Identification of the *endo,exo* Isomer of 6,9-$(PMe_2Ph)_2$-*arachno*-$B_{10}H_{12}$ by Nuclear Magnetic Resonance Spectroscopy

Xavier L. R. Fontaine and John D. Kennedy
School of Chemistry, University of Leeds, Leeds LS2 9JT

Reaction of PMe_2Ph with *nido*-$B_{10}H_{14}$ results in the formation of the previously unsuspected *endo,exo* isomer of *arachno*-$B_{10}H_{12}(PMe_2Ph)_2$ (*ca.* 85%) admixed with the expected *exo,exo* isomer (*ca.* 15%). Mild heating converts the *endo,exo* isomer into the *exo,exo* one. The mixture is readily analysed by multiple resonance and difference n.m.r. spectroscopy.

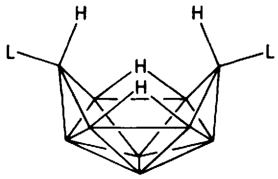
The *arachno* bis(ligand) decaborane compounds $B_{10}H_{12}L_2$, where L = NCR, SR_2, PR_3, *etc.*, are generally believed to have the 6,9-*exo,exo*-bis(ligand) configuration (I),[1,2] as established by single-crystal *X*-ray diffraction analysis for the bis(dimethyl sulphide) and bis(acetonitrile) compounds $B_{10}H_{12}(SMe_2)_2$ and $B_{10}H_{12}(NCMe)_2$.[3,4] It has recently been shown that the related *arachno* anion $[B_{10}H_{12}(PPh_2)]^-$ has a bridged structure [schematic configuration (II)][5,6] which effectively has the bidentate ligand PPh_2^- bound 6,9-*endo,endo* to the open decaboranyl cluster. This anion has long been recognized to be a species of particular stability,[7–9] and although contributions to this stability will arise from the (Lewis-acid) chelating ability of the neutral $B_{10}H_{12}$ fragment of ten-vertex *arachno* geometry,[6] it suggests that *endo,endo* and *endo,exo* isomers of $B_{10}H_{12}L_2$ [schematic configurations (III) and (IV) respectively] may also be stable providing that any steric interactions above the open face are not too severe. In this context we now report that the reaction of PMe_2Ph with $B_{10}H_{14}$, according to equation (1), in CD_2Cl_2 solution at <0 °C does in fact result in the initial formation of *endo,exo*-6,9-$(PMe_2Ph)_2$-*arachno*-$B_{10}H_{12}$ (*ca.* 85%) admixed with much smaller quantities (*ca.* 15%) of the symmetrical *exo,exo*-6,9 isomer.

$$B_{10}H_{14} + 2PMe_2Ph \longrightarrow B_{10}H_{12}(PMe_2Ph)_2 + H_2 \quad (1)$$

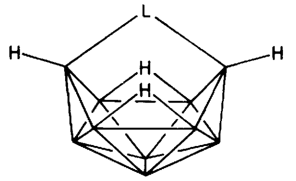
Results and Discussion

Addition of PMe_2Ph to a solution of *nido*-$B_{10}H_{14}$ in CD_2Cl_2 solution at *ca.* 200 K, followed by a slow warming to room temperature, resulted in the evolution of a colourless gas, presumably dihydrogen. The ^{11}B n.m.r. spectrum of the colourless solution [*e.g.* Figure 1(*b*)] showed that it contained two boron-containing compounds. Integrated n.m.r. spectroscopy [together with the subsequent identification (see below)] showed that these compounds were present in a molar ratio of 84:16, with only trace quantities of other boron-containing species being present. Interestingly, a similar product ratio was obtained when a sample of *exo,exo*-6,9-$(SMe_2)_2B_{10}H_{12}$ was treated with PMe_2Ph in CD_2Cl_2 solution [equation (2)]. In this case, however, the reaction occurred more slowly, being only *ca.* 50% complete after 24 h at *ca.* 293 K.

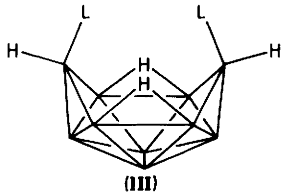
$$B_{10}H_{12}(SMe_2)_2 + 2PMe_2Ph \longrightarrow B_{10}H_{12}(PMe_2Ph)_2 + 2SMe_2 \quad (2)$$



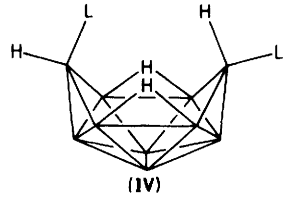
(I)



(II)



(III)



(IV)

Inspection of the ^{11}B n.m.r. spectrum of the product suggested that the minor component [compound (**1**)] was the expected *exo,exo*-6,9 isomer of $B_{10}H_{12}(PMe_2Ph)_2$ [configuration (I)]. This conclusion was also consistent with the results of selective ^1H-$\{^{11}B\}$ n.m.r. spectroscopy which related the observed ^1H resonances to their directly bound boron positions as summarized in the Table. Subtraction of the ^{11}B spectrum of a pure sample of compound (**1**) from that of the mixture (Figure 1) then more clearly revealed the ^{11}B spectrum of the major component [compound (**2**)]. These data for compound (**2**) are also summarised in the Table, together with the corresponding ^1H n.m.r. data which were again established by ^1H-$\{^{11}B\}$ spectroscopy. The Table also presents data for the *endo,endo* anionic species $[B_{10}H_{12}(PPh_2)]^-$ (**3**), configuration (II), for comparison.

The similarity of the ^{11}B and ^1H nuclear shielding patterns (Figure 2) suggests that the borane clusters of compounds (**1**)—(**3**) have closely related structures. In particular, the intermediacy of the n.m.r. properties of the new compound (**2**) compared to those of compounds (**1**) and (**3**) indicates that the detailed character of its structure is also intermediate. The 1:1:2:2:1:1:2 ^{11}B intensity pattern shows that compound (**2**) has effective mirror-plane symmetry, rather than the C_{2v} symmetry of the other two species, and the retention of ^{31}P coupling to $^{11}B(6)$ and $^{11}B(9)$ [these resonances being distinguished from those of $^{11}B(1,3)$ by the relative sharpness[10] of the latter] shows that it still retains PMe_2Ph ligands directly bound to B(6) and B(9). These considerations suggest the *endo,exo*-6,9 configuration (IV) for the phosphine ligands in compound (**2**).

This structure is confirmed by the comparative $^1H(6)$ and $^1H(9)$ shielding behaviour among the three species. For the *exo,exo* compound (**1**) the *endo*-6,9 proton resonance is some 2 p.p.m. above the approximately linear (^{11}B, ^1H) shielding-correlation plot for boron atoms and their directly bound *exo*-

Table. Measured n.m.r. parameters for *exo,exo*-6,9-$(PMe_2Ph)_2B_{10}H_{12}$ (**1**), *endo,exo*-6,9-$(PMe_2Ph)_2B_{10}H_{12}$ (**2**), and [*endo,endo*-μ(6,9)-(PPh_2)-$B_{10}H_{12}]^-$ (**3**) at +21 °C

	Compound (**2**)^{a}			Compound (**1**)^{a}			Compound (**3**)^{b}	
Assignment	$\delta(^{11}B)$/p.p.m.	$^{1}J(^{11}B-^{1}H)^{c}$/Hz	$\delta(^{1}H)^{d}$/p.p.m.	$\delta(^{11}B)$/p.p.m.	$^{1}J(^{11}B-^{1}H)^{c}$/Hz	$\delta(^{1}H)^{d}$/p.p.m.	$\delta(^{11}B)$/p.p.m.	$\delta(^{1}H)^{d}$/p.p.m.
2,4	+7.4 (1 B) +1.2 (1 B)	143 134	+3.09 (1 H)^{e} +2.37 (1 H)^{h}	−3.0 (2 B)	131	+2.24 (2 H)^{f}	+6.4 (2 B)	+2.50 (2 H)^{g}
5,7,8,10	−14.4 (2 B) −18.4 (2 B)	138 140	+1.76 (2 H) +1.65 (2 H) −4.91 (2 H)^{i}	−19.0 (4 B)	133	+1.65 (4 H), −4.16 (2 H)^{j}	−7.9 (4 B)	+1.95 (4 H), −4.19 (2 H)^{k}
6 9	−29.3 (1 B)^{l} *ca.* −34.5 (1 B)^{o}	114 *o*	+1.01 (1 H)(*exo*)^{j} −1.41 (1 H)(*endo*)^{j}	−35.2 (2 B)^{m}	114	−0.94 (2 H) (*endo*)^{i}	−26.8 (2 B)^{n}	+0.77 (2 H) (*exo*)
1,3	*ca.* −34.5 (2 B)	145	+0.85 (2 H)	−38.8 (2 B)	141	+0.59 (2 H)	−26.9 (2 B)	+0.98 (2 H)

[a] In $CDCl_3$ solution at +21 °C, this work. [b] In $(CD_3)_2CO$ solution, data from ref. 5. [c] ±8 Hz; measured from ^{11}B spectrum with line narrowing to achieve baseline separation of doublet components. [d] $\delta(^{1}H)$ related to directly bound B atoms by $^{1}H-\{^{11}B(selective)\}$ spectroscopy; fine structure in ^{1}H spectra (footnotes *e*—*i* and *k*) is observed under conditions of complete $\{^{11}B$(broad-band noise)$\}$ decoupling. [e] Doublet, $^{3}J(^{31}P-^{1}H)$ *ca.* 25 Hz. [f] Doublet, $^{3}J(^{31}P-^{1}H)$ *ca.* 24 Hz. [g] Doublet, $^{3}J(^{31}P-^{1}H)$ *ca.* 18 Hz. [h] Doublet, $^{3}J(^{31}P-^{1}H)$ *ca.* 28 Hz. [i] Possible doublet, $^{3}J(^{31}P-^{1}H)$ *ca.* 7 Hz. [j] No doublet structure observed, *i.e.* $^{3}J(^{31}P-^{1}H)$ < *ca.* 5 Hz. [k] Doublet, $^{3}J(^{31}P-^{1}H)$ *ca.* 52 Hz. [l] $^{1}J(^{31}P-^{11}B)$(*endo*) *ca.* 120 Hz. [m] $^{1}J(^{31}P-^{11}B)$(*exo*) *ca.* 105 Hz. [n] $^{1}J(^{31}P-^{11}B)$(*endo*) 97 Hz. [o] $^{1}J(^{31}P-^{11}B)$(*exo*) and $^{1}J(^{11}B-^{1}H)$(*endo*) both very approximately 100 Hz; not measurable more accurately due to overlap with $^{11}B(1,3)$ in the same compound and $^{11}B(6,9)$ of the *exo,exo* isomer.

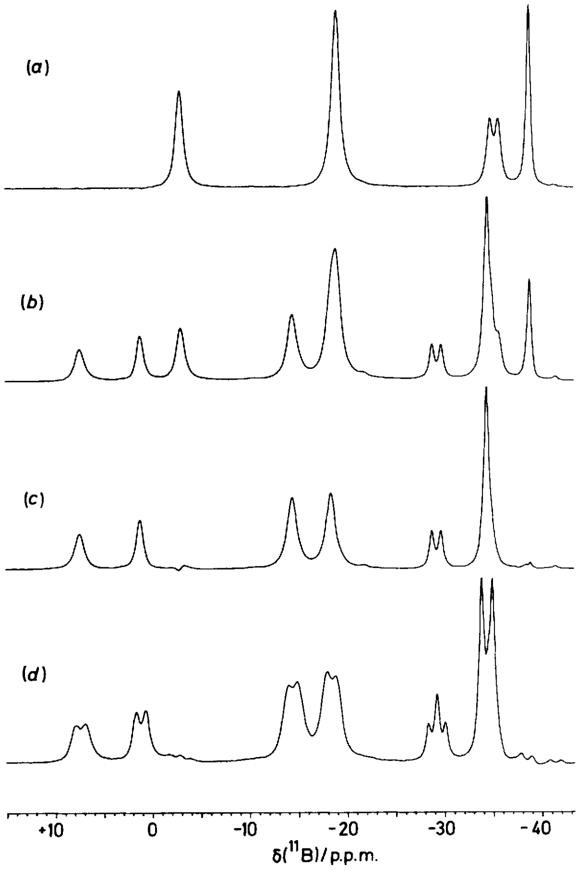


Figure 1. 128-MHz ^{11}B N.m.r. spectra of isomers of $B_{10}H_{12}(PMe_2Ph)_2$ in $CD_3C_6D_5$ solution at 294 K. Trace (*a*) shows the $^{11}B-\{^{1}H$(broad-band noise)$\}$ spectrum of the *exo,exo* isomer (**1**) [obtained by thermal isomerization of the mixture which gave trace (*b*)], and trace (*b*) shows the $^{11}B-\{^{1}H$(broad-band noise)$\}$ spectrum of a mixture of the *exo,exo* and *endo,exo* isomers (**1**) and (**2**) respectively. Trace (*c*) is a weighted subtraction of spectrum (*a*) from (*b*), and trace (*d*) is a similar subtraction of the equivalent ^{11}B spectra recorded without $\{^{1}H\}$ decoupling. Traces (*c*) and (*d*) respectively therefore represent the $^{11}B-\{^{1}H$-(broad-band noise)$\}$ and ^{11}B spectra of the *endo,exo* isomer (**2**)

hydrogen atoms (Figure 2, top). This is a diagnostic of *endo*-terminal hydrogen character.[11] For the *endo,endo* species (**3**) the *exo*-6,9 proton resonances lie close to the correlation plot, as expected from their *exo* nature. The *endo,exo*-6,9-bis(phosphine) compound (**2**), however, with a corresponding *exo,endo*-6,9-proton configuration, has one proton of each type.

A definitive precise spectroscopic assignment at the 2,4 and 5,7,8,10 positions in compound (**2**) is not possible on present evidence, although consideration of the shielding trends among compounds (**1**)—(**3**) suggests that $^{11}B(2)$ adjacent to the *endo*-phosphine-substituted vertex designated B(6) resonates at δ +7.4 p.p.m. and that the $^{11}B(5,7)$ resonance similarly is that at δ −14.4 p.p.m. In principle, precise assignments for the polyhedral borane species may be obtained by two-dimensional $[^{11}B-^{11}B]$-COSY[11—14] n.m.r., but in practice the resonance lines for the mixture of compounds (**1**) and (**2**) were so broadened by rapid ^{11}B relaxation that no correlations could be observed at ambient temperatures. Higher temperatures are often used to increase ^{11}B relaxation times and thus render $^{11}B-^{11}B$ cross-correlations more observable,[11,15—17] but in this case the *endo,exo* isomer (**2**) was found to be insufficiently thermally robust, and heating in $CD_3C_6D_5$ solution for a few minutes resulted in conversion into the symmetrical *exo,exo* isomer (**1**). The lack of robustness has so far precluded the mutual separation of these two isomers. They have very similar solubility and chromatographic properties, and there is a slow conversion of the asymmetric species (**2**) into the symmetric species (**1**) under the separatory conditions that we have previously found satisfactory for systems of this nature.

Experimental

Sample preparations were carried out under dry nitrogen by the addition of stoicheiometric quantities of PMe_2Ph [equation (1), scale *ca.* 10 mmol in *ca.* 0.5 cm^3 solvent] to solutions of $B_{10}H_{14}$ or $B_{10}H_{12}(SMe_2)_2$ in CD_2Cl_2 or $CD_3C_6D_5$ at *ca.* 203 K, followed by slow warming to room temperature. N.m.r. spectroscopy was carried out in the Fourier-transform mode at 2.35 and 9.40 T using commercially available instrumentation. $^{1}H-\{^{11}B\}$ N.m.r. spectroscopy at 2.35 T used a JEOL FX-100 instrument equipped with a $^{1}H-\{^{1}H\}$ probe in which the formal $\{^{1}H\}$-irradiation system had been tuned to accept the ^{11}B resonance frequency (32 MHz). That at 9.40 T used a Bruker AM-400 instrument equipped with a $^{11}B-\{^{1}H\}$ probehead that

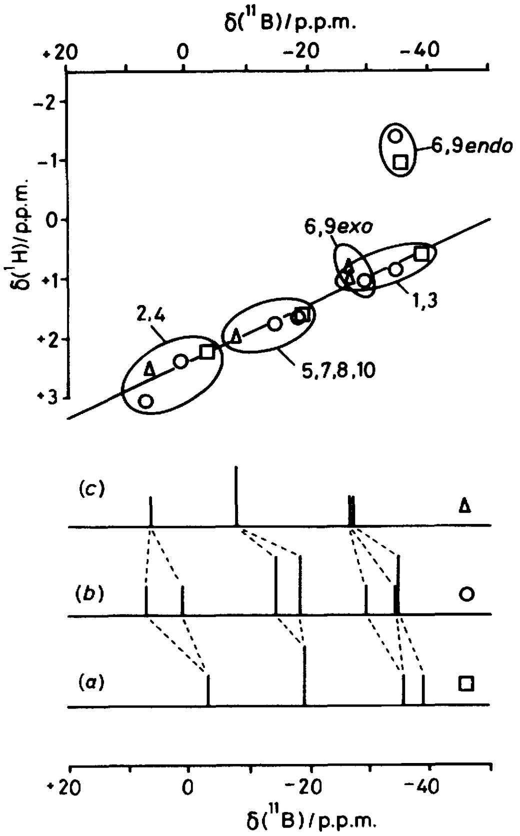


Figure 2. (*a*)—(*c*) Stick representations of the chemical shifts and relative intensities in the ^{11}B n.m.r. spectra of compounds (**1**) (*exo,exo*), (**2**) (*endo,exo*), and (**3**) (*endo,endo*), respectively, which illustrate the intermediate behaviour of (**2**). The upper diagram is a plot of δ(^{1}H) *versus* δ(^{11}B) for directly bound atoms in compounds (**1**) (□), (**2**) (○), and (**3**) (△); the line drawn has gradient δ(^{1}H)/δ(^{11}B) = 1/21

was used inversely: ^{1}H observation (400 MHz) was effected *via* the 'irradiation' coils and {^{11}B} decoupling (128 MHz) *via* the 'observation' coils. In both cases $\gamma B_2(^{11}\mathrm{B})/2\pi$ (γ = magnetogyric ratio, B_2 = irradiating field strength) for the selective decoupling experiments was *ca.* 300 Hz [estimated using residual splittings in ^{1}H-{^{11}B(off-resonance)} experiments on NaBH$_4$ solutions].[18] The indicated irradiation power in the AM-400 configuration under these conditions was about 0.15 W (Bird Thruline 43 Wattmeter), although precise adjustment of the power level was not critical in the experiments reported here. The n.m.r. spectroscopy was otherwise routine; ^{11}B chemical shifts are given to lower field (higher frequency) of Ξ 32.083 971 MHz [nominally BF$_3$(OEt$_2$) in CDCl$_3$],[11] measured using residual solvent-proton resonances as internal secondary standards relative to those of SiMe$_4$ (Ξ 100 MHz).

Acknowledgements

We thank the S.E.R.C. for support, Professor N. N. Greenwood for encouragement and facilities, and Dr. H. Fowkes for some technical assistance.

References

1 S. G. Shore, in 'Boron Hydride Chemistry,' ed. E. L. Muetterties, Academic Press, New York, 1976, ch. 3, pp. 136—141, and refs. therein.
2 L. Barton, T. Onak, R. J. Remmell, and S. G. Shore, in 'Borverbinding-Teil 20,' Gmelin Handbuch der Anorganischen Chemie, New Supplement Series, vol. 54, eds. K. Niedenzu and K-C. Buschbeck, Springer, Berlin, Heidelberg, and New York, 1979, pp. 151—165, and refs. therein.
3 J. Reddy and W. N. Lipscomb, *J. Chem. Phys.*, 1959, **31**, 610, 754.
4 D. E. Sands and A. Zalkin, *Acta Crystallogr.*, 1962, **15**, 410.
5 M. A. Beckett and J. D. Kennedy, *J. Chem. Soc., Chem. Commun.*, 1983, 575.
6 M. Thornton-Pett, M. A. Beckett, and J. D. Kennedy, *J. Chem. Soc., Dalton Trans.*, 1986, 303.
7 E. L. Muetterties and V. D. Aftandilian, *Inorg. Chem.*, 1962, **1**, 731.
8 H. Schroeder, *Inorg. Chem.*, 1963, **2**, 390.
9 C. B. Friedman and S. L. Perry, *Inorg. Chem.*, 1973, **12**, 288.
10 C. Naar-Colin and T. L. Heying, *Inorg. Chem.*, 1963, **2**, 659.
11 J. D. Kennedy, in 'Multinuclear NMR,' ed. J. Mason, Plenum, London and New York, ch. 8, in the press.
12 T L. Venable, W. C. Hutton, and R. N. Grimes, *J. Am. Chem. Soc.*, 1984, **106**, 29.
13 D. Reed, *J. Chem. Res.*, 1984, (*S*) 198.
14 I. J. Colquhoun and W. McFarlane, First and Third National Meetings of British Inorganic Boron Chemists, INTRABORON I, Strathclyde, May 1980; INTRABORON III, Leeds, September 1982.
15 M. A. Beckett, J. E. Crook, N. N. Greenwood, and J. D. Kennedy, *J. Chem. Soc., Dalton Trans.*, 1986, 1879.
16 X. L. R. Fontaine and J. D. Kennedy, *J. Chem. Soc., Chem. Commun.*, 1986, 779.
17 X. L. R. Fontaine, H. Fowkes, N. N. Greenwood, J. D. Kennedy, and M. Thornton-Pett, *J. Chem. Soc., Dalton Trans.*, 1987, 1431; *ibid.*, in the press.
18 T. C. Gibb and J. D. Kennedy, *J. Chem. Soc., Faraday Trans. 2*, 1982, 525.

Received 5*th August* 1986; *Paper* 6/1604