3). A frozen solution of **1** exhibits an interesting temperature dependence. The $g \sim 4$ signal reaches a maximum in intensity at 30 K and disappears at temperatures lower than 15 K. This signal probably arises from the thermally populated $S = {}^3/_2$ state. The $g \sim 2$ signal is barely noticeable at temperatures greater than 30 K. At 7.5 K, 29 manganese hyperfine lines are clearly resolved, which are due to the population of the $S = {}^1/_2$ state of the molecule arising from antiferromagnetic coupling between the high-spin Mn(II) ($S = {}^5/_2$) and high-spin Mn(III) ($S = 2$) ions. One expects 36 hyperfine lines for an $S = {}^1/_2$ state of a binuclear manganese complex. However, less lines may be observed due to overlap. Approximately 17–19 hyperfine lines have been observed for the $g \sim 2$ signal of the S_2 state of PS(II).[4a,19] We have observed similar spectral behavior for two additional mixed-valence Mn(II,III) dimers prepared from septadentate benzimidazole ligands.[20] In addition, similar magnetic behavior also has been reported for $[Mn_2(bpmp)(\mu\text{-}OAc)_2]^{2+}$.[15] Efforts to simulate the multiline EPR signals for compound **1** and related compounds are in progress, and a complete description of the structure and properties of **1** will be reported later.

Acknowledgment. We are thankful for support from the National Science Foundation, Grant RII-8610671, and the Commonwealth of Kentucky through the Kentucky EPSCoR program (R.M.B.). In addition, we would like to acknowledge the generous support from the University Research Foundation (Grant I.D. 61-102-9626). The authors acknowledge the helpful comments by the reviewers during the final preparation of the manuscript.

Supplementary Material Available: A table of fractional coordinates and isotropic thermal parameters for $[Mn(L\text{-}Im)(\mu\text{-}OAc)_2](ClO_4)_2$ (**1**) (4 pages). Ordering information is given on any current masthead page.

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[19] Dismukes, G. C.; Ferris, K.; Watnick, P. *Photochem. Photobiophys.* **1982**, *3*, 243.

[20] A total of 29 Mn hyperfine lines have been observed for a structurally similar mixed-valence dimer containing the ligand 2,6-bis[(bis(2-benzimidazolylmethyl)amino)methyl]-4-methylphenol while 19 lines are observed for the Mn(II,III) dimer of the ligand *N,N,N′,N′*-tetrakis-[(2-methylenebenzimidazolyl)]-1,3-diaminopropan-2-ol. The complete description of the structural and physiochemical properties of these compounds will be reported elsewhere.

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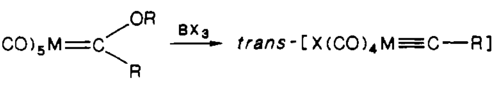
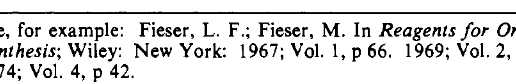
Alkoxy/Halogen Exchange Reaction of Molybdenum Complexes Containing Phosphite with Boron Trihalides

Sir:

Boron trihalides, BX_3, are known to have properties to abstract an OR group or halogens on a carbon atom.[1] This reactivity has been applied to the preparation of transition-metal carbyne complexes from Fischer-type carbene complexes (eq 1 and 2)[2] and to the halogen exchange of transition-metal perfluoroalkyl carbonyl complexes (eq 3).[3] In eq 1, an OR group on the carbene carbon



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



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

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

is abstracted as OR^- anion by BX_3, resulting in the bond order between the transition metal and the carbon atom being incremented by one from two to three. 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.

The reaction of transition-metal complexes containing a phosphite with BX_3 has not, to our knowledge, been reported. In this communication, we report the reaction of *fac*-$[Mo(bpy)(CO)_3\{P(OR)_3\}]$ (bpy = 2,2′-bipyridine) with $BF_3{\cdot}OEt_2$ and BCl_3. In the former reaction, one OR group was displaced by F with geometrical retention around the Mo atom, while in the latter reaction, two OR groups were replaced with two Cl atoms with a change in the geometry around the Mo atom.

A dichloromethane solution containing *fac*-$[Mo(bpy)(CO)_3\{P(OR)_3\}]$[4,5] was treated with 2 equiv of $BF_3{\cdot}OEt_2$ at −78 °C and allowed to warm to room temperature. The reaction mixture was passed through a silica gel column with dichloromethane. The violet fraction collected was precipitated from hexane to give a dark red powder. The spectroscopic data indicate the formation of *fac*-$[Mo(bpy)(CO)_3\{P(OR)_2F\}]$ (yield: **2a**, 80%; **2b**, 50%; **2c**, 20%).[6]

fac-$[Mo(bpy)(CO)_3\{P(OR)_3\}] \xrightarrow{2BF_3\cdot OEt_2}$
R = Me (**1a**)
R = Et (**1b**)
R = *i*-Pr (**1c**)

fac-$[Mo(bpy)(CO)_3\{P(OR)_2F\}]$
R = Me (**2a**)
R = Et (**2b**)
R = *i*-Pr (**2c**)

The reaction of **1a** with more than 3 equiv of $BF_3{\cdot}OEt_2$ or that of **2a** isolated with 1 equiv of $BF_3{\cdot}OEt_2$ did not yield two or more displaced $[Mo(bpy)(CO)_3\{P(OMe)_{3-n}F_n\}]$ (n = 2 or 3) complexes. The only detectable product containing a Mo atom in this reaction was $[Mo(bpy)(CO)_4]$.

The treatment of **1a** with 2 equiv of BCl_3 in dichloromethane at −78 °C resulted in a double OR/Cl exchange with the geometrical rearrangement around the Mo atom to produce *mer*-$[Mo(bpy)(CO)_3\{P(OMe)Cl_2\}]$ (**3a**) (80%).[7,8] The geometrical

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[1] 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.

[2] (a) Fischer, E. O. *Adv. Organomet. Chem.* **1976**, *14*, 1. (b) Schubert, U. In *The* Chemistry *of the Metal–Carbon Bond*; Hartley, F. R., Patai, S., Eds.; Wiley: New York, 1982; Vol. 1, p 233. (c) Fischer, E. O.; Schneider, J.; Neugebauer, D. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 820. (d) Fischer, H.; Motsch, A.; Markl, R.; Ackermann, K. *Organometallics* **1985**, *4*, 726.

[3] (a) Richmond, T. G.; Shriver, D. F. *Organometallics* **1983**, *2*, 1061. (b) Richmond, T. G.; Shriver, D. F. *Organometallics* **1984**, *3*, 305.

[4] **1a** and **1b** were prepared from $[Mo(bpy)(CO)_4]$ and the corresponding phosphite by the literature methods. Houk, L. W.; Dobson, G. R. *J. Chem. Soc. A* **1966**, 317. Houk, L. W.; Dobson, G. R. *Inorg. Chem.* **1966**, *5*, 2119. **1c** was prepared in a manner identical with that for **1a** or **1b**. For **1a**: IR (in dichloromethane) ν(CO) 1929, 1831, 1795 cm^{-1}; ^{1}H NMR (in acetone-d_6) δ 7.28–9.13 (m, 8 H, bpy), 3.30 (d, J = 10.0 Hz, 9 H, OCH_3); $^{31}P\{^1H\}$ NMR (in acetone) δ 153.3 (s). For **1b**: IR (in dichloromethane) ν(CO) 1925, 1826, 1792 cm^{-1}; ^{1}H NMR (in acetone-d_6) δ 7.22–9.10 (m, 8 H, bpy), 3.67 (m, 6 H, OCH_2CH_3), 0.93 (t, J = 7.0 Hz, 9 H, OCH_2CH_3); $^{31}P\{^1H\}$ NMR (in acetone) δ 149.1 (s). For **1c**: IR (in dichloromethane) ν(CO) 1920, 1822, 1790 cm^{-1}; ^{1}H NMR (in acetone-d_6) δ 7.27–9.10 (m, 8 H, bpy), 4.53 (m, 3 H, $OCH(CH_3)_2$), 0.97 (d, J = 6.0 Hz, 18 H, $OCH(CH_3)_2$); $^{31}P\{^1H\}$NMR (in acetone) δ 147.8 (s).

[5] The IR intensities of three bands in the ν(CO) region are equally strong. This can be also said for **2a**, **2b**, **2c**, and **3a**.

[6] For **2a**: IR (in dichloromethane) ν(CO) 1939, 1844, 1805 cm^{-1}; ^{1}H NMR (in acetone-d_6) δ 7.32–9.12 (m, 8 H, bpy), 3.46 (d, J = 10.0 Hz, 6 H, OCH_3); $^{31}P\{^1H\}$ NMR (in acetone) δ 151.9 (d, J = 1171 Hz); $^{19}F\{^1H\}$ NMR (in acetone) δ −48.9 (d, J = 1173 Hz). Anal. Calcd for $C_{15}H_{14}FMoN_2O_5P$: C, 40.20; H, 3.15; N, 6.25. Found: C, 40.60; H, 2.91; N, 6.08. For **2b**: IR (in dichloromethane) ν(CO) 1937, 1842, 1801 cm^{-1}; ^{1}H NMR (in acetone-d_6) δ 7.33–9.12 (m, 8 H, bpy), 3.88 (m, 4 H, OCH_2CH_3), 1.02 (t, J = 7.0 Hz, 6 H, OCH_2CH_3); $^{31}P\{^1H\}$ NMR (in acetone) δ 149.8 (d, J = 1169 Hz). Anal. Calcd for $C_{17}H_{18}FMoN_2O_5P$: C, 42.87; H, 3.81; N, 5.88. Found: C, 42.63; H, 3.75; N, 5.85. For **2c**: IR (in dichloromethane) ν(CO) 1934, 1839, 1800 cm^{-1}; ^{1}H NMR (in acetone-d_6) δ 7.30–9.10 (m, 8 H, bpy), 4.60 (m, 2 H, $OCH(CH_3)_2$), 0.97 (d, J = 7 Hz, 12 H, $OCH(CH_3)_2$); $^{31}P\{^1H\}$ NMR (in acetone) δ 152.0 (d, J = 1168 Hz).

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$$\underset{\mathbf{1a}}{fac\text{-}[\mathrm{Mo(bpy)(CO)_3\{P(OMe)_3\}}]} \xrightarrow{2\mathrm{BCl_3}} \underset{\mathbf{3a}}{mer\text{-}[\mathrm{Mo(bpy)(CO)_3\{P(OMe)Cl_3\}}]}$$

rearrangement is evidenced by the $^{13}C\{^1H\}$ NMR spectrum.[9] The rearrangement may be due to the strong trans influence of a $P(OMe)Cl_2$ ligand. The reaction of **1a** with 1 equiv of BCl_3 yielded **3a** (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 from **1a** and BCl_3, but it is very reactive; thus, some of the molecules react with the BCl_3 still existing in solution to give **3a**, and some of them decompose to afford $[Mo(bpy)(CO)_4]$, releasing free $P(OMe)_2Cl$.

$$\begin{tikzcd}
\mathbf{1a} \arrow[r, "BCl_3"] & {[\mathrm{Mo(bpy)(CO)_3\{P(OMe)_2Cl\}}]} \arrow[r, "BCl_3"] \arrow[dr] & \mathbf{3a} \\
 & & {[\mathrm{Mo(bpy)(CO)_4}] + \mathrm{P(OMe)_2Cl}}
\end{tikzcd}$$

The mechanism of replacement of OR group(s) on the phosphorus ligating to the Mo atom with X is not clear now, but it may involve an ionic intermediate containing a cationic phosphenium ligand or it may be of a concerted nature. 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).[3] If the electrophilic alkoxide abstraction from phosphorus by BX_3 takes place in the same manner as the halogen abstraction, then the cationic phosphenium complex is a more probable candidate as an intermediate.

Acknowledgment. We thank Akira Mizuno and Yoshihisa Toda at the Analytical Research Laboratory, Research Center, Mitsui Petrochemical Industries, Ltd., for ^{31}P, ^{19}F, and ^{13}C NMR measurements.

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(7) For **3a**: IR (in dichloromethane) ν(CO) 1960, 1880, 1840 cm^{-1}; ^1H NMR (in acetone-d_6) δ 7.60–9.23 (m, 8 H, bpy), 3.85 (d, J = 14.8 Hz, 2 H, OCH_3), 3.62 (d, J = 12.1 Hz, 1 H, OCH_3); $^{31}P\{^1H\}$ NMR δ 146.0 (s). Anal. Calcd for $C_{14}H_{11}Cl_2MoN_2O_4P$: 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.

(8) The reactions of **1b** and **1c** with 2 equiv of BCl_3 produce analogues of **3a**, though these reactions are not so clean.

(9) The $^{13}C\{^1H\}$ NMR spectrum for **3a** exhibits 10 sets of signals in the bpy region, out of which six sets are doublets. In the CO region, three singlets are observed. If the $P(OMe)Cl_2$ ligand rotates freely along the P–Mo bond, then carbonyl carbons cis to the both nitrogen atoms of the coordinated bpy would be magnetically equal. Thus, some interamolecular interaction between one of the carbonyl groups and presumably the OCH_3 group on the phosphorus atom may be expected. This is compatible with the fact that in the ^1H NMR spectrum one methoxy hydrogen is magnetically different from the other two methoxy hydrogens. The $^{13}C\{^1H\}$ NMR spectrum for **1a** containing facial geometry exhibits three singlets and two doublets with small coupling constants in the bpy region and two doublets in the terminal CO region. For **3a**: $^{13}C\{^1H\}$ NMR (in THF-d_8) δ 54.7 (d, J = 20.3 Hz, OCH_3) 122.6 (s, bpy), 123.3 (d, J = 61.8 Hz, bpy), 125.2 (s, bpy), 125.5 (d, J = 27.1 Hz, bpy), 137.4 (s, bpy), 138.4 (d, J = 108.5 Hz, bpy), 152.5 (d, J = 6.8 Hz, bpy), 152.6 (d, J = 13.6 Hz, bpy), 154.4 (d, J = 47.5 Hz, bpy), 154.7 (s, bpy), 219.8 (s, CO), 222.0 (d, J = 20.3 Hz, CO). For **1a**: $^{13}C\{^1H\}$ NMR (in THF-d_8) δ 49.5 (d, J = 1.6 Hz, OCH_3), 121.7 (s, bpy), 124.0 (s, bpy), 135.9 (s, bpy), 152.2 (d, J = 2.1 Hz, bpy), 154.7 (d, J = 1.0 Hz, bpy), 213.7 (d, J = 64.9 Hz, CO), 226.2 (d, J = 14.0 Hz, CO).

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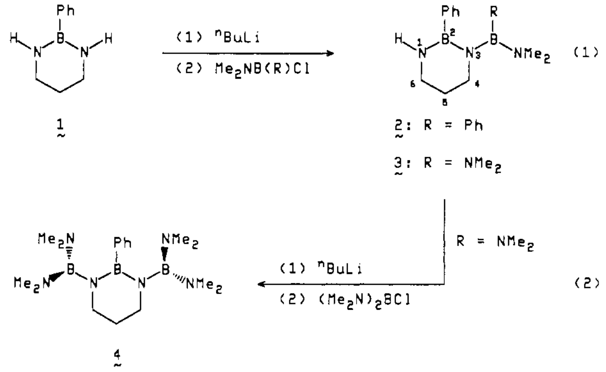
Boron–Nitrogen Polymer Precursors. Synthesis, Structure, and Stereochemistry of *N*-Boryl Derivatives of the 1,3,2-Diazaboracyclohexane Ring System

Sir:

In recent years, there has been an increasing level of interest in the use of small-molecule boron–nitrogen compounds as potential precursors to B–N polymers, BN-based ceramics, and other solid-state materials.[1] The possibility of preparing *linear* B–N polymers [i.e., poly(iminoboranes),[2] $(RBNR)_n$] is especially intriguing since such materials are not only preceramic polymers[3] but are also the isoelectronic analogues of polyacetylene and related organic conductors. In the 1950s and 1960s, the syntheses of numerous amine- and aminoboranes were reported along with many unsuccessful attempts to polymerize such reagents.[4] The high thermal stability of the cyclic trimers [i.e., borazines, $(RBNR)_3$] is generally cited as the reason for the failure of the B–N "monomers" to polymerize. In order to overcome the problem of borazine ring formation, two different approaches, both involving diborylamines as condensation monomers, are being studied in our laboratory. The incorporation of a linear N–B–N–B unit along with other structural features is intended to prevent these systems from condensing to the six-membered borazine rings upon thermolysis. In the first method, acyclic diborylamines containing both Si–N and B–X groups are the starting compounds. A few such species, having the sterically protecting *t*-Bu group on boron, have recently been prepared and characterized.[5]

This study is related to the second synthetic approach which involves linking the nitrogen atoms of the N–B–N–B backbone through bridging $-(CH_2)_n-$ units by use of the 1,3,2-diazaboracycloalkane[6] ring systems (e.g., **1**, eq 1). The bridges are intended to provide structural rigidity in order to prevent the boron–nitrogen backbone from condensing to the cyclic trimer. Specifically, we report here our preliminary findings on the synthesis, structural characterization, and dynamic stereochemistry of some new *N*-boryl derivatives of the 2-phenyl-1,3,2-diazaboracyclohexane ring system **1**.



Synthesis. Typically, the diazaboracyclohexane **1** [100 mmol, in THF (150 mL)] was deprotonated by treatment with an equimolar amount of *n*-BuLi at 0 °C (eq 1). Subsequent addition of the appropriate chloroborane, $Me_2NB(R)Cl$[7] (100 mmol),

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(1) See, for example, the following and references cited therein: (a) Narula, C. K.; Schaeffer, R.; Paine, R. T.; Dayte, A.; Hammetter, W. F. *J. Am. Chem. Soc.* **1987**, *109*, 5556. (b) Narula, C. K.; Paine, R. T.; Schaeffer, R. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1987**, *28*, 454. (c) Shaw, Y. S.; DuBois, D. A.; Neilson, R. H. *ACS Symp. Ser.*, in press. (d) Paciorek, K. J. L.; Harris, D. H.; Kratzer, R. H. *J. Polym. Sci., Polym. Chem. Ed.* **1986**, *24*, 173. (e) Narula, C. K.; Janil, J. F.; Duesler, E. N.; Paine, R. T.; Schaeffer, R. *Inorg. Chem.* **1986**, *25*, 3346. (f) Komm, R.; Geanangel, R. A.; Liepins, R. *Inorg. Chem.* **1983**, *22*, 1684.

(2) For the synthesis and structures of the *monomeric* and *dimeric* iminoboranes, see: Paetzold, P.; von Plotho, C. *Chem. Ber.* **1982**, *115*, 2819 (and references cited therein).

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(4) For a review, see: Atkinson, I. B.; Currell, B. R. *Inorg. Macromol. Rev.* **1971**, *1*, 203.

(5) Li, B.-L.; Neilson, R. H. *Inorg. Chem.* **1986**, *25*, 361.

(6) Niedenzu, K.; Fritz, P.; Dawson, J. W. *Inorg. Chem.* **1964**, *8*, 1077.

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