Dalton Transactions

ROYAL SOCIETY OF CHEMISTRY

COMMUNICATION

View Article Online
View Journal

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Cite this: DOI: 10.1039/d5dt02919h

Received 5th December 2025,
Accepted 6th May 2026

DOI: 10.1039/d5dt02919h

rsc.li/dalton

Accessing chiral NHC-boranes by abstraction of C_6F_5 from the $B(C_6F_5)_4^-$ weakly coordinating anion

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The prolonged heating of an *N*-heterocyclic carbene-stabilised borenium cation resulted in the abstraction of a $-C_6F_5$ group from its $B(C_6F_5)_4^-$ counter-anion. The resulting new chiral NHC-boranes presented an unusual *cis*/*trans* isomerism around the newly formed plane. The corresponding borenium cation, due to its Lewis superacidity, is a potentially interesting new chiral organocatalyst.

Boron cations have taken an important place in catalysis since the seminal work of Corey on cationic chiral oxazaborolidinium catalysts (Fig. 1, **1a**) and have gained increasing interest during the past decades with the development of Frustrated Lewis Pair (FLP) catalysed hydrogenations and of electrophilic borylations.[1,2] *N*-Heterocyclic carbene (NHC) stabilised borenium cations are appealing for their ability to heterolytically cleave dihydrogen and promote imine reduction in FLP systems.[3] They have also been shown to enable the reduction of unsaturated compounds and to borylate methane thanks to their strong Lewis acidity.[4] During the past decades, several examples of chiral NHC-boranes were reported, either through the sole coordination of four different ligands at the boron centre (**1b**, **1c**),[5] by the introduction of *C*-centered chiral centres (**1e**)[6a] or by both methods leading to the existence of diastereoisomers (**1d**, **1f**).[5h,6b] The corresponding *C*-centered chiral borenium cations of **1e** and **1f** were used in enantioselective reduction of imines with moderate enantiomeric excesses.[6]

With the intent of expanding the family of pyramidalised boron species, borenium cation **5** was targeted to increase the Lewis acidity from both the pyramidalisation and the cationisation of the boron centre.[7] NHC-borane **2**, bearing a benzhydryl group, was designed and synthesised to undergo two consecutive C–H borylation reactions leading to the desired cation **5** (Scheme 1).[8] Reacting NHC-borane **2** with the tritylium salt $[CPh_3][BArF_{20}]$ ($BArF_{20} = B(C_6F_5)_4^-$) led, as expected, to borenium cation **3** through a first intramolecular C–H borylation reaction of a phenyl group of the benzhydryl moiety (Scheme 1). This formation was witnessed by the spontaneous evolution of a gas (presumably H_2) and by ^{11}B NMR as the mixture gave a broad singlet at 54.4 ppm (see the SI, Fig. S-19). Upon heating, a second C–H borylation reaction was attempted to form the pyramidal borenium cation **5**. However, while **5** was not isolated nor observed, ^{11}B NMR of the reaction mixture revealed a doublet at −25.9 ppm.

After treatment and purification, **4-*trans*** and **4-*cis*** were isolated in 22% and 11% yields, respectively. These compounds result from the abstraction of a $-C_6F_5$ group from the $BArF_{20}$ counter-anion of **3**, releasing $B(C_6F_5)_3$. This kind of abstraction of a fluorophenyl ring has occasionally been reported on a $B(3,5\text{-}(CF_3)_2C_6H_3)_4^-$ ($BArF_{24}$) counter-anion using some transition metals and a cationic aluminium compound but has, to

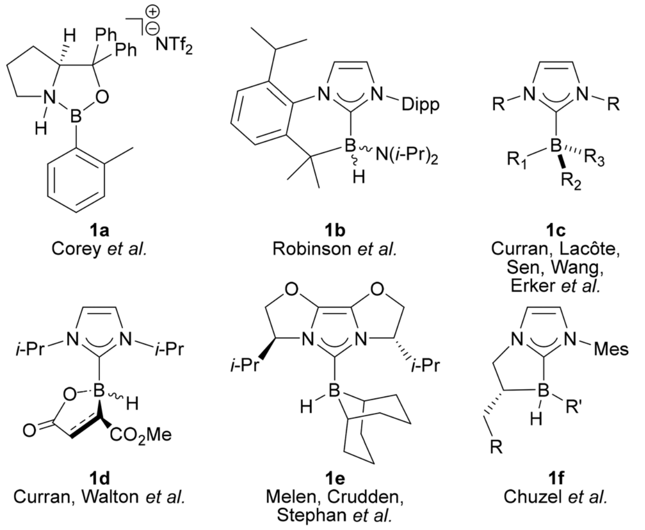

Fig. 1 Examples of a described chiral borenium cation and of chiral NHC-boranes, $NTf_2^- = N(SO_2CF_3)_2^-$.

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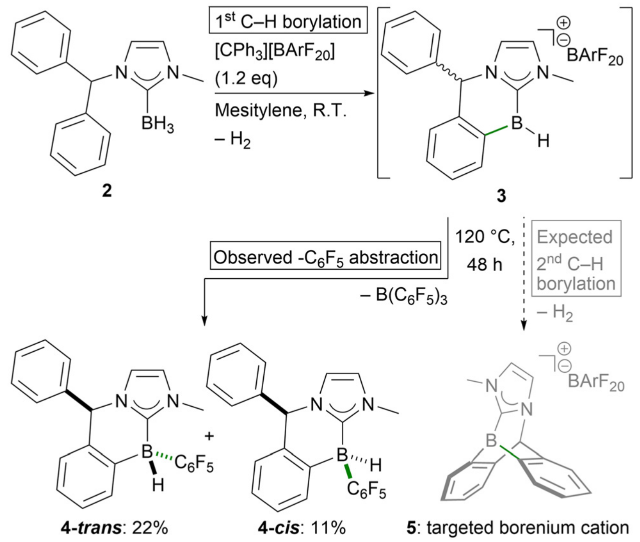


Scheme 1 Synthesis of **4-*trans*** and **4-*cis*** from $BArF_{20}$ abstraction, and structure of targeted pyramidal borenium cation **5**.

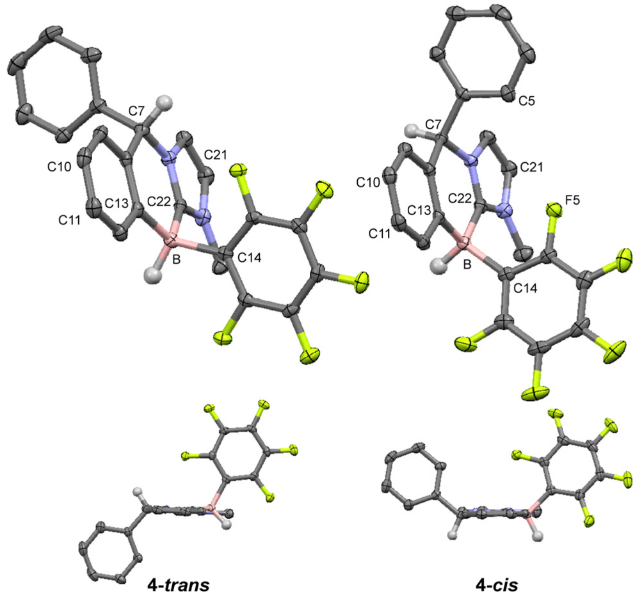


Fig. 2 X-ray diffraction structures of **4-*trans*** ($P2_1/c$ space group, *R*-factor: 2.91%) and **4-*cis*** ($P2_1/c$ space group, *R*-factor: 3.49%), ellipsoids at 50% probability; only one enantiomer is represented.

our knowledge, never been reported at a boron centre.[9] Interestingly, the C–H borylation followed by the abstraction resulted in the creation of a *C*-centred and a *B*-centred stereogenic centres. More than belonging to the family of NHC-boranes coordinated by four different ligands, **4-*trans*** and **4-*cis*** present a clear *cis*/*trans* isomerism around the newly formed 6-membered ring. This isomerism around a boron centre has been reported by Curran (**1d**) and Chuzel (**1f**) but, to our knowledge, no other examples have been described.[5h,6b]

Crystallographic data revealed similar C22–B and C13–B distances for **4-*trans*** and **4-*cis*** (1.598(2) *vs.* 1.600(2) Å and 1.613(2) *vs.* 1.612(2) Å respectively) (Fig. 2 and Table 1). However, the C14–B distance was elongated in the case of **4-*trans*** (1.647(2) *vs.* 1.638(2) Å). For **4-*trans***, the boron atom is 0.237 Å out of the (C10C11C21) plane, while it is only 0.121 Å away for **4-*cis***. This difference is due to steric repulsion between the $-C_6H_5$ and $-C_6F_5$ groups in **4-*cis*** forcing the boron atom into the plane as C5 and F5 are only 3.674 Å apart. This repulsion forces C7 out of the plane for **4-*cis*** compared to **4-*trans*** (0.131 *vs.* 0.047 Å respectively). The steric repulsion is also accountable for the greater C22^B^C14 angle observed for **4-*cis*** (112.2° *vs.* 107.9°). The doublet at −25.9 ppm observed in ^{11}B NMR for both compounds and the quartets observed at 3.55 ppm, for **4-*trans***, and 3.51 ppm, for **4-*cis***, in ^{1}H NMR are consistent with reported NHC-boranes.[4a,5]

DFT calculations of the diverse involved mechanisms were performed. **3** was indeed formed from a C–H borylation reaction of the corresponding borenium cation of **2** (see the SI, Fig. S-1). A 4-centered transition state was found, in accordance with the literature.[10] Calculations showed that the second C–H borylation, at **3**, forming the pyramidal borenium cation **5** presented an extreme activation barrier of 208 kJ mol^{-1} (Fig. 3). Concerning the formation of **4-*cis*** and **4-*trans***, two ion pair complexes (IPC), with the $BArF_{20}$ anion, presenting the lowest energies were obtained (Fig. 3). There, the $BArF_{20}$ anion was either on the same side of the phenyl group (**IPC-*cis***, Fig. 3) or on the opposite side (**IPC-*trans***). **IPC-*trans*** and **IPC-*cis*** were found to be in the same energy range with a small difference of only 4 kJ mol^{-1}.

The abstraction of the $-C_6F_5$ group from the $BArF_{20}$ anion proceeds in a concerted way, similarly to the $-C_6H_5$ group abstraction of a BPh_4^- anion by a phosphenium cation described by A. Růžička *et al.*[11] The *ipso* carbon of the abstracted $-C_6F_5$ group attacks the cationic boron centre of **3**, leading to the abstraction. The formation of **4-*cis*** presents an activation barrier of 139 kJ mol^{-1}, higher than the one required for the formation of **4-*trans***, 131 kJ mol^{-1}. **4-*trans***

Table 1 Atomic distances and angles in **4-*trans*** and **4-*cis*** from X-ray diffraction structures

	C22–B (Å)	C13–B (Å)	C14–B (Å)	C5···F5 (Å)	Plane···B[a] (Å)	Plane···C7[a] (Å)	Angle C22^B^C14
4-*trans*	1.598(2)	1.613(2)	1.647(2)	—	0.237	0.047	107.9°
4-*cis*	1.600(2)	1.612(2)	1.638(2)	3.674	0.121	0.131	112.2°

[a] Plane (C10C11C21).

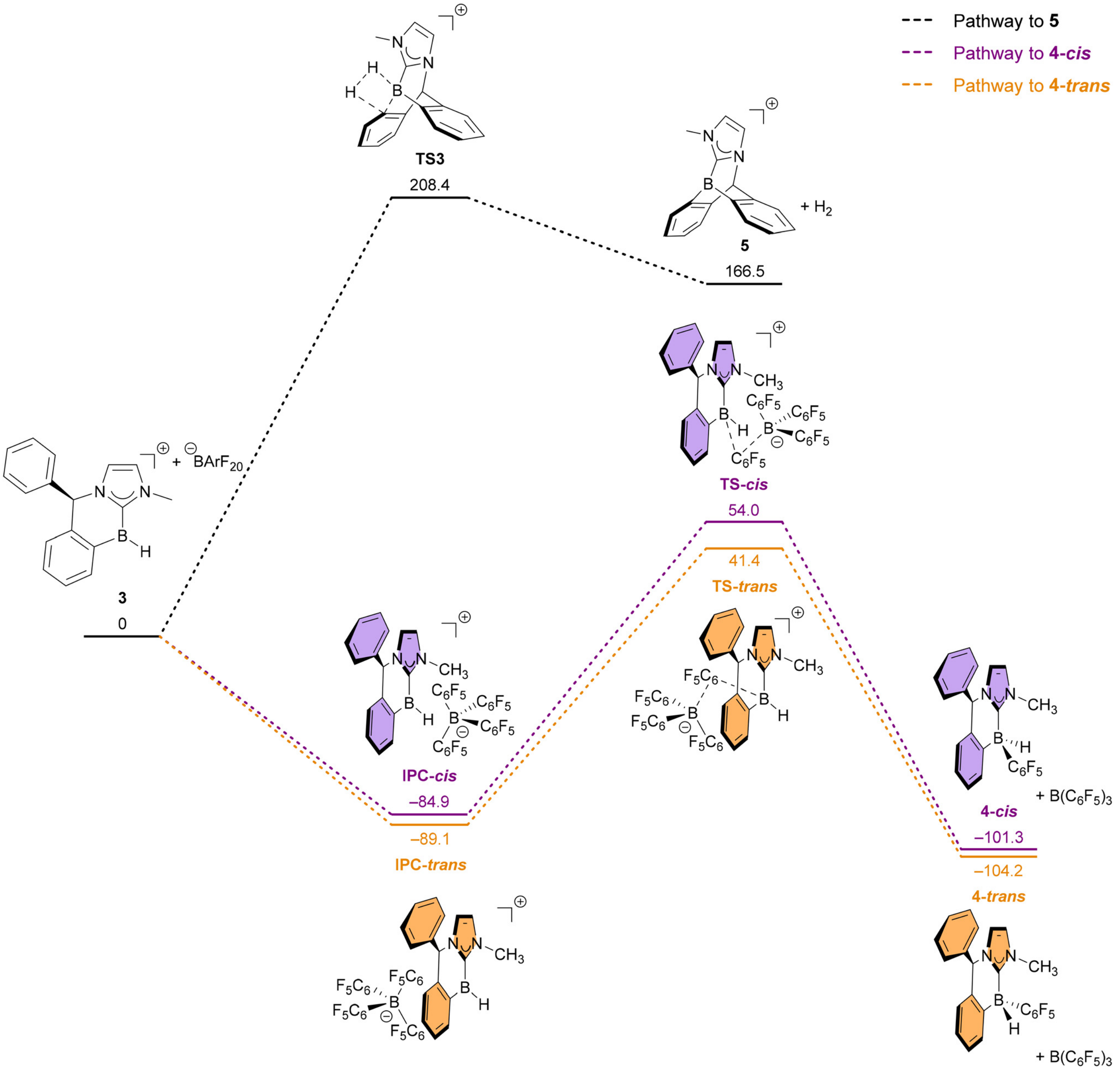
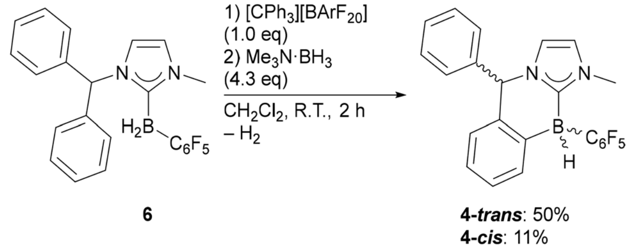


Fig. 3 Selected part of the DFT-estimated Gibbs free energy profile (kJ mol^{-1}) for the reaction mechanism of formation of **5**, **4-*trans*** and **4-*cis*** in mesitylene (M06-2X/6-311G(d), IEF-PCM (solvent = mesitylene)).

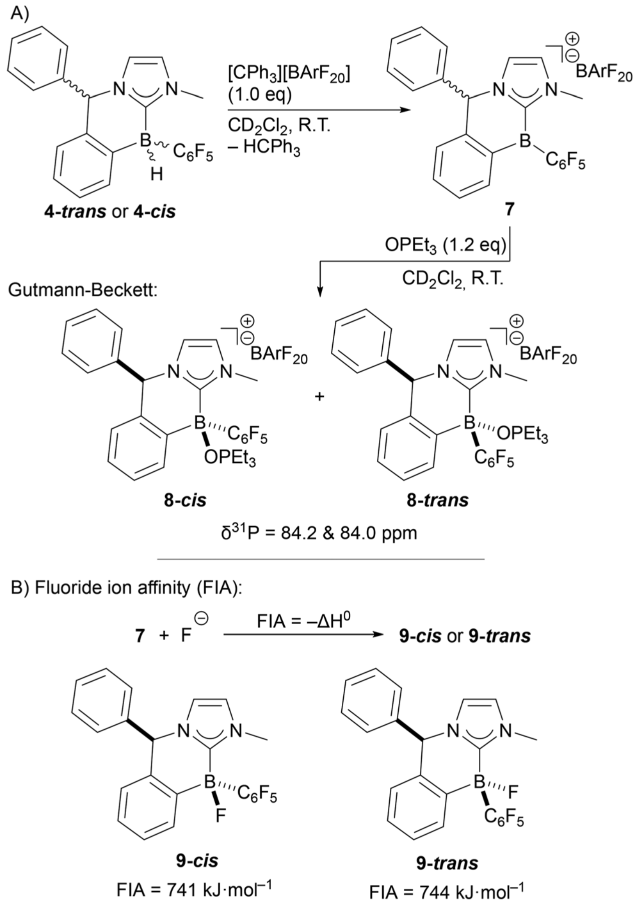
was found to be slightly lower in energy than **4-*cis***, by only 3 kJ mol^{-1}. The formations of **4-*trans*** and **4-*cis*** are both exergonic with global ΔG^0 of −15 and −16 kJ mol^{-1} respectively. These calculations indicate that the formation of **4-*trans*** *vs.* **4-*cis*** is driven by kinetic control of the reaction as **4-*trans*** was obtained in a higher yield than **4-*cis***.

Intending to obtain these new chiral NHC-boranes effectively, the C–H borylation was performed on **6**, an NHC-chelated Lancaster borane, synthesised from the corresponding imidazolium salt. The reaction of **6** with the tritylium salt [CPh$_3$][BArF$_{20}$] as a hydride abstractor led to the release of a gas (presumably H$_2$). After the gas release stopped, the reaction was quenched with a hydride donor, Me$_3$N·BH$_3$, which led, after treatment and purification, to **4-*trans*** and **4-*cis*** in 50% and 11% yields, respectively (Scheme 2). These higher yields are explained by the absence of –C$_6$F$_5$ abstraction in the reaction and the direct obtention of the compounds after C–H borylation and reduction. Interestingly, the hydride addition proceeded with high diastereoselectivity, in a 5 : 1 ratio, in favour of the *trans* isomer. The addition of a hydride to the same side as a bulky group on a borenium cation was witnessed by O. Chuzel *et al.*[6b] The corresponding NHC-borenium cation, **7**, was subsequently formed, from **4-*trans*** and **4-*cis***, by hydride abstraction using, once again, the tritylium salt. The



Scheme 2 Synthesis of ***4-trans*** and ***4-cis*** from C–H borylation of **6**.

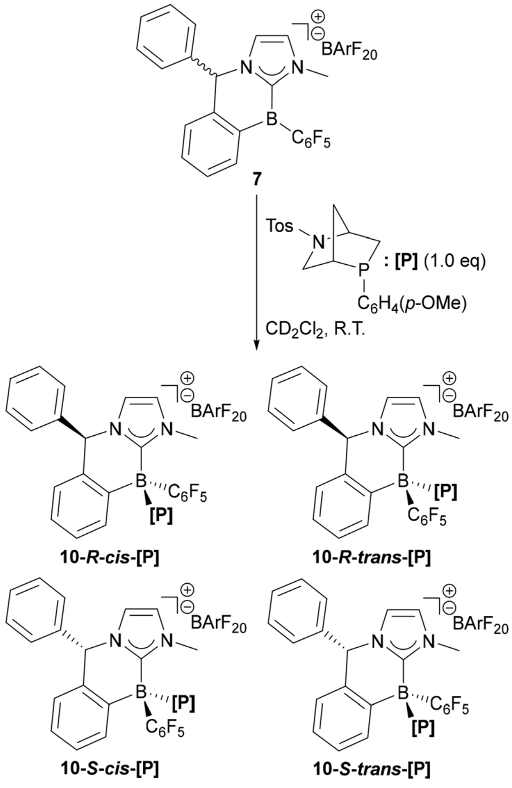
newly formed borenium cation presented a ^{11}B NMR signal at 51.6 ppm in CD_2Cl_2 but was not isolated. Its Lewis acidity was measured using the Gutmann–Beckett method and led to the obtention of two close signals at 84.2 and 84.0 ppm in ^{31}P NMR corresponding to the formation of the two possible diastereoisomers ***8-cis*** and ***8-trans*** (Scheme 3).[12,13] The shifts of 33.0 and 32.8 ppm of the phosphorus nucleus compared to the free $OPEt_3$ are in the range of Lewis acidities obtained for NHC-borenium cations.[4a,8b,13] The 84.2 and 84.0 ppm signals integrated in a 1 : 5.5 ratio presumably in favour of the less hindered ***8-cis*** adduct. The fluoride ion affinity (FIA) values were computed with the fluoride groups in both the *trans* and *cis* positions compared to the phenyl group.[14] Similar FIA values of 741 and 744 kJ mol^{-1} were obtained for the ***9-cis*** and ***9-trans*** isomers, respectively (Scheme 3). As the FIA values are above that of SbF_5 (500 kJ mol^{-1}), ***4-cis*** and ***4-trans*** are classified as Lewis superacids.[15] These values are again comparable to those of known NHC-borenium cations.[16]



Scheme 3 A) Formation of borenium cation **7**, structures of ***8-cis*** and ***8-trans***, $OPEt_3$ adducts for the Gutmann–Beckett experiment and obtained ^{31}P NMR chemical shifts (CD_2Cl_2, 300 K). δ^{31}P(free $OPEt_3$) = 51.2 ppm (CD_2Cl_2, 300 K). B) DFT calculated adducts for FIA determination. Calculated FIA values for NHC-borenium cation **7** (DFT at the M06-2X/6-311G(d) level of theory).

The racemic mixture of NHC-borenium **7** was combined with enantiopure Kwon's chiral phosphine **[P]** so as to perform a chiral derivatisation experiment (Scheme 4). The aim was to demonstrate the retention of the *C*-chiral centre, while the *B*-centred one was lost during the formation of the borenium cation, by the formation of the four different diastereoisomers of **10** (Scheme 4). After addition of Kwon's phosphine, only three signals were observed in ^{31}P NMR, two major ones at 19.6 and 17.9 ppm and a minor one at 15.0 ppm. Nonetheless, ^{19}F NMR revealed the presence of four different $–C_6F_5$ groups linked to the boron centres (see Fig. S38). The signals corresponding to the *ortho*-fluorines of **10** were obtained in a 1 : 1.5 : 1.5 : 1 ratio, proving the formation of the four possible diastereoisomers ***10-R-cis*-[P]**, ***10-R-trans*-[P]**, ***10-S-cis*-[P]** and ***10-S-trans*-[P]**.

While expecting a new pyramidal Lewis acid, the prolonged heating of a borenium cation resulted in the unexpected



Scheme 4 Chiral derivatization of a racemic mixture of borenium **7** using enantiopure Kwon's chiral phosphine **[P]**.

abstraction of a $-C_6F_5$ group of its $BArF_{20}$ counter-anion. This abstraction was never reported at a boron centre and led to the obtention of new chiral NHC-boranes. These new compounds, more than belonging to the family of chiral NHC-boranes, present a structurally interesting *cis*/*trans* diastereoisomerism around the newly formed plane. The corresponding NHC-borenium cation was formed and its chirality was confirmed through a chiral derivatisation experiment. This new chiral NHC-borenium cation was shown to be Lewis superacidic and could be an interesting candidate for enantioselective borenium-catalysed reactions as the chiral centre lies close to the boron centre. Moreover, the C–H borylation method should easily be tuneable for the obtention of different groups on the chiral carbon centre. The use of this chiral NHC-borenium cation and the introduction of different groups through a C–H borylation reaction are currently being studied in our laboratory.

Author contributions

N. N. performed the different syntheses and proofread the manuscript. A. I. A. performed the DFT determination of the mechanism. N. T. performed the XRD analysis. B. C. acquired funding, supervised A. I. A. and proofread the manuscript. G. B. acquired funding, helped in the writing of the manuscript and proofread the manuscript. K. B. designed the study, performed the preliminary experiments and FIA calculations, supervised N. N. and wrote the manuscript.

Conflicts of interest

There are no conflicts to declare.

Data availability

The data supporting this article have been included as part of the supplementary information (SI). See DOI: https://doi.org/10.1039/d5dt02919h.

CCDC 2495929 (**2**), 2495930 (**4-*trans***), 2495931 (**4-*cis***) and 2495932 (**6**) contain the supplementary crystallographic data for this paper.[17a–d]

Acknowledgements

The authors acknowledge the European Research Council (ERC, B-yond, grant agreement: 101044649, G. B.) and the Fond National de la Recherche Scientifique (F.R.S.-FNRS) for financial support (grant numbers: T.0012.21 (G. B.) and GEQ UG02222F (J. W.)). The calculations were performed on the computers of the "Consortium des Équipements de Calcul Intensif (CÉCI)" (https://www.ceci-hpc.be), including those of the "UNamur Technological Platform of High Performance Computing (PTCI)" (https://www.ptci.unamur.be), for which we gratefully acknowledge the financial support from the FNRS-FRFC, the Walloon Region, and the University of Namur (Convention No. U.G006.15, U.G018.19, U.G011.22, RW1610468, RW/GEQ2016, RW1117545, RW2110213, and RW2210148, B. C.). The authors thank the PC2 (UNamur) technological platforms for access to all characterization instruments.

References

1 (*a*) D. Ryu and E. Corey, *J. Am. Chem. Soc.*, 2003, **125**, 6388; (*b*) Y. Hayashi, J. Rohde and E. Corey, *J. Am. Chem. Soc.*, 1996, **118**, 5502; (*c*) E. Corey, *Angew. Chem., Int. Ed.*, 2002, **41**, 1650; (*d*) E. Corey, *Angew. Chem., Int. Ed.*, 2009, **48**, 2100.

2 (*a*) G. Welch, R. San Juan, J. Masuda and D. Stephan, *Science*, 2006, **314**, 1124; (*b*) D. Stephan and G. Erker, *Angew. Chem., Int. Ed.*, 2015, **54**, 6400; (*c*) T. Gazis, D. Willcox and R. Melen, Lewis Acidic Boranes in Frustrated Lewis Pair Chemistry, in *Frustrated Lewis Pairs*, ed. J. Slootweg and A. Jupp, Springer, Cham, 2021, 209–235; (*d*) T. De Vries, A. Prokofjevs, J. Harvey and E. Vedejs, *J. Am. Chem. Soc.*, 2009, **131**, 14679; (*e*) S. Iqbal, J. Pahl, K. Yuan and M. Ingleson, *Chem. Soc. Rev.*, 2020, **49**, 4564; (*f*) X. Feng, W. Meng and H. Du, *Chem. Soc. Rev.*, 2023, **52**, 8580.

3 (*a*) J. Farrell, J. Hatnean and D. Stephan, *J. Am. Chem. Soc.*, 2012, **134**, 15728; (*b*) J. Zheng, Z. Li and H. Wang, *Chem. Sci.*, 2018, **9**, 1433.

4 (*a*) C. Chen, J. Li, C. Daniliuc, C. Mück-Lichtenfeld, G. Kehr and G. Erker, *Angew. Chem., Int. Ed.*, 2020, **59**, 21460; (*b*) A. Prokofjevs, A. Boussonière, L. Li, H. Bonin, E. Lacôte, D. Curran and E. Vedejs, *J. Am. Chem. Soc.*, 2012, **134**, 12281; (*c*) Y. Liu, W. Dong, Z. Li and H. Wang, *Chem*, 2021, **7**, 1843.

5 (*a*) D. Lindsay and D. McArthur, *Chem. Commun.*, 2010, **46**, 2474; (*b*) D. Banerjee, C. Besnard and E. Kündig, *Organometallics*, 2012, **31**, 709; (*c*) Y. Wang and G. Robinson, *Inorg. Chem.*, 2011, **50**, 12326; (*d*) P. Bissinger, H. Braunschweig, K. Kraft and T. Kupfer, *Angew. Chem., Int. Ed.*, 2011, **50**, 4704; (*e*) X. Li and D. Curran, *J. Am. Chem. Soc.*, 2013, **135**, 12076; (*f*) T. Taniguchi and D. Curran, *Angew. Chem., Int. Ed.*, 2014, **53**, 13150; (*g*) T. Kawamoto, S. Geib and D. Curran, *J. Am. Chem. Soc.*, 2015, **137**, 8617; (*h*) W. Dai, S. Geib and D. Curran, *J. Am. Chem. Soc.*, 2019, **141**, 3623; (*i*) W. Dai, T. McFadden, D. Curran, H. Früchtl and J. Walton, *J. Am. Chem. Soc.*, 2018, **140**, 15868; (*j*) A.-L. Vallet and E. Lacôte, *Org. Biomol. Chem.*, 2019, **17**, 4234; (*k*) G. Kundu, S. Pahar, S. Tothadi and S. Sen, *Organometallics*, 2020, **39**, 4696; (*l*) G. Kundu, P. Amrutha, S. Tothadi and S. Sen, *Organometallics*, 2024, **43**, 1355; (*m*) K. Škoch, C. Chen, C. Daniliuc, G. Kerh and G. Erker, *Dalton Trans.*, 2022, **51**, 7695.

6 (*a*) J. Lam, B. Günther, J. Farrell, P. Eisenberger, B. Bestvater, P. Newman, R. Melen, C. Crudden and D. Stephan, *Dalton Trans.*, 2016, **45**, 15303; (*b*) C. Aupic, A. Abdou Mohamed, C. Figliola, P. Nava, B. Tuccio,

G. Chouraqui, J.-L. Parrain and O. Chuzel, *Chem. Sci.*, 2019, **10**, 6524.

7 (*a*) A. Ben Saida, A. Chardon, A. Osi, N. Tumanov, J. Wouters, A. I. Adjieufack, B. Champagne and G. Berionni, *Angew. Chem., Int. Ed.*, 2019, **58**, 16889; (*b*) A. Chardon, A. Osi, D. Mahaut, T.-H. Doan, N. Tumanov, J. Wouters, L. Fusaro, B. Champagne and G. Berionni, *Angew. Chem., Int. Ed.*, 2020, **59**, 12402; (*c*) N. Niessen, L. Mineur, A. Chardon, A. Osi, A. I. Adjieufack, D. Mahaut, N. Tumanov, J. Wouters, B. Champagne and G. Berionni, *ChemistryEurope*, 2025, **3**, e202500100; (*d*) M. Henkelmann, A. Omlor, M. Bolte, V. Schünemann, H.-W. Lerner, J. Noga, P. Hrobárik and M. Wagner, *Chem. Sci.*, 2022, **13**, 1608.

8 (*a*) R. Corberán, M. Sanaú and E. Peris, *Organometallics*, 2006, **15**, 4002; (*b*) J. Farrell and D. Stephan, *Angew. Chem., Int. Ed.*, 2015, **54**, 5214; (*c*) J. Lam, L. Cao, J. Farrell and D. Stephan, *Dalton Trans.*, 2020, **49**, 1839; (*d*) W. Jin, Z. Cheng, H. Chang, X. You, F. Zhou, S. Zhuang, H. Jin, C. Liu and J. Xuan, *Green Synth. Catal.*, 2025, DOI: 10.1016/j.gresc.2025.09.002, in press.

9 (*a*) W. Konze, B. Scott and G. Kubas, *Chem. Commun.*, 1999, 1807; (*b*) S. Weber, D. Zahner, F. Rominger and B. Straub, *Chem. Commun.*, 2012, **48**, 11325; (*c*) H. Salem, L. Shimon, G. Leitus, L. Weiner and D. Milstein, *Organometallics*, 2008, **27**, 2293; (*d*) M. Bochmann and M. Starsfield, *Organometallics*, 1998, **17**, 5908.

10 (*a*) J. Varela, D. Peña, B. Goldfuss, D. Denisenko, J. Kulhanek, K. Polborn and P. Knochel, *Chem. – Eur. J.*, 2004, **10**, 4252; (*b*) B. Goldfuss, P. Knochel, L. Bromm and K. Knapp, *Angew. Chem., Int. Ed.*, 2000, **39**, 4136.

11 M. Samsonov, J. Vrána, P. Švec, V. Němec, E. Procházková, J. Cvačka and A. Růžička, *Chem. – Eur. J.*, 2025, **31**, e00524.

12 (*a*) U. Mayer, V. Gutmann and W. Gerger, *Monatsh. Chem.*, 1975, **106**, 1235; (*b*) V. Gutmann, *Coord. Chem. Rev.*, 1976, **18**, 225; (*c*) M. Beckett, G. Strickland, J. Holland and K. Sukumar Varma, *Polymer*, 1996, **37**, 4629.

13 (*a*) C. Aupic, PhD Thesis, Université Aix-Marseille, 2018, https://theses.fr/2018AIXM0633; (*b*) K. Bijouard, PhD Thesis, Sorbonne Université, 2022, https://theses.fr/2022SORUS034.

14 (*a*) H. Böhrer, N. Trapp, D. Himmel, M. Schleep and I. Krossing, *Dalton Trans.*, 2015, **44**, 7489; (*b*) L. Greb, *Chem. – Eur. J.*, 2018, **24**, 17881.

15 (*a*) L. Müller, D. Himmel, J. Stauffer, G. Steinfeld, J. Slattery, G. Santiso-Quiñones, V. Brecht and I. Krossing, *Angew. Chem., Int. Ed.*, 2008, **47**, 7659; (*b*) L. Greb, *Chem. – Eur. J.*, 2018, **24**, 17881.

16 S. Ju, C. Zhang, B. Tang, L. L. Liu, D. W. Stephan and Y. Wu, *Chem. Commun.*, 2024, **60**, 698.

17 (*a*) CCDC 2495929: Experimental Crystal Structure Determination, 2026, DOI: 10.5517/ccdc.csd.cc2ps6vk; (*b*) CCDC 2495930: Experimental Crystal Structure Determination, 2026, DOI: 10.5517/ccdc.csd.cc2ps6wl; (*c*) CCDC 2495931: Experimental Crystal Structure Determination, 2026, DOI: 10.5517/ccdc.csd.cc2ps6xm; (*d*) CCDC 2495932: Experimental Crystal Structure Determination, 2026, DOI: 10.5517/ccdc.csd.cc2ps6yn.