

Direct Evidence for N→B π -Donation into a Polyhedral Borane Cluster

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The nitrogen atom of [1-(η^5 -C₅Me₅)-4-(NEt₂)-*isocloso*-1-RhB₁₀H₉] is planar, the N(4)–B(4) bond is short, and there is restricted rotation about this bond (ΔG^\ddagger_{272} ca. 54 kJ mol⁻¹), all implying significant N–B π -donation into the cluster.

Reaction between Et₂NH and the orange-yellow eleven-vertex *isocloso* metallaborane [1-(η^5 -C₅Me₅)-1-RhB₁₀H₁₀][†] in CH₂Cl₂ solution at room temperature for 1.5 h yields, *inter alia*, its dark purple air-stable 4-(NEt₂)-substituted derivative [1-(η^5 -C₅Me₅)-4-(NEt₂)-1-RhB₁₀H₉] in 66% yield. A single crystal X-ray diffraction analysis (Figure 1)[†] reveals an

[†] Crystal data: C₁₄H₃₄B₁₀NRh, *M* = 427.45, monoclinic, space group *P*2₁/*n*, *a* = 982.1(2), *b* = 1378.2(3), *c* = 1650.8(3) pm, β = 99.09(2)°, *U* = 2.2063(8) nm³, *Z* = 4, *D*_c = 1.29 g cm⁻³, *F*(000) = 880, μ = 6.91 cm⁻¹. *R* = 0.0435, *R*_w = 0.0470, for refinement of 294 parameters using 3423 unique absorption-corrected reflections with *F* > 4.0 σ (*F*) and 4.0 ≤ 2 θ ≤ 50.0°.

All crystallographic measurements were made on a Nicolet P3/F diffractometer using graphite monochromated Mo-*K*_α radiation (λ = 71.069 pm) operating in the ω -2 θ scan mode. The structure was solved by heavy atom methods and refined by full-matrix least-squares. All non-hydrogen atoms refined with anisotropic thermal parameters; methyl and methylene hydrogen atoms were included in calculated positions with fixed isotropic thermal parameters while the borane hydrogen atoms were located experimentally and were freely refined with individual isotropic thermal parameters. The weighting scheme $w = [\sigma^2(F_o) + 0.000125(F_o)^2]^{-1}$ was used at the end of refinement. Atomic co-ordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

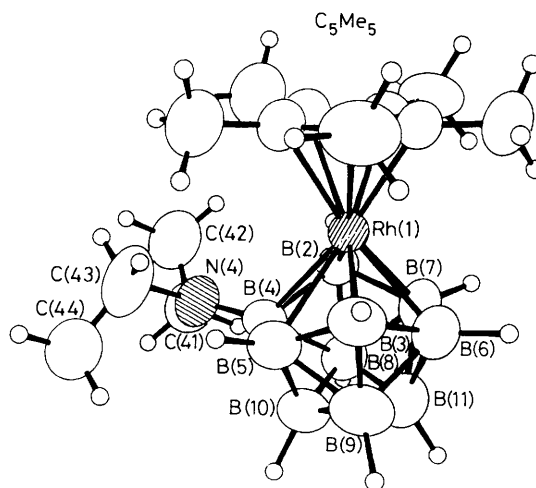


Figure 1. Drawing of the molecular structure of [1-(η^5 -C₅Me₅)-4-(NEt₂)-1-RhB₁₀H₉]. Distances from Rh(1) are: to B(2) 209.0(7), B(3) 208.4(8), B(4) 246.1(7), B(5) 227.6(8), B(6) 227.7(8), and B(7) 234.1(8) pm. Distances from B(4) are: to N(4) 142.7(8), B(2) 181.3(9), B(7) 172.0(10), B(8) 183.8(9), and B(10) 179.3(10) pm. Angles are C(41)–N(4)–C(43) 114.4(5), C(41)–N(4)–B(4) 125.2(5), and C(43)–N(4)–B(4) 120.2(5)°.

essentially planar nitrogen atom [sum of angles at N(4) 359.8°; deviation of N from the plane of attached atoms B(4)C(41)C(43) 4 pm]. Moreover, the B(4)–N(4) interatomic distance is short [142.7(8) pm, compared with the usual 'single-bond' distance of *ca.* 158 pm], and variable temperature proton n.m.r. spectroscopy shows that the barrier to 180° rotation about the B–N linkage is 53.8 ± 0.5 kJ mol⁻¹ at 272 K. We believe that all three observations directly indicate substantial N–B π -donation into the cluster. Further indirect manifestations of the N=B bonding are: (a) the lengthening, towards an *isonido* structure, of the Rh(1)–B(4) distance [to 246.1(7) pm compared to 227.6(8) and 227.7(8) pm for the Rh(1)–B(5) and Rh(1)–B(6) distances respectively], and (b) the slight tilting of the η^5 -C₅ plane away from B(4), the dihedral angle between η^5 -C₅ and B(4)B(5)N(6)B(7) being 5°.

Proton n.m.r. spectroscopy also reveals a barrier to rotation for the 6-(NEt₂) group in the ten-vertex *isocloso* analogue [1-(η^5 -C₅Me₅)-2,6-(NEt₂)₂-1-RhB₉H₇], with ΔG^\ddagger_{278} *ca.* 56 kJ mol⁻¹, but we have yet to confirm by X-ray diffraction analysis whether this is also accompanied by N-atom planarity and/or partial cluster opening.

The planarity of the three-co-ordinate N(4) atom, the short B–N distance, and restricted rotation about B(4)–N(4) observed in the sterically unconstricted compound [1-(η^5 -C₅Me₅)-4-(NEt₂)-1-RhB₁₀H₉] together constitute, so far as we are aware, the first direct evidence for *exo*-element → boron π -donation in a borane cluster compound. Although this partial double bonding has sometimes been invoked in the past to account for particular observed cluster phenomena such as spectroscopic properties, chemical reactivities, or partial cluster opening (as is also observed here), the evidence has previously been circumstantial and direct criteria invariably lacking.

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Reference

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