

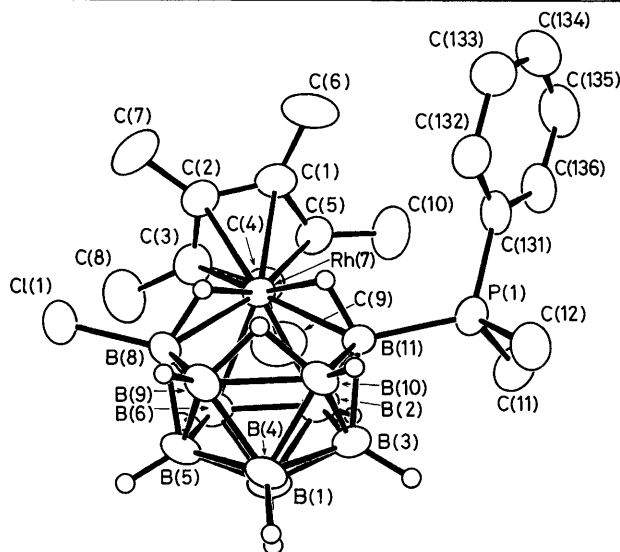
## Preparation and Structure of [7-( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)-8-Cl-11-(PMe<sub>2</sub>Ph)-*nido*-7-RhB<sub>10</sub>H<sub>11</sub>],<sup>†</sup> a Metallaborane Analogue of the Fluxional Borane Anion *nido*-B<sub>11</sub>H<sub>14</sub><sup>-</sup>

Xavier L. R. Fontaine, Hayat Fowkes, Norman N. Greenwood, John D. Kennedy, and Mark Thornton-Pett

Department of Inorganic and Structural Chemistry, University of Leeds, Leeds LS2 9JT, U.K.

[(C<sub>5</sub>Me<sub>5</sub>)RhB<sub>10</sub>H<sub>11</sub>Cl(PMe<sub>2</sub>Ph)] has a novel type of *nido*-7-metallaundecaborane structure which uniquely has one B–H–B and two M–H–B bridging H atoms rather than the usual two B–H–B bridging H atoms: these three H<sub>μ</sub> mutually exchange ( $\Delta G^\ddagger$  ca. 33 kJ mol<sup>-1</sup>) and this, together with the crystallographically determined molecular structure, suggests that the parent borane *nido*-B<sub>11</sub>H<sub>14</sub><sup>-</sup> has a conventional B–H–B bridge *styx* 3730 structure rather than one with an H<sub>3</sub><sup>+</sup> triangle perpendicular to the molecular axis.

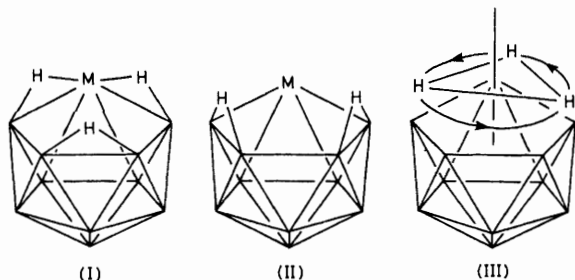
Reaction of *arachno*-[B<sub>10</sub>H<sub>12</sub>(PMe<sub>2</sub>Ph)<sub>2</sub>] with [(C<sub>5</sub>Me<sub>5</sub>)RhCl<sub>2</sub>]<sub>2</sub> in benzene for 1 hour at 60 °C results in a 25% yield of the orange, air-stable eleven-vertex *nido*-compound [(C<sub>5</sub>Me<sub>5</sub>)RhB<sub>10</sub>H<sub>11</sub>Cl(PMe<sub>2</sub>Ph)] (idealized equation 1). The compound crystallizes from methylene chloride as the 1:1 solvate and the molecular structure of the eleven-vertex rhodaborane (Figure 1), as determined by X-ray diffraction, shows a *nido*-7-metallaundecaborane configuration that has three bridging hydrogen atoms at B(9)B(10), Rh(7)B(8), and Rh(7)B(11) [schematic cluster configuration (I)]. This configuration of 3H<sub>μ</sub> is novel and contrasts with all other known transition metal *nido*-7-metallaundecaboranes, which have two B–H<sub>μ</sub>–B bridging hydrogen atoms at B(8)B(9) and B(10)B(11) [configuration (II)]. The considerably different cluster <sup>11</sup>B nuclear shielding properties<sup>‡</sup> indicate that the electronic structures within the



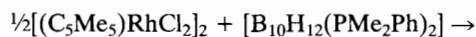
**Figure 1.** Drawing of the molecular structure of [(C<sub>5</sub>Me<sub>5</sub>)Rh<sub>10</sub>H<sub>11</sub>Cl(PMe<sub>2</sub>Ph)] with organyl hydrogen atoms omitted for clarity. Distances from Rh(7) are: to B(2) 225.2(7), to B(3) 222.1(7), to B(8) 231.0(7), and to B(11) 243.0(7) pm; B(9)–B(10) 187.8(9), B(11)–P(1) 194.8(7), B(8)–Cl(1) 186.2(7) pm. *Crystal data* for 7-(C<sub>5</sub>Me<sub>5</sub>)-8-Cl-11-(PMe<sub>2</sub>Ph)-*nido*-7-RhB<sub>10</sub>H<sub>11</sub> · CH<sub>2</sub>Cl<sub>2</sub>: *M* = 616.03, monoclinic, space group *P*2<sub>1</sub>/*n* (= *P*2<sub>1</sub>/*c*, no. 14), *a* = 1520.4(2), *b* = 1228.3(3), *c* = 1622.3(2) pm,  $\beta$  = 102.24(1)°, *U* = 2.9365 nm<sup>3</sup>, *Z* = 4, *D*<sub>c</sub> = 1.393 g cm<sup>-3</sup>, *F*(000) = 1240,  $\mu$ (Mo-*K*<sub>α</sub>) = 7.55 cm<sup>-1</sup>. The structure was solved by heavy atom methods and refined to *R* = 0.0388, *R*<sub>w</sub> = 0.0432 by full matrix least-squares. 4334 Reflections were measured on a Syntex *P*<sub>2</sub> diffractometer with Mo-*K*<sub>α</sub> radiation, and 3727 with *I* > 2.0σ(*I*) were used in refinement.

<sup>†</sup> 7-Pentamethylcyclopentadienyl-8-chloro-11-dimethylphenylphosphine-*nido*-7-rhodaundecaborane. The atomic co-ordinates for this compound are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

<sup>‡</sup> Values of  $\delta$ (<sup>11</sup>B)/p.p.m. for [(C<sub>5</sub>Me<sub>5</sub>)RhB<sub>10</sub>H<sub>11</sub>Cl(PMe<sub>2</sub>Ph)] (assigned from substituent positions and homonuclear <sup>11</sup>B COSY spectroscopy allied with heteronuclear <sup>1</sup>H{<sup>11</sup>B} selective and homonuclear <sup>1</sup>H COSY spectroscopy) compared with the corresponding values (in parentheses) for [(PMe<sub>2</sub>Ph)<sub>2</sub>PtB<sub>10</sub>H<sub>11</sub>-8-Cl]<sup>1</sup> as a typical example are: B(1) -17.0(+1.2), B(2) +2.5(+22.1), B(3) +14.2(+5.0), B(4) +1.7(-21.2), B(5) -18.5(+12.9), B(6) -9.5(-30.7), B(8) -5.6(+19.5), B(9) -13.2(-7.4), B(10) -16.9(-0.8), and B(11) -29.2(+4.4) [ $\delta$ (<sup>11</sup>B) with respect to BF<sub>3</sub> · OEt<sub>2</sub> taken as standard].



two cluster types also differ substantially. Proton magnetic resonance spectroscopy shows that the rhodaborane is fluxional with respect to non-dissociative exchange among these three bridging hydrogen sites with  $\Delta G^\ddagger$  ca. 33 kJ mol<sup>-1</sup> at -104 °C.<sup>§</sup>



Since  $\{(C_5Me_5)Rh\}$  and  $\{(PMe_2Ph)B\}$  are isolobal and isoelectronic in cluster terms with  $\{BH\}$  and  $\{BH^-\}$  respec-

§ In the <sup>1</sup>H n.m.r. spectrum, the H<sub>u</sub> resonance occurs at  $\delta(^1H) -6.70$  (3H; 21 °C, CD<sub>2</sub>Cl<sub>2</sub> solution), but on cooling this separates (coalescence temperature -104 °C at 400 MHz) to give an incipient 1:2 pattern with  $\delta(^1H) -6.47$  (1H) and  $-7.29$  (2H) (CD<sub>2</sub>Cl<sub>2</sub> at -112 °C); i.e.  $\Delta G^\ddagger$  ca. 33 kJ mol<sup>-1</sup> at -104 °C.

tively, the metallaborane is a direct analogue of the well-known *nido*-undecaborane anion B<sub>11</sub>H<sub>14</sub><sup>-</sup>. This anion is also fluxional,<sup>2</sup> but is generally held<sup>3,4</sup> to have a structure in which the three hydrogen atoms form a rotating H<sub>3</sub><sup>+</sup> triangle perpendicular to the fivefold axis of the eleven-vertex icosahedral fragment [schematic structure (III)]. The crystallographic location of the bridging hydrogen atoms in  $[(C_5Me_5)RhB_{10}H_{11}Cl(PMe_2Ph)]$ , together with their fluxionality in solution, now suggest that B<sub>11</sub>H<sub>14</sub><sup>-</sup> may also have the more straightforward triply-bridged structure of *styx* 3730 topology [structure (I), M = BH]. Although (III) could represent a transition state in the fluxionality, this is more likely to be one of *styx* 281 topology.<sup>5</sup>

We thank the S.E.R.C. for support.

Received, 6th June 1985; Com. 788

## References

- 1 J. E. Crook, N. N. Greenwood, J. D. Kennedy, and W. S. McDonald, *J. Chem. Soc., Dalton Trans.*, 1984, 2487.
- 2 V. D. Aftandilian, H. C. Miller, G. W. Parshall, and E. L. Muetterties, *Inorg. Chem.*, 1962, **1**, 734.
- 3 E. B. Moore, L. L. Lohr, and W. N. Lipscomb, *J. Chem. Phys.*, 1961, **35**, 1329.
- 4 L. Barton, in 'Topics of Current Chemistry—100. New Trends in Chemistry,' ed. F. L. Boschke, Springer, Berlin, Heidelberg, and New York, 1982, pp. 169—206.
- 5 W. N. Lipscomb, 'Boron Hydrides,' W. A. Benjamin, New York, 1963, p. 47.