$_3$)	146.0 (s)
fac-[Mo(bpy)(CO)$_3${P(OEt)$_2$Et}] (**4**)	1921, 1823, 1790	9.27–7.30 (m, 8 H, bpy)	181.5 (s)
[Mo(bpy)(CO)$_3${$\overline{\text{PN(Me)CH}_2\text{CH}_2\text{N}}$Me}]$^+$ (**5**)			268.2 (s)[b]
fac-[Mo(bpy)(CO)$_3${$\overline{\text{PN(Me)CH}_2\text{CH}_2\text{N}}$Me(OMe)}] (**6**)	1916, 1818, 1790 1902, 1801, 1778[e]	9.12–7.23 (m, 8 H, bpy) 3.01 (d, J = 12.5 Hz, 3 H, OCH$_3$) 2.82 (m, 4 H, CH$_2$) 2.32 (d, J = 13.0 Hz, 6 H, NCH$_3$)	138.0 (s)[b]
fac-[Mo(bpy)(CO)$_3${$\overline{\text{PN(Me)CH}_2\text{CH}_2\text{N}}$Me(OMe)}]·2BF$_3$ (**6·2BF$_3$**)	1953, 1846, 1803[e]		
fac-[Mo(bpy)(CO)$_3${$\overline{\text{PN(Me)CH}_2\text{CH}_2\text{N}}$Me(OEt)}] (**7**)	1916, 1816, 1788	9.10–7.33 (m, 8 H, bpy) 3.17–2.57 (m, 6 H, NCH$_2$ and OCH$_2$) 2.33 (d, J = 13.0 Hz, 6 H, NCH$_3$) 0.72 (t, J = 7.0 Hz, 3 H, OCH$_2$CH_3)	134.9 (s)[b]
fac-[Mo(phen)(CO)$_3${$\overline{\text{PN(Me)CH}_2\text{CH}_2\text{N}}$Me(OMe)}] (**8**)	1918, 1818, 1790	9.56–7.50 (m, 8 H, phen)[f] 2.87 (d, J = 9.7 Hz, 3 H, OCH$_3$) 2.73 (m, 4 H, CH$_2$) 2.10 (d, J = 10.4 Hz, 6 H, NCH$_3$)	138.1 (s) [f]
[Mo(phen)(CO)$_3${$\overline{\text{PN(Me)CH}_2\text{CH}_2\text{N}}$Me}]$^+$ (**9**)			269.0 (s)[b]
fac-[Mo(bpy)(CO)$_3${P(NEt$_2$)(OMe)$_2$}] (**10**)	1925, 1830, 1796	9.20–7.26 (m, 8 H, bpy) 3.32 (d, J = 10.0 Hz, 6 H, OCH$_3$) 3.05 (m, 4 H, NCH_2CH$_3$) 0.80 (t, J = 7.0 Hz, 6 H, NCH$_2$CH_3)	154.3 (s)[b]
fac-[Mo(bpy)(CO)$_3${P(NEt$_2$)$_2$(OMe)}] (**11**)	1931, 1835, 1799	9.20–7.27 (m, 8 H, bpy) 3.14 (d, J = 10.0 Hz, 3 H, OCH$_3$) 2.83 (m, 4 H, NCH_2CH$_3$) 0.83 (t, J = 7.0 Hz, 6 H, NCH$_2$CH_3)	156.7 (s)
fac-[Mo(bpy)(CO)$_3${$\overline{\text{PN(Me)CH}_2\text{CH}_2\text{N}}$Me(Me)}] (**12**)	1917, 1820, 1788	9.27–7.30 (m, 8 H, bpy) 2.70 (m, 4 H, CH$_2$) 2.20 (d, J = 16.0 Hz, 6 H, NCH$_3$) 1.06 (d, J = 2.2 Hz, 3 H, PCH$_3$)	134.1 (s)[b]

[a] At room temperature. [b] In CH$_2$Cl$_2$ solution. [c] In acetone-d_6 solution. [d] In acetone solution unless otherwise noted. [e] KBr disk. [f] In CD$_2$Cl$_2$ solution.

Results and Discussion

Reaction of *fac*-[Mo(bpy)(CO)$_3${P(OR)$_3$}] with BF$_3$·OEt$_2$. The treatment of *fac*-[Mo(bpy)(CO)$_3${P(OR)$_3$}] (R = Me (**1a**), Et (**2a**), and *i*-Pr (**3a**)) with 2 equiv of BF$_3$·OEt$_2$ at −78 °C yielded a dark red powder in each case. The spectroscopic data are summarized in Table I. The infrared spectrum of the product shows three absorptions in the ν_{CO} region, which are 9–17 cm^{-1} higher in frequency than those for the starting complex. The ^{1}H NMR data indicate that the product possesses only two OR groups. In the ^{31}P{^{1}H} NMR spectrum, one singlet is observed at about 150 ppm for the starting complex, while the product gives rise to a doublet with a coupling constant of about 1170 Hz, indicating that the product has a P–F bond. The existence of a P–F bond was also confirmed by measurement of ^{19}F NMR spectrum of **1b**; a doublet with a coupling constant of 1173 Hz was observed at −48.9 ppm relative to CFCl$_3$. These spectroscopic data, together with elemental analyses, ensure the formation of mono OR/F exchange products, *fac*-[Mo(bpy)(CO)$_3${P(OR)$_2$F}].

fac-[Mo(bpy)(CO)$_3${P(OR)$_3$}] $\xrightarrow{2\text{BF}_3\cdot\text{OEt}_2}$
1a: R = Me
2a: R = Et
3a: R = *i*-Pr
fac-[Mo(bpy)(CO)$_3${P(OR)$_2$F}] (8)
1b:R = Me
2b: R = Et
3b: R = *i*-Pr

The above reaction proceeds favorably when the molybdenum phosphite complexes are treated with 2 equiv of BF$_3$·OEt$_2$ at −78 °C. We then examined the effect of the reaction temperature and the amount of BF$_3$·OEt$_2$. When the reaction was carried out at room temperature, the system became complicated. When the molybdenum

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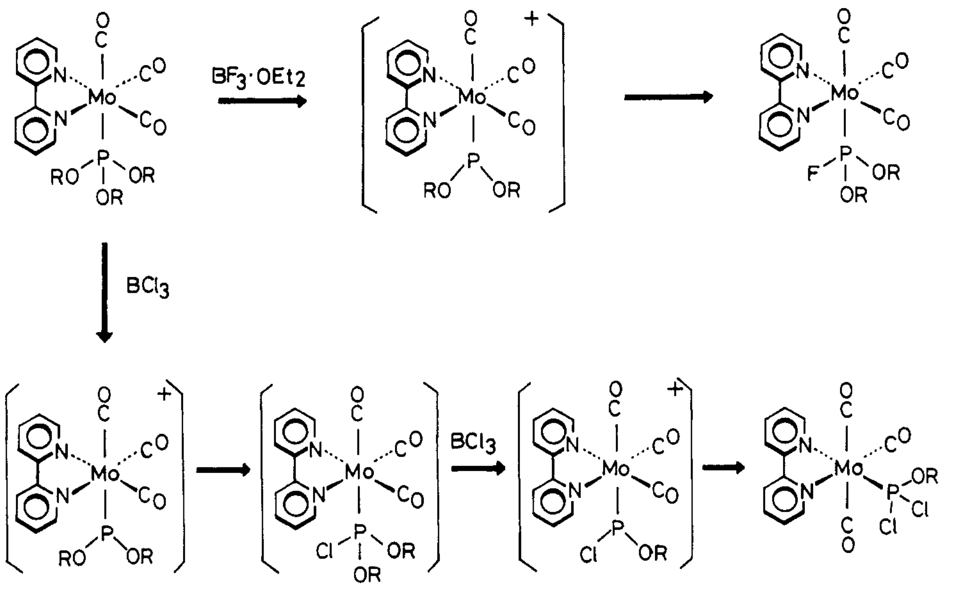
Scheme I



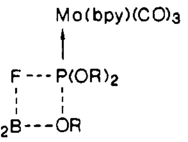
phosphite complexes were treated with more or less than 2 times an equimolar amount of $BF_3 \cdot OEt_2$, a lowering in the yield of the mono OR/F exchange product was observed.

Molybdenum complexes containing a phosphonite or a fluorophosphite in place of a phosphite were also allowed to react with 2 equiv of $BF_3 \cdot OEt_2$ at −78 °C. The reaction of *fac*-[Mo(bpy)(CO)$_3${P(OEt)$_2$Et}] (4) did not produce any OR/F exchange products, and the main Mo-containing product was [Mo(bpy)(CO)$_4$]. Similarly, in the reaction of *fac*-[Mo(bpy)(CO)$_3${P(OMe)$_2$F}] (**1b**), [Mo(bpy)(CO)$_4$] was the main product and *fac*-[Mo(bpy)(CO)$_3${P(OMe)F$_2$}] did not form. The presence of three OR groups on the phosphorus seems to be necessary for the above OR/F exchange.

$$fac\text{-}[\mathrm{Mo(bpy)(CO)_3\{P(OEt)_2Et\}}] \xrightarrow{2BF_3\cdot OEt_2} [\mathrm{Mo(bpy)(CO)_4}] \quad (9)$$

$$fac\text{-}[\mathrm{Mo(bpy)(CO)_3\{P(OEt)_2F\}}] \xrightarrow{2BF_3\cdot OEt_2} [\mathrm{Mo(bpy)(CO)_4}] \quad (10)$$

Now let us consider the OR/F exchange reaction mechanism. There are two possible pathways. One is the concerted mechanism via the intermediate like A. The

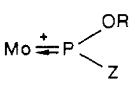


A

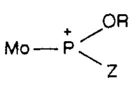
$[\mathrm{Mo(bpy)(CO)_3\{P(OR)_2\}}]^+$

B

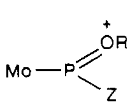
other is to involve an ionic intermediate containing a cationic phosphenium ligand (see B), which is generated by the abstraction of an OR group on the phosphorus as an anion by BX_3. The cationic intermediate can be described in the following resonance forms. B1 corresponds



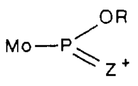
B1



B2



B3



B4

to a cationic complex containing the three-electron donor terminal phosphide as a ligand. The complex can effectively be considered as containing an M=P double bond. B2 corresponds to a transition-metal phosphenium complex where a phosphenium cation coordinates to a transition metal through its lone pair. When Z is OR, B3 is equivalent to B4, but when Z is alkyl, B4 may not contribute to the resonance. When Z is a strong electron-withdrawing group like F, both B2 and B4 probably contribute less to the resonance of the cationic intermediate, resulting in the facile decomposition of the intermediate before nucleophilic attack of X^- on the phosphorus atom. Although B has not been detected spectroscopically, we favor the mechanism via a cationic intermediate B (see Scheme I) because of the experimental results that the phosphite complexes **1a**, **2a**, and **3a** undergo OR/F exchange reactions, while the phosphonite complex **4** and the fluorophosphite complex **1b** do not undergo OR/F exchange reactions, together with the results mentioned later that an OR-abstracted cationic complex, [Mo(bpy)(CO)$_3${PN(Me)CH$_2$CH$_2$NMe}]$^+$, was detected in the reaction of *fac*-[Mo(bpy)(CO)$_3${PN(Me)CH$_2$CH$_2$NMe(OMe)}] with $BF_3 \cdot OEt_2$. Shriver et al. proposed the dihalocarbene complexes as an intermediate in the halogen exchange reaction of transition-metal perfluoroalkyl carbonyl complexes with BX_3 (eq 3).[5]

Reaction of *fac*-[Mo(bpy)(CO)$_3${P(OMe)$_3$}] (1a) with BCl$_3$. The bond energy of P–F in PF_3 (490 kJ/mol) is greater than that of P–Cl in PCl_3 (326 kJ/mol),[12] implying a possibility of detecting a cationic intermediate, B, in the reaction with BCl_3 in place of BF_3. Then, we examined the reaction of **1a** with 2 equiv of BCl_3 at −78 °C. On the basis of spectroscopic data (Table I) and elemental analysis data, it was found that the main product (yield 74%) was *mer*-[Mo(bpy)(CO)$_3${P(OMe)Cl$_2$}] (**1c**), where the two OMe groups were displaced by two Cl atoms and the geometry around the Mo atom changed from facial to meridional.

$$\underset{\mathbf{1a}}{fac\text{-}[\mathrm{Mo(bpy)(CO)_3\{P(OMe)_3\}}]} \xrightarrow{2BCl_3} \underset{\mathbf{1c}}{mer\text{-}[\mathrm{Mo(bpy)(CO)_3\{P(OMe)Cl_2\}}]} \quad (11)$$

The geometrical rearrangement is evidenced by the $^{13}C\{^1H\}$ NMR spectra (Table II). The spectrum for **1a** exhibits three singlets and two doublets with small coupling constants in the bpy region and two doublets in the terminal CO region, which is consistent with a facial geometry. On the other hand, the spectrum for **1c** exhibits four singlets

Table II. $^{13}C\{^1H\}$ NMR Data[a]

	CO	bpy	OCH_3
fac-$[Mo(bpy)(CO)_3\{P(OMe)_3\}]$ (**1a**)	226.2 (d, J = 14.0 Hz) 213.7 (d, J = 64.9 Hz)	154.7 (d, J = 1.0 Hz) 152.2 (d, J = 2.1 Hz) 135.9 (s) 124.0 (s) 121.7 (s)	49.5 (d, J = 1.6 Hz)
mer-$[Mo(bpy)(CO)_3\{P(OMe)Cl_2\}]$ (**1c**)	222.1 (s) 221.8 (s) 219.8 (s)	154.7 (s) 154.4 (d, J = 47.5 Hz) 152.6 (d, J = 13.6 Hz) 152.5 (d, J = 6.8 Hz) 138.4 (d, J = 108.5 Hz) 137.4 (s) 125.5 (d, J = 27.1 Hz) 125.2 (s) 123.3 (d, J = 61.8 Hz) 122.6 (s)	54.7 (d, J = 20.3 Hz)

[a] At room temperature. Chemical shifts in ppm. In THF-d_8 solution.

and six doublets in the bpy region and three singlets in the terminal CO region, indicating a meridional configuration. If the $P(OMe)Cl_2$ ligand rotates freely along the Mo–P bond, then two carbonyl carbons cis to the both nitrogen atoms of the coordinating bpy would be magnetically equivalent. The $^{13}C\{^1H\}$ NMR spectrum actually differentiates these two. In the ^1H NMR spectrum, two sets of doublets assigned to methoxy hydrogens are observed with a 1:2 intensity ratio. Therefore, some intramolecular interaction between one of the carbonyl groups cis to bpy nitrogens and one or two hydrogen(s) of the OCH_3 group on the phosphorus atom is expected even in solution at room temperature.

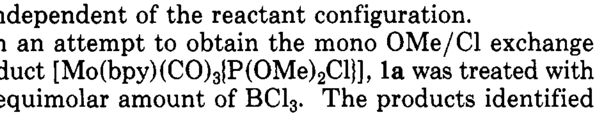
The geometrical rearrangement from facial to meridional may be explained in terms of the trans influence of the phosphorus ligands. That is, $P(OMe)Cl_2$ requires strong back-donation from a filled Mo d orbital, so it prefers situating trans to bpy rather than locating trans to a CO ligand which also requires strong back-donation.

The reaction of **1c** with an excess of NaOMe yielded **1a**, where two Cl atoms on the phosphorus are replaced by two OMe groups and the configuration around the Mo atom changed from meridional to facial. Therefore, it follows

$$\underset{\mathbf{1c}}{mer\text{-}[Mo(bpy)(CO)_3\{P(OMe)Cl_2\}]} \xrightarrow{\text{excess NaOMe}} \underset{\mathbf{1a}}{fac\text{-}[Mo(bpy)(CO)_3\{P(OMe)_3\}]} \quad (12)$$

that the configuration of the reaction product depends on the nature of the coordinating phosphorus compound and is independent of the reactant configuration.

In an attempt to obtain the mono OMe/Cl exchange product $[Mo(bpy)(CO)_3\{P(OMe)_2Cl\}]$, **1a** was treated with an equimolar amount of BCl_3. The products identified were **1c** (25%), $[Mo(bpy)(CO)_4]$ (20%), and free $P(OMe)_2Cl$ (25%). Although the monosubstituted complex $[Mo(bpy)(CO)_3\{P(OMe)_2Cl\}]$ was not obtained, it can be considered that $[Mo(bpy)(CO)_3\{P(OMe)_2Cl\}]$ forms momentarily from **1a** and BCl_3, but it is so reactive that it in part reacts further with the BCl_3 still present in solution to give **1c** and in part decomposes to give $[Mo(bpy)(CO)_4]$, releasing free $P(OMe)_2Cl$.



(13)

These OR/Cl exchanges mentioned above may take place via a cationic intermediate (see Scheme I).

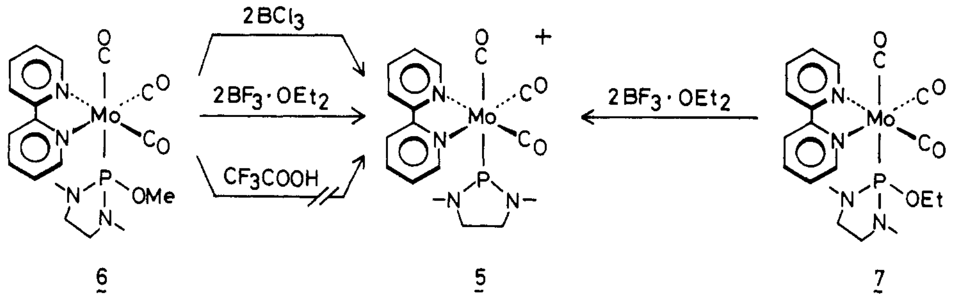
Formation of $[Mo(bpy)(CO)_3\{\overline{PN(Me)CH_2CH_2N}Me\}]^+$ (5). In order to obtain some evidence for the formation of molybdenum phosphenium complexes, a molybdenum complex containing a diaminophosphite in place of a phosphite as a ligand was treated with BX_3. In general, transition-metal alkylidene complexes are more stable when a substituent on a carbene carbon is an alkoxy group than when it is an alkyl group and are more stable when it is an amino group than when it is an alkoxy group. If this tendency holds for transition-metal phosphenium complexes, it seems to be appropriate to examine the reaction of *fac*-$[Mo(bpy)(CO)_3\{\overline{PN(Me)CH_2CH_2N}Me(OMe)\}]$ (**6**).

The reaction of **6** with 2 equiv of $BF_3\cdot OEt_2$ in CH_2Cl_2 at −78 °C resulted in the formation of a dark red powder. The elemental analysis data suggest a 1:2 adduct of **6** with BF_3. The powder is insoluble in CH_2Cl_2 and benzene but soluble in coordinating solvents such as Et_2O or THF. The IR signals of the KBr disk for the product (ν_{CO} = 1953, 1846, and 1803 cm^{-1}) are definitely different from those for **6** (ν_{CO} = 1902, 1801, and 1778 cm^{-1}). However, the IR data of the product in THF are identical with those of **6** in THF, indicating that **6** is re-formed in THF solution. Therefore, two BF_3 molecules in $\mathbf{6}\cdot 2BF_3$ seem to interact with the lone pair of the oxygen and/or nitrogen(s) of the coordinating $\overline{PN(Me)CH_2CH_2N}Me(OMe)$ ligand. The high-frequency shift in the ν_{CO} region is consistent with the above postulate.

The dark red precipitate was suspended in dichloromethane and stirred for ca. 1 h at room temperature, and the solution became homogeneous. The $^{31}P\{^1H\}$ NMR of the solution exhibits only one singlet at 268.2 ppm. The low-field resonance indicates the formation of a cationic phosphenium complex, $[Mo(bpy)(CO)_3\{\overline{PN(Me)CH_2CH_2N}Me\}]^+$ (**5**). The $^{31}P\{^1H\}$ NMR chemical shifts reported already for cationic phosphenium complexes have similar values;[7] 311 ppm for $[(CO)_4Fe\{P(NMe_2)_2\}]^+$, 307.6 ppm for $[(CO)_4Fe\{P(NEt_2)_2\}]^+$, 311.3 ppm for $[(CO)_4Fe\{P(N(i\text{-}Pr)_2)_2\}]^+$, 349.7 ppm for $[(CO)_4Fe\{P(N(SiMe_3)_2)_2\}]^+$, 441.5 ppm for $[(CO)_4Fe\{P(NMe_2)(t\text{-}Bu)\}]^+$, 300 ppm for $[(CO)_4Fe\{\overline{PN(Me)CH_2CH_2N}Me\}]^+$, and 286.8 ppm for $[(CO)_4Fe\{P(NMe_2)Cl\}]^+$.

The quantitative conversion to **5** is evidenced by the complete disappearance of the $^{31}P\{^1H\}$ resonance of **6** (δ 138.0 ppm) and its replacement by a singlet at 268.2 ppm. The formation of a coordinating phosphenium cation is caused presumably by the heterolitic P–O bond cleavage by BF_3. The treatment of **6** with 1 equiv of BF_3 led to no change in appearance and no IR change, indicating that

Scheme II



2 equiv of BF_3 is necessary to abstract one OR^- group from coordinating $PN(Me)CH_2CH_2N(OMe)$ in **6**.

The reaction of *fac*-[Mo(bpy)$(CO)_3${$PN(Me)CH_2CH_2NMe(OEt)$}] (**7**) with 2 equiv of $BF_3 \cdot OEt_2$ was also examined in the same manner as those for **6**. The $^{31}P\{^1H\}$ NMR of the resulting homogeneous solution showed exactly the same chemical shift (δ 268.2 ppm) as that obtained in the reaction of **6**. This indicates that the product does not contain Me nor Et group, consistent with the formation of **5**.

The OR^- abstraction by $BF_3 \cdot OEt_2$ also took place for a related complex, *fac*-[Mo(phen)$(CO)_3${$PN(Me)CH_2CH_2NMe(OMe)$}] (**8**). The $^{31}P\{^1H\}$ NMR of the product showed a singlet at 269.0 ppm, indicating the formation of [Mo(phen)$(CO)_3${$PN(Me)CH_2CH_2NMe$}]$^+$ (**9**).

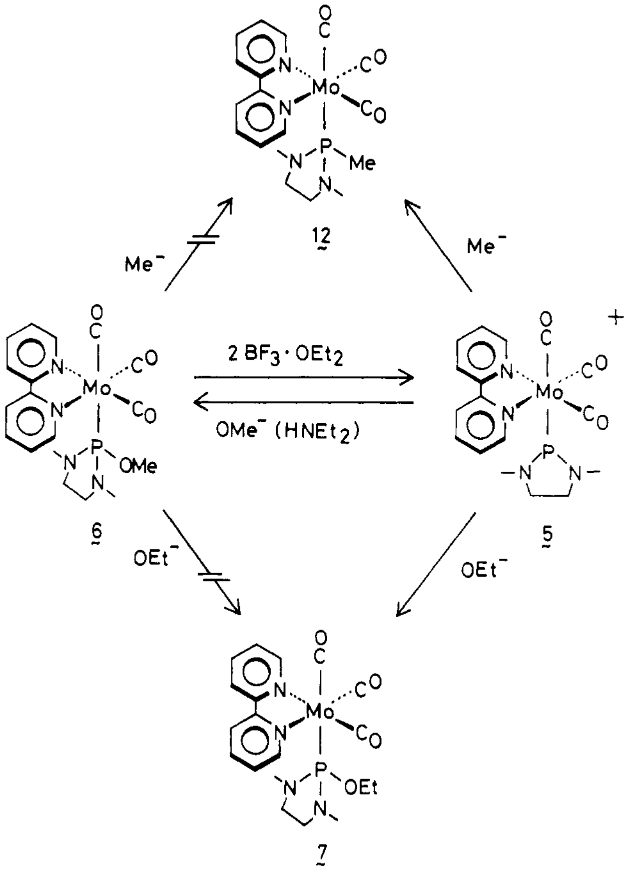
Complexes **5** and **9** are stable at room temperature for at least 1 day but are very sensitive toward air. Several trials to isolate **5** and **9** in the solid state were unsuccessful. Treatment of **6** with BCl_3 in place of $BF_3 \cdot OEt_2$ also resulted in the formation of **5** together with some other byproducts.

Since Muetterties et al.[10] reported the P–O bond cleavage for [M{$P(OMe)_3$}$_6$] (M = Mo, W) by protic attack to give [Mo{$P(OMe)_3$}$_5${$P(OMe)_2$}]$^+$, we examined the reaction of **6** with CF_3COOH. No indication of the formation of a cationic phosphenium complex was observed in our system, though some complicated reactions took place.

The formation reactions of **5** are summarized in Scheme II. The geometry of **5** around the Mo atom is not yet established. The facial configuration of the products in the reaction of **5** with some Lewis bases (vide infra) makes a facial configuration most plausible for **5**, but fluxional behavior cannot be ruled out. In Schemes II and III, **5** is tentatively described as a facial configuration.

Reaction of *fac*-[Mo(bpy)$(CO)_3${$P(NEt_2)(OMe)_2$}] (10) and *fac*-[Mo(bpy)$(CO)_3${$P(NEt_2)_2(OMe)$}] (11) with $BF_3 \cdot OEt_2$. It was found that a cationic phosphenium molybdenum complex is stable in solution when the substituent on the phosphorus is a chelated diamino group and unstable when the substituents are alkoxy groups only. Thus we tried the reactions of **10** and **11** with 2 equiv of $BF_3 \cdot OEt_2$ in the same manner as those for **6**. The products were found very complicated according to $^{31}P\{^1H\}$ NMR measurements. Therefore, neither an aminoalkoxyphosphenium complex nor an unchelated diaminophosphenium complex is stable in solution at room temperature. The chelate effect may play an important role in addition to amino substituents on the phosphorus in stabilizing a cationic phosphenium complex like **5**.

Scheme III



Reactivity of 5. Although electrophilic character is expected for cationic phosphenium complexes, no experimental evidence has been reported until recently.[13] We examined the reactions of **5** with some typical nucleophiles, Me^-, OEt^-, and $HNEt_2$, and found **5** to generate **12**, **7**, and **6**, respectively (Scheme III). The reactant **5** used in these reactions has been generated in solution from **6** and 2 equiv of $BF_3 \cdot OEt_2$ as described earlier. In the reaction with $HNEt_2$, **6** containing an OMe group was unexpectedly obtained from **5** and $HNEt_2$, both of which have no OMe group. **6** may be formed from the reaction of **5** with OMe^- which is released by the attack of $HNEt_2$ on the $BF_3(OMe)^-$ present. In the reaction of 5 with Me^- or OEt^-, there is a possibility that a trace amount of **6** still present in solution may react with the Lewis bases to give **12** or **7**. Thus, we examined also the reactions of **6** with LiMe and NaOEt and confirmed that **12** and **7** were not obtained by the direct reaction of **6**. Therefore, it was established that **5** is susceptible to nucleophilic attack at the phosphorus atom.

It is known that cationic carbonyl complexes react with OR^- to give alkoxy carbonyl complexes.[14] **5** can be re-

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garded as a cationic carbonyl complex. In this case, nonetheless, OR$^-$ and R$^-$ selectively attack the phosphorus atom but not the carbonyl carbon.

Experimental Section

General Remarks. All reactions were carried out under an atmosphere of dry nitrogen by using Schlenk tube technique. All solvents used were purified by distillation: Et$_2$O, THF, benzene, toluene, xylene, and hexane were distilled from sodium metal, and CH$_2$Cl$_2$ was distilled from P$_2$O$_5$. All solvents were stored under a nitrogen atmosphere. [Mo(bpy)(CO)$_4$] and [Mo(phen)(CO)$_4$] were prepared by the reported methods.[15] *fac*-[Mo(bpy)(CO)$_3${P(OMe)$_3$}], *fac*-[Mo(bpy)(CO)$_3${P(OEt)$_3$}], and *fac*-[Mo(bpy)(CO)$_3${P(O-*i*-Pr)$_3$}] were prepared according to the literature methods.[16] Phosphorus compounds were prepared according to the published methods: $\overline{\mathrm{PN(Me)CH_2CH_2N}}\mathrm{Me(OMe)}$[17] and P(OEt)$_2$Et.[18]

IR spectra were recorded on a Shimadzu FTIR-4000 spectrometer. JEOL PMX-60 and FX-100 spectrometers were used to obtain ^{1}H NMR and ^{31}P NMR spectra, respectively. ^{13}C NMR spectra were measured on a JEOL GX-270 spectrometer. ^{1}H NMR and ^{13}C NMR data were referred to (CH$_3$)$_4$Si, and ^{31}P NMR data were referred to 85% H$_3$PO$_4$.

***fac*-[Mo(bpy)(CO)$_3${P(OMe)$_2$F}] (1b).** A solution of *fac*-[Mo(bpy)(CO)$_3${P(OMe)$_3$}] (**1a**) (522 mg, 1.13 mmol) in CH$_2$Cl$_2$ (13 mL) was cooled to −78 °C, and BF$_3$·OEt$_2$ (280 μL, 2.28 mmol) was added. The mixture was allowed to warm to room temperature. After several hours the mixture was concentrated to 5 mL, and 10 mL of ether was added to give a dark red powder, which was filtered, washed with ether and hexane, and dried in vacuo. Thus obtained was *fac*-[Mo(bpy)(CO)$_3${P(OMe)$_2$F}] (**1b**) (255 mg, 0.79 mmol, 70%). Anal. Calcd for C$_{15}$H$_{14}$FMoN$_2$O$_5$P: C, 40.20; H, 3.15; N, 6.25. Found: C, 40.60, H, 2.91; N, 6.08.

***fac*-[Mo(bpy)(CO)$_3${P(OEt)$_2$F}] (2b).** A solution of *fac*-[Mo(bpy)(CO)$_3${P(OEt)$_3$}] (**2a**) (272 mg, 0.54 mmol) in CH$_2$Cl$_2$ (10 mL) was cooled to −78 °C, and BF$_3$·OEt$_2$ (133 μL, 1.08 mmol) was then added. The mixture was allowed to warm to room temperature. After several hours the mixture was put on a silica gel column and eluted with CH$_2$Cl$_2$. The first eluted orange fraction containing [Mo(bpy)(CO)$_4$] was discarded, and the second violet fraction was collected and concentrated. Hexane was added to the solution to afford a dark red powder, which was filtered, washed with hexane, and dried in vacuo. Thus obtained was *fac*-[Mo(bpy)(CO)$_3${P(OEt)$_2$F}] (**2b**) (129 mg, 0.27 mmol, 50%). Anal. Calcd for C$_{17}$H$_{18}$FMoN$_2$O$_5$P: C, 42.87; H, 3.81; N, 5.88. Found: C, 42.63; H, 3.75; N, 5.85.

***fac*-[Mo(bpy)(CO)$_3${P(O-*i*-Pr)$_2$F}] (3b).** A solution of *fac*-[Mo(bpy)(CO)$_3${P(O-*i*-Pr)$_3$}] (**3a**) (254 mg, 0.47 mmol) in CH$_2$Cl$_2$ (12 mL) was cooled to −78 °C, and BF$_3$·OEt$_2$ (116 μL, 0.94 mmol) was added. The mixture was allowed to warm to room temperature. After several hours the mixture was put on a silica gel column and eluted with CH$_2$Cl$_2$. The second fraction collected was concentrated, and hexane was added to afford a dark red powder, which was filtered, washed with hexane, and dried in vacuo. Thus obtained was *fac*-[Mo(bpy)(CO)$_3${P(O-*i*-Pr)$_2$F}] (47 mg, 0.09 mmol, 20%). Anal. Calcd for C$_{19}$H$_{22}$FMoN$_2$O$_5$P: C, 45.25; H, 4.40; N, 5.55. Found: C, 46.08; H, 4.49; N, 5.58.

***mer*-[Mo(bpy)(CO)$_3${P(OMe)Cl$_2$}] (1c).** A solution of *fac*-[Mo(bpy)(CO)$_3${P(OMe)$_3$}] (**1a**) (509 mg, 1.11 mmol) in CH$_2$Cl$_2$ (6 mL) was cooled to −78 °C, and BCl$_3$ (2.3 mL of BCl$_3$, 1.0 M hexane solution, 2.3 mmol) was added. After 2 h an orange precipitate formed, which was filtered, washed with CH$_2$Cl$_2$ and hexane, and dried in vacuo. Thus obtained was *mer*-[Mo(bpy)(CO)$_3${P(OMe)Cl$_2$}] (**1c**) (385 mg, 0.82 mmol, 74%). Anal. Calcd for C$_{14}$H$_{11}$Cl$_2$MoN$_2$O$_4$P: C, 35.83; H, 2.35; N, 5.97; Cl, 15.14. Found: C, 35.94; H, 2.62; N, 5.91; Cl, 15.98.

Reaction of *mer*-[Mo(bpy)(CO)$_3${P(OMe)Cl$_2$}] (1c) with NaOMe. To a solution of *mer*-[Mo(bpy)(CO)$_3${P(OMe)Cl$_2$}] (**1c**) (175 mg, 0.37 mmol) in THF (10 mL) was added NaOMe (200 mg, 3.70 mmol). After being stirred at room temperature for several hours, the resulting purple solution was filtered to remove unreacted NaOMe and NaCl formed, and the filtrate was concentrated to 3 mL. Hexane was added to generate a precipitate which was isolated by filtration, washed with hexane, and dried in vacuo. Thus obtained was *fac*-[Mo(bpy)(CO)$_3${P(OMe)$_3$}] (**1a**) (130 mg, 0.28 mmol, 77%).

***fac*-[Mo(bpy)(CO)$_3${P(OEt)$_2$Et}] (4).** To a solution of [Mo(bpy)(CO)$_4$] (500 mg, 1.37 mmol) in toluene (20 mL) was added P(OEt)$_2$Et (0.26 mL, 0.23 mg, 1.51 mmol), and the mixture was refluxed for 30 min. On cooling to room temperature a precipitate formed which was isolated by filtration. The powder was dissolved in a small amount of CH$_2$Cl$_2$, and the solution was loaded on a silica gel column and eluted with CH$_2$Cl$_2$. The purple fraction was collected and concentrated. Hexane was added to the solution to afford a precipitate which was filtered, washed with hexane, and dried in vacuo. Thus obtained was *fac*-[Mo(bpy)(CO)$_3${P(OEt)$_2$Et}] (**4**) (393 mg, 0.86 mmol, 63%). Anal. Calcd for C$_{19}$H$_{23}$MoN$_2$O$_5$P: C, 46.93; H, 4.77; N, 5.76. Found: C, 46.95; H, 5.00; N, 5.71.

***fac*-[Mo(bpy)(CO)$_3${$\overline{\mathrm{PN(Me)CH_2CH_2N}}\mathrm{Me(OMe)}$}] (6).** A solution of [Mo(bpy)(CO)$_4$] (3.2 g, 9.0 mmol) and $\overline{\mathrm{PN(Me)CH_2CH_2N}}\mathrm{Me(OMe)}$ (1.9 mL, 1.9 g, 13.0 mmol) in toluene (120 mL) was refluxed for 1 h. The reaction mixture was concentrated to about 60 mL, and hexane was added to give a dark purple precipitate, which was recrystallized from CH$_2$Cl$_2$/hexane. Thus obtained was *fac*-[Mo(bpy)(CO)$_3${$\overline{\mathrm{PN(Me)CH_2CH_2N}}\mathrm{Me(OMe)}$}] (**6**) (2.8 g, 5.78 mmol, 65%). Anal. Calcd for C$_{18}$H$_{21}$MoN$_4$O$_4$P: C, 44.63; H, 4.38; N, 11.57. Found: C, 44.42; H, 4.53; N, 11.29.

***fac*-[Mo(bpy)(CO)$_3${$\overline{\mathrm{PN(Me)CH_2CH_2N}}\mathrm{Me(OMe)}$}]·2BF$_3$ (6·2BF$_3$).** A solution of **6** (138 mg, 0.29 mmol) in CH$_2$Cl$_2$ was cooled to −78 °C, and BF$_3$·OEt$_2$ (70 μL, 0.57 mmol) was added. The reaction mixture was stirred for 2 h at −78 °C. The resulting dark red precipitate was isolated by filtration, washed with hexane, and dried in vacuo. Thus obtained was *fac*-[Mo(bpy)(CO)$_3${$\overline{\mathrm{PN(Me)CH_2CH_2N}}\mathrm{Me(OMe)}$}]·2BF$_3$ (**6·2BF$_3$**) (130 mg, 0.21 mmol, 74%). Anal. Calcd for C$_{18}$H$_{21}$B$_2$F$_6$MoN$_4$O$_4$P: C, 34.87; H, 3.42; N, 9.04. Found: C, 34.63; H, 3.70; N, 9.26.

***fac*-[Mo(bpy)(CO)$_3${$\overline{\mathrm{PN(Me)CH_2CH_2N}}\mathrm{Me(OEt)}$}] (7).** To a solution of [Mo(bpy)(CO)$_4$] (800 mg, 2.20 mmol) in xylene (35 mL) was added $\overline{\mathrm{PN(Me)CH_2CH_2N}}\mathrm{Me(OEt)}$ (0.50 mL, 3.39 mmol). The reaction mixture was refluxed for several hours and cooled to room temperature. The resulting precipitate was collected by filtration, loaded on an alumina column, and eluted with acetone to remove the unreacted [Mo(bpy)(CO)$_4$]. The first eluted violet fraction was collected and concentrated to afford a violet precipitate which was washed with hexane and dried in vacuo. Thus obtained was *fac*-[Mo(bpy)(CO)$_3${$\overline{\mathrm{PN(Me)CH_2CH_2N}}\mathrm{Me(OEt)}$}] (**7**) (787 mg, 1.58 mmol, 72%). Anal. Calcd for C$_{19}$H$_{23}$MoN$_4$O$_4$P: C, 45.79; H, 4.66; N, 11.24. Found: C, 46.51; H, 5.05; N, 10.89.

[Mo(bpy)(CO)$_3${$\overline{\mathrm{PN(Me)CH_2CH_2N}}\mathrm{Me}$}]$^+$ (5). A solution of *fac*-[Mo(bpy)(CO)$_3${$\overline{\mathrm{PN(Me)CH_2CH_2N}}\mathrm{Me(OMe)}$}] (**6**) (138 mg, 0.29 mmol) in CH$_2$Cl$_2$ (5 mL) was cooled to −78 °C, and BF$_3$·OEt$_2$ (70 μL, 0.57 mmol) was added. Within 2 h the dark red precipitate *fac*-[Mo(bpy)(CO)$_3${$\overline{\mathrm{PN(Me)CH_2CH_2N}}\mathrm{Me(OMe)}$}]·2BF$_3$ was formed. The heterogeneous solution was allowed to warm to room temperature to give an orange homogeneous solution containing [Mo(bpy)(CO)$_3${$\overline{\mathrm{PN(Me)CH_2CH_2N}}\mathrm{Me}$}]$^+$ (**5**) generated quantitatively.

***fac*-[Mo(phen)(CO)$_3${$\overline{\mathrm{PN(Me)CH_2CH_2N}}\mathrm{Me(OMe)}$}] (8).** A solution of [Mo(phen)(CO)$_4$] (1.0 g, 2.58 mmol) and $\overline{\mathrm{PN(Me)CH_2CH_2N}}\mathrm{Me(OMe)}$ (0.57 mL, 0.57 mg, 3.90 mmol) in toluene (30 mL) was refluxed for 6 h. The reaction mixture was allowed to cool to room temperature to give a precipitate, which was filtered

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and washed with hexane. Thus obtained was *fac*-[Mo(phen)(CO)$_3${PN(Me)CH$_2$CH$_2$NMe(OMe)}] (8) (1.07 g, 2.10 mmol, 81%). Anal. Calcd for $C_{20}H_{21}MoN_4O_4P$: C, 47.26; H, 4.16; N, 11.02. Found: C, 47.13; H, 4.22; N, 10.84.

[Mo(phen)(CO)$_3${PN(Me)CH$_2$CH$_2$NMe}]$^+$ (9). The synthesis was identical with that of 5 except that it was carried out by using 8 (162 mg, 0.32 mmol).

***fac*-[Mo(bpy)(CO)$_3${P(NEt$_2$)(OMe)$_2$}] (10).** A solution of [Mo(bpy)(CO)$_4$] (325 mg, 0.89 mmol) and P(NEt$_2$)(OMe)$_2$ (0.34 mL, 323 mg, 1.99 mmol) in toluene (15 mL) was refluxed for several hours. After the solution was cooled to room temperature, hexane was added to give a precipitate, which was recrystallized from CH$_2$Cl$_2$/hexane. Thus obtained was *fac*-[Mo(bpy)(CO)$_3${P(NEt$_2$)(OMe)$_2$}] (10) (308 mg, 0.61 mmol, 69%). Anal. Calcd for $C_{19}H_{24}MoN_3O_5P$: C, 45.52; H, 4.83; N, 8.38. Found: C, 45.56; H, 5.08; N, 8.09.

***fac*-[Mo(bpy)(CO)$_3${P(NEt$_2$)$_2$(OMe)}] (11).** A solution of [Mo(bpy)(CO)$_4$] (500 mg, 1.37 mmol) and P(NEt$_2$)$_2$(OMe) (0.7 mL, 3.05 mmol) in xylene (20 mL) was refluxed for about 1 h. After the solution was cooled to room temperature, hexane was added to give a precipitate, which was recrystallized from CH$_2$Cl$_2$/hexane. Thus obtained was *fac*-[Mo(bpy)(CO)$_3${P(NEt$_2$)$_2$(OMe)}] (11) (467 mg, 0.88 mmol, 64%). Anal. Calcd for $C_{22}H_{31}MoN_4O_4P$: C, 48.71; H, 5.76; N, 10.33. Found: C, 48.45, H, 6.02; N, 10.11.

Reaction of 5 with NaOEt. To a CH$_2$Cl$_2$ solution containing 5 (0.57 mmol) was added NaOEt (80 mg, 1.18 mmol) at −78 °C. The solution was allowed to warm to room temperature and stirred for 2 h. After removal of NaOEt which remained unreacted by filtration, the filtrate was loaded on a silica gel column. The violet portion eluted with CH$_2$Cl$_2$ was collected, and the solvent was removed. The resulting powder was recrystallized by CH$_2$Cl$_2$/hexane. Thus obtained was *fac*-[Mo(bpy)(CO)$_3${PN(Me)CH$_2$CH$_2$NMe(OEt)}] (7) (228 mg, 0.46 mmol, 80%).

Reaction of 5 with LiMe. To a CH$_2$Cl$_2$ solution containing 5 (0.61 mmol) was added a LiMe ether solution (0.61 mmol) at −78 °C. After being allowed to warm to room temperature, the solution was concentrated and loaded on a silica gel column. The violet portion eluted with CH$_2$Cl$_2$ was collected, and hexane was added to give a powder. Thus obtained was *fac*-[Mo(bpy)(CO)$_3${PN(Me)CH$_2$CH$_2$NMe(Me)}] (12) (173 mg, 0.37 mmol, 60%). Anal. Calcd for $C_{18}H_{21}MoN_4O_3P$: C, 46.16; H, 4.53; N, 11.97. Found: C, 45.92; H, 4.61; N, 11.82.

Reaction of 5 with HNEt$_2$. To a CH$_2$Cl$_2$ solution containing 5 (0.90 mmol) prepared from 6 and BF$_3$·OEt$_2$ was added HNEt$_2$ (0.3 mL, 0.36 g, 4.92 mmol) at −78 °C, and then the solution was allowed to warm to room temperature. The product was purified by column chromatography as in the case of 12. Thus obtained was 6 (339 mg, 0.70 mmol, 78%).

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Living Polymerization of 2-Butyne Using a Well-Characterized Tantalum Catalyst

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Ta(CHCMe$_3$)(DIPP)$_3$(THF) (DIPP = 2,6-diisopropylphenoxide) reacts with 1 equiv of 2-butyne, diphenylacetylene, bis(trimethysilyl)acetylene, or 2-methyl-1-buten-3-yne to give THF-free metallacyclobutene complexes **1**, **2**, **3a**, and **4a**, respectively. Addition of pyridine to **3a** and **4a** yields simple monoadducts **3b** and **4b** while addition of pyridine to **1** and **2** yields vinylalkylidene complexes **5** and **6** by opening of the metallacyclobutene ring. Ta[C(Me)C(Me)CHCMe$_3$](DIPP)$_3$(py) (**5**) crystallizes in the monoclinic system, space group $P2_1/n$, with $a = 14.791$ (4) Å, $b = 19.716$ (4) Å, $c = 16.115$ (5) Å, $V = 4668$ (4) Å, $\beta = 96.60$ (3)°, $Z = 4$, fw = 916.07, and $\rho = 1.30$ g/cm^3. The distorted trigonal-bipyramidal molecule contains an equatorial vinylalkylidene ligand (Ta═C = 1.99 (2) Å) in which the *tert*-butyl group is cis to the methyl group on the C═C linkage. **5** reacts with up to 200 equiv of 2-butyne readily to give living polymers Ta{[C(Me)C(Me)]$_x$CHCMe$_3$}(DIPP)$_3$(py) from which the organic polymer can be cleaved by treatment with benzaldehyde and shown to have a very low polydispersity (<1.05). If only 1 equiv of 2-butyne is added to **5**, then a side product, Ta{C(Me)C(Me)C[C(Me)(CH$_2$CMe$_3$)]CH$_2$}(DIPP)$_3$ (**8**), a tantalacyclopentene complex, forms virtually quantitatively. **8** crystallizes in the monoclinic system, space group $P2_1/c$, with $a = 10.632$ (4) Å, $b = 12.750$ (9) Å, $c = 34.144$ (9) Å, $V = 4627$ (6) Å, $\beta = 91.42$ (3)°, $Z = 4$, fw = 891.06, and $\rho = 1.279$ g/cm^3. **8** does not form in the presence of excess 2-butyne. Block copolymers containing 2-butyne and norbornene can be prepared. Analogous reactions between 2-butyne and Ta(CHCMe$_3$)(TIPT)$_3$(THF) (TIPT = 2,4,6-triisopropylbenzenethiolate) were not successful.

Introduction

Polymers made from acetylenes have received much attention in recent years. The interest in polyacetylene itself can be ascribed to the fact that it is a good conductor when doped,[1] while polymers made from substituted acetylenes have properties that make them desirable as selective membranes for gases and liquids.[2,3] The two most common mechanisms for polymerization of acetylenes by transition-metal catalysts are thought to be insertion of an acetylene into a metal–carbon single bond (eq 1)[4-7] and addition of an acetylene to a metal–carbon double bond to give a metallacyclobutene complex which opens to give a complex with a new metal–carbon double bond (eq 2).[2,8-11] (Other mechanisms have been proposed.[12,13]) Evidence for the "insertion" mechanism (eq 1) has been

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