# Oxidation of Tricarbonylmolybdacarborane. 1. First Examples of Oxomolybda(VI)carboranes

**Jae-Hak Kim, Eunkee Hong, Jinkwon Kim,[†] and Youngkyu Do***

Department of Chemistry and Center for Molecular Science, Korea Advanced Institute of Science and Technology,
Taejon 305-701, Korea, and Department of Chemistry, Kongju National University, Kongju 314-701, Korea

*Received February 29, 1996*

The chemistry of transition metal oxo complexes has drawn considerable interest due to its relevance to metal-centered oxygen-transfer reactions in biological systems,[1] metal-catalyzed oxidation processes for industrial catalysts,[2] and the synthesis of high oxidation state organometallics.[3] Synthesis of oxometals has been achieved by various means,[4] including oxidative decarbonylation,[3d,5] and hydrolysis followed by air oxidation.[3b,3c,6] In particular, cyclopentadienyl ligands, among others, have been used very often as ancillary ligands because of their ability to stabilize both low and high formal oxidation states.[5a] On the other hand, the dicarbollide anion $[\mathit{nido}\text{-}7,8\text{-}C_2B_9H_{11}]^{2-}$, which is isolobal with the $\eta^5$-cyclopentadienyl ligands, has not been employed in synthesizing metal oxo complexes in spite of its known ability to stabilize higher formal oxidation states in metallacarborane complexes.[7] Consequently, a synthetic search for oxometallacarboranes was undertaken. The work reported herein includes stepwise oxidation of $[(\eta^5\text{-}C_2B_9H_{11})Mo(CO)_3]^{2-}$ **(1)**[8] to $[(\eta^1\text{-}C_2B_9H_{11})MoO_3]^{2-}$ **(3)** and $[(\eta^5\text{-}C_2B_9H_{11})O_2Mo(\mu\text{-}O)MoO_2(\eta^5\text{-}C_2B_9H_{11})]^{2-}$ **(4)** via $[(\eta^5\text{-}C_2B_9H_{11})Mo(CO)_2(SPh)_2]^{2-}$ **(2)** as well as the molecular structures of three oxidized products.

To a yellow solution of **1**$(NMe_4)_2$ (460 mg, 1.0 mmol) in $CH_3CN$ was added 1 equiv of solid phenyl disulfide, resulting in a prompt color change from yellow to dark red. The reaction mixture was stirred for 12 h and filtered. The filtrate was treated with an excess amount of THF, affording analytically pure dark red microcrystalline **2**$(NMe_4)_2$ in 48% yield.[9a] The molecular structure of the anion **2**,[10a] shown in Figure 1, reveals a “four-legged piano-stool” coordination geometry about the molybdenum atom with two thiolates and two carbonyl groups consisting of a cis square base. The symmetry of anion **2** approaches $C_s$ with a plane containing Mo3, B6, B8, and B10 atoms as well as bisecting the C1−C2 bond. While the Mo−S bond distances in **2** are similar to those found in the analogous cyclopentadienyl complex $[TlMo(SC_6F_5)_2(CO)_2(Cp)]$, the C−O distances (1.166(11), 1.235(10) Å) in **2** are slightly longer than those (1.116(21), 1.121(22) Å) of the latter.[11] This is in good agreement with the lower carbonyl stretching frequencies observed for **2** compared to the Cp analog. In contrast to the anion **1** with zero formal oxidation state, the oxidized species **2**, where Mo is in the formal oxidation state of +2, undergoes a well-behaved oxidative decarbonylation reaction.

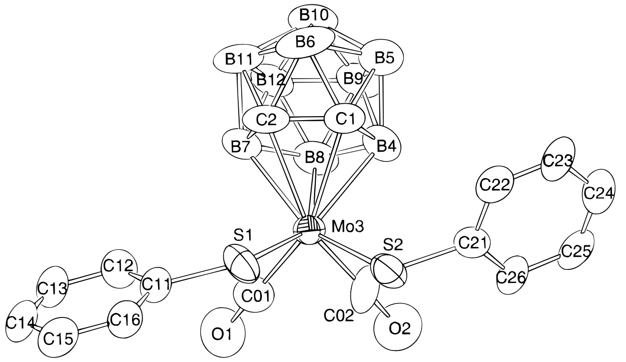

**Figure 1.** Molecular structure of $[(\eta^5\text{-}C_2B_9H_{11})Mo(CO)_2(SPh)_2]^{2-}$ **(2)** showing the atom-labeling scheme.

A dark red solution of **2**$(NMe_4)_2$ (650 mg, 1.0 mmol) in $CH_3CN$ was treated with a 4-fold molar amount of iodosylbenzene.

---

* To whom all correspondence should be addressed at the Korea Advanced Institute of Science and Technology.

[†] Kongju National University.

(1) (a) Enemark, J. H.; Young, C. G. *Adv. Inorg. Chem.* **1993**, *40*, 1. (b) Holm, R. H.; Berg, J. M. *Acc. Chem. Res.* **1986**, *19*, 363.

(2) (a) Holm, R. H. *Chem. Rev.* **1987**, *87*, 1401. (b) Basset, J.; Gates, B. C.; Candy, J.; Choplin, A.; Leconte, M.; Quignard, F.; Santin, C. *Surface Organometallic Chemistry: Molecular Approaches to Surface Catalysis*; Kluwer Academic Publishers: Dordrecht, The Netherlands, Boston, MA, and London, 1988.

(3) (a) Herrmann, W. A. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1297. (b) Rau, M. S.; Kretz, C. M.; Mercando, L. A.; Geoffroy, G. L. *J. Am. Chem. Soc.* **1991**, *113*, 7420. (c) Rau, M. S.; Kretz, C. M.; Geoffroy, G. L.; Rheingold, A. L. *Organometallics* **1993**, *12*, 3447. (d)Wolowiec, S.; Kochi, J. K. *Inorg. Chem.* **1991**, *30*, 1215.

(4) (a) Bottomley, F. *Polyhedron* **1992**, *11*, 1707. (b) Bottomley, F.; Sutin, L. *Adv. Organomet. Chem.* **1988**, *28*, 339.

(5) (a) Klahn-Oliva, A. H.; Sutton, D. *Organometallics* **1984**, *3*, 1313. (b) Herrmann, W. A.; Serrano, R.; Bock, H. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 383. (c) Wieghardt, K.; Pomp, C.; Nuber, B.; Weiss, J. *Inorg. Chem.* **1986**, *25*, 1659. (d) Faller, J. W.; Ma, Y. *J. Organomet. Chem.* **1988**, *340*, 59. (e) Leoni, P.; Pasquali, M.; Salsini, L.; di Bugno, C.; Braga, D.; Sabatino, P. *J. Chem. Soc. Dalton Trans.* **1989**, 155. (f) Harper, J. R.; Rheingold, L. *J. Am. Chem. Soc.* **1990**, *112*, 4037.

(6) Bottomley, F.; Boyle, P. D.; Karslioglu, S.; Thompson, R. C. *Organometallics* **1993**, *12*, 4090.

(7) (a) Wilson, R. J.; Warren, L. F., Jr.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1969**, *91*, 758. (b) Wing, R. M. *J. Am. Chem. Soc.* **1968**, *90*, 4828. (c) Clair, D. St.; Zalkin, A.; Templeton, D. H. *J. Am. Chem. Soc.* **1970**, *92*, 1173.

(8) (a) Hawthorne, M. F.; Young, D. C.; Andrews, T. D.; Howe, D. V.; Pilling, R. L.; Pitts, A. D.; Reintjes, M.; Warren, L. F., Jr.; Wegner, P. A. *J. Am. Chem. Soc.* **1968**, *90*, 879. (b) The structure of compound **1** was determined crystallographically in our group and will be reported in due course.

(9) (a) Data for **2**$(NMe_4)_2$: Anal. Calcd for $C_{24}H_{45}N_2B_9O_2S_2Mo$: C, 44.28; H, 6.97; N, 4.30. Found. C, 44.02; H, 7.32; N, 4.01. IR (KBr, $cm^{-1}$): $\nu_{BH} = 2582, 2542, 2523, 2489, 2447$; $\nu_{CO} = 1896, 1793$. $^1H$ NMR (ppm, $CD_3CN$): 3.10 (s, 24H, $NMe_4$), 3.18 (br, 2H, carbonyl CH), 7.4−6.7 (m, 10H, phenyl). $^{11}B\{^1H\}$ NMR (ppm, $CD_3CN$): 1.33, −5.96, −11.23, −13.52, −16.89, −19.92 (1:2:1:2:2:1). (b) Data for **3**$(NMe_4)_2$: Anal. Calcd for $C_{10}H_{35}N_2B_9O_3Mo$: C, 28.29; H, 8.31; N, 6.60. Found. C, 27.72; H, 8.26; N, 6.51. IR (KBr, $cm^{-1}$): $\nu_{BH} = 2570, 2536, 2516, 2497, 2472, 2460$; $\nu_{Mo=O} = 897, 855$. $^1H$ NMR (ppm, DMSO-$d_6$): 1.54 (br, 2H, carboranyl CH), 3.10 (s, 24H, $NMe_4$). $^{11}B\{^1H\}$ NMR (ppm, DMSO-$d_6$): −12.98, −17.66, −18.82, −20.46, −37.92 (2:3:1:2:1). (c) Data for **4**$(Ph_3P\text{-}p\text{-xylyl-}PPh_3)$: Anal. Calcd for $C_{48}H_{60}B_{18}O_5P_2Mo_2$: C, 49.47; H, 5.19. Found. C, 48.95; H, 5.03. IR (KBr, $cm^{-1}$): $\nu_{BH} = 2560, 2535, 2528, 2520$; $\nu_{Mo=O} = 927, 878$; $\nu_{Mo-O-Mo} = 776$. $^1H$ NMR (ppm, DMSO-$d_6$): 2.87 (br, 4H, carboranyl CH), 5.07 (d, 4H, $CH_2$), 6.75 (s, 4H, $C_6H_4$), 7.9−7.5 (m, 30H, phenyl). $^{11}B\{^1H\}$ NMR (ppm, DMSO-$d_6$): −2.22, −5.50, −9.91, −13.73, −20.89 (1:2:2:3:1).

(10) (a) Crystallographic data for **2**$(NMe_4)_2\cdot$THF: monoclinic, $P112_1/b$, $a = 10.307(1)$ Å, $b = 19.069(4)$ Å, $c = 19.608(2)$ Å, $\gamma = 95.67(1)°$, $V = 3835.0(10)$ Å$^3$, $Z = 4$, $R = 0.0714$. (b) Crystallographic data for **3**$(NMe_4)_2$: orthorhombic, $Pna2_1$, $a = 20.104(2)$ Å, $b = 7.0278(5)$ Å, $c = 30.648(3)$ Å, $V = 4330.1(7)$ Å$^3$, $Z = 4$, $R = 0.0881$. (c) Crystallographic data for **4**$\cdot(Ph_3P\text{-}p\text{-xylyl-}PPh_3)$: triclinic, $P\bar{1}$, $a = 10.059(2)$ Å, $b = 10.701(2)$ Å, $c = 13.3998(14)$ Å, $\alpha = 103.880(10)$, $\beta = 96.61(2)$, $\gamma = 100.84(2)°$, $V = 1355.8(3)$ Å$^3$, $Z = 1$, $R = 0.0285$.

(11) (a) Bakar, W. A. W. A.; Davidson, J. L.; Lindsell, W. E.; MaCullough, K. J.; Muir, K. W. *J. Organomet. Chem.* **1987**, *322*, C1. (b) Bakar, W. A. W. A.; Davidson, J. L.; Lindsell, W. E.; MaCullough, K. J.; Muir, K. W. *J. Chem. Soc., Dalton Trans.* **1989**, 991.

S0020-1669(96)00223-6 CCC: $12.00

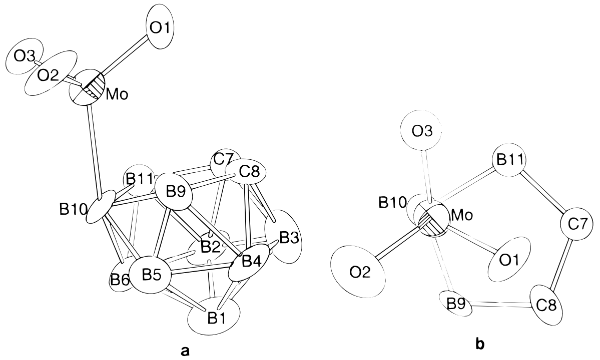

**Figure 2.** (a) Molecular structure of $[(\eta^1\text{-}C_2B_9H_{11})MoO_3]^{2-}$ **(3)** showing the atom-labeling scheme. (b) Projection of the $MoO_3$ fragment of **3** onto the open $C_2B_3$ pentagonal plane.

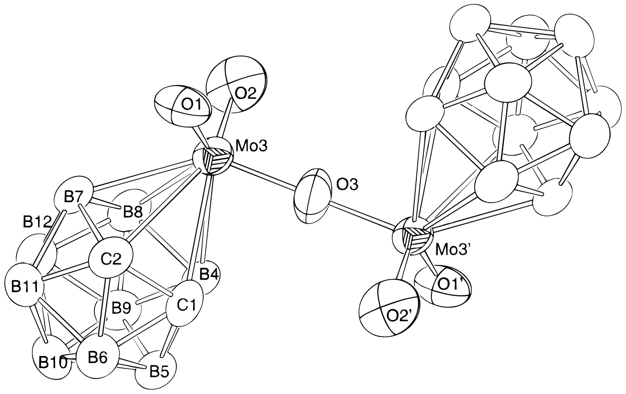

**Figure 3.** Molecular structure of $[(\eta^5\text{-}C_2B_9H_{11})O_2Mo(\mu\text{-}O)MoO_2(\eta^5\text{-}C_2B_9H_{11})]^{2-}$ **(4)** showing the atom-labeling scheme.

The reaction mixture was stirred for 12 h, causing gradual formation of a white precipitate, which was collected and washed with cold $CH_3CN$. The white solid was recrystallized from $DMF/CH_3NO_2/Et_2O$, giving colorless crystals of **3**$(NMe_4)_2$ in 45% yield.[9b] The use of the dicationic $Ph_3P-$*p*-xylyl$-PPh_3$ salt of **2** in the above reaction system gave a yellow solid which was collected and recrystallized from $DMF/CH_2Cl_2$, affording yellow crystals of **4**$(Ph_3P-$*p*-xylyl$-PPh_3)$ in 13% yield.[9c]

Shown in Figure 2a is the anionic molecular structure of one of the two independent **3**$(NMe_4)_2$ molecules in the asymmetric unit.[10b] In the anion **3**, an *endo*-$(MoO_3)$ moiety interacts with the unique boron atom of the *nido*-$C_2B_9$ cage vai a $\sigma$-Mo$-$B(10) bond, providing in **3** the first example of an oxometallacarborane as well as a $\sigma$-bonded dicarborane complex of the early transition metal series. Previous examples of $\sigma$-bonded heterocarboranes are limited to $C_2B_9H_{11}{}^{2-}$ complexes of Al(III),[12] M(IV) (M = Si,[13] Ge, and Sn[14]), and Ag(I).[15] The geometry about the molybdenum atom is slightly distorted tetrahedral with the large O1$-$Mo$-$B10 angle of 122.7(6)°. The distorted molybdenum center is slipped by an average 1.544 Å toward the unique boron atom B10 of the dicarbollide cage. One oxo group which forms a longer Mo$-$O bond (average 1.769 Å) compared with other two oxo groups (average 1.706 Å) in the $MoO_3$ moiety is situated on top of the $C_2B_3$ plane as shown in Figure 2b. The variance of Mo$=$O distances in **3** reflects different extent of $\pi$-donor ability of three oxo groups and two oxo groups associated with the shorter Mo$-$O bonds may act as formal $4e^-$ donors, leading to $\eta^1$ behavior of the dicarbollide anion.

In contrast to **3**, the structure[10c] of **4** reveals $\eta^5$ bonding of the dicarbollide anion as illustrated in Figure 3. The *closo*-$MoC_2B_9$ cages in the dinuclear anion **4** are related by a crystallographic inversion center lying at the bridging oxygen atom. The Mo$=$O and Mo$-\mu$-O bond distances are comparable with those in analogous complexes $[\{Cp^*Mo(O)_2\}_2(\mu\text{-}O)]$[5d,5e] and $[\{(Me_39N_3)Mo(O)_2\}_2(\mu\text{-}O)]^{2+}$ [16] where the multiple bond character in the interaction between molybdenum and oxygen atoms exists. The linear nature of oxo bridge in the anion **4** should provide efficient $d_\pi-p_\pi$ orbital overlap between the Mo atoms and the bridging oxygen.

The *in situ* $^{11}B$- and $^{13}C$-NMR experiments indicate simultaneous conversion of complex **2** to **3** and **4** with the formation of phenyl disulfide. While the role of **2** in the convenient stepwise oxidation of **1** to **3** and **4** remains as speculation, it is interesting to note that direct treatment of **1** with iodosylbenzene also provides **3** in low yield along with other new products. The nature of these and the reactivity studies of **3** and **4** are currently under investigation and will be the subject of future reports.

**Acknowledgment.** Support of this work by the Korea Science and Engineering Foundation (Y.D.) and the Nondirected Research Fund, Korea Research Foundation, 1994 (J.K.) is gratefully acknowledged.

**Supporting Information Available:** Tables giving details of the crystallographic data, positional and thermal parameters, and bond distances and angles for three reported compounds (24 pages). Ordering information is given on any current masthead page.

IC960223J

---

(12) Schubert, D. M.; Bandman, M. C.; Rees, W. S., Jr.; Knobler, C. B.; Lu, P.; Nam, W.; Hawthorne, M. F. *Organometallics* **1990**, *9*, 2046.
(13) Schubert, D. M.; Rees, W. S., Jr.; Knobler, C. B.; Hawthorne, M. F. *Organometallics* **1990**, *9*, 2938.
(14) Kim, J.; Kim, S.; Do, Y. *J. Chem. Soc., Chem. Commun.* **1992**, 938.
(15) Park, Y.-W.; Kim, J.; Do, Y. *Inorg. Chem.* **1994**, *33*, 1.
(16) Wieghardt, K.; Backes-Dahmann, G.; Herrmann, W. A.; Weiss, J. *Angew. Chem.* **1984**, *96*; 890; *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 899.