The fact that the nature of the polytelluride used as starting material does not affect the product suggests that there are facile and complex equilibria in solution. This is also in accord with NMR investigations of polyselenide and telluride solutions.[22] However, the simplicity of the reactions suggests that polytellurides extracted from Zintl phases are useful reagents for introducing polytellurium chains into metal complexes.

Acknowledgment. We are indebted to Chuck Campana and Nicolet Corp. for structural data on Ib. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the National Science Foundation for support of this research.

Registry No. Ia·THF, 112817-27-3; Ib·THF, 112817-31-9; $Cr(CO)_6$, 13007-92-6; $W(CO)_6$, 14040-11-0; K_2Te_3, 67488-76-0; K_2Te_2, 78547-42-9; K_2Te_4, 112817-28-4; $Mo(CO)_6$, 13939-06-5.

Supplementary Material Available: Tables of atomic coordinates and isotropic temperature factors, cation and solvent distances and angles, anisotropic temperature factors, and hydrogen atom parameters (17 pages); a table of observed and calculated structure factors (63 pages). Ordering information is given on any current masthead page.

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(22) Schrobilgen G. J.; Bjorgvinnson, M., in press.

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Synthesis and Characterization of a Mixed-Valence Binuclear Manganese(II,III) Complex of a Septadentate Polyimidazole Ligand[1]

Sir:

A multinuclear manganese center is known to play an integral role in the water-oxidizing complex of photosystem II (PS(II)).[2] The manganese center is capable of cycling between five oxidation levels (S_0–S_4) during the catalytic water oxidation cycle.[3] Two to four Mn ions are thought to participate directly in the oxidation process, and the S_2 state of the complex shows substantial Mn hyperfine structure in the EPR spectrum, which has been used to study the electronic structure of the manganese aggregate.[4] Because high-resolution structural data on the Mn site in PS(II) and other manganese-containing proteins are absent, efforts have focused on preparing and characterizing low molecular weight inorganic analogues[5-9] that mimic the spectral properties of the various S_n states. Therefore low molecular weight polymanganese complexes containing biologically relevant ligands such as imidazole, phenolates, and acetates that exhibit numerous manganese hyperfine EPR lines are of interest.

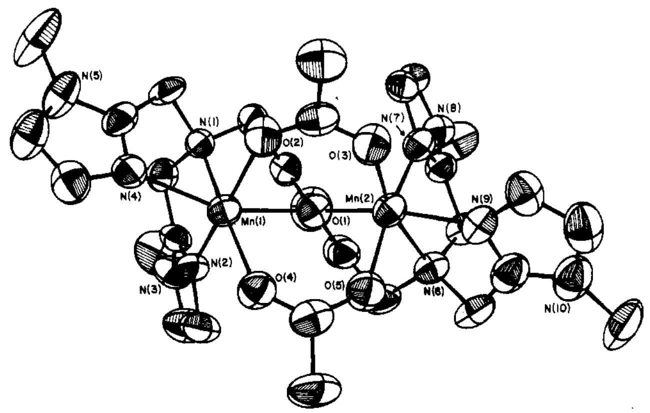
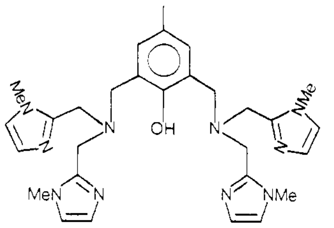


Figure 1. Structure of $[Mn_2(L\text{-}Im)(\mu\text{-}OAc)_2]^+$. The view is down the pseudo-2-fold axis of the dimer. Selected bond distances (Å) and angles (deg) are as follows: Mn(1)–O(1) = 2.258 (6); Mn(1)–O(2) = 2.107 (6); Mn(1)–O(4) = 2.091 (6); Mn(1)–N(1) = 2.364 (6); Mn(1)–N(2) = 2.186 (7); Mn(1)–N(4) = 2.229 (7); Mn(2)–O(1) = 1.887 (5); Mn(2)–O(3) = 1.995 (6); Mn(2)–O(5) = 2.036 (6); Mn(2)–N(6) = 2.270 (8); Mn(2)–N(7) = 2.100 (7); Mn(2)–N(9) = 1.998 (7); Mn(1)–O(1)–Mn(2) = 116.8 (3).

In the present study we wish to report the synthesis and characterization of a valence trapped binuclear mixed-valence Mn(II,III) complex prepared from a new septadentate ligand, HL-Im = 2,6-bis[(bis((1-methylimidazol-2-yl)methyl)amino)methyl]-4-methylphenol (I).[10] This ligand should provide a good



I

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(1) Complete description of crystal structure and properties of $[Mn_2(L\text{-}Im)(\mu\text{-}OAc)_2](ClO_4)_2$ will be described in a full paper submitted for publication in *Inorg. Chem.*

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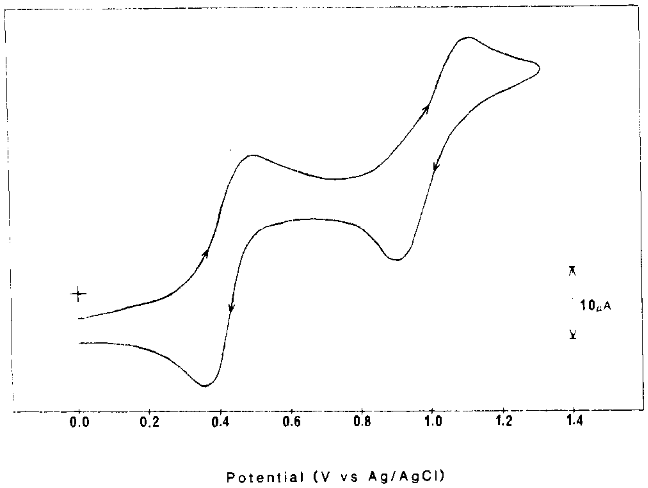

Figure 2. Cyclic voltammogram of $[Mn_2(L\text{-}Im)(\mu\text{-}OAc)_2]^+$ ($\mathbf{1}^{2+}$) (10^{-3} M) in acetonitrile (0.1 M $[n\text{-}Bu_4N]ClO_4$ supporting electrolyte, 20 °C) at a glassy-carbon electrode. The scan rate was 10 mV/s vs Ag/AgCl reference electrode. ΔE_p values of 120 and 180 mV are observed for the Mn(II,III)/Mn(II,III) and Mn(II,III)/Mn(III,III) processes, respectively.

chemical analogy of the coordination environment in several manganese proteins since histidine is found as a ligand in manganese superoxide dismutase[11] and presumed to be bound to a binuclear manganese center in the catalase from *L. plantarum*.[12] In addition, histidine has been proposed to play an integral role in the water oxidation cycle of PS(II).[2d,13] Recent EXAFS studies on the S_1 level of PS(II) indicates that two Mn ions are about 2.7 Å apart while additional Mn ions exceed 3.0 Å in separation.[3b,14]

The mixed-valence complex **1** is prepared by reaction of $Mn(CH_3COO)_3\cdot 2H_2O$ with HL-Im and $NaClO_4$ in methanol. The red-brown solution is then filtered and the filtrate cooled to 0 °C overnight whereupon black crystals of $[Mn_2(L\text{-}Im)(\mu\text{-}OAc)_2](ClO_4)_2$ deposited. The structure[15] of **1** has been determined by X-ray crystallography (Figure 1) and resembles that of the recently reported $[Mn_2(bpmp)(\mu\text{-}OAc)_2]^{2+}$ ion.[16] Both Mn ions in **1** are bridged by a phenoxide ion and two acetate ligands. The octahedral coordination sphere around each metal ion is completed by the bis((1-methylimidazol-2-yl)methyl)amine pendants. Metal–ligand bond lengths for Mn(1) are typical of high-spin Mn(II) while Mn(2) shows shorter equatorial and long axial lengths indicative of Jahn–Teller distortion expected for a high-spin d^4 Mn(III) ion. The Mn–Mn separation in **1** is 3.54 (1) Å.

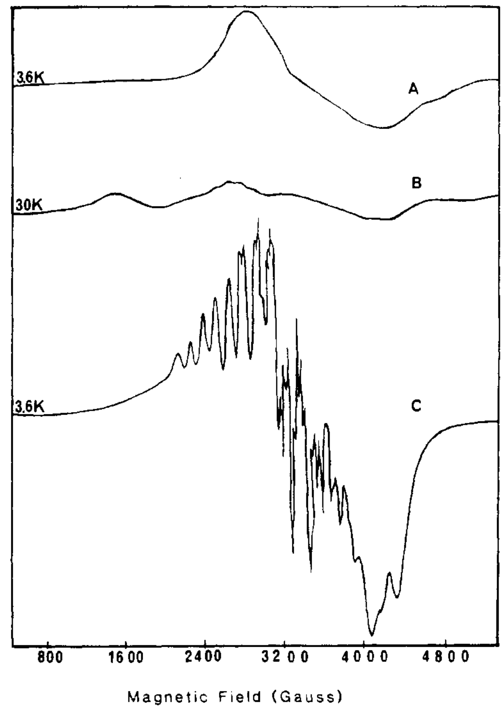

Figure 3. X-Band EPR spectra of complex **1**. Trace A corresponds to a 8000-G scan of a ground crystalline sample at 3.6 K. Conditions: microwave power, 10 mW; microwave frequency, 9.10 GHz; modulation amplitude, 2.0 G; modulation frequency, 100 KHz; gain, 6.3 × 10^2. Trace B is the (1:1:1) acetone–ethanol–toluene frozen-solution spectrum. Condtions: *T*, 30 K; microwave power, 10 mW; microwave frequency, 9.10 GHz; modulation amplitude, 1.6 G; modulation frequency, 100 KHz; gain, 5 × 10^3. Trace C corresponds to spectrum at T = 3.6 K with the same instrument settings as in trace B except the modulation amplitude was 2.0 G.

The complex shows two broad absorption bands in the visible region at 26 109 cm^{-1} (ϵ = 1050 M^{-1} cm^{-1}) and 16 500 cm^{-1} (ϵ = 430 M^{-1} cm^{-1}) tentatively assigned to phenolate to Mn(III) ion charge-transfer bands. No intervalence charge-transfer band has been observed in the near-IR region in solution.

The electrochemical properties of **1** have been studied by cyclic voltammetry. Two quasireversible redox processes are observed for the complex in acetonitrile (Figure 2). The redox waves correspond to successive one-electron-transfer steps forming Mn(II,II)/Mn(II,III) at +0.435 V and Mn(II,III)/Mn(III,III) at +1.01 V. Kida[17] and others[16] have reported similar electrochemical behavior for $[Mn_2(bpmp)(\mu\text{-}OAc)_2]^{2+}$.

The magnetic moment of **1** is 7.55 μB/complex at 297.2 K, decreasing to 1.86 μ_B at 2.5 K. The data are consistent with an isotropic magnetic exchange interaction ($\hat{H} = -2J\hat{S}_1\cdot\hat{S}_2$) between the high-spin Mn(II) and Mn(III) ions with $J = -4.5$ cm^{-1}.[18] The X-band EPR spectrum of **1** from powdered single crystals gives a broadened spectrum containing features of Mn hyperfine structures in the $g \sim 2$ region that are not well resolved (Figure

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[10] Prepared by stirring bis(1-methylimidazol-2-yl)methyl)amine (synthesis and characterization of this compound has been submitted for publication, a preliminary account of this work was reported at the 193rd National Meeting, of the American Chemical Society, Denver, CO April 1987; paper INORG 142) with 2,6-bis(chloromethyl)-*p*-cresol in THF containing triethylamine. Full details of the preparation of HL-Im will be provided in the full report of this work. *Caution!* Although the perchlorate salt of the complex was not found to be shock sensitive, care should be exercised in handling all perchlorate salts.

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[15] Anal. Calcd for $C_{33}H_{43}N_{10}O_{13}Cl_2Mn_2$: C, 40.92; H, 4.48; N, 14.46; Cl, 7.02. Found: C, 40.50; H, 4.53; N, 14.12; Cl, 6.87. Crystallographic data at 298 K: monoclinic space group $P2_1/n$; a = 15.545 (2) Å, b = 12.498 (2) Å, c = 21.694 (2) Å, β = 92.37 (1)°, V = 4211 $Å^3$, and Z = 4; R = 6.7%, R_w = 6.8%; d_{obsd} = 1.51 (1) g/cm^3; d_{calcd} = 1.53 g/cm^3. Data were collected on a red-brown 0.3 × 0.3 × 0.2 mm crystal coated with epoxy at 297 K with Mo Kα radiation (λ = 0.71073 Å, 2θ = 45° on an Enraf-Nonius CAD-4 diffractometer). The structure was solved and refined (SDP package) by using 3935 unique reflections ($I > 3\sigma(I)$). All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the final cycles of refinement as fixed contributions. Both perchlorate counterions showed rotational disorder about a 3-fold axis. Six partially occupied oxygen atom positions were used to model the disorder problem. An absorption correction using DIFABS (minimum value 0.12 to maximum value 1.25) was applied in the final cycles of least-squares refinement. The largest residue peak on the difference map was 0.80 e/$Å^3$, and GOF = 3.35.

[16] (a) Hendrickson, D. N., private communication. A preliminary account of the study of this complex was presented at the 192nd National Meeting of the American Chemical Society, Anaheim, CA, September 1986; paper INOR 205. A full account of the work has been reported: Diril, H.; Chang, H.-R.; Zhang, X.; Larsen, S. K.; Potenza, J. A.; Pierpont, C. G.; Schugar, H. J.; Isied, S. S.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1987**, 109, 6207.

[17] Suzuki, M.; Murata, S.; Uehara, A.; Kida, S. *Chem. Lett.* **1987**, *281*.

[18] Hendrickson, D. N., private communication. A complete description of magnetic properties of **1** will appear in a full paper.

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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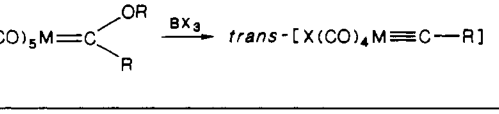
Received October 7, 1987

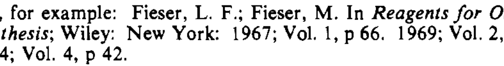
Alkoxy/Halogen Exchange Reaction of Molybdenum Complexes Containing Phosphite with Boron Trihalides

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



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



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

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

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]

$$fac\text{-}[Mo(bpy)(CO)_3\{P(OR)_3\}] \xrightarrow{2BF_3 \cdot OEt_2} fac\text{-}[Mo(bpy)(CO)_3\{P(OR)_2F\}]$$

R = Me (**1a**)
R = Et (**1b**)
R = *i*-Pr (**1c**)

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) $\nu(CO)$ 1929, 1831, 1795 cm^{-1}; ^1H 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) $\nu(CO)$ 1925, 1826, 1792 cm^{-1}; ^1H 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) $\nu(CO)$ 1920, 1822, 1790 cm^{-1}; ^1H 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 $\nu(CO)$ region are equally strong. This can be also said for **2a**, **2b**, **2c**, and **3a**.

(6) For **2a**: IR (in dichloromethane) $\nu(CO)$ 1939, 1844, 1805 cm^{-1}; ^1H 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) $\nu(CO)$ 1937, 1842, 1801 cm^{-1}; ^1H 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) $\nu(CO)$ 1934, 1839, 1800 cm^{-1}; ^1H 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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