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Preliminary communication

arachno-[(η^6-C_6Me_6)RuB_8H_{14}]; A NINE-VERTEX STRUCTURAL ANALOGUE OF n-B_9H_{15} RATHER THAN OF iso-B_9H_{15}

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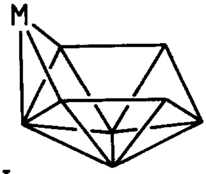
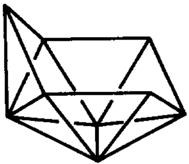
Summary

One of the products of the reaction of *arachno*-[B_6H_{11}]$^-$ with the versatile organometallic metallaborane synthon [(η^6-C_6Me_6)$RuCl_2$]$_2$ is the novel *arachno*-nine-vertex ruthenaborane [(η^6-C_6Me_6)RuB_8H_{14}] which, uniquely for a metallaborane, has the same skeletal configuration as n-B_9H_{15}.

Although a number of nine-vertex *arachno* metallaboranes are known [1], all have the configuration I based on the commonly encountered skeletal structure of iso-B_9H_{15} (configuration II), whereas the structural motif of n-B_9H_{15} (configuration III) [2] has not so far been reported in metallaborane chemistry. We now report preliminary results on an organometallaborane that does conform to this rarer structural motif. This compound is [1-(η^6-C_6Me_6)-n-*arachno*-1-RuB_8H_{14}] which has



I



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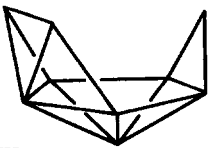

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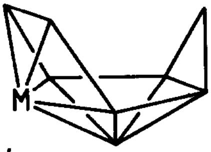

IV

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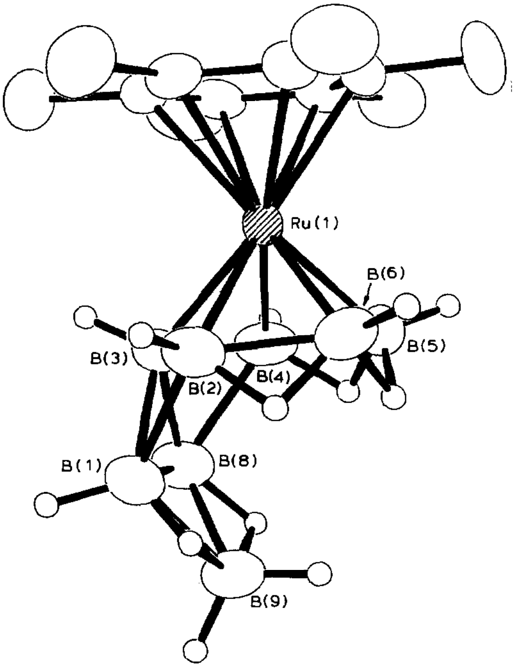
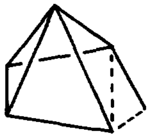


Fig. 1. Molecular structure of [1-(η^6-C_6Me_6)-n-*arachno*-1-RuB_8H_{14}]. Distances from the Ru(1) atom are as follows: to B(2) 218.0(6), to B(3) 214.1(6), to B(4) 217.7(6), to B(5) 208.7(6), and to B(6) 208.6(6) pm. Interboron distances are within typical polyhedral ranges at 174.4(8)–184.7(9) pm except for B(2)–B(7) and B(4)–B(8) which are somewhat longer at 195.6(8) and 196.0(9) pm respectively (compare the corresponding distances of 192.5(4) and 191.3(4) in n-B_9H_{15} itself). The dihedral angle between the aryl-C_6 plane and the B(2–6) plane is 2.8°. The eighteen methyl H atoms are omitted for clarity and the atom H(8) on the borane cluster is obscured in this projection.

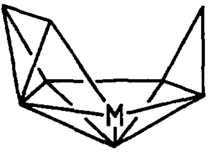
configuration IV: its identity was established by single-crystal X-ray diffraction analysis. Crystals were monoclinic, space group $P2_1/n$ ($= P2_1/c$, no.14), with a 856.8(1), b 1639.2(2), c 1324.3(2) pm, β 101.81(1)°, and $Z = 4$, D_c 1.33 g cm^{-3}, $F(000) = 752$, μ(Mo-K_α) 7.56 cm^{-1}. The structure was solved via standard heavy atom methods and refined by full-matrix least squares to $R = 0.0260$, $R' = 0.0287$. 2564 reflections were measured on a Nicolet P3/F diffractometer with Mo-K_α radiation (λ 71.069 pm), and 2151 reflections with $I > 2.0\sigma(I)$ were used in refinement. All methyl H atoms were included in calculated positions (C–H 108 pm); H atoms on the borane cluster were located in Fourier difference maps and freely refined.

The molecular structure (Fig. 1) is seen to be precisely analogous to that of n-B_9H_{15}, except that the BH moiety at the 2-position of the binary borane is replaced by the isoelectronic and isolobal Ru(η^6-C_6Me_6) moiety. (The structural analogy with dicyclopentadienyl- and arene-ruthenium organometallic sandwich compounds is also clear from Fig. 1.) In contrast to the iso-*arachno* metallanonaboranes of configuration I, in which the metal-to-boron bonding is based on a two orbital contribution from the metal centre to the cluster bonding [1], the ruthenium centre in the new metallaborane reported here contributes three orbitals to the cluster bonding. The bridging and *endo*-terminal hydrogen atom positions are as for n-B_9H_{15} and the NMR properties [*] are similar but, in contrast to n-B_9H_{15} which is an unstable liquid at ambient temperatures, the *arachno*-ruthenanonaborane is a yellow, air-stable, crystalline solid.

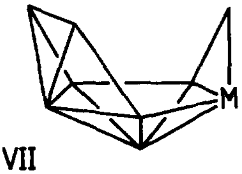
The ruthenaborane is formed in yields of up to 2% in the reaction of the *arachno*-$[B_6H_{11}]^-$ anion (of proposed configuration V [3]) with $[(\eta^6\text{-}C_6Me_6)RuCl_2]_2$ in THF/CH_2Cl_2 solution at −25°C for 2 h, and was separated by TLC on silica gel in air, followed by HPLC, also on silica (Lichromosorb). The detailed course of the reaction is not clear. The reaction mixture also yields a variety of other smaller ruthenaboranes that have generally precedented structures, as previously reported [4]. Also formed are a number of larger metallaboranes including (a) $[5\text{-}(\eta^6\text{-}C_6Me_6)\text{-}$*nido*-$5\text{-}RuB_9H_{13}]$; (b) its 2-subrogated analogue having the rarer ten-vertex *nido*-2-metalladecaborane configuration, known previously in metallaborane chemistry only for cobalt [5]; and (c) its 1-subrogated analogue of the previously unreported *nido*-1-metalladecaborane configuration. Preliminary NMR results also indicate a second isomer of the present nine-vertex $[(\eta^6\text{-}C_6Me_6)RuB_8H_{14}]$, probably of configuration VI or VII, and it is likely that further exploration of this and other closely related arene-metal type systems [4,6] will continue to yield many new metallaboranes of which some will exhibit novel structural features.



V



VI



VII

Acknowledgements

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[*] $\delta(^{11}B)$ values (with $\delta(^{1}H)$ values of directly bound H atoms in parentheses): B(2,4) +1.2(+2.33), B(3) +10.1(+3.54), B(5,6) −0.4(+2.28, −4.09); B(7,8) −36.9(+0.84), and B(9) +6.4(+3.42, +0.91); other (bridging) $\delta(^{1}H)$ values: H(4,5; 6,7) −4.23, H(7,9; 8,9) −1.09; $CDCl_3$ solution at 294 K; assignments by homonuclear $[^{11}B\text{–}^{11}B]$-COSY and heteronuclear $^{1}H\text{-}\{^{11}B(\text{selective})\}$ spectroscopy. n-B_9H_{15} had $\delta(^{11}B)$ as follows: B(1) −47.5, B(2,4) and B(5,6) +7.1 and +3.3, B(3) +17.2, B(7,8) −32.9, and B(9) +3.5 (A. Allerhand, A.O. Clouse, R.R. Rietz, T. Roseberry, and R. Schaeffer, J. Am. Chem. Soc., 94 (1972) 2445; A.O. Clouse, D.C. Moody, R.R. Rietz, T. Roseberry, and R. Schaeffer, ibid., 95 (1973) 2496). Numbering as in Fig. 1.

References

1 S.K. Boocock, N.N. Greenwood, M.J. Hails, J.D. Kennedy, and W.S. McDonald, J. Chem. Soc., Dalton Trans., (1981) 1415; J. Bould, J.E. Crook, N.N. Greenwood, J.D. Kennedy, and W.S. McDonald, J. Chem. Soc., Chem. Commun., (1982) 346; J. Bould, J.E. Crook, N.N. Greenwood, and J.D. Kennedy, J. Chem. Soc., Dalton Trans., (1984) 1903; J. Bould, N.N. Greenwood, and J.D. Kennedy, ibid., (1984) 2477; N.N. Greenwood, M.J. Hails, J.D. Kennedy, and W.S. McDonald, ibid., (1985) 953; M.A. Beckett, J.E. Crook, N.N. Greenwood, and J.D. Kennedy, ibid., (1984) 1427; R. Ahmad, J.E. Crook, N.N. Greenwood, and J.D. Kennedy, ibid., (1986) in press.

2 R.E. Dickerson, P.J. Wheatley, P.A. Howell, W.N. Lipscomb, and R. Schaeffer, J. Chem. Phys., 25 (1956) 606; R.E. Dickerson, P.J. Wheatley, P.A. Howell, and W.N. Lipscomb, ibid., 27 (1957) 200; P.G. Simpson and W.N. Lipscomb, ibid., 35 (1961) 1340; J.C. Huffman, Thesis, Indiana University, 1974.

3 R.J. Remmel, H.D. Johnson, I. Jaworiwski, and S.G. Shore, J. Am. Chem. Soc., 97 (1975) 5395.

4 M. Bown, N.N. Greenwood, and J.D. Kennedy, J. Organomet. Chem., 309 (1986) C67; M. Bown, X.L.R. Fontaine, N.N. Greenwood, J.D. Kennedy, and M. Thornton-Pett, J. Chem. Soc., Dalton Trans., 4, submitted, July 1986.

5 R. Wilczynski and L.G. Sneddon, Inorg. Chem., 18 (1979) 864; G.J. Zimmerman, L.W. Hall, and L.G. Sneddon, Inorg. Chem., 19 (1980) 3642; J.M. Gromek and J. Donohue, Crystal Struct. Commun., 10 (1981) 871; T.L. Venable, W.C. Hutton, and R.N. Grimes, J. Am. Chem. Soc., 106 (1984) 29.

6 X.L.R. Fontaine, H. Fowkes, N.N. Greenwood, J.D. Kennedy, and M. Thornton-Pett, J. Chem. Soc., Chem. Commun., (1985) 1165 and 1722; J. Chem. Soc., Dalton Trans., (1986) 547 and (1986) submitted; X.L.R. Fontaine, N.N. Greenwood, J.D. Kennedy, P. MacKinnon, and M. Thornton-Pett, J. Chem. Soc., Chem. Commun., (1986) 1111.