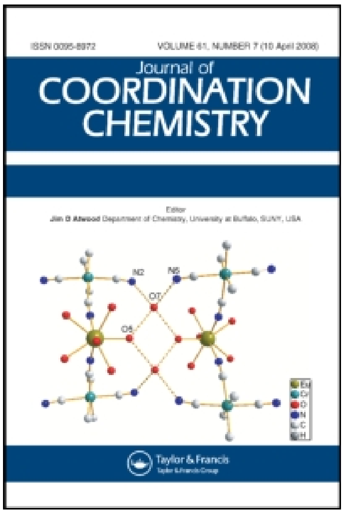

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ABSTRACTION OF OR GROUP FROM Mo-PHOSPHITE COMPLEXES BY BX_3

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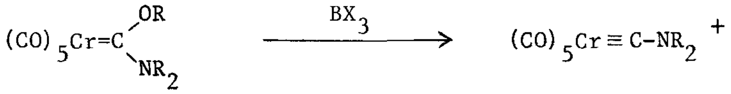
Fischer-type carbene complexes react with BX_3 to afford transition-metal carbyne complexes where an OR group on the carbene carbon is



$$(CO)_5Cr{=}C\begin{matrix}\diagup OR\\ \diagdown NR_2\end{matrix} \xrightarrow{BX_3} (CO)_5Cr\equiv C{-}NR_2{}^{+}$$

abstracted by BX_3 as an anion.[1] We have been interested in the reaction of BX_3 with a phosphite coordinating to a transition-metal in the hope of producing a complex containing a double bond between a transition-metal and phosphorus. The reaction of BX_3 with $P(OR)_3$ uncoordinated to transition-metal is known to produce stepwise $P(OR)_2X$, $P(OR)X_2$, or PX_3, depending on the reaction conditions.[2]

We have chosen $[Mo(bipy)(CO)_3P(OR)_3]$ (bipy = bipyridine)[3] as a transition-metal complex containing phosphite. The reaction of the molybdenum complex with 2 equiv of $BF_3{\cdot}OEt_2$ in dichloromethane at −78°C yielded a dark red powder. The $^{31}P\{^1H\}$ NMR data showing a doublet with about 1170 Hz coupling constant and $^{19}F\{^1H\}$ NMR data showing a doublet with the same coupling constant, and other spectroscopic data listed in Table 1 indicate the formation of fac-$[Mo(bipy)(CO)_3P(OR)_2F]$ (yield: 80%, 50%, 20% for R = Me, Et, i-Pr, respectively). The reaction of isolated fac-$[Mo(bipy)(CO)_3P(OR)_2F]$ with 1 equiv of $BF_3{\cdot}OEt_2$ caused an intractable oil in which $[Mo(bipy)(CO)_3P(OR)F_2]$ was not contained.

$$\text{fac-[Mo(bipy)(CO)}_3\text{P(OR)}_3] \xrightarrow{2BX_3\cdot OEt_2} \text{fac-[Mo(bipy)(CO)}_3\text{P(OR)}_2\text{F]}$$

(R = Me, Et, i-Pr)

The reaction of fac-[Mo(bipy)(CO)$_3$P(OMe)$_3$] with 2 equiv of BCl$_3$ generated mer-[Mo(bipy)(CO)$_3$P(OMe)Cl$_2$] (80% yield), where the two OR groups were displaced by two Cl atoms and geometrical rearrangement around the Mo atom took place. The reaction with 1 equiv of BCl$_3$ gave mer-[Mo(bipy)(CO)$_3$P(OMe)Cl$_2$] (25%) and free

$$\text{fac-[Mo(bipy)(CO)}_3\text{P(OMe)}_3] \xrightarrow{2BCl_3} \text{mer-[Mo(bipy)(CO)}_3\text{P(OMe)Cl}_2]$$

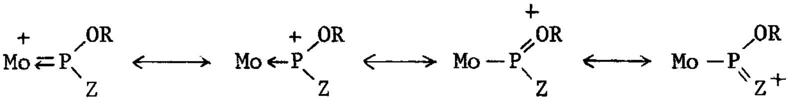
TABLE I Spectroscopic data of Mo(CO)$_3$(bipy)L

L	IR(cm^{-1})$^{a)}$ ν(CO)	^{1}H NMR(δ ppm)$^{b)}$	^{31}P NMR(δ ppm)$^{c)}$
P(OMe)$_3$	1929 1831 1795	7-9 (m, 8H, bipy) 3.30 (d, J=10.0Hz, 9H, CH$_3$)	153.3 (s)
P(OMe)$_2$F$^{d)}$	1939 1844 1805	7-9 (m, 8H, bipy) 3.46 (d, J=10.0Hz, 6H, CH$_3$)	151.9 (d, J=1171Hz)
P(OEt)$_3$	1925 1826 1792	7-9 (m, 8H, bipy) 0.93 (t, J=7.0Hz, 9H, CH$_3$) 3.67 (m, 6H, CH$_2$)	149.1 (s)
P(OEt)$_2$F	1937 1842 1801	7-9 (m, 8H, bipy) 1.02 (t, J=7.0Hz, 6H, CH$_3$) 3.88 (m, 4H, CH$_2$)	149.8 (d, J=1169Hz)
P(O-i-Pr)$_3$	1920 1822 1790	7-9 (m, 8H, bipy) 0.97 (d, J=6.0Hz, 18H, CH$_3$) 4.53 (m, 3H, CH)	147.8 (s)
P(O-i-Pr)$_2$F	1934 1839 1800	7-9 (m, 8H, bipy) 0.97 (d, J=6.0Hz, 12H, CH$_3$) 4.60 (m, 2H, CH)	152.0 (d, J=1168Hz)
P(OMe)Cl$_2$	1960 1880 1840	7-9 (m, 8H, bipy) 3.62 (d, J=12.1, 1H, CH$_3$) 3.85 (d, J=14.8, 2H, CH$_3$)	146.0 (s)

a) in CH$_2$Cl$_2$ b) in acetone-d$_6$ c) in acetone d) ^{19}F NMR (in acetone) -48.9ppm (d, J=1173Hz)

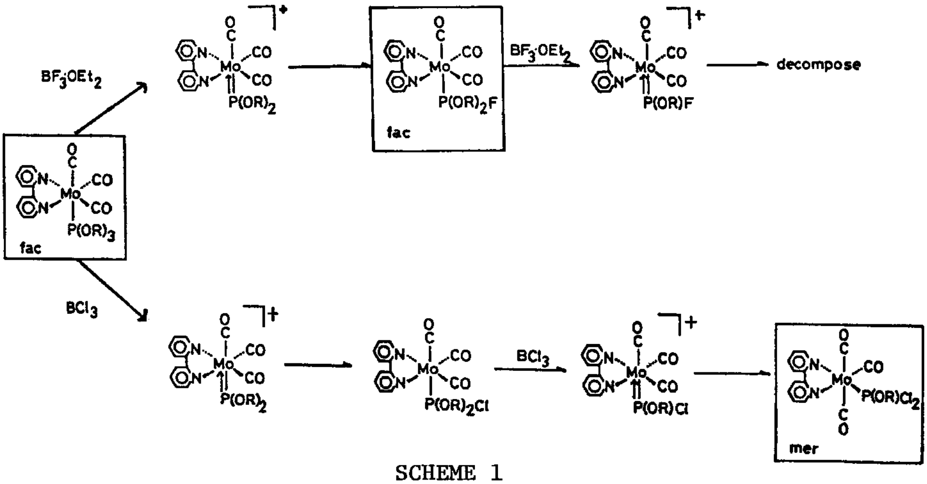
$P(OMe)_2Cl$ (25%), but did not yield mono-substituted product, $[Mo(bipy)(CO)_3P(OMe)_2Cl]$.

Two mechanisms in terms of the OR group(s) exchange by halogen(s) can be thought to be possible. One is a concerted process like a mechanism proposed in the reaction of free phosphite and BX_3, and the other is the process where a 3 electron donor terminal phosphide complex is formed as an intermediate owing to the abstraction of an OR group on the phosphorus as an anion by BX_3. If a 3 electron donor terminal phosphide complex is generated in the present reaction, it is cationic, and the following resonance can be considered. If Z is OR, the intermediate may be



$$\overset{+}{Mo}\rightleftharpoons P\begin{smallmatrix}OR\\Z\end{smallmatrix} \longleftrightarrow \overset{+}{Mo}\leftarrow P\begin{smallmatrix}OR\\Z\end{smallmatrix} \longleftrightarrow Mo-\overset{+}{P}\begin{smallmatrix}OR\\Z\end{smallmatrix} \longleftrightarrow Mo-P\begin{smallmatrix}OR\\Z^{+}\end{smallmatrix}$$

highly stabilized by the resonance, but if Z is a strong electron withdrawing group, such as F, the resonance would not stabilize the intermediate, thus the intermediate formed may decompose before nucleophilic attack of X^- on the phosphorus atom. Though it is difficult to rule out the concerted mechanism, the mechanism



SCHEME 1

via a terminal phosphide complex is compatible with the experimental results mentioned above. The reaction sequence we tentatively proposed is summarized in Scheme 1.

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