First tetrathiolate-bridged dinuclear molybdacarbaboranes: scission and formation of the C–C cluster bond during oxidation processes

Jae-Hak Kim, Mouad Lamrani, Jeong-Wook Hwang and Youngkyu Do*

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

Unprecedented tetrathiolate-bridged dinuclear ionic molybdacarbaboranes $[(C_2B_9H_{11})Mo(SPh)_2]_2^{n-}$ (n = 2, 1) are prepared by successive oxidation of $[(C_2B_9H_{11})Mo^{II}(CO)_2(SPh)_2]^{2-}$ with diphenyl disulfide and iodosylbenzene: X-ray crystal structure determinations and NMR studies show unusual scission and reformation of the C–C carborane cage bond.

We have recently demonstrated that the dicarbabollide anion $[nido\text{-}7,8\text{-}C_2B_9H_{11}]^{2-}$ is useful in synthesizing high oxidation state molybdenum oxo complexes.[1] In particular, the mononuclear thiolatomolybdacarbaborane $[(C_2B_9H_{11})Mo(CO)_2(SPh)_2]^{2-}$ **1**[1] coupled with iodosylbenzene as an oxygen-transfer agent was proven a convenient system in deriving oxometals, raising a possibility of using anion **1** as a synthon in preparing high oxidation state molybdenum thiolate complexes. To pursue this matter, the versatile oxidation reactivity of the synthon **1** has been exploited, leading to the first observation of tetrathiolate-bridged dinuclear molybdacarbaboranes $[(C_2B_9H_{11})Mo(\mu\text{-}SPh)_2]_2^{n-}$ (n = 2 **2**, n = 1 **3**) involving unusual scission and formation of the C–C bond of the unsubstituted carborane cage during oxidation processes.

Oxidation of a red solution of 0.5 mmol $[N(PPh_3)_2]_2$ **1** in 30 ml of MeCN with excess diphenyl disulfide (0.7 mmol) under refluxing for 24 h causes gradual precipitation of yellow product $[N(PPh_3)_2]_2$ **2**† (Scheme 1, path i) in 41% yield upon recrystallization from dmf–Et₂O. The dianionic **2** can be further oxidized to mixed-valence monoanionic **3** using PhIO [Scheme 1, path ii]: treatment of a dmf solution (30 ml) of 0.1 mmol $[N(PPh_3)_2]_2$ **2** with six fold excess of PhIO at 100 °C for 24 h, filtration and addition of Et₂O to the concentrated filtrate gave rise to a black precipitate. Recrystallization from dmf–Et₂O yielded analytically† pure black crystalline $[N(PPh_3)_2]$ **3** in a yield of 74%. The use of Br_2 instead of PhIO also affords the monoanionic **3** in 66% yield.

The structures‡ of **2** (Fig. 1) and **3** (Fig. 2) are seen to be based on discrete dimers oriented about a crystallographic inversion center. In both compounds, four bridging thiolate groups are arranged such that two planar MoSMoS rhombi are perpendicular to each other, the MoS(1)Mo′S(1′) plane bisects the cage C···C vector and the overall symmetry lacks a mirror plane. The observation of two well resolved singlets at δ 3.63 and 3.92 for carbaboranyl protons in the ¹H NMR spectrum of diamagnetic **2** in $(CD_3)_2SO$ at 23 °C is consistent with the expected magnetic inequivalency of two carboranyl CH protons. For **3**, similar observation was hampered by its paramagnetism (μ = 1.70 μ_B). It is interesting to note that at elevated temperature **2** becomes fluxional and two carboranyl CH proton signals coalesce at 93 °C, suggesting that the free energy of activation associated with the fluxional motion of **2** is 74.2 kJ mol⁻¹ which is comparable to those of other thiolate bridged dimers $[Fe_2(CO)_6(\mu\text{-}SBu^t)_2]_2$[2] (77 kJ mol⁻¹) and $[W_2O_2Cl_4(\mu\text{-}Cl)(\mu\text{-}SBu^i)_2]^-$[3] (75 kJ mol⁻¹) where inversion[4] at the three-coordinate bridging sulfur atoms is operative.
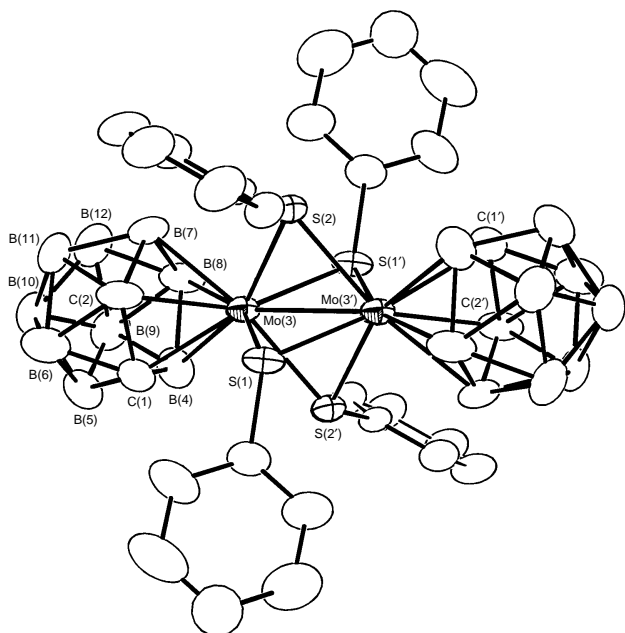
The C_2B_9Mo cage geometry in **2** is derived by the scission[5] of the C(1)–C(2) cage bond [C(1)···C(2), 2.55(6) Å] with concomitant movement of B(6) toward the molybdenum atom. The absence of the coupling peaks of carboranyl CH protons in the ¹H–¹H COSY NMR spectra of **2** is in good agreement with the X-ray structure. On the other hand, the C_2B_9Mo cage geometry in **3** is dictated by the formation of the C(1)–C(2) cage bond [1.65(2) Å]. The scission and the formation of the unsubstituted carborane C–C bond upon successive oxidation
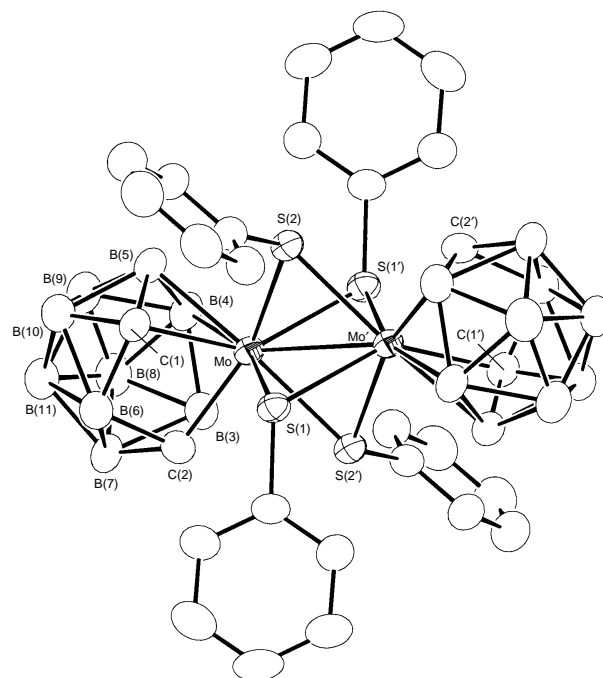
Fig. 1 ORTEP drawing of the $[(C_2B_9H_{11})Mo(SPh)_2]_2^{2-}$ dianion **2**. Selected bond distances (Å) and angles (°): Mo–Mo′ 2.8124(7), C(1)···C(2) 2.55(6), Mo–C(1) 2.174(4), Mo–C(2) 2.182(4), Mo–B(3) 2.377(5), Mo–B(4) 2.428(5), Mo–B(5) 2.371(5), Mo–B(6) 2.898, Mo–S(1) 2.5340(11), Mo–S(1′) 2.5098(11); C(1)–Mo-C(2) 72.8(2), S(1)–Mo–S(1′) 112.22(3), S(1)–Mo–Mo′ 55.70(3).
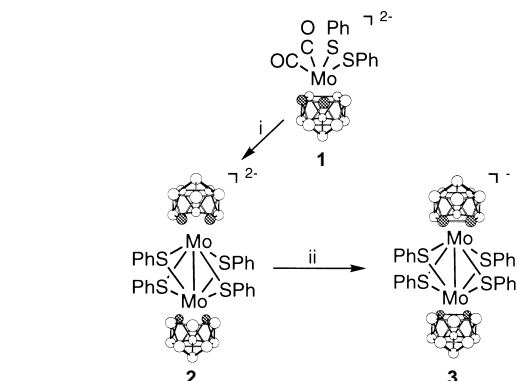
Scheme 1 Synthesis of $[N(PPh_3)_2]_2[(C_2B_9H_{11})Mo(SPh)_2]_2$ and $[N(PPh_3)_2][(C_2B_9H_{11})Mo(SPh)_2]_2$. *Reagents*: i, PhSSPh ; ii, 6PhIO.

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Fig. 2 ORTEP drawing of the [(C$_2$B$_9$H$_{11}$)Mo(SPh)$_2$]$_2^-$ monoanion. Selected bond distances (Å) and angles (°): Mo(3)–Mo(3′) 2.725(2), C(1)–C(2) 1.65(2), Mo(3)–C(1) 2.311(10), Mo(3)–C(2) 2.336(10), Mo(3)–B(4) 2.391(11), Mo(3)–B(6) 3.680, Mo(3)–B(7) 2.394(12), Mo(3)–B(8) 2.452(14), Mo(3)–S(1) 2.453(3), Mo(3)–S(1′) 2.485(3); C(1)–Mo(3)–C(2) 41.7(4), S(1)–Mo(3)–S(1′) 113.01(8), S(1)–Mo(3)–Mo(3′) 57.06(7).

processes, which constitutes the first example of its kind, are quite fascinating since it has often been surmised^5 that the presence of bulky and electron rich exo-cluster substituents at the cage carbon atoms induces the breaking of the C–C cage bond. It is interesting that the two-electron reduction of [PtW(CO)$_2$(PEt$_3$)$_2${η^6-C$_2$B$_9$H$_8$(CH$_2$C$_6$H$_4$Me-4)Me$_2$}],^{6} where the carbaborane C atoms are both substituted, causes the WC$_2$B$_9$ framework change from open to closed geometry with an exopolyhedral B(3)–Pt σ–bond formation ([PtW(μ-H){μ-σ,η^5-C$_2$B$_9$H$_7$(CH$_2$C$_6$H$_4$Me-4)Me$_2$}(CO)$_2$(PMe$_3$)(PEt$_3$)$_2$]). In our case, **2** was oxidized by a one-electron process and no rearrangement of the complex backbone has occurred. Additionally, the **2** and **3** are intriguing since no mixed metallacarbaboranes with bridged thiolate ligands have yet been reported in spite of the observation that the thiolate group bridging ligands have been previously shown to provide stable di- and poly-nuclear molybdenum compounds.$^{7–12}$

The *closo* MoC$_2$B$_9$ icosahedal framework in the oxidized derivative **3** suggests that the C$_2$B$_9$H$_{11}$ cages in **3** behave as *nido* dianionic ligands. Therefore, the observed paramagnetism is consistent with the expected mixed Mo^{III}Mo^{IV} valence for **3**. The closely interrelating features of the deltahedron nature^{13} of the MoC$_2$B$_9$ cages and the oxidation states of the metal centers in **2** remain to be clarified. The straightforward availability of these stable compounds from the dicarbabollide and thiolate ligands may make similar classes of compounds accessible for further investigations, such as connecting the two carbon cage atoms by various bridging aliphatic groups [-(CH$_2$)$_n$-; n = 3, 4] and in particular, tungsten homologue insertion reactions. We are currently investigating this possibility along with the XPS, electrochemical and electronic spectral studies on anions **2** and **3** to clarify the effects of electronic densities in these types of systems.