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ARTICLE TYPE

1,1 / 1,2 isomerisation in Lewis base adducts of B_2cat_2

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Reaction of bis-catecholatodiborane and 1 or 2 equivalents of 1,5-diazabicyclo[4.3.0]non-5-ene or 4-picoline yields Lewis acid-base adducts. Recrystallisation enabled identification of an unexpected isomerisation from the 1,1-isomer to the 1,2-isomer. This observation was probed computationally with significantly different dipole moments calculated for the two effectively isoenergetic isomeric forms.

Introduction

Much like their mono-boron analogues, diboranes (X_2B-BX_2) can react with an array of nucleophiles to form simple Lewis acid-base adducts, albeit often displaying complex dynamic coordination behaviour.[1] These systems have become the subject of significant interest since the discovery that they can behave as a source of nucleophilic boron. In particular bis-pinacolatodiborane (B_2pin_2), in the presence of suitable anionic nucleophiles, reacts with carbon electrophiles even in the absence of precious metal catalysts to give organo-borane products. Competent substrates for these reagents include α,β-unsaturated ketones, which form γ-borylketones, the product of a formal {Bpin}$^-$ transfer to carbon.[2] This methodology is proving to be a powerful route for forming C-B bonds, including enantioselective examples when a chiral Lewis base is present.[2g-k] We were interested in related systems based on bis-catecholatodiborane (B_2cat_2), **1**, as a source of nucleophilic {Bcat}$^-$. Despite the similarity to their pinacolato analogues, the chemistry of Lewis base adducts of B_2cat_2 has received less attention. However, one notable study confirmed that B_2cat_2 is a stronger Lewis acid than B_2pin_2 towards 4-picoline, consistent with the lower LUMO energy calculated for **1** relative to B_2pin_2.[3] It is also important to note that the activation of **1** with Cs_2CO_3 / MeOH enables the transfer of {Bcat}$^-$ to organic electrophiles, albeit with a slightly lower conversion relative to that using B_2pin_2.[2e]

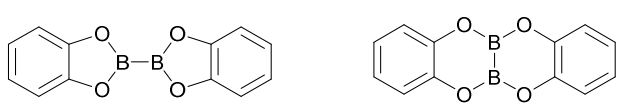


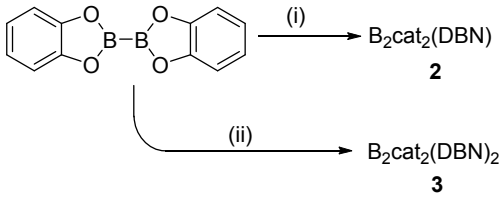
Figure 1. The two isomeric forms of $B_2(diolate)_2$ exemplified by B_2cat_2: 1,1-B_2cat_2, **1a** (left) and 1,2-B_2cat_2, **1b** (right).

Of the two isomers of $B_2(diolate)_2$, possessing 1,1- and 1,2-bound diolates (see Figure 1), all the solid state structures of **1**, B_2pin_2 and their respective Lewis base adducts have been found to be 1,1-isomers.[1b, 4] Indeed 1,2-isomers, where a diolate is bound to different boron atoms in the diborane, are rare,[5] with DFT calculations indicating that the 1,1-isomer is generally more stable.[5a] This is consistent with attempts to form the 1,2-isomer of B_2cat_2 by addition of catechol to 1,2-$B_2(NMe_2)_2$cat leading to isomerisation and exclusive formation of the 1,1-isomer of B_2cat_2.[5b] Examples of the reverse reaction, the 1,1 to 1,2 isomerisation of a chelating substituent on a diborane, are extremely rare, with the deprotonation of pinacolato diisopropanolaminato diboron providing a notable exception.[2d] It is also noteworthy that extensive isomerisation processes in diboranes have been elucidated by Braunschweig and co-workers, albeit for non-chelated substituents.[6]

Contrary to the, to date, sparse evidence of 1,2-$B_2(diolate)_2$ species, during the course of our investigation into Lewis base adducts of **1** we observed an unexpected isomerism of the diborane framework from 1,1- to 1,2-catecholato. This may have implications on the use of these materials as sources of boryl nucleophiles and in oxidative addition reactions with transition metals.

Results and Discussion

Compound **1** in the presence of one or two equivalents of 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) reacts to generate a mixture of isomeric mono-adducts, **2** and the doubly substituted adducts, **3**, respectively (Scheme 1).



Scheme 1. Reaction of **1** with DBN to give the corresponding mono and bis adducts, **2** and **3**, respectively. (i) One equivalent of DBN. (ii) Two equivalents of DBN.

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The ^{11}B NMR spectra of the mono adducts, **2** were characterised by a pair of major resonances consistent with the presence of both sp^2 and sp^3 boron centres (37.3 and 6.9 ppm). However, in addition to these major peaks there was also the persistent presence of a pair of minor sp^2 / sp^3 resonances shifted up-field that frustrated unambiguous identification and did not correspond to B_2cat_2 or $B_2cat_2L_2$. This behaviour contrasts with the single broad ^{11}B resonance displayed by the mono 4-picoline adduct of B_2cat_2 reported previously,[4b] which was indicative of the dynamic fluxional binding of 4-picoline in solution. Recrystallisation of the mono-adduct afforded the 1,1-isomer of **2**, termed **2a**, as expected (Figure 2). Dissolution of the crystals of **2a** led to identical spectra showing similar resonances to that observed for the crude reaction mixture consistent with an equilibrium process. The solid state structures of **2a** and the closely related mono-4-picoline[4a] adduct possess very similar, crystallographically indistinguishable B-B bonds with lengths 1.712(10) and 1.706(3) respectively. The B-N bond of **2a** is a little shorter than the mono-picoline analogue, 1.610(9) and 1.644(2), respectively, consistent with DBN being a stronger donor than 4-picoline.

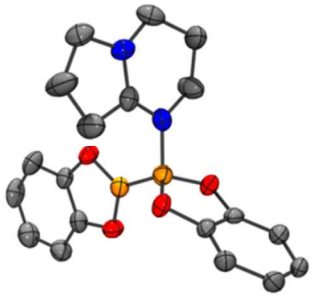

Figure 2. X-ray crystal structure of **2a** (ellipsoids at 50% probability and hydrogens omitted for clarity). Grey = carbon, blue = nitrogen, red = oxygen and orange = boron. Selected bond metrics: B-B 1.712(10) Å, B-N 1.610(9) Å, BB̂N 110.2(5)°,.

In contrast to the mono-adduct **2a**, the corresponding bis-adduct **3a** possesses only a 4-coordinate boron environment and was expected to give a single resonance in its ^{11}B NMR spectrum, provided only the 1,1 isomer was present. However, **3** gave a more complex ^{11}B NMR spectrum, with two resonances of approximately equal intensity at 12.3 and 4.0 ppm in DCM, indicative of two inequivalent 4-coordinate boron environments. These resonances did not coalesce on heating to 78°C (in *ortho*-dichlorobenzene, termed o-DCB). Recrystallization of **3** by layering a solution of **3** in DCM with pentane yielded two distinct crystalline products, the expected 1,1-isomer, **3a**, and the unexpected 1,2-isomeric form, termed **3b** (Figure 3). While the crystallographic data recorded for multiple crystals of **3b** was consistently of poor quality it was sufficient to create an unambiguous connectivity map for **3b** confirming its assignment. The particular product obtained by recrystallization was strongly determined by the solvents used. Compound **3a** was obtained as the dominant product from slow diffusion of pentane layered over a 1:1 DCM/DCB solution whereas isomeric **3b** was obtained by repeating this crystallisation process using only DCM and pentane. The isomeric purity of the bulk crystalline samples of **3a** and **3b** was probed by powder X-Ray diffraction with the room temperature results confirming that a microcrystalline sample of **3a** was phase pure. However, that of **3b** displayed a more complex powder X-Ray diffraction than expected, indicative of the presence of multiple crystalline species. Nevertheless, the solid state ^{13}C and ^{11}B MAS NMR spectra for both **3a** and **3b** confirmed the absence of three coordinate boron centers[7] in the bulk material and produced distinct isomer dependent resonances (see supporting information) that are comparable to that reported for $B_2cat_2(pic)_2$.[4b]

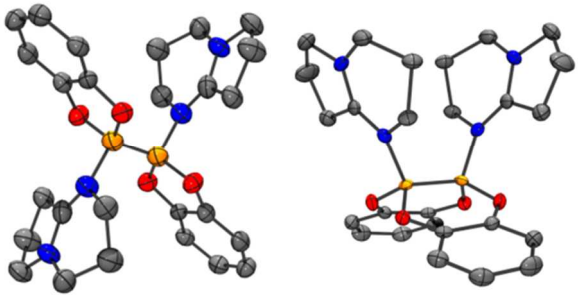

Figure 3. X-ray crystal structures of **3a** (left) and **3b** (right) (ellipsoids at 50% probability and hydrogens omitted for clarity). The data for **3b** was of poor quality precluding detailed analysis of bond metrics, but it does confirm formation of the 1,2-isomer. Selected bond metrics for **3a**: B-B 1.715(5) Å, B-N 1.631(3) Å, BB̂N 108.3(2)°.

The 1,2-isomer is uncommon for diboranes containing diolate substituents, indeed, to our knowledge there are only two previous examples of diolate substituted diboranes existing as a 1,2-isomer, B_2(BINOL)[5c] and $B_2cat(NMe_2)_2$.[5b] The propensity for BINOL to bind to diboranes in a 1,2-conformation may be due to its large bite angle and preference for forming eight membered rings over seven membered (required in the formation of the 1,1-isomer) as previously discussed.[5c] In contrast, the isolation of $B_2cat(NMe_2)_2$ with the unusual 1,2-conformation is likely to be facilitated by its synthesis from the unsymmetric precursor 1,2-$B_2(NMe_2)_2Cl_2$. Previous calculations (at the B3LYP/6-31G*//HF/6-31G level) on this and related structures show that while 1,2-$B_2cat(NMe_2)_2$ is 7.7 kcal mol^{-1} more stable than its 1,1-isomer (presumably due to the strongly π-donating dimethylamino ligands) the 1,2-isomers of related diolate and dithiolate compounds are the thermodynamically less stable forms (by 3.0-19.3 kcal mol^{-1}). Indeed, the unusual enhanced stability of the 1,2-catecholatodiboron core in 1,2-$B_2cat(NMe_2)_2$ is demonstrated by the reaction of 1,2-$B_2cat(NMe_2)_2$ with diols, with which it forms products adopting a 1,1-isomer structure.[5b]

It is notable that although only **3b** was isolated as a clear example of 1,2-isomerism, the 1,2-isomer of **2** (termed **2b**) was hinted at by the persistent presence of a second species observed in the ^{11}B NMR spectra (see Supporting Information). Based on the dearth of other known 1,2-catecholatodiborane isomers, our initial hypothesis was that 1,2-isomers were accessible by virtue of our use of the strong donor ligand DBN. Coordination could result in an increase in electron density at boron sufficient to weaken the boron oxygen bonds and allow for the facile rearrangement of the catechol diboron core. While the exact isomerisation mechanism for these diboranes is not known it is likely to occur between two boron centres that are three and four

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coordinate, respectively, by analogy to substituent redistribution reactions in CatBY(Lewis base) (Y = H or Cl).[8] In the latter when strongly nucleophilic amines are used as the Lewis base, e.g., Et_3N, which form strong dative bonds with CatBCl no ligand scrambling is observed. In contrast, the use of weaker nucleophiles towards boron in CatBCl (e.g., phosphines) results in rapid ligand redistribution due to reversible LB→B cleavage and the concomitant presence of both four coordinate and three coordinate CatB centres.[8] Despite being a strong Lewis base DBN binds reversibly to B_2cat_2 as demonstrated by the dissolution of microcrystalline samples of the bis-adduct **3** with **1** in THF leading to rapid formation of spectra consistent with the formation of the mono adducts **2** (by ^{11}B NMR spectroscopy). Thus both three and four coordinate boron centres will exist concomitantly in solution on combining B_2cat_2 with one and two equivalents of DBN.

In order to determine if the diolate isomerisation only proceeded with strong Lewis bases, we synthesised the known compound $B_2cat_2(pic)_2$, **4**,[4b] possessing weaker donor 4-picoline ligands and previously characterised in the solid state as the 1,1-isomer, **4a**. **4** is prepared by simply mixing **1** and 4-picoline in DCM and recrystallized by dissolution in DCB and layering with pentane. Despite the weaker donor capacity of 4-picoline relative to DBN, we observed formation of previously unknown 1,2-$B_2cat_2(pic)_2$ **4b** (Figure 4). This structure was shown to be representative of the bulk material by unit cell determinations of multiple single crystal samples and a powder X-Ray diffraction measurement of a microcrystalline sample. It is notable that our synthesis of **4b** differed in terms of solvent from the protocol for the 1,1-isomer, **4a**, which was synthesised in hexane (the product rapidly precipitating) and recrystallised from THF. To probe the reversibility of isomerisation, crystalline **4b** was dissolved in THF and stored for 7 days at ambient temperature. After this time crystals of sufficient quality for X-ray diffraction were grown by concentration and cooling (to -20^{O}C) the THF solution. These were shown to be still the 1,2-isomer albeit as a THF solvate. However, dissolution of crystals of the 1,2-isomer **4b** in either chloroform or THF yielded solutions, which when probed by multinuclear NMR spectroscopy showed resonances consistent with dynamic equilibria between the mono and bis-picoline adducts, as previously reported by Marder and co-workers,[4b] and presumably between the 1,1 and 1,2 isomers.

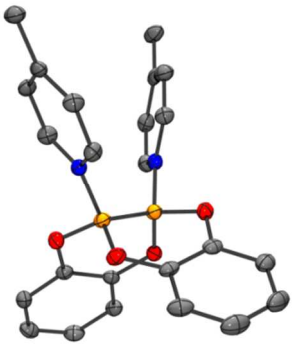

Figure 4. X-ray crystal structure of 1,2-$B_2cat_2(pic)_2$, **4b**, recrystallised from DCB (ellipsoids at 50% probability hydrogens and the molecule of DCB present in the asymmetric unit are omitted for clarity). Selected bond metrics: B-B 1.624(3) Å, B-N 1.624(3) Å, BB̂N 116.53(18) °.

The isolation of $B_2cat_2(pic)_2$ as its 1,2-isomer **4b** clearly indicated that the donor strength of the ligands is not a key factor controlling the barrier to isomerisation. In order to gain some insight into the unexpected isomerism observed for **3** and **4** and hinted at for **2** (by ^{11}B NMR spectroscopy), these systems were examined computationally. Four structures were probed, the 1,1-isomers **2a** and **3a**, and their 1,2-analogues **2b** and **3b**. These structures were modelled using M06-2X at the 6-311G(d,p) (PCM/DCM) level of theory. The optimised structures (Figure 5) were in very close agreement to the experimentally observed X-ray structures (full details of the comparisons between calculated and observed structures are presented in the supporting information). The most notable feature from the comparison of the calculated structures of the mono adducts is the near isoenergetic nature of pairs of 1,1- and 1,2- isomers. This was unexpected for the mono adducts as from simple inspection the 1,2-isomer **2b** might be expected to be somewhat strained, possessing a single sp^3-boron atom amongst nine sp^2-atoms in a pair of fused 6-membered rings (Figure 5, top right). However, any strain in the central fused 6-membered rings is either minimal or offset by opposing thermodynamically stabilising factors. Indeed, while the largest difference in energy is calculated for the mono-adducts **2a** and **2b**, the 1,2-isomer is calculated to be the more stable form by 2.7 kcalmol^{-1}. Whilst only the 1,1-isomer of the mono adduct **2a** was isolable and confirmed by X-ray crystallography, additional resonances in the NMR spectra of the DBN-mono-adduct indicate the presence of two isomers, presumably **2a** and **2b** as the sample is analytically pure (by combustion microanalysis).

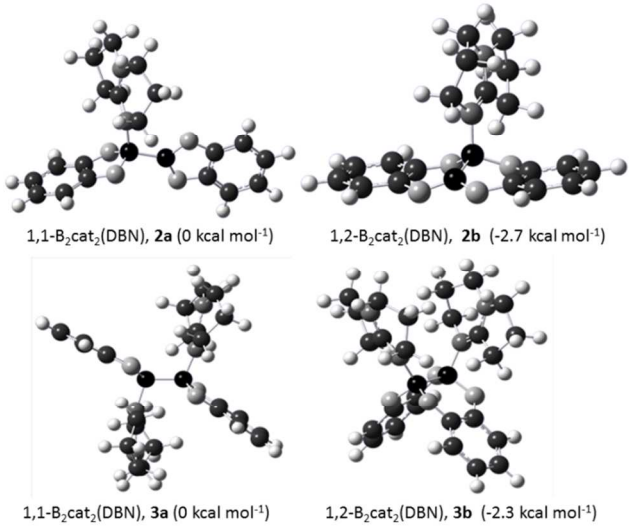

Figure 5. Comparison of the calculated structures of: **2a** and **2b**, **3a** and **3b**, note the distortion away from planarity of the central fused 6-membered rings of **2b**. Energies are quoted for each pair of structures, relative to the respective 1,1-isomers.

The 1,1 and 1,2 isomers of the bis-adduct are also energetically similar. However, there is a distinct difference between the isomeric bis-adduct structures, **3a** and **3b**. The 1,2-isomer was distinguished from the 1,1-analogue by virtue of significantly different calculated dipole moments. For **3a** the dipole moment was calculated to be very close to zero, consistent with the near

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inversion centre in the middle of the B-B bond. In contrast **3b** displays a dipole moment of 21 Debeye, and this distinguishing feature may be accountable for the observed solvent dependent isomerism. Considering the near isoenergetic structures calculated for the 1,1- and 1,2-isomers of the bis-adduct, the use of the moderately more polar solvents DCB / DCM (dielectric constants 9.9 and 9.1 D, respectively) relative to THF used previously (dielectric constant 7.5 D) may well be sufficient to alter equilibrium positions to favour the more polar isomer. In addition to the effects of solvent dielectric on the concentration of any one particular isomer in solution, the identity of the crystalline material isolated from a dynamic equilibrium is also likely to be dependent on the relative packing forces and solubility in a particular solvent. A full set of packing structures are provided in the supplementary information, however, a few particular structural features are worthy of note. Compounds **2a** and **3a** were isolated as co-crystals (from a reaction with a 1 : 2 ratio of **1** : DBN) with a molecule of each present in the asymmetric unit, indicative of at least two species present in solution. The molecular structure of **4b** includes a single molecule of DCB in the asymmetric unit, which has short contacts (< sum of vdW radii minus 0.1 Å) to both the picoline and catechol moieties of **4b**, again with potential implications for the observed crystallisation of the 1,2-isomer over the 1,1-isomer.

Conclusions

An unusual isomerism has been observed for Lewis base adducts of bis-catecholatodiborane. Isomerisation is rapid in the presence of moderate and strong Lewis bases. Mechanistically, the isomerisation presumably requires the presence of both four coordinate and three coordinate boron centers by analogy to ligand redistribution reactions for CatBCl(L) species. This rapid isomerisation may have implications in the chemistry of these materials and their closely related bis-pinacolatodiboranes and is especially significant considering the growing interest in the use of Lewis base adducts of diboranes as sources of nucleophilic boron.

Acknowledgements

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Experimental

All manipulations of air and moisture sensitive species were performed under an atmosphere of dry argon or nitrogen using standard Schlenk techniques. Glassware was dried in a hot oven overnight and heated under vacuum before use. Hexane and tetrahydrofuran were dried over sodium/potassium alloy and potassium respectively, *ortho*-dichlorobenzene, d_1-chloroform and d_2-dichloromethane were dried over calcium hydride and distilled under reduced pressure. Pentane and dichloromethane were dried by passing them through an alumina drying column incorporated into an Innovative Technology Inc. PD-MD-5 solvent purification system. All solvents were degassed under reduced pressure and stored over activated molecular sieves (3 Å) under inert atmosphere. $B_2cat_2pic_2$[4b] was synthesised using literature procedures. All other materials were purchased from commercial vendors and used as received. NMR spectra were recorded with a Bruker AvanceIII-400 (400 MHz ^{1}H; 128 MHz ^{11}B; 100 MHz ^{13}C) and Bruker AvanceII-500 (500 MHz ^{1}H; 160 MHz ^{11}B; 126 MHz ^{13}C) spectrometers. ^{1}H NMR chemical shifts are reported in ppm relative to *protio* impurities in the deuterated solvents and those of ^{13}C NMR relative to solvent resonances unless otherwise stated. ^{11}B NMR spectra were referenced to external BF_3:Et_2O. Elemental analysis of air sensitive materials was performed by the London Metropolitan University service.

2 - B_2cat_2(DBN)

DBN (50 µL, 0.4 mmol) was added to B_2cat_2 (200 mg 0.4 mmol) in DCM. The product could be recrystallised from DCM/DCB (90/10) by layering with pentane to obtain the title compound as a white solid. Yield: 206 mg 68%

Major resonances for the dominant solution isomer only listed. ^{1}H NMR (500 MHz, d_2-DCM,) δ 7.5-6.5 (8H overlapping br m), 3.42 (4H, m), 3.22 (2H, t, J = 5.0 Hz), 3.11 (2H, t, J = 7.3 Hz), 2.02 (2H, pent, 7.5 Hz) 1.90 (2H, t, 5.5 Hz). ^{11}B{^{1}H} NMR (128 MHz, d_2-DCM) δ 36.0 (br), 7.0 (br). ^{13}C{^{1}H} NMR (100 MHz, d_2-DCM) δ 164.2, 149.2 (br), 131.0, 128.5, 122.2 (br), 119.3 (br), 111.8 (br), 110.4 (br), 52.8, 43.5, 40.5, 31.5, 20.0, 19.7. Elemental analysis: Calculated for $C_{19}H_{20}B_2N_2O_4$: C, 63.04%; H, 5.57%; N, 7.74%, Found C, 62.92%; H, 5.70%; N, 7.81%

3-$B_2cat_2(DBN)_2$ (mixture of isomers)

DBN (100 µL, 0.8 mmol) was added to B_2cat_2 (100 mg, 0.4 mmol) in DCB (1ml). The mixture was stirred for 2 hours and the desired product precipitated as a microcrystalline solid. Yield: the yield was consistently above 100% due to the presence of tightly bound DCB solvent (also observed in the X-ray structure).

^{1}H NMR NMR (500 MHz, d_2-DCM) δ 7.47 (DCB), 7.24 (DCB), 6.64 (2H, m), 6.60(2H, m), 6.52 (4H, m), 3.28 (8H, br m), 3.00-3.09 (8H, br m), 1.88 (4H, pent) 1.72 (4H, br m). ^{11}B{^{1}H} NMR (MHz, d_2-DCM) δ 12.7 (br s), 4.6 (br s). ^{13}C{^{1}H} NMR (125 MHz, d_2-DCM,) δ 163.1 (br), 153.8, 148.8, 132.8, 131.0 (DCB), 128.5 (DCB), 118.8, 118.4, 118.2, 109.2, 51.4, 43.5 (br), 42.0 (br), 41.3 (br), 32.0 (br), 31.42 (br), 20.4 (br). Elemental analysis: Calculated for $C_{38}H_{40}B_2Cl_4N_4O_4$ ($B_2cat_2(DBN)_2$•$(DCB)_2$): C, 58.50%; H, 5.17%; N, 7.18%, Found C, 58.32%; H, 5.26%; N, 7.39%

3a-1,1-$B_2cat_2(DBN)_2$

DBN (100 µL, 0.8 mmol) was added to B_2cat_2 (100 mg, 0.4 mmol) in DCM/DCB (50/50). Crystals of the title compound were obtained by layering this mixture with pentane and filtering off the resulting white crystals.

3b-1,2-$B_2cat_2(DBN)_2$

DBN (100 µL, 0.8 mmol) was added to B_2cat_2 (100 mg, 0.4 mmol) in DCM. The mixture was heated in a 60°C oil bath for 5 min, and then layered with pentene to obtain, following filtration, the title compound as white crystals.

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4b$_{(DCB)}$-$B_2cat_2(pic)_2$•(DCB)

4-Picoline (163 μL, 1.6 mmol) was added to B_2cat_2 (200 mg, 0.8 mmol) in DCM (10 ml). The reaction mixture was stirred at room temperature for 90 mins then reduced to dryness under vacuum. The title compound was obtained by redissolving this in DCB (7 ml), filtering the supernatant, layering with pentane (approx. 7 ml) and filtering off the resulting large yellow crystalline blocks. NMR spectra, dynamic mixture consistent with that reported above and those previously reported by Marder *et al*.: ^{1}H NMR ($CDCl_3$) δ 8.40 (d, 4H), 7.17 (m, 4H), 7.01 (m, 4H), 6.75 (m 2H), 6.74 (m, 2H), 2.40 (s, 6H). $^{11}B\{^1H\}$ ($CDCl_3$) δ 20.2 (br s), 5.4 (br s). $^{13}C\{^1H\}$ ($CDCl_3$) δ 151.8, 149.8, 147.5, 143.9, 132.4, 130.5, 127.7, 125.7, 120.5, 119.3, 119.1, 111.2, 21.3. Elemental analysis: Calculated for $C_{24}H_{22}B_2N_2O_4$: C, 67.98%; H, 5.23%; N, 6.61%, Found C, 67.83%; H, 5.13%; N, 6.52%

4b$_{(THF)}$-1,2-$B_2cat_2(pic)_2$•(THF)

40 mg of 1,2-isomer obtained by recrystallization from DCB was redissolved in THF (approx. 3 ml), filtered and reduced in volume (to approximately 1 ml) under vacuum, the resulting solution was cooled to -20 ^{O}C overnight to yield yellow crystals of a distinctly different morphology (rough plates)

Notes and references

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† Electronic Supplementary Information (ESI) available: For detailed experimental conditions, single crystal and powder X-ray diffraction details, computational results and solution and solid state NMR data
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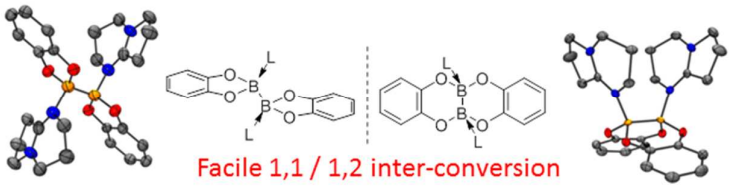

The unexpected 1,1/1,2 isomerisation of the diolate in B_2cat_2 is observed on addition of Lewis bases

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