

Formation of Three-vertex Metallaboranes from Monoborane Precursors: X-Ray Crystal Structures of the Molybdenum and Ruthenium Complexes $[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2\text{H}(\eta^2\text{-B}_2\text{H}_5)]$ and $[\text{Ru}(\eta\text{-C}_5\text{Me}_5)(\text{PMe}_3)(\eta^2\text{-B}_2\text{H}_7)]$

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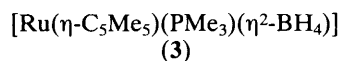
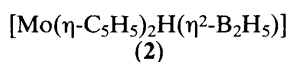
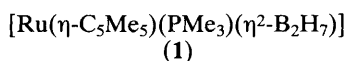
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The novel three-vertex metallaborane $[\text{Ru}(\eta\text{-C}_5\text{Me}_5)(\text{PMe}_3)(\eta^2\text{-B}_2\text{H}_7)]$ (**1**) has been synthesised by reaction of $[\text{Ru}(\eta\text{-C}_5\text{Me}_5)(\text{PMe}_3)\text{Cl}_2]$ with NaBH_4 ; homologation is also observed in the reaction of $[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2\text{H}_2]$ with $\text{BH}_3\cdot\text{THF}$, which forms $[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2\text{H}(\eta^2\text{-B}_2\text{H}_5)]$ (**2**); X-ray crystal structures of compounds (**1**) and (**2**) are reported.

The three-vertex metallaborane system $\{[\text{M}](\eta^2\text{-B}_2\text{H}_5)\}$ has been described:¹ e.g. $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})_2(\eta^2\text{-B}_2\text{H}_5)]^2$ and the anions $[\text{M}(\text{CO})_4(\eta^2\text{-B}_2\text{H}_5)]^-$ [$\text{M} = \text{Fe}$ (ref. 3), Ru (ref. 4), or Os (ref. 5)]. Here we report the synthesis and X-ray structure determination of $[\text{Ru}(\eta\text{-C}_5\text{Me}_5)(\text{PMe}_3)(\eta^2\text{-B}_2\text{H}_7)]$ (**1**), the first example of a three-vertex metallaborane of type $\{[\text{M}](\mu\text{-H})_2\text{B}_2\text{H}_5\}$, which may be regarded as a metalla derivative of the unknown parent neutral borane species $[\text{B}_3\text{H}_9]$.

Recently we have been studying metal-induced homologation reactions of monoborane species.⁶ We found that the prolonged reaction of $[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2\text{H}_2]$ with an excess of $\text{BH}_3\cdot\text{THF}$ ($\text{THF} = \text{tetrahydrofuran}$) in THF under photolytic conditions gave the yellow compound $[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2\text{H}(\eta^2\text{-B}_2\text{H}_5)]$ (**2**), which was isolated by column fractionation in ca. 20% yield. Interestingly, treatment of $[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2\text{Cl}_2]$ with $[\text{NaB}_3\text{H}_8]$ followed by column fractionation also gave (**2**), in



ca. 12% yield. The structure of (2), determined by single crystal X-ray diffractometry,[†] is shown in Figure 1, together with selected bond distances and angles. The structure consists of a {Mo}B₂ triangle with H(12) bridging the two BH₂ groups. The long B(1)–H(20) distance of 2.09 Å indicates that H(20) is not bridging to B(1). In the ¹H n.m.r. spectrum of (2), H(12) gives rise to a broad, unresolved resonance at δ –4.69, whereas the resonance at δ –6.65 assigned to H(20) is sharper and shows some quartet fine structure.

We noted striking similarities between the ¹H n.m.r. spectrum[‡] of (2) and that reported by Suzuki *et al.* for the ruthenium tetrahydroborate compound [Ru(η-C₅Me₅-

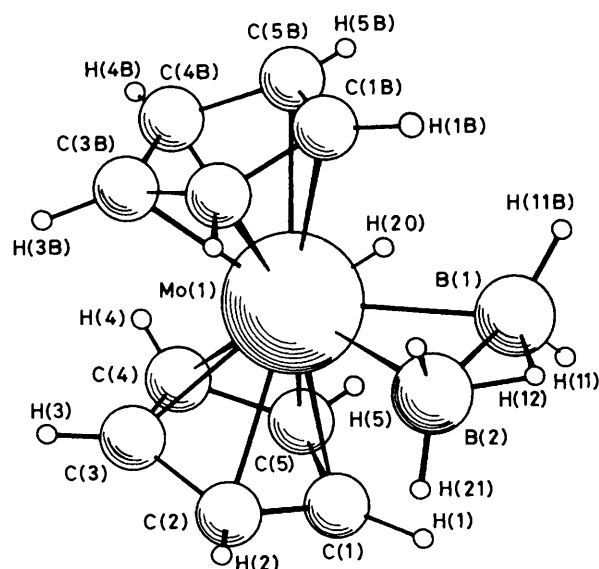


Figure 1. Crystal structure of the complex (2). The molecule lies across a crystallographic mirror plane. Atoms Mo(1), B(1), B(2), H(12), and H(20) lie on the mirror plane. Atoms with designation B are related to their counterparts by the symmetry operator $[x, y, 1/2 - z]$. Selected bond distances (Å) (Cp = η-C₅H₅): Mo(1)–Cp(centroid) 1.968, Mo(1)–B(1) 2.383(4), Mo(1)–B(2) 2.394(4), Mo(1)–H(20) 1.53(5), B(1)–B(2) 1.796(6), B(1)–H(11) 1.06(3), B(1)–H(12) 1.31(4), B(2)–H(21) 1.08(3), B(2)–H(12) 1.07(5), B(1)–H(20) 2.09(5). Selected bond angles (°): Cp(centroid)–Mo(1)–Cp(centroid) 139.8, B(1)–Mo(1)–B(2) 44.2(2), B(1)–H(12)–B(2) 97(3), Mo(1)–Mo(1)–H(20) 60(2), H(11)–B(1)–H(11B) 107(4), H(21)–B(2)–H(21B) 110(4), H(11)–B(1)–H(12) 107(2), H(21)–B(2)–H(12) 102(2).

[†] Crystal data for (2): C₁₀H₁₆MoB₂, *M* = 253.8, orthorhombic, space group *Pbnm* (non-standard setting of *Pnma*), *a* = 6.565(1), *b* = 12.199(4), *c* = 13.418(2) Å, *U* = 1074.5 Å³, *Z* = 4, *D_c* = 1.57 g cm⁻³, *F*(000) = 512, μ(Mo–K_α) = 11.4 cm⁻¹, crystal size ca. 1.0 × 0.9 × 1.0 mm. Data were collected (2θ_{max} = 84°) with an Enraf-Nonius CAD4 diffractometer using monochromated Mo–K_α radiation. An empirical absorption correction was applied and structure solution and refinement were carried out using 2831 observed reflections [*I* > 3σ(*I*)] from 3859 independent reflections measured. The structure was solved by Patterson and Fourier methods. All atoms were located and included in the refinement. Full-matrix least-squares refinement of 94 least-squares parameters has led to final agreement factors of *R* = 0.0417 and *R_w* = 0.0433.

[‡] Crystal data for (1): C₁₃H₃₁RuPB₂, *M* = 341.06, orthorhombic, space group *Pnma*, *a* = 16.589(5), *b* = 12.695(5), *c* = 8.234(1) Å, *U* = 1734 Å³, *Z* = 4, *D_c* = 1.31 g cm⁻³, *F*(000) = 712, μ(Mo–K_α) = 9.587 cm⁻¹, crystal size ca. 0.35 × 0.3 × 0.35 mm. Data were collected (2θ_{max} = 56°) with an Enraf-Nonius CAD4 diffractometer, using monochromated Mo–K_α radiation. Empirical absorption corrections were applied and structure solution and refinement were carried out using 1605 observed reflections [*I* > 3σ(*I*)] from 2741 independent reflections measured. The structure was solved by Patterson and Fourier methods. All non-hydrogen atoms were located and refined anisotropically. The methyl hydrogens were placed in calculated positions. The hydrogen atoms of the η²-B₂H₇ unit were located from the difference maps and their positional and isotropic thermal parameters were included in the refinement. Full-matrix least-squares refinement of 100 least-squares parameters has led to final agreement factors of *R* = 0.0277 and *R_w* = 0.0334.

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.

[†] *N.m.r. data* (solvent [²H₆]benzene unless otherwise stated): ¹H n.m.r. at 250 MHz and ¹¹B n.m.r. at 80.21 MHz; chemical shifts (δ) in p.p.m. and coupling constants in Hz; H_t and H_b refer to, respectively, terminal and bridging hydrogen attached to boron.

Compound (1): ¹H{¹¹B} n.m.r. 1.8 (m, 4H, 4BH_t), 1.7 (s, 15H, η-C₅Me₅), 0.85 [d, 9H, *J*(P–H) 10, PMe₃], –3.5 [br. s, 1H, H(43)], and –11.1 {2H, t, *J*[H(1)–P] = *J*[H(1)–BH_t]} 18, H(1) and H(1B)}; ¹¹B n.m.r. –21.4 [tt, *J*(B–H_t) 100, *J*(B–H_b–B) = *J*(B–H_b–Ru) 43, 2B].

Compound (2): ¹H{¹¹B} n.m.r. 4.22 (s, 10H, 2η-C₅H₅), 2.70 (br. s, 2H, 2BH_t), 2.41 (br. s, 2H, 2BH_b), –4.69 {sext, 1H, *J*[H(12)–BH_t] = *J*[H(12)–H(20)] 7.5, H(12)}, and –6.65 {q, 1H, *J*[H(20)–H(12)] = *J*[H(20)–BH_t] 7.5, H(20)}; ¹¹B n.m.r. –9.65 (t, 1B) and –11.12 (t, 1B).

Compound (3): ¹H{¹¹B} n.m.r. 6.58 [q, 1H, *J*(P–H) = *J*(H_t–H_b) 5, BH_t], 6.02 [q, 1H, *J*(P–H) = *J*(H_t–H_b) 9, BH_b], 1.68 [d, 15H, *J*(P–H) 1.4, η-C₅Me₅], 1.20 [d, 9H, *J*(P–H) 8.5, PMe₃], and –12.13 [ddd, 2H, *J*(P–H) 13, *J*(H_b–H_t) 9 and 5, 2Ru–H_b–B]; ¹¹B n.m.r. 34.8 [tt, *J*(B–H_t) 110, *J*(B–H_b) 61].

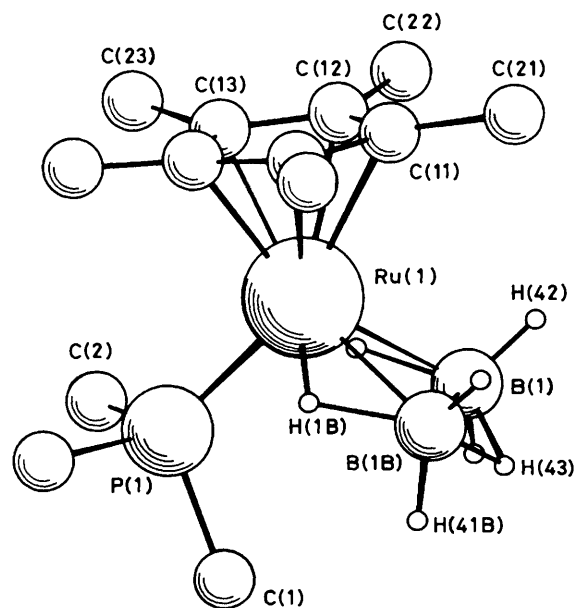


Figure 2. Crystal structure of the complex (1). The molecule lies across a crystallographic mirror plane. Atoms Ru(1), P(1), C(1), C(11), C(21), and H(43) lie on the mirror plane. Atoms with designation B are related to their counterparts by the symmetry operator $[x, 1/2 - y, z]$. Selected bond distances (Å) (Cp = η-C₅Me₅): Ru(1)–Cp(centroid) 1.88, Ru(1)–P(1) 2.2752(9), Ru(1)–B(1) 2.304(4), B(1)–B(1B) 1.93(1), Ru(1)–H(1B) 1.61(4), B(1B)–H(1B) 1.43(4), B(1B)–H(43) 1.363(4), B(1B)–H(41B) 1.13(3), B(1)–H(42) 1.08(3). Selected bond angles (°): Cp(centroid)–Ru(1)–P(1) 130.46, B(1)–H(43)–B(1B) 90.4(3), B(1)–Ru–B(1B) 49.6(3), Ru(1)–H(1B)–B(1B) 98.1(22), P(1)–Ru(1)–B(1B) 99.1(1), H(1B)–B(1B)–H(41B) 91.9(30), H(1)–B(1)–H(42) 112.9(30).

(PMe₃)(η²-BH₄)] (**3**).⁷ We reinvestigated the reported reaction of [Ru(η-C₅Me₅)(PMe₃)Cl₂] with an excess of NaBH₄ and found, as the minor product, the metallaborane complex [Ru(η-C₅Me₅)(PMe₃)(η²-B₂H₇)] (**1**) as well as (**3**). These compounds can be separated by fractional crystallisation.

The structure of (**1**) has been determined by single-crystal X-ray diffractometry† and is shown in Figure 2, together with selected bond distances and angles. The central unit consists of a {Ru}(μ-H)₂(B₂H₅) moiety, which is the first example of η²-B₂H₇ bonding geometry in three-vertex metallaborane species. The Ru–H(1) and B–H(1) distances of 1.61 and 1.43 Å, respectively, clearly indicate the presence of Ru–H–B bridges.

The ¹H n.m.r. spectrum of (**1**) is the same as that quoted by Suzuki *et al.* for compound (**3**). The ¹¹B n.m.r. spectrum‡ of (**1**) shows a complex symmetrical resonance at δ –21.4 approximating to a triplet of triplets, due to splitting of the BH₂ triplet (*J* 100 Hz) by two different adjacent bridging hydrogen atoms (*J ca.* 43 Hz). Heteronuclear decoupling of the resonance at δ –3.6 in the ¹H n.m.r. spectrum, assigned by Suzuki *et al.* to a terminal hydrogen attached to boron in (**3**), removed a small B–H_β coupling rather than a B–H_α coupling; this implies that this resonance is due to H(43). The ¹H n.m.r. spectrum of (**3**) showed a single broad resonance at δ –12.13 due to Ru–H–B, but no resonances in the region δ –3 to –5, which we consider may be characteristic of B–H–B bridges in these three-vertex metallaboranes. The terminal boron hydrogen atoms resonate at δ 6.02 and 6.58. We have determined the crystal structure of (**3**) and this will be

discussed in a subsequent publication. Comparison of the ¹H n.m.r. data of (**1**) and (**3**) with those reported by Suzuki *et al.* for the compounds [Ru(η-C₅Me₅)(PR₃)(η²-BH₄)] (PR₃ = PEt₃, Prⁱ₃, PCy₃, PPh₃, or PPh₂Me) suggests that the triethylphosphine compound is also a three-vertex metallaborane analogous to (**1**); the others have been correctly assigned tetrahydroborate structures.

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