# The Preparation of $[Ru(NCMe)_6][7-(\eta^6-C_6Me_6)$-*nido*-7-$RuB_{10}H_{13}]_2$ and its Characterization by Single-crystal *X*-Ray Diffraction Analysis and Nuclear Magnetic Resonance Spectroscopy: a Triply Hydrogen-bridged Eleven-vertex *nido*-7-Metallaundecaborane *

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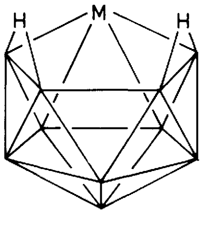
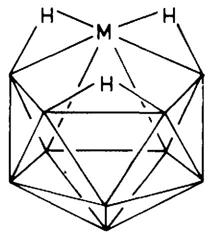
Reaction between $[\{Ru(\eta^6-C_6Me_6)Cl_2\}_2]$ and $[NEt_4]_2[B_{10}H_{14}]$ in MeCN solution gives an 86% yield of yellow $[Ru(NCMe)_6][7-(\eta^6-C_6Me_6)$-*nido*-7-$RuB_{10}H_{13}]_2$. Crystals were triclinic, space group $P\bar{1}$, with $a$ = 937.6(2), $b$ = 1 005.5(2), $c$ = 1 679.2(3) pm, $\alpha$ = 79.73(1), $\beta$ = 105.24(2), $\gamma$ = 115.59(2)°, and $Z$ = 1; the final $R$ factor was 0.0341 for 3 439 observed reflections. The unit cell contains two polyhedral anions, and a mononuclear cation which is situated on a centre of inversion. Each anion consists of a *nido*-7-metallaundecaboranyl open-faced cluster, with an $\eta^6-C_6Me_6$ ligand bound to the metal atom, and with two Ru(7)–H–B bridges and one B(9)–H–B(10) bridge which mutually exchange very readily in solution ($\Delta G_{183}^{\ddagger}$ < 34 kJ mol$^{-1}$). Geometrical and n.m.r. considerations indicate that the $B_{10}$ residue of the metallaborane cluster has *arachno*-decaboranyl character. The homoleptic cation $[Ru(NCMe)_6]^{2+}$ has also not previously been characterized by *X*-ray structural analysis.

Although over 100 *nido*-7-metallaundecaborane species, incorporating some 20 different metals, are known,[1-3] all generally have structure (I) with two bridging H atoms on the open face, at the B(8)–B(9) and B(10)–B(11) positions. A triply H-bridged structure(II), analogous to the structure of the binary borane exemplar $[B_{11}H_{14}]^-$, that has bridging H atoms at the M(7)–B(8), M(7)–B(11), and B(9)–B(10) positions, has only been substantiated for the rhodaborane $[7-(\eta^5-C_5Me_5)$-*nido*-7-$RhB_{10}H_{11}Cl(PMe_2Ph)$-8,11],[4] although the anionic nickelaborane species $[(\eta^5-C_5Me_5)NiB_{10}H_{13}]^-$ reported some time ago,[5] could have a related structure, and very recent results in our own laboratories have shown that molybdenum and tungsten analogues can also be synthesized.[6]

Here we report the characterization of the triply H-bridged anionic species $[7-(\eta^6-C_6Me_6)$-*nido*-7-$RuB_{10}H_{13}]^-$.



(I)



(II)

## Results and Discussion

The anion $[7-(\eta^6-C_6Me_6)$-*nido*-7-$RuB_{10}H_{13}]^-$ is isolable as its yellow $[Ru(NCMe)_6]^{2+}$ salt in 86% yield (based on Ru) from the reaction (75 μmol scale) between the *arachno*-$[B_{10}H_{14}]^{2-}$ anion and the versatile[7] ruthenaborane synthon $[\{Ru(\eta^6-C_6Me_6)Cl_2\}_2]$ in acetonitrile solution [idealized stoicheiometry as in equation (1)]. Reaction for 3 h at room temperature,

$$3[\{Ru(\eta^6-C_6Me_6)Cl_2\}_2] + 4[NEt_4]_2[B_{10}H_{14}] + 12\,MeCN \longrightarrow 2[Ru(NCMe)_6][(\eta^6-C_6Me_6)RuB_{10}H_{13}]_2 + 8[NEt_4]Cl + 4HCl + 2C_6Me_6 \quad (1)$$

followed by preparative-scale thin layer chromatography (t.l.c.) on silica yielded the air-stable ruthenaborane salt as the only metallaborane in viable yield. The open 11-vertex nature of the product contrasts with the closed 12-vertex product from the analogous reaction[8] between $[\{Rh(\eta^5-C_5Me_5)Cl_2\}_2]$ and *arachno*-$[SB_9H_{12}]^-$, which yields *closo*-$[(\eta^5-C_5Me_5)_2Rh_2SB_9H_8Cl]$ *via* loss of $H_2$ as well as HCl [idealized stoicheiometry as in equation (2)].

$$[\{Rh(\eta^5-C_5Me_5)Cl_2\}_2] + Cs[SB_9H_{12}] \longrightarrow [(\eta^5-C_5Me_5)_2Rh_2SB_9H_8Cl] + CsCl + 2HCl + H_2 \quad (2)$$

It is of interest that the ruthenium reaction [equation (1)] should stop at the *nido* 11-vertex stage whereas the rhodium reaction [equation (2)] adds a second metal vertex with loss of dihydrogen to form the *closo* species, and also incorporates a halogen substituent on the cluster. In view of this difference considerable interest attaches to a permutation of these reactants and we would hope to report at a later date on the products obtained on the one hand from reacting $[\{Rh(\eta^5-C_5Me_5)Cl_2\}_2]$ with *arachno*-$[B_{10}H_{14}]^{2-}$ and on the other from reacting $[\{Ru(\eta^6-C_6Me_6)Cl_2\}_2]$ with *arachno*-$[SB_9H_{12}]^-$.

A crystal of $[Ru(NCMe)_6][(\eta^6-C_6Me_6)RuB_{10}H_{13}]_2$ was obtained by slow evaporation from a solution in $CD_3CN$ and this was found to be suitable for a single-crystal *X*-ray diffraction analysis. The triclinic unit cell, space group $P\bar{1}$, contained a single formula weight of the compound with the two polyhedral anions in general positions and the cation located on a centre of inversion at $\frac{1}{2}$,0,0. All cluster hydrogen atoms were located. Drawings of the structure of the cation $[Ru(NCMe)_6]^{2+}$ and the anion $[(\eta^6-C_6Me_6)RuB_{10}H_{13}]^-$ are given in Figures 1 and 2 respectively and a packing diagram is shown in Figure 3. Interatomic distances and angles for the polyhedral metallaborane anion are in Tables 1 and 2 respectively.

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* Hexakis(methyl cyanide)ruthenium(II) bis [7-(η-hexamethylbenzene)-tridecahydro-7-ruthena-*nido*-undecaborate (1 – )].

*Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii—xx.

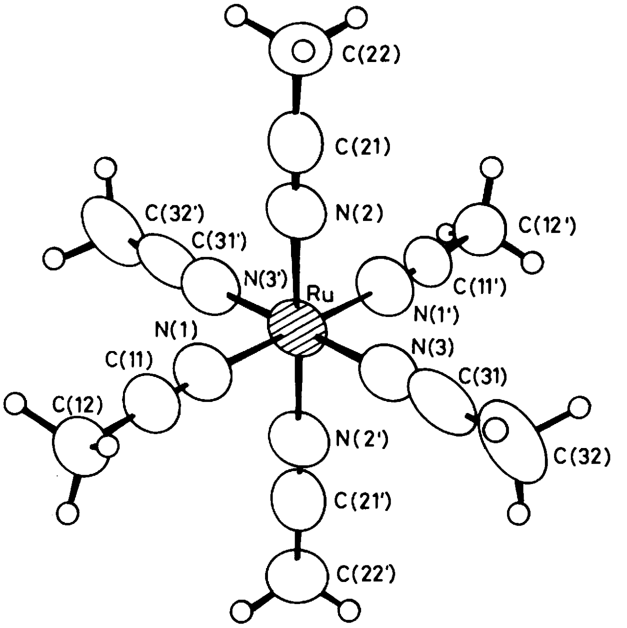

**Figure 1.** ORTEP drawing of the $[Ru(NCMe)_6]^{2+}$ cation in $[Ru(NCMe)_6][7\text{-}(\eta^6\text{-}C_6Me_6)\text{-}nido\text{-}7\text{-}RuB_{10}H_{13}]_2$. Distances: Ru(1)–N 202.2(5), 199.9(5), and 201.7(6); N–C 110.9(6), 110.7(6), and 110.3(7); C–C 146.2(6), 148.9(7), and 146.4(8) pm; numbering N(1), N(2), and N(3) respectively. The three independent angles at Ru(1) are 88.7(2), 90.6(2), and 91.3(2)°, at nitrogen 175.7(4), 178.4(3), and 176.3(4)°, and at nitrile carbon 178.7(5), 177.5(5), and 178.8(6)°

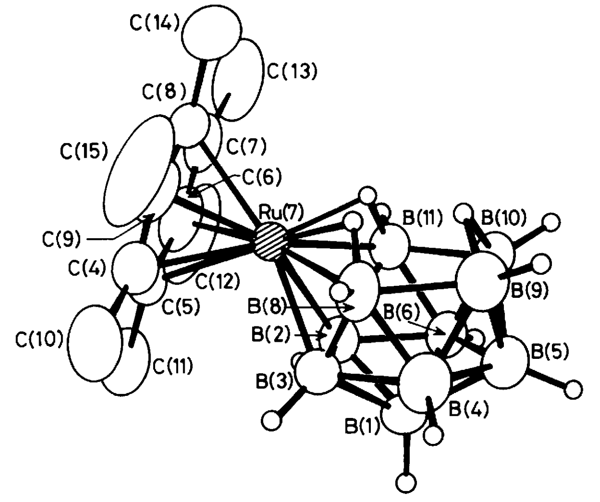

**Figure 2.** ORTEP drawing of the $[7\text{-}(\eta^6\text{-}C_6Me_6)\text{-}nido\text{-}7\text{-}RuB_{10}H_{13}]^-$ anion in $[Ru(NCMe)_6][7\text{-}(\eta^6\text{-}C_6Me_6)\text{-}nido\text{-}7\text{-}RuB_{10}H_{13}]_2$ with the methyl-hydrogen atoms omitted for clarity

The cation $[Ru(NCMe)_6]^{2+}$ has not previously been structurally characterized and is only the second homoleptic nitrogen-ligand ruthenium cation to be determined by single-crystal *X*-ray diffraction analysis, the previous example[9] being the hexakis(pyridine)ruthenium(II) cation in $[Ru(NC_5H_5)_6][BF_4]_2$. The three crystallographically independent Ru–N distances of 199.9(5), 201.7(6), and 202.2(5) pm are somewhat shorter than those in the pyridine complex, which lie in the range 209.9—214.4 pm, and, as expected, the C≡N distances of 110.3(7), 110.7(6), and 110.9(6) are somewhat longer than those in the unco-ordinated acetonitrile ligand.

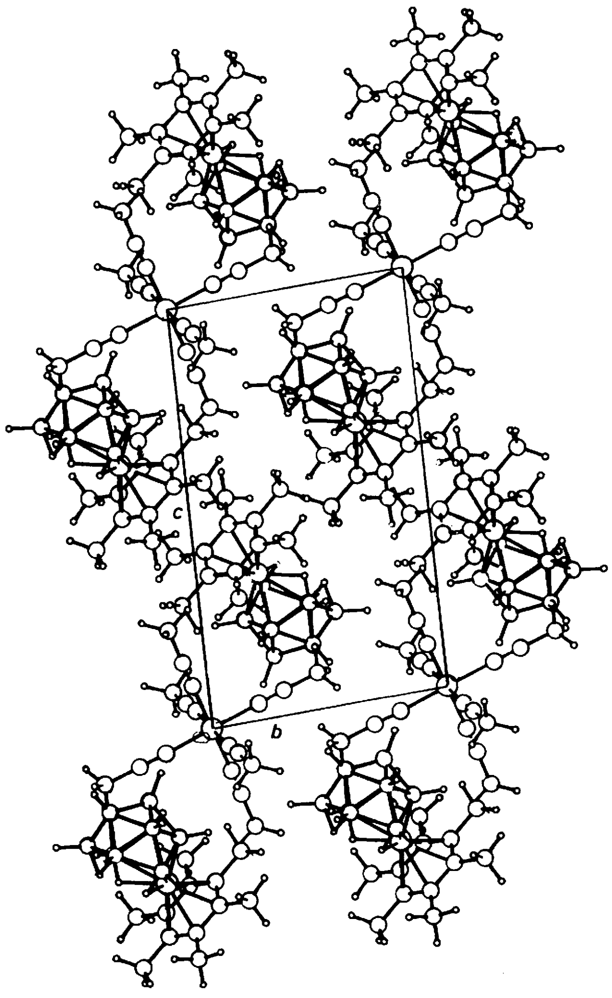

**Figure 3.** Packing diagram of $[Ru(NCMe)_6][7\text{-}(\eta^6\text{-}C_6Me_6)\text{-}nido\text{-}7\text{-}RuB_{10}H_{13}]_2$; view direction 1,0,0 (*h*,*k*,*l*)

The structure of the polyhedral ruthenaborane anion is seen to be based on a *nido* 11-vertex cluster derived from a closed triangulated icosahedron by removal of one vertex. The $RuB_{10}H_{13}$ cluster approximates closely to mirror-plane symmetry [through Ru(7), B(1), and B(5); see Tables 1 and 2], which it exhibits on time-average in solution (see n.m.r. considerations below). However, there is no crystallographically imposed mirror plane through the molecule and there is also a slight twist of the $C_6Me_6$ ligand away from this ideal in the solid state. Each boron atom has one *exo*-terminal hydrogen atom bound to it, and the ruthenium atom occupies a position in the *nido* open face (nominally position 7). There are three bridging hydrogen atoms in the open face, two of them bridging to ruthenium at Ru(7)–B(8) and Ru(7)–B(11), and the third bridging between the two boron atoms at B(9) and B(10). The $C_6Me_6$ ligand is bound to Ru(7) in a straightforward hexahapto manner with Ru–C distances in the range 218.9(6)—223.6(6) pm and the anion thus has sandwich character, with the aromatic $C_6$ plane and the B(2)B(3)B(11)B(8) plane being nearly parallel (dihedral angle 8.5°). The $C_6Me_6$ ligand is of interest when compared to other metallaborane congeners[4,10–13] because the six methyl carbon atoms are essentially coplanar with the arene $C_6$ ring [range of deviation 0.0—1.5° (away from the metal)]: by contrast the methyl groups in $C_5Me_5$ ligands in known pentamethylcyclopentadienylrhodaboranes bend away much more definitely from the metal atom (deviations 2.6—

**Table 1.** Interatomic distances (pm) [with estimated standard deviations (e.s.d.s) in parentheses] for the metallaborane anion in $[Ru(NCMe)_6]$-$[7\text{-}(\eta^6\text{-}C_6Me_6)\text{-}\textit{nido}\text{-}7\text{-}RuB_{10}H_{13}]_2$ *

(*i*) From the metal atom

| | | | |
|---|---|---|---|
| Ru(7)–B(2) | 224.8(6) | Ru(7)–B(3) | 224.9(6) |
| Ru(7)–B(11) | 235.5(6) | Ru(7)–B(8) | 232.9(6) |
| Ru(7)–H(7,11) | 178.4(14) | Ru(7)–H(7,8) | 180.2(10) |
| Ru(7)–C(7) | 220.8(6) | Ru(7)–C(9) | 223.2(6) |
| Ru(7)–C(6) | 218.9(6) | Ru(7)–C(4) | 220.7(6) |
| Ru(7)–C(5) | 219.6(6) | | |
| Ru(7)–C(8) | 223.6(6) | | |

(*ii*) Interboron

| | | | |
|---|---|---|---|
| B(1)–B(2) | 177.1(8) | B(1)–B(3) | 178.4(8) |
| B(1)–B(6) | 176.5(8) | B(1)–B(4) | 176.7(8) |
| B(1)–B(5) | 180.3(8) | | |
| B(2)–B(3) | 181.6(8) | | |
| B(2)–B(6) | 177.9(8) | B(3)–B(4) | 178.9(8) |
| B(2)–B(11) | 179.2(8) | B(3)–B(8) | 180.5(8) |
| B(5)–B(6) | 178.0(8) | B(5)–B(4) | 176.4(8) |
| B(5)–B(10) | 177.8(9) | B(5)–B(9) | 176.8(8) |
| B(6)–B(10) | 173.1(8) | B(4)–B(9) | 175.0(9) |
| B(6)–B(11) | 173.4(8) | B(4)–B(8) | 174.4(9) |
| B(9)–B(10) | 186.2(8) | | |
| B(10)–B(11) | 191.3(8) | B(9)–B(8) | 190.4(8) |

(*iii*) Boron hydrogen

| | | | |
|---|---|---|---|
| B(1)–H(1) | 117.6(15) | | |
| B(2)–H(2) | 115.3(10) | B(3)–H(3) | 104.7(15) |
| B(5)–H(5) | 118.3(12) | | |
| B(6)–H(6) | 110.2(10) | B(4)–H(4) | 113.8(14) |
| B(10)–H(10) | 113.2(13) | B(9)–H(9) | 119.5(10) |
| B(10)–H(9,10) | 145.2(9) | B(9)–H(9,10) | 125.7(16) |
| B(11)–H(11) | 118.3(14) | B(8)–H(8) | 107.5(10) |
| B(11)–H(7,11) | 123.6(10) | B(8)–H(7,8) | 117.8(16) |

(*iv*) Other

| | |
|---|---|
| C(aryl)–C(aryl) | 137.7(6)—142.1(7) |
| C(aryl)–C(alkyl) | 151.7(8)—154.7(8) |

* Horizontal rows comprise distances that would be equal if the anion conformed to the mirror-plane symmetry to which it approximates.

**Table 2.** Selected interatomic angles (°) for the metallaborane anion in $[Ru(NCMe)_6][7\text{-}(\eta^6\text{-}C_6Me_6)\text{-}\textit{nido}\text{-}7\text{-}RuB_{10}H_{13}]_2$, with e.s.d.s in parentheses *

(*i*) At the metal atom

| | | | |
|---|---|---|---|
| B(2)–Ru(7)–B(3) | 47.6(1) | | |
| B(2)–Ru(7)–B(8) | 82.1(2) | B(3)–Ru(7)–B(11) | 82.4(2) |
| B(2)–Ru(7)–B(11) | 45.8(2) | B(3)–Ru(7)–B(8) | 46.4(2) |
| B(11)–Ru(7)–B(8) | 87.6(2) | | |
| B(2)–Ru(7)–H(7,8) | 97.3(4) | B(3)–Ru(7)–H(7,11) | 100.4(5) |
| B(2)–Ru(7)–H(7,11) | 75.5(5) | B(3)–Ru(7)–H(7,8) | 74.4(6) |
| B(11)–Ru(7)–H(7,8) | 80.2(4) | B(8)–Ru(7)–H(7,11) | 82.2(5) |
| B(11)–Ru(7)–H(7,11) | 31.0(3) | B(8)–Ru(7)–H(7,8) | 29.8(5) |
| H(7,11)–Ru(7)–H(7,8) | 61.7(5) | | |
| C(aromatic)–Ru(7)–C(aromatic) | 35.9(2)—37.8(2), 65.1(3)—67.3(3), 77.6(2)—78.8(2) | | |

(*ii*) Ruthenium–boron–boron

| | | | |
|---|---|---|---|
| Ru(7)–B(2)–B(1) | 119.7(3) | Ru(7)–B(3)–B(1) | 119.0(4) |
| Ru(7)–B(2)–B(3) | 66.2(3) | Ru(7)–B(3)–B(2) | 66.2(3) |
| Ru(7)–B(2)–B(6) | 119.1(3) | Ru(7)–B(3)–B(4) | 118.2(4) |
| Ru(7)–B(8)–B(3) | 64.5(3) | Ru(7)–B(11)–B(2) | 64.0(3) |
| Ru(7)–B(8)–B(4) | 116.3(3) | Ru(7)–B(11)–B(6) | 115.8(4) |
| Ru(7)–B(8)–B(9) | 113.7(3) | Ru(7)–B(11)–B(10) | 113.7(4) |

(*iii*) Boron–boron–boron

| | | | |
|---|---|---|---|
| B(3)–B(2)–B(11) | 114.5(4) | B(2)–B(3)–B(8) | 112.3(4) |
| B(3)–B(8)–B(9) | 105.1(4) | B(2)–B(11)–B(10) | 104.6(4) |
| B(8)–B(9)–B(10) | 112.0(4) | B(11)–B(10)–B(9) | 110.5(4) |
| B–B–B (acute) | 56.9(3)—66.0(4) | (obtuse) | 105.7(4)—116.6(4) |

(*iv*) Others

| | | | |
|---|---|---|---|
| Ru(7)–H(7,8)–B(8) | 100.7(8) | Ru(7)–H(7,11)–B(11) | 100.9(9) |
| B(9)–H(9,10)–B(10) | 86.5(8) | | |

* Horizontal rows comprise angles that would be equal if the molecule conformed to the mirror-plane symmetry [through Ru(7)C(5)C(8)-H(9,10)B(1)B(5)] to which it approximates.

4.1°)[4,10–12] whereas in the known polymethylarene cobalta- and ferra-boranes the deviation is *towards* the metal atom.[13]

The Ru–B distances of 224.8(6)—235.5(6) pm are towards the middle of the ranges for previously reported ruthenaboranes,[3,14–17] *viz.* 203.0(11)—251.7(9) pm, although there are only few data for comparison. The somewhat longer (by *ca.* 10 pm) distances in the open face are also as observed[3] for the large variety of structurally characterized *nido*-7-metallaundecaboranes that have only two bridging hydrogen atoms [as in structure (**I**)]. The dihedral angle between the planes Ru(7)B(8)B(11) and B(8)B(9)B(10)B(11) is relatively flat at 14.7°. The B–B distances within the cluster [173.1(8)—181.6(8) pm] are within normal polyhedral ranges, but those in the open face are somewhat longer, the hydrogen bridged B(9)–B(10) being 186.2(8) pm and the two unbridged distances B(8)–B(9) and B(10)–B(11) averaging 191.4(8) pm. This last distance is similar to the corresponding distance[18] of 188.1(8) pm in *arachno*-$[B_{10}H_{14}]^{2-}$, consistent with the conclusion that the $B_{10}$ unit has *arachno*-decaboranyl character (see also n.m.r. discussion below).

The presence of three bridging hydrogen atoms in the open face is noteworthy as this configuration is rare.[3–6] It is analogous to that presumed for the binary analogue $[B_{11}H_{14}]^-$, for which the bridging hydrogen atoms have not been located by crystallography, and this lends additional support to the conclusion[4] that this latter anion has a conventional (*styx* 3730) triply-bridged structure rather than a delocalized '$\mu$-$H_3$ triangle' type of behaviour as previously postulated.[19,20] This structural analogy also shows that in cluster terms the neutral $(\eta^6\text{-}C_6Me_6)Ru$ moiety contributes three orbitals and two electrons to the cluster-bonding scheme, just like neutral BH, and the structure is therefore entirely in accord with the Wade–Williams[21–24] cluster-geometry electron-counting rules. Overall, the metallaborane anion can be regarded as an 18-electron octahedral ruthenium(II) complex, or as a *conjuncto* cluster compound comprising a *nido* seven-vertex cluster and a *nido* 11-vertex cluster conjoined at the common metal atom.

The n.m.r. properties of the metallaborane cluster (Table 3) are consistent with the solid-state structure, thereby confirming the identity of the selected crystal with the bulk sample. Selective $^1H$-$\{^{11}B\}$ spectroscopy shows that each boron atom has an *exo*-terminal hydrogen atom associated with it and that, in addition, there is a single high-field proton resonance of relative intensity 3 H attributable to the three bridging hydrogen atoms undergoing mutual exchange. In contrast to the behaviour of the rhodium, molybdenum, and tungsten analogues,[4,6] but in accord with that of $[B_{11}H_{14}]^-$,[19,20] cooling the sample to low temperatures [*ca.* 183 K in $(CD_3)_2CO$ solution at

**Table 3.** Measured n.m.r. data for the $[7\text{-}(\eta^6\text{-}C_6Me_6)\text{-}\textit{nido}\text{-}7\text{-}RuB_{10}H_{13}]^-$ anion in $[Ru(NCMe)_6][7\text{-}(\eta^6\text{-}C_6Me_6)\text{-}\textit{nido}\text{-}7\text{-}RuB_{10}H_{13}]_2$; saturated solution in $CD_3CN$ at ambient temperature

| Tentative assignment[a] | $\delta(^{11}B)$/p.p.m.[b] | $[^{11}B\text{–}^{11}B]$ COSY correlations[c] | $^1J(^{11}B\text{–}^1H)$/Hz[d] | $\delta(^1H)$/p.p.m.[e] |
|---|---|---|---|---|
| 1 | −17.2 (1 B) | (2,3)s, (4,6)s | 131 | +1.07 (1 H) |
| 2,3 | −0.8 (2 B) | (1)s, (4,6)m, (5)vw?, (8,11)s | 127 | +1.44 (2 H) |
| 4,6 | −7.2 (2 B) | (1)s, (2,3)m, (5)m, (8,11)s, (9,10)s | 131 | +1.97 (2 H) |
| 5 | −22.8 (1 B) | (4,6)m, (9.10)s | 132 ± 15[f] | +1.2 (1 H) |
| 8,11 | −23.8 (2 B) | (2,3)s, (4,6)s, (9,10)w? | 124 ± 15[f] | +0.50 (2 H) |
| 9,10 | −17.7 (2 B) | (4,6)s, (5)s, (8,11)w? | 139 | +1.2 (2 H) |
| Bridge | | | *g* | −8.75 (3 H)[h] |
| $C_6Me_6$ | | | | +2.12 (18 H) |

[a] Based on $^1H\text{-}\{^{11}B(\text{selective})\}$ spectroscopy (see footnotes *e* and *g*) and $[^{11}B\text{–}^{11}B]$ COSY correlations. [b] ±0.5 p.p.m. to low field (high frequency) of $BF_3(OEt_2)$ in $CDCl_3$. [c] Obtained with $\{^1H(\text{broad-band noise})\}$ decoupling; COSY-45 sequence at 293 K; s, m, w, and vw indicate strong, medium, weak, and very weak observed correlations. [d] ±8 Hz unless otherwise indicated; measured from $^{11}B$ spectrum with resolution enhancement to achieve baseline separation of doublet components. [e] ±0.05 p.p.m. to low field (high frequency) of $SiMe_4$; proton resonances related to directly bound boron positions by $^1H\text{-}\{^{11}B(\text{selective})\}$ spectroscopy. [f] Uncertainty arises from overlap of $^{11}B(5)$ and $^{11}B(8,11)$ resonances. [g] Not measurable under experimental conditions used. [h] Proton resonance sharpened (markedly) by irradiation at $\nu[^{11}B(8,11)]$ and (somewhat) by $\nu[^{11}B(9,10)]$, but *not* by $\nu[^{11}B(2,3)]$ or $\nu[^{11}B(4,6)]$ in $^1H\text{-}\{^{11}B(\text{selective})\}$ experiments; assigned to (rapidly exchanging) $^1H(7,8; 8,11)$ and $^1H(9,10)$; no separation, or incipient separation, observed in $(CD_3)_2CO$ solution at 183 K (9.4 T).

2.35 T] did not arrest this fluxionality on the n.m.r. time-scale. Estimates of $\delta(^1H)$ for the Ru–H–B and B–H–B hydrogen atoms, based on analogous 11-vertex metallaundecaboranes[4,6] and other Ru–H–B bridged species[15,25] are *ca.* −6 and −9 p.p.m. respectively, implying an upper limit to the activation energy $\Delta G_{183}^{\ddagger}$ for the fluxional process of *ca.* 34 kJ mol$^{-1}$ (*cf. ca.* 35 and *ca.* 60 kJ mol$^{-1}$ for analogous rhodaborane[4] and wolfraborane[6] species respectively). In a process not necessarily related to this, the presence of only one proton resonance position for the methyl groups of the $\eta^6\text{-}C_6Me_6$ ligand shows that there is rapid rotation of the arene about its six-fold axis in solution. This may be contrasted to the behaviour of those transition-metal *nido*-7-metallaundecaboranes which have only two bridging hydrogen atoms and which are often fluxional *via* what is regarded as an effective rotation of the effective tetrahapto borane ligand.[3,26–30]

In n.m.r. experiments, the selective sharpening of the bridging proton resonance observed during $^1H\text{-}\{^{11}B\}$ spectroscopy upon irradiation of the two highest-field (lowest frequency) $^{11}B$ resonances of relative intensity 2 B established these as arising from the B(8,11) and B(9,10) atoms in the open face. Relative intensities in the $^{11}B$ spectrum combined with the off-diagonal correlations observed in two-dimensional $[^{11}B\text{–}^{11}B]\text{-}\{^1H(\text{broad-band noise})\}$ COSY experiments[31–33] thence permitted the assignment of resonances to the positions listed in Table 3.

Two further aspects of the n.m.r. behaviour merit mention. First, there is a general parallel between $\delta(^{11}B)$ and $\delta(^1H)$ for the *exo* B–H groupings in the metallaborane anion, as is generally observed in polyhedral boron compounds,[34,35] although the close distribution of the $^{11}B$ resonances (+12 ± 12 p.p.m.), combined with the expected minor deviations [*e.g.* of up to *ca.* 0.7 p.p.m. in $\delta(^1H)$] from the correlation, renders the parallel only approximate in this case. Furthermore, any anisotropic effect of the $CD_3CN$ solvent (required for adequate solubility) would serve additionally to confuse a more detailed interpretation. Secondly, it is apparent that the magnitudes and the orderings of the $^{11}B$ chemical shifts [*e.g.* $^{11}B(4,6)$ at lower field, $^{11}B(1)$, $^{11}B(5)$, and $^{11}B(8,11)$ at higher field] are similar to those[35,36] in the starting *arachno*-$[B_{10}H_{14}]^{2-}$ substrate, which indicates again that the overall *arachno* character is retained throughout the $B_{10}$ unit in the metallaborane cluster (see also geometric considerations discussed above). This tendency is to be compared with the behaviour of doubly-bridged *nido*-7-metallaundecaboranes in which any tendency towards *arachno* character is thought to be more localized in the metal-to-borane interface[3,4,27] so that a tendency to *nido*-decaboranyl character is shown by those parts of the cluster that are not adjacent to the metal atom.

## Experimental

*General.*—Reactions were carried out under an atmosphere of dry nitrogen using dried and degassed solvents. Subsequent manipulations and separations were carried out in air. $[\{Ru(\eta^6\text{-}C_6Me_6)Cl_2\}_2]$ was prepared according to the published method.[37] $[NEt_4]_2[\textit{arachno}\text{-}B_{10}H_{14}]$ was prepared from $B_{10}H_{14}$, $NaBH_4$, and $NEt_4OH$ in water essentially according to the procedure described for $Cs_2[B_{10}H_{14}]$.[38] Preparative t.l.c. was carried out using 1-mm layers of silica (Kieselgel GF54; Fluka) on glass plates of dimensions 200 × 200 mm; these were prepared as required from an acetone slurry, followed by drying in air at *ca.* 80 °C.

*Preparation of* $[Ru(NCMe)_6][7\text{-}(\eta^6\text{-}C_6Me_6)\text{-}\textit{nido}\text{-}7\text{-}RuB_{10}H_{13}]_2$.—$[\{Ru(\eta^6\text{-}C_6Me_6)Cl_2\}_2]$ (50 mg, 0.075 mmol) was added to a solution of $[NEt_4]_2[B_{10}H_{14}]$ (81 mg, 0.30 mmol) in MeCN (40 cm$^3$) and the resulting mixture stirred under nitrogen at room temperature for 3 h, during which time its colour changed from red to yellow. The solvent was removed under reduced pressure, and the solid residue extracted with $CH_2Cl_2$ (10 cm$^3$) and filtered over silica with MeCN to remove chromatographically immobile components. The solvent was reduced to a volume of *ca.* 5 cm$^3$ under reduced pressure and the product purified by t.l.c. using MeCN–$CH_2Cl_2$ (1:1) as the liquid phase. The yellow product eluted as the major band ($R_f$ *ca.* 0.65) and was identified as described above (yield 48 mg, 86%). A crystal suitable for a single-crystal *X*-ray diffraction analysis was obtained by slow evaporation from $CD_3CN$. $^{11}B$ N.m.r. spectroscopy on the reaction mixtures and on some of the partially purified minor reaction products suggested that some of these were also ruthenaborane species, but most were unstable under the separatory conditions used. One of the more stable was tentatively identified as a *closo*-1-ruthenaundecaborane of the $[(\eta^6\text{-}C_6Me_6)RuB_{10}H_{10}]$-based family and another, which was less stable, was possibly a 10-vertex *nido*-ruthenadecaborane species.

*Single-crystal X-Ray Diffraction Analysis.*—All crystallographic measurements were made on a Nicolet P3/F diffractometer operating in the ω–2θ scan mode using graphite-

**Table 4.** Atomic co-ordinates ($\times 10^4$)[a] for $[Ru(NCMe)_6][7-(\eta^6-C_6Me_6)$-*nido*-$7-RuB_{10}H_{13}]_2$

| Atom | *x* | *y* | *z* |
|---|---|---|---|
| Ru(1) | 5 000[b] | 0[b] | 0[b] |
| Ru(7) | 3 936.0(3) | 2 625.9(3) | 3 445.8(2) |
| N(1) | 5 914(4) | 2 057(4) | 386(2) |
| C(11) | 6 503(5) | 3 198(4) | 590(2) |
| C(12) | 7 316(5) | 4 699(4) | 862(3) |
| N(2) | 3 828(4) | 631(4) | −1 070(2) |
| C(21) | 3 152(5) | 949(4) | −1 663(3) |
| C(22) | 2 297(5) | 1 378(5) | −2 479(3) |
| N(3) | 6 980(4) | 604(4) | −471(2) |
| C(31) | 8 108(6) | 983(5) | −695(3) |
| C(32) | 9 588(6) | 1 499(6) | −1 011(3) |
| C(4) | 5 742(5) | 1 700(5) | 3 582(3) |
| C(5) | 4 258(5) | 551(4) | 3 606(3) |
| C(6) | 3 344(4) | 494(4) | 4 174(3) |
| C(7) | 4 000(5) | 1 620(5) | 4 728(3) |
| C(8) | 5 559(5) | 2 756(5) | 4 698(3) |
| C(9) | 6 394(4) | 2 791(4) | 4 119(3) |
| C(10) | 6 691(6) | 1 740(6) | 2 956(4) |
| C(11) | 3 554(7) | −670(5) | 3 000(4) |
| C(12) | 1 676(6) | −781(6) | 4 200(5) |
| C(13) | 3 078(7) | 1 617(7) | 5 349(3) |
| C(14) | 6 329(7) | 3 975(6) | 5 315(4) |
| C(15) | 8 064(5) | 4 030(6) | 4 088(5) |
| B(1) | 1 773(5) | 2 942(5) | 1 441(3) |
| B(2) | 1 753(4) | 1 892(4) | 2 407(3) |
| B(3) | 3 641(5) | 2 950(5) | 2 061(3) |
| B(4) | 3 506(5) | 4 627(5) | 1 552(3) |
| B(5) | 1 618(5) | 4 632(5) | 1 532(3) |
| B(6) | 572(4) | 2 956(4) | 2 089(3) |
| B(8) | 4 781(5) | 4 696(5) | 2 525(3) |
| B(9) | 3 378(5) | 5 700(5) | 2 223(3) |
| B(10) | 1 428(5) | 4 600(5) | 2 562(3) |
| B(11) | 1 404(5) | 2 768(5) | 3 133(3) |
| H(1) | 1 215(9) | 2 362(9) | 815(9) |
| H(2) | 1 088(9) | 622(9) | 2 408(9) |
| H(3) | 4 169(9) | 2 492(9) | 1 772(9) |
| H(4) | 4 234(9) | 5 181(9) | 1 050(9) |
| H(5) | 871(9) | 5 216(9) | 1 038(9) |
| H(6) | −754(9) | 2 526(9) | 1 996(9) |
| H(8) | 6 019(9) | 5 355(9) | 2 480(9) |
| H(9) | 3 905(9) | 7 018(9) | 2 122(9) |
| H(10) | 715(9) | 5 166(9) | 2 701(9) |
| H(11) | 558(9) | 2 080(9) | 3 606(9) |
| H(7,8) | 4 563(9) | 4 588(9) | 3 198(8) |
| H(7,11) | 2 704(9) | 3 471(9) | 3 588(9) |
| H(9,10) | 3 121(9) | 5 366(9) | 2 945(9) |

[a] Non-borane H-atom co-ordinates available as supplementary data.
[b] Co-ordinate fixed on special position.

monochromated Mo-$K_\alpha$ ($\lambda = 71.069$ pm) radiation and following a standard procedure described elsewhere in detail.[39] The data were corrected for absorption empirically after the structure had been solved.[40]

The structure was determined *via* heavy-atom methods and refined by full-matrix least squares using the SHELX program system.[41] All non-hydrogen atoms were refined with anisotropic thermal parameters. All methyl hydrogens were included in calculated positions and assigned to an overall isotropic thermal parameter for each ion. The boron-attached hydrogens were all located in subsequent Fourier difference maps and were 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 the refinement with the parameter $g$ included to give a flat analysis of variance with increasing sinθ and $(F/F_{max.})^{\frac{1}{2}}$. Non-hydrogen atomic co-ordinates and borane-hydrogen atomic co-ordinates are given in Table 4.

*Crystal data.* $C_{36}H_{80}B_{20}N_6Ru_3$, $M = 1\,116.53$, triclinic, $a = 937.6(2)$, $b = 1\,005.5(2)$, $c = 1\,679.2(3)$ pm, $\alpha = 79.73(1)$, $\beta = 105.24(2)$, $\gamma = 115.59(2)°$, $U = 3.639$ nm$^3$, space group $P\bar{1}$, $Z = 1$, $D_c = 1.35$ g cm$^{-3}$, $\mu(\text{Mo-}K_\alpha) = 7.57$ cm$^{-1}$, $F(000) = 572$, and $T = 290$ K.

*Data collection.* Scans from 1° below $K_{\alpha 1}$ to 1° above $K_{\alpha 2}$, scan speeds 2.0—29.3° min$^{-1}$, $4.0 \leqslant 2\theta \leqslant 45.0°$, 3 522 unique data, 3 439 observed $[I > 2.0\sigma(I)]$.

*Structure refinement.* Number of parameters 376, weighting factor $g = 0.0004$, $R = 0.0341$, $R' = 0.0387$.

*N.M.R. Spectroscopy.*—Experiments at 2.35 and 9.40 T were carried out on commercially available instruments. The $[^{11}B-^{11}B]$ COSY experiment[31–33] was performed at 128 MHz (9.40 T) with a 45° mixing pulse (4.2 μs in the instrumental configuration used) and with 512 and 64 words of data in the $t_2$ and $t_1$ dimensions respectively: 128 transients were collected for each of the 64 $t_1$ values (recycling delay time 50 ms), giving a total acquisition time of *ca.* 15 min. Uninterrupted $\{^1H$(broad-band noise)$\}$ decoupling was applied throughout. The time-domain matrix was multiplied by a sine-bell-squared function and zero-filled ×4 in the $t_1$ dimension prior to Fourier transformation; the frequency-domain matrix was symmetrized along its F1 = F2 diagonal. The selective $^1H-\{^{11}B\}$ technique has been described elsewhere,[42–46] use being made of the procedure in which the $^1H-\{^{11}B$(off-resonance)$\}$ spectrum is subtracted from the $^1H-\{^{11}B$(on-resonance)$\}$ spectrum in order to remove lines arising from protons which are not coupled to the $^{11}B$ nucleus of interest.[44,47] Other n.m.r. spectroscopy was straightforward, chemical shifts $\delta(^1H)$ and $\delta(^{11}B)$ being given in p.p.m. to high frequency (low field) of Ξ 100 (nominally internal $SiMe_4$) and 32.083 971 MHz [nominally $BF_3(OEt_2)$ in $CDCl_3$],[35] respectively.

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## References

1 R. N. Grimes, in 'Comprehensive Organometallic Chemistry,' eds. G. Wilkinson, F. G. A. Stone, and E. Abel, Pergamon, Oxford, 1982, Part 1, ch. 5.5, pp. 459—542.

2 N. N. Greenwood and J. D. Kennedy, in 'Metal Interactions with Boron Clusters,' ed. R. N. Grimes, Plenum Press, New York, 1982, ch. 2, p. 43; N. N. Greenwood, *Pure Appl. Chem.*, 1983, **55**, 1415.

3 J. D. Kennedy, *Prog. Inorg. Chem.*, 1984, **32**, 519; 1986, **34**, 211 and refs. therein.

4 X. L. R. Fontaine, H. Fowkes, N. N. Greenwood, J. D. Kennedy, and M. Thornton-Pett, *J. Chem. Soc., Chem. Commun.*, 1985, 1165; *J. Chem. Soc., Dalton Trans.*, in the press.

5 R. N. Leyden, B. P. Sullivan, R. T. Baker, and M. F. Hawthorne, *J. Am. Chem. Soc.*, 1978, **100**, 3758.

6 I. Macpherson, unpublished observations, University of Leeds, 1984—1986; X. L. R. Fontaine, N. N. Greenwood, J. D. Kennedy, I. Macpherson, and M. Thornton-Pett, unpublished work.

7 M. Bown, N. N. Greenwood, and J. D. Kennedy, *J. Organomet. Chem.*, 1986, **309**, C67.

8 G. Fergusson, M. F. Hawthorne, B. Kaitner, and F. J. Lalor, *Acta Crystallogr., Sect. C*, 1984, **40**, 1707.

9 J. L. Templeton, *J. Am. Chem. Soc.*, 1979, **101**, 4906.

10 X. L. R. Fontaine, H. Fowkes, N. N. Greenwood, J. D. Kennedy, and M. Thornton-Pett, *J. Chem. Soc., Dalton Trans.*, 1986, 547.

11 X. L. R. Fontaine, H. Fowkes, N. N. Greenwood, J. D. Kennedy, and M. Thornton-Pett, *J. Chem. Soc., Dalton Trans.*, in the press.

12 X. L. R. Fontaine, N. N. Greenwood, J. D. Kennedy, P. MacKinnon, and M. Thornton-Pett, *J. Chem. Soc., Chem. Commun.*, 1986, 1111.

13 See, for example, J. J. Briguglio, and L. G. Sneddon, *Organometallics*, 1986, **5**, 327 and refs. therein.

14 J. E. Crook, M. Elrington, N. N. Greenwood, J. D. Kennedy, M. Thornton-Pett, and J. D. Woollins, *J. Chem. Soc., Dalton Trans.*, 1985, 2407.

15 N. N. Greenwood, J. D. Kennedy, M. Thornton-Pett, and J. D. Woollins, *J. Chem. Soc., Dalton Trans.*, 1985, 2397.

16 M. Elrington, N. N. Greenwood, J. D. Kennedy, and M. Thornton-Pett, *J. Chem. Soc., Chem. Commun.*, 1984, 1398.

17 M. Elrington, N. N. Greenwood, J. D. Kennedy, and M. Thornton-Pett, *J. Chem. Soc., Dalton Trans.*, 1987, 451.

18 D. S. Kendall and W. N. Lipscomb, *Inorg. Chem.*, 1973, **12**, 546.

19 E. B. Moore, L. L. Lohr, and W. N. Lipscomb, *J. Chem. Phys.*, 1961, **35**, 1329.

20 L. Barton, in 'Topics of Current Chemistry—100: New Trends in Chemistry,' ed. F. L. Boschke, Springer, Berlin, 1982, pp. 169—206 and refs. therein.

21 R. E. Williams, *Inorg. Chem.*, 1971, **10**, 210.

22 K. Wade, *Chem. Commun.*, 1971, 792.

23 R. E. Williams, *Adv. Inorg. Chem. Radiochem.*, 1976, **18**, 67.

24 K. Wade, *Adv. Inorg. Chem. Radiochem.*, 1976, **18**, 1.

25 M. Bown and X. L. R. Fontaine, unpublished work, University of Leeds 1984—1986.

26 S. K. Boocock, N. N. Greenwood, and J. D. Kennedy, *J. Chem. Soc., Chem. Commun.*, 1980, 305.

27 S. K. Boocock, N. N. Greenwood, J. D. Kennedy, W. S. McDonald, and J. Staves, *J. Chem. Soc., Dalton Trans.*, 1981, 2573.

28 J. E. Crook, N. N. Greenwood, J. D. Kennedy, and W. S. McDonald, *J. Chem. Soc., Dalton Trans.*, 1984, 2487.

29 J. E. Crook, Ph.D. Thesis, University of Leeds, 1982.

30 R. Ahmad, N. N. Greenwood, and J. D. Kennedy, unpublished work; R. Ahmad, Ph.D. Thesis, University of Leeds, 1983.

31 I. J. Colquhoun and W. McFarlane, findings communicated to the First and Third National Meetings of British Inorganic Boron Chemists, INTRABORON I, Strathclyde, May 1980, and INTRABORON III, Leeds, September 1982.

32 T. L. Venable, W. C. Hutton, and R. N. Grimes, *J. Am. Chem. Soc.*, 1982, **104**, 4716; 1984, **106**, 29.

33 D. Reed, *J. Chem. Res. S*, 1984, 198.

34 G. R. Eaton and W. N. Lipscomb, 'N.M.R. Studies of Boron Hydrides and Related Compounds,' Benjamin, New York, 1969.

35 J. D. Kennedy, in 'Multinuclear N.M.R.,' ed. J. Mason, Plenum Press, London, ch. 8, in the press.

36 R. R. Rietz, A. R. Siedle, R. O. Schaeffer, and L. J. Todd, *Inorg. Chem.*, 1973, **12**, 2100.

37 M. A. Bennett, T. N. Huang, T. W. Matheson, and A. K. Smith, *Inorg. Synth.*, 1982, **21**, 75.

38 E. L. Muetterties, *Inorg. Chem.*, 1963, **2**, 647.

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

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

41 G. M. Sheldrick, SHELX 76, program system for *X*-ray structure determination, University of Cambridge, 1976.

42 J. D. Kennedy and B. Wrackmeyer, *J. Magn. Reson.*, 1980, **38**, 529.

43 J. D. Kennedy and N. N. Greenwood, *Inorg. Chim. Acta*, 1980, **38**, 93.

44 S. K. Boocock, N. N. Greenwood, M. J. Hails, J. D. Kennedy, and W. S. McDonald, *J. Chem. Soc., Dalton Trans.*, 1981, 1415.

45 S. K. Boocock, J. Bould, N. N. Greenwood, J. D. Kennedy, and W. S. McDonald, *J. Chem. Soc., Dalton Trans.*, 1982, 713.

46 J. Bould, N. N. Greenwood, J. D. Kennedy, and W. S. McDonald, *J. Chem. Soc., Dalton Trans.*, 1985, 1843.

47 J. D. Kennedy and J. Staves, *Z. Naturforsch., Teil B*, 1979, **34**, 808.

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