

## Metal Carbonyl Derivatives of 1,4-Quinone and 1,4-Hydroquinone

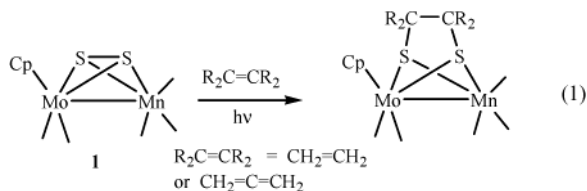
Richard D. Adams\* and Shaobin Miao

Department of Chemistry and Biochemistry, University of South Carolina Columbia, South Carolina 29208

Received February 15, 2004; E-mail: adams@mail.chem.sc.edu

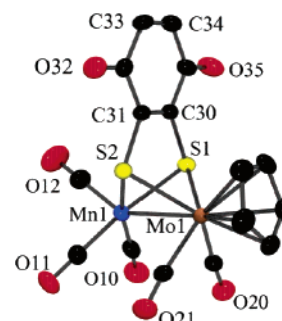
Quinones are a class of compounds that have widespread importance in biology and chemistry. Quinone derivatives are active in cellular respiration,<sup>1</sup> photosynthesis,<sup>2</sup> and blood coagulation.<sup>3</sup> Their biological action is often linked to their electron-transfer rates and redox potentials.<sup>4</sup> In organic synthesis, quinones are valuable reagents for the dehydrogenation of polycyclic hydroaromatic compounds,<sup>5</sup> cyclic ketones, and nitrogen heterocycles.<sup>6</sup> Quinone/hydroquinone redox couples have been widely used in electrochemical studies because they are readily available and exhibit “well-behaved” electrochemistry. In aprotic solvents, quinones are reduced in two successive one-electron steps to form the radical anion ( $Q^-$ ) and hydroquinone dianion ( $Q^{2-}$ ).<sup>7</sup> Sweigart<sup>8</sup> and Amouri<sup>9</sup> have recently reported some  $\pi$ -bonded organometallic quinone complexes.

We have recently shown that mixed-metal disulfido compound  $CpMoMn(CO)_5(\mu-S_2)$ , **1** readily reacts with small unsaturated hydrocarbons in the presence of light by insertion into the S–S bond to yield complexes containing dithiolato ligands, eq 1.<sup>10</sup>



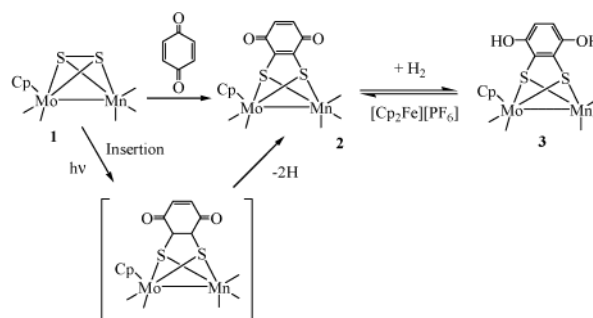
To investigate the potential of **1** to add to a wider range of unsaturated hydrocarbons, we have now investigated the reaction of **1** with 1,4-benzoquinone. The new compound  $CpMoMn(CO)_5(\mu-S_2C_6H_2O_2)$ , **2** was obtained in 67% yield by the reaction of **1** with 1,4-benzoquinone at 25 °C in the presence of visible light for 24 h.<sup>11</sup> The molecular structure of **2** was established by a single-crystal X-ray diffraction analysis, and an ORTEP diagram of its structure is shown in Figure 1.<sup>12</sup> The structure of **2** is similar to that of **1** except for the presence of a 1,4-quinone-2,3-dithiolato ligand that bridges the two metal atoms. The manganese and molybdenum atoms are joined by a metal–metal single bond. The Mn–Mo bond distance, 2.7050(6) Å, is slightly shorter than that found in **1**, 2.8421(10) Å.<sup>10</sup> The S(1)⋯S(2) distance, 3.042(3) Å, is nonbonding and is longer than the S(1)–S(2) distance, 2.959(4) Å, found in the related compound  $CpMoMn(CO)_5(\mu-SCH_2CH_2S)$ .<sup>10</sup> The C–O bond lengths in the quinone group are typical of C–O double bonds, 1.221(4) Å and 1.218(5) Å. Two of the C–C bonds in the six-membered ring, C(30)–C(31) = 1.338(5) Å and C(33)–C(34) = 1.316(6) Å, are short and double in character. These are not significantly different from those found in 1,4-benzoquinone, 1.334(3) Å.<sup>13</sup> The other C–C bonds are long and single: C(30)–C(35) = 1.474(4) Å, C(31)–C(32) = 1.474(5) Å, C(32)–C(33) = 1.474(5) Å, C(34)–C(35) = 1.476(5) Å.

The 1,4-quinonedithiolato ligand was obviously formed by the replacement of two of the hydrogen atoms on one of the C–C double bonds of the quinone with the two sulfur atoms of the



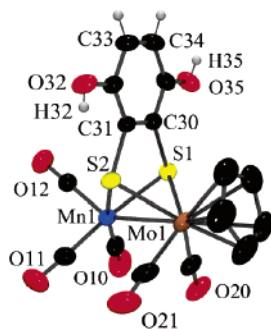
**Figure 1.** Povray diagram of the molecular structure of **2** showing 40% thermal ellipsoid probability. Selected interatomic distances (Å): Mo(1)–S(1) = 2.4931(9), Mo(1)–S(2) = 2.5096(9), Mo(1)–Mn(1) = 2.7050(6), Mn(1)–S(1) = 2.3557(9), Mn(1)–S(2) = 2.3582(11), S(1)–C(30) = 1.776(3), S(2)–C(31) = 1.781(3), O(32)–C(32) = 1.221(4), O(35)–C(35) = 1.218(5), C(30)–C(31) = 1.338(5), C(30)–C(35) = 1.474(4), C(31)–C(32) = 1.474(5), C(32)–C(33) = 1.474(5), C(33)–C(34) = 1.316(6), C(34)–C(35) = 1.476(5), S(1)⋯S(2) = 3.042(3).

### Scheme 1



disulfido ligand in **1**. In the process the S–S bond in **1** was cleaved. The mechanism for this process has not yet been established, but we believe that it probably proceeds first by an insertion of a C–C double bond of the quinone into the S–S bond, as previously observed for olefins,<sup>10</sup> and is then followed by elimination of the two hydrogen atoms from the two carbon atoms, see Scheme 1. The reaction does not proceed in the absence of light. This is consistent with the light-promoted concerted addition mechanism.<sup>14</sup> Hydroquinone is formed in this reaction and could account for the fate of the two hydrogen atoms lost in the formation of **2**. There was no evidence for hydrogen formation by <sup>1</sup>H NMR spectroscopy of reaction solutions. The  $S_2C_6H_2O_2$  ligand in **2** appears to be completely quinone-like in its structure. This is supported by reactivity studies.

Treatment of **2** with  $H_2$  at 25 °C yielded the new compound  $CpMoMn(CO)_5[\mu-S_2C_6H_2(OH)_2]$ , **3**, in 86% yield.<sup>15</sup> Compound **3** was characterized crystallographically, and an ORTEP diagram of its molecular structure is shown in Figure 2.<sup>16</sup> The structure of **3** is similar to that of **2** except that the quinone group has been reduced to a hydroquinone group. The Mn–Mo bond distance, 2.7418(3) Å, is longer than that in **2**, but still shorter than that in **1**. The sulfur



**Figure 2.** Povray diagram of the molecular structure of **3** showing 40% thermal ellipsoid probability. Selected interatomic distances (Å): Mo(1)–S(1) = 2.4824(5), Mo(1)–S(2) = 2.4851(5), Mo(1)–Mn(1) = 2.7418(3), Mn(1)–S(1) = 2.3236(5), Mn(1)–S(2) = 2.3341(5), S(1)–C(30) = 1.7866(17), S(2)–C(31) = 1.7826(17), O(32)–C(32) = 1.363(2), O(35)–C(35) = 1.366(2), C(30)–C(31) = 1.390(2), C(30)–C(35) = 1.375(2), C(31)–C(32) = 1.385(2), C(32)–C(33) = 1.393(3), C(33)–C(34) = 1.377(3), C(34)–C(35) = 1.396(3), S(1)⋯S(2) = 2.989(3).

atoms are not mutually bonded, S⋯S = 2.989(3) Å, in **3**. The C<sub>6</sub> ring appears to be fully delocalized. The C–C distances in the ring span the narrow range: 1.375(2)–1.396(3) Å. One hydrogen atom was observed on each of the oxygen atoms O(32) and O(35). These appear in the <sup>1</sup>H NMR spectrum at 4.82 ppm. The C–O bond distances, 1.363(2) and 1.366(2) Å, are typical C–O single bonds. In the solid state, the hydroxyl groups are hydrogen bonded to neighboring molecules and to the oxygen atoms of cocrystallized diethyl ether molecules to form zigzag chains that run parallel to the *c*-axis.

Compound **3** was reoxidized to **2** in 84% yield by treatment with ferrocenium hexafluorophosphate, see Scheme 1.<sup>17</sup> Cyclic voltammograms of basic solutions of **3** in acetonitrile show two quasi-reversible one-electron redox processes: one at  $E_{1/2} = -0.34$  V and a second at approximately  $E_{1/2} = -1.0$  V. Solutions of 1,4-quinone, **Q** exhibit redox processes at  $E_{1/2} = -0.56$  and  $-1.05$  V under these same conditions. The latter have been assigned to the reductions **Q** → **Q<sup>•-</sup>** and **Q<sup>•-</sup>** → **Q<sup>2-</sup>**, respectively.<sup>18</sup> Accordingly, we assign the process at  $E_{1/2} = -0.34$  V to **2** → **2<sup>•-</sup>**, and the one at  $-1.0$  V to **2<sup>•-</sup>** → **2<sup>2-</sup>**, respectively, which indicates that **2** is a slightly stronger oxidant than 1,4-quinone. Similar redox behavior was observed for some quinone-substituted metal complexes.<sup>19</sup>

The derivatization of quinones with organometallic moieties opens new directions for the chemistry of this important family of molecules. Their physical properties, redox chemistry, and applications to inorganic and bioinorganic chemistry will be of great interest. Further investigations involving the derivatization of other quinones and synthesis of other metal complexes of them are in progress.

**Acknowledgment.** This research was supported by a grant from the National Science Foundation, Grant No. CHE-9909017 and the USC NanoCenter. We express our appreciation to the reviewers for useful comments.

**Supporting Information Available:** Details of the synthesis and characterizations of the products, packing diagram of the structure of **3** and CIF files for the structural analyses. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## References

- (1) (a) Larsen, P. L.; Clarke, C. F. *Science* **2002**, *295*, 120–123. (b) Do, T. Q.; Hsu, A. Y.; Jonassen, T.; Lee, P. T.; Clarke, C. F. *J. Biol. Chem.* **2001**, *276*, 18161.
- (2) Steinberg-Yfrach, G.; Liddell, P. A.; Hung, S.-C.; Moore, A. L.; Gust, D.; Moore, T. A. *Nature* **1997**, *385*, 239.
- (3) Cross, J. V.; Deak, J. C.; Rich, E. A.; Qian, Y.; Lewis, M.; Parrott, L. A.; Mochida, K.; Gustafson, D.; Vande Pol, S.; Templeton, D. J. *J. Biol. Chem.* **1999**, *274*, 31150.
- (4) Voet, D.; Voet, J. B.; Pratt, C. W. *Fundamentals of Biochemistry*, Wiley: New York, 1999.
- (5) Fu, P. P.; Harvey, R. G. *Chem. Rev.* **1978**, *78*, 317.
- (6) Becker, H.-D.; Turner, A. B. In *The Chemistry of Quinonoid Compounds*; Patai, S.; Rappoport, Z., Eds.; Wiley: New York, 1988; Vol. 2, Chapter 23, pp 1351–1384.
- (7) Chambers, J. Q. In *The Chemistry of Quinonoid Compounds*; Patai, S.; Rappoport, Z., Eds.; Wiley: New York, 1988; Vol. 2, Chapter 12, pp 719–757.
- (8) Oh, M.; Carpenter, G. B.; Sweigart, D. A. *Organometallics* **2002**, *21*, 1290.
- (9) Le Bras, J.; Amouri, H.; Vaissermann, J. *Organometallics* **1998**, *17*, 1116.
- (10) (a) Adams, R. D.; Captain, B.; Kwon, O.; Miao, S. *Inorg. Chem.* **2003**, *42*, 3356. (b) Adams, R. D.; Kwon, O. *Inorg. Chem.* **2003**, *42*, 6175.
- (11) Compound **2** was obtained in 67% yield from the reaction of 1,4-benzoquinone with **1** in benzene under irradiation from a 150-W tungsten lamp for 24 h. For **2**: IR  $\nu_{\text{CO}}$  (cm<sup>-1</sup> in CH<sub>2</sub>Cl<sub>2</sub>) 2035 (vs), 1994 (m), 1959 (m), 1931 (m), 1651 (m). <sup>1</sup>H NMR ( $\delta$  in CDCl<sub>3</sub>) 6.62 (s, 2H), 5.98 (s, 5H). <sup>13</sup>C NMR ( $\delta$  in CD<sub>2</sub>Cl<sub>2</sub>) 235.22, 180.88, 169.06, 136.70, 96.27. MS (ES)  $m/z$  528 (M<sup>+</sup>).
- (12) For **2**: Space Group: *Pbca*,  $a = 13.1057(7)$  Å,  $b = 16.3648(8)$  Å,  $c = 16.8605(8)$  Å,  $V = 3616.1(3)$  Å<sup>3</sup>, formula: C<sub>16</sub>H<sub>7</sub>MnMoO<sub>7</sub>S<sub>2</sub>, for 3772 reflections ( $I > 2\sigma(I)$ ),  $R = 0.0394$ ;  $R_w = 0.1017$ .
- (13) Van Bolhuis, F.; Kiers, C. T. *Acta Crystallogr., Sect. B* **1978**, *34*, 1015.
- (14) Kramer, A.; Lorenz, I.-P. *J. Organomet. Chem.* **1990**, *388*, 187.
- (15) Hydrogen was purged through a solution of 15.0 mg **2** (0.0285 mmol) in CH<sub>2</sub>Cl<sub>2</sub> for 12 h; 13.0 mg (86% yield) of the product **3** was isolated by TLC. For **3**: IR  $\nu_{\text{CO}}$  (cm<sup>-1</sup> in CH<sub>2</sub>Cl<sub>2</sub>) 2030 (vs), 1989 (m), 1954 (m), 1923 (m). <sup>1</sup>H NMR ( $\delta$  in CDCl<sub>3</sub>) 6.22 (s, 2H), 5.68 (s, 5H), 4.82 (s, 2H). <sup>13</sup>C NMR ( $\delta$  in CD<sub>2</sub>Cl<sub>2</sub>) 235.02, 148.94, 133.85, 116.34, 95.82. MS (ES)  $m/z$  530 (M<sup>+</sup>).
- (16) For **3**: Space Group: *P2<sub>1</sub>/c*,  $a = 8.7934(4)$  Å,  $b = 21.9625(9)$  Å,  $c = 12.7233(6)$  Å,  $\beta = 97.497(1)^\circ$ ,  $V = 2436.18(19)$  Å<sup>3</sup>, formula: C<sub>16</sub>H<sub>6</sub>MnMoO<sub>7</sub>S<sub>2</sub>·1.0 O(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>, for 5353 reflections ( $I > 2\sigma(I)$ ),  $R = 0.0267$ ;  $R_w = 0.0637$ .
- (17) Ferrocenium hexafluorophosphate, [Cp<sub>2</sub>Fe][PF<sub>6</sub>], (47 mg, 0.142 mmol) was added to a solution of **3** (15.0 mg, 0.0284 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (30 mL) at 25 °C under nitrogen for 12 h. This yielded 12.5 mg of **2** (84% yield) after the usual workup.
- (18) (a) Eggins, B. R. *Chem. Commun.* **1969**, 1267. (b) Parker, V. D. *Chem. Commun.* **1969**, 716.
- (19) (a) Sembiring, S. B.; Colbran, S. B.; Craig, D. C. *J. Chem. Soc., Dalton Trans.* **1999**, 1543. (b) Storrier, G. D.; Colbran, S. B.; Craig, D. C. *J. Chem. Soc., Dalton Trans.* **1998**, 1351.

JA049170S