

Terminal Substitution and Cage Incorporation of an η -Cyclopentadienyl Ring into Borane Cage Structures; Crystal Structures of $[\text{Mo}(\eta\text{-C}_5\text{H}_5)(\eta^5 : \eta^1\text{-C}_5\text{H}_4)\text{B}_4\text{H}_7]$ and $[\text{Mo}(\eta\text{-C}_5\text{H}_5)(\eta^3 : \eta^2\text{-C}_3\text{H}_3)\text{C}_2\text{B}_9\text{H}_9]$

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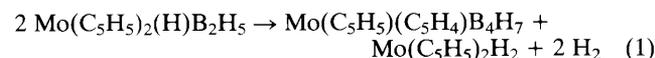
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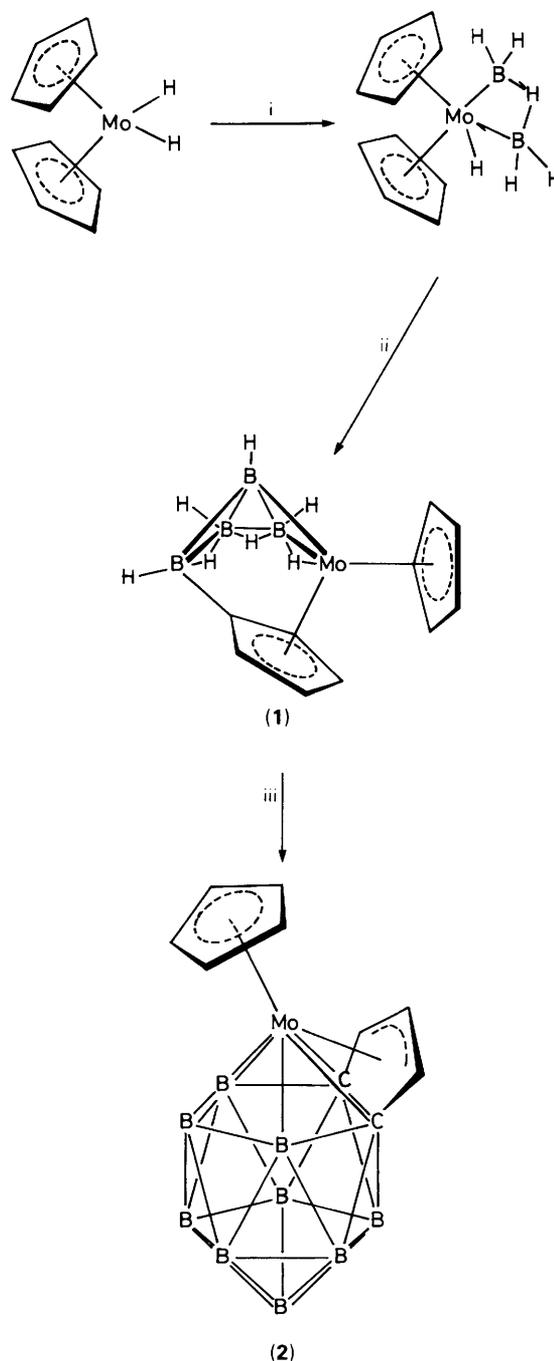
The synthesis and crystal structure of the molybdaborane $[\text{Mo}(\eta\text{-C}_5\text{H}_5)(\eta^5 : \eta^1\text{-C}_5\text{H}_4)\text{B}_4\text{H}_7]$ (**1**) and of the molybdacarbaborane $[\text{Mo}(\eta\text{-C}_5\text{H}_5)(\eta^3 : \eta^2\text{-C}_3\text{H}_3)\text{C}_2\text{B}_9\text{H}_9]$ (**2**) formed *via* cyclopentadienyl ring activation are reported.

We are exploring the metal-mediated oligomerisation of boranes.¹ Previously we have reported the synthesis of $[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2(\text{H})\text{B}_2\text{H}_5]$ by the photolysis of $[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2\text{H}_2]$ in the presence of $[\text{BH}_3 \cdot \text{THF}]$ (THF = tetrahydrofuran).² Here we report that prolonged photolysis and thermolysis of this reaction mixture gives a deep red solution from which the compounds $[\text{Mo}(\eta\text{-C}_5\text{H}_5)(\eta^5 : \eta^1\text{-C}_5\text{H}_4)\text{B}_4\text{H}_7]$ (**1**) and $[\text{Mo}(\eta\text{-C}_5\text{H}_5)(\eta^3 : \eta^2\text{-C}_3\text{H}_3)\text{C}_2\text{B}_9\text{H}_9]$ (**2**) can be isolated by column chromatography.[†] The reactions are shown in Scheme 1. Compounds (**1**) and (**2**) are mildly air-sensitive, solutions decomposing in air in a few hours; crystals of (**2**) appear to be air-stable.

Thermolysis of pure $[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2(\text{H})\text{B}_2\text{H}_5]$ also gives (**1**) together with $[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2\text{H}_2]$ in a 1 : 1 ratio, as determined from ¹H n.m.r. integration; the presumed reaction is given in equation (1).



Compound (**1**) has been characterised by single crystal X-ray crystallography.[‡] The molecular structure (Figure 1) may be viewed as an analogue of the neutral *arachno*-



[†] In a typical experiment, $[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2\text{H}_2]$ (10 g) dissolved in $[\text{BH}_3 \cdot \text{THF}]$ (220 cm³ of a 1 M solution) was irradiated (medium pressure Hg lamp) for 6 h, then heated to 70 °C for 12 h, and this cycle was repeated six times. Column chromatography, followed by crystallisation from toluene or diethyl ether, gave (**1**) (2.4 g, 20%) and (**2**) (70 mg, 0.5%).

[‡] Data were collected on an Enraf-Nonius CAD4 diffractometer ($3 < 2\theta < 50^\circ$). The structures were solved from Patterson and Fourier syntheses and refined by full matrix least squares procedures with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms bonded to carbon atoms were included in calculated positions and refined riding on their attached atom. Hydrogen atoms bonded to boron atoms were located from difference syntheses and their co-ordinates and isotropic thermal parameters refined. Crystallographic calculations were carried out using the Oxford 'CRYSTALS' package.⁷

Crystal data for (**1**): $\text{C}_{10}\text{H}_{16}\text{B}_4\text{Mo}$, $M = 275.4$, orthorhombic, space group $Pna2_1$, $a = 11.710(2)$, $b = 10.956(2)$, $c = 9.202(9)$ Å, $U = 1180.7$ Å³, $Z = 4$, $D_c = 1.55$ g cm⁻³, $\mu = 10.5$ cm⁻¹, $F(000) = 552$, $R = 0.023$ and $R_w = 0.026$ for 903 observed reflections $I > 3\sigma(I)$ and 165 refined least squares parameters, $\lambda(\text{Mo-K}\alpha) = 0.71069$ Å, crystal size ca. $0.25 \times 0.15 \times 0.20$ mm.

For (**2**): $\text{C}_{10}\text{H}_{17}\text{B}_9\text{Mo}$, $M = 330.5$, monoclinic, space group $P2_1/c$, $a = 7.012(3)$, $b = 15.029(8)$, $c = 13.460(5)$ Å, $\beta = 91.57(3)$, $U = 1417.9$ Å³, $Z = 4$, $D_c = 1.55$ g cm⁻³, $\mu = 8.8$ cm⁻¹, $F(000) = 656$, $R = 0.024$ and $R_w = 0.025$ for 2255 observed reflections $I > 3\sigma(I)$ and 219 refined least squares parameters, $\lambda(\text{Mo-K}\alpha) = 0.71069$ Å, crystal size ca. $0.40 \times 0.30 \times 0.45$ mm.

Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

Scheme 1. i, $\text{BH}_3 \cdot \text{THF}$ (1.0 M) $h\nu$ (medium pressure Hg) 8 h, 60% (ref. 2). ii, $\text{BH}_3 \cdot \text{THF}$, $h\nu$ for 4 h, heat 80 °C, 12 h, 12%. iii, $\text{BH}_3 \cdot \text{THF}$, as for ii, 0.5%.

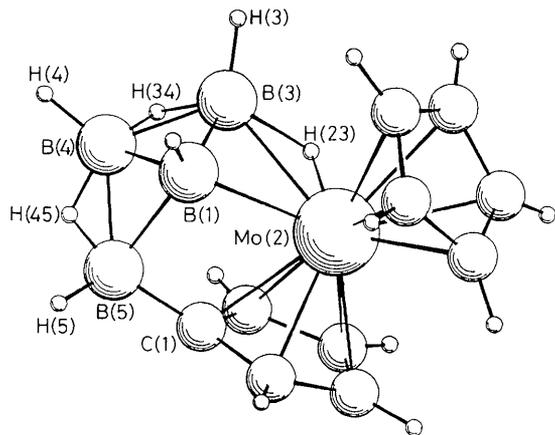


Figure 1. Crystal structure of compound (1). Selected bond distances (Å): Mo(2)–(C₅H₅ centroid) 1.927, Mo(2)–(C₅H₄ centroid) 1.964, Mo(2)–B(1) 2.374(9), Mo(2)–B(3) 2.399(10), Mo(2)–C(1) 2.294(7), C(1)–B(5) 1.556(11), B(1)–B(3) 1.688(14), B(1)–B(4) 1.683(12), B(1)–B(5) 1.800(14), B(3)–B(4) 1.772(13), B(4)–B(5) 1.794(13). Selected bond angles (°): (C₅H₅ centroid)–Mo(2)–(C₅H₄ centroid) 144.24, Mo(2)–C(1)–B(5) 107.0(5), Mo(2)–B(3)–B(4) 109.6(5), B(3)–B(4)–B(5) 106.2(6).

pentaborane(11) in which basal substitution of one of the {BH₂} groups by a {Mo(η-C₅H₅)(η⁵:η¹-C₅H₄)} fragment has occurred.³ One of the C₅-ring hydrogen atoms has been replaced giving a boron–carbon σ-bond with the carbon atom substituting for the *endo* terminal H on the B(5) of the parent B₅H₁₁. Thus, the {C₅H₄} fragment acts as an η⁵-ligand to Mo(2) and as an η¹-ligand to B(5). From an electron counting view, the {Mo(η-C₅H₅)(η⁵:η¹-C₅H₄)} fragment contributes three orbitals and a total of five electrons to the cage. The possibility of considering (1) as a *nido*-pentagonal pyramidal structure is excluded by the observation that C(1) lies *ca.* 0.7 Å below the Mo(2), B(3), B(4), B(5) best plane.

Compound (1) has been characterised in solution by ¹H, ¹¹B, and ¹³C n.m.r. spectroscopy. § The ¹¹B n.m.r. spectrum shows four inequivalent boron resonances which, unusually for an *arachno* structure, all occur as doublets due to terminal hydrogen couplings, and is consistent with the absence of a {BH₂} fragment which often helps to characterise an *arachno* structure. Consistent with the proposed structure the ¹H n.m.r. spectrum shows three different bridging hydrogens. Selective heteronuclear ¹¹B{¹H} decoupling experiments show that these occupy bridging positions between the basal atoms, Mo(2) and B(3), B(3) and B(4), and B(4) and B(5). An interesting feature is that spin–spin coupling is observed

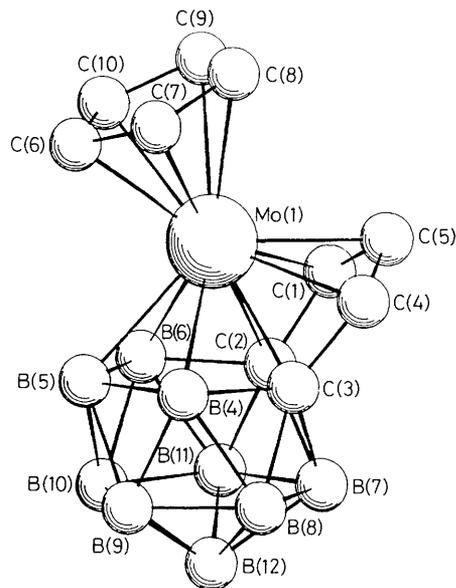


Figure 2. Crystal structure of compound (2). Selected bond distances (Å): Mo(1)–(C₅H₅ centroid) 1.985, Mo(1)–C(1) 2.225(2), Mo(1)–C(2) 2.155(2), Mo(1)–C(5) 2.310(2), Mo(1)–B(4) 2.344(2), Mo(1)–B(5) 2.428(2), C(1)–C(2) 1.450(3), C(1)–C(5) 1.413(3), C(2)–C(3) 1.682(2). Selected bond angle (°): (C₅H₅ centroid)–Mo(1)–(C₅H₃ centroid) 145.01. Average deviation from calculated best planes (Å): C(2)C(3)B(4)B(5)B(6) 0.016(8), B(7)B(8)B(9)B(10)B(11) 0.0012(8), Mo(1)B(6)B(11)B(7)C(3) 0.15(5), C(1)C(2)C(3)C(4)C(5) 0.02(1), C(6)C(7)C(8)C(9)C(10) 0.0006(5).

between basal bridging protons and the apex terminal proton in addition to the expected ²J couplings from adjacent terminal and bridging protons. In both the ¹H and ¹³C n.m.r. spectra, one resonance is observed for the η-C₅H₅ ligand, and four separate resonances are observed for the C₅H₄ ligand. The quaternary C(1) has not been located in the ¹³C n.m.r. spectrum.

Compound (2) has been characterised by single crystal X-ray crystallography. ‡ A striking feature of the molecular structure (Figure 2) is the presence of a MoC₂B₉ *closo*-icosahedral cage. This is the first example of the partial incorporation of a C₅ ring into a cage while retaining co-ordination to the metal atom. In a previous report of partial incorporation of a C₅ ring into a metallocarbaborane, in the compound [Co₂(η-C₅H₅)₂(μ-C₃H₄)C₂B₃H₅],⁴ the three *exo* carbons of the C₅ unit are not interacting with the metal atoms and form a {C₃H₄} fragment, compared with {C₃H₃} in compound (2). We note that boron–carbon bond formation *via ortho*-cycloboronation has been described in an iridaplatina–borane system.⁵ Of interest from the crystal structure of (2) is the C(2)–C(3) interatomic cage distance of 1.682(2) Å, which is consistent with that found in other equivalent MC₂B₉ cages⁶ and is considerably larger than normal bonded C–C distances. Compound (2) possesses a non-crystallographic plane of symmetry through atoms Mo(1), C(5), B(7), B(12), B(5), and C(6).

Compound (2) has also been characterised in solution by ¹H, ¹¹B, and ¹³C n.m.r. spectroscopy. § The ¹¹B n.m.r. spectrum shows six inequivalent boron resonances in intensity ratios 1:1:2:2:2:1 and the selective ¹H{¹¹B} n.m.r. spectrum shows six terminal B–H proton resonances in intensity ratios 1:2:2:1:2:1, in addition to a single resonance intensity 5 for the η-C₅H₅ ring and a doublet and triplet, intensities 2:1, resulting from the coupled *exo*-cage C₃H₃ group co-ordinated to the molybdenum and cage carbon

§ Selected spectroscopic data {solvent [2H₂] toluene for compound (1)}. ¹H n.m.r. at 200 MHz and ¹¹B n.m.r. at 64 MHz, chemical shifts (δ) in p.p.m. and coupling constants in Hz.

Compound (1): ¹H{¹¹B} n.m.r., 4.7 (t d, 1H, C₅H₄), 4.5 (sextet, 1H, C₅H₄), 4.3 [s, 1H(4)], 4.3 [s, 5H(Cp)], 3.6 [s, 1H(5)], 3.5 (quartet, 1H, C₅H₄), 3.1 [t, 1H(3)], 1.8 (quintet, 1H, C₅H₄), 0.2 [s, 1H(1)], –1.2 [quintet, 1H(u_{4,5})], –2.4 [sextet, 1H(u_{3,4})], –11.6 [triplet, 1H(u_{2,3})]; ¹¹B n.m.r. (*J* ¹¹B–¹H), 9.7 [d, 1B(4), (142)], –0.3 [d, 1B(3), (129)], –8.5 [d, 1B(5), (125)], –50.9 [d, 1B(1), (151)]. ¹³C{¹H} n.m.r., 74.96 (s, 1C), 79.21 (s, 1C), 82.58 (s, 1C), 86.16 [s, 5C(Cp)], 86.33 (s, 1C).

Compound (2): ¹H{¹¹B} n.m.r., 4.6 [s, 5H(Cp)], 4.3 [s, 1H(12)], 3.7 [d, 2H(21,24)], *J*_{H(21,24)–H(25)} 3.3 Hz], 3.2 [s, 2H(9,10)], 2.9 [t, 1H(25)], *J*_{H(21,24)–H(25)} 3.3 Hz], 2.63 [s, 2H(4,6)], 2.58 [s, 1H(5)], 2.57 [s, 2H(8,11)], 1.0 (s, 1H(7)); ¹¹B n.m.r., 6.0 [d, 1B(12)], 4.4 [d, 1B(5)], 5.1 [d, 2B(4,6)], –8.1 [d, 2B(9,10)], –21.0 [d, 2B(8,11)], –28.4 [d, 1B(7)]; ¹³C{¹H} n.m.r., 90.3 {5C(Cp), C(6)–C(10)}, 89.8 [1C(C5)], 61.8 [2C(C1, 4)].

atoms. The ^{13}C n.m.r. spectrum shows one resonance for the $\eta\text{-C}_5\text{H}_5$ ligand, and two separate resonances for the C(1,4) and C(5) of the C_5H_3 ligand. As in the case of compound (1), the quaternary C(1) and C(2) resonances have not been located.

In compound (2), the structure can be considered as a MoC_2B_9 icosahedron with the molybdenum(II) co-ordinated to an $\eta\text{-C}_5\text{H}_5$ ring and to an η^3 -allylic C_3H_3 unit. The allylic unit is also η^2 -co-ordinated to the icosahedral cage *via* the cage C atoms. The resulting cluster count of 26 electrons is consistent with that required for a *closo* icosahedron.

In conclusion, the compounds (1) and (2) contain surprising and unique C_5 -ring-borane ligands derived initially from $[\text{BH}_3\cdot\text{THF}]$ and presumably formed *via* metal-mediated processes.

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