

Contribution from The Bristol-Myers Squibb Pharmaceutical Research Institute,  
P.O. Box 191, New Brunswick, New Jersey 08903

## Syntheses, Characterization, and Reactivity of Manganese and Rhenium Dioxime Complexes. X-ray Crystal Structures of $\text{Mn}^{\text{II}}(\text{CDO})(\text{CDOH})_2(\text{BPh}(\text{OCH}_3))_2$ , an Unusual Pseudoclathrochelate Complex, and $\text{Re}^{\text{III}}\text{Cl}(\text{CDO})(\text{CDOH})_2\text{BPh}$

S. Jurisson, L. Francesconi,<sup>†</sup> K. E. Linder, E. Treher, M. F. Malley, J. Z. Gougoutas, and A. D. Nunn\*

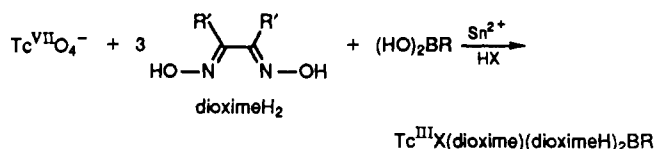
Received March 28, 1990

A number of uncapped and monocapped rhenium(III) complexes and a biscapped manganese(II) tris(dioxime) complex have been synthesized and fully characterized. The uncapped rhenium(III) tris(dioxime) complexes,  $\text{ReCl}(\text{dioximeH})_2(\text{dioximeH}_2)$ , are neutral, seven-coordinate complexes with a chloride occupying the seventh site. They can be capped at one end with a boronic acid to give  $\text{ReCl}(\text{dioxime})(\text{dioximeH})_2\text{BR}$ . These complexes are analogous to the previously reported technetium BATO complexes.<sup>1,2</sup> The Mn(II) complex is neutral, six-coordinate, and biscapped with a tetrahedral boron derivative bound at each end to only two of the three oximes.  $\text{ReCl}(\text{CDO})(\text{CDOH})_2\text{BPh} \cdot \frac{1}{2}\text{C}_6\text{H}_{14}$  ( $\text{CDOH}_2 = 1,2$ -cyclohexanedione dioxime),  $\text{ReClC}_{24}\text{H}_{31}\text{N}_6\text{O}_6\text{B} \cdot \frac{1}{2}\text{C}_6\text{H}_{14}$ , crystallizes from  $\text{CH}_2\text{Cl}_2/\text{hexane}$  (1:1) in the triclinic space group  $P\bar{1}$  with  $a = 12.393$  (2) Å,  $b = 13.350$  (4) Å,  $c = 11.539$  (4) Å,  $\alpha = 115.14$  (2)°,  $\beta = 113.53$  (2)°,  $\gamma = 92.63$  (2)°,  $Z = 2$ ,  $R = 0.050$ , and  $R_w = 0.058$ .  $\text{Mn}(\text{CDO})(\text{CDOH})_2(\text{BPh}(\text{OCH}_3))_2$ ,  $\text{MnC}_{32}\text{H}_{42}\text{N}_6\text{O}_6\text{B}_2$ , crystallizes from  $\text{CH}_2\text{Cl}_2/\text{MeOH}$  (1:1) in the triclinic space group  $P\bar{1}$  with  $a = 11.804$  (1) Å,  $b = 15.155$  (1) Å,  $c = 10.609$  (1) Å,  $\alpha = 105.45$  (1)°,  $\beta = 103.70$  (1)°,  $\gamma = 98.71$  (1)°,  $Z = 2$ ,  $R = 0.044$ , and  $R_w = 0.050$ .

### Introduction

Complexes containing encapsulated metal ions (clathrochelates) of the form  $[\text{M}(\text{dioxime})_3(\text{BR})_2]$  ( $\text{M} = \text{Fe}, \text{Co}, \text{Ru}$ ) are well-known<sup>3-8</sup> (Figure 1a). These clathrochelates are prepared by template synthesis, during which both ends of the intermediate tris(dioxime) complex are capped by a boron derivative. Each cap results from the formation of three covalent boron-oxygen (oxime) bonds. Recently, we reported the synthesis of a number of technetium(III) tris(dioxime) complexes that are capped at only one end of the molecule with a boron derivative<sup>1,2</sup> (Figure 1b). These boronic acid adducts of technetium dioximes (BATOs) have proven very useful in nuclear medicine; two compounds from this class of Tc(III) compounds are currently in clinical trials, as myocardial<sup>9</sup> and cerebral<sup>10</sup> perfusion tracers. The myocardial perfusion tracer has recently been approved for routine clinical use by the FDA under the tradename Cardiotec.

The BATOs, like the clathrochelates, are prepared by template synthesis via the following simplified reaction scheme:



Three vicinal dioxime ligands, a boronic acid, a halogen, and the technetium atom react in solution to form a neutral, seven-coordinate monocapped Tc(III) complex,  $\text{TcX}(\text{dioxime})(\text{dioximeH})_2\text{BR}$ . The formation of the BATOs from pertechnetate in the presence of Sn(II) proceeds through two technetium(III) tris(dioxime) intermediates: a Sn-monocapped technetium(III) tris(dioxime) complex,  $\text{Tc}(\text{dioxime})_3(\mu\text{-OH})\text{SnCl}_3$ , and an uncapped technetium(III) tris(dioxime) complex,  $\text{TcX}(\text{dioximeH}_2)(\text{dioximeH})_2$ .<sup>2</sup> The Sn-capped species is formed initially, followed by acid decomposition to the uncapped tris(dioxime) complex, which is subsequently capped by the boronic acid. All attempts to prepare the biscapped Tc complexes (by way of Cl<sup>-</sup> abstraction with  $\text{Ag}^+$ , for example<sup>1</sup>) analogous to the Co and Fe clathrochelates (Figure 1a) have failed.

In an attempt to understand why the BATOs are formed with only one cap, we have extended this chemistry to include Mn and Re, the two other members of group VIIB. We now report the syntheses and characterization of an uncapped rhenium(III) tris(dioxime) complex, several monocapped boronic acid adducts of the rhenium(III) dioxime complexes (BAREOs), and an unusual

manganese(II) dioxime complex having a pseudoclathrochelate structure<sup>11,12</sup> (Figure 1c).

### Experimental Section

**General Details.** Manganese(III) acetate (Aldrich Chemical Co.), phenylboronic acid ((HO)<sub>2</sub>BPh; Aldrich Chemical Co.), methylboronic acid ((HO)<sub>2</sub>BMe; Aldrich Chemical Co.), boric acid ((HO)<sub>3</sub>B; Aldrich Chemical Co.), butylboronic acid ((HO)<sub>2</sub>BBu; Aldrich Chemical Co.), 1,2-cyclohexanedione dioxime (CDOH<sub>2</sub>; Eastern Chemical Co.), dimethylglyoxime (DMGH<sub>2</sub>; Eastern Chemical Co.), ammonium perchlorate (NH<sub>4</sub>ReO<sub>4</sub>; Aesar Chemical Co.), stannous chloride (MCI), triphenylphosphine (PPh<sub>3</sub>; Strem), sodium sulfate (anhydrous, Fisher Scientific), and magnesium sulfate (anhydrous, Fisher Scientific) were used without purification.  $\text{ReCl}_3(\text{CH}_3\text{CN})(\text{PPh}_3)_2$  was prepared by using a literature method.<sup>13,14</sup> Silica gel (grade 60, 230-400 mesh) and silica gel TLC plates (1B-F, Baker-flex) were obtained from Aldrich Chemical Co. and J. T. Baker, respectively. Dichloromethane (certified ACS grade), chloroform (certified ACS grade), acetonitrile (pesticide grade), methanol (certified ACS grade), and hexane were obtained from Fisher Scientific and used as received. Absolute ethanol was obtained from General Laboratories, and all water used was obtained from a Millipore Super Q system.

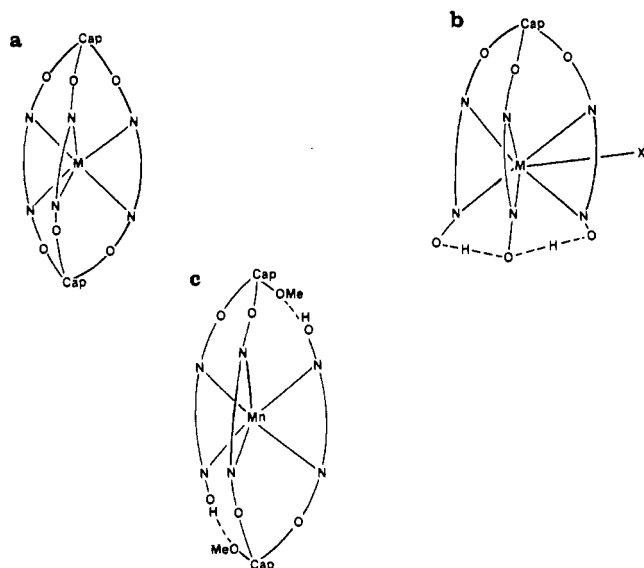
**Physical Measurements.** The HPLC separations were made on a 15-cm Hamilton PRP-1 10 μm column (4.1-mm i.d.) or a 25-cm Hibar Licrosorb RP-18 5 μm (4.6-mm i.d.) column, using a dual pump system and a mobile phase consisting of 90% acetonitrile and 10% 0.1 M ammonium acetate buffer (pH 4.6), except where noted, flow rates of 2 and 1 mL/min, respectively, and detection at 450 or 250 nm. The HPLC *k'* values are reported; nitrate was used as the void volume standard.

UV-visible spectra were recorded on a Hewlett-Packard HP 8451A diode-array spectrophotometer. Conductivity was measured with a YSI Model 32 conductance meter.

- (1) Treher, E. N.; Francesconi, L. C.; Malley, M. F.; Gougoutas, J. Z.; Nunn, A. D. *Inorg. Chem.* **1989**, *28*, 3411.
- (2) Linder, K. E.; Malley, M. F.; Gougoutas, J. Z.; Unger, S. E.; Nunn, A. D. *Inorg. Chem.* **1990**, *29*, 2428.
- (3) Boston, D. R.; Rose, N. J. *J. Am. Chem. Soc.* **1968**, *90*, 6859.
- (4) Boston, D. R.; Rose, N. J. *J. Am. Chem. Soc.* **1972**, *96*, 4163.
- (5) Zakrzewski, G. A.; Ghilardi, C. A.; Lingafelter, E. C. *J. Am. Chem. Soc.* **1971**, *93*, 4411.
- (6) Jackals, S.; Rose, N. J. *Inorg. Chem.* **1973**, *12*, 1232.
- (7) Robbins, M. K.; Naser, D. W.; Heiland, J. L.; Grzybowski, J. J. *Inorg. Chem.* **1985**, *24*, 3381.
- (8) Muller, J. G.; Grzybowski, J. J.; Takeuchi, K. J. *Inorg. Chem.* **1986**, *25*, 2665.
- (9) Narra, R. K.; Nunn, A. D.; Kuczynski, B. L.; Feld, T.; Wedeking, P.; Eckelman, W. C. *J. Nucl. Med.* **1989**, *30*, 1830.
- (10) Narra, R. K.; Nunn, A. D.; Kuczynski, B. L.; DiRocco, R. J.; Feld, T.; Silva, D.; Eckelman, W. C. *J. Nucl. Med.* **1990**, *31*, 1370.
- (11) A fully biscapped clathrochelate structure, by the Busch<sup>12</sup> definition, requires that a bicyclic ligand system be formed about the metal. In this context, the capping in the Mn structure is incomplete.
- (12) Busch, D. H. *Rec. Chem. Prog.* **1964**, *25*, 107.
- (13) Chatt, J.; Rowe, G. A. *J. Chem. Soc.* **1962**, 4019.
- (14) Rouschias, G.; Wilkinson, G. *J. Chem. Soc. A* **1967**, 993.

\* To whom correspondence should be addressed.

<sup>†</sup> Present address: 305 University Science Center, University of Pennsylvania, 3700 Market Street, Philadelphia, PA 19104.



**Figure 1.** (a) Schematic representation of a biscapped clathrochelate complex (e.g.,  $[M(\text{dioxime})_3(\text{BR})_2]$ , where  $M = \text{Co(II)}, \text{Fe(II)}, \text{Ru(II)}$ ). (b) Schematic representation of the monocapped seven-coordinate technetium and rhenium tris(dioxime) complexes. Dashed lines at the uncapped end represent two bridging hydrogen bonds. (c) Schematic representation of the biscapped structure of the tris(dioxime) complex of Mn. Dashed lines within the ligand framework represent hydrogen bonds.

Infrared spectra were obtained from KBr pellets and recorded on a Sirius 100 FT-IR spectrometer.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were obtained in  $\text{CD}_2\text{Cl}_2$  by using a 270-MHz JEOL-FX-270 spectrometer.

Fast atom bombardment (FAB) mass spectra were run from a thio-glycerol matrix on a VG-ZAB-2F spectrometer. Chemical ionization (CI) mass spectra were run in a glycerol matrix on a Finnigan TSQ spectrometer. Elemental analyses were performed by the Squibb Microanalytical laboratory, Princeton, NJ.

Magnetic susceptibility measurements were made by using the Gouy method.

X-ray photoelectron spectroscopy (XPS) measurements were made by using either an SSI, a VG Scientific, or a Perkin-Elmer instrument.

**Synthesis of  $\text{Mn}^{\text{II}}(\text{CDO})(\text{CDOH})_2(\text{BPh}(\text{OCH}_3))_2$ .**  $\text{CDOH}_2$  (0.8032 g, 5.7 mmol) and  $(\text{HO})_2\text{BPh}$  (0.4739 g, 3.9 mmol) were dissolved in 30 mL of MeOH.  $\text{Mn}^{\text{III}}(\text{OAc})_3 \cdot \text{H}_2\text{O}$  (0.5096 g, 1.9 mmol), suspended in 15 mL of MeOH, was added, followed by 15 mL of  $\text{CH}_2\text{Cl}_2$ . An intense golden brown color was observed. The reaction mixture was heated for ca. 1 h, during which time a beige precipitate formed. The reaction mixture was cooled, and the beige precipitate was collected, washed with MeOH, and air-dried. The crude product was purified by dissolution in  $\text{CH}_2\text{Cl}_2$ , followed by filtration to remove the undissolved solids (a small amount of a dark brown material that may be  $\text{MnO}_2$ ), addition of an equal volume of MeOH, and crystallization by slow evaporation at room temperature. A 1.23-g amount (90%, based on Mn) of pale salmon-colored  $\text{Mn}(\text{CDO})(\text{CDOH})_2(\text{BPh}(\text{OCH}_3))_2$  was collected, washed with MeOH, and dried in vacuo. The crystals isolated were suitable for diffraction studies. Anal. Calc for  $\text{MnC}_{32}\text{H}_{42}\text{N}_6\text{O}_8\text{B}_2$ : C, 53.72; H, 5.92; N, 11.75. Found: C, 53.58; H, 5.99; N, 11.57.

Following the procedure described above and substituting acetone for methanol (to eliminate methanol addition to the boron cap atoms) yielded a beige product that was similar in appearance to  $\text{Mn}(\text{CDO})(\text{CDOH})_2(\text{BPh}(\text{OCH}_3))_2$ . The product was collected by filtration, washed with acetone, and dried in vacuo. Yield of  $\text{Mn}(\text{CDO})(\text{CDOH})_2(\text{BPh} \cdot 3\text{H}_2\text{O})$ : 0.1275 g (9.5%). Anal. Calc for  $\text{MnC}_{30}\text{H}_{40}\text{N}_6\text{O}_9\text{B}_2$ : C, 51.06; H, 5.39; N, 11.91. Found: C, 51.31; H, 5.37; N, 11.87.

Following the above procedure and adding  $\text{H}_2\text{O}_2$  and NaOH in an attempt to promote formation of a Mn(III) complex yielded only the Mn(II) product,  $\text{Mn}(\text{CDO})(\text{CDOH})_2(\text{BPh}(\text{OCH}_3))_2$ , described above (as determined by UV-visible spectrophotometry and mass spectrometry). Addition of  $\text{H}_2\text{O}_2/\text{NaOH}$  to the Mn(II) product dissolved in  $\text{CH}_2\text{Cl}_2/\text{MeOH}$  did not yield the Mn(III) complex. Some unidentified dark brown precipitate was observed in this reaction, in addition to starting compound.

**Synthesis of  $\text{ReCl}(\text{CDOH})_2(\text{CDOH}_2)$ .**  $\text{ReCl}_3(\text{CH}_3\text{CN})(\text{PPh}_3)_2$  (0.152 g, 0.18 mmol) and  $\text{CDOH}_2$  (0.103 g, 0.72 mmol) in 30 mL of  $\text{CH}_2\text{Cl}_2$  were refluxed under  $\text{N}_2$  for 3 h. The reaction mixture (orange-brown in

color) was adsorbed onto a silica gel column (2 cm  $\times$  20 cm). Elution with  $\text{CH}_2\text{Cl}_2$  quickly displaced unreacted starting material (lemon yellow in color) and then, much more slowly, the orange  $\text{ReCl}(\text{CDOH})_2(\text{CDOH}_2)$ . This fraction was collected and filtered to remove silica fines. An equal volume of hexane was added, and the  $\text{ReCl}(\text{CDOH})_2(\text{CDOH}_2)$  precipitated on slow evaporation at room temperature. The product was collected by filtration, washed with hexane, and vacuum-dried. Yield: 0.089 g (42%). Anal. Calc for  $\text{ReClCl}_{18}\text{H}_{28}\text{N}_6\text{O}_6$ : C, 33.46; H, 4.34; N, 13.01. Found: C, 33.41; H, 4.18; N, 12.79. Conductivity in  $\text{CH}_3\text{CN}$ :  $1.38 \Omega^{-1} \text{mol}^{-1} \text{cm}^2$ . Observed HPLC  $k'$  values: 6.4 (PRP-1) and 5.7 (Licrosorb RP-18).

**Synthesis of  $\text{ReCl}(\text{CDO})(\text{CDOH})_2\text{BPh}$ .**  $\text{ReCl}_3(\text{CH}_3\text{CN})(\text{PPh}_3)_2$  (1.013 g, 1.18 mmol),  $\text{CDOH}_2$  (0.652 g, 4.60 mmol), and  $(\text{HO})_2\text{BPh}$  (0.296 g, 2.42 mmol) in 120 mL of  $\text{CH}_2\text{Cl}_2$  were refluxed under  $\text{N}_2$  for 3 h. The intense orange-brown reaction mixture was concentrated to ca. 20 mL and purified by silica gel chromatography (2 cm  $\times$  15 cm). Elution with  $\text{CH}_2\text{Cl}_2$  rapidly displaced unreacted starting material (lemon yellow in color) and then the orange-brown  $\text{ReCl}(\text{CDO})(\text{CDOH})_2\text{BPh}$ . The fraction containing the product was collected, concentrated to a volume of 20–30 mL by rotary evaporation (without heat), and filtered. Equal volumes of ethanol and 1 M HCl were added, and the product crystallized on slow evaporation at room temperature. The crystals were collected by filtration, washed with 1 M HCl, and vacuum-dried. Yield: 0.264 g (30.5%). Anal. Calc for  $\text{ReClCl}_{24}\text{H}_{31}\text{N}_6\text{O}_6\text{B}^{1/2}\text{EtOH}$ : C, 39.76; H, 4.51; N, 11.13. Found: C, 39.72; H, 4.27; N, 10.74. The crystal used for X-ray structural analysis was obtained from  $\text{CH}_2\text{Cl}_2/\text{hexane}$  (1:1) and found to be  $\text{ReCl}(\text{CDO})(\text{CDOH})_2\text{BPh} \cdot \frac{1}{2}\text{C}_6\text{H}_{14}$ . Conductivity in  $\text{CH}_3\text{CN}$ :  $7.71 \Omega^{-1} \text{mol}^{-1} \text{cm}^2$ . Observed HPLC  $k'$  values: 8.8 (PRP-1) and 7.4 (Licrosorb RP-18).

**Synthesis of  $\text{ReCl}(\text{CDO})(\text{CDOH})_2\text{BMe}$ .**  $\text{ReCl}(\text{CDO})(\text{CDOH})_2\text{BPh}$  was prepared by the method described for  $\text{ReCl}(\text{CDO})(\text{CDOH})_2\text{BPh}$  by substituting the equivalent molar quantity of methylboronic acid for phenylboronic acid and maintaining the reaction temperature below 40  $^\circ\text{C}$  (otherwise, methylboronic acid would sublime from the reaction mixture). The product was crystallized from  $\text{Et}_2\text{O}/\text{MeOH}/1 \text{ M HCl}$  (1:1:1), collected by filtration, washed with 1 M HCl, and vacuum-dried. Yield: 0.036 g (23%). Anal. Calc for  $\text{ReClCl}_{19}\text{H}_{29}\text{N}_6\text{O}_6\text{B}^{1/4}\text{Et}_2\text{O}$ : C, 34.89; H, 4.57; N, 12.21. Found: C, 34.97; H, 4.17; N, 12.24. Conductivity in  $\text{CH}_3\text{CN}$ :  $1.75 \Omega^{-1} \text{mol}^{-1} \text{cm}^2$ . Observed HPLC  $k'$  value: 6.6 (Licrosorb RP-18).

**Synthesis of  $\text{ReCl}(\text{CDO})(\text{CDOH})_2\text{BOH}$ .**  $\text{ReCl}(\text{CDO})(\text{CDOH})_2\text{BPh}$  was prepared by the method described for  $\text{ReCl}(\text{CDO})(\text{CDOH})_2\text{BPh}$  by substituting the equivalent molar quantity of boric acid for phenylboronic acid. The fraction containing the desired product was evaporated to dryness, taken up in ether, and allowed to crystallize by very slow evaporation over several days. The deep red-brown solid was collected by filtration, washed with  $\text{H}_2\text{O}$ , and vacuum-dried. Yield: 0.046 g (28%). Anal. Calc for  $\text{ReClCl}_{18}\text{H}_{27}\text{N}_6\text{O}_7\text{B}^{1/4}\text{Et}_2\text{O}$ : C, 33.04; H, 4.28; N, 12.17. Found: C, 33.26; H, 4.16; N, 12.10. Conductivity in  $\text{CH}_3\text{CN}$ :  $2.10 \Omega^{-1} \text{mol}^{-1} \text{cm}^2$ . Observed HPLC  $k'$  value: 6.3 (Licrosorb RP-18, 65:35  $\text{CH}_3\text{CN}/0.1 \text{ M NH}_4\text{OAc}$ ).

**Synthesis of  $\text{ReCl}(\text{CDO})(\text{CDOH})_2\text{BBu}$ .** Method a from  $\text{ReCl}_3(\text{CH}_3\text{CN})(\text{PPh}_3)_2$ . The method described above for  $\text{ReCl}(\text{CDO})(\text{CDOH})_2\text{BPh}$  was used by substituting an equivalent molar quantity of butylboronic acid for phenylboronic acid. Yield: 0.030 g (15%). (This product was indistinguishable from that prepared by method b as determined by HPLC and UV-visible spectral analyses.)

**Method b from  $\text{NH}_4\text{ReO}_4$ .**  $\text{CDOH}_2$  (3.0 g, 21 mmol) and  $(\text{HO})_2\text{BBu}$  (1.3 g, 13 mmol) were dissolved in 250 mL of EtOH.  $\text{NH}_4\text{ReO}_4$  (0.8 g, 3 mmol) dissolved in 10 mL of concentrated HCl was added, followed by dropwise addition of  $\text{SnCl}_2$  (1.1 g, 5 mmol) in 5 mL of concentrated HCl. The resultant solution gradually became deep red in color. After being stirred for 1 h, the solution was concentrated to an oil (5–10 mL) and 20 mL of ethanol was added. The addition of 30 mL of 1.5 M HCl and 30 mL of  $\text{H}_2\text{O}$  resulted in the precipitation of crude product. The orange solid was collected by filtration, washed with  $\text{H}_2\text{O}$ , and dried in vacuo for 2 h. The solid was dissolved in  $\text{CH}_2\text{Cl}_2$  and purified by silica gel chromatography. The desired product was eluted as an orange band with  $\text{CHCl}_3$ . This fraction was filtered, an equal volume of EtOH/1 M HCl (1:1) was added, and the product was allowed to crystallize by slow evaporation. The orange product was collected by filtration, washed with  $\text{H}_2\text{O}$ , and dried in vacuo. Yield: 0.110 g (5%). Anal. Calc for  $\text{ReClCl}_{22}\text{H}_{35}\text{N}_6\text{O}_6\text{B}^{1/2}\text{EtOH}$ : C, 37.58; H, 5.21; N, 11.43; Cl, 4.82. Found: C, 37.41; H, 5.14; N, 11.47; Cl, 4.84. Conductivity in  $\text{CH}_3\text{CN}$ :  $0.20 \Omega^{-1} \text{mol}^{-1} \text{cm}^2$ . Observed HPLC  $k'$  value: 10.8 (Licrosorb RP-18).

**Synthesis of  $\text{ReCl}(\text{DMG})(\text{DMGH})_2\text{BBu}$ .** Method a from  $\text{ReCl}_3(\text{CH}_3\text{CN})(\text{PPh}_3)_2$ .  $\text{ReCl}_3(\text{CH}_3\text{CN})(\text{PPh}_3)_2$  (0.681 g, 0.79 mmol),  $\text{DMGH}_2$  (0.401 g, 3.45 mmol), and  $(\text{HO})_2\text{BBu}$  (0.180 g, 1.77 mmol) were placed in a 250-mL 3-necked round-bottom flask fitted with a condenser,  $\text{N}_2$  inlet, and a stir bar. The system was flushed with  $\text{N}_2$ , and

100 mL of  $\text{CH}_2\text{Cl}_2$  was added, followed by 20 mL of MeOH to dissolve the DMGH<sub>2</sub>. The reaction mixture was refluxed for 4 h, maintaining a slight positive pressure of N<sub>2</sub>. The reaction mixture was rotary evaporated to dryness (at room temperature), taken up in a minimum volume of  $\text{CH}_2\text{Cl}_2$  (10–15 mL), and purified by silica gel chromatography. Elution with  $\text{CH}_2\text{Cl}_2$  displaced unreacted starting material (bright yellow band) and then, more slowly, the  $\text{ReCl}(\text{DMG})(\text{DMGH})_2\text{BBu}$  (orange band). The product was collected, filtered to remove silica fines, and allowed to crystallize from a mixture of  $\text{CH}_2\text{Cl}_2/\text{MeOH}/0.1 \text{ M HCl}$  (1:1:1) by slow evaporation. The orange solid was collected by filtration, washed with  $\text{H}_2\text{O}/\text{MeOH}$  (95:5), and dried in vacuo. Yield: 0.007 g (1.4%). (The product was indistinguishable from that prepared by method b as determined by HPLC and UV-visible spectral analyses.)

**Method b from  $\text{NH}_4\text{ReO}_4$ .** DMGH<sub>2</sub> (2.16 g, 18.6 mmol) and  $(\text{HO})_2\text{BBu}$  (2.40 g, 23.5 mmol) were dissolved in 30 mL of boiling MeOH.  $\text{NH}_4\text{ReO}_4$  (0.564 g, 2.1 mmol) dissolved in 20 mL of warm  $\text{H}_2\text{O}$  was added with stirring.  $\text{SnCl}_2$  (0.765 g, 4 mmol) in 3 mL of 4 M HCl was added dropwise over 1 min. The reaction mixture was removed from the heat, sealed under N<sub>2</sub>, and stirred for 3 h. The mixture rapidly turned deep red-orange, and a yellow-orange precipitate formed.  $\text{H}_2\text{O}$  (20 mL) was added and the nonpolar products were extracted into 2 × 25 mL of  $\text{CH}_2\text{Cl}_2$ . The orange organic layer was dried over  $\text{MgSO}_4$ , filtered, and rotary evaporated to dryness at room temperature. The resultant red-orange solid was dried in vacuo for 12 h to remove excess  $(\text{HO})_2\text{BBu}$  by sublimation. The solid was redissolved (incompletely) in 2 mL of  $\text{CH}_2\text{Cl}_2$  and the mixture purified by silica gel chromatography. Elution with  $\text{CH}_2\text{Cl}_2$  displaced the red-orange product,  $\text{ReCl}(\text{DMG})(\text{DMGH})_2\text{BBu}$ . This was collected, rotary evaporated to dryness, and crystallized by slow evaporation from 5 mL of MeOH containing 4 drops of 0.1 M HCl. Yield: 0.036 g (3%). Anal. Calc for  $\text{ReClC}_{16}\text{H}_{29}\text{N}_6\text{O}_6\text{B}$ : C, 30.32; H, 4.61; N, 13.26. Found: C, 30.87; H, 4.33; N, 13.07. Observed HPLC *k'* value: 2.1 (PRP-1).

**Synthesis of  $\text{ReCl}(\text{CDO})(\text{CDOH})_2\text{BPh}$  from  $\text{ReCl}(\text{CDOH})_2(\text{CDOH})_2$ .**  $\text{ReCl}(\text{CDOH})_2(\text{CDOH})_2$  (0.004 g, 0.0056 mmol) was dissolved in 4 mL of  $\text{CH}_3\text{CN}$  and 1 mL of 1 M HCl. Phenylboronic acid (0.004 g, 0.033 mmol) was added, and the reaction mixture was gently heated with stirring. The progress of the capping process was monitored by HPLC. Within 20 min the capping reaction was nearly complete. Addition of dilute HCl (1 M) and evaporation of the  $\text{CH}_3\text{CN}$  at room temperature yielded 0.004 g (98% crude yield) of  $\text{ReCl}(\text{CDO})(\text{CDOH})_2\text{BPh}$  as a precipitate. The same method was used to prepare  $\text{ReCl}(\text{CDO})(\text{CDOH})_2\text{BBu}$  and  $\text{ReCl}(\text{CDO})(\text{CDOH})_2\text{BMe}$  in nearly quantitative yields, as determined by HPLC and silica gel TLC.

**Crystal Structure Analyses.** Crystal cell parameters and some details of data collection and refinement are summarized in Table I. The general comments here apply to both analyses; differences in the individual refinement procedures are described in the following two paragraphs. Unit cell parameters were obtained through a least-squares analysis of more than 15 high-angle reflections. Crystal densities were measured by flotation in carbon tetrachloride/hexane/bromoform mixtures. Reflections were measured diffractometrically at 23 °C with the  $\theta$ - $2\theta$  variable-scan technique and were corrected for Lorentz-polarization factors and for absorption. Background counts were collected at the extremes of the scan for half the time of the scan. Two standard reflections were monitored for decay; no decrease of intensity was observed during the course of the measurements. Structures were solved by heavy-atom techniques and refined on the basis of "observed" reflections with  $I \geq 3\sigma(I)$ . All calculations utilized the SDP program package with minor local modifications.<sup>15</sup> Least-squares weights,  $w = \sigma^{-2}(F_o)$ , were calculated with the assumption that  $\sigma^2 = \epsilon^2 + (pI)^2$ , where  $\epsilon$  is the statistical counting error and  $p = 0.04$ . The function minimized in the least squares refinements was  $\sum w(|F_o| - |F_c|)^2$ . *R* is defined as  $\sum ||F_o| - |F_c|| / \sum |F_o|$ , while  $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$ .

**$\text{Mn}(\text{CDO})(\text{CDOH})_2(\text{BPh}(\text{OCH}_3))_2$ .** Although most hydrogen positions were evident on difference maps during the latter stages of refinement, only the bridging hydrogens on O2B and O3F were introduced in their observed positions. All other hydrogens were introduced in idealized positions and assigned isotropic temperature factors. The coordinates and anisotropic temperature factors of all atoms except hydrogen were refined.

**$\text{ReCl}(\text{CDO})(\text{CDOH})_2\text{BPh}$ .** Density measurements and proton NMR spectroscopy indicated that the crystals contained hexane of crystallization. ( $D_{\text{obs}} = 1.70 \text{ g cm}^{-3}$ ;  $D_{\text{calc}} = 1.59 \text{ g cm}^{-3}$  for  $\text{ReClC}_{24}\text{H}_{31}\text{N}_6\text{O}_6\text{B}$ .) The calculated mass difference (51 amu) corresponds to one molecule

**Table I.** Crystal Data, Data Collection Parameters, and Refinement Parameters

	$\text{ReCl}(\text{CDO})(\text{CDOH})_2\text{BPh}$	$\text{Mn}(\text{CDO})(\text{CDOH})_2(\text{BPh}(\text{OCH}_3))_2$
formula	$\text{ReClC}_{24}\text{H}_{31}\text{N}_6\text{O}_6\text{B} \cdot \frac{1}{2}\text{C}_6\text{H}_{14}$	$\text{MnC}_{32}\text{H}_{42}\text{N}_6\text{O}_6\text{B}_2$
fw	775.1	715.28
solvent	$\text{CH}_2\text{Cl}_2/\text{hexane}$ (1:1)	$\text{MeOH}/\text{CH}_2\text{Cl}_2$ (1:1)
color	violet	beige
space group	$P\bar{1}$	$P\bar{1}$
<i>a</i> , Å	12.393 (2)	11.804 (1)
<i>b</i> , Å	13.350 (3)	15.155 (1)
<i>c</i> , Å	11.539 (4)	10.609 (1)
$\alpha$ , deg	115.14 (2)	105.45 (1)
$\beta$ , deg	113.53 (2)	103.70 (1)
$\gamma$ , deg	92.63 (2)	98.71 (1)
<i>V</i> , Å <sup>3</sup>	1530 (2)	1729.9 (7)
<i>Z</i>	2	2
$D_{\text{calc}}$ , g/cm <sup>3</sup>	1.68	1.37
$D_{\text{obs}}$ , g/cm <sup>3</sup>	1.70	1.35
cryst size, mm	0.3 × 0.1 × 0.15	0.18 × 0.04 × 0.03
$\mu$ , cm <sup>-1</sup>	41.6	35.8
min-max transm factors	0.74–1.47	0.93–1.00
abs cor	DIFABS <sup>a</sup>	PSI <sup>b</sup>
diffractometer	Syntex P2 <sub>1</sub>	CAD4S
$\lambda$ source, Å	0.71069	1.5418
$2\theta$ , max	55	140
octants measured	+ <i>h</i> , ± <i>k</i> , ± <i>l</i>	+ <i>h</i> , ± <i>k</i> , ± <i>l</i>
no. of reflns measd	5987	6805
no. of indep reflns	5657	6125
no. of reflns used in refinements	3682	4079
no. of refined variables	308	442
<i>R</i> ( <i>F</i> )	0.050	0.044
<i>R</i> <sub>w</sub> ( <i>F</i> )	0.058	0.050
error in an observn of unit wt	1.51	1.30
max shift/error on final cycle	0.01	0.01

<sup>a</sup> Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A* **1983**, *A39*, 159.

<sup>b</sup> North, A. C. T.; Phillips, D. C.; Matthews, F. S. *Acta Crystallogr., Sect. A* **1968**, *A24*, 351.

of hexane in the unit cell (the hexane was found to be situated on the center of symmetry at 0, 0, 1/2). Since the crystals lose some solvent on standing ( $D_{\text{obs}} = 1.63 \text{ g cm}^{-3}$  after ca. 36 h of exposure), they were coated with epoxy cement prior to data collection. The cyclohexyl rings show conformational disorder with unreasonably large apparent temperature factors of the outwardmost (C15, C16, C25, C26, C35, C36) methylene carbon atoms. This is probably due to the presence of two half-chair conformations. While two distinct positions were observed for C36 (C36'), it was not possible to resolve the disorder of the other CDO rings, and these atoms were refined with isotropic temperature factors. The three unique atoms of the solvent (1/2 molecule of hexane) were also refined with isotropic temperature factors. The disorder of the CDO ligands implies disorder of the hydrogen atoms, and no reliable hydrogen positions were evident on difference maps. Hydrogens were introduced in idealized positions on the phenyl substituent. The coordinates of all other atoms were refined together with their anisotropic temperature factors.

## Results

The rhenium(III) tris(dioxime) complexes,  $\text{ReCl}(\text{dioximeH})_2(\text{dioximeH}_2)$  and  $\text{ReCl}(\text{dioxime})(\text{dioximeH})_2\text{BR}$ , were prepared, for the most part, by direct substitution onto  $\text{ReCl}_3(\text{CH}_3\text{CN})(\text{PPh}_3)_2$  under an inert atmosphere. The combined reduction/substitution method of synthesis from  $\text{ReO}_4^-$  was also used, but the resultant yields were much lower. The biscapped manganese(II) tris(dioxime) complex,  $\text{Mn}(\text{CDO})(\text{CDOH})_2(\text{BPh}(\text{OCH}_3))_2$ , was synthesized in nearly quantitative yield from manganese(III) acetate. No reductant was added. Attempts to prepare the manganese(III) dioxime complex,  $\text{MnCl}(\text{CDO})(\text{CDOH})_2\text{BPh}$ , analogous to the Re(III) and the previously reported Tc(III)<sup>1,2</sup> complexes, under oxidizing conditions ( $\text{H}_2\text{O}_2$  and high pH), yielded only the Mn(II) complex reported here. Attempts to obtain the biscapped clathrochelate Mn(II) complex (Figure 1a), either by using acetone/ $\text{CH}_2\text{Cl}_2$  as the solvent of

(15) SDP, *Structure Determination Package*, B. Frenz & Associates: College Station, TX 77840. Scattering factors, including *f'* and *f''*, in the SDP software were taken from: *International Tables for Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, Tables 2.2A and 2.3.1.

**Table II.** UV-Visible Spectral Results (in CH<sub>3</sub>CN for the Re Complexes and CH<sub>2</sub>Cl<sub>2</sub> for the Mn Complex)

	$\lambda$ , nm ( $\epsilon$ )
ReCl(CDOH) <sub>2</sub> (CDOH <sub>2</sub> )	464 (10970), 398 (12540), 275 (sh), 206 (22940)
ReCl(CDO)(CDOH) <sub>2</sub> BMe	478 (9660), 398 (15730), 330 (6870), 284 (7750), 245 (sh), 200 (28200)
ReCl(CDO)(CDOH) <sub>2</sub> BOH	476 (7800), 398 (12330), 330 (5420), 282 (6160), 245 (sh), 202 (22410)
ReCl(CDO)(CDOH) <sub>2</sub> BPh	478 (8740), 398 (14050), 328 (7300), 278 (sh), 242 (sh), 208 (29130)
ReCl(CDO)(CDOH) <sub>2</sub> BBu	478 (9910), 400 (15110), 328 (7420), 284 (8150), 245 (sh), 214 (19400)
ReCl(DMG)(DMGH) <sub>2</sub> BBu	472 (5700), 392 (9030), 328 (5330), 275 (sh), 245 (sh), 204 (19400)
Mn(CDO)(CDOH) <sub>2</sub> (BPh(OCH <sub>3</sub> )) <sub>2</sub>	270 (17160)

reaction (vide infra) or by vacuum drying the compound, were unsuccessful.

The UV-visible spectral data are given in Table II. Four UV-visible transitions are observed for the uncapped ReCl(CDOH)<sub>2</sub>(CDOH<sub>2</sub>) complex. On capping, two additional transitions are observed for the various Re complexes at ca. 330 and 245 nm. The spectra of the Re complexes are very similar to those observed for the analogous Tc complexes.<sup>16</sup> Mn(II) has no allowed d-d transitions (high-spin d<sup>5</sup>), and thus, all such transitions should be very weak.<sup>17</sup> Only one transition is observed for Mn(CDO)(CDOH)<sub>2</sub>(BPh(OCH<sub>3</sub>))<sub>2</sub> at 270 nm; considering the magnitude of its extinction coefficient, this is probably a charge-transfer transition.

The <sup>1</sup>H NMR spectra for the various Re complexes were similar. All the CDO-containing rhenium complexes had broad multiplets (integrating for 24 H) at 1.6–3.2 ppm. When the dioxime was DMG, four methyl singlets were observed between 2.5 and 2.8 ppm (integrating for 6:3:6:3 H). The chemical shifts for the hydrogen bond protons between oxime oxygens were observed as a singlet at ca. 15.5 ppm (integrating for 2 H for the BAReOs and for 4 H for the uncapped ReCl(CDOH)<sub>2</sub>(CDOH<sub>2</sub>)). <sup>13</sup>C NMR spectra were obtained for the CDO-containing BAReOs. The eight alkyl CDO carbon signals were observed between 20 and 31 ppm, while the four oxime CDO carbon signals were observed between 148 and 162 ppm. The phenyl carbon signals were observed in the 125–133 ppm region.

The IR spectra of the various Mn and Re complexes show the expected C=N stretches in the 1550–1650-cm<sup>-1</sup> range, the N-O stretches in the ranges 950–1160 and 1190–1210 cm<sup>-1</sup>, and the B-O stretches at ca. 810–820 and 1045–1225 cm<sup>-1</sup>.<sup>6</sup>

Magnetic susceptibility measurements, using the Gouy method, show that the Mn(II) complex is paramagnetic and the Re(III) complex is diamagnetic. For Mn(CDO)(CDOH)<sub>2</sub>(BPh(OCH<sub>3</sub>))<sub>2</sub>,  $\chi$  (gram susceptibility) was found to be  $18.69 \times 10^{-6}$  cgs units, which gives a spin-only magnetic moment ( $\mu_{\text{eff}}$ ) of  $5.67 \mu_{\text{B}}$  (Bohr magnetons). Magnetic susceptibility measurements for ReCl(CDO)(CDOH)<sub>2</sub>BPh gave a negative  $\chi$  (gram susceptibility) value ( $-0.37 \times 10^{-6}$  cgs units), indicative of a diamagnetic Re(III).<sup>17</sup>

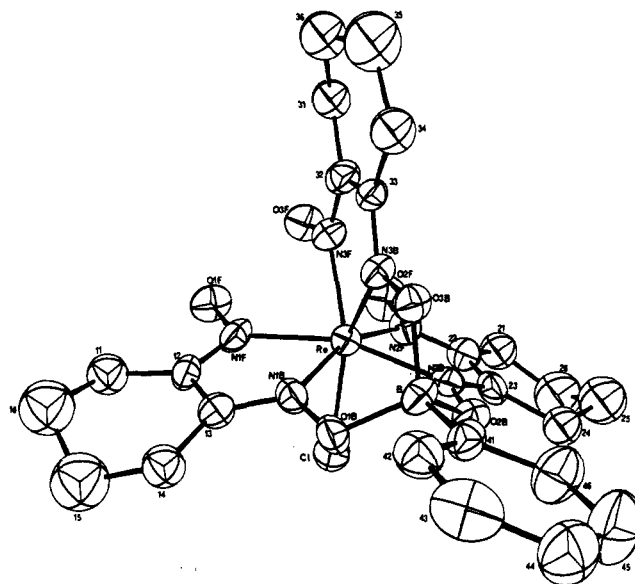
The XPS results gave a value for Cl 2p<sub>3/2</sub> of 197.6 eV for ReCl(CDO)(CDOH)<sub>2</sub>BMe and 197.7 eV for ReCl(CDO)(CDOH)<sub>2</sub>BOH. These values are slightly less than the values recorded for a large set of covalent Re(III)-Cl compounds by Chatt and co-workers (197.9 eV).<sup>18</sup>

The mass spectral results are given in Table III. A molecular ion cluster is observed for the Re(III) complexes; the major

**Table III.** Mass Spectral (*m/e*) Results

A. Rhenium Complexes				
	MW	(M + H) <sup>+</sup> and M <sup>++</sup>	-18 (-H <sub>2</sub> O)	-36 (-2H <sub>2</sub> O)
ReCl(CDOH) <sub>2</sub> (CDOH <sub>2</sub> )	646.13	644–649	n.o. <sup>a</sup>	n.o.
ReCl(CDO)(CDOH) <sub>2</sub> BMe	669.96	667–673	649–655	631–636
ReCl(CDO)(CDOH) <sub>2</sub> BOH	671.93	669–675	651–657	n.o.
ReCl(CDO)(CDOH) <sub>2</sub> BBu	712.05	709–715	691–697	673–679
ReCl(CDO)(CDOH) <sub>2</sub> BPh	732.04	729–735	711–717	693–699
ReCl(DMG)(DMGH) <sub>2</sub> BBu	633.93	631–637	613–619	595–601
B. Manganese Complex				
	MW	M <sup>++</sup> and (M + H) <sup>+</sup>	-32 (-MeOH)	-64 (-2 MeOH)
Mn(CDO)(CDOH) <sub>2</sub> (BPh(OCH <sub>3</sub> )) <sub>2</sub>	715.32	n.o.	683, 684	651, 652

<sup>a</sup> n.o. = not observed.

**Figure 2.** ORTEP representation of ReCl(CDO)(CDOH)<sub>2</sub>BPh.

fragment ion clusters observed are for the loss of 18 and 36 mass units (this could be H<sub>2</sub>O or OH + H). The isotope pattern observed is consistent with Re, Cl, and B isotopes. The molecular ion is not observed for the Mn(II) complex; however, fragment ions indicating the loss of one and two methanol molecules are observed.

The conductivity results for the Re(III) complexes show that they are neutral molecules in solution. The lack of solubility in polar solvents prevented this determination for the Mn(II) complex.

ORTEP<sup>19</sup> representations for ReCl(CDO)(CDOH)<sub>2</sub>BPh and Mn(CDO)(CDOH)<sub>2</sub>(BPh(OCH<sub>3</sub>))<sub>2</sub> are shown in Figures 2 and 3, respectively. Atomic fractional coordinates are listed in Table IV. Selected bond lengths and bond angles for the two structures are given in Tables V and VI, respectively. Parameters for the hydrogen atoms, thermal parameters, listings of observed and calculated structure factors, and bond distances and angles are available as supplementary material.

## Discussion

The chemical properties of the second and third transition series metals are more closely related to each other than either is to the first transition series metal of a particular group.<sup>17</sup> Our results are in accord with this observation; the manganese tris(dioxime) complex is very different from those of Tc and Re. The Re(III) complexes, like the Tc(III)-BATO complexes,<sup>1,2</sup> are seven-coordinate and monocapped (Figure 1b). In contrast, Mn appears

(16) Unpublished data.

(17) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 5th ed.; Interscience Publishers: New York, 1988.

(18) Chatt, J.; Elson, C. M.; Hooper, N. E.; Leigh, G. J. *J. Chem. Soc., Dalton Trans.* 1975, 2393.

(19) Johnson, C. K. *ORTEP, A Fortran Thermal Ellipsoid Plot Program for Crystal Structure Illustrations*; Report ORNL-5138 (Third Revision); Oak Ridge National Laboratory: Oak Ridge, TN, 1976.

Table IV. Atomic Fractional Coordinates for the Non-Hydrogen Atoms

atom	x	y	z	atom	x	y	z
<b>[Mn(CDO)(CDOH)<sub>2</sub>(BPh(OCH<sub>3</sub>)<sub>2</sub>)<sub>2</sub>]</b>							
Mn	0.37979 (5)	0.18311 (4)	0.75951 (5)	C31	0.5666 (4)	0.2911 (3)	1.2097 (3)
N1F	0.2757 (2)	0.0458 (2)	0.5977 (2)	C32	0.5385 (3)	0.2468 (2)	1.0589 (3)
N1B	0.4479 (2)	0.1644 (2)	0.5708 (2)	C33	0.6221 (3)	0.2767 (2)	0.9863 (2)
N2F	0.1954 (2)	0.1741 (2)	0.7947 (3)	C34	0.7512 (3)	0.3195 (3)	1.0613 (3)
N2B	0.3416 (2)	0.3295 (2)	0.8208 (3)	C35	0.7778 (4)	0.3437 (3)	1.2150 (4)
N3F	0.4444 (2)	0.1837 (2)	0.9815 (2)	C36	0.6755 (4)	0.3725 (3)	1.2643 (4)
N3B	0.5758 (2)	0.2637 (2)	0.8581 (2)	B1F	0.1477 (3)	0.0052 (3)	0.7314 (4)
O1F	0.1762 (2)	-0.0154 (2)	0.5986 (2)	B1B	0.6131 (3)	0.3037 (3)	0.6626 (4)
O1B	0.5492 (2)	0.2138 (2)	0.5537 (2)	O40	0.2530 (2)	0.0161 (2)	0.8435 (2)
O2F	0.1069 (2)	0.0943 (1)	0.7632 (2)	C41	0.3094 (4)	-0.0604 (3)	0.8382 (4)
O2B	0.4277 (2)	0.4128 (2)	0.8621 (3)	C42	0.0357 (3)	-0.0772 (2)	0.7138 (3)
O3F	0.3671 (2)	0.1586 (2)	1.0534 (3)	C43	-0.0428 (3)	-0.1326 (2)	0.5886 (4)
O3B	0.6608 (2)	0.2901 (2)	0.7970 (2)	C44	-0.1400 (4)	-0.2010 (3)	0.5792 (4)
C11	0.2118 (3)	-0.0491 (2)	0.3549 (3)	C45	-0.1608 (4)	-0.2147 (3)	0.6947 (5)
C12	0.2911 (3)	0.0284 (2)	0.4782 (3)	C46	-0.0853 (4)	-0.1597 (3)	0.8216 (4)
C13	0.3963 (3)	0.0904 (2)	0.4681 (3)	C47	0.0121 (4)	-0.0917 (3)	0.8302 (4)
C14	0.4376 (3)	0.0651 (3)	0.3436 (3)	O48	0.5338 (2)	0.3682 (2)	0.6804 (2)
C15	0.3721 (4)	-0.0296 (3)	0.2423 (4)	C49	0.4732 (4)	0.3881 (3)	0.5631 (5)
C16	0.2433 (4)	-0.0487 (3)	0.2248 (4)	C50	0.7294 (3)	0.3433 (2)	0.6237 (3)
C21	0.0422 (3)	0.2568 (3)	0.8571 (4)	C51	0.7899 (3)	0.2857 (3)	0.5535 (3)
C22	0.1621 (3)	0.2510 (2)	0.8379 (3)	C52	0.8974 (3)	0.3213 (3)	0.5320 (4)
C23	0.2534 (3)	0.3381 (2)	0.8703 (3)	C53	0.9442 (3)	0.4161 (3)	0.5783 (4)
C24	0.2424 (4)	0.4287 (3)	0.9598 (4)	C54	0.8845 (4)	0.4754 (3)	0.6444 (4)
C25	0.1157 (4)	0.4319 (3)	0.9567 (5)	C55	0.7799 (3)	0.4393 (3)	0.6671 (4)
C26	0.0470 (4)	0.3478 (3)	0.9665 (5)				
<b>ReCl(CDO)(CDOH)<sub>2</sub>BPh</b>							
Re	0.27149 (4)	0.25033 (3)	0.05097 (4)	C23	0.0090 (9)	0.1299 (8)	-0.1079 (9)
Cl	0.2153 (3)	0.2853 (2)	0.2389 (3)	C24	-0.100 (1)	0.0367 (9)	-0.176 (1)
N1F	0.4295 (7)	0.3772 (7)	0.2266 (8)	C25	-0.218 (1)	0.075 (1)	-0.256 (1)
N2F	0.1185 (7)	0.3131 (7)	-0.0183 (8)	C26	-0.214 (1)	0.194 (1)	-0.171 (2)
N3F	0.3198 (7)	0.3385 (6)	-0.0372 (8)	C31	0.384 (1)	0.3493 (9)	-0.211 (1)
N1B	0.3817 (7)	0.1700 (6)	0.1442 (7)	C32	0.3479 (9)	0.2885 (8)	-0.142 (1)
N2B	0.1215 (7)	0.1152 (6)	-0.0655 (7)	C33	0.3409 (8)	0.1714 (8)	-0.1859 (9)
N3B	0.3061 (7)	0.1394 (6)	-0.1119 (8)	C34	0.375 (1)	0.0944 (9)	-0.297 (1)
O1F	0.4536 (7)	0.4933 (5)	0.2659 (7)	C35	0.419 (1)	0.161 (1)	-0.359 (1)
O1B	0.3502 (6)	0.0528 (5)	0.0919 (6)	C36	0.457 (2)	0.279 (2)	-0.288 (2)
O2F	0.1183 (7)	0.4230 (6)	0.0038 (9)	C36'	0.371 (2)	0.260 (2)	-0.362 (2)
O2B	0.1316 (6)	0.0073 (5)	-0.0880 (6)	B	0.255 (1)	-0.0101 (9)	-0.065 (1)
O3F	0.3251 (7)	0.4528 (5)	0.0157 (7)	C41	0.2447 (9)	-0.1437 (8)	-0.1153 (9)
O3B	0.2960 (6)	0.0240 (5)	-0.1486 (6)	C42	0.3465 (9)	-0.1840 (8)	-0.076 (1)
C11	0.623 (1)	0.4329 (9)	0.445 (1)	C43	0.335 (1)	-0.2998 (9)	-0.115 (1)
C12	0.5102 (8)	0.3488 (8)	0.314 (1)	C44	0.227 (1)	-0.3763 (9)	-0.188 (1)
C13	0.4815 (9)	0.2273 (8)	0.2654 (9)	C45	0.122 (1)	-0.341 (1)	-0.235 (1)
C14	0.561 (1)	0.1751 (9)	0.349 (1)	C46	0.134 (1)	-0.2243 (9)	-0.194 (1)
C15	0.659 (1)	0.270 (1)	0.503 (2)	Cl'	-0.022 (2)	-0.056 (2)	-0.531 (2)
C16	0.719 (1)	0.371 (1)	0.503 (1)	C2'	0.023 (3)	-0.147 (2)	-0.519 (3)
C21	-0.102 (1)	0.287 (1)	-0.122 (1)	C3'	-0.026 (2)	-0.264 (2)	-0.585 (2)
C22	0.0106 (9)	0.2456 (9)	-0.080 (1)				

Table V. Selected Bond Distances in Å

<b>Mn(CDO)(CDOH)<sub>2</sub>(BPh(OCH<sub>3</sub>)<sub>2</sub>)<sub>2</sub></b>			
Mn-N1F	2.260 (2)	Mn-N1B	2.295 (3)
Mn-N2F	2.284 (3)	Mn-N2B	2.285 (3)
Mn-N3F	2.294 (3)	Mn-N3B	2.293 (2)
O1F-B1F	1.490 (5)	O1B-B1B	1.483 (4)
C13-B11	1.613 (5)	C50-B1B	1.602 (6)
O2F-B1F	1.483 (5)	O48-B1B	1.459 (5)
O40-B1F	1.457 (4)	O3B-B1B	1.485 (4)
<b>ReCl(CDO)(CDOH)<sub>2</sub>BPh</b>			
Re-N1F	2.103 (6)	Re-N1B	2.028 (9)
Re-N2F	2.108 (9)	Re-N2B	2.038 (7)
Re-N3F	2.05 (1)	Re-N3B	2.061 (8)
Re-Cl	2.404 (4)		
B-O1B	1.51 (1)	B-O3B	1.46 (2)
B-O2B	1.49 (2)	B-C41	1.60 (2)

in the +2 oxidation state rather than the +3 oxidation state observed with Tc and Re. The six-coordinate Mn(II) complex contains two caps rather than one, but in a pseudoclatrocholate arrangement. Each cap is covalently bonded to only two of the three oxime oxygen atoms (Figure 1c).

#### Synthesis of the Manganese Dioxime Complex. Mn<sup>II</sup>.

Table VI. Selected Bond Angles in Degrees

<b>Mn(CDO)(CDOH)<sub>2</sub>(BPh(OCH<sub>3</sub>)<sub>2</sub>)<sub>2</sub></b>			
N1F-Mn-N1B	70.3 (1)	N1B-Mn-N3B	79.06 (9)
N1F-Mn-N2B	133.1 (1)	N2F-Mn-N2B	69.5 (1)
N1F-Mn-N3B	137.8 (1)	N2F-Mn-N3B	141.70 (9)
N1F-Mn-N2F	79.13 (9)	N2F-Mn-N3F	84.9 (1)
N1F-Mn-N3F	118.2 (1)	N2B-Mn-N3F	93.3 (1)
N1B-Mn-N2F	134.66 (9)	N2B-Mn-N3B	83.7 (1)
N1B-Mn-N3F	139.1 (1)	N3F-Mn-N3B	69.4 (1)
N1B-Mn-N2B	108.8 (1)		
<b>ReCl(CDO)(CDOH)<sub>2</sub>BPh</b>			
N1F-Re-N2F	114.4 (3)	N3F-Re-N3B	71.2 (4)
N1F-Re-N3F	76.9 (3)	N1B-Re-N2B	94.0 (3)
N1F-Re-N1B	73.2 (3)	N1B-Re-N3B	77.2 (3)
N1F-Re-N2B	160.3 (4)	N2B-Re-N3B	78.2 (3)
N1F-Re-N3B	112.1 (3)	Cl-Re-N1F	81.6 (3)
N2F-Re-N3F	77.6 (4)	Cl-Re-N2F	80.3 (3)
N2F-Re-N1B	159.0 (4)	Cl-Re-N3F	139.1 (2)
N2F-Re-N2B	73.0 (3)	Cl-Re-N1B	81.6 (3)
N2F-Re-N3B	114.7 (3)	Cl-Re-N2B	82.0 (3)
N3F-Re-N1B	123.3 (4)	Cl-Re-N3B	149.7 (3)
N3F-Re-N2B	122.7 (3)		

(CDO)(CDOH)<sub>2</sub>(BPh(OCH<sub>3</sub>)<sub>2</sub>)<sub>2</sub> is formed in very high yield (ca. 90%) from manganese(III) acetate in the absence of added re-

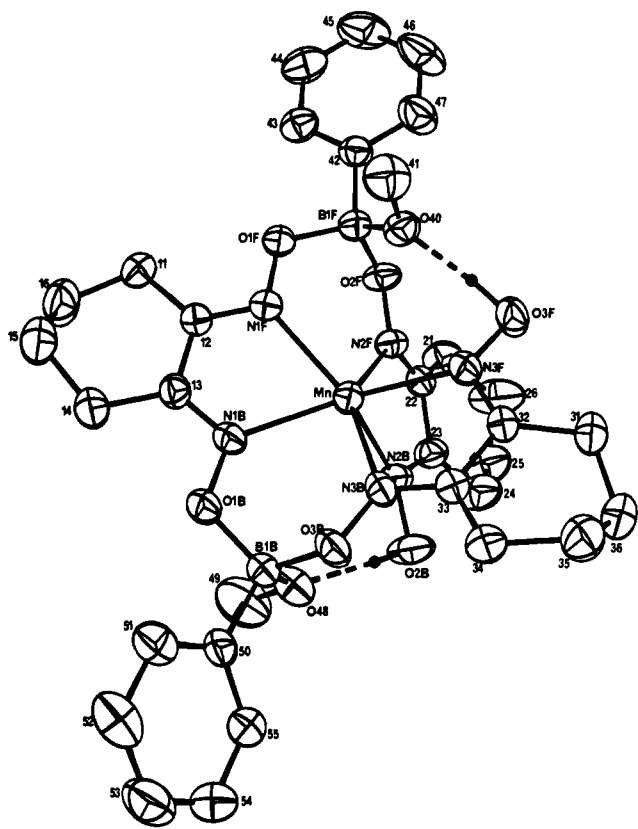
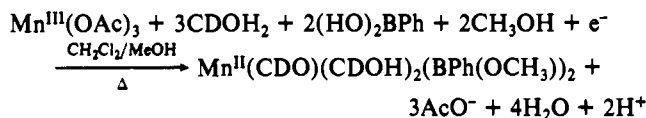


Figure 3. ORTEP representation of  $\text{Mn}(\text{CDO})(\text{CDOH})_2(\text{BPh}(\text{OCH}_3)_2)$ .

ductant, even under oxidizing conditions (alkaline hydrogen peroxide). The scheme for this reaction is shown as follows:



Although no reductant was added to the reaction mixture to take the Mn(III) to Mn(II), Mn(III) is known to oxidize various organic compounds, often by way of free-radical reactions.<sup>20–23</sup> As alcohols are known substrates for this reaction,<sup>20,23</sup> methanol may have been oxidized by manganese(III) acetate, thereby yielding the Mn(II) product. Subsequent attempts to oxidize the manganese(II) dioxime complex (with  $\text{H}_2\text{O}_2$  and high pH) were not successful. Preparation of the Mn(II) complex in the absence of methanol (acetone as solvent) yielded a product that analyzed for  $\text{Mn}^{\text{II}}(\text{CDO})(\text{CDOH})_2(\text{BPh})_2 \cdot 3\text{H}_2\text{O}$  (again, no reductant was added, but acetone is also known to be involved in oxidation reactions with manganese(III) acetate<sup>23</sup>). Whether the water molecules were coordinated in a fashion similar to that for the methoxy groups in  $\text{Mn}(\text{CDO})(\text{CDOH})_2(\text{BPh}(\text{OCH}_3)_2)$  could not be determined from either mass spectra, elemental analyses, or IR results. Vacuum drying the product overnight did not remove the water molecules.

**Characterization of  $\text{Mn}(\text{CDO})(\text{CDOH})_2(\text{BPh}(\text{OCH}_3)_2)$ .** A molecular ion was not observed in either the positive or negative CI or FAB mass spectrum. Fragment ions were, however, observed corresponding to the loss of one and two methanol molecules

(Table III). Magnetic susceptibility measurements confirmed the presence of high-spin,  $d^5$  Mn(II). The spin-only magnetic moment ( $\mu_{\text{eff}}$ ) was determined to be  $5.67 \mu_{\text{B}}$  indicative of a high-spin  $d^5$  environment (theoretical value  $5.92 \mu_{\text{B}}$ ).<sup>17</sup>

**Syntheses of the Rhenium Dioxime Complexes.** Syntheses of the uncapped and monocapped rhenium(III) tris(dioxime) complexes were best achieved by substitution from  $\text{ReCl}_3 \cdot (\text{CH}_3\text{CN})(\text{PPh}_3)_2$ . The capped dioxime complexes can be prepared by the method of reduction and substitution from  $\text{ReO}_4^-$ , albeit in lower yields (1–5% vs ca. 25–50% for the direct substitution). The perrhenate reduction route resulted in the formation of many side products (as determined by TLC). The DMG analogues gave low yields regardless of the method of synthesis (the low yields observed during the substitution route may be a result of the fact that  $\text{DMGH}_2$  is not soluble in  $\text{CH}_2\text{Cl}_2$  or  $\text{CHCl}_3$  and  $\text{ReCl}_3(\text{CH}_3\text{CN})(\text{PPh}_3)_2$  hydrolyzes in MeOH or EtOH). In contrast, the analogous Tc complexes are best prepared by using the reduction/substitution route from  $\text{TcO}_4^-$ .<sup>1,2</sup> This marked difference between Tc and Re may be a result of the fact that  $\text{ReO}_4^-$  is more difficult to reduce than  $\text{TcO}_4^-$ .<sup>17</sup>

The  $\text{BAReOs}$  can also be prepared by capping  $\text{ReCl}(\text{CDOH})_2(\text{CDOH})_2$  under slightly acidic conditions. This capping step of the synthesis is nearly quantitative (as demonstrated also for uncapped technetium tris(dioxime) complexes<sup>2</sup>), yielding exclusively a monocapped product.

**Characterization of the Rhenium Dioxime Complexes.** The rhenium(III) tris(dioxime) complexes (uncapped and capped) are analogous to the technetium complexes previously reported.<sup>1,2</sup> The symmetry of these molecules is such that two of the dioximes are equivalent, the unique dioxime being trans to the chloride (Figure 2). This symmetry is retained in solution, as shown by the NMR results. The chemical shifts for the methyl groups in  $\text{ReCl}(\text{DMG})(\text{DMGH})_2\text{BBu}$  (2.52–2.75 ppm) show a 2:1:2:1 ratio for the six DMG methyl group signals. The CDO complexes show a similar pattern, but it is less apparent due to the complexity of the methylene signals. The protons on the carbon directly bonded to the boron atom are observed at an unusually high upfield position due to the shielding effect of the tetrahedral boron atom. The chemical shifts of the protons attached to carbon atoms further removed from the boron are unaffected. The bridging oxime protons in the dioxime complexes are observed at ca. 15 ppm. Comparison of the  $^1\text{H}$  NMR spectra of the Tc and Re complexes shows that the signals for protons on the carbon adjacent to the imine carbon and for the oxime protons of the Re complexes are observed slightly downfield (ca. 0.2–0.4 ppm and ca. 0.5 ppm, respectively; less shielded) relative to those of the analogous Tc complexes. The chemical shift positions of the remaining protons, which are further removed from the metal, are unaffected by the metal.

The XPS results for the Cl  $2p_{3/2}$  binding energy (vide supra) imply close to a covalent metal–chlorine bond for the Re complexes.<sup>18</sup> The Tc compounds display binding energies intermediate to those of covalent and ionic Tc–Cl bonds.<sup>24</sup>

Conductivity measurements indicate that these seven-coordinate rhenium dioxime complexes (capped and uncapped) are neutral in solution ( $0\text{--}8 \Omega^{-1} \text{M}^{-1} \text{cm}^2$ ).<sup>25</sup> The magnetic susceptibility measurement for  $\text{ReCl}(\text{CDO})(\text{CDOH})_2\text{BPh}$  ( $\chi = -0.37 \times 10^{-6}$  cgs units) indicates that the Re(III) complexes are diamagnetic spin-paired  $d^4$ .<sup>17</sup>

A molecular ion cluster is observed for the capped and uncapped rhenium dioxime complexes in the positive and/or negative FAB mass spectra (Table III). A major fragment ion cluster observed is the loss of  $\text{H}_2\text{O}$  (or  $\text{OH} + \text{H}$ ). Another fragment ion cluster is the loss of 36 mass units. The observed isotope pattern is consistent with the loss of two  $\text{H}_2\text{O}$  molecules. In contrast, the spectra of the technetium analogues<sup>1,2</sup> clearly showed the loss of  $\text{HCl}$  as major fragment ions (by isotope patterns), and no loss of  $\text{H}_2\text{O}$  (without the loss of  $\text{Cl}^-$ ) was observed. This difference might be explained by the expected reduction in lability for the

(20) Waters, W. A.; Littler, J. S. Oxidation by Vanadium(V), Cobalt(III), and Manganese(III). In *Oxidation in Organic Chemistry*; Wiberg, K., Ed.; Academic Press: New York, 1965; Vol. 5-A, 185–241.

(21) Anderson, J. M.; Kochi, J. K. *J. Am. Chem. Soc.* **1970**, *92*, 2450.

(22) Heiba, E. I.; Dessau, R. M.; Koehl, W. J., Jr. *J. Am. Chem. Soc.* **1969**, *91*, 138.

(23) De Klein, W. J. Reactions with Manganese(III) Acetate. In *Organic Syntheses by Oxidation with Metal Compounds*; Mijs, W. J., De Jonge, C. R. H. I., Eds.; Plenum Press: New York, 1986; pp 261–314.

(24) Thompson, M.; Nunn, A. D.; Treher, E. N. *Anal. Chem.* **1986**, *58*, 3100.

(25) Geary, W. H. *Coord. Chem. Rev.* **1971**, *7*, 81.

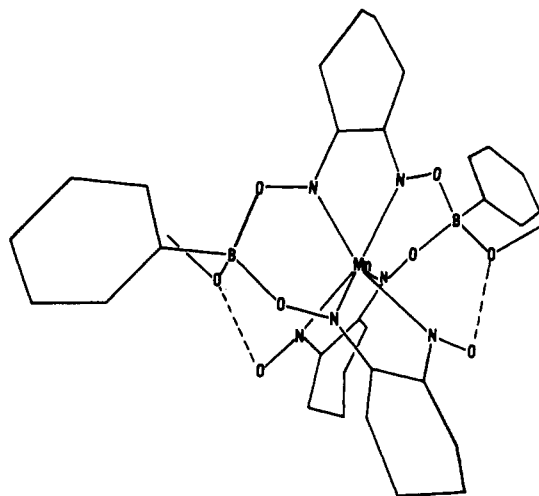


Figure 4. View of  $\text{Mn}(\text{CDO})(\text{CDOH})_2(\text{BPh}(\text{OCH}_3))_2$  showing the noncrystallographic  $C_2$  molecular symmetry ( $C_2$  axis is vertical).

analogous complexes in going from a second- to a third-row transition metal.

The uncapped  $\text{ReCl}(\text{CDOH})_2(\text{CDOH}_2)$  is an intermediate in the synthesis of  $\text{ReCl}(\text{CDO})(\text{CDOH})_2\text{BR}$  from  $\text{ReCl}_3 \cdot (\text{CH}_3\text{CN})(\text{PPh}_3)_2$ , and probably also from  $\text{ReO}_4^-$ , although the uncapped complex has not been isolated during syntheses from  $\text{ReO}_4^-$ . The uncapped Re complex is readily capped by boronic acids, as are the Tc analogues.<sup>2</sup> Under mild acidic conditions, in the presence of boronic acid, the tris(dioxime) complex is monocapped very efficiently (near-quantitative yields as evidenced by TLC and HPLC) to give  $\text{ReCl}(\text{CDO})(\text{CDOH})_2\text{BR}$ . This method of synthesis is useful when the boronic acid or the resultant monocapped complex is sensitive (unstable) to the conditions necessary for the direct synthesis of the  $\text{BAReO}$  from either  $\text{ReCl}_3(\text{CH}_3\text{CN})(\text{PPh}_3)_2$  or  $\text{ReO}_4^-$ .

**X-ray Structural Characterizations of  $\text{Mn}(\text{CDO})(\text{CDOH})_2(\text{BPh}(\text{OCH}_3))_2$  and  $\text{ReCl}(\text{CDO})(\text{CDOH})_2\text{BPh}$ .** The nearly  $C_2$  symmetric Mn(II) structure is unusual, since the complex is only partially capped at each end. Only one of the three CDO ligands is covalently bonded to both boron atoms in the two caps (Figures 3 and 1c). The two remaining CDO ligands are directly involved in only one of the two caps (these two CDO ligands are covalently bonded to different boron atoms). Each boron atom forms covalent bonds with only two of the three proximate dioxime oxygens. The third "free" hydroxyl oxygen is intramolecularly hydrogen bonded to a methoxyl substituent of the tetrahedral boron cap (average  $\text{HO} \cdots \text{OCH}_3$  distance is 2.55 Å). Since the hydrogen bonds effect topological closure of the cap, the structure may loosely be considered as a clathrochelate and described in terms of distortions from the known trigonal-prismatic clathrochelate structure  $\text{Co}^{\text{II}}(\text{dioxime})_3(\text{BF})_2$  (Figure 1a). The Mn complex retains only a noncrystallographic  $C_2$  axis of symmetry (Figure 4) when compared to the  $D_3$  symmetric Co complex. In order to accommodate the "extra" hydrogen bonds of the ligand cage, the two partially capped CDO groups are twisted about the Mn, while the caps are forced up toward the unique CDO group ( $\text{B}-\text{Mn}-\text{B}$  angle =  $157^\circ$ ). The triangles of nitrogen atoms at each cap are parallel and isosceles (average N-N distances are 2.91, 3.07, and 3.82 Å) with the long side involving the nitrogens of the unique and uncapped CDO groups. The average Mn-N distance is 2.285 (3) Å, consistent with previously reported Mn(II)-N distances (2.2-2.3 Å).<sup>26,27</sup> The usual coordination number of Mn(II) is 6, and since high-spin Mn(II) obtains no ligand field stabilization in either an octahedral or tetrahedral environment, the geometry about the Mn is dictated by the ligand constraints.<sup>17</sup> In this case,

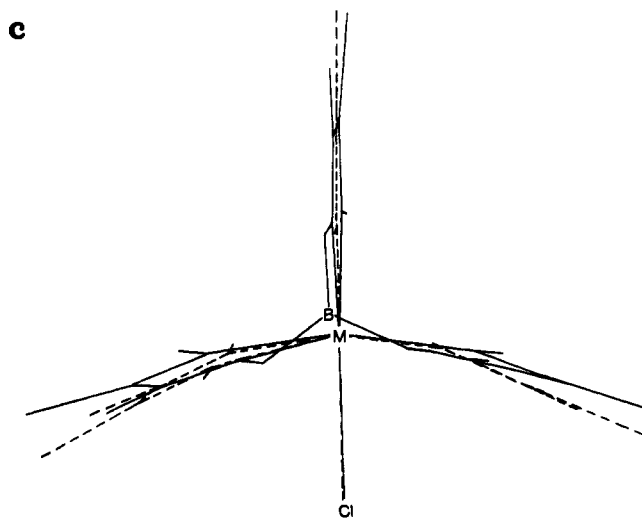
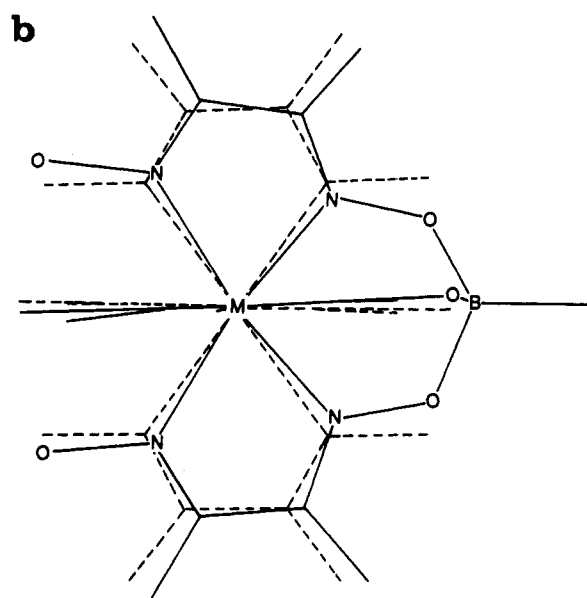
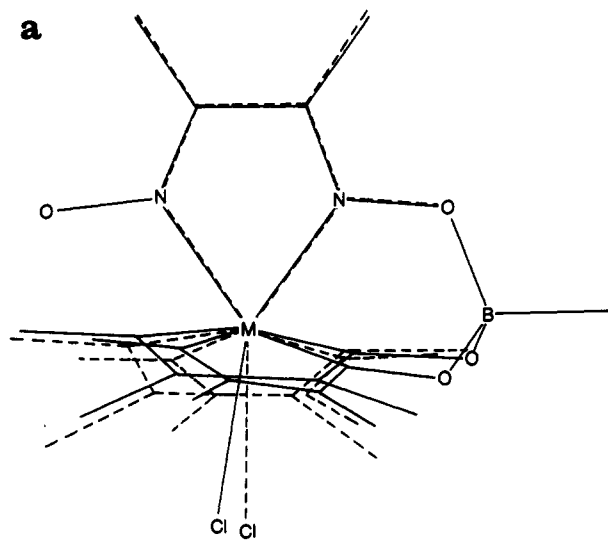


Figure 5. Distortions (changes) that occur on going from the uncapped (dotted lines)  $\text{TcCl}(\text{DMGH})_2(\text{DMGH}_2)^2$  to the monocapped (solid lines) Tc or Re complexes: (a) view superimposing the metal and unique dioxime ligand of the two structures; (b) view of (a) looking down at the metal from the unique dioxime with the chlorine below the metal; (c) end-on view of (a) from the metal to the boron cap.

(26) Wiegardt, K.; Schoffmann, E.; Nuber, B.; Weiss, J. *Inorg. Chem.* **1986**, *25*, 4877.

(27) Donaldson, P. B.; Tasker, P. A.; Alcock, N. W. *J. Chem. Soc., Dalton Trans.* **1977**, 1160.

we observe a six-coordinate complex with close to trigonal geometry.

It seems likely that under different conditions all three dioximes could be capped completely by a boron atom at *one* end, given the reported structure of the Mn(II) complex of 1,1,1-tris(((pyridyl-2-methylene)amino)methyl)ethane (Mn–N distance = 2.21 Å; the average distance between the pyridyl  $\alpha$ -carbons at the uncapped end is 3.83 Å).<sup>27</sup> However, our observed Mn–N distances are clearly too long for a clathrochelate structure (Figure 1a) with *two* completely formed boron caps (e.g., Co(II)–N = 1.973 Å).<sup>5</sup> The size of the cavity for this type of clathrochelate is most sensitive to the bond distances and angles at the cap atoms;<sup>28</sup> even the expanded cavity of the clathrochelate ligand FB(ONCHC<sub>5</sub>H<sub>3</sub>N)<sub>3</sub>P is too small for Mn(II).<sup>29,30</sup> (Co(II)–N = 2.12 Å at the phosphorus “capped” end; average cap C–P distance = 1.85 Å, and Co(II)–N = 2.06 Å at the boron-capped end; average cap B–O distance = 1.55 Å).<sup>29</sup>

As expected,<sup>31</sup> the monocapped Re complex is virtually superimposable on the previously reported Tc–BATO structures.<sup>1,2</sup> The Re is coordinated to six nitrogen atoms from the three CDO ligands; a chlorine occupies the seventh coordination site. Seven-coordination is known for Re(III), although six-coordinate complexes are much more common.<sup>17</sup> The Re–Cl distance, 2.404 (4) Å, is within the range (2.2–2.6 Å) reported for other chlorine-containing Re(III) complexes.<sup>32–38</sup> Coordination of the six

nitrogen atoms about the metal is distorted from trigonal-prismatic geometry by the seventh, halogen ligand, which spreads the angle between the planes of the two flanking dioxime groups; this distortion is augmented by the presence of two intramolecular hydrogen bonds, which bridge the two flanking uncapped dioxime oxygens with the third (O–O distances = 2.50 and 2.47 (1) Å) and pull them toward the unique dioxime. Similar distortions have been observed in a crystal structure of the uncapped hepta-coordinate technetium tris(dioxime) complex, TcCl(DMGH)<sub>2</sub>(DMGH<sub>2</sub>),<sup>2</sup> which is a precursor of the BATO complexes.<sup>2</sup> It is clear, though, that some relaxation of the initial C<sub>2v</sub> symmetric geometry of the uncapped complex is required for the introduction of a cap (see Figure 5). Metal (Re or Tc)<sup>2</sup> to nitrogen distances are somewhat compressed at the capped end (2.05 Å) though unchanged (2.10 Å) at the uncapped end (Tc–N distance = 2.10 Å for TcCl(DMGH)<sub>2</sub>(DMGH<sub>2</sub>)).<sup>2</sup> At the capped end the two flanking dioxime groups are drawn in (Figure 5b) and twisted down (ca. 8°) and away from the unique dioxime group. The halogen is similarly bent away from the cap (B–M–Cl angle = 101°) toward the uncapped end (Figure 5a), where the distance between the two flanking dioxime oxygens increases from 3.4 to 3.8 Å. The additional distortions and relaxation required for the introduction of a second cap apparently are not possible for the relatively rigid monocapped Re and Tc complexes.

### Conclusion

The manganese(II), rhenium(III), and previously reported technetium(III)<sup>1,2</sup> tris(dioxime) complexes capped with boronic acid derivatives do not form the well-known biscapped clathrochelate structures reported for Co(II), Co(III), Fe(II), and Ru(II).<sup>3–8</sup> Mn(II) is too large to fit in the cavity of the completely biscapped free-ligand cage, and thus an unusual biscapped structure is observed in which only two of the three oxime oxygens at each end of the molecule are covalently bonded to the capping boron atoms. The distortions resulting from seven coordination prevent further capping of the monocapped Tc(III) and Re(III) complexes.

**Acknowledgment.** We thank Dr. M. Thompson at the University of Toronto for obtaining the magnetic susceptibility and XPS data.

**Supplementary Material Available:** Tables listing all bond distances, all bond angles, anisotropic thermal parameters, isotropic temperature factors, and hydrogen positional parameters for the two structures (12 pages); tables listing observed and calculated structure factors (40 pages). Ordering information is given on any current masthead page.

- (28) Dawson, J. W.; Lane, B. C.; Mynott, R. J.; Venanzi, L. M. *Inorg. Chim. Acta* **1971**, *5* (1), 25.  
 (29) Churchill, M. R.; Reis, A. H. *J. Chem. Soc., Dalton Trans.* **1973**, 1570.  
 (30) Parks, J. E.; Wagner, B. E.; Holm, R. H. *J. Am. Chem. Soc.* **1970**, *92*, 3500.  
 (31) The Cambridge Structural Database (CSD, July 1990 release) contains 148 structures of Tc complexes and 1018 structures of Re complexes. Of these, eight pairs of structures represent exact Tc–Re analogues. Exact here denotes a one-to-one correspondence between the bond connectivity graph(s) of all atoms (including any ions and solvents) in the unit cell of one member with the connectivity graph(s) of the other member of the pair. The (isographic) members of a pair differ formally only through the replacement of one or more Tc atoms by Re atoms. We find that for each of the eight pairs, the Tc and Re analogues are crystallographically isostructural (CSD refcodes (Tc analogue first); ratio of the unit cell volumes,  $V_{\text{Re}}/V_{\text{Tc}}$ ): (1) BAGWAH, NREDTC10, 0.993; (2) BECDDES, CETCRE, 0.997; (3) BEWRIE, REOENC10, 0.999; (4) DANNIP, BINVOJ, 0.999; (5) VACSUN, BOCLOU, 0.999; (6) CUZCEF, PASNRE, 1.009; (7) FOKCIR, FUZTOJ, 0.983; (8) TPPTCC, TPPOREC20, 0.999. The above pairs of isographic structures were uncovered through a general computer program that classifies, sorts, and compares the unit cell graphs and crystal structures of the ca. 82 000 entries in the CSD database (J. Z. Gougoutas and M. A. Hermsmeier, manuscript in preparation). Further, there are 25 pairs of isographic Mn–Re analogues in the CSD database, of which 13 represent crystallographically isostructural pairs (average  $V_{\text{Re}}/V_{\text{Mn}} = 1.025$ ). There are two pairs of isographic Mn–Tc analogues, of which one has isostructural members ( $V_{\text{Mn}}/V_{\text{Tc}} = 0.937$ ).  
 (32) Hiller, W.; Mohyla, J.; Strahle, J.; Hauck, H. G.; Dehnik, K. *Z. Anorg. Allg. Chem.* **1984**, *72*.  
 (33) Lock, C. J. L.; Murphy, C. N. *Acta Crystallogr., Sect. B* **1979**, *35*, 951.  
 (34) Drew, M. G. B.; Tisley, D. G.; Walton, R. A. *J. Chem. Soc., Chem. Commun.* **1970**, 600.

- (35) Duckworth, V. F.; Douglas, P. G.; Mason, R.; Shaw, B. L. *J. Chem. Soc., Chem. Commun.* **1970**, 1083.  
 (36) Cotton, F. A.; Cage, L. D. *Inorg. Chem.* **1979**, *18*, 1716.  
 (37) Collins, D. M.; Cotton, F. A.; Cage, L. D. *Inorg. Chem.* **1979**, *18*, 1712.  
 (38) Calvo, C.; Hayadevan, N. C.; Lock, C. J. L. *Can. J. Chem.* **1969**, *47*, 4213.