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Preliminary communication

Niobium metallaboranes: a novel metallaborane analogue of pentaborane(11) *

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Abstract

Treatment of $[\text{Nb}(\eta\text{-C}_5\text{H}_5)_2\text{H}_3]$ with pentaborane(9) gives the novel *arachno*-metallaboranes $[\text{Nb}(\eta\text{-C}_5\text{H}_5)_2\text{B}_4\text{H}_9]$ (**1**) and $[\text{Nb}(\eta\text{-C}_5\text{H}_5)_2\text{B}_3\text{H}_8]$ (**2**). Compound **1** is the first reported base subrogated analogue of the neutral *arachno*-pentaborane(11) and has an apex to niobium hydrogen bridge. Compound **2**, for which the X-ray crystal structure has been determined, is an analogue of the neutral *arachno*-tetra-borane(10).

Arachno-pentaborane(11) is exceptional among simple boranes in having a hydrogen atom bridging asymmetrically across the open B(1)B(2)B(5) apex-base face [1,2]. In the three reported metallaborane analogues of pentaborane(11), $[\text{Ir}(\text{CO})(\text{PR}_3)_2\text{B}_4\text{H}_9]$ ($\text{PR}_3 = \text{PMe}_3$ and PMe_2Ph) [3,4] and $[\text{RuH}(\text{C}_6\text{Me}_6)\text{B}_4\text{H}_9]$ [5], the metal atoms occupy apex positions. Here we report the first characterised example of a basal metal subrogated analogue of *arachno*-pentaborane(11). Interestingly, it contains an apex to basal niobium hydrogen bridge.

Treatment of $[\text{Nb}(\eta\text{-C}_5\text{H}_5)_2\text{H}_3]$ with pentaborane(9) at ca. 0 °C leads to the formation of $[\text{Nb}(\eta\text{-C}_5\text{H}_5)_2\text{B}_4\text{H}_9]$ (**1**) (Fig. 1), $[\text{Nb}(\eta\text{-C}_5\text{H}_5)_2\text{B}_3\text{H}_8]$ (**2**) (Fig. 2), and the previously known $[\text{Nb}(\eta\text{-C}_5\text{H}_5)_2\text{BH}_4]$ (**3**) which were separated by fractional crystallisation **. In solution, at ca. 50 °C **1** decomposes to form **2**; at room temperature **1** reacts slowly with $[\text{Nb}(\eta\text{-C}_5\text{H}_5)_2\text{H}_3]$ to form **2** and **3**, and with **3** to form **2** along with further unidentified products.

* Dedicated to Prof. G. Wilke on the occasion of his 65th birthday.

** In a typical experiment 2.2 mmol $[\text{Nb}(\eta\text{-C}_5\text{H}_5)_2\text{H}_3]$ was treated with 20 cm³ B₅H₉/toluene solution (5 mmol). Crystallisation from 40/60 petroleum ether and toluene gave the following solids: $[\text{Nb}(\eta\text{-C}_5\text{H}_5)_2\text{B}_4\text{H}_9]$ (**1**) (0.49 mmol), $[\text{Nb}(\eta\text{-C}_5\text{H}_5)_2\text{B}_3\text{H}_8]$ (**2**) (0.66 mmol), $[\text{Nb}(\eta\text{-C}_5\text{H}_5)_2\text{BH}_4]$ (**3**) (0.35 mmol).

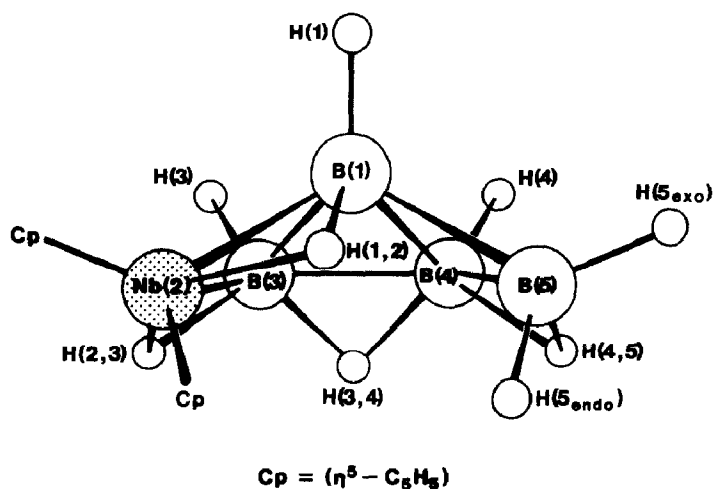


Fig. 1. Proposed structure of $[\text{Nb}(\eta^5\text{-C}_5\text{H}_5)_2\text{B}_4\text{H}_9]$ (1).

Compound **1** has been characterised by elemental analysis and ^1H , ^{11}B , and ^{13}C NMR spectroscopy*. The ^{11}B NMR shows the presence of four inequivalent boron positions (Fig. 3). Three of these resonances occur as doublets due to terminal hydrogen couplings. The low frequency of the doublet at $\delta -55.7$ is characteristic of the apex position in a pentaborane(11) species. The remaining resonance occurs as a triplet $\delta -1.4$ and is characteristic of the basal BH_2 unit in this structure. The ^1H NMR shows four different bridging hydrogen atoms. Selective heteronuclear $^{11}\text{B}\{^1\text{H}\}$ decoupling experiments show three of these to occupy bridging positions between the basal niobium (2) and boron atom (3) and between the basal boron atoms (3&4) and (4&5) respectively. The chemical shift of the remaining bridge at $\delta -8.5$ shows that it is bonded to Nb while selective heteronuclear $^{11}\text{B}\{^1\text{H}\}$ and $^1\text{H}\{^{11}\text{B}\}$ decoupling experiments establish coupling to the apex boron atom (1). We have found no evidence of coupling between this Nb(2)–H(1,2)–B(1) proton and the basal boron B(5). The exact location of this apex to base bridging hydrogen remains to be determined. Two cyclopentadienyl resonances are evident in both the ^1H and ^{13}C NMR spectra corresponding to *exo*- and *endo*-dispositions for these rings.

Compound **2** has been characterised by single crystal X-ray crystallography. The

* Analytical data for compound **1**: Found: C, 43.69; H, 7.01. $\text{C}_{10}\text{H}_{19}\text{B}_4\text{Nb}$ calcd.: C, 43.61; H, 6.95%.

Selected NMR data (solvent benzene- d_6 for compound **1** and toluene- d_8 for compound **2**): ^1H NMR at 200 MHz and ^{11}B NMR at 64.2 MHz; chemical shifts δ in ppm and coupling constants in (Hz).

Compound **1**: $^1\text{H}\{^{11}\text{B}\}$ NMR, δ 5.6 (s, 1H(4)), 4.3 (s, 5H(Cp^a)), 4.1 (s, 5H(Cp^b)), 3.7 (s, 1H(3)), 3.4 (s, 1H(5_{exo/endo})), 2.6 (s, 1H(5_{exo/endo})), -1.1 (s, 1H(1)), -1.4 (s, 1H($\mu_{4,5}$)), -2.5 (s, 1H($\mu_{3,4}$)), -8.5 (s, 1H($\mu_{1,2}$)), -10.2 (s, 1H($\mu_{2,3}$)); ^{11}B NMR ($J(^{11}\text{B}-^1\text{H})$), δ 21.4 (d, 1B(4), (154)), 6.9 (d, 1B(3), (127)), -1.4 (t, 1B(5), (119)), -55.7 (d, 1B(1), (178)); $^{13}\text{C}\{^1\text{H}\}$ NMR δ 93.5 (s, 5C(Cp^a)), 92.4 (s, 5C(Cp^b)).

Compound **2**: $^1\text{H}\{^{11}\text{B}\}$ NMR δ 4.5 (s, 5H(p^a)), 4.29 (s, 5H(Cp^b)), 4.26 (s, 1H_{exo/endo}(4/5)), 2.7 (s, H_{exo/endo}(4/5)), 0.3 (s, 2H(1,3)), -1.1 (s, 2H($\mu_{3,4}$; $\mu_{1,4}$)), -12.7 (s, 2H($\mu_{1,2}$; $\mu_{2,3}$)). ^{11}B NMR ($J(^{11}\text{B}-^1\text{H})$) δ 6.0 (t, 1B(4), (105)), -42.5 (d, 2B(1,3), (111)); $^{13}\text{C}\{^1\text{H}\}$ NMR δ 92.7 (s, 5C(Cp^a)), 91.3 (s, 5C(Cp^b)).

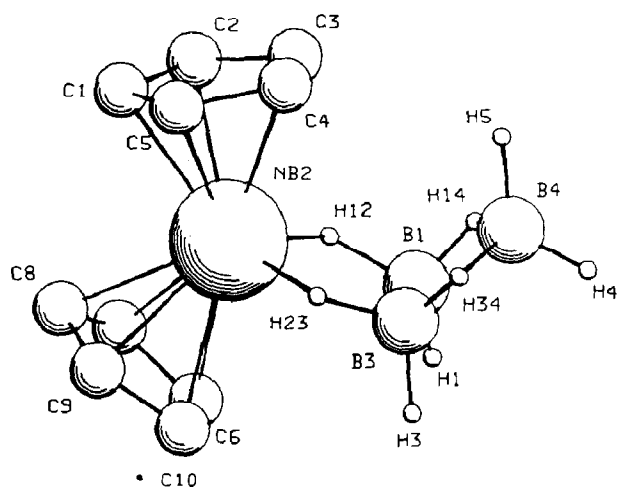


Fig. 2. Crystal structure of $[\text{Nb}(\eta\text{-C}_5\text{H}_5)_2\text{B}_3\text{H}_8]$ (**2**). Hydrogen atoms on the Cp rings have been excluded for clarity. Selected bond distances and angles are from one of the molecules in the asymmetric unit only. Selected bond distances (\AA) (Cp = $\eta\text{-C}_5\text{H}_5$): Nb(2)–Cp(centroid) 2.047, Nb(2)–B(1) 2.555(6), Nb(2)–B(3) 2.566(6), B(1)–B(3) 1.727(8), B(1)–B(4) 1.804(9), B(3)–B(4) 1.79(1). Selected bond angles ($^\circ$): Cp(centroid)–Nb(2)–Cp(centroid) 137.95, B(1)–Nb(2)–B(3) 39.4(2), Nb(2)–B(1)–B(4) 108.1(4), Nb(2)–B(3)–B(4) 108.1(4), B(1)–B(4)–B(3) 61.6(4), dihedral angle between planes B(1),Nb(2),B(3) and B(1),B(4),B(3) 124.93.

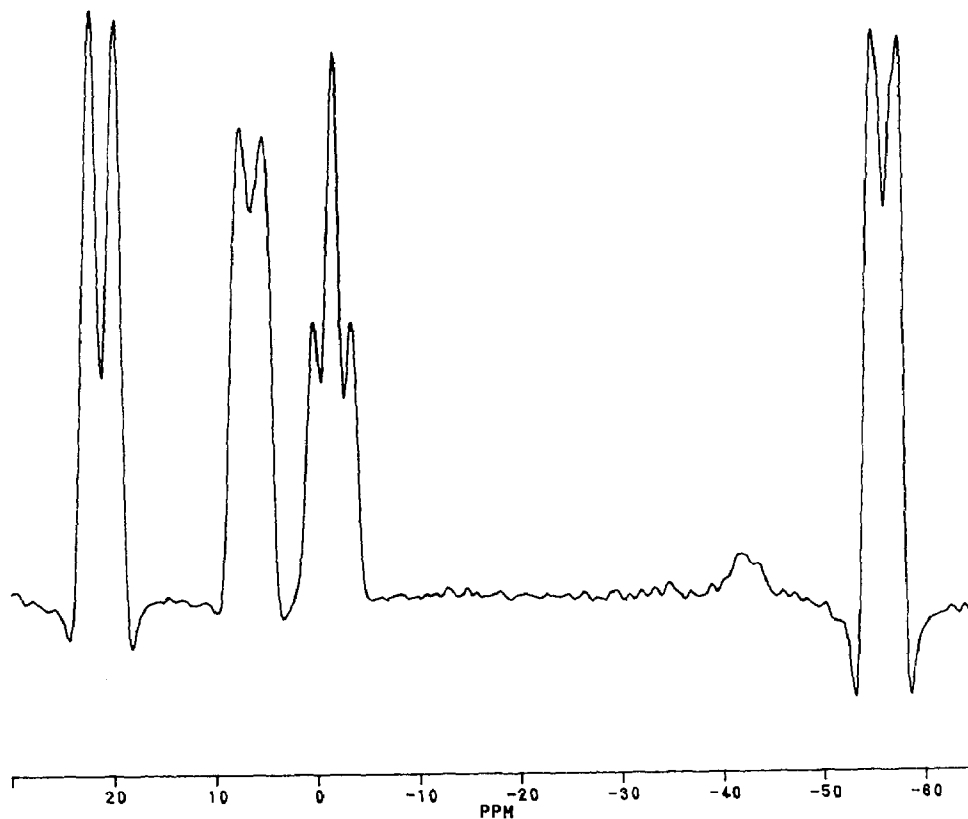


Fig. 3. ^{11}B NMR at 64.2 MHz of $[\text{Nb}(\eta\text{-C}_5\text{H}_5)_2\text{B}_4\text{H}_9]$ (**1**).

crystal structure * showed two independent molecules of **2** in the asymmetric unit. There are no significant differences between the structural parameters of the two molecules. The butterfly geometry, shown for one of the molecules in the asymmetric unit (Fig. 2), is well established for *arachno*-2-metallaborane analogues of tetraborane(10). The solution ^1H , ^{11}B and ^{13}C NMR spectra are consistent with the solid state structure, but interestingly, spin saturation transfer experiments show the presence of scrambling processes involving exchange of the terminal protons on B(1,3), one of the *exo/endo* protons on B(4) and the bridging protons H(1,4) and H(3,4). Similar processes have been observed in compound **1** involving the terminal protons on B(5) and B(4) with the bridging proton H(4,5). Previously reported systems showing bridge/terminal exchange processes include the $[\text{3,3,3,3-(CO)}_4\text{-arachno-WB}_7\text{H}_{12}]^-$ anion [6] and B_4H_{10} [7].

The $\{\text{Nb}(\eta\text{-C}_5\text{H}_5)_2\}$ fragment can be considered to subrogate for a $\{\text{BH}_2\}$ fragment and to contribute three orbitals and three electrons towards the skeletal electron count. Thus, from electron counting procedures, **1** can be considered to be an analogue of the *arachno*- B_5H_{11} cluster whereas **2** can be considered to be an analogue of the *arachno*- B_4H_{10} cluster.

Previously reported metalla subrogated analogues of pentaborane(11) are apex subrogated. In the absence of any obvious steric effects to explain the subrogation position in compound **1**, we suggest that the planar spatial disposition of the frontier orbitals of the $\{\text{Nb}(\eta\text{-C}_5\text{H}_5)_2\}$ fragment favours base subrogation, whereas the pyramidal arrangement of the frontier orbitals of the $\{\text{Ir}(\text{CO})(\text{PR}_3)_2\}$ and $\{\text{RuH}(\text{C}_6\text{Me}_6)\}$ fragments is more compatible with apex subrogation.

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* Crystal data: $\text{C}_{10}\text{H}_{18}\text{NbB}_3$, $M = 263.6$, monoclinic, space group $C_{2/c}$, a 24.684(4), b 8.039(1), c 24.433(3) Å, β 101.71(1)°, U 4748 Å³, $Z = 16$, D_c 1.47 g cm⁻³, $F(000) = 2144$, $\mu(\text{Mo-K}\alpha)$ 9.3 cm⁻¹. crystal size ca. 0.30 × 0.25 × 0.05 mm. Data were collected ($2\theta_{\text{max}} 50^\circ$) on an Enraf-Nonius CAD4 diffractometer, using graphite monochromated Mo- K_α radiation. An empirical absorption correction was applied and structure solution and refinement were carried out using 3057 observed reflections ($I > 3\sigma(I)$) from the 4183 independent reflections measured. The structure was solved using SHELXS and routine Fourier methods. Hydrogen atoms on the B_3H_8 fragment were located from a Fourier difference map and included in the refinement subject to soft restraints. Hydrogen atoms attached to the cyclopentadienyl rings were included in calculated positions. Full matrix least squares refinement of 316 least squares parameters has led to final agreement factors of $R = 0.0268$ and $R_w = 0.0298$ (unit weights). The atomic coordinates, bond lengths, angles and thermal parameters are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

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