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A New Synthesis of Charge-Neutral Tris-Pyrazolyl and -Methimazolyl Borate Ligands**

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Supporting information:
CCDC-747521 (11), 747522 (12), 747523 (13), and 749089 (8) 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

Synopsis:
The substitution of the $HNMe_2$ in $(HNMe_2)B(Azolyl)_3$ (Azolyl = pyrazolyl, methimazolyl) by a range of N-donors provides a high yielding route to neutral tripodal ligands. The IR spectra of Mn(I) tricarbonyl complexes of the ligands allows comparison of their donor properties with the anionic parent Tp and Tm ligands and shows them to be only marginally weaker donors.

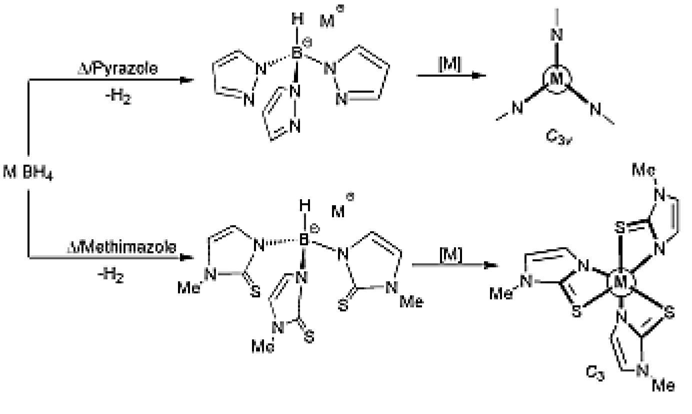
Keywords:
ligand design; manganese; ruthenium; scorpionates; tripodal ligands

Abstract

The dimethylamine in the adducts [$(HNMe_2)B(azolyl)_3$] (azolyl = methimazolyl, pyrazolyl), obtained by reaction of the azole with $B(NMe_2)_3$, can readily be substituted with a range of nitrogen donors to provide new charge-neutral, tripodal ligands in high yield. This observation has lead to a revision of an earlier interpretation of the mechanism of the formation of these species. The donor properties of the ligands [$(NMI)B(azolyl)_3$] (NMI = N-methylimidazole) have been compared with their anionic analogues $[HB(azolyl)_3]^-$ by synthesis of their manganese(I)tricarbonyl complexes and comparison of their infra red ν_{co} energies. This comparison indicates that the new neutral ligands are only marginally weaker donors than the corresponding anionic hydrotris(azolyl)borate ligands. This may be explained by the ability of the attached NMI ring to stabilize a positive charge remote from the coordinated metal, which may also account for the fact that the [$(NMI)B(pyrazolyl)_3$] ligand is a substantially stronger donor than the similarly neutral tris(pyrazolyl)methane ligand.

Introduction

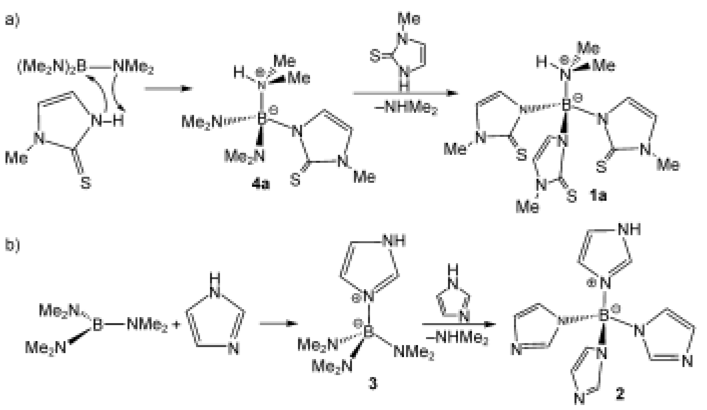
The synthesis of tripodal borate-centered ligands through reaction of a tetrahydroborate salt with an azole heterocycle is well established and follows Trofimenko's original methodology for the preparation of the hydrotris(pyrazolyl)borate (Tp) ligand (Scheme 1).[1] The reaction is conventionally conducted in the absence of a solvent in a so called melt reaction, but high boiling hydrocarbon or ether solvents have also been used. Ligands synthesized from a wide range of substituted pyrazoles are accessible via this route.[2] Analogous neutral tripods such as the tris(pyrazolyl)methanes [$RC(pz)_3$][3] and phosporyl centered ligands [$O{=}P(pz)_3$][4] have also been developed. More recently a new family of sulfur donor ligands with the methimazolyl group (1-methylimidazolyl-2-thione) and its derivatives as the donor heterocycles, $[HB(methimazolyl)_3]^-$ (Tm), has been developed based upon a similar synthetic methodology (Scheme 1).[5]



Scheme 1. The synthesis of hydrotris(azolyl)borate ligands from a BH_4^- salt and the structure of their complexes.

The Tm ligand system provides an interesting alternative ligand topology to that provided by the Tp ligands. The presence of an extra atom in each arm of the tripod provides a system which forms a bicylo[3.3.3] cage on κ^3-coordination to a metal ion, and this contrasts with the bicyclo[2.2.2] cage present in Tp ligand complexes. Thus, while the latter forms a C_3v symmetric TpM cage structure containing 6-membered rings, angle strain within the 8-membered rings contained within the TmM cage results in a twisted C_3-symmetric, and consequently chiral, structure (Scheme 1).[6] Our interest in directing this chirality, with a view to exploiting Tm complexes in asymmetric catalysis, prompted our exploration of routes to tris(methimazolyl)borate ligands which will allow the introduction of chiral groups in place of the methimazolyl N-methyl groups. However, we have found that, although reaction of 2-mercapto-1-benzylimidazole with tetrahydroborate salts successfully provides the corresponding $\mathrm{Tm^{Bn}}$ ligand in a melt reaction,[7] the chiral 2-mercapto-1-(s-)α-methylbenzylimidazole does not undergo a similar reaction, a result which we must attribute to the increased steric bulk resulting from the introduction of the α-methyl group.[8] An alternative, and possibly preferable, route for the introduction of chirality into the Tm ligand is to replace the remaining B-H hydride with a chiral group. Our initial approach to this goal involved the use of $(\mathrm{Ipc})\mathrm{BCl_2}$ (Ipc = isopinocampheyl) as the boron precursor, and while its reaction with pyrazolyl sodium successfully provided the $[(\mathrm{Ipc})\mathrm{B(pz)_3}]^-$ ligand, treatment with methimazolyl sodium resulted in the formation of the parent Tm ligand through dehydroboration of the Ipc group and elimination of pinene. Reaction of $[(\mathrm{Ipc})\mathrm{BH_3}]^-$ with methimazole also provided the Tm ligand.[9] As a consequence of these failures of the known routes to tris(azolyl)borates to provide our desired chiral Tm derivatives we have explored routes starting from an alternative boron precursor.

In 1981 Niedenzu reported that tris(dimethylamino)borane, $\mathrm{B(NMe_2)_3}$, provides the dimethylamino aduct of tris(pyrazolyl)borane, $[(\mathrm{HNMe_2})\mathrm{B(pz)_3}]$,[10] on reaction with pyrazole, and we found that a similar adduct, $[(\mathrm{HMe_2N})\mathrm{B}(\text{methimazolyl})_3]$ (**1a**), is formed in its reaction with methimazole (Scheme 2a).[11] This prompted us to further explore the reactivity of $\mathrm{B(NMe_2)_3}$ with a range of azole heterocycles. We found that with more basic heterocycles, such as imidazole, an alternative type of product is formed in which the dimethyl amine is replaced by imidazole, $[(\text{imidazole})\mathrm{B}(\text{imidazolyl})_3]$ (**2**) (Scheme 2b). Furthermore, this product is formed no matter what the reaction stoichiometry. At this time we interpreted these observations in terms of the operation of two alternative mechanisms for the reaction between $\mathrm{B(NMe_2)_3}$ and azoles dependent upon the azole basicity.[11] We have since revised our views on this and report here evidence for an alternative view of the formation of the species $[(\text{donor})\mathrm{B}(\text{azolyl})_3]$ which opens up a very flexible route to a wide range of tripodal ligands of this type. Never-the-less, a review of our earlier interpretation of the process will place the current work into context.

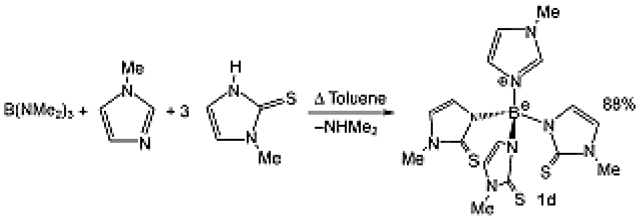


Scheme 2. The previously postulated mechanisms accounting for the formation of different products on reaction of $B(NMe_2)_3$ with azoles of differing basicity: (a) azoles with basic pKa < 3.5; (b) azoles with basic pKa > 3.5 as exemplified by methimazole and imidazole respectively.

In contrast to its pyramidal group 15 analogues $E(NMe_2)_3$ (E = As, Sb) which are very strongly basic systems capable, for example, of doubly metallating primary amines through transamination,[12] the planar $B(NMe_2)_3$ is a relatively weak base due to the involvement of the nitrogen lone pairs in B-N π-bonding. A further consequence of this π-bonding is the low Lewis acidity of the boron center. Consequently, we argued that in its reactions with weakly basic azoles such as pyrazole (basic $pK_a = 2.5$)[13] and methimazole (basic $pK_a = -1$)[14] there is no coordination of the heterocycle to the boron and the reaction proceeds via direct transamination steps to provide **1a**; the initial transamination to provide **4a** would be slow due to the low basicity of $B(NMe_2)_3$ (Scheme 2a). The formation of the alternative species of the type represented by [(imidazole)B(imidazolyl)$_3$] (**2**) from azoles with a basic pK_a higher than ca. 3.5, lead us to suggest that a preliminary coordination to the boron occurs providing a tetrahedral reactive intermediate [(azole)$B(NMe_2)_3$] (**3**), formally isoelectronic with the group 15 $E(NMe_2)_3$ species. The greatly increased basicity of this system, resulting from the boron rehybridization from sp^2 to sp^3, and consequent removal of the B-N π-bonding, would result in rapid transamination with the remaining azole present in the reaction solution providing [(azole)B(azolyl)$_3$] as the ultimate product (Scheme 2b). The reactions are conveniently conducted in toluene solution under reflux where the product precipitates from solution in high yield on completion and may be monitored by detection of $HNMe_2$ gas released by the reaction. Indeed, the loss of $HNMe_2$ from the reaction will shift the equilibrium for what may otherwise be rather thermodynamically unfavourable transamination processes.

Whilst the synthesis of hydrotris(pyrazolyl)borate (Tp) and hydrotris(methimazolyl)borate (Tm) ligands starting from a tetrahydroborate salt has proved to be quite flexible, there are a number of factors which limit its use for the synthesis of ligands containing alternative azolyl donor groups. For the melt reaction the melting point of the azole heterocycle must be considered, and those which readily sublime can cause problems in the synthesis. The acidity of the azole is also a factor; the less acidic systems either not reacting with tetrahydroborate or the reaction not progressing to the desired trisubstituted product. The derivatization of the ligands by replacing the remaining boron-bound hydride with alternative groups cannot be achieved by simple substitution; this B-H group displaying no acidity and only very limited basicity. Although the extended high temperature melt reaction of alkali metal tetrahydroborate salts with pyrazole provides the tetrakis(pyrazolyl)borate system $[B(pz)_4]^-$,[1] the substitution of the remaining B-H group in $[HB(azolyl)_3]^-$ systems has not been otherwise achieved in a controlled fashion. The preparation of such substituted ligands requires the use of $[RBH_3]^-$ salts or $RB(OR)_2$ systems. Such ligands have attracted increasing attention and the replacement of the remaining B-H with an alternative group has been shown to provide ligands which differ substantially from the parent Tp ligand in their steric and electronic properties.[2]

We have previously reported that the reactivity of $B(NMe_2)_3$ with imidazole described above may be adapted to provide a convenient and high yielding one-pot synthesis of [(N-methylimidazole)B(methimazolyl)$_3$] from a mixture of $B(NMe_2)_3$, methimazole and N-methylimidazole (Scheme 3).[11] There is clearly scope for variation in this strategy to provide a wide variety of ligands; indeed we have already reported the synthesis of one of our target ligands containing homotopic α-methylbenzyl groups in place of the methimazole N-methyl groups. The pseudo-C_3-symmetric complex of this ligand, [{(N-methylimidazole)B(1-(*S*-)α-methylbenzyl-2-mercapto-imidazolyl)$_3$}Ru(*p*-cymene)]$^{2+}$ forms on reaction with [RuCl$_2$(*p*-cymene)]$_2$ as a single diastereomer with the twist of the bicyclo[3.3.3] metal-ligand cage adopting only the λλλ conformation.[8] As discussed above, this heterocycle failed to react with $[BH_4]^-$ and this therefore provides an encouraging indication of the flexibility of the new synthetic route. We describe here our further exploration of the scope of this synthetic methodology and the resulting reinterpretation of the mechanism of the reaction of azoles with $B(NMe_2)_3$. The donor properties of the charge neutral [(N-donor)B(methimazolyl)$_3$] and [(N-donor)B(pyrazolyl)$_3$] ligands in comparison to their anionic Tm and Tp analogues are also explored.



Scheme 3. The ‘one-pot’ synthesis of ligand **1d**.

Results and Discussion

Mechanism of ligand formation

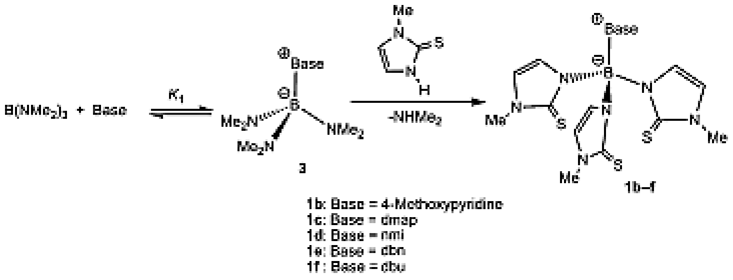
In our previous work we had concluded that an imine base with a basic pKa of >3.5 is required to coordinate to $B(NMe_2)_3$ and provide the reactive intermediates **3** (Scheme 4).[11] A number of bases were therefore selected (Table 1) and employed in the reaction with $B(NMe_2)_3$ and methimazole (1:1:3 stoichiometry) under reflux in toluene which provided the products (**1**) as colorless precipitates on completion of the reaction (Scheme 4). Attempts to observe the reactive intermediates **3** in mixtures of $B(NMe_2)_3$ and the bases by NMR at ambient temperatures provided spectra consistent only with mixtures of the two components, even for the strongest base examined (DBU), and we therefore concluded that the equilibrium concentration of the adducts (Base)$B(NMe_2)_3$ is insufficient to be observed spectroscopically, and thus that K_1 is small. It was noted however that increased basicity resulted in increased rates of reaction, as measured by the time taken for cessation of the evolution of $HNMe_2$ from the reaction mixture (Table 1). In our original interpretation of the mechanism this could be explained either by increased basicity of the NMe_2 groups in the adducts **3**, or by higher values of the equilibrium constant K_1, as the basicity of the 'activator' is increased, or a combination of the two. Triethylamine was included in the series to examine whether tertiary amines of suitable basicity could be employed in place of heterocyclic imines, however it was found that its use provided only the dimethylamine adduct **1a** and we therefore concluded that the steric bulk of NEt_3 prevents its coordination to $B(NMe_2)_3$.

Added Base	Basic pKa (MeCN)[a][15]	Reaction time /h	Isolated Yield	Ligand
None	-	2	82%	**1a**
4-methoxypyridine	14.23	8	85%	**1b**
4-N,N-dimethyl-aminopyridine (DMAP)	17.95	6	87%	**1c**
1-Methylimidazole	Not available[b]	3	88%	**1d**
Triethylamine	18.4	-	-	-
1,5-diazabicyclo-[4.3.0]non-5-ene (DBN)	23.79[16]	1	72%	**1e**
1,8-Diazabicyclo-[5.4.0]undec-7-ene (DBU)	24.34	1	92%	**1f**

[a] The basic pKa is defined as the pKa of the conjugate acid of the base, that of $[HPy]^+$ for pyridine for example, and is therefore a measure of its Brönsted basicity. T. Rodima, I. Kaljurand, A. Pihl, V. Mäemets, I. Leito, I. A. Koppel, *J. Org. Chem*., 2002, **67**, 1873.

[b] Unfortunately the basic pKa of N-methylimidazole in MeCN appears not to have been reported.

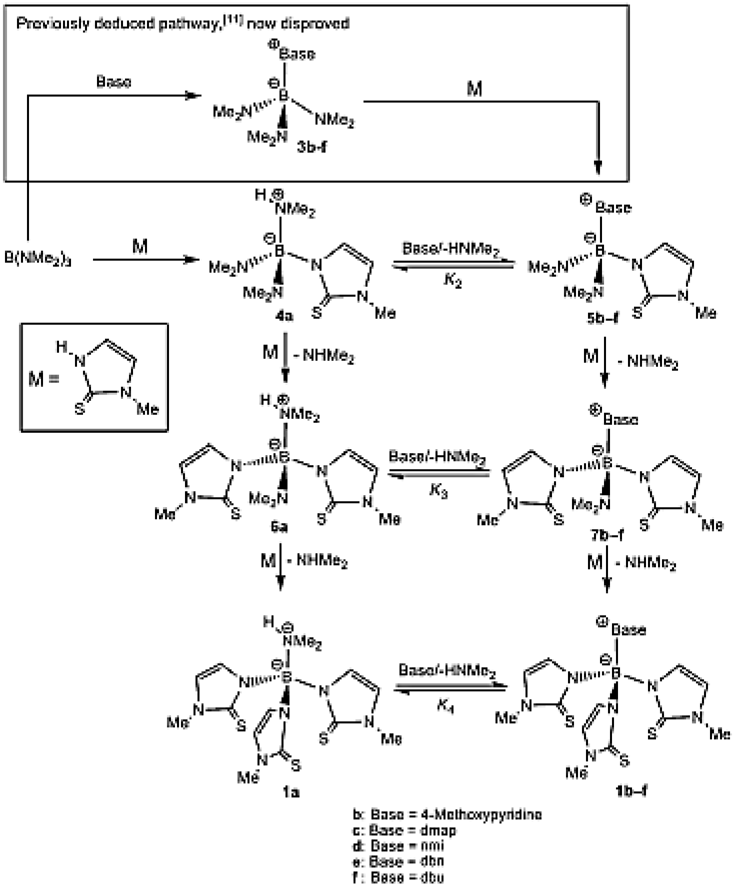
Table 1. Correlation of added base pKa and reaction time for the synthesis of the ligands **1**.



Scheme 4. Previously assumed mechanism for the formation of the ligands **1** via the reactive intermediate **3**.

Under the same toluene reflux reaction conditions the reaction between $B(NMe_2)_3$ and methimazole in the absence of an added base provides the dimethylamine adduct **1a**, a reaction which requires only 2 hours for completion. It was therefore surprising that, for the reactions with added bases which require longer periods than this, the products **1b-d** are not contaminated with **1a** which, in the absence of the added base, is formed more quickly. Given our failure to observe the adducts **3** in mixtures of $B(NMe_2)_3$ and the activating bases, this cannot be due to the absence of $B(NMe_2)_3$ in the reaction solutions. The explanation must lie in the details of the reaction between methimazole and the boron-bound NMe_2 groups (Scheme 5). In the absence of the added base it is reasonable to postulate progress of the reaction via the intermediate **4a** and subsequently through sequential transamination of the remaining two NMe_2 groups to provide **1a**. However, in the reactions containing an added base the products **1b-f** may be formed via the intermediates **5b-f**, which are those previously proposed to be formed via the intermediates **3**, but which may also be accessible from **4a** through an $HNMe_2$/base exchange with its associated equilibrium constant K_2. This equilibrium would be driven towards **5b-f** by the volatility of $HNMe_2$ which would readily be lost from the toluene solution under reflux.

Since the intermediate **4a** cannot be isolated, whether the $HNMe_2$ group in this species can be substituted by an added base cannot be proved. However, we find that reaction of DMAP with **1a** in toluene under reflux does result in substitution to provide [(DMAP)B(methimazolyl)$_3$] (**1c**), thus establishing that the formation of ligands **1b-f** does not require the previously suggested intermediacy of the $B(NMe_2)_3$ adducts **3**. The correlation of reaction time with the pKa of the added base (Table 1) reflects the significance of this factor in determining the rate of $HNMe_2$ substitution. The non-aqueous (MeCN) pKa of $HNMe_2$, which is required to compare with the other bases studied on a consistent basis, has not been reported; the most closely related secondary amine to have its pKa determined in this solvent is HNMePr which has a value of 18.92.[17] Accepting that this will be close to that for $HNMe_2$, the fact that it can be substituted by weaker bases (Table 1) which presumably bind less strongly to boron,[18] must reflect a shifting of the substitution equilibrium due to the loss of $HNMe_2$ gas from the reaction. The duration of the reactions has been determined by monitoring the evolution of $HNMe_2$ and thus, although the formation of **1a** may be complete in 2 h, the liberation of the free amine will continue until the formation of the final products **1b-f** is complete.

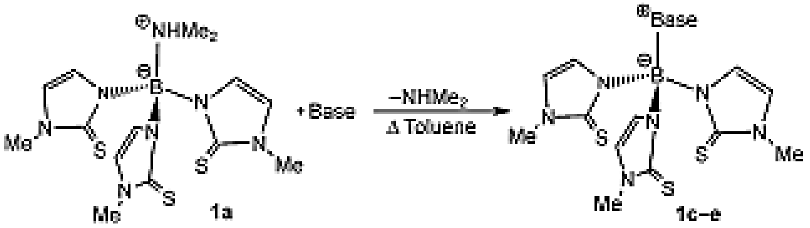


Scheme 5. Mechanism for the formation of the ligands **1** via substitution of $HNMe_2$ at boron by an added base.

The above discussion presupposes that the substitution of $HNMe_2$ does not occur until the species **1a** is formed. Whether this is the case or the substitution occurs from a species with one (**4a**) or two (**6a**) methimazolyl groups is perhaps a moot point; however it is possible to speculate about the most likely stage at which the substitution occurs. Studies on the substitution of Lewis base adducts of boron derivatives suggest that both S_N1 and S_N2 pathways may be involved in such processes.[19] Given the B-N π-bonding which will stabilise the boranes produced on dissociation of $HNMe_2$ from **4a**, and to a lesser extent **6a**, and the combined steric bulk of the groups attached to boron in **1a**, S_N1 processes would seem most likely to be operating in this system. Given this, the availability of two NMe_2 groups in **4a** to provide stabilisation of the trigonal borane intermediate via B-N π- interactions would make this the most likely stage at which substitution occurs. The fact that the reactions with the very strongly basic DBN and DBU are complete to form **1e** and **1f** in 1 h (faster than the formation of **1a** in the absence of an added base) indicates that this substitution of $HNMe_2$ must be occurring at an early stage of the reaction. For the weaker bases, which form their products (**1b-d**) more slowly than **1a** is formed, it seems that the transamination steps with methimazole compete with the $HNMe_2$

substitution in **4a** such that at least a proportion of the final products are formed via **1a**, thus accounting for the correlation between the reaction duration and basicity in these cases.

These observations provide a potentially very flexible route to new ligands by substitution of the $HNMe_2$ in $[(HNMe_2)B(methimazolyl)_3]$ (**1a**). To establish the general applicability of this route we have synthesised the ligands **1c-e** (Scheme 4 and Table 1) by treatment of **1a** with the selected base in toluene under reflux (Scheme 6). We have no reason to suspect that this route will not succeed for any ligand which may be synthesised via the 'one-pot' route, as would be anticipated from our foregoing discussion of the mechanism. We have further extended this synthesis to incorporate chiral bases into the ligand and details of this work will appear in a subsequent publication.



Scheme 6. Substitution of $HNMe_2$ in **1a** by added bases to form the ligands **1c-e**.

A ruthenium^{II} complex of ligand 1e

A Ru^{II} complex of the ligand **1e** containing DBN coordinated to boron was synthesised by reaction with the dimer $[(p\text{-cymene})RuCl_2]_2$ in ethanol. The resulting chloride salt of the complex was then treated with NH_4PF_6 to provide $[\{\kappa^3\text{-(DBN)B(methimazolyl)}_3\}Ru(p\text{-cymene})][PF_6]_2$ (**8**). The positive ion FAB mass spectrum of this complex shows an ion at M/z = 501.9 corresponding to $M^+/2$; the ^1H and ^{13}C NMR spectra are consistent with the anticipated structure showing signals for the *p*-cymene, DBN and methimazolyl components. The X-ray crystal structure of the salt was determined and the structure of the dicationic complex is shown in Figure 1. Selected bond-distances and angles are provided in Table 2. The ligand **1e** is κ^3-S,S,S-coordinated to the ruthenium center. There are 4 molecules in the unit cell related pairwise by inversion centres and these therefore represent the two enantiomeric λλλ and δδδ forms of the C_3-symmetric metal-ligand bicyclo[3.3.3] cage structure. The coordinate B-N bond to the DBN [1.569(6) Å] is marginally longer than those to the covalently bound methimazolyl nitrogen atoms [range 1.538(5) – 1.561(4) Å], a feature we have found to be common to these types of ligand. The three contiguous carbon atoms in the 6-membered ring of the DBN and their attached hydrogen atoms are disordered over two sites representing the presence of this ring in two different conformations. We have previously noted the flexibility of the C-S-M angles in Tm metal complexes manifest in the variability of these angles in different complexes. The structures of many Tm metal complexes are constrained by crystallographically imposed 3-fold symmetry and in these all three such angles are thus equivalent, however this is not possible when the boron bound hydride in Tm is replaced by a donor such as DBN. In the structure of **8** the C-S-Ru angles range from 114.23(11) to 100.14(11)° representing a substantial distortion of the metal-ligand cage structure. This range may be compared with those in $[(Tm)Ru(p\text{-cymene})]^+$ [108.34(10) – 113.33(10)°][20] and $[(Tm^{Et})Ru(p\text{-cymene})]^+$ [108.41(9) – 110.68(10)°].[6] The 14° range found for the C-S-Ru angles thus appears to be exceptionally large in **8** and it is a further illustration of the substantial flexibility of the M-S coordination geometry in these ligands which we have discussed previously.[6]

8	**11**	**12**	**13**
Ru-S(1) 2.4540(9)	Ru(1)-N(11A) 2.076(2)	Mn(1)-S(11) 2.4327(16)	Mn(1)-N(21) 2.053(4)
Ru-S(2) 2.4031(9)	Ru(1)-N(16A) 2.086(2)	Mn(1)-S(12) 2.4138(16)	Mn(1)-N(22) 2.051(4)
Ru-S(3) 2.4256(8)	Ru(1)-Cl(1C) 2.3908(7)	Mn(1)-S(13) 2.4603(16)	Mn(1)-N(23) 2.035(4)
B-N(11)1.553(4)	N(7A)-B(10A) 1.569(3)	B(1)-N(31) 1.535(8)	N(11)-B(1) 1.543(6)
B-N(12) 1.561(4)	B(10A)-N(21A) 1.521(4)	B(1)-N(32) 1.542(7)	N(12)-B(1) 1.538(6)
B-N(13) 1.538(5)	B(10A)-N(12A) 1.531(4)	B(1)-N(33) 1.548(7)	N(13)-B(1) 1.544(6)
B-N(14) 1.569(5)	B(10A)-N(17A) 1.540(4)	B(1)-N(14) 1.591(7)	N(14)-B(1) 1.543(6)
S(2)-Ru(1)-S(3) 87.08(3)	N(21A)-B(10A)-N(12A) 111.9(2)	S(11)-Mn(1)-S(12) 91.11(5)	N(21)-Mn(1)-N(22) 85.97(16)
S(2)-Ru(1)-S(1) 90.90(3)	N(21A)-B(10A)-N(17A) 109.7(2)	S(11)-Mn(1)-S(13) 93.53(5)	N(21)-Mn(1)-N(23) 84.77(15)
S(3)-Ru(1)-S(1) 95.69(3)	N(12A)-B(10A)-N(17A) 111.4(2)	S(12)-Mn(1)-S(13) 93.22(5)	N(22)-Mn(1)-N(23) 85.71(16)
N(13)-B(1)-N(11) 109.6(3)	N(21A)-B(10A)-N(7A) 110.4(2)	N(31)-B(1)-N(32) 115.0(4)	N(13)-B(1)-N(14) 104.4(4)
N(13)-B(1)-N(12) 116.7(3)	N(12A)-B(10A)-N(7A) 105.9(2)	N(31)-B(1)-N(33) 113.0(4)	N(13)-B(1)-N(11) 108.2(3)
N(11)-B(1)-N(12) 105.0(3)	N(17A)-B(10A)-N(7A) 107.4(2)	N(32)-B(1)-N(33) 108.0(4)	N(14)-B(1)-N(11) 116.4(4)
N(13)-B(1)-N(14) 104.5(3)	N(11A)-Ru(1)-N(16A) 86.75(8)	N(31)-B(1)-N(14) 103.3(4)	N(13)-B(1)-N(12) 108.9(4)
N(11)-B(1)-N(14) 111.5(3)		N(32)-B(1)-N(14) 108.5(4)	N(14)-B(1)-N(12) 110.6(4)
N(12)-B(1)-N(14) 109.6(3)		N(33)-B(1)-N(14) 108.9(4)	N(11)-B(1)-N(12) 108.0(3)

Table 2. Selected bond lengths (Å) and angles (°) for $[\{(DBN)B(methimazolyl)_3\}Ru(p\text{-cymene})][PF_6]_2$ (**8**) $[\{(DMAP)B(pz)_3\}Ru(p\text{-cymene})Cl][PF_6]$ (**11**), $[\{(N\text{-methyl-imidazole})B(methimazolyl)_3\}Mn(CO)_3][PF_6]$ (**12**) and $[\{(N\text{-methylimidazole})B(pyrazolyl)_3\}Mn(CO)_3][PF_6]$ (**13**).

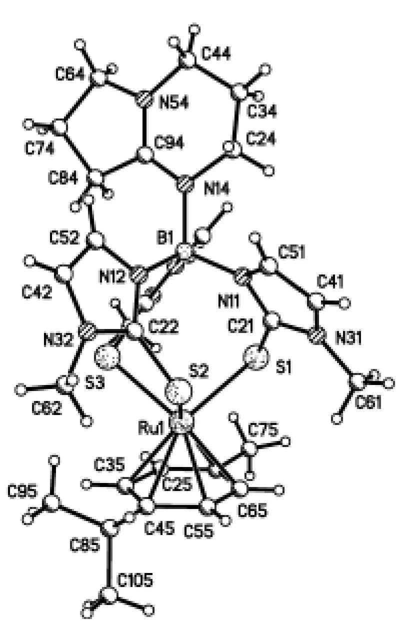
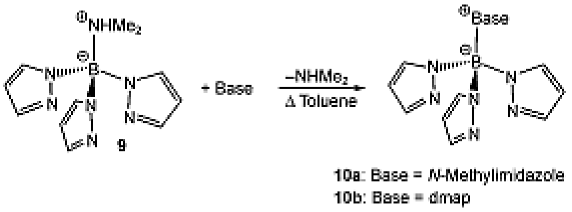


Figure 1. Structure of the dication in [{κ^3-(DBN)B(methimazolyl)$_3$}Ru(*p*-cymene)][PF_6]$_2$ (**8**). PF_6^- counterions not shown. Selected bond lengths and angles are provided in Table 2.

Tris(pyrazolyl)borate ligands

The possibility that this synthetic method may be employed for the preparation of analogous tris(pyrazolyl)borate ligands has also been explored. The substantial literature concerning the chemistry and applications of tris(pyrazolyl)borate ligands and their various derivatives attests to their significance in coordination chemistry, catalysis and a variety of other fields.[2] A flexible route to their boron substituted derivatives would provide a potentially valuable new addition to the synthetic toolkit available for the design of such ligands for specific applications. The required precursor for this study [($HNMe_2$)B(pz)$_3$] (**9**) is readily available by reaction of B(NMe_2)$_3$ with pyrazole according to the procedure developed by Niedenzu.[10] Reaction of **9** with both 1-methylimidazole and DMAP proceeds smoothly under reflux in toluene to liberate $HNMe_2$ and provide the new ligands (**10a** and **10b**) in very high yield (Scheme 7).



Scheme 7. Substitution of $HNMe_2$ in **9** by added bases to form the new ligands **10a** and **10b**.

To establish the coordination chemistry of these new ligands **10b** was reacted with the dimer [(*p*-cymene)$RuCl_2]_2$ in methanol solution followed by salt metathesis with NH_4PF_6 to provide the yellow salt **11**. We anticipated the formation of the complex $[\{\kappa^3\text{-(DMAP)B(pz)}_3\}$Ru(*p*-cymene)]$[PF_6]_2$; however, the +FAB mass spectrum of **11** showed a molecular ion at m/z = 605 consistent with the formulation $[\{\kappa^2\text{-(DMAP)B(pz)}_3\}$RuCl(*p*-cymene)$]^+$ indicating that the ligand adopts a κ^2-N,N-coordination mode and one chloride remains coordinated to ruthenium. ^1H and ^{13}C nmr spectra of **11** are consistent with this and show signals due to two different pyrazolyl ring environments (2:1 ratio). The X-ray crystal structure of **11** was obtained and the structure of the cationic complex is shown in Figure 2. The structure found confirms the observations from the mass and nmr spectra; the ligand coordinates to ruthenium through two of its pyrazolyl rings and the third remains uncoordinated. The retention of the chloride ligand at ruthenium results in the coordination of the ligand in such a way that the uncoordinated pyrazolyl ring is orientated away from the metal. This structure is similar to that of $[\{\kappa^2\text{-HB(pz)}_3\}$RuCl(arene)] which may be isolated from the reaction of NaTp with [(arene)$RuCl_2]_2$ (arene = *p*-xylene, mesitylene, hexamethylbenzene) in MeCN.[21] The Ru-N bond distances to the two coordinated pyrazolyl rings are very similar [2.086(2) and 2.076(2) Å] and compare with values of 2.081(5) and 2.083(5) Å in $[\{\kappa^2\text{-HB(pz)}_3\}$RuCl-(hexamethylbenzene)]. The Ru-Cl distances in these two complexes are also very similar at 2.3908(7) Å in **11** and 2.397(2) Å in the Tp complex.

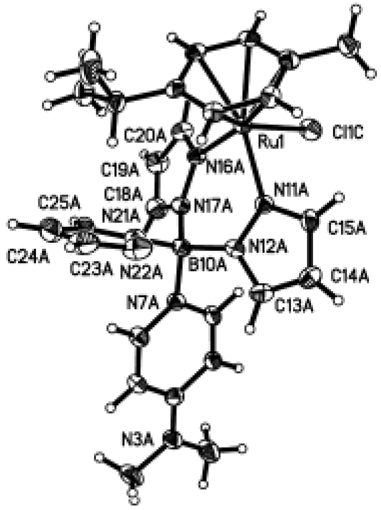


Figure 2. Structure of the cation in $[\{\kappa^2\text{-(DMAP)B(pz)}_3\}$RuCl(*p*-cymene)]$[PF_6]$ (**11**). PF_6^- counterion not shown. Selected bond lengths and angles are provided in Table 2.

Donor Properties of the Ligands

Wishing to be able to compare the donor properties of the ligands **1**, [(Base)B(methimazolyl)$_3$] and **10**, [(Base)B(pyrazolyl)$_3$] with their anionic hydrotris(azolyl)borate counterparts (Tp and Tm) we have synthesised manganese tricarbonyl complexes of the ligands, [(1-methylimidazole)B(methimazolyl)$_3$] (**1d**) and [(1-methylimidazole)B(pyrazolyl)$_3$] (**10a**) by treatment with [Mn(CO)$_3$(NCMe)$_3$][PF$_6$] in MeCN solution. These reactions proceed smoothly to provide the salts [{(1-methylimidazole)B(methimazolyl)$_3$}Mn(CO)$_3$][PF$_6$] (**12**) and [{(1-methylimidazole)B(pyrazolyl)$_3$}Mn(CO)$_3$][PF$_6$] (**13**) in high yield. Spectroscopic characterisation of these complexes is consistent with κ^3-S,S,S and κ^3-N,N,N coordination of the ligands in **12** and **13** respectively and this is confirmed by X-ray crystallography. The structure of the cation in **12** is shown in Figure 3 and that in **13** in Figure 4. Selected bond-distances and angles are provided in Table 2.

Describing the structure of complex (**12**) containing the methimazolyl donor ligand first; the crystals contain two molecules per unit cell related by an inversion centre, and these therefore represent the λλλ and δδδ enantiomeric forms of the complex in which the C_3-symmetric twist of the metal-ligand cage adopts either a left or right handed twist. We have previously published the structure of the analogous charge-neutral Mn(CO)$_3$ complex containing the anionic hydrotris(methimazolyl)borate (Tm) ligand, [(Tm)Mn(CO)$_3$] (**14**), in which the 1-methylimidazole of **12** is replaced by a hydride on boron. For the purposes of comparing the characteristics of the two ligands it is useful to compare the bond lengths and angles in the two complexes, however, this is complicated by the fact that there are two independent molecules in the unit cell of **14** which differ substantially in their metrical parameters. For the purposes of this comparison therefore, the mean values for the data for this complex will be used. In **12** the mean Mn-S distance is 2.4356 Å (esds of individual values = 0.0016) while in **14** the corresponding mean is 2.4146 Å (esds of individual values = 0.0005), a difference of 0.021 Å. While this might be interpreted as weaker S-Mn interactions in **12**, it has previously been noted that M-S bond lengths in Tm complexes may vary substantially in closely related systems.[6] This is best illustrated by the fact that in the two independent molecules present in the crystal of **14** the mean Mn-S distances are 2.4015 and 2.4277 Å (esds as above), a difference of 0.0262 Å. Similarly, in the complexes [(Tm)Cu(PAr$_3$)] (Ar = Ph, *m*-tolyl, *p*-tolyl) the mean Cu-S distances differ by 0.055 Å, a variation which is not correlated with the steric bulk or donor properties of the phosphine ligands.[22] Consequently caution is required in interpreting M-S bond distances in Tm and related complexes in terms of the donor properties of the ligands and a more reliable comparison is provided by the energy of the CO stretching vibrations (*vide infra*).

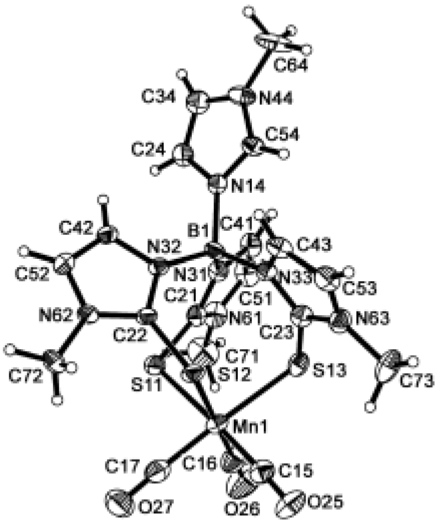


Figure 3. Structure of the cation in [{(1-methylimidazole)B(methimazolyl)$_3$}Mn(CO)$_3$][PF$_6$] (**12**). PF$_6^-$ counterion not shown. Selected bond lengths and angles are provided in Table 2.

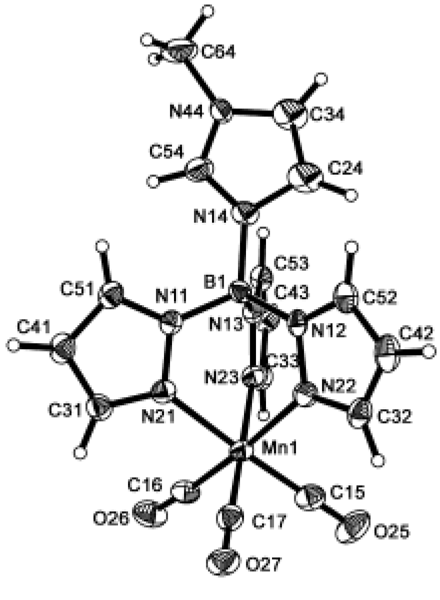


Figure 4. Structure of the cation in [{(1-methylimidazole)B(pyrazolyl)$_3$}Mn(CO)$_3$][PF$_6$] (**13**). PF$_6^-$ counterion not shown. Selected bond lengths and angles are provided in Table 2.

Given the replacement of H$^-$ in **14** by 1-methylimidazole in **12** the other bonds which are worthy of comparison between these two complexes are the B-N distances to the methimazolyl rings. In **14** the mean distance for the two independent molecules is 1.5501 Å (individual esds = 0.0017) while in **12** the mean is 1.542 Å (max. individual esds = 0.008) and the two values are not therefore crystallographically distinguishable. The B-N distance to the N-methylimidazole in **12** is 1.591(7) Å, slightly longer than the distances to the methimazole nitrogen atoms. It may be concluded from these data that the replacement of the hydride in **14** by N-methylimidazole in **12**, and the resulting change in ligand charge, does not have a significant effect on the bond distances to the methimazolyl nitrogen atoms. This may be rationalised by the ability of the imidazole to stabilise a positive charge, and there is thus little difference between the boron centred charge in the two ligands (Figure 5). On this basis it might be anticipated that there should be little difference between the sulfur donor properties of the two ligands.

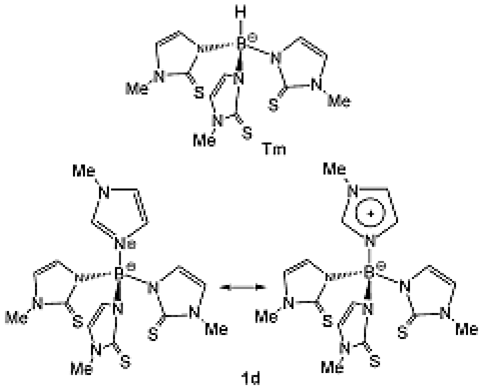


Figure 5. Location of charge in the Tm ligand and its neutral analogue, ligand **1d**.

The 1-methylimidazole in [{(1-methylimidazole)B(pz)$_3$}-Mn(CO)$_3$][PF$_6$] (**13**) is disordered over two sites approximately related by a 90° rotation about the B-N axis. One carbon atom in the ring is common to both sites, as is the methyl carbon. The mean Mn-N distance in **13** is 2.046 Å (individual esds = 0.004) while that in the two independent molecules present in the unit cell of [(Tp)Mn(CO)$_3$] (**15**) is 2.070 Å; however, this disguises the fact that the mean Mn-N bond distances in the two molecules of **15** in the unit cell are 2.177 and 1.963 Å and it is not therefore reasonable to interpret the differences between the mean values for **13** and **15** in terms of the donor properties of the pz rings in the two ligands. Again, a better measure is available from a comparison of the CO stretching energies. The mean B-N(pz) distance in **13** is 1.542 Å (individual esds = 0.006) which is indistinguishable from the value of 1.541 Å in **15**.

The overall picture which emerges from the structural comparison of the these complexes is one in which the variation between bond lengths in complexes of Tm and Tp complexes (even between the same complexes within unit cells of crystals) is too large to be able to distinguish any pattern of variation in comparison with their analogues containing the N-methylimidazole substituted ligands **1d** and **10a**. Thus, there is no structural evidence for differences in donor properties between the anionic Tm and Tp ligands and the charge neutral **1d** and **10a**. Fortunately there is a much more sensitive means of assessing the donor properties of ligands.

It has become common practice to compare the donor properties of ligands by indirectly sensing the donor/acceptor properties of the coordinated metal via the CO stretching energies of attached carbonyl ligands. This provides a sensitive measure of the ability of the metal to partake in the acceptor and donor interactions with its CO ligands and thus the metal centred electron density provided by the ligands under study. In the current context we are fortunate in there being available a wide range of $Mn(CO)_3$ complexes of tripodal borate and related ligands to serve as comparators with our new ligands [(1-methylimidazole)-B(methimazolyl)$_3$] (**1d**) and [(1-methyl-imidazole)B(pz)$_3$] (**10a**), and it should therefore be possible to assess their donor properties and place them in context with their related ligands. The infra-red data for a selected group of complexes along with those for **12** and **13** are provided in Table 3. It is unfortunate that spectra for the various complexes are reported in different solvents and only a solid state spectum (KBr) is reported for one of the complexes; notwithstanding this however, a consistent picture is provided for the situation as discussed below. The energy of the A symmetry (higher energy) C-O vibration mode provides the best measure of the C-O bond strength in these complexes, being the simultaneous stretching of all three CO ligands, and the energy of this vibration for each complex will therefore be compared as a measure of the donor properties of the various ligands.

Complex[a]	ν_{co}/cm^{-1}	Medium	Ref
[{HB(methimazolyl)$_3$}Mn(CO)$_3$]	2003, 1905	Toluene	[20]
[{(NMI)B(methimazolyl)$_3$}Mn(CO)$_3$] [PF$_6$] (**12**)	2007, 1914	MeCN	This work
[{HB(3,5-Me$_2$Pz)$_3$}Mn(CO)$_3$]	2023, 1912	KBr	[23]
[{HB(pz)$_3$}Mn(CO)$_3$]	2036, 1932	MeCN	[24]
[{pzB(pz)$_3$}Mn(CO)$_3$]	2039, 1936	MeCN	[24]
[{(NMI)B(pz)$_3$}Mn(CO)$_3$][PF$_6$] (**13**)	2041, 1941	MeCN	This work
[{HC(3,5-Me$_2$pz)$_3$}Mn(CO)$_3$][OTf]	2044, 1949	CH_2Cl_2	[25]
[{HC(pz)$_3$}Mn(CO)$_3$][OTf]	2051, 1956	CH_2Cl_2	[25]

[a] NMI = 1-methylimidazole

Table 3. IR data (ν_{co}) for manganese tricarbonyl complexes bearing tripodal tris(azolyl)-borate and -methane ligands.

It should be borne in mind that the new ligands **1d** and **10a** are charge neutral systems and thus provide cationic complexes with the Mn^I tricarbonyl unit, while the anionic Tm and Tp ligands and their derivatives give neutral complexes. In the absence of other factors the introduction of a positive charge into a carbonyl complex will result in an increase in CO stretching energy for the attached carbonyl ligands; in the present context this is illustrated by a comparison of the ν_{co} values for the complexes containing the [HB(pz)$_3$]$^-$ (Tp) and HC(pz)$_3$ ligands where a difference of 15 cm^{-1} is observed due to the isoelectronic replacement of HB$^-$ by HC in these species. In light of this the difference of only 5 cm^{-1} between the cationic complex **13**, containing the neutral ligand [(N-methylimidazole)B(pz)$_3$] (**10a**), and the neutral Tp complex is worthy of note. A comparison between **13** and the similarly cationic complex with the neutral $HC(pz)_3$ ligand shows that the CO ligands in **13** vibrate 10 cm^{-1} lower in energy, and even those in the complex with the stronger donor $HC(3,5\text{-}Me_2pz)_3$ have an energy which is 3 cm^{-1} higher. On this basis therefore it appears that the donor properties of the ligand **10a** lies approximately mid way between that of Tp and $HC(3,5\text{-}Me_2pz)_3$, and is thus a substantially stronger donor than might have been predicted at first sight. This may be attributed to the ability of the boron-bound N-methylimidazole ring to stabilize a positive charge (illustrated for ligand **1d** in Figure 5), thus in cationic complexes such as those of the $Mn(CO)_3^+$ unit considered here, the positive charge is substantially located remote from the metal. Such a charge localisation is not possible in the tris(pyrazolyl)methane ligands and these are therefore effectively weaker donors.

A similar situation is revealed in the comparison of the complex [{(1-methylimidazole)B(methimazolyl)$_3$} $Mn(CO)_3$] [PF_6] (**12**) and its neutral analogue containing the Tm ligand, [{HB(methimazolyl)$_3$}$Mn(CO)_3$]. The energy of the A-symmetry ν_{co} vibration for **12** is only 4 cm^{-1} higher than that for the Tm complex, indicating only a slight decrease in donor properties on replacement of $H\text{-}B^-$ by $^+N\text{-}B^-$ which may again be attributed to the localisation of the positive charge within the 1-methylimidazole ring remote from the coordinated metal. The tris(methimazolyl)methane ligand has recently been reported,[26] but unfortunately its $Mn(CO)_3$ complex has not been prepared and a comparison with this ligand in the present context is therefore not possible.

Conclusions

The ease with which the $HNMe_2$ may be substituted by alternative N-donors in both ($HNMe_2$)B(methimazolyl)$_3$ (**1a**) and ($HNMe_2$)B(pyrazolyl)$_3$ (**9**) provides a flexible and high-yielding route to new ligands. The extension of this methodology to introduce functionality in this position could lead to a range of possibilities for incorporating these tris(azolyl) tripods (and their complexes) into larger systems, by incorporation of additional metal-binding or polymerizable groups for example. We are continuing to explore the range of donors which may be used to substitute the $HNMe_2$ in these systems.

Experimental Section

General: All reactions were carried out under an atmosphere of dry, oxygen-free dinitrogen, using standard Schlenk techniques. Solvents were distilled and dried by standard methods or used directly from a Glass Contour solvent purification system and further degassed before use where necessary. Mass spectra were recorded on Kratos MS50TC (FAB) and Micromass Platform II (ES-MS) spectrometers. NMR spectra were recorded on a Bruker 250AC spectrometer operating at room temperature. ^1H 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. Infra red spectra were recorded from solution using cells with CaF_2 windows on a Jasco FT-IR 410 spectrometer. The compounds [$(HMe_2N)B(methimazolyl)_3$] (**1a**),[11] [$(HMe_2N)B$-(pyrazolyl)$_3$],[10a] [(*p*-cymene)$RuCl_2]_2$[27] and [$Mn(CO)_3(NCMe)_3$][$PF_6$][28] were synthesised according to the literature procedures. All other chemicals were obtained from Sigma-Aldrich and used as received.

Synthesis of ligands (Method A): The tris(methimazolyl) ligands were synthesised by two routes. In the 'one-pot' reaction (Method A) $B(NMe_2)_3$, methimazole and the added base (1:3:1 stiochiometry) are heated to reflux in toluene until evolution of $HNMe_2$ ceases, as judged by testing of the evolved gasses with damp pH paper. The duration of the reactions for ligands **1a-f** are given in Table 1. The detailed procedure for **1b** is provided below, others followed a similar protocol. All ligands are colorless solids.

[(4-methoxypyridine)B(methimazolyl)$_3$] (1b): 4-methoxypyridine (156 µl, 1.43 mmol), tris(dimethylamino) borane (250 µl, 1.43 mmol) and methimazole (0.444 g, 3.90 mmol) were heated to reflux in dry toluene (10 mL). The evolution of $HNMe_2$ ceased after 8h at which time a colourless solid had formed in the solution. The reaction mixture was cooled and the solid product filtered and washed with hexane (2 x 10 mL). Yield 0.506 g, 1.10 mmol, 85%. ^{1}H-NMR (250.1 MHz, $CDCl_3$), δ: 8.62 (br, 2H), 7.01 (t, 1H, J = 1.56 Hz), 6.97 (t, 1H, J = 1.56 Hz), 6.78 (br, 3H), 6.61 (d, 3H, = 2.34 Hz), 3.95 (s, 3H), 3.47 (s, 9H); ^{13}C-NMR (62.9 MHz, $CDCl_3$), δ: 170.7 (C=S), 165.9 (C_{quat}), 1478.0 (CH), 128.6 (CH), 118.2 (CH), 110.2 (CH), 57.3 (CH_3), 35.3 (CH_3); ^{11}B-NMR (80.3 MHz, $CDCl_3$), δ: 5.43; MS (EI +25eV): M^+= 459.88 (M^++1); Anal. Calcd for $C_{18}H_{22}BN_7OS_3$; C, 47.06; H, 4,83; N, 21.34. Found: C, 46.87; H, 4,60; N, 21.69.

[(4-dimethylaminopyridine)B(methimazolyl)$_3$] (1c): Yield 87%. ^{1}H-NMR (250.1 MHz, $CDCl_3$), δ: 8.12 (br, 2H), 6.59 (d, 3H, J= 2.34 Hz), 6.54 (t, 1H, J= 1.43 Hz), 6.51 (t, 1H, J= 1.43 Hz), 3.48 (s, 9H), 3.09 (s, 6H); ^{13}C-NMR (62.9 MHz, $CDCl_3$), δ: 165.77 (C=S), 156.7 (C_{quat}); 146.6 (CH), 123.1 (CH), 117.9 (CH), 105.9 (CH), 40.1 (CH_3), 35.2 (CH_3); ^{11}B-NMR (80.3 MHz, $CDCl_3$), δ: 5.08; MS (EI +25eV): M^+= 473.04; Anal. Calcd for $C_{19}H_{25}BN_8S_3B$; C, 48.30; H, 5.33; N, 23.72. Anal. Calcd for $C_{19}H_{25}BN_8S_3$; C, 48.30; H, 5.33; N, 23.72. Found: C, 48.09; H, 5.10; N, 23.91.

[(N-methylimidazole)B(methimazolyl)$_3$] (1d): Yield 88%. ^{1}H-NMR (250.1 MHz, $CDCl_3$), δ: 3.49 (s, 9H), 3.81 (s, 3H), 6.61-6.65 (m, 6H), 6.95 (s, 1H), 7.19 (s, 1H), 8.97 (s, 1H); ^{13}C-NMR (62.9 MHz, $CDCl_3$), δ: 35.10 (CH_3*met*), 36.05 (CH_3*Imi*), 114.36 (CH*Imi*), 117.9 (CH*met*), 121.6 (CH*Imi*), 124.6 (CH*Met*), 142.7 (CH*Imi*), 164.7 (C=S); ^{11}B-NMR (80.3 MHz, $CDCl_3$), δ: 8.05; MS (EI +25eV): M^+= 433; Anal. 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.

[(DBN)B(methimazolyl)$_3$] (1e): Yield 72%. ^{1}H nmr (500.1 MHz, $CDCl_3$): δ_H 6.71 (3H, d J = 2.5 Hz), 6.67 (3H, d, J = 2.2 Hz), 6.6-6.5 (2H, m), 3.6 (9H, s), 3.56-3.49 (6H, m), 3.39-3.33 (2H, m), 2.05-1.9 (2H, br); ^{13}C nmr (90.5 MHz, DMSO): δ_C 161.0 (C=S), 129.3 ($C_{q\ DBN}$), 120.1 (CH_{met}), 114.1 (CH_{met}), 46.9 (CH_{2DBN}), 43.9

(CH_{2DBN}), 42.9 (CH_{2DBN}), 34.9 (CH_{2DBN}), 30.7 (CH_{2DBN}), 24.1 (CH_{3met}), 18.3 (CH_{2DBN}); MS (FAB^+): *m/z* = 474.6; Anal. Calcd. for $C_{19}H_{27}BN_8S_3$ (474.16): C, 48.10; H, 5.74; N, 23.61; found: C, 47.60; H, 5.46; N, 23.36 %.

[(DBU)B(methimazolyl)₃] (1f): Recrystallised from MeOH. Yield 92%.^{1}H-NMR (250.1 MHz, DMSO-d_6), δ: 7.10 (d, 3H, *J* = 2.34Hz), 6.79 (d, 3H, *J* = 2.34Hz), 4.15 (m, 2H), 3.88 (m, 2H), 3.54 (s, 9H), 2,33 (m, 2H), 1.93 (m, 2H), 1.73 (m, 2H), 1.70 (m, 2H), 1.10 (m, 4H); ^{13}C-NMR (62.9 MHz, DMSO-d_6), δ:165.70 ($C_{quatDBU}$), 161.4 (C=S); 119.8 (CH*met*), 114.6 (CH*met*), 55.4 (CH_{2DBU}) 53.7 (CH_{2DBU}) 48.3 (CH_{2DBU}) 33.9 (CH_3*met*), 31.7 (CH_{2DBU}) 28.7 (CH_{2DBU}) 26.4 (CH_{2DBU}) 23.8 (CH_{2DBU}) 19.4 (CH_{2DBU}); ^{11}B-NMR (80.3 MHz, DMSO-d_6), δ: 7.57; MS (EI +25eV): M^+= 503.05, 389.07 (M-het); Anal. Calcd for $C_{21}H_{31}BN_8S_3B\cdot MeOH$; C, 49.43; H, 6.60; N, 20.96. Found: C, 49.22; H, 6.42; N, 21.54.

Method B of ligand synthesis involves substitution of $HNMe_2$ in [($HNMe_2$)B(azolyl)$_3$] (azolyl = methimazolyl, pyrazolyl). The procedure for ligand **1c** is given below and the other ligands followed a similar protocol.

[(4-dimethylaminopyridine)B(methimazolyl)₃] (1c): To a solution of 4-dimethylaminopyridine (62 mg, 0.506 mmol) in toluene (15 mL) was added [($HNMe_2$)B(methimazolyl)$_3$] (**1a**) (200 mg, 0.506 mmol). The mixture was heated under reflux for 4 h with the solution becoming cloudy after 2 h. After cooling the solid product was isolated by filtration and washed with diethyl ether (3 x 5 mL) Yield 181 mg of **1c** (76%) as a colorless powder.

[{(DBN)B(methimazolyl)₃}Ru(p-cymene)][PF₆]₂ (8): [Ru(p-cymene)Cl_2]$_2$ (64.6 mg, 0.105 mmol) was dissolved in ethanol (15 mL) and stirred at room temperature for 45 minutes. The ligand **1e** (100 mg, 0.210 mmol) was added as a solid in small portions and the mixture stirred for 12 h at room temperature. After this period NH_4PF_6 (171 mg, 1.05 mmol) was added and the precipitation of an orange solid was observed. After filtration by cannula, the solid was washed with ethanol (3 x 7 mL) and then with diethyl ether (2 x 5mL). Drying under vacuum provided 171 mg of **8** (76%). Crystals suitable for X-ray were obtained by slow diffusion of diethyl ether in a concentrated solution of the complex in acetonitrile. δ_H (250.1 MHz, CD_3CN): 7.15 (3H, d, *J*=3.0 Hz), 6.77 (3H , d, *J*=3.1 Hz,), 5.53-5.39 (4H, m), 3.91 (1H, sept, *J*=6.7 Hz), 3.77-3.71 (2H, m), 3.67 (9H, s),

3.64-3.39 (4H, m), 2.47-2.38 (2H, m), 2.18 (3H, s), 1.30 (2H, m), 1.17 ppm (6H, t, *J*=7 Hz); δ_C (125.7 MHz, $(CH_3)_2CO$): 172.2 ($C_{q\ DBN}$), 148.9 ($C_{q\ met}$), 124.4 (CH_{met}), 124.1(CH_{met}), 107.8 ($C_{q\ p\text{-cym}}$), 103.5 ($C_{q\ p\text{-cym}}$), 87.3 ($2CH_{p\text{-cym}}$), 86.3 ($CH_{p\text{-cym}}$), 85.3 ($2CH_{p\text{-cym}}$), 55.3 ($CH_{2\ DBN}$), 46.7 ($CH_{2\ DBN}$), 45.4 ($CH_{2\ DBN}$), 37.1 ($CH_{2\ DBN}$), 36.9 ($CH_{2\ DBN}$), 32.0 ($CH_{3\ met}$), 23.5 ($CH_{3\ p\text{-cym}}$), 21.3 ($2CH_{3\ p\text{-cym}}$), 19.5 ($CH_{2\ DBN}$); δ_B(115.5 MHz, DMSO): 4.15; MS (FAB^+): *m/z* = 501.9 [(M+1)/2]; Anal. Calcd for $C_{29}H_{41}BF_{12}N_8P_2RuS_3$: C, 34.89; H, 4.13; N, 11.21; found: C, 34.16; H, 4.02; N, 11.15%.

[(N-methylimidazole)B(pyrazolyl)$_3$] (10a): 92% yield. ^{1}H-NMR (250.1 MHz, CDCl$_3$), δ: 8.52 (s, 1H), 7.65 (dd, 3H, *J* = 1.56Hz, *J* = 0.51Hz), 7.48 (t 1H, *J* = 1.53 Hz), 6.88 (dd, 3H, *J* = 2.34 Hz, *J* = 0.51Hz), 6.85 (t 1H, *J* = 1.53 Hz), 6.17 (dd, 3H, *J* = 2.34Hz, 1.56 Hz), 3.68 (s, 3H); ^{13}C-NMR (62.9 MHz, CDCl$_3$), δ:140.9 (CH*imi*), 137.4 (CH*imi*); 133.6 (CH*imi*), 125.5 (CH*py*), 119.6 (CH*py*), 104.1 (CH*py*), 34.4 (CH$_3$*imi*); ^{11}B-NMR (80.3 MHz, CDCl$_3$), δ: 3.76; MS (EI +25eV): M$^+$= 295.13 (M+1); Anal. Calcd for $C_{13}H_{15}N_8B$; C, 53.09; H, 5.14; N, 38.10. Found: C, 53.24; H, 5.03; N, 38.29.

[(4-dimethylaminopyridine)B(pyrazolyl)$_3$] (10b): 90% yield. ^{1}H nmr (360.1 MHz, CDCl$_3$): δ_H 8.31 (2H, d, *J* = 7.4 Hz), 7.74 (3H, d, *J* = 0.8 Hz), 7.12 (3H, d, *J* = 2.2 Hz), 6.56 (2H, d, *J* = 7.8 Hz), 6.25 (3H, t, *J* = 1.7 Hz and *J* = 0.9 Hz), 3.16 (6H, s); ^{13}C nmr (90.5 MHz, CD$_3$CN): δ_C 156.1 ($C_{q\ \mathrm{DMAP}}$), 145.4 ($CH_{\ \mathrm{pz}}$), 135.3 ($CH_{\ \mathrm{pz}}$), 129.1 ($CH_{\ \mathrm{DMAP}}$), 106.6 ($CH_{\ \mathrm{pz}}$), 105.7 ($CH_{\ \mathrm{DMAP}}$), 39.9 ($CH_{3\ \mathrm{DMAP}}$); MS (FAB$^+$): *m*/ *z* = 335.3 (M+1); $C_{16}H_{19}BN_8$: C, 57.50; H, 5.73; N, 33.53; found: C, 57.01; H, 5.39; N, 33.38 %.

[{(DMAP)B(pz)$_3$}Ru(p-cymene)Cl]PF$_6$ (11): [(*p*-cymene)-RuCl$_2$]$_2$ (110 mg, 0.0179 mmol) was dissolved in methanol (10 mL) and stirred for 1 h. [(DMAP)B(pz)$_3$] (9b) (120 mg, 0.36 mmol) was then added in small portions and a colour change from orange to yellow was observed. The reaction was stirred for a further 24 h at room temperature. NH$_4$PF$_6$ (60 mg, 0.37 mmol) was added to the solution and a yellow precipitate was formed. The precipitate was isolated by cannula filtration, dried and washed with ether to afford 120 mg of a yellow solid (37%). The product was crystallized by slow diffusion of diethyl ether into an acetonitrile solution to obtain crystals suitable for X- ray crystallography. ^{1}H nmr (360.1 MHz, DMSO): δ_H 8.18 (3H, d, *J* = 2.2 Hz), 7.46 (3H, *J* = 2.6 Hz), 7.03 (2H, d, *J* = 7.8 Hz), 6.90 (2H, d, *J* = 7.4 Hz), 6.68 (3H, t, *J* = 2.2 Hz), 5.77 (2H, d, *J* = 6.1 Hz), 4.92 (2H d, *J* = 6.1 Hz), 3.22 (6H, s), 2.66 (1H, sept, *J* = 6.5 Hz), 1.56 (3H, s), 1.76 (6H, d, *J* = 6.5 Hz); ^{13}C nmr (90.5 MHz, DMSO): δ_C 156.7 ($C_{q\ \mathrm{DMAP}}$), 148.5 ($C_{q\ p\text{-cym}}$), 142.2 ($CH_{\ \mathrm{pz}}$), 138.2 ($CH_{\ \mathrm{pz}}$), 128.7 ($CH_{\ q\ p\text{-cym}}$), 108.3 ($CH_{\ \mathrm{DMAP}}$), 107.8 ($CH_{\ p\text{-cym}}$), 102.6 ($CH_{\ \mathrm{pz}}$), 101.9 ($CH_{\ p\text{- cym}}$), 107.2 ($C_{\ \mathrm{DMAP}}$), 80.3 ($CH_{3\ \mathrm{pz}}$), 29.9 ($CH_{3\ \mathrm{DMAP}}$), 22.1 ($CH_{3\ P\text{-cym}}$), 17.4 ($CH_{3\ p\text{-cym}}$); MS (FAB$^+$) *m/z* = 605.2 (M$^+$); Anal. Calcd. for $C_{26}H_{33}BClF_6N_8PRu$: C, 41.64; H, 4.44; N, 14.94; found: C, 41.53; H, 4.35; N, 14.56 %.

[{(N-methylimidazole)B(methimazolyl)$_3$}Mn(CO)$_3$][PF$_6$] (12): Ligand **9a** (0.100 g, 0.23 mmol) was added in small portions to a solution of [Mn(CO)$_3$(MeCN)$_3$]PF$_6$ (0.094 g, 0.23 mmol) dissolved in MeCN (10 mL) and the mixture was then heated to reflux for 2 hours providing a yellow precipitate. After cooling the solid was filtered via cannula, washed with hexane (10 mL) and dried under vacuum to yield **12** as a yellow solid.(0.095 g, 0.17 mmol, 70%). ^{1}H-NMR (250.1 MHz, CDCl$_3$), δ: 8.83 (s, 1H), 7.70 (s, 1H), 7.67 (s, 1H), 7,38 (d, 3H, *J* =2.34Hz), 6.82 (d, 3H, *J* = 2.34Hz), 3.83 (s, 3H), 3.55 (s, 9H); ^{13}C-NMR (62.9 MHz, CDCl$_3$), δ: 209.45 (C=O), 162.7 (C=S), 141.4 (CH*imi*); 125.6 (CH*imi*), 124.3 (CH*met*), 122.6 (CH*imi*), 121.5 (CH*met*), 40.4 (CH$_3$*imi*), 35.1 (CH$_3$*met)*; ^{11}B-NMR (80.3 MHz, DMSO-d$_6$), δ: 4.07; MS (EI +25eV): M$^+$= 571.9; IR (MeCN solution): 2007, 1914 cm^{-1} (CO); Anal. Calcd for $C_{19}H_{21}BN_8S_3O_3MnPF_6$; C, 31.86; H, 2.95; N, 15.64. Found: C, 31.72; H, 2.89; N, 15.70.

[{(N-methylimidazole)B(pyrazolyl)$_3$}Mn(CO)$_3$][PF$_6$] (13): To a solution of [Mn(CO)$_3$(MeCN)$_3$]PF$_6$ (0.141 g, 0.34 mmol) in acetonitrile (10 mL), ligand **9b** (0.100 g, 0.34 mmol) was added in small portions. The mixture was heated to reflux and the reaction was monitored by ES mass spectrometry. After 5h starting materials were no longer detected and the mixture was cooled to room temperature. Half of the solvent was removed under vacuum and the remaining solution was layered with dry Et$_2$O (15 mL) and stored at 5ºC overnight. A pale yellow solid precipitated, which was filtered off, washed with Et$_2$O (10 mL) and dried under vacuum to yield (**13**) as a pale yellow solid. (0.110 g, 0.25 mmol, 75%). Crystals suitable for X-ray were obtained by slow diffusion of Et$_2$O into a solution of **13** in acetone. ^{1}H-NMR (250.1 MHz, DMSO-d$_6$), δ: 9.69 (s, 1H), 8.36 (s, 1H), 8.23 (s, 1H), 8.17 (s, 3H), 8.09 (s, 3H), 6.55 (s, 3H), 3.86 (s, 3H); ^{13}C-NMR (62.9 MHz, CDCl$_3$), δ: 206.9 (CO), 147.2 (CH*imi*); 141.5 (CH*imi*), 136.2 (CH*imi*), 125.4 (CH*py*), 125.1 (CH*py*), 108.0 (CH*py*), 36.4 (CH$_3$*imi*); ^{11}B-NMR (80.3 MHz, DMSO-d$_6$), δ: 1.90.; MS (EI +25eV): M$^+$= 433 (M+1); IR(MeCN): 2041, 1941 cm^{-1} (CO); Anal. Calcd for $C_{16}H_{15}N_8BO_3MnPF_6$: C, 33.24; H, 2.62; N, 19.38. Found: C, 33.06; H, 2.50; N, 19.45.

X-ray crystallography: Crystal data for **8**, **11**, **12** and **13** are presented in Table 4. All data sets were collected with Mo-Kα 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 using the multi-scan procedure SADABS.[29] The structures were solved by Patterson methods for **8** and **11**, DIRDIF[30] and by direct methods for **12** and SIR-92[31] for **13**. All structures were refined by full-matrix least-squares against F^2 using SHELXL-97[32] for **8** and **11** and CRYSTALS[33] for **12** and **13**. All non-hydrogen 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)= 1.2U_{iso} for aromatic carbons and 1.5U_{iso} for methyl atoms]. In **8** the PF$_6^-$ anion based on P2 is disordered about one F-P-F axis. The occupancies of each component were fixed at 0.5 after competitive refinement. The geometries of the components were restrained to be similar. C34 is disordered over two positions, also in the ratio 0.5:0.5. The C24-C34-C44 and C23- C34'-C44 fragments were restrained to be geometrically similar. The structures of **8** and **12** contained disordered solvent regions which were were treated using the Squeeze procedure.[34] In **8** the number of electrons treated equates to 1 MeCN per formula unit; in **12** the number equates to 1 MeCN and 1 CH$_2$Cl$_2$ per formula unit. The values of F(000), D, M and mu are all calculated on this assumption. The imidazole ring in **13** is disordered over two orientations in the ratio 0.68:0.32. One carbon atom in the ring is common to both sites, as is the methyl carbon. The PF$_6^-$ counterion is also disordered. The 4 equatorial F atoms have been modelled as a torus of electron density as described by Schroder *et al*.[35]

	8	**11**	**12**	**13**
Crystal Description	Red block	Orange block	Yellow needle	Yellow block
Empirical Formula	$C_{31}H_{44}BF_{12}N_9P_2RuS_3$ $[RuL(cymene)][PF_6]_2.MeCN$	$C_{26}H_{33}BClF_6N_8PRu$ $[Ru(C_{16}H_{19}BN_8)(C_{10}H_{14})Cl]^+ PF_6^-$	$C_{22}H_{26}BCl_2F_6MnN_9O_3PS_3$ $[MnL(CO)_3][PF_6].MeCN.CH_2Cl_2$	$C_{16}H_{15}BF_6MnN_8O_3P$ $[Mn(CO)_3(C_{13}H_{15}BN_8)][PF_6]$
M_W	1040.75	749.9	842.31	578.05
T(K)	150(2)	150(2)	150(2)	150(2)
Crystal system	Monoclinic	monoclinic	triclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$	P-1	$P2_1/c$
a (Å)	16.7640(5)	15.3059(5)	10.1485(4)	22.6630(9)
b (Å)	13.0602(4)	10.1443(3)	10.5216(4)	7.7096(3)
c (Å)	20.5423(6)	20.8293(7)	17.4682(7)	13.3115(6)
α(°)	90	90	103.199(2)	90
β(°)	94.485(2)	106.854(2)	94.290(2)	101.201(2)
γ(°)	90	90	106.470(2)	90
V(Å^3)	4483.8(2)	3095.20(17)	1721.88(12)	2281.52(16)
Z	4	4	2	4
μ(Cu-Kα) (mm^{-1})	0.646	0.713	0.841	0.735
Independent reflections	8811 [R(int) = 0.0674]	6359 [R(int) = 0.0578]	9595 [R(int) = 0.041]	6286 [R(int) = 0.040]
Data with $\|F\| > 4\sigma(\|F\|)$]	7122	5123	4373	4627
Absorption correction	Multiscan (T_{min} = 0.334, T_{max} = 0.827)	Semi-empirical from equivalents (T_{min} = 0.7707, T_{max} = 0.9168)	Semi-empirical from equivalents (T_{min} = 0.74, T_{max} = 0.93)	Semi-empirical from equivalents (T_{min} = 0.61, T_{max} = 0.90)
R	0.0452	0.0347	0.0664	0.0915

Table 4. Crystallographic data for [{(DBN)B(methimazolyl)$_3$}Ru(*p*-cymene)][PF$_6$]$_2$ (**8**), [{(DMAP)B(pz)$_3$}Ru(p-cymene)Cl]PF$_6$ (**11**), [{(1-methylimidazole)-B(methimazolyl)$_3$}Mn(CO)$_3$][PF$_6$] (**12**) and [{(1-methylimidazole)B(pyrazolyl)$_3$}Mn(CO)$_3$][PF$_6$] (**13**).

References

[1] S. Trofimenko, *Inorganic Syntheses*, **1970**, *12*, 99-109.

[2] a) S. Trofimenko, *Scorpionates: The Coordination of Polypyrazolylborate Ligands*, Imperial College Press, London, **1999**; b) S. Trofimenko, *Chem. Rev.,* **1993**, *93*, 943; c) C. Pettinari, *Scorpionates II: Chelating Borate Ligands*, Imperial College Press, London, **2008**.

[3] H. R. Bigmore, S. C. Lawrence, P. Mountford, Philip, C. S. Tredget, *Dalton Trans*., **2005**, 635.

[4] D. D. LeCloux, C. J. Tokar, M. Osawa, R. P. Houser, M. C. Keyes, W. B. Tolman, *Organometallics,* **1994**, *13*, 2855.

[5] a) J. Reglinski, M. Garner, I. D. Cassidy, P. A. Slavin, M. D. Spicer, D. R. Armstrong, *J. Chem. Soc., Dalton Trans.,* **1999**, 2119; b) Ref. 2 c) pp 381-415; c) M. D. Spicer, J. Reglinski, *Eur. J. Inorg. Chem*., **2009**, 1553.

[6] P. J. Bailey, A. Dawson, C. McCormack, S. A. Moggach, I. D. H. Oswald, S. Parsons, D. W. H. Rankin, A. Turner, *Inorg. Chem.,* **2005**, *44*, 8884.

[7] S. Bakbak, V. K. Bhatia, C. D. Incarvito, A. L. Rheingold, D. Rabinovich, *Polyhedron*, **2001**, *20*, 3343.

[8] P. J. Bailey, C. McCormack, A. Sanchez-Perucha, S. Parsons, F. Rudolfi, P. Wood, *Dalton Trans.,* **2007**, 476.

[9] P. J. Bailey, S. Parsons and P. Pinho, *Inorg. Chem.* **2003**, *42*, 8872.

[10] a) K. Niedenzu, S. S. Seelig, W. Weber*, Z. Anorg. Allg. Chem*., **1981**, *483*, 51; b) K. Niedenzu, S. Trofimenko*, Inorg. Chem*., **1985**, *24*, 4222.

[11] P. J. Bailey, D. Lorono-Gonzales, C. McCormack, F. Millican, S. Parsons, R. Pfeifer, P. P. Pinho, F. Rudolphi, A. Sanchez-Perucha. *Chem. Eur. J.,* **2006**, *12*, 2593.

[12] a) M. A. Beswick, S. J. Kidd, M. A. Paver, P. R. Raithby, A. Steiner, D. S. Wright, *Inorg. Chem. Comm.* **1999**, *2,* 612; b) A. Hopkins, A. J. Wood, D. S. Wright, *Coord. Chem. Rev.*, **2001**, *216 – 217,* 155; c) M. A. Beswick, D. S. Wright, *Coord. Chem. Rev.*, **1998,** *176*, 373.

[13] B. Barszcz, *Pol. J. Chem*. **1989**, *63*, 9.

[14] H. N. Po, Z. Shariff, J. A. Masse, F. Freeman, M. C. Keindl-Yu, *Phosphorus Sulfur Silicon Relat. Elem*., **1991**, *63*, 1.

[15] L. Sooväli, I Kaljurand, A. Kütt, I Leito, *Anal. Chim. Acta*., **2006**, *566*, 290.

[16] T. Ishikawa (Ed.)*, Superbases for Organic Synthesis: Guanidines, Amidines, Phosphazenes and Related Organocatalysts*, Wiley, Chichester, **2009**.

[17] E-I. Rõõm, A. Kütt, I. Kaljurand, I. Koppel, I. Leito, I. A. Koppel, M. Mishima, K. Goto, Y. Miyahara, *Chem Eur J*, **2007**, *13*, 7631.

[18] This argument presupposes that bacicity is a reliable measure of the affinity of the added base for the boron centre. On the basis of the position of boron towards the hard end of the hard and soft acids scale, we think that this is a reliable first approximation for a tetrahedral boron centre.

[19] a) A. H. Cowley, J. L. Mills, *J. Am. Chem. Soc.,* **1969**, *91*, 2911; b) W. L. Budde, M. F. Hawthorne, *J. Am. Chem. Soc.,* **1971**, *93*, 3147; c) D. E. Walmsley, W. L. Budde, M. F. Hawthorne, *J. Am. Chem.Soc.,* **1971**, *93*, 3150; d) F. J. Lalor, T. Paxson, M. F. Hawthorne, *J. Am. Chem. Soc.* **1971**, *93*, 3156; e) E. Müller, H.-B. Bürgi, *Helv.Chim. Acta,* **1987**, *70*, 499; f) S. Toyota, M. Oki, *Bull. Chem. Soc. Jpn.,***1990**, *63*, 1168; g) S. Toyota, T. Futawaka, H. Ikeda, M. Oki, *J.Chem. Soc., Chem. Commun.,* **1995**, 2499; h) M. DiMare, *J. Org. Chem.,***1996**, *61*, 8378.

[20] P. J. Bailey, D. J. Lorono-Gobzales, C. McCormack, S. Parsons, M. Price, *Inorg. Chim. Acta*,, **2003**, *354*, 61.

[21] S. Bhambri, D. A. Tocher, *J. Chem. Soc., Dalton Trans.,* **1997**, 3367.

[22] G. Gioia Lobbia, C. Pettinari, C. Santini, N. Somers, B. Skelton, A. H. White, *Inorg. Chim. Acta*,, **2001**, *319*, 15.

[23] J. E. Joachim, C. Apostolidis, B. kanellakopulos, R. MaierN. Marques, D. Meyer, J. Muller, A. Pires de Matos, B. Nuber, J. Rebizant, M. L. Ziegler*, J. Organometal. Chem*., **1993**, *448*, 119.

[24] J. H. MacNeil, A. W. Roszak, M. C. Baird, . F. Preston, A. L. Rheingold, *Organometallics*, **1993**, *12*, 4402.

[25] D. L. REger, T. C. Grattan, K. J. Brown, J. J. S. Lamba, A. L. Rheingold, R. D. Sommer, *, J. Organometal. Chem*., **2000**, *607*, 120.

[26] C. Gwengo, R. M. Silva, M. D. Smith, S. V. Lindeman, J. R. Gardinier, *Inorg. Chim. Acta*, **2009**, *326*, 4127.

[27] S. B. Jensen, S. J. Rodger, M. D. Spicer, *J. Organometal. Chem*., **1998**, *556*, 151.

[28] R. H. Reimann, E. Singleton, *J. Chem. Soc., Dalton Trans.,* **1974***,* 808.

[29] Software Reference Manual (Bruker AXS, Madison, Wisconsin, USA, 1997)

[30] P. T. Beurskens, G. Beurskens, R. de Gelder, S. Garcia-Granda, R. O. Gould, R. Israel and J. M. M. Smits, Crystallography Laboratory, University of Nijmegen, The Netherlands. **1999**.

[31] A. Altomare, G. Cascarano, C. Giacovazzo and A. Guagliardi*, J. Appl. Crystallogr*. **1993**, *26*, 343.

[32] G. M. Sheldrick, Institüt für Anorganische Chemie der Universität, Tammanstrasse 4, D-3400 Göttingen, Germany, **1998**.

[33] P. W. Betteridge, J. R. Carruthers, R. I. Cooper, K. Prout, D. J. Watkin, *J. Appl. Cryst*. **2003**, *36*, 1487.

[34] P. v.d. Sluis and A. L. Spek, *Acta Crystallogr., Sect A*, **1990**, *46*, 194.

[35] L. Schröder, D. J. Watkin, A. Cousson, R. I. Cooper, W. Paulus, *J. Appl. Cryst.*, **2004**, *37*, 545.