A Novel Eleven-vertex *closo*-type Azametallaborane: $[1\text{-}(\eta^6\text{-MeC}_6\text{H}_4\text{-4-Pr}^i)\text{-}closo\text{-1,2-RuNB}_9\text{H}_{10}]$

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Reaction between *nido*-6-NB_9H_{12} and $[(\eta^6\text{-MeC}_6\text{H}_4\text{-4-Pr}^i)\text{RuCl}_2]_2$ in tetrahydrofuran yields a variety of azaruthenaboranes of which one is the novel *closo*-type eleven-vertex species $[1\text{-}(\eta^6\text{-MeC}_6\text{H}_4\text{-4-Pr}^i)\text{-}closo\text{-1,2-RuNB}_9\text{H}_{10}]$.

We report the first fully contiguous azametallaborane, the eleven-vertex *closo*-type ruthenium compound $[1\text{-}(\eta^6\text{-MeC}_6\text{H}_4\text{-4-Pr}^i)\text{-}closo\text{-1,2-RuNB}_9\text{H}_{10}]$. This air-stable orange—red crystalline solid was isolated in 15% yield (unoptimised) from the products of the reaction between $[(\eta^6\text{-MeC}_6\text{H}_4\text{-4-Pr}^i)\text{RuCl}_2]_2$ and *nido*-6-NB_9H_{12} in the presence of *N,N,N′,N′*-tetramethylnaphthalene-1,8-diamine in tetrahydrofuran solution. N.m.r. spectroscopy† suggested the closed eleven-vertex structural type, and this was confirmed by a single-crystal *X*-ray diffraction analysis (Figure 1).‡

The molecular structure is seen to be based upon the closed C_{2v} eleven-vertex structure generally presumed for $[B_{11}H_{11}]^{2-}$, with the ruthenium atom in the high-connectivity 1-position, and with an NH vertex in the adjacent low-connectivity 2-position. As far as we are aware this is the first metallaborane that exhibits complete incorporation of a nitrogen vertex within the cluster framework {in the only azametallaborane previously reported, the ten-vertex platinum species $[6,6\text{-(PPh}_3)_2\text{-}arachno\text{-6,9-PtNB}_8\text{H}_{11}]$,[1] the nitrogen vertex is an NH grouping [formally equivalent to a $\{BH_2\}^-$ unit] in an open-face *arachno* position}. A closed structure for the azaruthenaborane is in accord with the Williams–Wade[2,3] cluster-geometry and electron-counting rules, but in this context the long Ru(1)–N(2) distance of 208.8(6) pm is of interest, particularly in view of the shorter B(4)–N(2) and B(5)–N(2) distances of *ca.* 155 pm [compared to B(6)–B(3) and B(7)–B(3) of *ca.* 170 pm], and suggests a 'slippage' from true *closo*, probably related to the slippage observed[4] in the more open cluster structure adopted by $[1\text{-}(\eta^6\text{-MeC}_6\text{H}_4\text{-4-Pr}^i)\text{-2,4-Me}_2\text{-1,2,4-RuC}_2\text{B}_8\text{H}_8]$.

Preliminary results from n.m.r. spectroscopy show that the other products from the reaction include substituted derivatives of the *closo*-type species described here (combined yields *ca.* 14%), and a variety of (less stable) open *nido* and/or *arachno*-type $\{RuNB_9\}$ cluster species (combined yields *ca.* 18%).

Although metallaheteroborane chemistry where the heteroatom is carbon has been an important and extensively examined area of inorganic chemistry for nearly a quarter of a

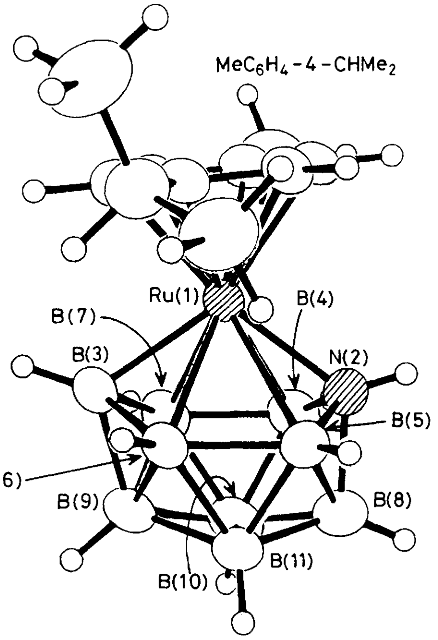

Figure 1. Crystallographically determined molecular structure of $[1\text{-}(\eta^6\text{-MeC}_6\text{H}_4\text{-4-Pr}^i)\text{-}closo\text{-1,2-RuB}_9\text{H}_{10}]$, determined on the $0.75CH_2Cl_2$ solvate (the molecule represented is one of two very similar molecules in the unit cell; the other differs principally in the relative twist of the aromatic ring *vs.* the $RuNB_9$ cluster, and in the rotamer conformations of the methyl and isopropyl groups). Selected distances from Ru(1) are as follows; to N(2) 208.6(6), to B(3) 214.0(8), to B(4) 241.6(7), to B(5) 243.2(8), to B(6) 235.8(8), and to B(7) 236.5(8) pm. Boron–nitrogen distances are: B(4)–N(2) 154.2(10), B(5)–N(2) 155.4(10), and B(8)–N(2) 167.4(9) pm. Selected interboron distances are: B(3)–B(6) 170.3(10), B(3)–B(7) 174.6(11), B(4)–B(7) 182.7(11), B(5)–B(6) 183.9(10), B(4)–B(8) 185.6(12), B(5)–B(8) 185.3(11), B(6)–B(9) 180.7(10), B(7)–B(9) 182.1(10), and B(10)–B(11) 182.3(12) pm, the others being in the range 170.3(10)—180.2(11) pm. The angle between the planes of the aromatic ring and of the B(4)B(5)B(6)B(7) unit is 4.4°.

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† *N.m.r. data* at 294 K {ordered as: assignment, $\delta(^{11}B)$ in CD_2Cl_2 [$\delta(^1H)$ in CD_2Cl_2]}: BH(3), +53.2[+7.68]; BH(9), +19.6[+3.92]; BH(4,5), +0.6[+2.54]; BH(8), −13.8[+2.50]; BH(6,7), −22.5[+0.15]; BH(10,11), −25.7[+0.09]; NH(2), —[+5.02]; $\delta(^{11}B)$ and $\delta(^1H)$ in p.p.m. to low field (high frequency) of $[(BF_3(OEt_2))]$ and $SiMe_4$ respectively; assignments by [^1H-^1H]-COSY and by ^1H-{^{11}B(selective)} n.m.r. experiments. In the [^1H-^1H]-COSY experiments it was of interest[9] to observe correlations between $^1H(2)$ on N(2) and the $^1H(4,5)$ and/or $^1H(8)$ resonances at $\delta(^1H)$ +2.52, ±0.02 p.p.m.

‡ *Crystal data* for $C_{10}H_{24}B_9NRu\cdot 0.75CH_2Cl_2$: M = 420.38, monoclinic, space group $C2/c$, a = 3874.9(6), b = 1251.9(3), c = 1737.7(2) pm, β = 112.49(2)°, U = 7.788(2) nm^3, Z = 16, μ = 9.05 cm^{-1}, $F(000)$ = 3384. Scans widths 1.6° + α-doublet splitting, scan speeds 2.0—29.3° min^{-1} and $4.0 < 2\theta < 50.0°$. Total data collected = 7833, no. observed = 6978 [$I > 2.0\sigma(I)$], R = 0.0502, R_w = 0.0518 (g = 0.0002).

All crystallographic measurements were made on a Nicolet P3/F diffractometer operating in the ω/2θ scan mode using graphite monochromated Mo-K_α radiation following a procedure described elsewhere.[10] The data set was corrected for absorption empirically.[11] The structure was solved by standard heavy atom methods and refined by full-matrix least-squares using SHELX76.[12] All non-hydrogen atoms were refined anisotropically (except for a slightly disordered chlorine atom and the carbon atoms of the solvent molecules). The organyl hydrogen atoms were included in calculated positions (C–H = 108 pm) and refined with an overall isotropic thermal parameter while all the hydrogen atoms associated with the borane cage were located in Fourier difference maps and freely refined with individual isotropic thermal parameters. The weighting scheme $w = [\sigma^2(F_o) + g(F_o)^2]^{-1}$ was used at the end of refinement. 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.

century,[5] contiguous metallaheteroborane chemistry where the heteroatom is an electronegative first-row element other than carbon is very limited indeed, and only three examples where the heteroatom is nitrogen or oxygen have previously been established.[1,6,7] The present work now presages an extensive new azametallaborane cluster chemistry that is derived, in the first instance, from an azaborane precursor that can be readily made[8] from commercially available $B_{10}H_{14}$ in high yield.

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References

1 K. Baše, A. Petřina, B. Štíbr, V. Petríček, K. Malý, A. Línek, and I. A. Zakharova, *Chem. Ind.*, 1979, 212; K. Baše, B. Štíbr, and I. A. Zakharova, *Synth. React. Inorg. Metal-Org. Chem.*, 1980, **10**, 509.

2 R. E. Williams, *Inorg. Chem.*, 1971, **10**, 210; *Adv. Inorg. Chem. Radiochem.*, 1976, **18**, 67.

3 K. Wade, *Chem. Commun.*, 1971, 792; *Adv. Inorg. Chem. Radiochem.*, 1976, **18**, 1.

4 M. Bown, X. L. R. Fontaine, N. N. Greenwood, J. D. Kennedy, and M. Thornton-Pett, *Organometallics*, 1987, **6**, 2254.

5 R. N. Grimes, in 'Comprehensive Organometallic Chemistry,' eds. G. Wilkinson, F. G. A. Stone, and E. Abel, Pergamon, 1982, Part I, Ch. 5.5., pp. 459—542, and references cited therein.

6 R. P. Micchiche, J. J. Briguglio, and L. G. Sneddon, *Inorg. Chem.*, 1984, **23**, 3992.

7 X. L. R. Fontaine, H. Fowkes, N. N. Greenwood, J. D. Kennedy, and M. Thornton-Pett, *J. Chem. Soc., Chem. Commun.*, 1985, 1722; *J. Chem. Soc., Dalton Trans.*, 1986, 2417.

8 K. Baše, F. Hanousek, J. Plešek, B. Štíbr, and A. Lyčka, *J. Chem. Soc., Chem. Commun.*, 1981, 1162; K. Basě, *Collect. Czech. Chem. Commun.*, 1983, **48**, 2593.

9 X. L. R. Fontaine and J. D. Kennedy, *J. Chem. Soc., Chem. Commun.*, 1986, 779.

10 A. Modinos and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 1974, 2065.

11 N. Walker and D. Stuart, *Acta Crystallogr., Sect. A*, 1983, **39**, 158.

12 G. M. Sheldrick, SHELX 76, Program System for *X*-ray Structure Determination, University of Cambridge, 1976.