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Cationic Phosphenium Complexes of Group 6 Transition Metals. Systematic Approach to Elucidation of Influence of Substituents of the Phosphenium Phosphorus on the Stability of the Complexes

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Group 6 transition-metal phosphite complexes, *fac*-$[(bpy)(CO)_3M\{PXY(OMe)\}]$ (M=Cr, Mo, and W; XY=$(NEt_2)_2$, **1a**; $N(Me)CH_2CH_2O$, **2a**; $(NEt_2)(OMe)$, **3a**; $OCMe_2CMe_2O$, **4a**; $(OMe)_2$, **5a**) have been prepared and subjected to the reaction with $BF_3\cdot OEt_2$. In these reactions, cationic phosphenium complexes $[(bpy)(CO)_3M\{PXY\}]^+$ are formed by an OMe abstraction as an anion from the phosphorus ligand for **1a**, **2a**, and **3a** (M=Mo, W). The reaction of **3a** (M=Cr) yields *fac*-$[(bpy)(CO)_3Cr\{P(OMe)_2F\}]$ (**Cr-5c**) and $[(bpy)(CO)_3Cr\{P(NEt_2)F_2\}]$ (**Cr-7d**). In the reaction of **4a** and **5a** for all group 6 congeners, an OMe/F substitution reaction takes place to give *fac*-$[(bpy)(CO)_3M\{\overline{POCMe_2CMe_2O}(F)\}]$ and *fac*-$[(bpy)(CO)_3M\{P(OMe)_2F\}]$. These results 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.

Cationic phosphenium compounds depicted as $^+PR_2$ have both lone pair electrons and a vacant p orbital on a phosphorus atom. There is growing interest in the chemistry of transition metal complexes possessing a cationic phosphenium compound as a ligand because it serves as a strong π-acceptor due to its empty p orbital in addition to as a σ-donor.[1] Transition metal phosphenium chemistry dates back to the synthesis and characterization of an iron complex reported by Parry's group in 1978.[2] After that, some such complexes have been reported for several kinds of transition metals.[3—5] We started the chemistry of these complexes a decade after the first discovery by Parry and have reported the preparative methods, structures, properties, and reactivities of cationic phosphenium complexes for group 6[5] and 8[6] transition metals. The results obtained so far involving ours have revealed that a bond between a transition metal and a phosphenium phosphorus bears a significant double bond character.

The stability of transition metal phosphenium complexes is expected to be affected appreciably by the nature of substituents on the phosphenium phosphorus: a transition metal and two organic substituents. However, there is no systematic study on the influence of these substituents on the stability of the complexes. This paper shows our results of somewhat qualitative but systematic approach concerning the stability of cationic phosphenium complexes of group 6 transition metals.

Results and Discussion

Cationic Phosphenium Compound   Cationic Phosphenium Complex

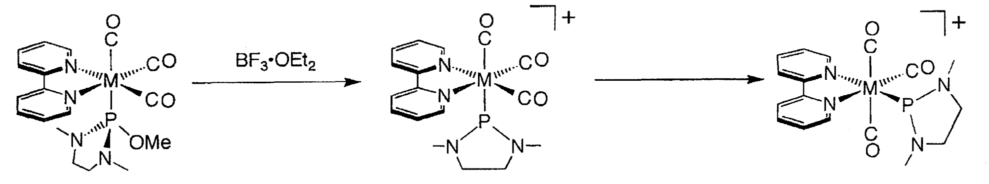
Chart 1.

We already have reported a preparative method of cationic phosphenium complexes where an OR group on a coordinating phosphorus ligand is abstracted as an anion by a Lewis acid such as $BF_3\cdot OEt_2$ or BCl_3.[5b,5c] The results are shown in Scheme 1 with ^{31}P NMR data. The resulting phosphenium complexes with chelated diamino substituents on the phosphenium phosphorus isomerize from the *fac* form to the *mer* form, and the isomerization rate is in the order Cr > Mo > W. The products are very stable in a CH_2Cl_2 solution under an inert atmosphere at room temperature for several days. The diamino substituents and the ethylene bridge between the two amino groups seem to play an important role to stabilize the resulting phosphenium complexes; for example, $[(bpy)(CO)_3Mo\{P(OMe)_2\}]^+$ having no such moieties has not been detected presumably due to its less stability. Therefore, this paper focuses on the effect of the following points on the stability of the phosphenium complexes $[(bpy)(CO)_3M\{PXY\}]^+$: (i) variation of M; Cr, Mo, W. (ii) variation of X and Y; NR_2 or OR. (iii) whether an ethylene bridge between X and Y exists or not. The above combination provides 18 kinds of complexes formulated as $[(bpy)(CO)_3M\{PXY(OMe)\}]$ as a starting complex. Since the results of three complexes out of the 18 complexes, $[(bpy)(CO)_3M\{\overline{PN(Me)CH_2CH_2NMe}$-

(OMe)}] (M=Cr, Mo, W) have already been reported,[5c] the rest 15 species were synthesized and then subjected to the reaction with $BF_3 \cdot OEt_2$.

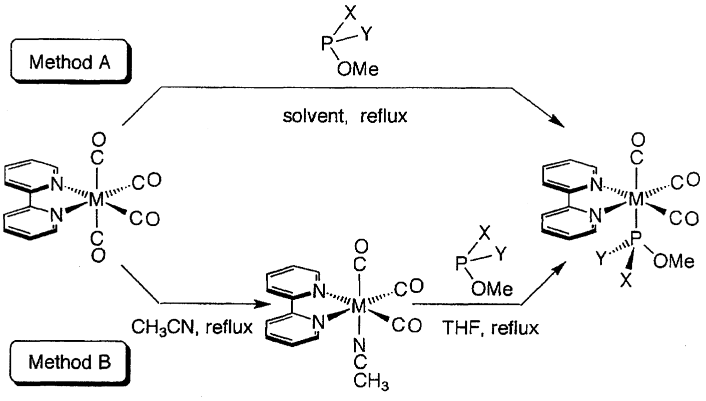
Preparation of a Series of *fac*-[(bpy)(CO)$_3$M{PXY(OMe)}]. Several complexes of *fac*-[(bpy)(CO)$_3$ML] (M=Cr, Mo, W; L=phosphine, phosphite) have been prepared by thermolysis of M(bpy)(CO)$_4$ in the presence of L in toluene or xylene.[7] This method was applied to the preparation of the title complexes (Method A in Scheme 2). However, this method was not suitable for the following three complexes, **Cr-1a**, **Mo-4a**, and **W-5a**, because **Cr-1a** was accompanied by unidentified products and it was difficult to separate from them, **Mo-4a** was accompanied by the disubstituted product, [(bpy)(CO)$_2$Mo{$\overline{\text{POCMe}_2\text{CMe}_2\text{O}}$(OMe)}$_2$] which reduced the yield of **Mo-4a**, and for **W-5a** the xylene reflux temperature caused vaporization of P(OMe)$_3$. Therefore, these three complexes were obtained from a more substitution-active complex, *fac*-[(bpy)(CO)$_3$M(NCMe)] (Method B in Scheme 2).

The IR, ^{1}H NMR, and ^{31}P NMR data of the complexes thus prepared are summarized in Table 1. The ^{31}P NMR chemical shifts (143—182 ppm) fall in the range covered by transition-metal phosphite complexes. In the series of these



^{31}P NMR Data			
M = Cr ;	153.9	263.8	277.3
Mo ;	138.0	252.5	268.2
W ;	129.8	233.7	242.6
	($^1J_{PW}$ = 334.6 Hz)	($^1J_{PW}$ = 441.7 Hz)	($^1J_{PW}$ = 561.1 Hz)

Scheme 1. Reaction sequence and ^{31}P NMR data.



M	X, Y		Method (solvent)	Yield (%)
Cr	NEt$_2$, NEt$_2$	**(Cr-1a)**	B	93
Cr	N(Me)CH$_2$CH$_2$O	**(Cr-2a)**	A (toluene)	95
Cr	NEt$_2$, OMe	**(Cr-3a)**	A (toluene)	73
Cr	OCMe$_2$CMe$_2$O	**(Cr-4a)**	A (toluene)	80
Cr	OMe, OMe	**(Cr-5a)**	A (toluene)	77
Mo	NEt$_2$, NEt$_2$	**(Mo-1a)**	A (xylene)	64
Mo	N(Me)CH$_2$CH$_2$O	**(Mo-2a)**	A (toluene)	56
Mo	NEt$_2$, OMe	**(Mo-3a)**	A (toluene)	69
Mo	OCMe$_2$CMe$_2$O	**(Mo-4a)**	B	97
Mo	OMe, OMe	**(Mo-5a)**	A (toluene)	79
W	NEt$_2$, NEt$_2$	**(W-1a)**	A (xylene)	62
W	N(Me)CH$_2$CH$_2$O	**(W-2a)**	A (xylene)	57
W	NEt$_2$, OMe	**(W-3a)**	A (xylene)	71
W	OCMe$_2$CMe$_2$O	**(W-4a)**	A (xylene)	75
W	OMe, OMe	**(W-5a)**	B	85

Scheme 2.

Table 1. Spectroscopic Data[a]

Complex[b]	IR (ν_{CO}/cm^{-1})[c]	^{1}H NMR (δ/ppm)[d]	^{31}P NMR (δ/ppm)[e]
fac-[(Cr){P(NEt$_2$)$_2$(OMe)}] (**Cr-1a**)	1907, 1814, 1783	0.81 (t, $^3J_{\mathrm{HH}} = 7.3$ Hz, 12H, $\mathrm{CH_2C}H_3$) 2.51—3.26 (m, 8H, NCH$_2$) 3.20 (d, $^3J_{\mathrm{PH}} = 12.0$ Hz, 3H, OCH$_3$) 7.25—9.48 (m, 8H, bpy)	171.1 (s)
fac-[(Mo){P(NEt$_2$)$_2$(OMe)}] (**Mo-1a**)[f]	1915, 1813, 1788	0.83 (t, $^3J_{\mathrm{HH}} = 7.0$ Hz, 12H, $\mathrm{CH_2C}H_3$) 2.83 (m, 8H, NCH$_2$) 3.14 (d, $^3J_{\mathrm{PH}} = 10.0$ Hz, 3H, OCH$_3$) 7.27—9.20 (m, 8H, bpy)	157.6 (s)
fac-[(W){P(NEt$_2$)$_2$(OMe)}] (**W-1a**)	1907, 1808, 1784	0.81 (t, $^3J_{\mathrm{HH}} = 7.3$ Hz, 12H, $\mathrm{CH_2C}H_3$) 2.77 (m, 8H, NCH$_2$) 3.27 (d, $^3J_{\mathrm{PH}} = 12.2$ Hz, 3H, OCH$_3$) 7.52—9.34 (m, 8H, bpy)	147.8 (s) ($^1J_{\mathrm{PW}} = 313.7$ Hz)
fac-[(Cr){$\overline{\mathrm{PN(Me)CH_2CH_2O}}$(OMe)}] (**Cr-2a**)	1919, 1826, 1790	2.49 (d, $^3J_{\mathrm{PH}} = 10.0$ Hz, 3H, NCH$_3$) 3.18 (d, $^3J_{\mathrm{PH}} = 10.4$ Hz, 3H, OCH$_3$) 3.34 (m, 2H, NCH$_2$) 4.20 (m, 2H, OCH$_2$) 7.23—9.48 (m, 8H, bpy)	172.3 (s)
fac-[(Mo){$\overline{\mathrm{PN(Me)CH_2CH_2O}}$(OMe)}] (**Mo-2a**)[g]	1924, 1827, 1794	2.53 (d, $^3J_{\mathrm{PH}} = 10.6$ Hz, 3H, NCH$_3$) 2.72—3.50 (m, 2H, NCH$_2$) 3.21 (d, $^3J_{\mathrm{PH}} = 10.4$ Hz, 3H, OCH$_3$) 3.51—4.56 (m, 2H, OCH$_2$) 7.34—9.26 (m, 8H, bpy)	157.0 (s)
fac-[(W){$\overline{\mathrm{PN(Me)CH_2CH_2O}}$(OMe)}] (**W-2a**)	1915, 1821, 1788	2.54 (d, $^3J_{\mathrm{PH}} = 10.7$ Hz, 3H, NCH$_3$) 2.80 (m, 1H, NCH$_2$) 3.10 (m, 1H, NCH$_2$) 3.22 (d, $^3J_{\mathrm{PH}} = 10.7$ Hz, 3H, OCH$_3$) 3.56 (m, 1H, OCH$_2$) 4.08 (m, 1H, OCH$_2$) 7.48—9.25 (m, 8H, bpy)	145.0 (s) ($^1J_{\mathrm{PW}} = 352.8$ Hz)
fac-[(Cr){P(NEt$_2$)(OMe)$_2$}] (**Cr-3a**)	1914, 1822, 1789	0.82 (t, $^3J_{\mathrm{HH}} = 7.5$ Hz, 6H, $\mathrm{CH_2C}H_3$) 2.79 (m, 4H, NCH$_2$) 3.15 (d, $^3J_{\mathrm{PH}} = 10.6$ Hz, 6H, OCH$_3$) 7.42—9.44 (m, 8H, bpy)	174.0 (s)
fac-[(Mo){P(NEt$_2$)(OMe)$_2$}] (**Mo-3a**)[f]	1925, 1830, 1796	0.80 (t, $^3J_{\mathrm{HH}} = 7.0$ Hz, 6H, $\mathrm{CH_2C}H_3$) 3.05 (m, 4H, NCH$_2$) 3.32 (d, $^3J_{\mathrm{PH}} = 10.0$ Hz, 6H, OCH$_3$) 7.26—9.20 (m, 8H, bpy)	154.3 (s)
fac-[(W){P(NEt$_2$)(OMe)$_2$}] (**W-3a**)	1914, 1817, 1788	0.77 (t, $^3J_{\mathrm{HH}} = 7.0$ Hz, 6H, $\mathrm{CH_2C}H_3$) 2.90 (m, 4H, NCH$_2$) 3.07 (d, $^3J_{\mathrm{PH}} = 10.6$ Hz, 6H, OCH$_3$) 7.17—9.12 (m, 8H, bpy)	144.6 (s) ($^1J_{\mathrm{PW}} = 341.8$ Hz)
fac-[(Cr){$\overline{\mathrm{POCMe_2CMe_2O}}$(OMe)}] (**Cr-4a**)	1924, 1835, 1796	0.72 (s, 6H, CCH$_3$) 1.21 (s, 6H, CCH$_3$) 3.48 (d, $^3J_{\mathrm{PH}} = 10.6$ Hz, 3H, OCH$_3$) 7.22—9.34 (m, 8H, bpy)	182.0 (s)
fac-[(Mo){$\overline{\mathrm{POCMe_2CMe_2O}}$(OMe)}] (**Mo-4a**)	1930, 1835, 1798	0.76 (s, 6H, CCH$_3$) 1.20 (s, 6H, CCH$_3$) 3.53 (d, $^3J_{\mathrm{PH}} = 12.2$ Hz, 3H, OCH$_3$) 7.55—9.16 (m, 8H, bpy)	165.3 (s)
fac-[(W){$\overline{\mathrm{POCMe_2CMe_2O}}$(OMe)}] (**W-4a**)	1922, 1828, 1793	0.73 (s, 6H, CCH$_3$) 1.20 (s, 6H, CCH$_3$) 3.54 (d, $^3J_{\mathrm{PH}} = 11.7$ Hz, 3H, OCH$_3$) 7.53—9.25 (m, 8H, bpy)	154.0 (s) ($^1J_{\mathrm{PW}} = 374.0$ Hz)

Table 1. (Continued)

Complex[b]	IR (ν_{CO}/cm^{-1})[c]	^{1}H NMR (δ/ppm)[d]	^{31}P NMR (δ/ppm)[e]
fac-[(Cr){POCMe$_2$CMe$_2$O(F)}] (**Cr-4c**)	1937, 1848, 1805	1.04 (s, 6H, CH$_3$) 1.25 (s, 6H, CH$_3$) 7.45—9.33 (m, 8H, bpy)	175.5 (d, $^1J_{PF}$ = 1264.8 Hz)
fac-[(Mo){POCMe$_2$CMe$_2$O(F)}] (**Mo-4c**)	1942, 1851, 1810	1.06 (s, 6H, CH$_3$) 1.25 (s, 6H, CH$_3$) 7.57—9.14 (m, 8H, bpy)	156.5 (d, $^1J_{PF}$ = 1242.7 Hz)
fac-[(W){POCMe$_2$CMe$_2$O(F)}] (**W-4c**)	1934, 1843, 1803	1.07 (s, 6H, CH$_3$) 1.24 (s, 6H, CH$_3$) 7.58—9.25 (m, 8H, bpy)	144.3 (d, $^1J_{PF}$ = 1260.2 Hz) ($^1J_{PW}$ = 412.4 Hz)
fac-[(Cr){P(OMe)$_3$}] (**Cr-5a**)	1924, 1830, 1793	3.31 (d, $^3J_{PH}$ = 10.6 Hz, 9H, CH$_3$) 7.28—9.41 (m, 8H, bpy)	169.7 (s)
fac-[(Mo){P(OMe)$_3$}] (**Mo-5a**)[f]	1929, 1831, 1795	3.30 (d, $^3J_{PH}$ = 10.0 Hz, 9H, CH$_3$) 7.28—9.13 (m, 8H, bpy)	153.3 (s)[h]
fac-[(W){P(OMe)$_3$}] (**W-5a**)	1920, 1825, 1790	3.33 (d, $^3J_{PH}$ = 10.9 Hz, 9H, CH$_3$) 7.37—9.33 (m, 8H, bpy)	143.3 (s) ($^1J_{PW}$ = 371.1 Hz)
fac-[(Cr){P(OMe)$_2$(F)}] (**Cr-5c**)	1935, 1845, 1801	3.51 (d, $^3J_{PH}$ = 10.3 Hz, 6H, CH$_3$) 7.46—9.34 (m, 8H, bpy)	170.6 (d, $^1J_{PF}$ = 1198.7 Hz)
fac-[(Mo){P(OMe)$_2$(F)}] (**Mo-5c**)[f]	1939, 1844, 1805	3.46 (d, $^3J_{PH}$ = 10.0 Hz, 6H, CH$_3$) 7.32—9.12 (m, 8H, bpy)	151.9 (d, $^1J_{PF}$ = 1171.0 Hz)[h]
fac-[(W){P(OMe)$_2$(F)}] (**W-5c**)	1932, 1839, 1800	3.47 (d, $^3J_{PH}$ = 11.0 Hz, 6H, CH$_3$) 7.20—9.22 (m, 8H, bpy)	141.2 (d, $^1J_{PF}$ = 1160.0 Hz) ($^1J_{PW}$ = 407.0 Hz)
fac-[(Cr){PN(Me)CH$_2$CH$_2$O(NEt$_2$)}] (**Cr-6a**)	1910, 1815, 1785	0.88 (t, $^3J_{HH}$ = 8.0 Hz, 6H, CH$_2$CH_3) 2.18 (d, $^3J_{PH}$ = 10.0 Hz, 3H, NCH$_3$) 2.90 (m, 2H, NCH_2CH$_2$O), 3.00 (m, 4H, NCH_2CH$_3$) 3.98 (m, 2H, OCH$_2$) 7.24—9.45 (m, 8H, bpy)	169.7 (s)
fac-[(Mo){PN(Me)CH$_2$CH$_2$O(NEt$_2$)}] (**Mo-6a**)	1916, 1816, 1789	0.82 (t, $^3J_{HH}$ = 7.1 Hz, 6H, CH$_2$CH_3) 2.35 (d, $^3J_{PH}$ = 9.8 Hz, 3H, NCH$_3$) 2.61 (m, 1H, NCH_2CH$_2$O), 3.03 (m, 5H, NCH_2CH$_2$O and NCH_2CH$_3$) 3.18 (m, 1H, OCH$_2$) 3.89 (m, 1H, OCH$_2$) 7.48—9.24 (m, 8H, bpy)	153.2 (s)
fac-[(W){PN(Me)CH$_2$CH$_2$O(NEt$_2$)}] (**W-6a**)	1908, 1810, 1784	0.82 (t, $^3J_{HH}$ = 7.1 Hz, 6H, CH$_2$CH_3) 2.34 (d, $^3J_{PH}$ = 9.8 Hz, 3H, NCH$_3$) 2.65 (m, 1H, NCH_2CH$_2$O), 3.05 (m, 5H, NCH_2CH$_2$O and NCH_2CH$_3$) 3.15 (m, 1H, OCH$_2$) 3.88 (m, 1H, OCH$_2$) 7.49—9.24 (m, 8H, bpy)	144.9 (s) ($^1J_{PW}$ = 316.2 Hz)

a) At room temperature. b) (Cr)=(bpy)(CO)$_3$Cr, (Mo)=(bpy)(CO)$_3$Mo, and (W)=(bpy)(CO)$_3$W. c) In CH$_2$Cl$_2$ solution. d) In acetone-d_6 solution. e) In CH$_2$Cl$_2$ solution unless otherwise noted. f) Ref. 5b. g) Ref. 5d. h) In acetone solution.

complexes, the chemical shifts for chromium complexes are roughly 15 ppm lower in magnetic field than those for the corresponding molybdenum complexes which are about 10 ppm lower than those for the corresponding tungsten complexes. This tendency is similar to the previous indication.[8] In the cases of tungsten complexes, the ^{31}P–^{183}W spin–spin coupling is observed as satellite peaks due to ^{183}W of 14.4% natural abundance. The values observed here (313—374 Hz) fall in the reported range (200—500 Hz),[9] and increase with increasing the number of OR groups on the phosphorus. The IR and ^{1}H NMR spectra and elemental analyses as well as ^{31}P NMR spectra support the formation of these complexes.

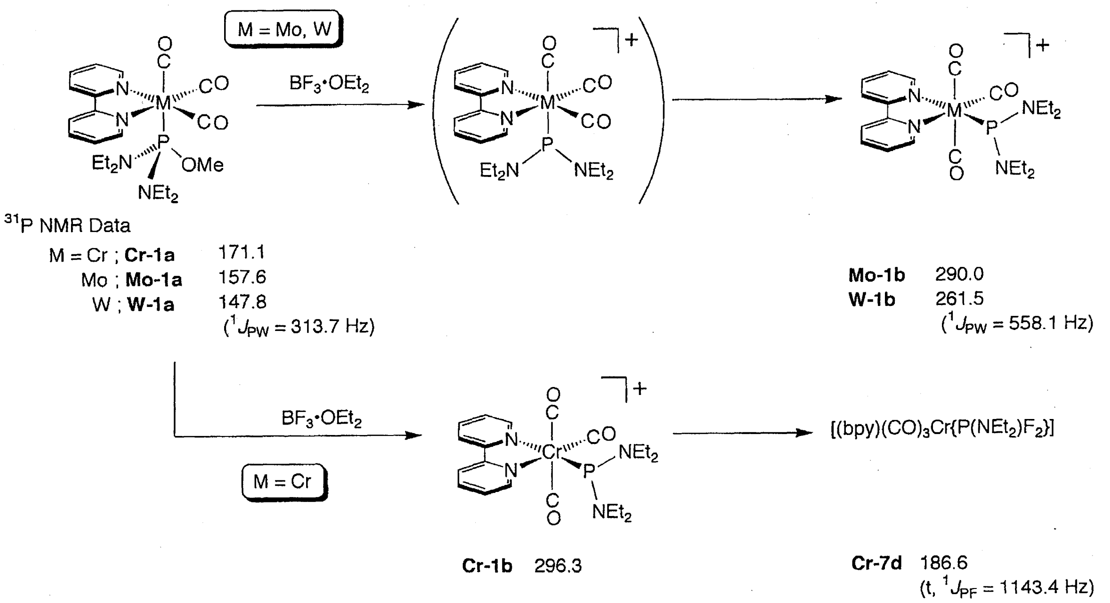
Reaction of *fac*-[(bpy)(CO)$_3$M{PXY(OMe)}] with BF$_3$·OEt$_2$. A series of *fac*-[(bpy)(CO)$_3$M{PXY(OMe)}] were subjected to the reaction with BF$_3$·OEt$_2$ in CH$_2$Cl$_2$ at −78 °C in an inert atmosphere. Cationic phosphenium complexes thus formed were very air sensitive and several trials of the isolation were unsuccessful. However, since the ^{31}P NMR data show reliable diagnosis as to the formation of cationic phosphenium complexes, the reaction sequences were followed mainly by the ^{31}P NMR measurements, and in some cases also by IR and ^{13}C NMR measurements.

(i) In the Case of *fac*-[(bpy)(CO)$_3$M{P(NEt$_2$)$_2$(OMe)}]. The results are shown in Scheme 3 with ^{31}P NMR data. With the tungsten complex **W-1a**, the ^{31}P NMR spectrum of the resulting solution showed only one singlet at 261.5 ppm, which is 113.7 ppm lower in magnetic field than that for the starting complex, accompanied by satellite peaks with a coupling constant of 558.1 Hz being 244.4 Hz larger than that for the starting complex. The IR spectrum showed three ν_{CO} stretchings (1934, 1838, and 1805 cm^{-1}), which are about 20 cm^{-1} higher than those for the starting complex. These data indicate the formation of the cationic phosphenium complex, $[(bpy)(CO)_3W\{P(NEt_2)_2\}]^+$. These signals remained unchanged with time. In order to elucidate the geometry around the tungsten, the ^{13}C NMR spectrum was measured, and showed the following resonances: (in CH_2Cl_2) δ=11.5 (d, $^3J_{PC}$=14.7 Hz, CH_3), 42.6 (d, $^2J_{PC}$=14.7 Hz, NCH_2), 123.0 (s, bpy), 126.0 (s, bpy), 126.1 (s, bpy), 127.9 (s, bpy), 139.6 (s, bpy), 140.3 (s, bpy), 152.2 (s, bpy), 152.7 (s, bpy), 153.7 (s, bpy), 155.9 (s, bpy), 197.5 (d, $^2J_{PC}$=9.2 Hz, CO), 218.3 (d, $^2J_{PC}$=9.1 Hz, CO). In the region of the carbonyl carbon, two doublets with similar coupling constants were observed, and in the bpy region, ten singlets were observed. These observations clearly show that the cationic complex **W-1b** has a meridional geometry.

With **Mo-1a**, the product exhibited only one singlet at 290.0 ppm in the ^{31}P NMR spectrum. This is 132.4 ppm lower than that for the starting complex, indicating the formation of $[(bpy)(CO)_3Mo\{P(NEt_2)_2\}]^+$, **Mo-1b**. With **Cr-1a**, the ^{31}P NMR spectrum showed a singlet at 296.3 ppm, which is 125.2 ppm lower than that for the starting complex, indicating the formation of $[(bpy)(CO)_3Cr\{P(NEt_2)_2\}]^+$, **Cr-1b**. The *fac*-to-*mer* isomerization of $[(bpy)(CO)_3M\{PN(Me)CH_2CH_2NMe\}]^+$ is known faster for Cr than for Mo and faster for Mo than for W.[5c)] And **W-1b** has a meridional form. Therefore, **Mo-1b** and **Cr-1b** are thought to have a meridional form. In the ^{31}P NMR spectrum the singlet due to **Cr-1b** decreased in intensity with growing a new triplet at 186.6 ppm with a coupling constant of 1143.4 Hz. This triplet with such a large coupling constant implies that the P has two F atoms. The new triplet is ascribed to $[(bpy)(CO)_3Cr\{P(NEt_2)F_2\}]$ (**Cr-7d**). This complex may be produced by F introduction to **Cr-1b**, followed by an NEt_2/F exchange reaction.

In short for non-bridged diamino-substituted phosphite complexes, the cationic phosphenium complexes are formed, and they (M=W and Mo) are stable in solution, but for M=Cr a further reaction takes place to give the fluorinated complex.

(ii) In the Case of *fac*-$[(bpy)(CO)_3M\{PN(Me)CH_2CH_2O(OMe)\}]$. The results are summarized in Scheme 4 with ^{31}P NMR data. With **W-2a**, only one singlet at 230.1 ppm (85.1 ppm lower in magnetic field than that for the starting complex) accompanied by satellite peaks with a coupling constant of 621.4 Hz (286.6 Hz larger than that for the starting complex) was observed in the ^{31}P NMR spectrum. The IR spectrum showed three ν_{CO} stretchings (1965, 1872, and 1819 cm^{-1}) which were about 50 cm^{-1} higher than those for the starting complex. These results show the formation of the cationic phosphenium complex $[(bpy)(CO)_3W\{PN(Me)CH_2CH_2O\}]^+$ (**W-2b**). The ^{13}C NMR spectrum indicates its meridional geometry because of two doublets with the similar coupling constant in a terminal CO region and ten resonances due to bpy; (in CH_2Cl_2) δ=32.6 (d, $^2J_{PC}$=12.9 Hz, NCH_3), 52.0 (s, NCH_2), 70.6 (d, $^2J_{PC}$=9.2 Hz, OCH_2), 122.8 (s, bpy), 124.1 (s, bpy), 124.3 (s, bpy), 125.9 (s, bpy), 140.2 (s, bpy), 140.5 (s, bpy), 152.7 (s, bpy), 154.8 (s, bpy), 155.4 (s, bpy), 155.4 (s, bpy), 196.8 (d, $^2J_{PC}$=9.2 Hz, CO), 210.5 (d, $^2J_{PC}$=12.8 Hz, CO). The facial isomer was not detected even right after the reaction started.



Scheme 3. Reaction sequence and ^{31}P NMR data.

With **Mo-2a**, the ^{31}P NMR spectrum showed only one singlet at 253.8 ppm indicating the formation of a phosphenium complex $[(bpy)(CO)_3Mo\{PN(Me)CH_2CH_2O\}]^+$ (**Mo-2b**), presumably with a meridional geometry.

With **Cr-2a**, the ^{31}P NMR spectrum showed a singlet at 258.7 ppm assigned to *mer*-$[(bpy)(CO)_3Cr\{PN(Me)CH_2CH_2O\}]^+$ (**Cr-2b**). But in addition, some unidentified resonances were also observed.

The cationic phosphenium complexes are similarly formed when they have monoaminomonoalkoxy substituents on the phosphorus. The reactions for Mo and W are clean. But, for the chromium complex, some unidentified compounds are also formed.

(iii) In the Case of *fac*-$[(bpy)(CO)_3M\{P(NEt_2)(OMe)_2\}]$. The results obtained are shown in Scheme 5, together with ^{31}P NMR data. With **W-3a**, the ^{31}P NMR spectrum showed mainly a singlet at 249.6 ppm (105.0 ppm lower than that for the starting complex) accompanied by satellite peaks with a coupling constant of 606.3 Hz (265.4 Hz larger than that for the starting complex). This result indicates the formation of the cationic phosphenium complex, $[(bpy)(CO)_3W\{P(NEt_2)(OMe)\}]^+$ (**W-3b**). The ^{31}P NMR spectrum showed also the formation of some unidentified products. Although the ^{13}C NMR resonances were very complicated due to the impurities, the meridional geometry of the phosphenium complex was deduced from the $^1J_{PW}$ value. As shown in Table 2, the conversion of *fac*-$[(bpy)(CO)_3W\{PN(Me)CH_2CH_2NMe(OMe)\}]$ into *fac*-$[(bpy)(CO)_3W\{PN(Me)CH_2CH_2NMe\}]^+$ causes the increasing of $^1J_{PW}$ by 107 Hz and the conversion of *fac*- to *mer*-$[(bpy)(CO)_3W\{PN(Me)CH_2CH_2NMe\}]^+$results in the increasing of $^1J_{PW}$ by 119 Hz. The conversions of **W-1a** into **W-1b** and of **W-2a** into **W-2b**, where **W-1b** and **W-2b** were confirmed to have a meridional geometry by the ^{13}C NMR spectra, cause the increasing of $^1J_{PW}$ by 245 and 269 Hz, respectively. Therefore, the increasing of $^1J_{PW}$ by 265 Hz on going from **W-3a** to **W-3b** indicates that the **W-3b** has a meridional geometry.

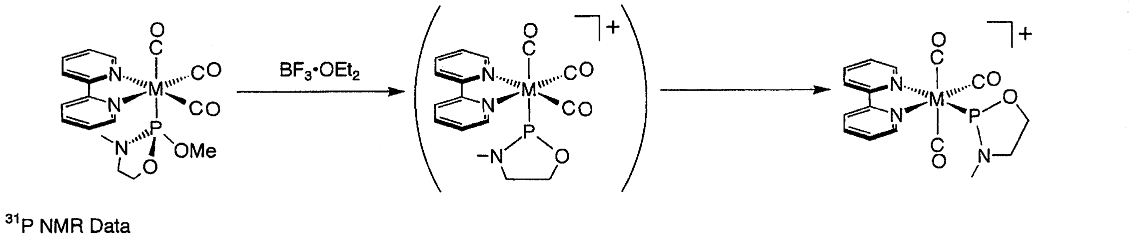
With **Mo-3a**, the ^{31}P NMR spectrum showed many resonances involving a singlet at 272.6 ppm assignable to *mer*-$[(bpy)(CO)_3Mo\{P(NEt_2)(OMe)\}]^+$ (**Mo-3b**).

With **Cr-3a**, a singlet corresponding to a cationic phosphenium complex was not observed in the ^{31}P NMR spectrum, but a doublet at 170.4 ppm with a coupling constant of 1198.7 Hz and a triplet at 186.6 ppm with a coupling constant of 1143.4 Hz were observed. The former is identical to the resonance observed in the reaction of **Cr-5a** with $BF_3{\cdot}OEt_2$ (vide infra), and the latter is identical to that observed in the reaction of **Cr-1a** with $BF_3{\cdot}OEt_2$ (vide supra), which, together with the coupling patterns and the coupling constants, indicates that the former is due to *fac*-$[(bpy)(CO)_3Cr\{P(OMe)_2F\}]$ (**Cr-5c**) and the latter to $[(bpy)(CO)_3Cr\{P(NEt_2)F_2\}]$ (**Cr-7d**).

In the case of non-bridged monoamino-substituted phosphite complexes, the cationic phosphenium complexes of W and Mo are formed with some unidentified products. In the case of the chromium complex, the cationic complex is not observed but two kinds of fluorinated complexes are formed.

(iv) In the Cases of *fac*-$[(bpy)(CO)_3M\{POCMe_2CMe_2O(OMe)\}]$ and *fac*-$[(bpy)(CO)_3M\{P(OMe)_3\}]$. The results are shown in Scheme 6 and the spectroscopic data are summarized in Table 1. The ^{31}P NMR and IR spectra of the reaction mixture showed that all reactions proceeded very cleanly. In all cases, the products were isolated as reddish violet powders. The infrared spectra showed three absorptions in the ν_{CO} region, which are 8—16 cm^{-1} higher in frequency than those for the parent complex. The ^{1}H NMR spectra showed that the product has one $OCMe_2CMe_2O$ group for **4c** and two OMe groups for **5c**. In the ^{31}P NMR spectra, a doublet with a coupling constant of about 1200 Hz, indicating that the product has one P–F bond, is observed at 141—175 ppm. These spectroscopic data, together with elemental analyses, confirm the formation of mono OMe/F exchange complexes. A signal assignable to a cationic phosphenium complex was not observed in ^{31}P NMR spectrum irrespective of the presence of the bridging between two O substituents.

The reactions of $[(bpy)(CO)_3M(phosphite)]$ with $BF_3{\cdot}OEt_2$ where the phosphite has more than one amino group

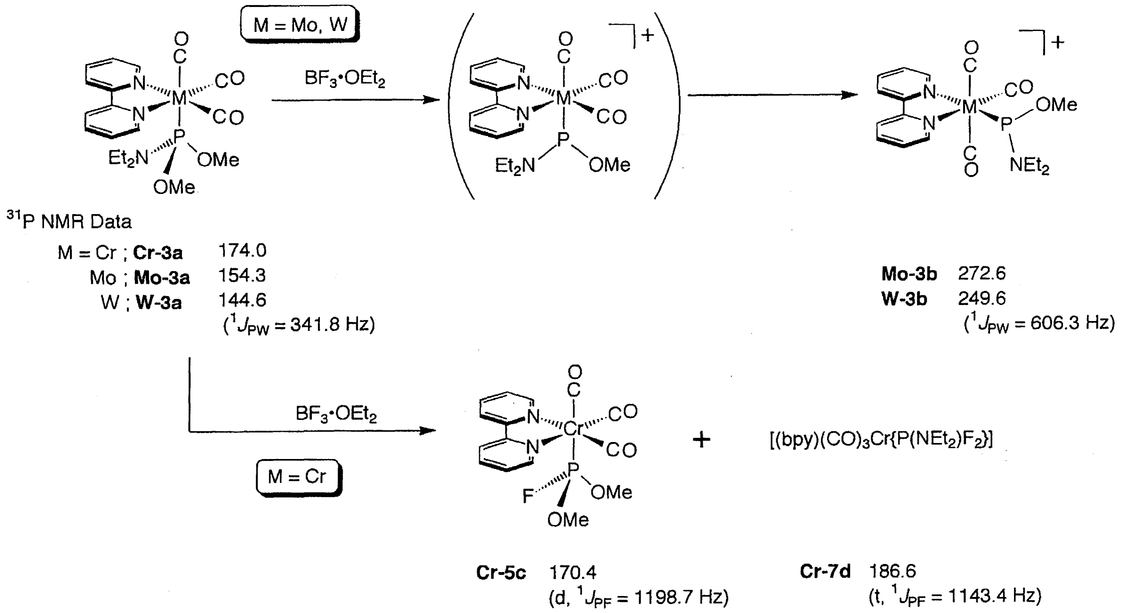


^{31}P NMR Data

M = Cr ; **Cr-2a**	172.3	**Cr-2b**	258.7
Mo ; **Mo-2a**	157.0	**Mo-2b**	253.8
W ; **W-2a**	145.0 ($^1J_{PW}$ = 352.8 Hz)	**W-2b**	230.1 ($^1J_{PW}$ = 621.4 Hz)

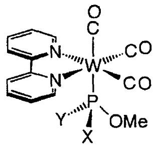
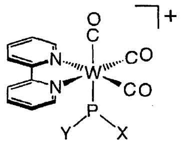
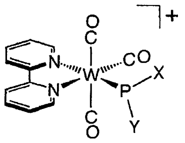
Scheme 4. Reaction sequence and ^{31}P NMR data.

have been mentioned above and revealed that an OR group on the phosphite is abstracted as an anion by $BF_3 \cdot OEt_2$ to give a cationic phosphenium complex. Therefore, it may be reasonably postulated that $[(bpy)(CO)_3M\{\overline{POCMe_2CMe_2O}\}]^+$ and $[(bpy)(CO)_3M\{P(OMe)_2\}]^+$ are formed from **4a** and **5a**, respectively by an OMe abstraction. However, since resulting cationic phosphenium complexes may be too reactive toward a nucleophilic attack such as F^- to be detected, only F introduced products are eventually observed.

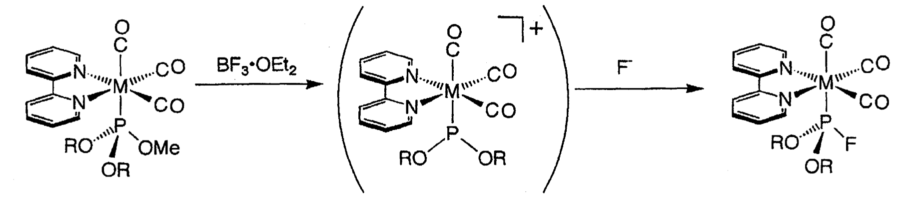


Scheme 5. Reaction sequence and ${}^{31}P$ NMR data.

Table 2. Coupling Constant ${}^1J_{PW}$ (Hz)

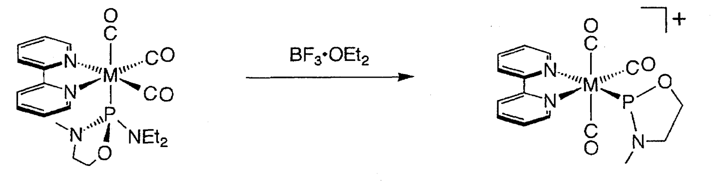
			
X,Y=N(Me)CH_2CH_2NMe [a)]	334.6	441.7	561.1
NEt_2, NEt_2	313.7 (**W-1a**)	—	558.1 (**W-1b**)
N(Me)CH_2CH_2O	352.8 (**W-2a**)	—	621.4 (**W-2b**)
NEt_2, OMe	341.8 (**W-3a**)	—	606.3 (**W-3b**)

a) Ref. 5c.



	M	OR, OR	
(Cr-4a)	Cr	$OCMe_2CMe_2O$	**(Cr-4c)**
(Mo-4a)	Mo	$OCMe_2CMe_2O$	**(Mo-4c)**
(W-4a)	W	$OCMe_2CMe_2O$	**(W-4c)**
(Cr-5a)	Cr	OMe, OMe	**(Cr-5c)**
(Mo-5a)	Mo	OMe, OMe	**(Mo-5c)**
(W-5a)	W	OMe, OMe	**(W-5c)**

Scheme 6.



^{31}P NMR Data

M = Cr ; **Cr-6a**	169.7	**Cr-2b**	259.0
Mo ; **Mo-6a**	153.2	**Mo-2b**	254.1
W ; **W-6a**	144.9	**W-2b**	231.1
	($^1J_{PW}$ = 316.2 Hz)		($^1J_{PW}$ = 620.2 Hz)

Scheme 7. Reaction sequence and ^{31}P NMR data.

Reaction of *fac*-[(bpy)(CO)$_3$M{PN(Me)CH$_2$CH$_2$O(NEt$_2$)}] with BF$_3$•OEt$_2$. In the reaction of **Cr-1a** and **Cr-3a** with BF$_3$•OEt$_2$, NEt$_2$/F substitution products such as **Cr-5c** and **Cr-7d** were formed, implying that an NEt$_2$ group is abstracted as an anion by BF$_3$•OEt$_2$ to give the corresponding cationic phosphenium complexes. In order to examine whether an NR$_2$ abstraction from the coordinating phosphorus compound by BF$_3$•OEt$_2$ actually takes place or not, we prepared *fac*-[(bpy)(CO)$_3$M{PN(Me)CH$_2$CH$_2$O(NEt$_2$)}] (M=Cr (**Cr-6a**), Mo (**Mo-6a**), W (**W-6a**)) by the thermolysis of M(bpy)(CO)$_4$ in the presence of PN(Me)CH$_2$CH$_2$O(NEt$_2$), and then subjected to the reaction with BF$_3$•OEt$_2$. These results are shown in Scheme 7 with ^{31}P NMR data.

In all cases, the amino group abstraction took place to form the cationic phosphenium complexes **2b** (The ^{31}P NMR data of the products are in agreement with those in Scheme 4 within an experimental error). This result clearly shows that BF$_3$ can abstract the amino group on the phosphorus as well.

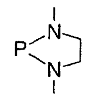
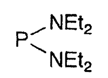
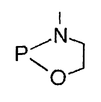
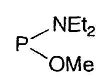
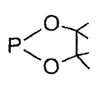
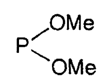
Now let us consider again the reaction of *fac*-[(bpy)(CO)$_3$M{P(NEt$_2$)$_2$(OMe)}] (**1a**) and *fac*-[(bpy)(CO)$_3$M{P(NEt$_2$)(OMe)$_2$}] (**3a**) with BF$_3$•OEt$_2$ in terms of the possibility for an NEt$_2$ abstraction. Supposed that the amino substituent is selectively abstracted as an anion by BF$_3$•OEt$_2$, cationic phosphenium complexes [(bpy)(CO)$_3$M{P(NEt$_2$)(OMe)}]$^+$ (**3b**) and [(bpy)(CO)$_3$M{P(OMe)$_2$}]$^+$ would be formed, respectively. However, as mentioned above, the dimethoxy phosphenium complex [(bpy)(CO)$_3$M{P(OMe)$_2$}]$^+$ can not be detected from [(bpy)(CO)$_3$M{P(OMe)$_3$}] (**5a**). Therefore, a cationic phosphenium complex prepared from **3a** has to be **3b**, and a cationic phosphenium complex prepared from **1a** has to be **1b**. These phosphenium complexes result from the selective OR abstraction. Therefore, BF$_3$•OEt$_2$ can abstract an NR$_2$ group on a coordinating phosphorus to give a cationic phosphenium complex, but it prefers OR abstraction to NR$_2$ abstraction.

Stability of Cationic Phosphenium Complexes. The results obtained previously[5c)] and here show a tendency about the stability of cationic phosphenium complexes, which is, though somewhat qualitative, shown in Table 3. 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 byproducts, whereas that of Cr is not detected but F-introduced complexes are 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) Adding the ethylene bridge between an amino and an alkoxy substituents contributes to stabilization of a cationic phosphenium complex roughly to the same extent as the substitution of one OMe group by an NEt$_2$ group.

It is generally said that transition metal complexes become more stable on going to a heavier congener. This trend seems to hold true for the cationic phosphenium complexes. The stability difference 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.

Amino substituents stabilize the phosphenium complexes. We have proposed the reason based on the X-ray structures of *trans*-[(bpy)(CO)$_2$Mo{PN(Me)CH$_2$CH$_2$NMe(OMe)}{PN(Me)CH$_2$CH$_2$NMe}]OTf and *trans*-[(phen)(CO)$_2$Mo{PN(*t*-Bu)CH$_2$CH$_2$O(OMe)}{PN(*t*-Bu)CH$_2$CH$_2$O}]OTf•CH$_2$Cl$_2$.[5d)] In these complexes the bond lengths of Mo–P(phosphenium) are clearly shorter than those of Mo–P(phosphite), indicating that a Mo–P(phosphenium) bond bears a significant double bond character. An amino nitro-

Table 3. Stability of Cationic Phosphenium Complexes Formulated as $[(bpy)(CO)_3M\{PXY\}]^+$

PXY / M						
Cr	⊚	○	○	🄵	🄵	🄵
Mo	⊚	◎	◎	○	🄵	🄵
W	⊚	◎	◎	○	🄵	🄵

⊚ 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.

🄵 A phosphenium complex is not detected but a fluorinated complex, $[(bpy)(CO)_3M\{PXYF\}]$, is formed.

gen 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 P. 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 P. The role of an amino substituent on a phosphenium phosphorus for stabilizing the phosphenium complex has been proposed to protect the approach of a nucleophile to a phosphenium P by high pπ lone pair density flanking the phosphenium center.[5d)] This may be the reason for a tendency observed for a series of the complexes examined in this paper: Diamino phosphenium complexes are more stable than monoaminomonoalkoxy phosphenium complexes, which is 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 P. This orientation exerts the most effective inhibitory action of the amino lone pair electrons on a nucleophilic attack toward a phosphenium P. Supposed 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 P, it is reasonably understood that the stability of $[(bpy)(CO)_3M\{P(NEt_2)_2\}]^+$ and $[(bpy)(CO)_3M\{\overline{PN(Me)CH_2CH_2O}\}]^+$ are similar, and the stability of $[(bpy)(CO)_3M\{\overline{PN(Me)CH_2CH_2NMe}\}]^+$ is greater than that of $[(bpy)(CO)_3M\{P(NEt_2)_2\}]^+$. These features are schematically shown in Fig. 1. An alkoxy substituent may not effectively protect a nucleophilic attack to a phosphenium P. Therefore, a dialkoxy phosphenium complex is not detected but F-introduced complex is obtained.

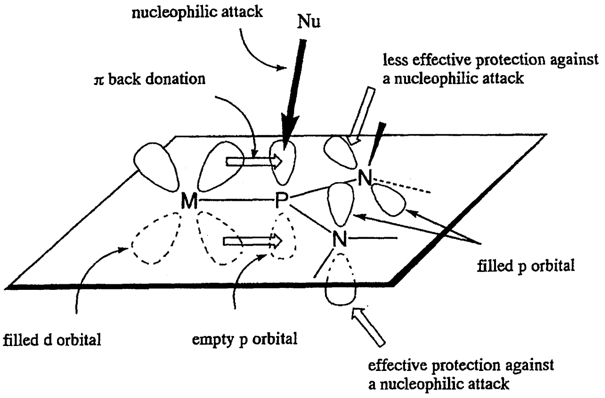
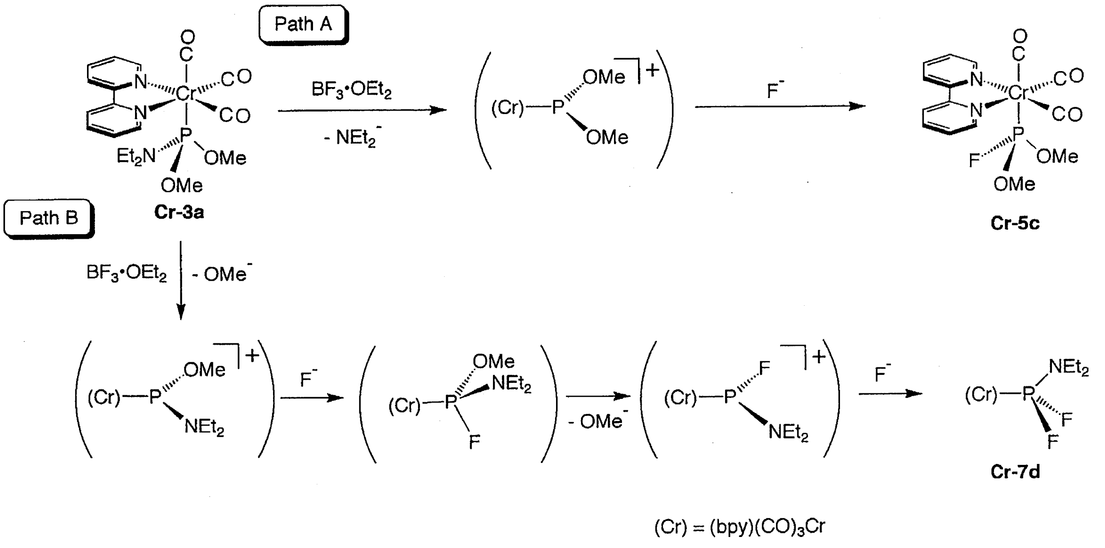


Fig. 1. Bonding feature of a cationic phosphenium complex with two amino substituents on a phosphenium phosphorus.

We have proposed the reason for stabilization of a cationic phosphenium complex by an amino substituent on a phosphenium phosphorus for $[(bpy)(CO)_2M(phosphite)(phosphenium)]^+$ type complexes. And we thought that the same applies to $[(bpy)(CO)_3M(phosphenium)]^+$ type complexes. However, it should be noted that the possibility can not be ruled out for $[(bpy)(CO)_3M(phosphenium)]^+$ type complexes that the amino group donates its lone pair electron density to some extent toward the empty p orbital of phosphenium P. This also reasonably explain the stability tendency observed in this paper.

Let us consider why the *fac* isomer was detected only for $[(bpy)(CO)_3M\{\overline{PN(Me)CH_2CH_2NMe}\}]^+$. Although the mechanism of the *fac–mer* isomerization is not clear now, it



Scheme 8.

has been reported that addition of a Lewis base such as phosphine, alcohol, or $CF_3SO_3^-$ promotes the isomerization.[5d)] The reaction mixtures of cationic phosphenium complexes in this paper have also not strong but potential Lewis bases such as BF_3OR^- and BF_4^-. If a nucleophilic attack of such a Lewis base at the phosphenium P introduces the isomerization, it is reasonably understood that the *fac* isomer was detected only for [(bpy)(CO)$_3$M{PN(Me)CH$_2$CH$_2$NMe}]$^+$ having ethylene bridged diamino substituents on the phosphenium P.

Let us finally consider why **Cr-5c** and **Cr-7d** were formed in the reaction of **Cr-3a** with $BF_3\cdot OEt_2$ (see Scheme 8). An OMe abstraction by BF_3 may take place to give [(Cr)–P(NEt$_2$)(OMe)]$^+$ (Path B), where (Cr) stands for (bpy)(CO)$_3$Cr, which readily reacts with F^- to give [(Cr)–P(NEt$_2$)(OMe)F]. If this Cr complex again reacts with $BF_3\cdot OEt_2$ present in a solution, [(Cr)–P(NEt$_2$)F]$^+$ would be formed, which may react with F^- to yield [(Cr)–P(NEt$_2$)F$_2$] (**Cr-7d**). If an NEt$_2$ group is firstly abstracted from **Cr-3a** by $BF_3\cdot OEt_2$ (Path A), then [(Cr)–P(OMe)$_2$]$^+$ is formed, which readily reacts with F^- to give [(Cr)–P(OMe)$_2$F] (**Cr-5c**). The NEt$_2$ abstraction is probable because it has been reported that *trans*-[(CO)$_4$Mo(PPh$_2$NH$_2$)$_2$] reacts with $BF_3\cdot OEt_2$ to give *trans*-[(CO)$_4$Mo(PPh$_2$NH$_2$)(PPh$_2$F)],[10)] and we also showed examples in this paper in which cationic phosphenium complexes are prepared by NEt$_2$ abstraction as an anion by $BF_3\cdot OEt_2$ from *fac*-[(bpy)(CO)$_3$M{PN(Me)CH$_2$CH$_2$O(NEt$_2$)}]. In the reaction of **Cr-3a** with $BF_3\cdot OEt_2$, OMe abstraction and NEt$_2$ abstraction may proceed simultaneously.

Formation of **Cr-7d** in the reaction of **Cr-1a** with $BF_3\cdot OEt_2$ may be similarly understood. That is, a phosphenium complex firstly generated (**Cr-1b**) is attacked by F^- to give [(Cr)–P(NEt$_2$)$_2$F]. Then, NEt$_2$ abstraction by $BF_3\cdot OEt_2$ present in the solution takes place to give [(Cr)–P(NEt$_2$)F]$^+$, followed by F^- attack to yield [(Cr)–P(NEt$_2$)F$_2$] (**Cr-7d**).

Experimental

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: Toluene, xylene, and THF were distilled from sodium/benzophenone, hexane was distilled from sodium metal, and CH_2Cl_2 and CH_3CN were distilled from P_2O_5. Acetone was distilled from $CaCl_2$. All solvents were stored under a nitrogen atmosphere. $BF_3\cdot OEt_2$ was distilled under reduced pressure and was stored under a nitrogen atmosphere.

P(NEt$_2$)$_2$(OMe),[11a)] PN(Me)CH$_2$CH$_2$O(OMe),[11a)] P(NEt$_2$)(OMe)$_2$,[11a)] POCMe$_2$CMe$_2$O(OMe),[11b)] and PN(Me)CH$_2$CH$_2$O(NEt$_2$)[11c)] were prepared according to the literature method. Complexes M(bpy)(CO)$_4$ (M=Cr, Mo, W),[12)] **Mo-1a**,[5b)] **Mo-2a**,[5d)] **Mo-3a**,[5b)] and **Mo-5a**[5a)] were prepared in the literature methods. IR spectra were recorded on a Shimadzu FTIR-4000 spectrometer. ^{1}H NMR and ^{31}P NMR spectra were measured on JEOL PMX-60, GSX-270, and GSX-500 spectrometers. ^{13}C NMR spectra were recorded on a JEOL EX-400 spectrometer. ^{1}H and ^{13}C NMR data were referenced to Si(CH$_3$)$_4$ as an internal standard, and ^{31}P NMR data were referenced to 85% H$_3$PO$_4$ as an external standard. Elemental analyses were performed on a Perkin-Elmer 2400CHN elemental analyzer.

Preparation of *fac*-[(bpy)(CO)$_3$Cr{P(NEt$_2$)$_2$(OMe)}] (Cr-1a). A solution of Cr(bpy)(CO)$_4$ (200 mg, 6.25 mmol) in CH_3CN (100 ml) was refluxed for 17 h to give *fac*-[(bpy)(CO)$_3$Cr(NCMe)] (IR (KBr, in CH_3CN) ν_{CO}=1906, 1787 cm^{-1}). The solvent was removed under reduced pressure. The residual powder was dissolved in THF (50 ml), and P(NEt$_2$)$_2$(OMe) (3.0 ml, 13.0 mmol) was added to the solution. After being refluxed for 1.5 h, the solution was concentrated to ca. 25 ml. Addition of hexane (50 ml) and then cooling at 0 °C overnight resulted in the formation of a purple powder, which was washed with hexane several times and dried in vacuo to give **Cr-1a** (2910 mg, 5.84 mmol, 93%). Found: C, 52.80; H, 5.99; N, 10.94%. Calcd for $C_{22}H_{31}CrN_4O_4P$: C, 53.01; H, 6.27; N, 11.24%.

Preparation of *fac*-[(bpy)(CO)$_3$W{P(NEt$_2$)$_2$(OMe)}] (W-1a). To a solution of W(bpy)(CO)$_4$ (2055 mg, 4.55 mmol) in xylene

(100 ml) was added $\mathrm{P(NEt_2)_2(OMe)}$ (1.5 ml, 6.52 mmol). After being refluxed for 4.5 h, the solution was kept for several hours at room temperature. The resulting reddish purple precipitates were isolated by filtration, washed with hexane, and dried in vacuo to give **W-1a** (1788 mg, 2.84 mmol, 62%). Found: C, 42.05; H, 5.05; N, 8.68%. Calcd for $\mathrm{C_{22}H_{31}N_4O_4PW}$: C, 41.92; H, 4.96; N, 8.89%.

Preparation of *fac*-[(bpy)(CO)$_3$Cr{$\overline{\mathrm{PN(Me)CH_2CH_2O}}$(OMe)}] (Cr-2a). To a solution of Cr(bpy)(CO)$_4$ (3000 mg, 9.37 mmol) in toluene (100 ml) was added $\overline{\mathrm{PN(Me)CH_2CH_2O}}$(OMe) (2.0 ml, 16.1 mmol). After being refluxed for 2 h, the solution was allowed to stand for several hours at room temperature. The reaction mixture was then cooled in a refrigerator through overnight. The resulting deep green precipitates were isolated by filtration, washed with hexane, and dried in vacuo to give **Cr-2a** (3800 mg, 8.89 mmol, 95%). Found: C, 47.48; H, 4.37; N, 9.97%. Calcd for $\mathrm{C_{17}H_{18}CrN_3O_5P}$: C, 47.78; H, 4.25; N, 9.83%.

Preparation of *fac*-[(bpy)(CO)$_3$W{$\overline{\mathrm{PN(Me)CH_2CH_2O}}$(OMe)}] (W-2a). The complex **W-2a** was prepared in a similar manner to that of **W-1a** from W(bpy)(CO)$_4$ and $\overline{\mathrm{PN(Me)CH_2CH_2O}}$(OMe). Reddish purple powders were yielded in 57%. Found: C, 36.46; H, 3.25; N, 7.43%. Calcd for $\mathrm{C_{17}H_{18}N_3O_5PW}$: C, 36.50; H, 3.24; N, 7.51%.

Preparation of *fac*-[(bpy)(CO)$_3$Cr{P(NEt$_2$)(OMe)$_2$}] (Cr-3a). The complex **Cr-3a** was prepared in a similar manner to that of **Cr-2a** from Cr(bpy)(CO)$_4$ and $\mathrm{P(NEt_2)(OMe)_2}$. Deep green powders were yielded in 73%. Found: C, 49.67; H, 5.28; N, 9.20%. Calcd for $\mathrm{C_{19}H_{24}CrN_3O_5P}$: C, 49.89; H, 5.29; N, 9.19%.

Preparation of *fac*-[(bpy)(CO)$_3$W{P(NEt$_2$)(OMe)$_2$}] (W-3a). The complex **W-3a** was prepared in a similar manner to that of **W-1a** from W(bpy)(CO)$_4$ and $\mathrm{P(NEt_2)(OMe)_2}$. Reddish purple powders were yielded in 71%. Found: C, 38.51; H, 4.10; N, 6.97%. Calcd for $\mathrm{C_{19}H_{24}N_3O_5PW}$: C, 38.73; H, 4.11; N, 7.13%.

Preparation of *fac*-[(bpy)(CO)$_3$Cr{$\overline{\mathrm{POCMe_2CMe_2O}}$(OMe)}] (Cr-4a). The complex **Cr-4a** was prepared in a similar manner to that of **Cr-2a** from Cr(bpy)(CO)$_4$ and $\overline{\mathrm{POCMe_2CMe_2O}}$(OMe). Deep green powders were yielded in 80%. Found: C, 50.91; H, 4.98; N, 6.08%. Calcd for $\mathrm{C_{20}H_{23}CrN_2O_6P}$: C, 51.07; H, 4.93; N, 5.95%.

Preparation of *fac*-[(bpy)(CO)$_3$Mo{$\overline{\mathrm{POCMe_2CMe_2O}}$(OMe)}] (Mo-4a). A solution of Mo(bpy)(CO)$_4$ (1800 mg, 4.94 mmol) in $\mathrm{CH_3CN}$ (100 ml) was refluxed for 5 h to give *fac*-[(bpy)(CO)$_3$Mo(NCMe)] (IR (KBr, in $\mathrm{CH_3CN}$) ν_{CO}=1908, 1788 cm^{-1}). The solvent was removed under reduced pressure. The residue was dissolved in THF (50 ml), and $\overline{\mathrm{POCMe_2CMe_2O}}$(OMe) (1.26 ml, 7.41 mmol) was added to the solution. After being refluxed for 1 h, the solvent was removed under reduced pressure. The residue was recrystallized from $\mathrm{CH_2Cl_2}$/hexane to give reddish powders, which were washed with hexane several times and dried in vacuo to give **Mo-4a** (2470 mg, 4.80 mmol, 97%). Found: C, 46.70; H, 4.46; N, 5.29%. Calcd for $\mathrm{C_{20}H_{23}MoN_2O_6P}$: C, 46.70; H, 4.51; N, 5.45%.

Preparation of *fac*-[(bpy)(CO)$_3$W{$\overline{\mathrm{POCMe_2CMe_2O}}$(OMe)}] (W-4a). The complex **W-4a** was prepared in a similar manner to that of **W-1a** from W(bpy)(CO)$_4$ and $\overline{\mathrm{POCMe_2CMe_2O}}$(OMe). Reddish purple powders were yielded in 75%. Found: C, 39.66; H, 3.81; N, 4.91%. Calcd for $\mathrm{C_{20}H_{23}N_2O_6PW}$: C, 39.89; H, 3.85; N, 4.65%.

Preparation of *fac*-[(bpy)(CO)$_3$Cr{P(OMe)$_3$}] (Cr-5a). The complex **Cr-5a** was prepared in a similar manner to that of **Cr-2a** from Cr(bpy)(CO)$_4$ and $\mathrm{P(OMe)_3}$. Deep green powders were yielded in 77%. Found: C, 46.02; H, 4.31; N, 6.83%. Calcd for $\mathrm{C_{16}H_{17}CrN_2O_6P}$: C, 46.16; H, 4.12; N, 6.73%.

Preparation of *fac*-[(bpy)(CO)$_3$W{P(OMe)$_3$}] (W-5a). A solution of W(bpy)(CO)$_4$ (1490 mg, 3.30 mmol) in $\mathrm{CH_3CN}$ (150 ml) was refluxed for 24 h to give *fac*-[(bpy)(CO)$_3$W(NCMe)] (IR (KBr, in $\mathrm{CH_3CN}$) ν_{CO}=1898, 1783 cm^{-1}). The solvent was removed under reduced pressure. The residual powder was dissolved in THF (50 ml), and $\mathrm{P(OMe)_3}$ (0.50 ml, 4.23 mmol) was added to the solution. After being refluxed for 1 h, the solution was filtrated. Addition of hexane (50 ml) to the filtrate formed the blackish purple powder, which was washed with hexane several times and dried in vacuo to give **W-5a** (1542 mg, 2.81 mmol, 85%). Found: C, 34.93; H, 3.08; N, 5.26%. Calcd for $\mathrm{C_{16}H_{17}N_2O_6PW}$: C, 35.06; H, 3.13; N, 5.11%.

Preparation of *fac*-[(bpy)(CO)$_3$Cr{$\overline{\mathrm{PN(Me)CH_2CH_2O}}$(NEt$_2$)}] (Cr-6a). The complex **Cr-6a** was prepared in a similar manner to that of **Cr-2a** from Cr(bpy)(CO)$_4$ and $\overline{\mathrm{PN(Me)CH_2CH_2O}}$(NEt$_2$). Deep green powders were yielded in 86%. The product was further purified for elemental analysis by recrystallization from $\mathrm{CH_2Cl_2}$/hexane. Found: C, 51.12; H, 5.27; N, 11.60%. Calcd for $\mathrm{C_{20}H_{25}CrN_4O_4P}$: C, 51.28; H, 5.38; N, 11.96%.

Preparation of *fac*-[(bpy)(CO)$_3$Mo{$\overline{\mathrm{PN(Me)CH_2CH_2O}}$(NEt$_2$)}] (Mo-6a). The complex **Mo-6a** was prepared in a similar manner to that of **Cr-2a** from Mo(bpy)(CO)$_4$ and $\overline{\mathrm{PN(Me)CH_2CH_2O}}$(NEt$_2$). Reddish purple powders were yielded in 69%. It was further purified by recrystallization from acetone/hexane for elemental analysis. Found: C, 46.62; H, 4.84; N, 10.81%. Calcd for $\mathrm{C_{20}H_{25}MoN_4O_4P}$: C, 46.88; H, 4.92; N, 10.93%.

Preparation of *fac*-[(bpy)(CO)$_3$W{$\overline{\mathrm{PN(Me)CH_2CH_2O}}$(NEt$_2$)}] (W-6a). The complex **W-6a** was prepared in a similar manner to that of **W-1a** from W(bpy)(CO)$_4$ and $\overline{\mathrm{PN(Me)CH_2CH_2O}}$(NEt$_2$). Reddish purple powders were yielded in 77%. Found: C, 39.76; H, 4.15; N, 9.44%. Calcd for $\mathrm{C_{20}H_{25}N_4O_4PW}$: C, 40.02; H, 4.20; N, 9.33%.

Reactions of Phosphite Complexes with $\mathrm{BF_3\cdot OEt_2}$. In general, a solution of the phosphite complex (ca. 0.5—1.5 mmol) in $\mathrm{CH_2Cl_2}$ (ca. 10 ml) was cooled to −78 °C and 2 equiv of $\mathrm{BF_3\cdot OEt_2}$ was added. The solution was then allowed to warm to room temperature. The resulting solution was subjected to ^{31}P NMR measurement and, in some cases, also to ^{13}C NMR and IR measurements. Yields of cationic phosphenium complexes estimated from ^{31}P NMR data are as follows: 42% (**Cr-1b**), 100% (**Mo-1b**), 100% (**W-1b**), 25% (**Cr-2b**), 100% (**Mo-2b**), 100% (**W-2b**), 14% (**Mo-3b**), 32% (**W-3b**).

Preparation of *fac*-[(bpy)(CO)$_3$Cr{$\overline{\mathrm{POCMe_2CMe_2O}}$(F)}]

(Cr-4c). A solution of *fac*-[(bpy)(CO)$_3$Cr{$\overline{POCMe_2CMe_2O}$-(OMe)}] (**Cr-4a**) (406 mg, 0.863 mmol) in CH_2Cl_2 (10 ml) was cooled to −78 °C, and then $BF_3\cdot OEt_2$ (0.12 ml, 0.955 mmol) was added. The mixture was allowed to warm to room temperature. After several hours, the mixture was concentrated to ca. 4 ml, which was put on a silica gel column and eluted with CH_2Cl_2. The first eluted reddish orange fraction containing Cr(bpy)(CO)$_4$ was discarded, and the second bluish violet fraction was collected and dried in vacuo. Thus obtained was *fac*-[(bpy)(CO)$_3$Cr{$\overline{POCMe_2CMe_2O}$-(F)}] (152 mg, 0.332 mmol, 38%). The product was further purified for elemental analysis by recrystallization from acetone/hexane. The complex **Cr-4c** was isolated by filtration, washed with hexane, and dried in vacuo. Found: C, 49.66; H, 4.41; N, 6.07%. Calcd for $C_{19}H_{20}CrFN_2O_5P$: C, 49.79; H, 4.40; N, 6.11%.

Preparation of *fac*-[(bpy)(CO)$_3$Mo{$\overline{POCMe_2CMe_2O}$(F)}] (Mo-4c). A solution of *fac*-[(bpy)(CO)$_3$Mo{$\overline{POCMe_2CMe_2O}$-(OMe)}] (**Mo-4a**) (416 mg, 0.809 mmol) in CH_2Cl_2 (10 ml) was cooled to −78 °C, and then $BF_3\cdot OEt_2$ (0.11 ml, 0.876 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_2Cl_2. The first eluted reddish orange fraction containing Mo(bpy)(CO)$_4$ was discarded, and the second reddish violet fraction was collected and dried in vacuo. Thus obtained was *fac*-[(bpy)(CO)$_3$Mo{$\overline{POCMe_2CMe_2O}$(F)}] (**Mo-4c**) (110 mg, 0.219 mmol, 27%). For elemental analysis, further purification was done by recrystallization from CH_2Cl_2/hexane. The complex **Mo-4c** was isolated by filtration, washed with hexane, and dried in vacuo. Found: C, 45.46; H, 3.90; N, 5.53%. Calcd for $C_{19}H_{20}FMoN_2O_5P$: C, 45.43; H, 4.01; N, 5.58%.

Preparation of *fac*-[(bpy)(CO)$_3$W{$\overline{POCMe_2CMe_2O}$(F)}] (W-4c). A solution of *fac*-[(bpy)(CO)$_3$W{$\overline{POCMe_2CMe_2O}$-(OMe)}] (**W-4a**) (247 mg, 0.410 mmol) in CH_2Cl_2 (10 ml) was cooled to −78 °C, and then $BF_3\cdot OEt_2$ (0.10 ml, 0.796 mmol) was added. The mixture was allowed to warm to room temperature. After several hours, the mixture was concentrated to ca. 3 ml, which was put on a silica gel column and eluted with CH_2Cl_2. The first eluted orange fraction containing W(bpy)(CO)$_4$ was discarded, and the second reddish violet fraction was collected and dried in vacuo. *fac*-[(bpy)(CO)$_3$W{$\overline{POCMe_2CMe_2O}$(F)}] (**W-4c**) was obtained (104 mg, 0.176 mmol, 43%). In order to perform satisfactory elemental analysis, the complex was further purified by recrystallization with acetone/hexane. Found: C, 38.83; H, 3.33; N, 4.72%. Calcd for $C_{19}H_{20}FN_2O_5PW$: C, 38.67; H, 3.42; N, 4.75%.

Preparation of *fac*-[(bpy)(CO)$_3$Cr{P(OMe)$_2$(F)}] (Cr-5c). A solution of *fac*-[(bpy)(CO)$_3$Cr{P(OMe)$_3$}] (576 mg, 1.38 mmol) in CH_2Cl_2 (12 ml) was cooled to −78 °C, and $BF_3\cdot OEt_2$ (0.20 ml, 1.87 mmol) was added. The reaction mixture was allowed to warm to room temperature. After several hours, the solution was concentrated to ca. 5 ml, which was loaded to a silica gel column and eluted with CH_2Cl_2. The first eluted reddish orange fraction was discarded, and the second bluish violet fraction was collected and concentrated to dryness. The complex **Cr-5c** was obtained in 42% yield (236 mg, 0.584 mmol). The product was further purified for elemental analysis by recrystallization from acetone/hexane. The complex **Cr-5c** was isolated by filtration, washed with hexane, and dried in vacuo. Found: C, 44.51; H, 3.42; N, 6.87%. Calcd for $C_{15}H_{14}CrFN_2O_5P$: C, 44.57; H, 3.49; N, 6.93%. The complex **Cr-5c** was also obtained from the reaction of **Cr-3a** with $BF_3\cdot OEt_2$ (31%).

Preparation of *fac*-[(bpy)(CO)$_3$W{P(OMe)$_2$(F)}] (W-5c). A solution of *fac*-[(bpy)(CO)$_3$W{P(OMe)$_3$}] (191 mg, 0.348 mmol) in CH_2Cl_2 (10 ml) was cooled to −78 °C, and $BF_3\cdot OEt_2$ (0.09 ml, 0.717 mmol) was added. The reaction mixture was allowed to warm to room temperature. After several hours, the solution was concentrated to dryness. The residual powder was dissolved in THF, which was loaded to a silica gel column and eluted with CH_2Cl_2. The purple fraction was collected and concentrated to 10 ml, and hexane was added to form a purple powder, which was isolated by filtration, washed with hexane, and dried in vacuo to give **W-5c** (70 mg, 0.131 mmol, 38%). Found: C, 33.77; H, 2.51; N, 5.13%. Calcd for $C_{15}H_{14}FN_2O_5PW$: C, 33.61; H, 2.63; N, 5.22%.

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