Selective Syntheses of Bipentaboranes: $1,2'-(B_5H_8)_2$ and $2,2'-(B_5H_8)_2$

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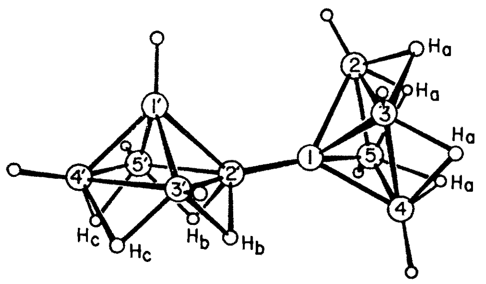
Summary The Friedel–Crafts catalysed reaction of 2-Br-B_5H_8 with B_5H_9 produces $1,2'-(B_5H_8)_2$, whereas metathesis of KB_5H_8 with $2-BrB_5H_8$ produces $2,2'-(B_5H_8)_2$.

Though the $1,1'-(B_5H_8)_2$,[1] $1,2'-(B_5H_8)_2$,[2] and $2,2'-(B_5H_8)_2$[2–4] isomers have been characterized, no viable synthetic routes to these compounds have been reported. This has resulted in severely limited systematic chemical studies of these compounds. As part of our study of rational borane cluster syntheses we report here two reaction pathways that allow discrete coupling of pentaborane(9) molecular units to form selectively $1,2'-(B_5H_8)_2$ or $2,2'-(B_5H_8)_2$.

The selective synthesis of $1,2'-(B_5H_8)_2$ is accomplished by the Friedel–Crafts catalysed reaction of $2-BrB_5H_8$ with B_5H_9. Typically 9·0 mmol of $2-BrB_5H_8$[5] and a 10 fold excess of B_5H_9 are heated in the presence of catalytic amounts of freshly prepared $AlBr_3$ and excess of Al foil at 65 °C for 4 days in a 1 l flask (equation 1). The $1,2-(B_5H_8)_2$,

$$B_5H_9 + 2\text{-}BrB_5H_8 \xrightarrow{AlBr_3(cat)} 1,2'\text{-}(B_5H_8)_2 + HBr \qquad (1)$$

isolated by high vacuum fractional condensation at −30 °C in yields of 20%, was characterized by ^1H and ^{11}B n.m.r., i.r., and high resolution mass spectroscopy.[2] Its ^1H n.m.r. spectrum contains quartet resonances assigned to H(3′–5′), δ 2·62 (*J* 160 Hz); H(2–5) δ 2·28 (164); H(1′), δ 1·16 (169), and broad overlapping singlet resonances assigned to H_b and H_c at δ −2·12 and −2·43 and H_a at δ −2·70. This Friedel–Crafts catalysed coupling of borane polyhedral units is apparently unprecedented.



$1,2'-(B_5H_8)_2$ numbering scheme

The metathesis reaction of KB_5H_8[6] with $2-BrB_5H_8$ to yield selectively $2,2'-(B_5H_8)_2$ may be an example of a broadly applicable reaction. In a typical reaction, a slurry of 8 mmol of KB_5H_8 and an excess of $2-BrB_5H_8$ in *ca.* 30 ml of pentane were rapidly stirred and warmed from −78 °C to room temperature (equation 2). The 2,2′-$(B_5H_8)_2$, purified

$$KB_5H_8 + 2\text{-}BrB_5H_8 \rightarrow 2,2'\text{-}(B_5H_8)_2 + KBr \quad (2)$$

by fractional condensation at −30 °C, is typically obtained in 35% yield based on KB_5H_8. Its ^{11}B n.m.r., i.r., and high resolution mass spectra are identical with those reported previously.[2]

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