

An N.M.R. Study of the *arachno*-[B₁₀H₁₂PPh₂]⁻ Anion: an Interesting *arachno* → *arachno* Topological Transition induced by Deprotonation

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The compound [B₁₀H₁₃PPh₂] is remarkably acidic: n.m.r. studies now show that its conjugate base [B₁₀H₁₂PPh₂]⁻ derives its stability from an *arachno*-decaboranyl cluster structure with, uniquely, a bridging {Ph₂P} moiety between the B(6) and B(9) positions.

In the eleven-vertex cluster compound *arachno*-[B₁₀H₁₃PPh₂], two cluster bonding electron pairs are localized in two direct two-electron two-centre phosphorus-boron linkages at B(5) and B(6) and the structure resembles that of a *nido*-decaborane species (structure A).¹ It is a surprisingly strong protic acid, the conjugate base [B₁₀H₁₂PPh₂]⁻ being remarkably stable towards reprotonation.² The reason for this strong acidity has long remained puzzling,¹⁻³ even though it has been generally presumed that the anion also retains the *nido*-decaboranyl configuration.^{4,5} We now show by n.m.r. spectroscopy that the deprotonation is in fact accompanied by a substantial topological transformation to give an *arachno*-decaboranyl sub-cluster structure with, uniquely, the {Ph₂P} moiety bridging the B(6) and B(9) positions (structure B).

Selected ¹H, ¹¹B, and ³¹P n.m.r. properties of the neutral species and the anion are summarized in Table 1. Those of the neutral compound [B₁₀H₁₃PPh₂] are similar to those of an

asymmetrically substituted *nido*-decaboranyl cluster,^{2,3} and are thus in accord with the molecular, and proposed electronic, structures.¹ Upon deprotonation, there is a dramatic change: there is an inversion of the ordering of the resonance positions, together with an overall increase of *ca.* 9 p.p.m. in

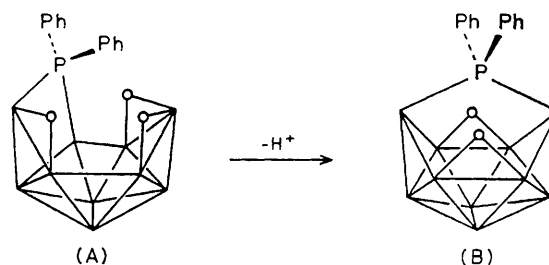


Table 1. Selected n.m.r. parameters for [B₁₀H₁₃PPh₂] and its conjugate base [B₁₀H₁₂PPh₂]⁻.

Assignment ^e	[B ₁₀ H ₁₃ PPh ₂] ^{a, b}		[B ₁₀ H ₁₂ PPh ₂] ^{- c, d}		
	δ(¹¹ B) ^f	δ(¹ H) ^g	δ(¹¹ B) ^f	δ(¹ H) ^g	Relative intensity
1,3	+14.2, +5.0	+4.23, +3.29	-26.9	+0.98	2
9	+9.0	+2.98	-26.8 ^h	+0.77	2
6	+2.7 ^h	+3.52			
7,8,10	+4.3, +3.1, +1.8	+3.43, +2.72, +2.83	-7.9	+1.95	4
5	-10.2 ^j	+2.80	+6.4	+2.50 ^k	2
2,4	-31.3, -36.4	+0.80, +0.63		-4.19 ^l	2
Bridge		-2.30, -2.60, -3.33			2

^a In CDCl₃ at +21 °C. ^b δ(³¹P) *ca.* -55 p.p.m. (relative to 85% H₃PO₄). ^c [C₁₀H₈(NMe₂)(NMe₂H)]⁺ salt in (CD₃)₂CO at 21 °C. ^d δ(³¹P) *ca.* +33 p.p.m. (rel. 85% H₃PO₄). ^e *nido*-B₁₀H₁₄ numbering convention used throughout. ^f In p.p.m. relative to BF₃·OEt₂ (15% in CDCl₃). ^g In p.p.m. relative to SiMe₄; terminal ¹H resonances assigned to corresponding boron positions by selective ¹H-¹¹B experiments (ref. 7). ^h ¹J(³¹P-¹¹B) *ca.* 145 Hz. ⁱJ(³¹P-¹¹B) *ca.* 97 Hz. ^jJ(³¹P-¹¹B) *ca.* 88 Hz. ^kJ(³¹P-H)(*transoid*) 17.7 Hz. ^lJ(³¹P-¹¹H)(*cisoid*) 51.2 Hz.

the average boron nuclear shielding, $\sigma(^{11}\text{B})$. This is diagnostic of a ten-vertex *nido* \rightarrow *arachno* transition. In addition the ^{11}B and ^1H n.m.r. spectra are considerably simplified, and the 2:4:2:2 intensity ratios for the ^{11}B resonances of the anion indicate a decaboranyl cluster with effective C_{2v} symmetry. In particular, the overall pattern is very similar to that⁶ of the C_{2v} *arachno*- $\text{B}_{10}\text{H}_{14}^{2-}$ anion, except that in the phosphine compound the $^{11}\text{B}(6,9)$ nuclei are less shielded (by ca. 10 p.p.m.) and also exhibit coupling to ^{31}P , with $J(^{31}\text{P}-^{11}\text{B})$ ca. 97 Hz. The magnitude of this coupling is consistent with a direct phosphorus-boron bond.

The structure of the anion $[\text{B}_{10}\text{H}_{12}\text{PPh}_2]^-$ is thus reasonably formulated as that of an *arachno*- $\text{B}_{10}\text{H}_{14}^{2-}$ cluster in which the two formal *endo*-terminal hydride ions at B(6) and B(9) are notionally replaced by two two-electron bonds to a bridging $\{\text{Ph}_2\text{P}\}^-$ moiety (structure B). It is novel in that a decaborane species which has a one-atom bridge between the B(6) and B(9) positions has not previously been substantiated.

In view of the uniquely strong acidity of the neutral conjugate $[\text{B}_{10}\text{H}_{13}\text{PPh}_2]$, the bridged structure appears to be a particularly stable one, and this bridged structural type may therefore have significance in a number of other reaction processes. For example, a species $[\text{B}_{10}\text{H}_{12}\text{SMe}_2]$, of unknown structure, but isoelectronic in cluster terms with $[\text{B}_{10}\text{H}_{12}\text{PPh}_2]^-$, has been postulated from kinetic evidence to be a key intermediate in the synthesis of the dicarbadodecaboranes $\text{RC}_2\text{B}_{10}\text{H}_{11}$ from $[\text{B}_{10}\text{H}_{12}(\text{SMe}_2)_2]$ and $\text{RC}\equiv\text{CH}$.⁵ With the present system we have found that, although $[\text{B}_{10}\text{H}_{13}\text{PPh}_2]$ itself

reacts readily with selected monosubstituted acetylenes, the anion $[\text{B}_{10}\text{H}_{12}\text{PPh}_2]^-$ is much less reactive, and the major product is often the *arachno* nine-vertex compound $[\text{B}_9\text{H}_{13}\text{PPh}_2]$ rather than the appropriate carborane species. We hope to report more fully on aspects of this system in the future.

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