Unprecedented tetrathiolate-bridged dinuclear molybdacarbaboranes [(C_{2}B_{9}H_{11})Mo(SPh)_{2}]^{2−} (n = 2, n = 1) are prepared by successive oxidation of [(C_{2}B_{9}H_{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 carbaborane cage bond.

We have recently demonstrated that the dicarbabollide anion [nido-7,8-C_{2}B_{9}H_{11}]^{2−} is useful in synthesizing high oxidation state molybdenum oxo complexes. In particular, the mononuclear thiolatomolybdacarbaborane [(C_{2}B_{9}H_{11})Mo(CO)(SPh)_{2}]^{2−} 1 coupled with iodosylbenzene as an oxygen-transfer agent was proven a convenient system in deriving synthon preparing high oxidation state molybdenum thiolate complexes.

The structures of C_{2}B_{9}Mo cage geometry in 2 is derived by the scission 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 carbonyl 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_{2}B_{9}Mo 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 carbaborane C−C bond upon successive oxidation

Reagents: i, PhSSPh; ii, 6PhIO.

Scheme 1 Synthesis of [(C_{2}B_{9}H_{11})Mo(SPh)_{2}]^{2−} and [(C_{2}B_{9}H_{11})Mo(SPh)_{2}]: Reagents: i, PhSSPh; ii, 6PhIO.

Fig. 1 ORTEP drawing of the [(C_{2}B_{9}H_{11})Mo(SPh)_{2}]^{2−} dianion 2. Selected bond distances (Å) and angles (°): Mo−Mo′ 2.8124(7), C(1)−C(2) 2.55(6), Mo−C(12) 1.74(4), Mo−C(2) 1.82(4), Mo−B(3) 2.37(5), Mo−B(4) 2.42(5), Mo−B(5) 2.37(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).

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processes, which constitutes the first example of its kind, is quite fascinating since it has often been surmised that the presence of bulky and electron rich exo-cluster substituents at an exopolyhedral B(3)°MoC 2 B 9 cages and the oxidation states of the metal centers are currently investigating this possibility along with the XPS, electron chemical and electronic spectral studies on anions 2 and 3 to clarify the effects of electronic densities in these types of systems.

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Footnotes and References
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† Elemental analysis: for 2, C 54.95 H 9.53 N 1.93 P 2.55 S 2.05 Mo 14.95; C 60.54 H 2.19 N 1.71 P 2.45 S 2.40 Mo 14.53. Found: C 54.95 H 9.62 N 2.34 P 2.47 S 2.57 Mo 15.03. The following arguments are consistent with the expected mixed MoIII Mo IV valence for 3. The closely interrelating features of the deltahedron nature 13 of systems.

Fig. 2 ORTEP drawing of the [C 6 H 14 ] 2 Mo(SPh) 2 ] − monoaion. Selected bond distances (Å) and angles (°): Mo(3)–Mo(3) 3.275(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).

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