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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 [(HNMe₂)B(azolyl)₃] (azolyl = methimazolyl, pyrazolyl), obtained by reaction of the azole with B(NMe₂)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 νco 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). 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. Analogous neutral tripods such as the tris(pyrazolyl)methanes [RC(pz)₃] and phosphoryl centered ligands [O=P(pz)₃] 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).

Scheme 1. The synthesis of hydrotris(azolyl)borate ligands from a BH₄⁻ 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 bicyclo[3.3.3] cage on \(\kappa^3\)-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\(_3\)v 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 Tm\(^{18}\) ligand in a melt reaction,\(^7\) the chiral 2-mercapto-1-(s-)\(\alpha\)-methylbenzylimidazole does not undergo a similar reaction, a result which we must attribute to the increased steric bulk resulting from the introduction of the \(\alpha\)-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 (Ipc)BCl\(_2\) (Ipc = isopinocampheyl) as the boron precursor, and while its reaction with pyrazolyl sodium successfully provided the [(Ipc)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 [(Ipc)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, B(NMe\(_2\))\(_3\), provides the dimethylamino aduct of tris(pyrazolyl)borane, [(HNMe\(_2\))B(pz)\(_3\)],\(^10\) on reaction with pyrazole, and we found that a similar adduct, [(HMe\(_2\)N)B(methimazolyl)\(_3\)] (1a), is formed in its reaction with methimazole (Scheme 2a).\(^11\) This prompted us to further explore the reactivity of 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, [(imidazole)B(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 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 [(donor)B(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 $[HB(azoly)_3]$ 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 $\alpha$-methylbenzyl groups in place of the methimazole N-methyl groups. The pseudo-$C_3$-symmetric complex of this ligand, $\{((N$-methylimidazole)B(1-$\alpha$-$\alpha$-methylbenzyl-2-mercapto-imidazolyl)$_3$)Ru($p$-cymene)$\}_2^{2+}$ 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 $\bar{\lambda}\bar{\lambda}\bar{\lambda}$ 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](image-url)  
**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(NMe₂)₃ and provide the reactive intermediates 3 (Scheme 4). A number of bases were therefore selected (Table 1) and employed in the reaction with B(NMe₂)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(NMe₂)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(NMe₂)₃ is insufficient to be observed spectroscopically, and thus that K₁ 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 HNMe₂ from the reaction mixture (Table 1). In our original interpretation of the mechanism this could be explained either by increased basicity of the NMe₂ groups in the adducts 3, or by higher values of the equilibrium constant K₁, 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 NEt₃ prevents its coordination to B(NMe₂)₃.

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


[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(NMe₂)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(NMe₂)₃ and the activating bases, this cannot be due to the absence of B(NMe₂)₃ in the reaction solutions. The explanation must lie in the details of the reaction between methimazole and the boron-bound NMe₂ 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 NMe₂ 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 HNMe₂/base exchange with its associated equilibrium constant K₂. This equilibrium would be driven towards 5b-f by the volatility of HNMe₂ which would readily be lost from the toluene solution under reflux.

Since the intermediate 4a cannot be isolated, whether the HNMe₂ 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(NMe₂)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 HNMe₂ substitution. The non-aqueous (MeCN) pKa of HNMe₂, 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.

Accepting that this will be close to that for HNMe₂, the fact that it can be substituted by weaker bases (Table 1) which presumably bind less strongly to boron, must reflect a shifting of the substitution equilibrium due to the loss of HNMe₂ gas from the reaction. The duration of the reactions has been determined by monitoring the evolution of HNMe₂ 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 HNMe₂ at boron by an added base.

The above discussion presupposes that the substitution of HNMe₂ 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 Sₘ¹ and Sₘ² pathways may be involved in such processes. Given the B-N π-bonding which will stabilise the boranes produced on dissociation of HNMe₂ from 4a, and to a lesser extent 6a, and the combined steric bulk of the groups attached to boron in 1a, Sₘ¹ processes would seem most likely to be operating in this system. Given this, the availability of two NMe₂ 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 HNMe₂ 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 HNMe₂
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 HNMe₂ in [(HNMe₂)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 HNMe₂ in 1a by added bases to form the ligands 1c-e.

A ruthenium⁰⁺ complex of ligand 1e

A Ru⁺⁺ complex of the ligand 1e containing DBN coordinated to boron was synthesised by reaction with the dimer [(p-cymene)RuCl₂]₂ in ethanol. The resulting chloride salt of the complex was then treated with NH₄PF₆ to provide [{κ³-(DBN)B(methimazolyl)]Ru(p-cymene)][PF₆]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 ^13C 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 κ³-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 λλλλ and δδδδ forms of the C₃-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-cymene)]+ [108.34(10) – 113.33(10)°][20] and [(Tm13)Ru(p-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]

Figure 1. Structure of the dication in [{κ³-(DBN)B(methimazolyl)}₃Ru(p-cymene)][PF₆]₂ (8). PF₆⁻ 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 [(HNMe₂)B(pz)] (9) is readily available by reaction of B(NMe₂)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 HNMe₂ and provide the new ligands (10a and 10b) in very high yield (Scheme 7).

Scheme 7. Substitution of HNMe₂ 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)RuCl₂]₂ in methanol solution followed by salt metathesis with NH₄PF₆ to provide the yellow salt 11. We anticipated the formation of the complex [{κ³-(DMAP)B(pz)₃}Ru(p-cymene)][PF₆]₂; however, the +FAB mass spectrum of 11 showed a molecular ion at m/z = 605 consistent with the formulation [{κ²-(DMAP)B(pz)₃}RuCl(p-cymene)]⁺ indicating that the ligand adopts a κ²-N,N-coordination mode and one chloride remains coordinated to ruthenium. ¹H and ¹³C 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 [{κ²-HB(pz)₃}RuCl(arene)] which may be isolated from the reaction of NaTp with [(arene)RuCl₂]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 [{κ²-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 [{κ²-(DMAP)B(pz)₃}RuCl(p-cymene)][PF₆] (11). PF₆⁻ counterion not shown. Selected bond lengths and angles are provided in Table 2.](image)

**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][PF₆] in MeCN solution. These reactions proceed smoothly to provide the salts [{(1-methylimidazole)B(methimazolyl)₃}Mn(CO)₃][PF₆] (12) and [{(1-methylimidazole)B(pyrazolyl)₃}Mn(CO)₃][PF₆] (13) in high yield. Spectroscopic characterisation of these complexes is consistent with κ³-S,S,S and κ³-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 λλλλ and δδδδ enantiomeric forms of the complex in which the C₃-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(PAr₃)] (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][PF₆] (12). PF₆⁻ 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][PF₆] (13). PF₆⁻ 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][PF₆] (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 spectrum (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.

<table>
<thead>
<tr>
<th>Complex[a]</th>
<th>$\nu_{CO}$/cm⁻¹</th>
<th>Medium</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>[{HB(methimazolyl)₃}Mn(CO)₃]</td>
<td>2003, 1905</td>
<td>Toluene</td>
<td>[20]</td>
</tr>
<tr>
<td>[{(NMI)B(methimazolyl)₃}Mn(CO)₃][PF₆] (12)</td>
<td>2007, 1914</td>
<td>MeCN</td>
<td>This work</td>
</tr>
<tr>
<td>[{HB(3,5- Me₂Pz)₃}Mn(CO)₃]</td>
<td>2023, 1912</td>
<td>KBr</td>
<td>[23]</td>
</tr>
<tr>
<td>[{HB(pz)₃}Mn(CO)₃]</td>
<td>2036, 1932</td>
<td>MeCN</td>
<td>[24]</td>
</tr>
<tr>
<td>[{pzB(pz)₃}Mn(CO)₃]</td>
<td>2039, 1936</td>
<td>MeCN</td>
<td>[24]</td>
</tr>
<tr>
<td>[{(NMI)B(pz)₃}Mn(CO)₃][PF₆] (13)</td>
<td>2041, 1941</td>
<td>MeCN</td>
<td>This work</td>
</tr>
<tr>
<td>[{HC(3,5-Me₂Pz)₃}Mn(CO)₃][OTf]</td>
<td>2044, 1949</td>
<td>CH₂Cl₂</td>
<td>[25]</td>
</tr>
<tr>
<td>[{HC(pz)₃}Mn(CO)₃][OTf]</td>
<td>2051, 1956</td>
<td>CH₂Cl₂</td>
<td>[25]</td>
</tr>
</tbody>
</table>

[a] NMI = 1-methylimidazole

Table 3. IR data ($\nu_{CO}$) 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⁺ 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 $\nu_{CO}$ 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-Me₂pz)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-Me₂pz)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] [PF₆] (12) and its neutral analogue containing the Tm ligand, [{H(B(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-B’ by ‘N-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, 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 HNMe₂ may be substituted by alternative N-donors in both (HNMe₂)B(methimazolyl)₃ (1a) and (HNMe₂)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 HNMe₂ 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 MSS50TC (FAB) and Micromass Platform II (ES-MS) spectrometers. NMR spectra were recorded on a Bruker 250AC spectrometer operating at room temperature. ¹H and ¹³C chemical shifts are reported in ppm relative to SiMe₄ (δ = 0) and were referenced internally with respect to the protio solvent impurity or the ¹³C 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 CaF₂ windows on a Jasco FT-IR 410 spectrometer. The compounds [(HMe₂N)B(methimazolyl)]₃ (1a),[(HMe₂N)B-(pyrazolyl)]₃ [10a] [(p-cymene)RuCl₂] [27] and [Mn(CO)₅(NCMe)₃][PF₆] [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(NMe₂)₃, methimazole and the added base (1:3:1 stoichiometry) are heated to reflux in toluene until evolution of HNMe₂ 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)](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 HNMe₂ 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%. ¹H-NMR (250.1 MHz, CDCl₃), 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); ¹³C-NMR (62.9 MHz, CDCl₃), δ: 170.7 (C=S), 165.9 (C automated), 1478.0 (CH), 128.6 (CH), 118.2 (CH), 110.2 (CH), 57.3 (CH₃), 35.2 (CH), 35.1 (CH₃), 11B-NMR (80.3 MHz, CDCl₃), δ: 5.43; MS (EI +25eV): M⁺ = 459.88 (M⁺+1); Anal. Calcd for C₁₉H₂₂BN₆OS₃; C, 47.06; H, 4.83; N, 21.34. Found: C, 46.87; H, 4.60; N, 21.69.

[(4-dimethylaminopyridine)B(methimazolyl)](1c): Yield 87%. ¹H-NMR (250.1 MHz, CDCl₃), δ: 8.12 (br, 2H), 6.59 (d, 3H, = 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); ¹³C-NMR (62.9 MHz, CDCl₃), δ: 165.77 (C=S), 156.7 (C automated), 146.6 (CH), 123.1 (CH), 117.9 (CH), 105.9 (CH), 40.1 (CH₃), 35.2 (CH₃), 11B-NMR (80.3 MHz, CDCl₃), δ: 5.08; MS (EI +25eV): M⁺ = 473.04; Anal. Calcd for C₁₉H₂₂BN₆S₂B; C, 48.30; H, 5.33; N, 23.72. Anal. Calcd for C₁₉H₂₂BN₆S₂; C, 48.30; H, 5.33; N, 23.72. Found: C, 48.09; H, 5.10; N, 23.91.

[(N-methylimidazole)B(methimazolyl)](1d): Yield 88%. ¹H-NMR (250.1 MHz, CDCl₃), 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); ¹³C-NMR (62.9 MHz, CDCl₃), δ: 35.10 (CH₃met), 36.05 (CH₂Imi), 114.36 (CHImi), 117.9 (CHmet), 121.6 (CHImi), 124.6 (CHMet), 142.7 (CHImi), 164.7 (C=S); ¹¹B-NMR (80.3 MHz, CDCl₃), δ: 8.05; MS (EI +25eV): M⁺ = 433; Anal. Calcd for C₁₆H₁₉BN₆S₃C₇H₅; C, 52.66; H, 5.57; N, 21.36. Found: C, 52.57; H, 5.52; N, 21.39.

[(DBN)B(methimazolyl)](1e): Yield 72%. ¹H nmr (500.1 MHz, CDCl₃): δH 6.71 (3H, d, D = 2.5 Hz), 6.67 (3H, d, D = 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); ¹³C nmr (90.5 MHz, DMSO): δC 161.0 (C=S), 129.3 (Cq DBN), 120.1 (CHmet), 114.1 (CHmet), 46.9 (CH₂DBN), 43.9
(CH$_2$DBN), 42.9 (CH$_2$DBN), 34.9 (CH$_2$DBN), 30.7 (CH$_2$DBN), 24.1 (CH$_3$met), 18.3 (CH$_2$DBN); MS (FAB$^+$): $m/z$ = 474.6; Anal. Calcd. for C$_{19}$H$_29$BN$_8$S$_3$(474.16): C, 48.10; H, 5.74; N, 23.61; found: C, 47.60; H, 5.46; N, 23.36%.

[(DBU)B(methimazolyl)$_2$] (If): 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 (CHmet), 114.6 (CHmet), 55.4 (CH$_2$DBU) 53.7 (CH$_2$DBU) 48.3 (CH$_2$DBU) 33.9 (CH$_3$met), 31.7 (CH$_2$DBU) 28.7 (CH$_2$DBU) 26.4 (CH$_2$DBU) 23.8 (CH$_2$DBU) 19.4 (CH$_2$DBU); $^{1}$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$_{27}$BN$_8$S$_3$B 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 If is given below and the other ligands followed a similar protocol.

[(4-dimethylaminopyridine)B(methimazolyl)$_2$] (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)][PF$_6$]$_2$ (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$_2$PF$_6$ (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$_3$CN): 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$_3$)$_2$CO): 172.2 (C$_q$DBN), 148.9 (C$_q$met), 124.4 (CH$_3$met), 124.1(CH$_3$met), 107.8 (C$_p$-cym), 103.5 (C$_q$-p-cym), 87.3 (2CH$_p$-cym), 86.3 (CH$_p$-cym), 85.3 (2CH$_p$-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-cym), 21.3 (2CH$_3$-p-cym), 19.5 (CH$_2$DBN); δ$_H$(115.5 MHz, DMSO): 4.15; MS (FAB$^+$): $m/z$ = 501.9 [(M+1)/2]; Anal. Calcd for C$_{28}$H$_{41}$BF$_4$N$_8$P$_3$Ru$_3$: C, 34.89; H, 4.13; N, 11.21; found: C, 34.16; H, 4.02; N, 11.15%.

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[(N-methylimidazole)B(pyrazolyl)]₂ (10a): 92% yield. ¹H-NMR (250.1 MHz, CDCl₃): δ: 8.52 (s, 1H), 7.65 (dd, 3H, J = 1.55Hz, J = 0.51Hz), 7.48 (t 1H, J = 1.55 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); ¹³C-NMR (62.9 MHz, CDCl₃), δ: 140.9 (CHim), 137.4 (CHim); 133.6 (CHpy), 125.5 (CHpy), 104.1 (CHpy), 34.4 (CH₃im); ¹¹B-NMR (80.3 MHz, CDCl₃), δ: 3.76; MS (EI +25eV): M⁺ = 295.13 (M+1); Anal. Calcd for C₁₃H₁₉N₃B; C, 53.09; H, 5.14; N, 38.10. Found: C, 53.24; H, 5.03; N, 38.29.

[(4-dimethylaminopyridine)B(pyrazolyl)]₂ (10b): 90% yield. ¹H nmr (360.1 MHz, CDCl₃): δ₁ 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); ¹³C nmr (90.5 MHz, CD₂Cl₂): δc 156.1 (Cq DMAP), 145.4 (CHpy), 135.3 (CHpy), 129.1 (CH DMAP), 106.6 (CHpy), 105.7 (CH DMAP), 39.9 (CH₃ DMAP); MS (FAB⁺): m/z = 335.3 (M+1); C₁₆H₁₈BN₅; C, 57.50; H, 5.73; N, 33.53; found: C, 57.01; H, 5.39; N, 33.38 %.

[(DMAP)B(pz)]₂Ru(p-cymene)ClPF₆ (11): [(p-cymene)-RuCl₂]₂ (110 mg, 0.0179 mmol) was dissolved in methanol (10 mL) and stirred for 1 h. [(DMAP)B(pz)]₂ (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. NH₄PF₆ (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. ¹H nmr (360.1 MHz, DMSO): δ₁ 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); ¹³C nmr (90.5 MHz, DMSO): δc 156.7 (Cq DMAP), 148.5 (C₃p-cym), 142.2 (CHp), 138.2 (CHpy), 128.7 (CH q-p-cym), 108.3 (CH DMAP), 107.8 (CH p-cym), 102.6 (CHpy), 101.9 (CH p-cym), 107.2 (CDMAP), 80.3 (CH₃ py), 29.9 (CH₃ DMAP), 22.1 (CH₃ p-cym), 17.4 (CH₃ p-cym); MS (FAB⁺) m/z = 605.2 (M⁺); Anal. Calcd for C₂₀H₂₃BClF₆N₈PRu: C, 41.64; H, 4.44; N, 14.94; found: C, 41.53; H, 4.35; N, 14.56 %.

[(N-methylimidazole)B(methylazolyl)]₃Mn(CO)₃[PF₆] (12): Ligand 9a (0.100 g, 0.23 mmol) was added in small portions to a solution of [Mn(CO)₃(MeCN)]₃PF₆ (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%). ¹H-NMR (250.1 MHz, CDCl₃), 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); ¹³C-NMR (62.9 MHz, CDCl₃), δ: 209.45 (C=O), 162.7 (C=S), 141.4 (CHim); 125.6 (CHim), 124.3 (CHmet), 122.6 (CHim), 121.5 (CHmet), 40.4 (CH₃im), 35.1 (CH₃met); ¹¹B-NMR (80.3 MHz, DMSO-d₆), δ: 4.07; MS (EI -25eV): M⁺ = 571.9; IR (MeCN solution): 2007, 1914 cm⁻¹ (CO); Anal. Calcd for C₁₉H₂₁BN₃S₃O₃MnPF₆; C, 31.86; H, 2.95; N, 15.64. Found: C, 31.72; H, 2.89; N, 15.70.
[(N-methylimidazole)B(pyrazolyl)]₃Mn(CO)₃[PF₆] (13): To a solution of [Mn(CO)₃(MeCN)₃]PF₆ (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 Et₂O (15 mL) and stored at 5ºC overnight. A pale yellow solid precipitated, which was filtered off, washed with Et₂O (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 Et₂O into a solution of 13 in acetone.

1H-NMR (250.1 MHz, DMSO-d₆), 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);

13C-NMR (62.9 MHz, CDCl₃), δ: 206.9 (CO), 147.2 (CHimi); 141.5 (CHimi), 136.2 (CHimi), 125.4 (CHpy), 125.1 (CHpy), 108.0 (CHpy), 36.4 (CH₃imi);

11B-NMR (80.3 MHz, DMSO-d₆), δ: 1.90.; MS (EI +25eV): M⁺ = 433 (M+1); IR(MeCN): 2041, 1941 cm⁻¹ (CO);


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 F² 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 Uiso values assigned [Uiso(H) = 1.2Uiso for aromatic carbons and 1.5Uiso for methyl atoms]. In 8 the PF₆⁻ 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 fragments were restrained to be geometrically similar. The structures of 8 and 12 contained disordered solvent regions which 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 CH₂Cl₂ 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 PF₆⁻ counterion is also disordered. The 4 equatorial F atoms have been modelled as a torus of electron density as described by Schröder et al.[35]
<table>
<thead>
<tr>
<th>Crystal Description</th>
<th>8</th>
<th>11</th>
<th>12</th>
<th>13</th>
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<tr>
<td>Empirical Formula</td>
<td>C₃₁H₄₄BF₁₂N₉P₂RuS₃[RuL(cymene)][PF₆]₂·MeCN</td>
<td>C₂₆H₃₃BClF₆N₈P₂Ru[Ru(C₁₀H₁₄BN₈)C₁₀H₁₄]⁺PF₆⁻</td>
<td>C₂₂H₂₆BCl₂F₆MnN₉O₃PS₃[MnL(CO)₃][PF₆]₂·MeCN.CH₂Cl₂</td>
<td>C₁₆H₁₅BF₆MnN₉O₃P[Mn(CO)₃(C₁₃H₁₅BN₈)][PF₆]</td>
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<tr>
<td>Mw</td>
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<td>749.9</td>
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<tr>
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<td>a(Å)</td>
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<td>15.3059(5)</td>
<td>10.1485(4)</td>
<td>22.6630(9)</td>
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<tr>
<td>b(Å)</td>
<td>13.0602(4)</td>
<td>10.1443(3)</td>
<td>10.5216(4)</td>
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<td>c(Å)</td>
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<td>β(°)</td>
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<td>106.854(2)</td>
<td>94.290(2)</td>
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<td>γ(°)</td>
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<tr>
<td>F(A⁺)</td>
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<td>3095.20(17)</td>
<td>1721.88(12)</td>
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<td>6359 [R(int) = 0.0578]</td>
<td>9595 [R(int) = 0.041]</td>
<td>6286 [R(int) = 0.040]</td>
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<td>Absorption correction</td>
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<td>Semi-empirical from equivalents Tₘᵢₙ = 0.7707, Tₘₐₓ = 0.9168</td>
<td>Semi-empirical from equivalents Tₘᵢₙ = 0.74, Tₘₐₓ = 0.93</td>
<td>Semi-empirical from equivalents Tₘᵢₙ = 0.61, Tₘₐₓ = 0.90</td>
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<td>0.0347</td>
<td>0.0664</td>
<td>0.0915</td>
</tr>
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</table>

**Table 4.** Crystallographic data for [(DBN)B(methimazolyl)₃]Ru(p-cymene)][PF₆]₂ (8), [(DMAP)B(pz)₃]Ru(p-cymene)Cl][PF₆] (11), [(1-methylimidazole)-B(methimazolyl)₃]Mn(CO)₃][PF₆] (12) and [(1-methylimidazole)B(pyrazolyl)₃]Mn(CO)₃][PF₆] (13).
References


[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.


