Oxidation of Tricarbonylmolybdacarborane. 3.[1] A New Entry to the First Examples of Sulfido-Bridged Dinuclear Molybda(V)carboranes[§]

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Received March 5, 2002

$[(C_2B_9H_{11})Mo(CO)_3]_2PPN_2$ (**2**·PPN_2), a new precursor for the oxidative decarbonylation reaction, was synthesized in high yield by the one-electron oxidation reaction of $[(C_2B_9H_{11})Mo(CO)_3]PPN_2$. **2**·$PPN_2$ was structurally characterized, showing a dimeric nature with long (3.321 Å) Mo-Mo bonding. Reaction of **2**·PPN_2 with sulfur gave the completely decarbonylated product $[(C_2B_9H_{11})Mo(\mu\text{-}S)(S)]_2PPN_2$ (**3**·PPN_2). The ligand substitution of the terminal sulfur ligands in **3**·PPN_2 to oxygen ligands was carried out with the use of PhIO to give $[(C_2B_9H_{11})Mo(\mu\text{-}S)(O)]_2PPN_2$ (**4**·PPN_2). The structures of **3**·PPN_2 and **4**·PPN_2 were also studied.

Key Words : Molybdenum, Sulfur, Carborane, Oxidative decarbonylation

Introduction

Metallacarborane chemistry has expanded in both scope and diversity and has provided a rich field of study and applications.[2] Recently, the use of carborane clusters has been directed toward broadening their applications in materials science such as, among others, molecular recognition systems,[3] display devices,[4] modular construction systems,[5] NLO materials,[6] special polymers,[7] olefin polymerization catalysts,[8] and luminescent functional materials.[9] In contrast to the application in materials chemistry, the use of carborane clusters in probing the chemistry of high oxidation state complexes, an important basic subject, has been recently documented: For example, the dicarbabollide anion [*nido*-7,8-$C_2B_9H_{11}$]$^{2-}$ has been successfully employed in developing the first novel examples of high oxidation state Group 6 metallacarboranes containing Group 16 donor ligands.[1,10] Oxo-[1] and tetrathiolate-bridged dinuclear[10] molybdacarboranes are the cases in point. The scarcity of such examples coupled with the richness of the chemistry of oxo- and sulfido-molybdenum complexes in their structures,[11] their relevance in biological systems,[12] and as catalysts in industries[13] spurred us to further the subject of high oxidation state Group 6 metallacarboranes.

In our recent papers, we have demonstrated that $[(C_2B_9H_{11})Mo(CO)_3]^{2-}$ (**1**) shows various oxidative decarbonylation activities with iodosyl benzyl or disulfides and thus acts as an excellent starting materials for the synthesis of molybdacarboranes with group 16 donor ligands.[1,10] However, the attempt to synthesize the completely decarbonylated sulfido-rich molybdacarborane was not successful since the reaction of **1** with elemental sulfur as an oxidant resulted in the formation of partially decarbonylated product [*closo*-3,3-$(CO)_2$-3-(η^2-S_2)-3,1,2-$Mo(C_2B_9H_{11})$]$^{2-}$.[14] In order to overcome this matter, we have exploited the synthesis and the reactivity of a new precursor $[(C_2B_9H_{11})Mo(CO)_3]_2(PPN)_2$ (**2**·PPN_2). Herein, we report the details of the synthesis and structures of the first molybdacarboranes containing the sulfido ligand $[(C_2B_9H_{11})Mo(\mu\text{-}S)(E)]_2PPN_2$ (E = S, **3**·PPN_2 and O, **4**·PPN_2) as well as their precursor **2**·PPN_2.

Experimental Section

General Procedures and Materials. All manipulations were carried out under dinitrogen atmosphere by using standard Schlenk techniques. Reagent grade solvents were distilled from the appropriate drying agents[15] and deuterated DMSO was dried from the activated molecular sieve 3A. The chemicals $Mo(CO)_6$, $(CH_3)_3NO\cdot 2H_2O$, bis(triphenylphosphoranylidene)ammonium chloride (PPNCl), and AgBr were purchased from Aldrich and used as received. Isodosyl benzene (PhIO)[16] and $[(C_2B_9H_{11})Mo(CO)_3]PPN_2$ (**1**·PPN_2)[1(a),17] were prepared according to the literature.

$[(C_2B_9H_{11})Mo(CO)_3]_2PPN_2$ (**2**·PPN_2). (a) 4.2 g of **1**·PPN_2 (3.0 mmol) in 50 mL CH_3CN was reacted with excess of AgBr (970 mg, 5.2 mmol) for 24 hrs. The reaction mixture was filtered, washed with 5 mL CH_3CN and with 10 mL CH_3OH twice. The residue was extracted with 50 mL CH_2Cl_2 and the extractant was treated with 100 mL CH_3OH. The resulting red crystalline precipitate was collected, washed with 10 mL CH_3OH (2 times) and with 10 mL Et_2O (3 times), and dried in vacuum. The analytically pure product was obtained in a yield of 80% (2.0 g, 1.2 mmol). Anal. Calcd for $[C_{41}H_{41}B_9NO_3P_2Mo]_2$: C, 57.87; H, 4.86; N, 1.65. Found: C, 57.78; H, 4.90; N, 1.42. IR (KBr, cm^{-1}): ν_{BH} = 2557, 2501, and 2467. ν_{CO} = 1985, 1926, 1886, and 1858. ^1H NMR (ppm, DMSO-d_6): 3.14 (4H, br, carboranyl CH)

[§] This paper is dedicated to Professor Sang Chul Shim with admiration and respect.

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and 7.70-7.52 (60H, m, phenyl). ^{11}B{^{1}H} NMR (ppm, CH$_2$Cl$_2$, *ext.* CDCl$_3$): -2.92, -8.66, -10.61, -14.63, and -20.15 (2:2:1:2:2).

(b) A methanol solution (30 mL) of excess amount of (CH$_3$)$_3$NO·2H$_2$O (1.5 g, 14 mmol) was added to an orange-yellow solution of 4.2 g (3.0 mmol) **1**·PPN$_2$ in 50 mL of CH$_3$CN. Slow formation of red crystalline precipitate was observed. The reaction mixture was stirred at room temperature for 12 hours. The red precipitate was collected, washed with 20 mL CH$_3$OH (3 times) and with 20 mL Et$_2$O (3 times). Recrystallization of this crude product from CH$_2$Cl$_2$/CH$_3$OH gave red crystals of **2**·PPN$_2$ in a yield of 26%. (0.67 g, 0.39 mmol). All spectroscopic data are the same as those from the reaction of **1**·PPN$_2$ with AgBr.

[(C$_2$B$_9$H$_{11}$)Mo(μ-S)(S)]$_2$PPN$_2$ (**3**·PPN$_2$). A solution of **2**·PPN$_2$ (310 mg, 0.18 mmol) in CH$_2$Cl$_2$ was treated with excess sulfur (60 mg, 1.9 mmol of S) and was stirred for 12 hours at ambient temperature. The resulting brown slurry was evaporated to dryness by vacuum, and washed with Et$_2$O. The crude brown solid was recrystallized from DMF/Et$_2$O, affording analytically pure brown crystals in a yield of 37% (110 mg, 0.066 mmol). Anal. Calcd for [C$_{38}$H$_{41}$NB$_9$P$_2$-S$_2$Mo]$_2$: C, 54.92; H, 4.97; N, 1.69. Found: C, 54.81; H, 4.95; N, 1.76. IR (KBr, cm^{-1}): ν_{BH} = 2581, 2568, 2545, 2534, 2524 (sh), and 2504. ^{1}H NMR (ppm, DMSO-*d*$_6$): 1.20 (4H, br, carboranyl CH) and 7.71-7.49 (60H, m, phenyl). ^{11}B{^{1}H} NMR (ppm, DMSO-*d*$_6$): 4.94, -7.90, -13.05, and -22.17 (1:2:5:1). Electronic spectrum (DMF): 483 (ε 4100, sh), 432 (ε 8800), 388 (ε 14000), 285 (ε 37000, sh), and 275 nm (ε 43000 M^{-1}cm^{-1}).

[(C$_2$B$_9$H$_{11}$)Mo(μ-S)(O)]$_2$PPN$_2$ (**4**·PPN$_2$). A solution of **3**·PPN$_2$ (330 mg, 0.20 mmol) in CH$_2$Cl$_2$ was treated with excess PhIO (450 mg, 2.0 mmol) and was stirred for overnight at ambient temperature. The resulting orange solution was concentrated to dryness by vacuum, and then washed with Et$_2$O. The crude orange solid was recrystallized from DMF/Et$_2$O, affording analytically pure reddish orange crystals in a yield of 70% (230 mg, 0.14 mmol). Anal. Calcd for [C$_{38}$H$_{41}$NB$_9$OP$_2$SMo]$_2$: C, 56.00; H, 5.07; N, 1.72. Found: C, 55.85; H, 5.12; N, 1.86. IR (KBr, cm^{-1}): ν_{BH} = 2585, 2561, 2530, and 2513. $\nu_{Mo=O}$ = 923 and 907. ^{1}H NMR (ppm, DMSO-*d*$_6$): 1.49 (4H, br, carboranyl CH) and 7.71-7.49 (60H, m, phenyl). ^{11}B{^{1}H} NMR (ppm, DMSO-*d*$_6$): 6.79, -7.90, -11.93, -15.95, and -21.39 (1:2:1:4:1). Electronic spectrum (DMF): 384 (ε 6700, sh), 342 (ε 23000), 294 (ε 38000), and 275 nm (ε 35000 M^{-1}cm^{-1}).

X-ray Structural Determination. Reflection data were collected on an Enraf-Nonius CAD4TSB diffractometer with graphite-monochromated MoKα radition (λ = 0.71073 Å) at 20 °C. The accurate cell parameters and the orientation matrices were determined from the least-square fit of 25 accurately centered reflections. Data were collected with the ω/θ scan mode for **2**·PPN$_2$ and $\omega/2\theta$ scan mode for **3**·PPN$_2$ and **4**·PPN$_2$. The data were corrected for *Lp* effects and ψ-scan absorption correction were applied. The structures of the compounds were solved by Patterson's heavy atom method (SHELXS-86).[18] Non-hydrogen atoms were refined by full-matrix least-square techniques (SHELXL-93)[19] with anisotropic displacement parameters. Phenyl hydrogens were placed at their geometrically calculated positions (d$_{CH}$ = 0.930 Å) and refined riding on the corresponding carbon atoms with isotropic thermal parameters (U = 1.2 U(C$_{phenyl}$)). Carboranyl hydrogens were refined isotropically for **2**·PPN$_2$ or placed at their geometrically calculated positions (d$_{C(or\ B)H}$ = 1.10 Å) and refined riding on the corresponding carbon atoms with isotropic thermal parameters (U = 1.2 U(C(or B)$_{carboranyl}$)) for the remaining compounds. Details of crystallographic data are given in Table 1. The crystallographic data for the structures reported here have been deposited with the Cambridge Crystallographic Data Centre (Deposition No. CCDC 183428, CCDC 183429, and CCDC 183430 for **2**·PPN$_2$, **3**·PPN$_2$, and **4**·PPN$_2$, respectively.). The data can be obtained free of charge via http://www.ccdc.cam.ac.uk/perl/catreq/catreq.cgi (or from CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; Fax +44 1223 336033; e-mail: deposit@

Table 1. Details of the Crystallographic Data for **2**·PPN$_2$, **3**·PPN$_2$ and **4**·PPN$_2$

	2·PPN$_2$	**3**·PPN$_2$	**4**·PPN$_2$
Formular	[C$_{41}$H$_{41}$B$_9$NO$_3$P$_2$Mo]$_2$	[C$_{38}$H$_{41}$NB$_9$P$_2$S$_2$Mo]$_2$	[C$_{38}$H$_{41}$NB$_9$OP$_2$SMo]$_2$
FW	1701.84	1662.02	1629.90
Temperature (K)	293(2)	293(2)	293(2)
Radiation source	MoKα	MoKα	MoKα
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	triclinic	triclinic	monoclinic
Space group	*P*-1 (No. 2)	*P*-1 (No. 2)	*P*112$_1$/*b* (No. 14)
a (Å)	11.301(2)	11.613(1)	10.090(1)
b (Å)	13.419(4)	12.026(1)	15.855(2)
c (Å)	15.542(3)	15.274(1)	25.404(4)
α (deg)	112.35(2)	79.04(1)	90
β (deg)	95.53(2)	74.46(1)	90
γ (deg)	99.66(2)	88.60(1)	91.37(1)
V (Å^3)	2115.7(9)	2016.9(3)	4062.9(7)
Z	1	1	2
d_{calc} (g/cm^3)	1.336	1.368	1.332
μ (mm^{-1})	0.425	0.538	0.485
F(000)	870	850	1668
2θ range (deg)	$4 \le 2\theta \le 50$	$4 \le 2\theta \le 50$	$4 \le 2\theta \le 50$
h	$0 \le h \le 13$	$0 \le h \le 13$	$0 \le h \le 11$
k	$-15 \le k \le 15$	$-14 \le k \le 14$	$-18 \le k \le 18$
l	$-18 \le l \le 18$	$-17 \le l \le 18$	$0 \le l \le 30$
No. of indep rflns	6718	5854	5971
No. of obsd rflns (|F_o| > 4σ(F_o))	5507	4388	4734
No. of params refined	486	407	406
R_1 (|F_o| > 4σ(F_o))	0.0522	0.0557	0.0414
wR_2 (|F_o| > 4σ(F_o))	0.1244	0.1060	0.0859
GOF (|F_o| > 4σ(F_o))	1.121	1.110	1.077
Max, Min peak (eÅ^3)	+0.740, -0.324	+0.469, -0.365	+0.334, -0.301
x	0.0719	0.0490	0.0360
y	0.6611	0.9793	3.3103

$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR_2 = [\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$, where $w = 1/[\sigma^2(F_o^2) + (xP)^2 + yP]$, $P = (F_o^2 + 2F_c^2)/3$.

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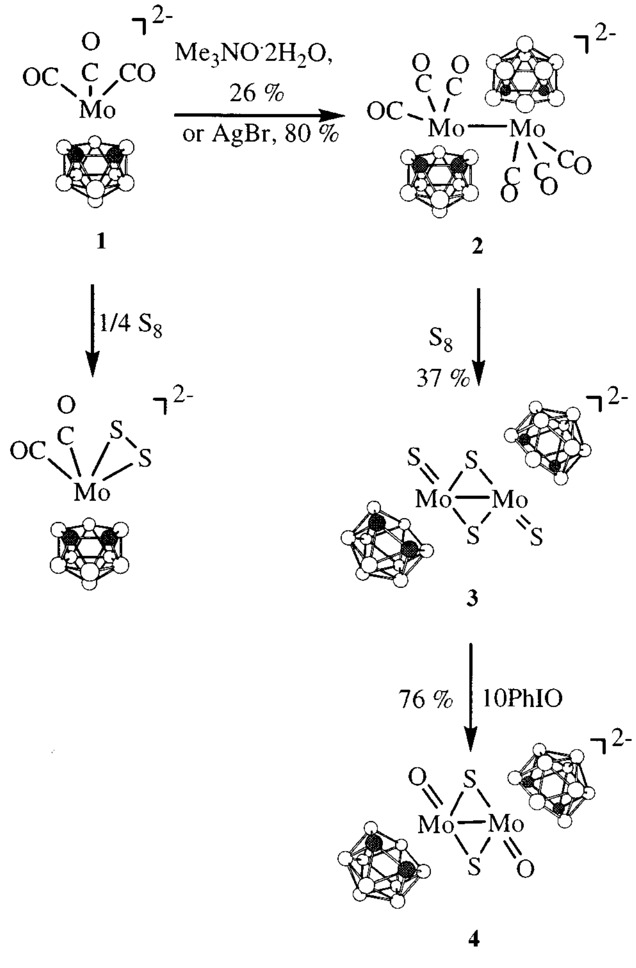
Physical Measurements. Infrared spectra were measured as KBr pellets on a Bomem MB-100 FTIR spectrometer. ^{1}H-NMR spectra were obtained at 300.13 MHz on a Bruker AM 300 spectrometer, and were referenced to internal solvent peaks. ^{11}B NMR spectra were recorded at 96.295 MHz on a Bruker AM 300 instrument and referenced to external $BF_3 \cdot OEt_2$. All chemical shifts downfield of the reference are designated as positive. The Korea Basic Science Institute, Seoul Branch, Korea, provided the elemental analyses for C, H and N. The electronic absorption spectra were recorded on a Shimadzu UV-3100S spectrophotometer.

Results and Discussion

Reactions. In a former study, we have found that the reaction of **1**·PPN$_2$ with elemental sulfur gave partially decarbonylated species [*closo*-3,3-$(CO)_2$-3-(η^2-S_2)-3,1,2-$Mo(C_2B_9H_{11})]^{2-}$, as outlined in Scheme 1, raising the necessity of a new starting material susceptible to the complete decarbonylation. This matter was tackled by pursuing the generation of oxidized but non-decarbonylated product of **1**·PPN$_2$. In fact, when **1**·PPN$_2$ was treated with oxidants AgBr or $(CH_3)_3NO \cdot 2H_2O$, a desirable new synthon was formed as shown in Scheme 1. The reaction with AgBr gave **2**·PPN$_2$ in high yield (80%) and the reaction with $(CH_3)_3NO \cdot 2H_2O$ led to the same product in lower yield (26 %). Since $(CH_3)_3NO \cdot 2H_2O$ is known as an oxo-transfer reagent[20] and decarbonylation reagent,[21] it is interesting that even in a coordinating solvent (CH_3CN), the reaction proceeds in an one-electron oxidation process with the carbonyl ligands left intact.



Scheme 1

The Scheme 1 also shows that the reaction of **2**·PPN$_2$ with sulfur led to the oxidation of Mo from +1 to +5 state with complete decarbonylation to give **3**·PPN$_2$ in 37% yield. It should be noted that the analogous reaction of $[CpMo(CO)_3]_2$ with sulfur led to a mixture of uncharacterizable species[22] and the reaction of $[Cp'Mo(CO)_3]_2$ ($Cp'=C_5H_4Me$) with sulfur gave $[Cp'MoS(m\text{-}S)]_2$ in only 2.1% yield.[23] The high yield synthesis of the cyclopentadienyl analogue ($[Cp^*MoS(m\text{-}S)]_2$) of **3**·PPN$_2$ was achieved by oxidative decarbonylation of $Cp^*Mo(CO)_3H$ with sulfur[23] (65%) or by substitution reaction of Cp^*MoCl_4 with Li_2S_2 (88%).[24]

The terminal sulfur ligands of **3**·PPN$_2$ was replaced by oxygen with the use of PhIO. The sulfido/oxo exchange reaction in these kinds of complexes has been reported: $[Cp^*MoS(\mu\text{-}S)]_2$ undergoes exchange reaction with air to give $[Cp^*MoO(\mu\text{-}S)]_2$ in 15-20% yield, with concomitant formation of isomers.[23] However, the reaction was monitored only by *in situ* NMR study and the products were not isolated. The high yield (70%) of the substitution reaction in

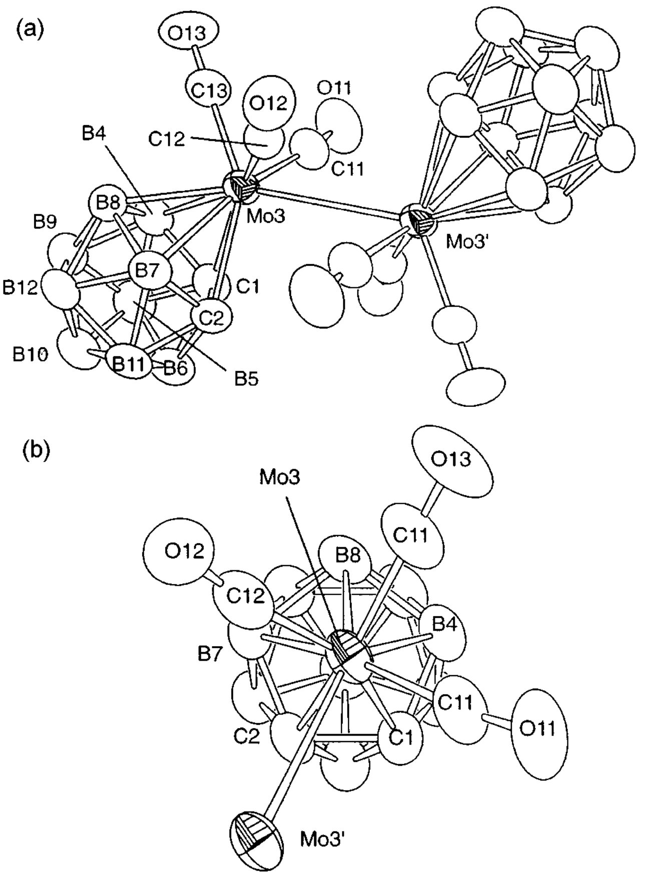


Figure 1. (a) ORTEP drawing of **2**. (b) Projection of the Mo atom in **2** onto the open C_2B_3 pentagonal plane. All hydrogen atoms have been omitted for clarity.

Table 2. Selected Bond Distances (Å) and Angles (deg) of **2**·PPN$_2$

Mo3 --- C13	1.945(5)	Mo3 --- C11	1.964(6)
Mo3 --- C12	1.970(5)	Mo3 --- C1	2.374(5)
Mo3 --- B4	2.389(5)	Mo3 --- C2	2.402(4)
Mo3 --- B8	2.413(5)	Mo3 --- B7	2.418(5)
Mo3 --- Mo3'	3.321	C11 --- O11	1.153(5)
C12 --- O12	1.162(6)	C13 --- O13	1.143(6)
C13 - Mo3 - C12	76.9(2)	C13 - Mo3 - C11	76.1(2)
C12 - Mo3 - C11	106.8(2)	O11 - C11 - Mo3	170.9(4)
O12 - C12 - Mo3	171.7(4)	O13 - C13 - Mo3	179.6(5)

our study suggests that PhIO, which was proven to be a useful reagent in the synthesis of oxo-complexes from carbonyl complexes,[1(b)] may also serve as a useful reagent in sulfido → oxo conversion reactions.

Structural Analysis. The molecular geometry of **2** (Figure 1, Table 2) can be best described as two four-legged piano stools sharing one leg, the center of the Mo3-Mo3' bond being the shared leg. The overall structure strongly resembles the cyclopentadienyl analogue [CpMo(CO)$_3$]$_2$.[25] The Mo3-Mo3' distance in **2** is 3.321 Å, which is slightly longer than the twice of the covalent radius of Mo (1.62 Å)[26] and Mo-Mo distance in the related complex [CpMo(CO)$_3$]$_2$ (3.235 Å).[25] This is presumably the consequence of the steric repulsion between the two half-fragments. The C11-C12' (or C12-C11') interatomic distance which can indicate the extent of steric crowding between the two half fragments is 2.672 Å in **2** which is considerably shorter than that found in [CpMo(CO)$_3$]$_2$ (2.810 Å) and even shorter than that found in [CpCr(CO)$_3$]$_2$ (2.720 Å), where elongation of the Cr-Cr distance via steric repulsion is suggested.[25] The angles of Mo3-C11-O11 (170.9°) and Mo3-C12-O12 (171.9°) show considerable nonlinearity whereas Mo3-C13-O13 (179.6°) shows almost perfect linearity. This bending of the carbonyl ligands, suggested as a consequence of steric repulsion, is a well-known feature in these kinds of complexes.[25]

The anion **2** has the center of symmetry but its projection view of the Mo atom onto the C$_2$B$_3$ pentagonal plane, illustrated in Figure 1(b), reveals that it lacks mirror plane in the solid state. On the other hand, the observations of five signals in the ^{11}B-NMR spectrum and one signal corresponding to the carboranyl portons in the ^{1}H-NMR spectrum are clear indication of C_s symmetry nature of the carborane cages presumably caused by the rotation of the cage in the solution state.

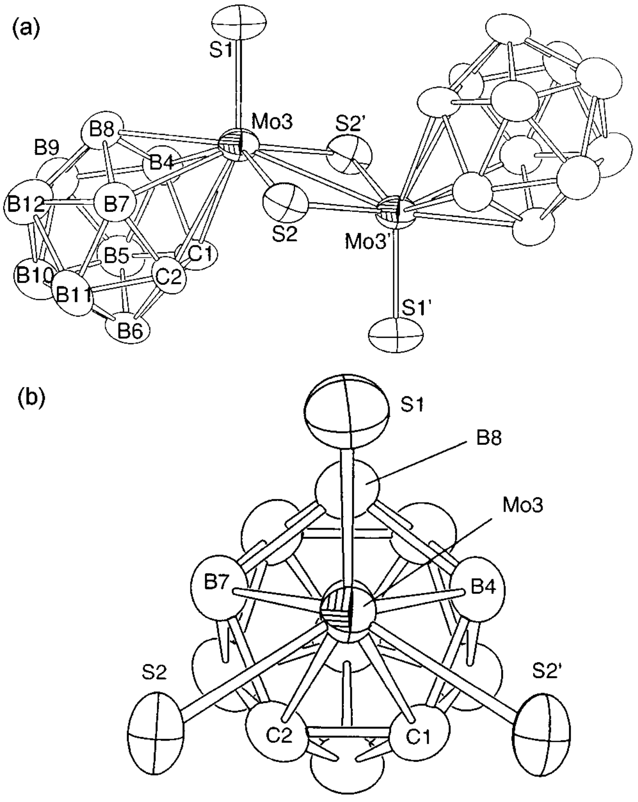


Figure 2. (a) ORTEP drawing of **3**. (b) Projection of the Mo atom in **3** onto the open C$_2$B$_3$ pentagonal plane. All hydrogen atoms have been omitted for clarity.

The overall structures of **3** and **4** can be best described as an edge-sharing bi-octahedral configuration with an *anti*-arrangement of the suldifo (or oxo) ligands with the common edge bisecting the direct Mo3-Mo3' bond. The structural features of **3** (Figure 2, Table 3) are similar to those found in [CpMoS(*μ*-S)]$_2$,[27] [Cp*MoS(*μ*-S)]$_2$,[23] and [Cp'MoS(*μ*-S)]$_2$ (Cp' = C$_5$H$_4$Me),[23] and the structural features of **4** (Figure 3, Table 4) are similar to those found in [CpMoO(*μ*-S)]$_2$,[28] [Cp'MoO(*m*-S)]$_2$ (Cp' = C$_5$H$_4$Me),[29] [Cp*MoO(*μ*-S)]$_2$,[23] and {[MoO([9]aneN$_3$)]$_2$(*μ*-S)$_2$}$^{2+}$ ([9]aneN$_3$ = 1, 4, 7-triazacyclononane).[30] However, the Mo3-Mo3' distances in **3** and **4** are shorter by ~0.05 Å than the values in the reported cases. As seen in Figures 2(b) and 3(b), the Mo3S1Mo3'S1' (or Mo3O1Mo3'O1') plane bisects the carborane cage as a mirror plane, which is in agreement of the NMR spectra: The ^{11}B-NMR spectra show 5 (in **3**) or 4 (in **4**) peaks and the ^{11}H-NMR spectra show only one peak corresponding to the carboranyl protons.

Conclusion

The synthesis and structural characterization of **2**·PPN$_2$ is reported in this paper. Reaction of **2**·PPN$_2$ with sulfur gave **3**·PPN$_2$, the first molybdacarborane with terminal and bridging sulfur ligands, proving that **2**·PPN$_2$ is a useful starting material for the preparation of sulfur-rich molybdacarborane. The conversion of the terminal sulfur to oxygen using PhIO

Table 3. Selected Bond Distances (Å) and Angles (deg) of 3·PPN$_2$

Mo3 --- S1	2.125(2)	Mo3 --- S2	2.307(2)
Mo3 --- S2'	2.3117(15)	Mo3 --- B4	2.412(7)
Mo3 --- B8	2.429(7)	Mo3 --- B7	2.398(7)
Mo3 --- C2	2.497(5)	Mo3 --- C1	2.500(5)
Mo3 --- Mo3'	2.9503(11)		
S1 - Mo3 - S2	101.78(6)	S1 - Mo3 - S2'	101.84(7)
S2 - Mo3 - S2'	100.60(5)	S2' - Mo3 - Mo3'	50.23(4)
S1 - Mo3 - Mo3'	108.69(6)	S2 - Mo3 - Mo3'	50.37(4)
Mo3 - S2 - Mo3'	79.40(5)		

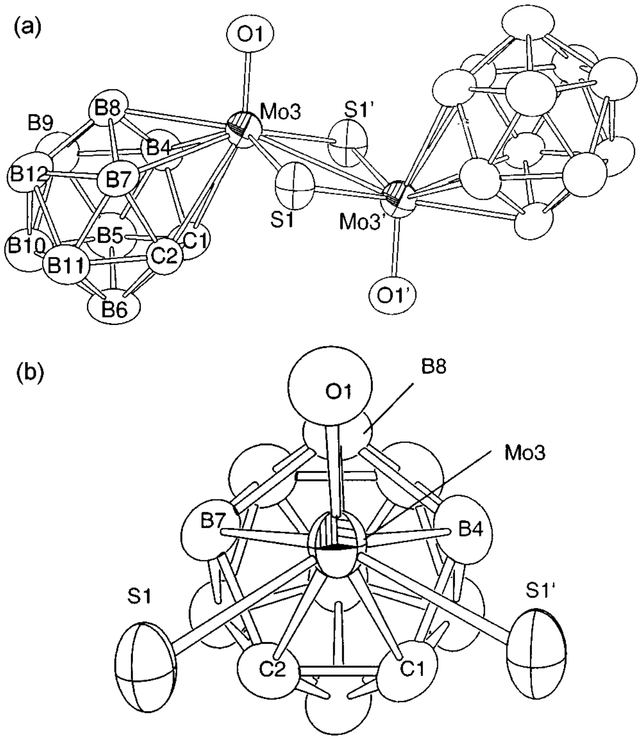


Figure 3. (a) ORTEP drawing of **4**. (b) Projection of the Mo atom in **4** onto the open C_2B_3 pentagonal plane. All hydrogen atoms have been omitted for clarity.

Table 4. Selected Bond Distances (Å) and Angles (deg) of **4**·PPN_2

Mo3 --- O1	1.684(3)	Mo3 --- S1	2.3243(11)
Mo3 --- S1'	2.3278(11)	Mo3 --- B4	2.419(5)
Mo3 --- B8	2.419(5)	Mo3 --- B7	2.420(5)
Mo3 --- C2	2.556(4)	Mo3 --- C1	2.559(4)
Mo3 --- Mo3'	2.9508(8)		
O1 - Mo3 - S1'	100.98(11)	O1 - Mo3 - S1	100.52(11)
S1' - Mo3 - S1	101.27(3)	S1 - Mo3 - Mo3'	50.69(3)
O1 - Mo3 - Mo3'	107.10(10)	S1' - Mo3 - Mo3'	50.58(3)
Mo3' - S1 - Mo3	78.73(3)		

gave the first oxo- and sulfido- containing molybdacarborane **4**·PPN_2.

Acknowledgment. This research was supported by grant R03-2001-00029 from the Korea Science and Engineering Foundation and the Brain Korea 21 Project. JK acknowledges the financial support from MOST (NRL).

Supporting Information Available: The listings of the experimental crystallographic data, the positional and equivalent isotropic thermal parameters, the anisotropic thermal parameters, the bond distances and angles are available from the corresponding author upon request.

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