

Tuneable reduction of cymantrenylboranes to diborenes or borylenes

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

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Whereas the reduction of N-heterocyclic carbene (NHC)-stabilised cymantrenyldibromoboranes, (NHC)BBR₂Cym, in benzene results in formation of the corresponding diborenes (NHC)₂B₂Cym₂, a change of solvent to THF yields a borylene of the form (NHC)₂BCym, stabilised through its boratafulvene resonance form.

Since the isolation of the first metal-free boron(I) compounds, Robinson's diborene (NHC)₂B₂H₂ (NHC = N-heterocyclic carbene)¹ and Bertrand's borylene (CAAC)₂BH (CAAC = cyclic (alkyl)(amino)carbene),² the targeted synthesis of low-oxidation-state boron compounds has greatly advanced.³ The most straightforward route to organoboron(I) compounds proceeds via the twofold reduction of a Lewis-base-stabilised dihaloborane precursor of the form LBX₂Y (L = Lewis base; X = halide or triflate; Y = anionic substituent, e.g. hydride, halide, (hetero)aryl, alkyl or amino group). The outcome of these reactions is essentially dependent on the electronic nature of L and the combined steric profile of L and Y. If the latter are too bulky, the reduction of LBX₂Y tends to lead to intramolecular C–H or C–C bond activation by an intermediate dicoordinate borylene, [LBY] (Fig. 1a).⁴ Conversely, if the intermediate borylene [LBY] is sufficiently kinetically stable, the boron coordination sphere not excessively crowded, and L is a pure σ donor, [LBY] tends to dimerise to yield a doubly base-stabilised diborene of the form L₂B₂Y₂ (Fig. 1b). Thus, the reduction of aryl-, heteroaryl- and alkyl dihaloboranes stabilised by relatively small NHCs leads to the formation of the corresponding diborenes,⁵ while the reduction of trihaloboranes stabilised by large NHCs may yield dihydrodiborenes through additional radical hydrogen abstraction.^{1,6} If L, however, is a π -accepting Lewis base, e.g. CAAC⁷ or oxazol-2-ylidene,⁸ the intermediate [LBY] is stabilised by π backdonation of the lone pair at boron into the empty p orbital of L (Fig. 1c). Moreover, if Y is an electron-donating substituent, e.g. an amine, additional π donation into the empty p orbital at boron affords a stable dicoordinate borylene (Fig. 1d).⁹ Finally, if Y is not an electron donor, the [LBY] intermediate can be stabilised by adduct formation with a second Lewis base, L'. The latter may be added from the outset to the reduction mixture,^{5a,10} present as a pendant

donor within the precursor itself,¹¹ or scavenged from another [LBY] equivalent,² yielding a doubly base-stabilised tricoordinate borylene (Fig. 1e). The reduction of a (CAAC)BBR₂H precursor to the corresponding diborene, (CAAC)₂B₂H₂, rather than the expected borylene, (CAAC)₂BH, marks a rare exception to these rules.¹²

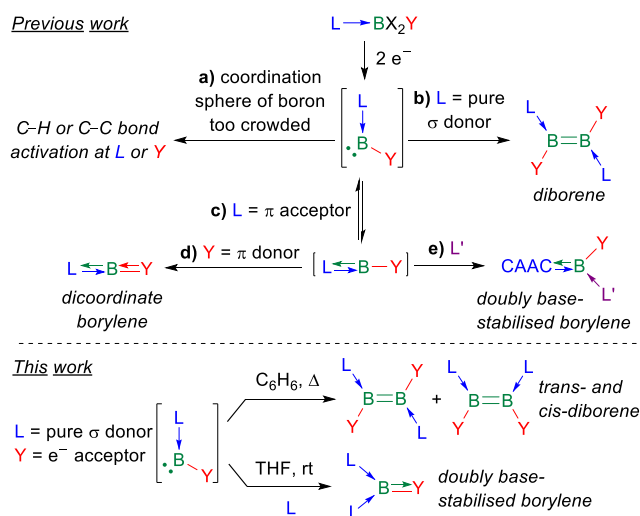


Figure 1. Various outcomes for the reduction of LBX₂Y, depending on the sterics and electronics of L and Y. L, L' = Lewis bases, X = halide or triflate, Y = anionic substituent.

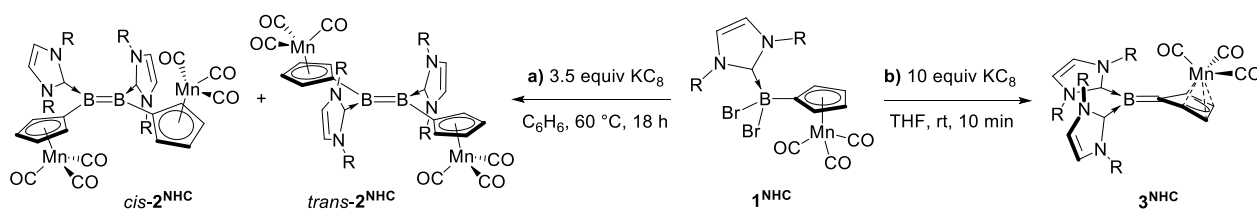
In this contribution we report the first example of a (NHC)BX₂Y precursor (Y = cymantrenyl), which may be reduced selectively either to the corresponding diborene, (NHC)₂B₂Y₂, or the

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† Electronic supplementary information (ESI) available: General experimental details, NMR spectra, details of the DFT calculations and crystallographic data. CCDC 2033095–2033098. For ESI and crystallographic data in CIF or other electronic format see DOI: xxx



Scheme 1. Selective reduction of 1^{NHC} to the corresponding *cis*- and *trans*-diborenes (2^{NHC}) and borylene (3^{NHC}). R = Me: 2^{IMe} *cis/trans* = 1:1; R = *i*Pr: 2^{IPr} *cis/trans* = 1:2.

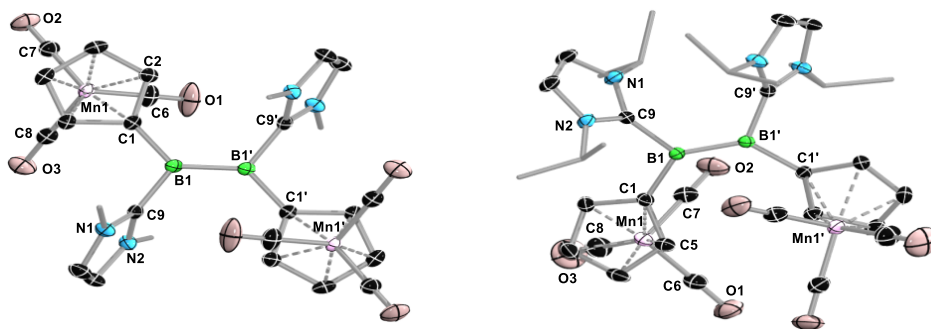


Figure 2. Crystallographically-derived molecular structures of *trans*-2^{IMe} (left) and *cis*-2^{IPr} (right). Atomic displacement ellipsoids at 50% probability. Ellipsoids of ligand periphery and hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (°) for *trans*-2^{IMe}: B1–B1' 1.588(3), B1–C1 1.570(2), B1–C9 1.591(2), Mn⋯Cp_{plane} 1.784, Mn–C_{CO} 1.7845(16)–1.7909(17), ∑∠_{B1} 360.0(2), torsion (C1,B1,B1',C9') 0.8(2), (C2,C1,B1,B1') 6.4(3), (N2,C9,B1,B1') –74.8(2); for *cis*-2^{IPr}: B1–B1' 1.591(6), B1–C1 1.583(4), B1–C9 1.596(4), Mn⋯Cp_{plane} 1.777, Mn–C_{CO} 1.777(3)–1.788(4), ∑∠_{B1} 359.8(2), torsion (C1,B1,B1',C1') –3.3(6), (C9,B1,B1',C9') –14.5(4), (C5,C1,B1,B1') 26.2(6), (N1,C9,B1,B1') 63.7(5).

tricoordinate borylene, (NHC)₂BY, depending on the reduction conditions (Fig. 1, bottom).

The reduction of (NHC)BBr₂Cym (1^{NHC}, NHC = IMe = 1,3-dimethylimidazol-2-ylidene; *i*Pr = 1,3-diisopropylimidazol-2-ylidene; Cym = cymantrenyl = (C₅H₄)Mo(CO)₃) with 3.5 equiv. K_{C₈} in benzene at 60 °C yielded purple suspensions, the work-up of which afforded the purple diborenes (NHC)₂B₂Cym₂ (2^{NHC}) in moderate yields (2^{IMe} 38%; 2^{IPr} 51%, Scheme 1a). The ¹¹B NMR resonance of 2^{NHC} at ca. 19 ppm is significantly upfield-shifted compared to the related dibora[2]ferrocenophane (*i*Pr)₂B₂(μ-Fc) at 28 ppm,^{5e} but similar to the NHC-stabilised dithienyl- and difuryldiborenes (18–22 ppm).^{5d,g} The IR spectra of 2^{NHC} show strong CO stretching bands in the 1880–2000 cm⁻¹ region, while the UV-vis spectra show an absorption maximum at 581 nm accounting for their purple colour. To our surprise, X-ray crystallographic analyses of 2^{IMe} and 2^{IPr} revealed a *trans*- and a *cis*-diborene, respectively.[‡] While the *trans* geometry is prevalent in most known diborenes, the *cis* conformation of an acyclic diborene has only been observed recently in (*i*Pr)₂B₂Ar^F₂ (Ar^F = 3,5-(CF₃)₂C₆H₃).^{5a} Examination of the ¹H NMR spectra of the crude reduction products showed that 2^{IMe} and 2^{IPr} were formed as 1:1 and 2:1 *trans/cis* mixtures, respectively.[†] The relative thermodynamic stability of *cis*- and *trans*-2^{NHC} was examined by density functional theory (DFT) calculations. While *trans*-2^{IPr} is more stable than *cis*-2^{IPr} by 5.0 kcal mol⁻¹ at the PBE¹³-D3¹⁴(BJ)¹⁵ / def2-SVP,def2-TZVP(Mn)¹⁶ level of theory, this energy difference drops down to 3.3 kcal mol⁻¹ for 2^{IMe}. In both cases the two isomers are thus energetically accessible, the calculated energy differences correlating with the experimentally observed ratios. In both diborenes the B–B bond length of ca. 1.59 Å is that of a typical B=B double bond (Fig. 2).[‡] Whereas in *trans*-2^{IMe} the diborene

core and Cp rings are virtually coplanar (torsion (C1,B1,B1',C9') 0.8(2)°), the diborene core of *cis*-2^{IPr} is slightly distorted from planarity (torsion (C9,B1,B1',C9') –14.5(4)°) and not coplanar with the Cp rings (torsion (C5,C1,B1,B1'): 26.2(6)°). These distortions most likely arise from the strong steric repulsion between the two *i*Pr ligands in *cis* conformation.

Besides *cis*- and *trans*-2^{NHC} the NMR spectra of the crude reduction products revealed a minor by-product, 3^{NHC} (ca. 10%, δ(¹¹B) = –13 ppm).[‡] For the reduction of 1^{IPr}, changing the reaction solvent from apolar benzene to polar THF and using 10 equiv. K_{C₈} yielded blue-coloured 3^{IPr} as the sole reaction product (Scheme 1b). NMR-spectroscopic and X-ray crystallographic analyses (*vide infra*) identified 3^{IPr} as the doubly NHC-stabilised borylene (*i*Pr)₂BCym.[‡] 3^{IPr} is, to our knowledge, the first example of a neutral doubly NHC-stabilised borylene, this class of compounds having only been the object of DFT calculations on the model system (IMe)₂BH thus far.¹⁷ Cationic bis(NHC)-stabilised borylenes of the form [(NHC)₂B(C≡NR)]⁺ had previously been obtained by Driess through the addition of isocyanides to a bis(NHC)-hydroborylene complex of Ni(II).¹⁸

Whereas the reduction of 1^{NHC} to diborene 2^{NHC} is to be expected according to the selectivity rules laid out in Fig. 1, the formation of borylene 3^{NHC} as the sole product in THF and as the minor product in benzene is more surprising, given that *i*Pr is not sufficiently π-accepting to stabilise an intermediate [(*i*Pr)BCym] borylene. Examination of the solid-state structure of 3^{IPr} (Fig. 3b) provides an answer to this unusual selectivity. While the boron centre is stabilised by two essentially σ-donating *i*Pr ligands (B–C_{NHC} ca. 1.57 Å), the B–C_{Cp} distance of 1.491(5) Å is in the range of a partial B–C double bond.¹⁹ In this

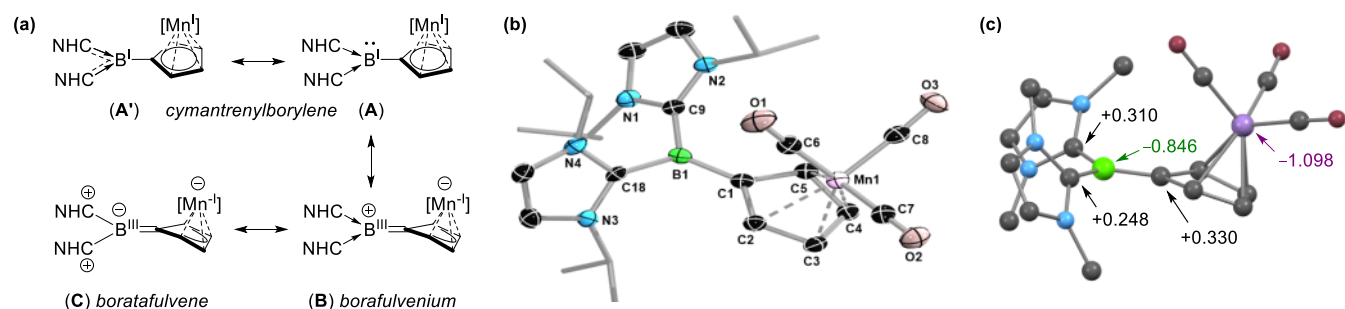


Figure 3. (a) Selected resonance forms of 3^{NHC} . [Mn] = Mn(CO)₅. (b) Crystallographically-derived structure of 3^{IPr} . Atomic displacement ellipsoids at 50% probability. Ellipsoids of ligand periphery and hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (°): B1–C9 1.572(5), B1–C18 1.567(5), B1–C1 1.491(5), C1–C2 1.466(5), C2–C3 1.420(5), C3–C4 1.420(5), C4–C5 1.428(5), C5–C1 1.452(5), Mn1···C1 2.530(4), Mn···Cp_{plane} 1.837, Mn–C_{CO} 1.766(4)–1.795(4), torsion (C9,B1,C1,C5) 6.2(6), (N1,C9,B1,C1) 57.2(5), (N4,C18,B1,C1) 50.0(5). (c) Calculated Mulliken charges for 3^{IPr} . *i*Pr methyl groups omitted for clarity.

case, the Cym ligand acts as the π acceptor stabilising the intermediate dicoordinate borylene. As a result, the Cp ring switches to an envelope conformation, with the C1 *endo*-carbon tilted ca. 16° out of the (C2,C3,C4,C5) plane, and the Mn centre switches to an η^4 coordination mode. A similar envelope conformation and η^4 coordination to the C₅ ring is also found in some transition metal cyclopentadienone²⁰ and fulvene²¹ complexes. Rather than a B(I)–Mn(I) cymantrenylborylene, stabilised by π backdonation to the NHC ligands (Fig 3a, A/A'), 3^{IPr} may thus be described as a B(III)–Mn(–I) borafulvenium (B) or boratafulvene (C) complex, stabilised by B-to-Mn charge transfer via the Cym ligand. A similar electronic situation was observed for the cationic borylenes [(NHC)₂B(C≡NR)]⁺, for which theoretical data suggest a predominant B(III) boraketiminium resonance form.¹⁸

In order to assess the bonding situation in 3^{IPr} , we performed DFT calculations in conjunction with energy decomposition analysis with natural orbitals of chemical valence (EDA-NOCV)²² calculations, as well as Mayer bond order (MBO)²³ and Mulliken²⁴ charge analyses. The best agreement between X-ray structure and calculations was obtained at the BLYP²⁵-D3(BJ)/def2SVP,def2TZVP(Mn)+SMD²⁶(THF) level of theory, with the calculated B–C_{Cp} bond (1.51 Å) being only slightly longer than the experimental one (1.491(5) Å).¹¹ The HOMO of 3^{IPr} (Fig. 4a) is concentrated at the B–C_{Cp} π space, with some delocalisation through the B–C_{NHC} bonding regions. Inspection of the NOCV deformation densities (Fig. 4b–d) indicates that the orbital interaction is dominated to 64% by two contributions related to σ donation from the carbenes ($\Delta\rho_1$ and $\Delta\rho_3$), π backdonation from the B–C_{Cp} double bond to the carbenes ($\Delta\rho_2$) accounting for ~18% of the orbital interaction. Furthermore, the Mulliken charges on Mn, B and the two NHC carbene carbon atoms are –1.098, –0.846, 0.310 and 0.248, respectively (Fig. 3c), while the MBO values of B–C_{Cp} and the two B–C_{NHC} bonds are 1.39, 1.23 and 1.15, respectively. These results suggest that 3^{IPr} is mainly stabilised through its boratafulvene resonance form C (Fig. 3a). The use of polar THF in the synthesis of 3^{IPr} may help stabilise the dicoordinate intermediate [(*i*Pr)BCym] and its zwitterionic resonance form, thus favouring the formation of the borylene/boratafulvene.

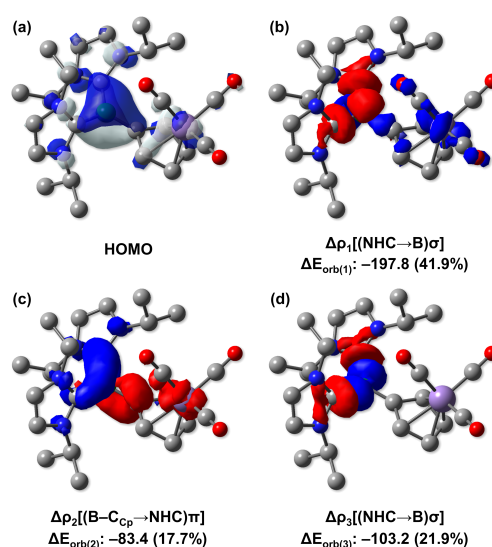


Figure 4. (a) HOMO of 3^{IPr} . (b), (c) and (d) Deformation density plots of the three main bonding configurations contributing to the total orbital interactions in the EDA-NOCV description of 3^{IPr} from (NHC)₂ and BCym fragments. Charge flows from red to blue.

To conclude, we have shown that a (NHC)BX₂Y precursor with an electron-accepting Y ligand may be selectively reduced to either the corresponding (NHC)₂B₂Y₂ diborene or (NHC)₂BY borylene, the latter being stabilised by π donation from the borylene to Y and the resulting zwitterionic resonance form.

Conflict of interest

The authors declare no conflict of interest.

Acknowledgments

This project was funded by the European Research Council (ERC) under the European Union Horizon 2020 Research and Innovation Program (grant agreement no. 669054). F. F. thanks the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES) and the Alexander von Humboldt (AvH) Foundation for a Capes-Humboldt postdoctoral fellowship.

Notes and references

‡ This was confirmed in repeated experiments, which always yielded single crystals of *trans*-**2**^{IME} and *cis*-**2**^{IPr}.

† No *cis/trans*-isomerisation was observed upon heating solutions of the isolated diborenes to 80 °C.

§ The proportion of **3**^{NHC} increased when the reduction was carried out at rt.

¶ **3**^{IME} could not be isolated as it rapidly decomposed in solution.

|| The geometrical parameters of **3**^{IPr}, especially the B–C_{CP} distance, are very sensitive to the type of functional, and are improved if solvent effects are taken into consideration during the geometry optimisation procedure. Moreover, BLYP performs well for first-row transition metal systems.²⁷

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