

THE REACTION OF Cp^*ReH_6 , $\text{Cp}^* = \text{C}_5\text{Me}_5$, WITH MONOBORANE TO YIELD A NOVEL RHENABORANE. SYNTHESIS AND CHARACTERIZATION OF *arachno*- $\text{Cp}^*\text{ReH}_3\text{B}_3\text{H}_8$

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Dedicated to Professor Jaromír Plešek on the occasion of his 75th birthday. His imaginative synthetic chemistry has been an inspiration to all.

The rhenaborane $\text{Cp}^*\text{ReH}_3\text{B}_3\text{H}_8$, which is generated by the reaction of Cp^*ReH_6 with $\text{BH}_3\cdot\text{THF}$, has been characterized spectroscopically in solution and by a single-crystal X-ray diffraction study in the solid state as a hydrogen-rich *arachno*-metallatetraborane.

Keywords: Boranes; Metallaboranes; Metal complexes; Rhenium; Half-sandwich complexes.

The reaction of monocyclopentadienyl metal halides with monoboranes has been established as a useful route to metallaboranes containing transition metals of groups 4–9 (ref.¹). The method features build-up of the polyborane on a transition metal fragment. In the case of two metals of the ones thus far examined, the isolation of the first formed metallaborane is made more difficult by the concurrent formation of a mononuclear hydride. In the case of Ir (ref.²), this problem can be avoided by the utilization of $[\text{Cp}^*\text{IrHCl}]_2$, $\text{Cp}^* = \text{C}_5\text{Me}_5$, in place of $[\text{Cp}^*\text{IrCl}_2]_2$. No similar back door is available for Cp^*ReCl_4 and the coproduct Cp^*ReH_6 causes significant extra work as well as diverting about half the Re to an unwanted product³. There are a few instances in the literature where metal hydrides have been used as precursors to metallaboranes^{4–6}; however, none involve rhenium. Hence, we have investigated the reaction of Cp^*ReH_6 (ref.⁷) with $\text{BH}_3\cdot\text{THF}$ and show that it can be converted to a new *arachno*-rhenatetraborane that does not result from the reaction of Cp^*ReCl_4 with monoboranes.

Heating Cp^*ReH_6 with $\text{BH}_3\cdot\text{THF}$ leads to the formation of a single metallaborane product that was separated from residual hydride by sublimation. The mass spectrum suggested a minimal composition $\text{Cp}^*\text{ReB}_3\text{H}_7$;

however, the 1H , $^1H\{^{11}B \text{ selective}\}$, and variable temperature NMR data showed the actual composition to be $Cp^*ReB_3H_{11}$, a hydrogen-rich metallaborane. The chemical shifts and multiplicities of the two signals in the ^{11}B NMR are more characteristic of those observed for a metal- B_3H_8 complex rather than an isomeric "borallyl" complexes. As shown in Chart 1, both are formal metal derivatives of B_4H_{10} in which the former has the metal in a "wing-tip" position and the latter in a "hinge" position. The postulated framework structure was confirmed with a solid-state, single-crystal X-ray diffraction study (Fig. 1).

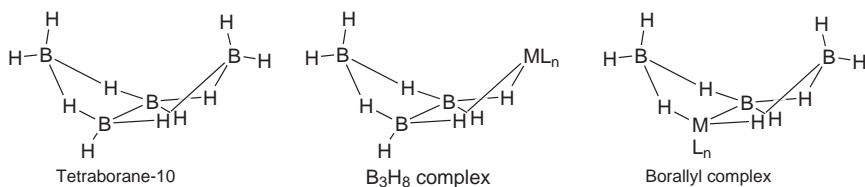


CHART 1

In the structure determination, only eight of the hydrogen positions could be located and the 1H NMR data was necessary to locate all eleven hydrogen atoms. Selective decoupling of boron allows the BH_{term} , BH_{bridge} hydrogens to be assigned and, by a process of elimination, the remaining two signals at $\delta -0.4$ (1 H) and -8.2 (2 H) are assigned to ReH_{term} hydrogens. The

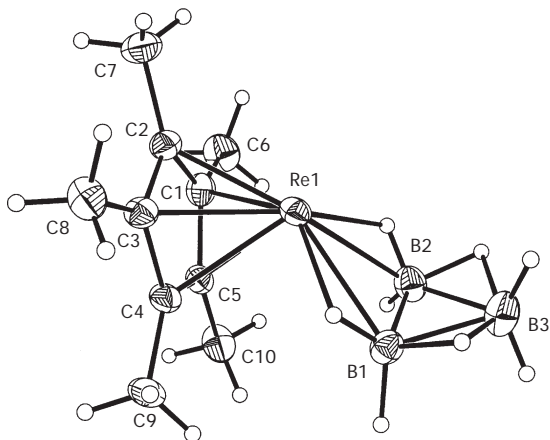


FIG. 1

Molecular structure of $Cp^*ReH_3B_3H_8$ (1), 30% probability ellipsoids. Selected bond lengths in Å: $Re(1)-B(1)$ 2.420(8), $Re(1)-B(2)$ 2.453(9), $B(1)-B(2)$ 1.707(10), $B(1)-B(3)$ 1.801(12), $B(2)-B(3)$ 1.772(12)

new compound is thus formulated as *arachno*-Cp*ReH₃B₃H₈ (**1**) and, considering that the structure of Cp*ReH₆ is described as a distorted pentagonal bipyramid⁸, we suggest an approximately octahedral environment for Re in Cp*Re(H₃)B₃H₈ with the unique lower-field ReH_{term} resonance trans to the Cp* ligand (Chart 2). The difference in chemical shifts of the two ReH_{term} resonances is notable as is the fact that the resonance for the two equivalent ReH_{term} shows 7 Hz geminal coupling (doublet at low temperature, 90% valley). However, the shoulders on the low-field resonance of the expected triplet were not resolved (the broad BHB resonance is only 0.5 ppm downfield of this hydride resonance).

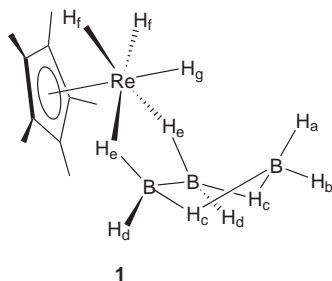


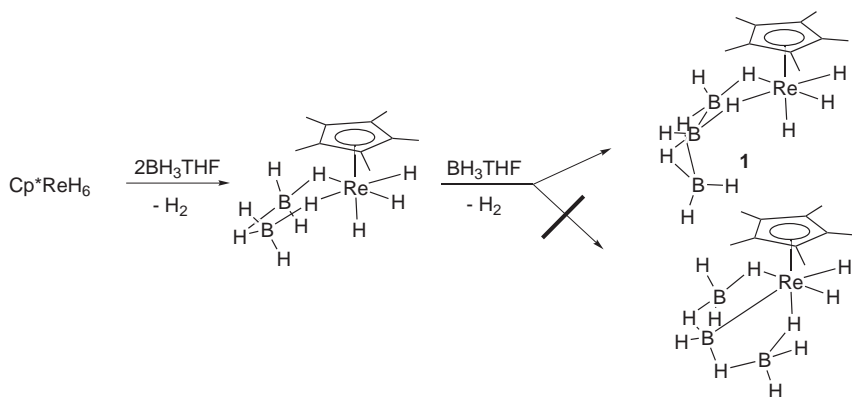
CHART 2

(PMe₃)₃WH₃B₃H₈, which is formed from the reaction of (PMe₃)₃WH₆ with BH₃·THF (ref.⁴), constitutes a precedent for **1** both in terms of structure and method of synthesis. In contrast to **1**, the three W-H_{term} protons of (PMe₃)₃WH₃B₃H₈ exhibit much more similar chemical shifts and are fluxional at room temperature. Otherwise the NMR spectroscopic properties of Cp*ReH₃B₃H₈ and (PMe₃)₃WH₃B₃H₈ are remarkably similar. Reemphasizing the comment of the earlier workers, direct generation of L_nMH₃B₃H₈ from L_nMH₆, L_nM = (PMe₃)₃W and Cp*Re, illustrates the fact that polyborane fragments can be built up on metal hydride frameworks thereby making metallaboranes more accessible.

Compound **1** is also isoelectronic with (PPh₃)₂IrH₂B₃H₈ with analogous structure⁹; however, the isoelectronic (CO)(PPh₃)₃IrHB₃H₇ (ref.¹⁰) and Cp*IrH₂B₃H₇ (ref.²) possess the borallyl structure (Chart 1). In the case of the last example, Cp*IrH₂B₃H₇ is generated from [Cp*IrCl₂]₂ with Cp*IrH₄ as a coproduct. Clearly this has mechanistic implications concerning the build-up of the B₃ fragment in the two cases. As shown in Scheme 1 for the rhenium hydride, addition of the first two boranes to ReH_{term} bonds may lead to Cp*ReH₃B₂H₇ (isoelectronic to known Cp*Ru(PMe₃)B₂H₇) (ref.⁵). The third borane adds preferentially to the boron fragment of the intermediate rather than to the other ReH_{term} sites. Compound **1** is unreactive towards

further borane addition whereas $Cp^*IrH_2B_3H_7$ readily adds borane to give the *arachno*-iridapentaborane $Cp^*IrB_4H_9$.

Rhenaboranes are unusual^{11–14} and it was only recently that the fascinating chemistry of dinuclear compounds could be accessed *via* $Cp^*_2Re_2B_4H_8$ (refs^{3,15–18}). In terms of structure **1** is analogous to $(CO)_4ReB_3H_8$ (ref.¹¹) and thus is a B_3H_8 derivative of a type that is well known for other metals¹⁹. Nearly all of these compounds are generated by a metathesis reaction of $[B_3H_8]^-$ salts with metal halides and the ancillary ligands on the metal rarely are hydrides. As we have shown that hydrogen-rich metallaboranes can be precursors to hypoelectronic clusters^{20,21}, synthetic access to $Cp^*ReH_3B_3H_8$ gains added significance.



SCHEME 1

In contrast to the established set of M–C bond-forming reactions of organometallic chemistry, there are few general routes to the synthesis of compounds containing direct M–B bonds. It is now clear that metal hydrides must be considered as potential metal precursors for metallaboranes. For Cp^*MX_n ($X = H, Cl$), n , as well as the nuclearity of the complex, depends on X and M . Hence, the metallaboranes generated by hydride *vs* halide may well differ as illustrated by the chemistry reported here. In the case of rhenium, it constitutes a method complementary to the halide route. The generality of the hydride route remains to be established.

EXPERIMENTAL

Synthesis of $Cp^*ReH_3B_3H_8$ (1). A 100 ml Schlenk flask containing 0.15 g (0.45 mmol) of Cp^*ReH_6 , obtained as a byproduct of the reaction of Cp^*ReCl_4 with borane³, in 10 ml toluene was prepared and a 5-fold excess of 1 M $BH_3 \cdot THF$ was added. The solution was heated at 75 °C for 15 h after which volatiles were removed. Extraction with hexane, filtration, and

sublimation of the residue yielded light yellow **1** (0.04 g, 28% based on Re). MS (EI): (P - 4)⁺ 360 (isotope distribution for ReB₃), calculated for ¹²C₁₀¹H₂₂¹¹B₃¹⁸⁷Re 360.1405; found 360.1415. ¹¹B NMR (C₆D₆, 96 MHz, 22 °C): 6.2 t, 1 B, *J*(BH) = 136; -39.9 d, 2 B, *J*(BH) = 138. ¹H NMR (C₆D₆, 400 MHz, 22 °C): 6.35 q, 1 H_{a/b}, *J*(BH) = 132; 3.45 q, 1 H_{b/a}, *J*(BH) = 132; 1.66 s, 15 H, Cp*; 0.65 q, 1 H_d, *J*(BH) = 131; 0.1 br s, 2 H_d; -0.36 s, 1 H_g; -8.17 s, 2 H_f; -10.3 partially collapsed quartet, 2 H_e.

X-Ray crystal structure of 1. Non-hydrogen atoms were found by successive full-matrix least-squares refinement on *F*² and refined with anisotropic thermal parameters. The Cp* methyl hydrogen atoms were placed at calculated positions, while B-H hydrogen atoms were located from difference Fourier maps. Re-H atoms were not located. Hydrogen atoms were refined using a riding model with fixed thermal parameters. CCDC 182201 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).

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