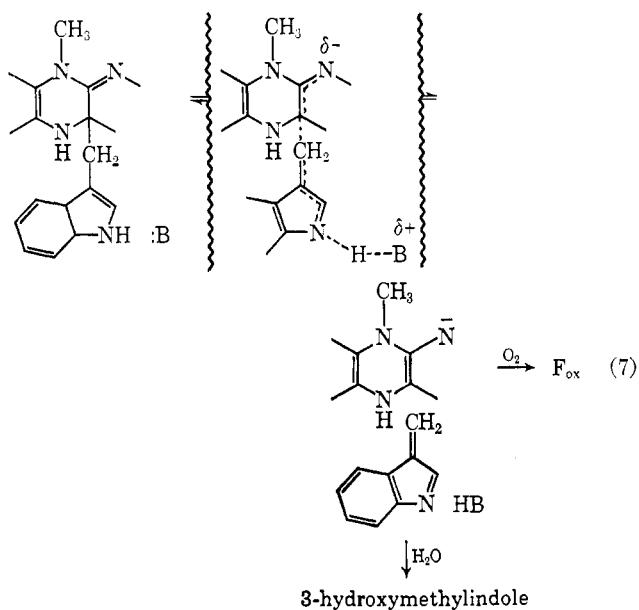


Since the HO<sup>-</sup> catalyzed conversion of 4a-InH to both F<sub>ox</sub> and FH<sub>2</sub> (not seen with 4a-InMe) is dependent upon the same rate constant, the mechanism can only represent an E-2 elimination to provide FH<sub>2</sub> (eq 7). The



log of the second-order rate constants for HO<sup>-</sup>, CO<sub>3</sub><sup>2-</sup>, and HPO<sub>4</sub><sup>2-</sup> dictate a Brønsted line (deviation = 0.0) of slope +0.5<sup>16</sup> in accord with general-base catalysis as in eq 7.

These results suggest that in some flavin oxo-reduction reactions: (1) formation of a 5-adduct may lead to a 4a-adduct (dependent upon the carbonium ion stability of the migrating group<sup>3</sup>) prior to base catalyzed formation of oxidized substrate and FH<sub>2</sub>, (2) formation of FH<sub>2</sub> from 5- and (appropriate) 4a-adducts is general-acid and general-base catalyzed, (3) formation of either a 4a- or 5-adduct may lead to oxidized substrate without reduction of F<sub>ox</sub>, and (4) the stabilities of the 4a- and 5-adduct are such that, as intermediates, they should be observable, particularly in a model reaction. The elimination reaction of eq 7 represents an experimental verification of the feasibility of the Hamilton<sup>4</sup> mechanism for flavin catalysis in appropriate cases.<sup>3</sup>

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(16) Second-order rate constants for HO<sup>-</sup> = 112 M<sup>-1</sup> min<sup>-1</sup>, for CO<sub>3</sub><sup>2-</sup> = 1.88 × 10<sup>-1</sup> M<sup>-1</sup> min<sup>-1</sup>, and for HPO<sub>4</sub><sup>2-</sup> = 5.1 × 10<sup>-3</sup> M<sup>-1</sup> min<sup>-1</sup>.

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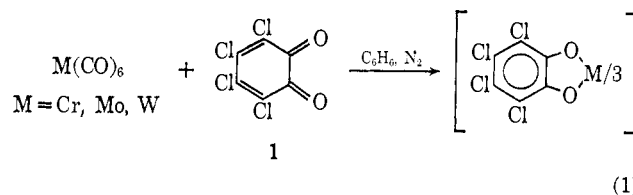
### Neutral Tris(*o*-benzoquinone) Complexes of Chromium, Molybdenum, and Tungsten

Sir:

Considerable attention has been directed at the coordination properties of bidentate ligands which form

unsaturated five-membered chelate rings with metal ions.<sup>1</sup> Interest in these systems stems, in part, from the facile electrochemical properties observed for such complexes. A large majority of the ligands used in these studies have contained nitrogen and sulfur donor atoms. In an effort to investigate the chemical and structural properties of various related oxygen donor ligands, we have begun a study of simple binary metal-*o*-benzoquinone complexes.

Reflux of *o*-tetrachlorobenzoquinone (1) with carbonyls of Cr, Mo, and W in benzene yields diamagnetic, neutral tris complexes of the metals according to reaction 1.<sup>2</sup> The complexes are only slightly soluble in



benzene and may be isolated from the reaction mixture by reducing the volume of the cooled solution.<sup>3</sup> In solid they are moderately air stable<sup>4</sup> and are highly colored: red-purple for Cr(O<sub>2</sub>C<sub>6</sub>Cl<sub>4</sub>)<sub>3</sub>, violet and brown for the Mo and W complexes. Infrared spectra show no bands above 1550 cm<sup>-1</sup> consistent with oxygen-bonded, reduced *o*-benzoquinone ligands.<sup>5</sup> Spectral bands for Cr(O<sub>2</sub>C<sub>6</sub>Cl<sub>4</sub>)<sub>3</sub> are sharp and agree with spectra reported previously for chelated *o*-tetrachlorobenzoquinone complexes.<sup>6</sup> Spectra for Mo(O<sub>2</sub>C<sub>6</sub>Cl<sub>4</sub>)<sub>3</sub> and its W analog contain broader bands which in some cases are split into two distinct sets. Electronic spectra of the complexes show similar trends.<sup>7</sup> The spectrum of the Cr complex is well resolved while the Mo and W complexes show only large broad bands. The electrochemical properties of all three complexes have been examined using cyclic voltammetry.<sup>8</sup> The Mo and W complexes undergo one electron reduction reactions irreversibly while the Cr complex undergoes three reversible oxidation steps at +0.12, +0.54, and +0.88 V, with reduction of Cr(O<sub>2</sub>C<sub>6</sub>Cl<sub>4</sub>)<sub>3</sub><sup>3+</sup> occurring at +0.07, +0.41, and +0.77 V. Attempts are currently underway to examine each member of this series.

The complex Cr(O<sub>2</sub>C<sub>6</sub>Cl<sub>4</sub>)<sub>3</sub> is clearly different from its Mo and W analogs and also from related 1,2-dithiolene

(1) (a) J. A. McCleverty, *Progr. Inorg. Chem.*, **10**, 49 (1968); (b) G. N. Schrauzer, *Accounts Chem. Res.*, **2**, 72 (1969).

(2) A reaction time of about 36 hr is required for the Cr complex. The Mo and W complexes require about 12 hr.

(3) *Anal.* Calcd for Cr(O<sub>2</sub>C<sub>6</sub>Cl<sub>4</sub>)<sub>3</sub>·4C<sub>6</sub>H<sub>6</sub>: C, 45.7; H, 2.2; Cl, 38.6; Cr, 4.7. Found: C, 45.8; H, 2.2; Cl, 38.9; Cr, 4.5. Calcd for Mo<sub>2</sub>(O<sub>2</sub>C<sub>6</sub>Cl<sub>4</sub>)<sub>6</sub>·3C<sub>6</sub>H<sub>6</sub>: C, 34.1; H, 1.0; Cl, 44.8; Mo, 10.1. Found: C, 33.2; H, 1.1; Cl, 44.6; Mo, 10.4. Calcd for W<sub>2</sub>(O<sub>2</sub>C<sub>6</sub>Cl<sub>4</sub>)<sub>6</sub>·3C<sub>6</sub>H<sub>6</sub>: C, 31.2; H, 0.9; Cl, 41.0; W, 17.7. Found: C, 28.2; H, 0.7; Cl, 41.2; W, 16.7. The presence of solvent of crystallization has been verified by mass spectra.

(4) The Cr complex is quite stable in solid or in solution. The Mo and W complexes decompose in air over the period of a few weeks as solid samples.

(5) Principal infrared bands (cm<sup>-1</sup>): Cr(O<sub>2</sub>C<sub>6</sub>Cl<sub>4</sub>)<sub>3</sub> 1440, 1330, 1270, 1245, 1210, 983, 813, 792; Mo<sub>2</sub>(O<sub>2</sub>C<sub>6</sub>Cl<sub>4</sub>)<sub>6</sub> 1505, 1355, 1200, 960, 815, 800, 777, 757; W<sub>2</sub>(O<sub>2</sub>C<sub>6</sub>Cl<sub>4</sub>)<sub>6</sub> 1530, 1375, 1250, 980, 825, 805, 795, 773.

(6) Y. S. Sohn and A. L. Balch, *J. Amer. Chem. Soc.*, **94**, 1144 (1972).

(7) Electronic spectra (λ<sub>max</sub>, nm (ε); measured in dichloromethane): Cr(O<sub>2</sub>C<sub>6</sub>Cl<sub>4</sub>)<sub>3</sub> 1190 (1100), 1000 (1600), 765 (5600), 525 (17,600), 495 (11,400) (sh), 460 (5900) (sh), 313 (14,300) (sh); Mo<sub>2</sub>(O<sub>2</sub>C<sub>6</sub>Cl<sub>4</sub>)<sub>6</sub> 730 (6800), 560 (5000) (sh), 510 (4400) (sh), 290 (12,000) (sh); W<sub>2</sub>(O<sub>2</sub>C<sub>6</sub>Cl<sub>4</sub>)<sub>6</sub> 620 (1600) (sh), 560 (2300) (sh), 405 (4200), 290 (23,300) (sh).

(8) Cyclic voltammetry performed in dichloromethane with (C<sub>4</sub>H<sub>9</sub>)N-CIO<sub>4</sub> as supporting electrolyte vs. Ag/AgCl reference electrode.

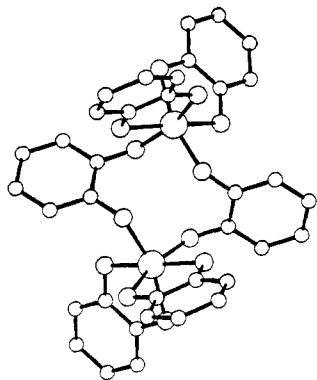


Figure 1. View of  $\text{Mo}_2(\text{O}_2\text{C}_6\text{Cl}_4)_6$  down the twofold axis of the molecule. Ring chlorine atoms have been omitted.

complexes. Spectral properties of the complex suggest a highly symmetric coordination geometry of  $D_3$  or higher symmetry. Structurally,  $\text{Cr}(\text{O}_2\text{C}_6\text{Cl}_4)_3$  is iso-electronic with 1,2-dithiolene complexes known to possess trigonal prismatic ( $D_{3h}$ ) coordination geometries.<sup>9</sup> If effects which stabilize this geometry with related S and Se donor ligands are significant in the present case, a  $D_{3h}$  molecular structure is expected. The electrochemical properties of  $\text{Cr}(\text{O}_2\text{C}_6\text{Cl}_4)_3$ , however, are quite different from similar 1,2-dithiolene complexes. Neutral complexes of related sulfur donor ligands readily undergo reversible reduction reactions with the S analog of the present complex  $\text{Cr}(\text{S}_2\text{C}_6\text{Cl}_4)_3$  undergoing reduction to complexes with charges of  $-1$ ,  $-2$ , and  $-3$ .<sup>10</sup> The oxidation reactions observed for  $\text{Cr}(\text{O}_2\text{C}_6\text{Cl}_4)_3$  are more similar to the oxidation of  $\text{M}(\text{PPh}_3)_2(\text{O}_2\text{C}_6\text{Cl}_4)$ ,  $\text{M} = \text{Pd}, \text{Pt}$ .<sup>11</sup> Balch has recently reported the chemical and electrochemical formation of  $[\text{M}(\text{PPh}_3)_2(\text{O}_2\text{C}_6\text{Cl}_4)]^+$  with evidence to show that the unpaired electron is localized mainly on the partially reduced *o*-benzoquinone ligand. Thus, oxidation of  $\text{Cr}(\text{O}_2\text{C}_6\text{Cl}_4)_3$  probably involves oxidation of the reduced benzoquinone ligands. It is surprising that reduction of the Cr(VI) metal ion is not observed.

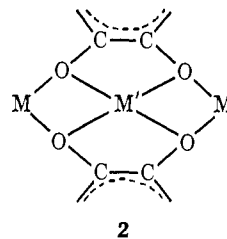
The properties of  $\text{Mo}(\text{O}_2\text{C}_6\text{Cl}_4)_3$  and  $\text{W}(\text{O}_2\text{C}_6\text{Cl}_4)_3$  are mutually similar and indicate much lower symmetry than the Cr analog. The preliminary results of a crystallographic study on the Mo complex show this to be the case.<sup>12</sup> The molecule is dimeric with crystallographic  $C_2$  symmetry. Each Mo atom is chelated by two terminal  $\text{C}_6\text{Cl}_4\text{O}_2^{2-}$  ligands and bonded to one oxygen of two bridging ligands (Figure 1) with a distorted octahedral coordination geometry about the metal. The bridging ligands bond to the metals through outer electron pairs of the oxygen donors creating a puckered 10-membered  $\text{Mo}_2\text{O}_4\text{C}_4$  ring. The inner donor orbitals normally used for chelated coordination are available for coordination to an additional metal at the center of the ring, 2. However, attempts to prepare such a compound have, so far, been unsuccessful. The effects resulting in the preferred dimeric configuration of the

(9) R. Eisenberg, *Progr. Inorg. Chem.*, **12**, 925 (1970).

(10) E. J. Wharton and J. A. McCleverty, *J. Chem. Soc. A*, 2258 (1969).

(11) A. L. Balch, *J. Amer. Chem. Soc.*, **95**, 2723 (1973).

(12) Crystallographic data are:  $C_{2h}^2-C2/c$ ;  $\rho_{\text{calc}} = 1.833$ ,  $\rho_{\text{expt}} = 1.83$  (1)  $\text{g}/\text{cm}^3$ ;  $Z = 4$  for  $\text{Mo}_2(\text{O}_2\text{C}_6\text{Cl}_4)_6 \cdot 3\text{C}_6\text{H}_6$ ;  $a = 22.450$  (3),  $b = 11.592$  (3),  $c = 27.303$  (3) Å;  $\beta = 104.27$  (5)°. The conventional *R* factor obtained from the full-matrix least-squares refinement of 2891 reflections measured on a Picker diffractometer is currently 0.065.



2

complex over a monomeric molecule of either  $D_3$  or  $D_{3h}$  symmetry are not clear but appear related to the restrictive chelate bite of the *o*-benzoquinone ligand.

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### New Transition Metal Derivatives of the Triborohydride Ion and the First Example of Reversible Bidentate-Tribidentate Borane Ligand Functionality

Sir:

In recent years there has been a great deal of interest in the preparation of metal derivatives of the triborohydride ion,  $\text{B}_3\text{H}_8^-$ .<sup>1-4</sup> We wish to report here the preparation of several new neutral transition metal triborohydride derivatives and to illustrate the previously unknown fact that the  $\text{B}_3\text{H}_8^-$  group can function as both a bidentate and a tridentate ligand.

Salts of  $\text{B}_3\text{H}_8^-$  react with equimolar quantities of  $\text{Mn}(\text{CO})_5\text{Br}$  or  $\text{Re}(\text{CO})_5\text{Br}$  in  $\text{CH}_2\text{Cl}_2$  solvent at room temperature to produce the volatile yellow liquids  $(\text{CO})_4\text{-MnB}_3\text{H}_8$  and  $(\text{CO})_4\text{-ReB}_3\text{H}_8$ , respectively, in good yield. For example,  $(\text{CH}_3)_4\text{NB}_3\text{H}_8$  and  $\text{Mn}(\text{CO})_5\text{Br}$  react to form a 76% yield of  $(\text{CO})_4\text{-MnB}_3\text{H}_8$  in 69 hr. Reaction of  $(\text{CH}_3)_4\text{NB}_3\text{H}_8$  with  $\text{Re}(\text{CO})_5\text{Br}$  requires ultraviolet radiation to produce a 43% yield in 27 hr. The yellow  $(\text{CO})_4\text{-MnB}_3\text{H}_8$  is purified by high-vacuum distillation through a trap at  $-10^\circ$  and condensation in a trap at  $-36^\circ$ . The rhenium complex is a colorless liquid which is purified by distillation through a  $0^\circ$  trap and condensation in a  $-30^\circ$  trap. The composition of each of these products was confirmed by mass spectrometry. The following parent fragment ions were identified:  $(\text{CO})_4\text{-MnB}_3\text{H}_8$ , ( $^{12}\text{C}^{16}\text{O}$ )<sub>4</sub><sup>55</sup> $\text{Mn}^{11}\text{B}_3^1\text{H}_8$ , found 208.0086 (calcd 208.0083);  $(\text{CO})_4\text{-ReB}_3\text{H}_8$ , ( $^{12}\text{C}^{16}\text{O}$ )<sub>4</sub><sup>187</sup> $\text{Re}^{11}\text{B}_3^1\text{H}_8$ , found 340.0256 (calcd 340.0262); ( $^{12}\text{C}^{16}\text{O}$ )<sub>4</sub><sup>187</sup> $\text{Re}^{11}\text{B}_3^1\text{H}_6$ , found 338.0109 (calcd 338.0105); ( $^{12}\text{C}^{16}\text{O}$ )<sub>4</sub><sup>185</sup> $\text{Re}^{11}\text{B}_3^1\text{H}_6$ , found 336.0078 (calcd 336.0075). The loss of each of the four carbonyls is observed for both of these complexes. The infrared spectra of these two species are almost identical. For example the prominent gas phase absorptions from  $(\text{CO})_4\text{-MnB}_3\text{H}_8$

(1) (a) F. Klanberg and L. J. Guggenberger, *Chem. Commun.*, 1293 (1967); (b) F. Klanberg, E. L. Muetterties, and L. J. Guggenberger, *Inorg. Chem.*, **7**, 2272 (1968); (c) L. J. Guggenberger, *ibid.*, **9**, 367 (1970).

(2) (a) S. J. Lippard and D. A. Ucko, *Inorg. Chem.*, **7**, 1051 (1968); (b) S. J. Lippard and K. M. Melmed, *ibid.*, **8**, 2755 (1969); (c) E. L. Muetterties, W. G. Peet, P. A. Wegner, and C. W. Alegranti, *ibid.*, **9**, 2447 (1970); (d) H. Beall, C. H. Bushweller, W. J. Dewkett, and M. Grace, *J. Amer. Chem. Soc.*, **92**, 3484 (1970); (e) C. H. Bushweller, H. Beall, M. Grace, W. Dewkett, and H. Bilofsky, *J. Amer. Chem. Soc.*, **93**, 2145 (1971).

(3) J. Borlin and D. F. Gaines, *J. Amer. Chem. Soc.*, **95**, 1367 (1972).

(4) (a) A. R. Kane and E. L. Muetterties, *J. Amer. Chem. Soc.*, **93**, 1041 (1971); (b) L. J. Guggenberger, A. R. Kane, and E. L. Muetterties, *ibid.*, **94**, 5665 (1972).