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Reaction of Azole Heterocycles with Tris(dimethylamino)borane, a New Method for the Construction of Tripodal Borate-Centred Ligands

Philip J. Bailey,* Daniel Lorono-Gonzales, Chiara McCormack, Frances Millican, Simon Parsons, Robert Pfeifer, Pedro P. Pinho, Felix Rudolphi, and Alejandro Sanchez Perucha[a]

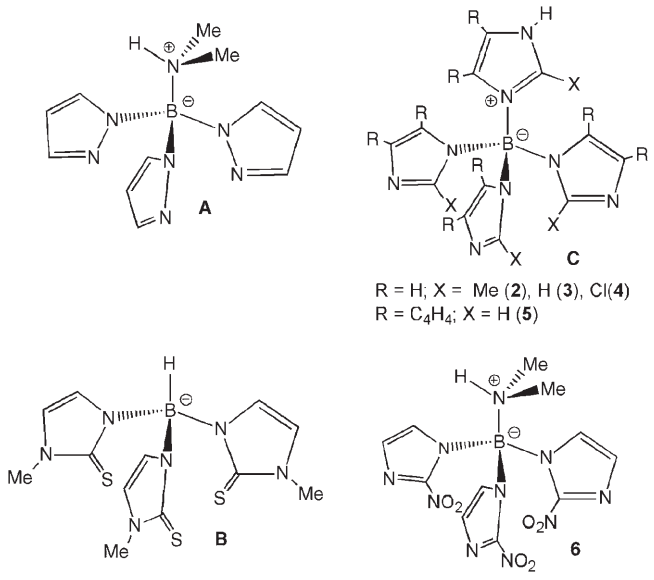
Abstract: Reaction of 2-mercapto-1-methylimidazole (methimazole) with tris(dimethylamino)borane, $B(NMe_2)_3$, provides the tetrahedral dimethylamine adduct of tris(methimazolyl)borane, $[(Me_2HN)B(methimazolyl)_3]$. By contrast, imidazole, 2-methylimidazole, 2-chloroimidazole and benzimidazole provide the homoleptic tetra-azolyl systems $H[B(azolyl)_4]$, and the same product is obtained even when a substoichiometric quantity of the heterocyle is employed. The change in reaction outcome is correlated with the variation of basic pK_a for the heterocycles. A simple acid-base reaction with elimination of $HNMe_2$ is proposed for the reaction with the weakly basic, but more strongly acidic, methimazole. However, for the more strongly basic imidazoles, initial coordination of the heterocycle imine nitrogen to the weakly Lewis acidic boron centre in $B(NMe_2)_3$ to form the tetrahedral adduct $[(azole)B(NMe_2)_3]$ is proposed. The greater availability of the NMe_2 lone pairs in this species results in increased basicity and a rapid reaction with further heterocycle to provide the observed $H[B(azolyl)_4]$ products. For 2-nitroimidazole, the low basicity (and increased N–H acidity) results in the formation of $[(HNMe_2)B(2\text{-nitroimidazolyl})_3]$ on reaction with $B(NMe_2)_3$, analogous to the product formed with methimazole. Both $[(HNMe_2)B(methimazolyl)_3]$ and $H[B(benzimidazolyl)_4]$ have been structurally characterised by single crystal X-ray crystallography. This chemistry has been exploited to provide a new synthesis of borate-centred tripod ligands, whereby *N*-methylimidazole is used to activate $B(NMe_2)_3$ to reaction with methimazole to form the new ligand $[(N\text{-methylimidazole})B(methimazolyl)_3]$ in good yield and a complex of this ligand with Ru^{II} has been structurally characterised.

Keywords: imidazoles · ligand design · ruthenium · scorpionates · tripod ligands

Introduction

The hydrotris(pyrazolyl)borate system and its various derivatives are ubiquitous among tripod ligands and displays a remarkable flexibility in coordinating to a variety of metals in a range of oxidation states and a strong preference for *fac*-tridentate (κ^3) coordination to both tetrahedral and octahedral metal ions.[1] The synthesis of these ligands by reaction of the chosen pyrazole with an alkali metal tetrahydroborate, either in a solvent-free (melt) reaction or in a suitable high-boiling solvent, is well established.[2] Alternative routes that provide tris(pyrazolyl)borates in which the boron-bound hydrogen has been replaced by an alternative group by using boron sources, such as boronic acids and boron trihalides, have also been established.[3] An interesting alternative route to systems of this type involves treatment of $B(NMe_2)_3$ with pyrazole, providing $[(HNMe_2)B(pyrazolyl)_3]$ **A** from which the N–H proton may readily be removed to provide an anionic ligand, which has received very little attention.[4] We were attracted by the outcome of this reaction as a result of our interest in the boron derivatisation of Reglinski's hydrotris(methimazolyl)borate (Tm) ligand system **B**,[5] reasoning that, if a similar species could be formed containing methimazolyl in place of pyrazolyl groups, suitable derivatisation of the remaining boron-bound $HNMe_2$ may provide a leaving group susceptible to substitution by a range of nucleophiles. Intrigued also by the possibilities of this reaction for the construction of other borate-centred ligands, we have undertaken a study of the reaction of imidazole and some of its derivatives with $B(NMe_2)_3$ to establish the

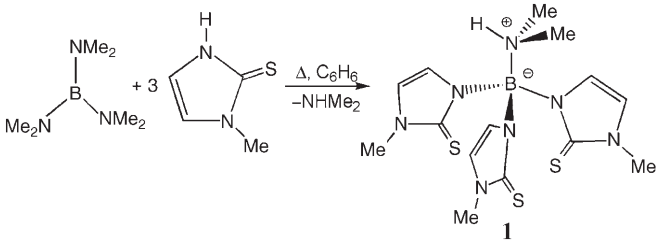
[a] Dr. P. J. Bailey, D. Lorono-Gonzales, C. McCormack, F. Millican, Dr. S. Parsons, Dr. R. Pfeifer, Dr. P. P. Pinho, F. Rudolphi, A. Sanchez Perucha
School of Chemistry, University of Edinburgh
West Mains Road, Edinburgh, EH9 3 JJ (UK)
Fax: (+44) 131-650-4743
E-mail: Philip.Bailey@ed.ac.uk



extent of its applicability. However, we find that these heterocycles provide an alternative product, H[B(azolyl)$_4$] (azole = imidazole, 2-methylimidazole, 2-chloroimidazole, benzimidazole) **C**, the formation of which we discuss here. Only with 2-nitroimidazole is there evidence for the formation of [(HNMe$_2$)B(2-nitroimidazolyl)$_3$] (**6**), a product analogous to that formed with methimazole and pyrazole. In a further elaboration of this chemistry we have employed *N*-methylimidazole to activate B(NMe$_2$)$_3$ towards reaction with methimazole to provide a new tripodal borate ligand [(*N*-methylimidazole)B(methimazolyl)$_3$] in good yield. We have also prepared and structurally characterised a Ru^{II} complex of this ligand. This approach therefore provides a new and promising methodology for the construction of a range of ligands of this type.

Results and Discussion

Reaction of B(NMe$_2$)$_3$ with three molar equivalents of methimazole in benzene solution under reflux for 2 h provides the adduct [(HNMe$_2$)B(methimazolyl)$_3$] (**1**) as a white precipitate on cooling the solution (Scheme 1). The ^{1}H NMR spectrum of this product contains only one singlet at $\delta = 3.48$ ppm, which can be assigned to the NHMe$_2$ and



Scheme 1. Reaction of methimazole with B(NMe$_2$)$_3$.

methimazolyl methyl groups; however, the ^{13}C NMR spectrum contains two signals ($\delta = 34.7$ and 34.9 ppm) due to these methyl groups, and the signals in the ^{1}H NMR spectrum for these different methyl groups must therefore be coincident; this is supported by the integral of this peak which corresponds to 15 hydrogen atoms. The reaction of B(NMe$_2$)$_3$ with methimazole therefore follows the same course as that for pyrazole[4] to provide the dimethylamine adduct of the tris(azolyl)borane.

Crystals of **1** were obtained by cooling a hot benzene solution to room temperature. X-ray crystal structure determination (Figure 1) confirms the formation of **1** in a similar

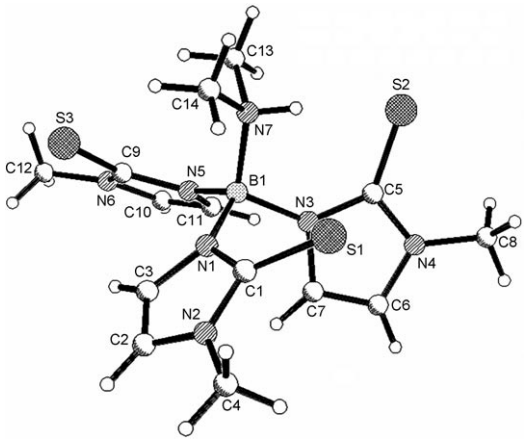


Figure 1. Structure of [(HNMe$_2$)B(methimazolyl)$_3$] (**1**). Selected bond lengths and angles are provided in Table 1.

manner to its previously reported pyrazole analogue;[4] selected bond lengths and angles are presented in Table 1. Direct comparison of the structure with the hydrotris(methimazolyl)borate (Tm) ligand is hampered by the fact that **1** is a neutral species and is not metal-coordinated, while all reported structures of the anionic Tm involve coordination to a metal counter ion. However for the purposes of comparison, the complex [ZnCl(Tm)][6] will be taken as a model system. The B–N(methimazole) bond lengths in **1** (range 1.542(3)–1.560(3) Å) are slightly shorter than those to the amine nitrogen (1.605(3) Å) reflecting the covalent and coordinate bonding of the two different groups, respectively, and the difference in nitrogen hybridisation. The B–N bond lengths in [ZnCl(Tm)] are very similar and range from 1.547–1.555 Å. The C=S bond lengths in **1** range from 1.694(2)–1.700(2) Å and are significantly shorter than those in [ZnCl(Tm)] (1.715–1.723 Å), consistent with metal coordination of the sulfur atoms in the complex. The N-B-N angles between methimazole groups in **1** are smaller than those between the NHMe$_2$ and methimazole groups reflecting the greater steric bulk of the amine, although the distortion is not severe, the smallest and largest angles being 106.49 and 112.50°. The orientation of the methimazole groups places their sulphur atoms towards the NHMe$_2$ group and the presence of two hydrogen bonds is indicated

Table 1. Selected bond lengths [Å] and angles [°] for [$(HNMe_2)$B(methimazolyl)$_3$] (**1**), H[B(benzimidazolyl)$_4$] (**5**) and [Ru(*p*-cymene)(*N*-methylimidazole)B(methimazolyl)$_3$][Cl]$_2$ (**9**).

1	**5**	**9**
B–N(11) 1.547(6)	B–N(1) 1.542(3)	B–N14 1.567(12)
B–N(12) 1.524(6)	B–N(3) 1.559(3)	B–N11 1.559(12)
B–N(13) 1.527(6)	B–N(5) 1.556(3)	B–N12 1.538(12
B–N(14) 1.536(6)	B–N(7) 1.605(3)	B–N13 1.551(12)
N(11)–C(21) 1.357(4)	N(1)–C(1) 1.373(3)	C21–S21 1.721(9)
C(21)–N(31) 1.313(4)	C(1)–N(2) 1.356(3)	C22–S22 1.734(8)
N(12)–C(22) 1.362(5)	C(1)–S(1) 1.694(2)	C23–S23 1.735(8)
C(22)–N(32) 1.302(5)	N(3)–C(5) 1.359(3)	S21–Ru 2.441(2)
N(13)–C(23) 1.384(5)	C(5)–N(4) 1.358(3)	S22–Ru 2.428(2)
C(23)–N(33) 1.338(5)	C(5)-S(2) 1.700(2)	S23–Ru2.409(2)
N(14)–C(24) 1.354(5)	N(5)–C(9) 1.370(3)	N11-B-N12 113.3(7)
C(24)–N(34) 1.360(6)	C(9)–N(6) 1.365(3)	N11-B-N13 111.3(7)
N(11)-B-N(12) 110.9(3)	C(9)–S(3) 1.686(2)	N11-B-N14 105.0(7)
N(11)-B-N(13) 110.4(3)	N(1)-B-N(3) 106.49(17)	N12-B-N13 110.0(7)
N(11)-B-N(14) 105.6(3)	N(1)-B-N(5) 109.92(18)	N12-B-N14 105.2(7)
N(12)-B-N(13) 109.9(3)	N(1)-B-N(7) 112.51(18)	N13-B-N14 111.9(7)
N(12)-B-N(14) 111.2(4)	N(3)-B-N(5) 107.80(18)	C21-S21-Ru 103.1(3)
N(13)-B-N(14) 108.8(3)	N(3)-B-N(7) 109.53(18)	C22-S22-Ru 105.9(3)
	N(5)-B-N(7) 110.40(17)	C23-S23-Ru 109.8(3)

by one relatively short S···H distance of 2.294 Å (to S2) and a longer one of 3.153 Å (to S1) from a second methimazole group.

All attempts at derivatisation of **1** by removal of the $HNMe_2$ proton with base and reaction with a range of electrophiles (MeI, Me_3OBF_4, MeCOCl, PhCOCl) failed and resulted only in isolation of free methimazole and/or the product of the addition of the electrophile to the methimazolyl anion. The decomposition appears to occur at the deprotonation stage, and despite the exploration of a range of bases (BuLi, MeLi, NaH, NaOMe, LDA), we have been unable to isolate or trap the borate [(Me_2N)B(methimazolyl)$_3$]$^-$. This is somewhat surprising given the ready formation of the stable pyrazolyl analogue [(Me_2N)B(pyrazolyl)$_3$]$^-$,[4b] and may indicate weaker coordination of the methymazolyl rings to the boron centre leading to decomposition via a trigonal borane species and ejection of a methimazolyl anion. This difference in reactivity is consistent with the stability of the heterocycle anions as indicated by the acidic pK_a values for pyrazole and methimazole (see Table 2).

Wishing to explore the scope of this reaction of azoles with $B(NMe_2)_3$, we have studied the reaction with a range of imidazoles. Reaction of three molar equivalents of 2-methylimidazole with tris(dimethylamino)borane in toluene or benzene solution at reflux does not provide the expected [$(HNMe_2)$B(azolyl)$_3$] product, but instead gives H[B(2-methylimidazolyl)$_4$] (**2**), a species which has previously been prepared employing tetrahydroborate as the boron source.[7] At a lower temperature in THF at reflux, the reaction did not proceed and only starting materials could be isolated. The reaction of equimolar quantities of 2-methylimidazole and $B(NMe_2)_3$ in toluene at reflux also produced the borate **2** exclusively. These observations were reproduced for reactions with imidazole, 2-chloroimidazole and benzimidazole to provide H[B(azolyl)$_4$] products **3**, **4** and **5**, respectively (Scheme 2). The synthesis of **3** from sodium tetrahydroborate followed by treatment with acid has previously been reported.[8] Similarly, salts of the [N(Benzimidazolyl)$_4$]$^-$ anion have been prepared before;[8] however, the free acid **5** has not previously been reported. No evidence for the formation or intermediacy of [$(HNMe_2)$B(azolyl)$_3$], nor indeed any other species, could be obtained by removing samples for MS analysis during the reactions or conducting the reactions at lower temperatures in the same or different solvents. Only molecular ions and fragments which could be assigned to either B(azolyl)$_4^-$ or the starting imidazole and $B(NMe_2)_3$ were observed. Only in the case of reaction with 2-nitroimidazole could an ion due to [$(HNMe_2)$B(2-nitroimidazolyl)$_3$] be observed in a mass spectrum of the reaction solution; however, this was never formed in sufficient quantities to allow its isolation due to apparent thermal decomposition over the longer reaction times, which would be necessary for its formation in appreciable yield.[9]

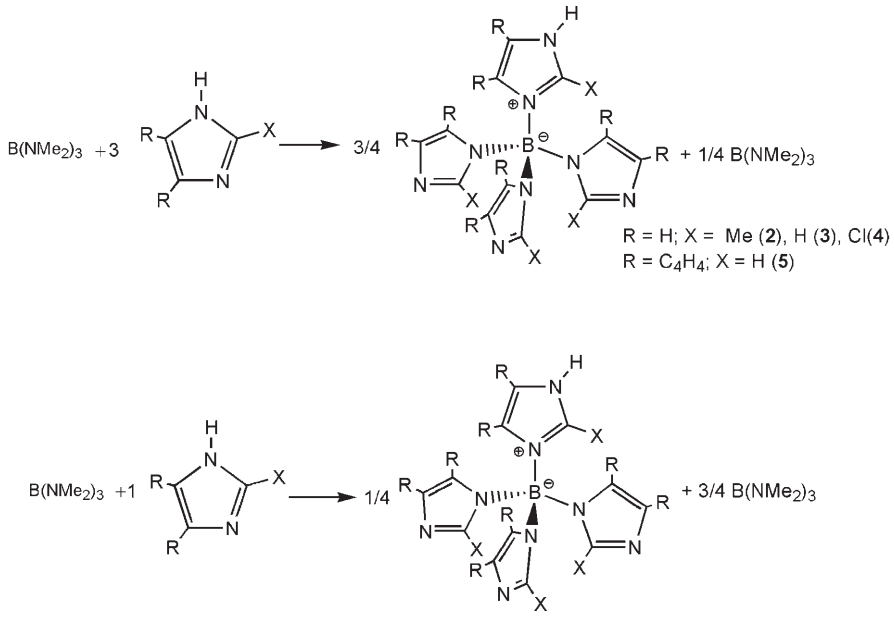
Table 2. pK_a data for the heterocycles employed in this work.

	Basic pK_a[a]	Acid pK_a[a]
methimazole	−1.05[28a]	12[28b]
2-nitroimidazole	−0.8 (DMF/H_2O)[28c]	7.15 (MeOH/H_2O)[28d]
pyrazole	2.79 (H_2O)[28e]	14.0 (EtOH/H_2O)[28f]
2-chloroimidazole	3.55 (H_2O)[28g]	10.5[28h]
benzimidazole	5.7 (H_2O)[28i]	13.2 (MeOH/H_2O)[28j]
imidazole	7.0 (DMF/H_2O)[28k]	14.9 (DMF/H_2O)[28k]
2-methylimidazole	7.85 (DMF/H_2O)[28k]	15.1[28l]

[a] The basic pK_a is defined as the pK_a of the conjugate acid of the heterocycle, the pK_a of $[H_2Pz]^+$ for pyrazole for example, and is therefore a measure of its Brønsted basicity. The acid pK_a is that of the parent heterocycle, HPz for example, and is therefore a measure of its Brønsted acidity.

The X-ray crystal structure of H[B(benzimidazolyl)$_4$] (**5**) was determined and its structure is illustrated in Figure 2. Selected bond lengths and angles are presented in Table 1. The position of the proton to balance the charge on the borate anion was not evident from the data and it has been split equally between N31 and N32 as a result of unfavourable contacts when it is located on the other two nitrogen atoms (N33 and N34). The B–N bond lengths to the benzimidazole groups containing these nitrogen atoms (1.547(6) and 1.536(6) Å) are marginally longer than those to the other ones (1.525(6) and 1.527(6) Å), providing some support for this assignment. In other respects the structure is quite symmetrical, the N-B-N angles deviate only slightly from the ideal (range 105.56–111.18°), for example.

On the basis of the products isolated from the above reactions it is clear that the reactions between $B(NMe_2)_3$ and



Scheme 2. Reaction of imidazole and its derivatives with $B(NMe_2)_3$.

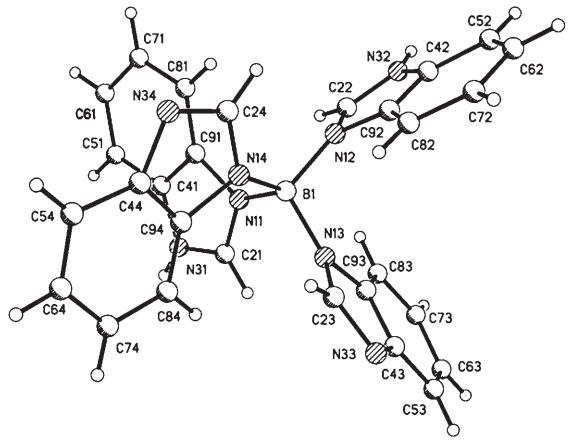
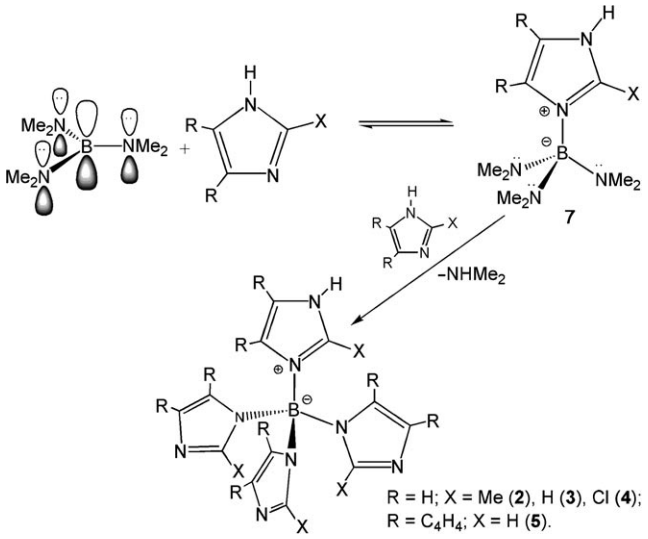


Figure 2. Structure of H[B(benzimidazolyl)$_4$] (**5**). The N–H proton is placed upon N31 and N32 with equal weighting. Selected bond lengths and angles are provided in Table 1.

pyrazole, methimazole or 2-nitroimidazole on the one hand, and imidazole, 2-methylimidazole and 2-chloroimidazole on the other, follow different mechanisms. The most obvious difference between these two sets of azoles is their basicity (Table 2). Methimazole is only very weakly basic ($pK_a = -1.05$), which is perhaps not surprising given the dominance of the thione tautomer.[10] Pyrazole is also only weakly basic with a pK_a of just 2.79 in water. Imidazole and its derivatives are, however, considerably stronger bases, with even the 2-chloro-substituted derivative ($pK_a = 3.55$) being more basic than pyrazole. Only nitro-substitution reduces the pK_a to a value similar to that of methimazole and it is therefore significant that reaction with this species is found to provide the same product as that observed with methimazole and pyrazole.

One of the interesting features of $B(NMe_2)_3$ is the presence of significant B–N pπ-bonding, and the effect of this on its Lewis acid/base properties is significant. In comparison to group 15 analogues $E(NMe_2)_3$ (E = P, As, Sb, Bi), in which the electronic saturation of the central atom precludes any π-bonding, $B(NMe_2)_3$ is only very weakly basic. This is illustrated by the absence of any reaction with amines or considerably more acidic species, such as methimazole, under ambient conditions, which contrasts with the double metallation that can occur on reaction of $E(NMe_2)_3$ with primary amines under the same conditions.[11] The availability of nitrogen lone pairs in these species makes them very strong bases compared to systems, such as lithium alkyls in which the basic lone pair is restricted in its availability by metal coordination, and only monolithiation of primary amines by *n*BuLi is typically observed.[12] The increased E–N bond strength and the occupation of the nitrogen lone pairs engendered by B–N π-bonding in $B(NMe_2)_3$ results in greatly reduced basicity for both kinetic and thermodynamic reasons.[13] Nevertheless, reaction with moderately acidic species, such as the azoles considered here, can be observed under forcing conditions to provide the observed [$(HNMe_2)B(azolyl)_3$] products, such as **1**.

The formation of the alternative products H[$B(azolyl)_4$] with the more basic imidazoles, and in particular their formation from substoichiometric quantities of the azole, requires an alternative explanation, which we suggest is as follows. The Lewis acidity of $B(NMe_2)_3$ is very low due to its modulation by the B–N π-bonding.[14] As a consequence, the weakly basic pyrazole and indeed methimazole, does not coordinate to the boron centre, even under forcing conditions (toluene reflux), before the onset of the acid-base reaction leading to the [$HNMe_2B(azolyl)_3$] products with elimination of $NHMe_2$. However, for the more strongly basic imidazoles coordination to the boron occurs before this stage is reached and a tetrahedral intermediate **7** is formed (Scheme 3). The absence of B–N π-bonding in this species results in the full availability of the nitrogen lone pairs and basic behaviour similar to that found for the $E(NMe_2)_3$ species discussed above should be anticipated. Under the conditions required to form **7** therefore, its reaction with all remaining azole is rapid, providing the tetra-azolylborates, even when a substoichiometric ratio of $B(NMe_2)_3$ and azole is employed. It is unfortunate that the product from the reaction with 2-nitroimidazole could not be isolated due to its apparent low stability under the reaction conditions. However, the obser-



Scheme 3. Reaction of imidazoles with $B(NMe_2)_3$ to provide homoleptic borates $H[B(azolyl)_4]$.

vation of an ion at $m/z = 392$ due to $[(HNMe_2)B(2\text{-nitroimidazolyl})_3]$ in samples withdrawn from the reaction mixture, and the absence of an ion due to the $H[B(2\text{-nitroimidazolyl})_4]$, indicates that the mechanism adopted by pyrazole and methimazole is accessible to 2-substituted imidazoles if their basicity is sufficiently low. It seems therefore that at an azole pK_a between those for pyrazole (2.79) and 2-chloroimidazole (3.55), the mechanism of the reaction between $B(NMe_2)_3$ and azoles changes from one in which coordination of the azole to provide an intermediate **7** does not occur before the acid-base reaction to one in which it does. This mechanistic change will also be dependent on the acidic pK_a of the azole as the direct acid-base reaction will clearly be favoured by increased azole N–H acidity.

We have sought to exploit our understanding of the reactivity of $B(NMe_2)_3$ with azoles in the synthesis of new borate-centred tripod ligands by reaction with the chosen N–H acid in the presence of *N*-methylimidazole acting as a simple Lewis base to coordinate to, and activate, $B(NMe_2)_3$ towards reaction with acidic heterocyclic donor groups. On the basis of the mechanism shown in Scheme 3, we anticipated initial formation of a species analogous to **7** with the *N*-methylimidazole, which would then subsequently react rapidly with the N–H acid present in solution under the reaction conditions. The reaction between $B(NMe_2)_3$ and methimazole (1:3) in the presence of 1 equivalent of *N*-methylimidazole under reflux in toluene solution provides the new ligand [(*N*-methylimidazole)B(methimazolyl)$_3$] (**8**) in good yield as a colourless precipitate from the reaction mixture. This ligand is of the generic type $E(L_2D)_3$ (E = central tripod atom, L = linking atom and D = donor atom), providing a bicyclo[3.3.3]-cage which adopts a chiral twisted C_3-symmetric structure. These complexes exhibit a particular type of atropisomerism in which there is restricted rotation about the 3-fold axis and they can therefore exist in chiral mirror-image forms (Figure 3).[3a,15]

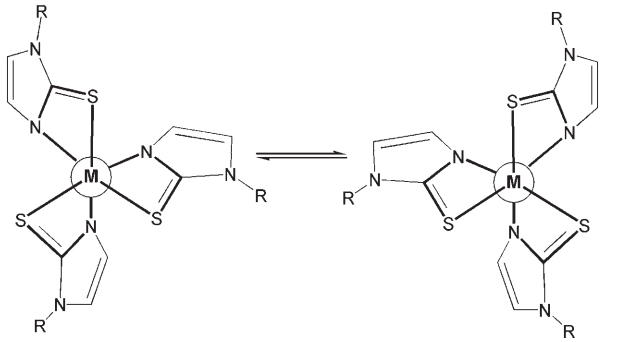


Figure 3. The C_3-symmetric chiral structures of complexes of ligands of the type $E(L_2D)_3$ as exemplified by tris(methimazolyl)borate ligands.

Complexation of **8** to Ru^{II} was achieved by reaction with $[\{Ru(p\text{-cymene})Cl_2\}_2]$ in CH_2Cl_2 solution. The chirality of the resulting complex [Ru(*p*-cymene)(*N*-methylimidazole)B-(methimazolyl)$_3$][Cl]$_2$ (**9**) is revealed in its ^{1}H NMR spectrum which shows a pair of singlets for the diastereotopic *p*-cymene *i*Pr methyl groups and four doublets for the *p*-cymene arene CH protons that normally produce an $(AB)_2$ pattern in achiral systems.[16] The X-ray crystal structure of **9** shows the unit cell to contain two mirror-image pairs of complexes displaying $\delta\delta\delta$ and $\lambda\lambda\lambda$-stereochemistry for the three ligand arms with θ^m values (mean N-B-M-S torsion angles[16]) of 49.8 and −49.5°, respectively. The other torsional parameter (ω^m, the mean angle made by the normal to the methimazole rings with the B-M vector[17]), 57.75 and −56.28° for the $\delta\delta\delta$ and $\lambda\lambda\lambda$ complexes, respectively, fall in the range observed for Tm complexes of octahedral metals.[17,18] The $\delta\delta\delta$ enantiomer is illustrated in Figure 4, and selected bond lengths and angles are given in Table 1. The dipositive charge of the complexes is balanced by four chloride ions displaying short hydrogen bond contacts with the two water and four CH_2Cl_2 molecules also

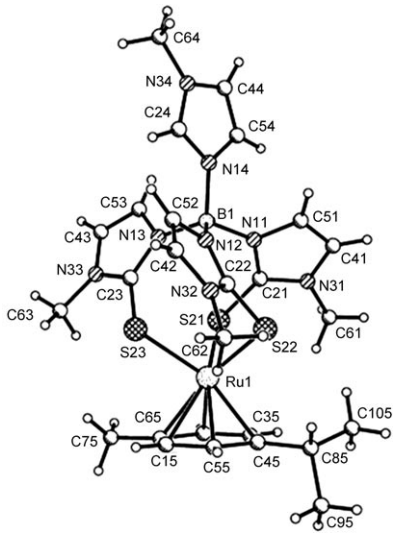


Figure 4. Molecular structure of the $\delta\delta\delta$ enantiomer of **9**. Selected bond lengths and angles are provided in Table 1.

present in the unit cell. There are only minor differences in the metric parameters between the two enantiomers and only those for the $\delta\delta\delta$ isomer will be discussed below. The coordinate B–N (*N*-methylimidazole) bond (1.575 Å) is slightly longer than the covalent bonds to the methimazole rings (mean 1.540 Å). The C–S and S–Ru bond lengths (mean 1.720 and 2.425 Å, respectively) do not differ significantly from those found in the corresponding complex containing the Tm ligand [Ru(*p*-cymene)(Tm)]Cl (mean C–S = 1.723 and mean S-Ru = 2.411 Å),[15a] indicating that the binding of ligand **8** to the ruthenium centre is similar to that for Tm.

Conclusion

It is evident from this study that the activation of $B(NMe_2)_3$ to reaction with heterocyclic N–H acids by Lewis bases with a basic $pK_a > 3$ provides a novel route to tetrahedral borate species. The formation of the new system [(*N*-methylimidazole)B(methimazolyl)$_3$] (**8**) illustrates the application of this methodology to the construction of a new borate-centred tripod ligand of the $E(L_2D)_3$ type. We are currently exploring the flexibility of this approach in the synthesis of a range of new ligand systems of this type, employing alternative donor heterocycles and activating Lewis bases and will report on these in subsequent publications.

Experimental Section

General: All reactions were carried out under an atmosphere of dry, oxygen-free dinitrogen by using standard Schlenk techniques. Solvents were freshly distilled over an appropriate drying agent and further degassed before use when necessary. MS were recorded on Kratos MS50TC (FAB) and Micromass Platform II (ES-MS) spectrometers. NMR spectra were recorded on a Bruker 250 AC spectrometer operating at room temperature. ^{1}H and ^{13}C chemical shifts are reported in ppm relative to $SiMe_4$ ($\delta = 0$) and were referenced internally with respect to the protio solvent impurity or the ^{13}C resonances, respectively. Multiplicities and peak types are abbreviated: singlet, s; doublet, d; triplet, t; multiplet, m; broad, br; aromatic, ar. 2-Chloroimidazole was prepared by a modification of the literature method by using hexachloroethane in place of *N*-chlorosuccinimide as the chlorinating agent.[19] [{Ru(*p*-cymene)Cl$_2$}$_2$] was prepared according to the literature procedure.[20] All other chemicals were obtained from Sigma-Aldrich and used as received.

General procedure for the reaction of azoles with $B(NMe_2)_3$: In a typical reaction the azole was added in one portion to a solution of the required quantity of $B(NMe_2)_3$ in the chosen solvent, and the solution was then heated to reflux. After the specified period, the reaction mixture was allowed to cool and the solvent removed from the resulting colourless solid by the use of a cannula under nitrogen. Finally, the product was dried under vacuum. For the cases in which the product was soluble in the reaction solvent, the solvent was removed under vacuum to provide the crude product.

[(HNMe$_2$)B(methimazolyl)$_3$] (1): In a dry two-neck flask adapted with a reflux condenser, methimazole (978 mg, 8.57 mmol) was suspended under nitrogen in benzene (10 mL). $B(NMe_2)_3$ (0.500 cm^3, 2.86 mmol) was then added to the mixture at room temperature in one portion and the mixture set to reflux for 2 h. During reflux, a clear solution was first obtained (after a few minutes), followed by precipitation with time (after approximately 20 min). After 2 h the reaction was cooled to room temperature and the solvent removed from the remaining white solid. If precipitation did not occur, even after cooling the mixture, the volume of solvent was slightly reduced to induce precipitation of the product (927 mg, 82%). Crystals for X-ray analysis (see Figure 1) were obtained by dissolving a small amount of the product in hot benzene and allowing the solution to slowly cool to room temperature. ^{1}H NMR ($CDCl_3$): $\delta = 3.48$ (s, 15H), 6.36 (s, 3H), 6.52–6.62 (m, 3H), 9.72 ppm (br s, 1H); ^{13}C NMR ($CDCl_3$): $\delta = 34.7$, 34.9, 117.4, 120.6, 165.4 ppm; MS (FAB+): *m/z*: 396 $[M]^+$; elemental analysis calcd for $C_{14}H_{22}BN_7S_3 \cdot C_6H_6$: C 50.73, H 5.96, N 20.71; found: C 50.67, H 5.94, N 20.79.

H[B(2-methylimidazolyl)$_4$] (2): 2-methylimidazole (0.703 g, 8.57 mmol) was added to a solution of $B(NMe_2)_3$ (0.500 cm^3, 2.86 mmol) in toluene (10 cm^3), and the resulting mixture was heated to reflux. The reaction was monitored by mass spectrometry, and after 8 h ions due to the reactants were absent. The solvent was then removed under vacuum, the product washed with dry hexane (2×10 mL), and then dried to give **2** (0.720 g, 2.14 mmol, 75%) as a colourless crystalline solid. ^{1}H NMR (CD_3OD): $\delta = 1.99$ (s, 12H; C*H*$_3$), 6.92 (d, 4H; 4- or 5-C*H*), 7.23 ppm (d, 4H; 4- or 5-C*H*); ^{13}C NMR (CD_3OD): $\delta = 12.45$ (*C*H$_3$), 121.88 (4- or 5-*C*H), 124.25 (4- or 5-*C*H), 147.53 ppm (C_{quat}); MS (ES): *m/z*: 335 $[M-H]^+$; elemental analysis calcd for $C_{16}H_{21}N_8B$: C 57.15, H 6.29, N 33.32; found: C 56.97, H 6.15, N 33.04.

H[B(imidazolyl)$_4$] (3): Freshly sublimed imidazole (0.585 g, 8.6 mmol) was added to a solution of $B(NMe_2)_3$ (0.500 cm^3, 2.86 mmol) in toluene (10 cm^3) and heated to reflux. After 8 h the precipitated white powder was isolated by filtration. The crude product was purified by dissolving in the minimum amount of methanol, followed by the dropwise addition of diethyl ether until precipitation commenced, after which the mixture was stored at −5 °C. The product was filtered by the use of a cannula and the solid dried under vacuum to give **3** (0.60 g, 2.15 mmol, 75%) as a white powder. Spectroscopic data were consistent with the literature values:[20] ^{1}H NMR ($CDCl_3$): $\delta = 7.04$ (s, 1H), 6.93 (d, 1H), 6.78 (d, 1H); MS (FAB): *m/z*: 280.9 $[M]^+$.

H[B(2-chloroimidazolyl)$_4$] (4): 2-chloroimidazole (0.878 g, 8.57 mmol) is added to a solution of $B(NMe_2)_3$ (0.50 cm^3, 2.86 mmol) in toluene (10 cm^3) and heated to reflux. After 1 h mass spectrometry indicated that the reaction was complete. Half of the solvent was then removed under vacuum to precipitate a white solid, which was filtered by the use of a cannula, washed with dry hexane (2×10 mL) and dried to give **4** (0.693 g, 1.66 mmol, 58%) as a white solid. ^{1}H NMR ($CDCl_3$): $\delta = 6.84$ (s, 1H), 6.63 ppm (s, 1H); ^{13}C NMR ($CDCl_3$): $\delta = 138.2$ (C–Cl), 133.01 (CH), 129.92 ppm (CH); MS (EI, +25 eV): 418.8 $[M]^+$; elemental analysis calcd for $C_{12}H_9BN_8Cl_4 \cdot 3H_2O$: C 34.87, H 3.29, N 25.42; found: C 34.82, H 3.40, N 25.63.

H[B(benzimidazolyl)$_4$] (5): Benzimidazole (1.01 g, 8.57 mmol) was added to a solution of $B(NMe_2)_3$ (0.50 cm^3, 2.86 mmol) in toluene (10 cm^3), and the resulting mixture was heated to reflux. Mass spectrometry indicated that the reaction was complete after 5 h, and the solvent was then removed under vacuum. The crude product was purified by dissolving it in the minimum amount of methanol, followed by the dropwise addition of diethyl ether until precipitation commenced, after which the mixture was stored at −5 °C. The white solid product was filtered by the use of a cannula and dried under vacuum to give **5** (0.700 g, 1.45 mmol, 51%). A sample of the product was recrystallized by slow diffusion of pentane into a methanol solution to produce a crystal suitable for X-ray crystallography. ^{1}H NMR ($CDCl_3$): $\delta = 7.73$ (s, 1H), 7.64 (d, 1H), 7.09 (t, 1H), 6.90 (t, 1H), 6.57 ppm (d, 1H); ^{13}C NMR ($CDCl_3$): $\delta = 145.7$ (quat), 144.6 (quat), 136.4 (CH), 121.8 (CH), 120.9 (CH), 118.9 (CH), 112.3 ppm (CH); MS (FAB): 479 $[M]^+$; elemental analysis calcd for $C_{28}H_{21}BN_8 \cdot 0.5\,C_5H_{12} \cdot 0.5\,CH_3OH$: C 69.93, H 5.49, N 21.04; found: C 69.89, H 5.45, N 21.09.

[(*N*-methylimidazole)B(methimazolyl)$_3$] (8): Tris(dimethylamino)borane (128 µl, 105 mg, 0.73 mmol), *N*-Methylimidazole (58 µl, 60 mg, 0.73 mmol) and methimazole (250 mg, 2.20 mmol) were refluxed in toluene (5 cm^3) under nitrogen. After 3 h, a colourless solid precipitated, which was washed with dry hexane (2×10 mL) and dried in vacuo to yield **8** (280 g, 0.64 mmol, 88%). ^{1}H NMR ($CDCl_3$): $\delta = 3.49$ (s, 9H), 3.81 (s, 3H), 6.61–6.65 (m, 6H), 6.95 (s, 1H), 7.19 (s, 1H), 8.97 ppm (s, 1H);

Table 3. Crystallographic data for [(HNMe$_2$)B(methimazolyl)$_3$] (**1**), H[B(benzimidazolyl)$_4$] (**5**) and [Ru(*p*-cymene)(*N*-methylimidazole)B(methimazolyl)$_3$][Cl]$_2$ (**9**).

	1	**5**	**9**
crystal description	colourless block	colourless block	red block
empirical formula	$C_{20}H_{28}BN_7S_3$	$C_{31}H_{29}BN_8O_{0.5}$	$C_{28}H_{41}BCl_6N_8ORuS_3$
M_w	395.41	532.43	926.45
T [K]	150(2)	150(2)	150(2)
crystal system	monoclinic	orthorhombic	triclinic[a]
space group	$C2/c$	$Fdd2$	$P\bar{1}$
a [Å]	27.290(2)	25.987(2)	14.4174(17)
b [Å]	11.8268(10)	48.046(4)	16.8641(19)
c [Å]	13.4467(11)	9.4624(6)	17.1528(19)
α [°]	90	90	93.237(3)
β [°]	97.663(5)	90	112.814(2)
γ [°]	90	90	91.016(3)
V [Å^3]	4301.2(6)	11814.3(15)	3834.5(8)
Z	8	16	4
μ(Cu$_{K\alpha}$) [mm^{-1}]	0.356	0.075	0.71073
independent reflections	5203 (R_{int} = 0.0420)	3824 (R_{int} = 0.0737)	15602 (R_{int} = 0.0711)
data with $\|F\| > 4\sigma(\|F\|)$	1664	2839	13091
absorption correction	semiempirical from equivalents	multiscan	multiscan
min/max transmission	0.9597/0.8965	0.629/1.00	0.341/0.810
R	0.0572	0.0586	0.0747

[a] Twinned through 2 [0 1 0].

^{13}C NMR ($CDCl_3$): δ = 35.10 (CH_3-Methymazole), 36.05 (CH_3-imid), 114.36 (CH-Imi), 117.94 (CH-Met), 121.63 (CH-Imi), 124.59 (CH-Met), 142.66 (CH-Imi), 164.70 ppm (C=S); ^{11}B NMR ($CDCl_3$): δ = 8.05 ppm (s); MS *m/z*: (EI, +25 eV): 433 $[M]^+$; elemental analysis calcd for $C_{16}H_{21}BN_8S_3{\cdot}C_7H_8$: C 52.66, H 5.57, N 21.36; found: C 52.57, H 5.52, N 21.39.

[Ru(*p*-cymene)(*N*-methylimidazole)B(methimazolyl)$_3$][Cl]$_2$ (9): [{RuCl(*p*-cymene)(μ-Cl)}$_2$] (100 mg, 0.16 mmol) and ligand **7** (141 mg, 0.33 mmol) were stirred in dry ethanol (5 cm^3) overnight. For the next step, the solution was stirred for 4 h at 70 °C, after which time, the solvent was removed in vacuo to give **9** (97 mg, 0.13 mmol, 82 %) as a red-brown solid. Crystals suitable for X-ray analysis were obtained by diffusion of hexane into a solution of the complex in dichloromethane. ^{1}H NMR (DMSO): δ = 1.39 (d, 6H), 2.38 (s, 3H), 3.11 (sept, 1H), 3.91 (s, 9H), 4.09 (s, 3H); 5.84–5.94 (m, 4H), 7.27 (d, 3H), 7.82 (d, 3H), 8.03 (d, 1H), 8.11 (d, 1H), 9.31 ppm (s, 1H); ^{13}C NMR (DMSO): δ = 30.44 (CH_3-Met), 35.47 (CH_3-Imi), 39.78 (CH_3 *i*Pr or Me), 40.13 (CH_3 *i*Pr or Me), 95.31 (*i*Pr), 106.22 (CH-Ar), 114.28 (CH-Met), 122.39 (CH-Met), 122.95 (CH-Imi), 124.47 (CH-Imi), 128.50 (CH-Ar), 133.26 (C_{quat}-Ar), 139.48 (CH-2-Imi), 141.60 (C_{quat}-Ar), 159.51 ppm (C=S); ^{11}B NMR (DMSO): δ = 3.32 (s); MS (EI, +25 eV): *m/z*: 334; elemental analysis calcd for $C_{26}H_{35}BN_8S_3Ru{\cdot}Cl_2{\cdot}(CH_2Cl_2)_2{\cdot}H_2O$: C 36.29, H 4.46, N 12.09; found: C 37.13, H 4.79, N 13.27; elemental analysis of this compound was hampered by gradual loss of CH_2Cl_2. The crystals used for the analysis were the same as those used in the X-ray analysis. The calculated analysis for the compound with loss of one mole of CH_2Cl_2 is: C 38.53, H 4.67, N 13.31.

X-ray crystallography: Crystal data for **1**, **5** and **9** are presented in Table 3. All data sets were collected with Mo$_{K\alpha}$ radiation (λ = 0.71073 Å) on a Bruker SMART APEX CCD diffractometer equipped with an Oxford Cryosystems low-temperature device operating at 150 K. Absorption corrections were carried out by using the multi-scan procedure SADABS.[21] The structures of **1** and **5** were solved by direct methods (SHELXS-97),[22] and that of **9** was solved by Patterson methods (DIRDIF)[23] and refined by full-matrix least-squares against F^2 (SHELXL-97).[24]

The benzene solvent of crystallization in **1** was disordered over several positions and was treated in the manner described by van der Sluis and Spek.[25] All nonhydrogen atoms were refined anisotropically, while hydrogen atoms were placed in calculated positions, constrained to ride on their carbon atoms with group U_{iso} values assigned [U_{iso}(H) = 1.20 U_{iso} for aromatic carbons and 1.50 U_{iso} for methyl atoms].

The crystal of **5** diffracted only weakly, and only data to 2θ = 45° were used for analysis. Most H-atoms could be placed in calculated positions. The position of the H-atom needed to balance the charge of the zwitterion was less obvious, and it was not evident in a difference map. Neither were plausible positions recognizable from considerations of intermolecular H-bonding. Possible H-positions were calculated and those on N33 and N34 ruled out on the basis of unfavourable contacts (e.g. H33··H22′ = 1.96 Å). The proton was therefore split equally over the remaining sites on N31 and N32. The solvent of crystallization in **5**, was unrecognizably disordered, and was treated by using the procedure of van der Sluis and Spek,[25] accounting for 750 e per cell. Assuming 0.5 pentane and 0.5 MeOH per formula unit yields 720 e per cell, and the formulae, M_r, μ etc. were calculated according to this assumption.

The crystal of **9** was nonmerohedrally twinned by a two-fold rotation about [0 1 0],[26] the twin-scale factor refined to 0.4652(14). O1w and O2w were assigned as water on the basis that (1) when assigned as Cl their isotropic displacement parameters increased to 0.15, much larger than the other Cl atoms and (2) the presence of contacts of approximately 3 Å to the Cl$^-$ anions. The water H-atoms were included in positions based on favourable intermolecular contacts.[27] CCDC-285496–285498 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[9] 2-nitroimidazole (250 mg, 2.21 mmol) was added to a solution of tris(dimethylamino)borane (129 µl, 105 mg, 0.74 mmol) and *N*-Methylimidazole (61 µl, 63 mg, 0.74 mmol) in dry toluene (5 mL). The mixture was then heated to reflux and samples were extracted for analysis by mass spectrometry every 10 min. After 40 min, a weak ion corresponding to $[NHMe_2B(2\text{-nitroimidazolyl})_3]$ (**6**) (MS (EI, + 25 eV): *m/z*: 392 $[M]^+$) was detected for the first time, and after 70 min it was detected with the same intensity as the nitroimidazole starting material. Beyond this point the reaction mixture became progressively darker in colour, until after 90 min the ion due to **6** was absent from the mass spectrum and only a small peak corresponding to the nitroimidazole was seen. All attempts at isolation of the product **6** failed and further analysis was therefore not possible.

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