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Insertion and substitution chemistry at the boron fourth position in charge-neutral zwitterionic tripodal tris(methimazolyl)borate ligands**

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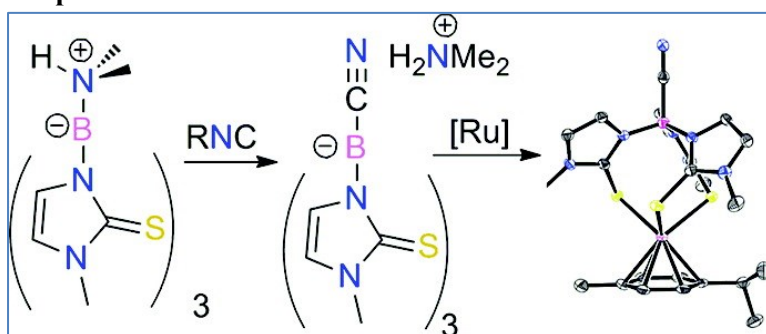
Supporting information:

Crystallographic data in CIF format and the variable temperature ¹H NMR spectra of compound 9/9b. This material is available free of charge via the Internet at <http://pubs.acs.org>. CCDC refs. 867276–867282 contain the supplementary crystallographic data for the structures in this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif

Synopsis:

The synthesis of novel anionic and zwitterionic charge-neutral tripodal tris(methimazolyl)borate ligands is described. In the course of this study unusual reactivity of these ligands with nitriles and isocyanides was observed the results of which are described herein.

Graphical abstract:



Keywords:

Scorpionate; tripod ligand; ligand design; nitrile insertion; isocyanide insertion; ruthenium

Abstract

Poly(azolyl)borates, the most common of which is the hydrotris(pyrazolyl)borate (Tp), are some of the most popular chelating ligands in coordination chemistry.¹ The analogous hydrotris(methimazolyl)borate (Tm) ligand was developed by Reglinski and Spicer in 1996 and has since been shown to be capable of complexation to a wide variety of metal centres.² Complexes of this ligand exhibit an unusual type of chirality as the metal-ligand cage formed twists into a helical structure to relieve torsional strain which arises as a result of the 8-membered bicyclic rings which form upon complexation. The result is that complexes of this ligand have C_3 -symmetry and exist in *P*- and *M*-helical enantiomeric forms (Figure 1).

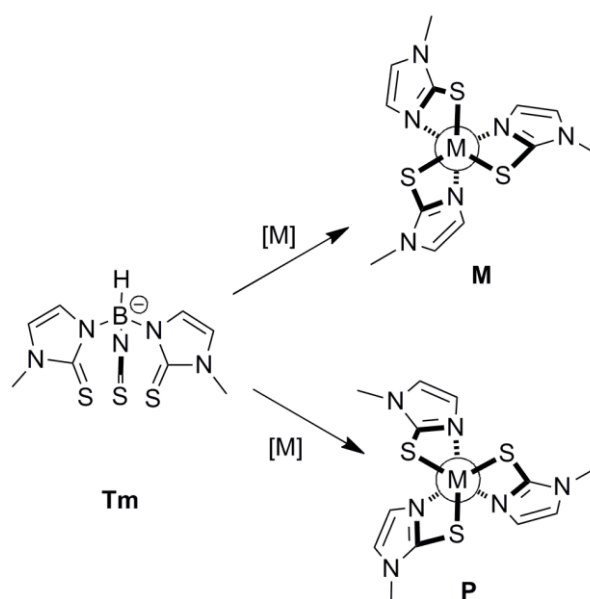
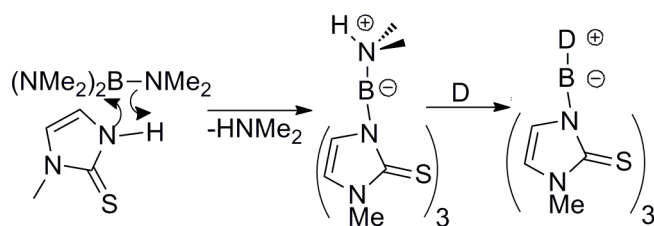


Figure 1. *P* and *M* enantiomers of a complex of the Tm ligand.

Hydrotris(azolyl)borates are typically synthesised via a solventless melt reaction between the chosen heterocycle and a group 1 metal tetrahydridoborate. The resulting anionic ligand contains three azolyl groups and a hydride in the boron fourth position. However, a number of alternative routes to such ligands exist. In 1985 Niedenzu reported the synthesis of a charge-neutral zwitterionic analogue of Tp [(HNMe₂)B(pz)₃], in which the hydride is replaced by dimethylamine, achieved by reaction of pyrazole with tris(dimethylamino)borane.³ Over recent years we have developed this approach to provide a range of such neutral zwitterionic ligands of both the tris(methimazolyl) [ZTm] and tris(pyrazolyl) [ZTp] type.⁴ The dimethylamine in (HNMe₂)B(methimazolyl)₃ (**1**) formed by this reaction may be substituted with a wide range of neutral, mostly nitrogen, donors (D) to provide new ligands [(D)ZTm] (Scheme 1). The substitution is aided by the loss of HNMe₂ gas from the reaction mixture which drives the equilibrium towards the product and enables the use of donors considerably less basic than HNMe₂ (e.g. pyridine).



Scheme 1. Synthesis and Substitution of [(HMe₂N)ZTm]. (D=Donor).

This synthetic route provides access to a much wider range of ligands than the conventional borohydride melt reaction since, not only can a range of groups be placed at the boron fourth position in place of hydride, but the use of B(NMe₂)₃ as the boron source enables use of substituted methimazoles for which the borohydride route fails. Thus, replacing the N-methyl group in methimazole with homochiral N- α -methylbenzyl provides a ligand which forms single diastereomer complexes in which the helical twist of the metal-ligand cage adopts the *M*- or *P*- conformation exclusively dependent on the chirality of the α -methylbenzyl groups.⁵

A potential alternative means of directing the helical twist involves the use of a chiral donor at the boron fourth position chosen to maximise its interaction with the three methimazolyl groups, and thus to relay chirality to the rest of the ligand. This would leave the choice of methimazolyl N-substituent to modify the steric environment, or introduce functionality, around the metal coordination site. For this reason we have explored the range of donor types which can be incorporated at this site to replace the dimethylamine in (HNMe₂)ZTm (**1**) and we report here some results from this study. The donors used in this work are shown in Figure 2.

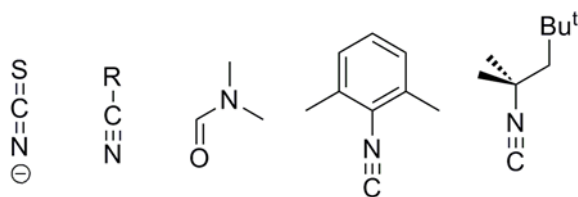


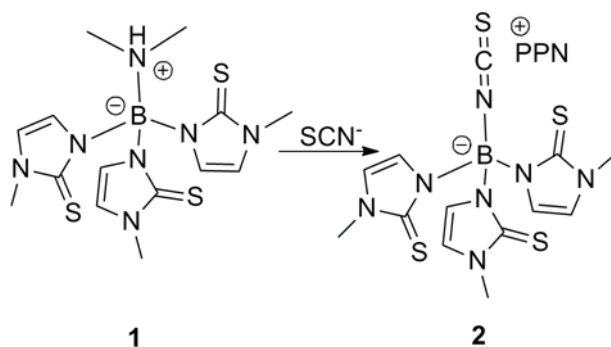
Figure 2. Donors used in this work. R = Me, Ph.

Results and Discussion

Anionic tris(methimazolyl)borate ligands from (HNMe₂)ZTm (1)

Having demonstrated the broad scope of the synthesis of charge-neutral ZTm ligands by substitution of the amine in (HNMe₂)ZTm (**1**) with neutral donors,⁴ we also wished to explore the possibility of forming new

anionic “XTm” ligands by similar substitution with anionic donors. Parkin has previously demonstrated that complexes of these ligands can be accessed by treating [TmNiX] (X = N₃, NCS, NCO) with iodine.⁶ Thus the pseudo-halides N₃⁻, NCS⁻ and NCO⁻ were chosen as potential donors in this role. Due to the insolubility of the [PPN]⁺ and [PPh₄]⁺ salts of these anions in toluene, the usual solvent for our substitution reactions, acetonitrile was employed as the reaction medium. Reaction with both N₃⁻ and NCO⁻ resulted in the degradation of **1** upon dissolution even under ambient conditions. We have previously shown that strong bases such as NaOH, NaOR and NaNH₂ cause degradation of **1** by deprotonation of the dimethylamine functionality leading to the anion [(Me₂N)B(mt)₃]⁻, which appears to be unstable as only free methimazole is isolated in these reactions. However, N₃⁻ and NCO⁻ are not strong Brønsted bases and are in fact weaker Lewis bases than thiocyanate. The reason for the instability of **1** in the presence of these anions remains unclear at this time. However, the [PPN]⁺ salt of (thiocyanate)tris(methimazolyl)borate [(SCN)Tm]⁻ (**2**) could be isolated in 51% yield after reflux for 24 hours (*Scheme 2*).



Scheme 2. Reaction of ZTm(**1**) with [PPN][NCS].

The ¹H-NMR spectrum of **2** shows no signals due to N-H or NMe₂ groups indicating the loss of HNMe₂. The methimazolyl proton signals show small shifts relative to **1** reflecting minor changes in electronic structure between the neutral zwitterionic **1** and anionic **2**. Mass spectrometry (ESI) shows a molecular ion peak at *m/z* = 408 consistent with the presence of the [(SCN)B(mt)₃]⁻ anion. Additionally, the IR spectrum showed a strong absorption at 2158 cm⁻¹ assigned to the SCN C=N stretching vibration (*c.f.* 2058 cm⁻¹ in [PPN]SCN), thus indicating a strengthening of this bond upon coordination to the boron centre.

A complex of ligand **2** was obtained by reaction of [PPN] [(SCN)B(mt)₃] with [(*p*-cymene)RuCl₂]₂ at room temperature in methanol for 2 hours followed by addition of sodium tetraphenylborate. After filtration of the precipitated salts and work-up of the solution the salt [{"(SCN)B(mt)₃} Ru(*p*-cymene)] [BPh₄] (**3**) was obtained as red needles in 30% yield. X-ray crystallography of this complex confirmed the structure of the ligand (Figure 3). The complex crystallises in space group I2/a with two independent molecules in the unit cell corresponding to the two helical enantiomers. Metric data for the two do not differ substantially and only

those for the complex containing Ru1 will be discussed. The B1a-N22a (NCS) bond [1.518(3)Å] is shorter than the other B-N bonds within this complex [1.542(4), 1.536(4), 1.545(3) Å] demonstrating its covalency. The N22a-C23a (NCS) bond [1.153(3) Å] is comparable with the same bond in KSCN [1.149(14) Å], although the C23a-S24a bond [1.597(3) Å] is slightly shorter than in the salt [1.689(13) Å].⁷ The angle around N22a is slightly bent [167.2(2)°], although the S24a-C23a-N22a bond angle is essentially linear [178.2(3)°]. The mean $N_{\text{mt}}\text{-B-Ru-S}$ torsion in this complex is relatively large ($\theta = -49.1^\circ$) compared to the literature value ($\theta = 45.1^\circ$) for [TmRu(p-cymene)]Cl.⁸ However, the displacement of the metal from the plane of the methimazole ring ($\omega = 58.6^\circ$) compares favourably with reported values ($\omega = -58.0^\circ$).^{9, 10}

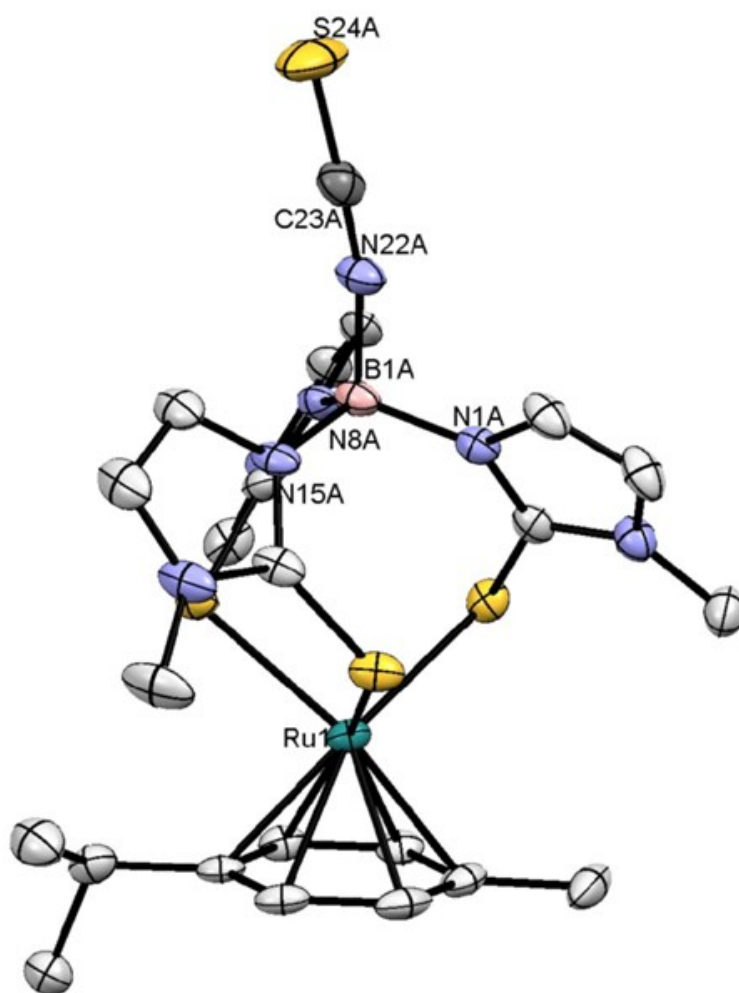


Figure 3. Structure of $[(\kappa^3\text{-[S,S,S]-(thiocyanate)-B(methimazoly)}_3)\text{Ru(p-cymene)}]^-$ (**3**). Hydrogen atoms and counter ion omitted for clarity. Selected bond lengths and angles are provided in **Table 1**.

3		5		7		9b	
Ru1—S10A	2.4208 (7)	Ru(1) S(1A)	2.4258(7)	Ru(1)-S(3)	2.4111(11)	S1—C1	1.835 (2)
Ru1—S17A	2.4318 (6)	Ru(1) S(1B)	2.4218(7)	Ru(1)-S(2)	2.4143(11)	S1—C2	1.721 (3)
Ru1—S3A	2.4387 (7)	Ru(1) S(1C)	2.4257(6)	Ru(1)-S(1)	2.4373(11)	S2—C14	1.700 (3)
N1A—B1A	1.542 (4)	B(1) N(1C)	1.541(3)	B(1)-N(4)	1.525(6)	S3—C18	1.686 (3)
B1A—N22A	1.518 (3)	B(1) N(1D)	1.545(3)	B(1)-N(2)	1.544(5)	N1—C2	1.331 (3)
B1A—N8A	1.536 (4)	B(1) N(1A)	1.558(3)	B(1)-N(8)	1.567(6)	N2—C2	1.342 (3)
B1A—N15A	1.545 (3)	B(1) N(1B)	1.560(3)	B(1)-N(6)	1.580(6)	N2—B1	1.547 (3)
N22A—C23A	1.156 (3)	N(1D) C(2D)	1.337(3)	N(2)-C(3)	1.340(5)	N3—C1	1.255 (3)
C23A—S24A	1.597 (3)	C(2D) C(3D)	1.496(4)	C(3)-C(4)	1.473(6)	N3—C6	1.431 (3)
		C(2D) N(4D)	1.315(3)	N(1)-C(3)	1.326(5)	N4—B1	1.535 (4)
		N(4D) C(6D)	1.468(4)	N(1)-C(2)	1.461(5)	N6—B1	1.537 (3)
		N(4D) C(5D)	1.471(4)	N(1)-C(1)	1.472(5)	C1—B1	1.652 (3)
S10A-Ru1-S17A	90.84 (2)	S(1B)-Ru(1)-S(1C)	88.95(2)	S(3)-Ru(1)-S(2)	88.51(4)	C1—S1—C2	89.37 (11)
S10A-Ru1-S3A	91.67 (2)	S(1B)-Ru(1)-S(1A)	90.38(2)	S(3)-Ru(1)-S(1)	95.19(4)	C2—N2—B1	116.5 (2)
S17A-Ru1-S3A	90.66 (2)	S(1C)-Ru(1)-S(1A)	94.11(2)	S(2)-Ru(1)-S(1)	89.92(4)	C4—N2—B1	136.5 (2)
N22A-B1A-N8A	107.4 (2)	N(1C)-B(1)-N(1D)	108.64(19)	N(4)-B(1)-N(2)	109.8(3)	C1—N3—C6	120.6 (2)
N22A-B1A-N1A	107.4 (2)	N(1C)-B(1)-N(1A)	109.46(19)	N(4)-B(1)-N(8)	108.0(3)	C18—N6—B1	127.2 (2)
N22A-B1A-N15A	106.87 (19)	N(1D)-B(1)-N(1A)	105.94(19)	N(2)-B(1)-N(8)	108.5(3)	C20—N6—B1	125.0 (2)
N8A-B1A-N15A	113.5 (2)	N(1C)-B(1)-N(1B)	115.12(19)	N(4)-B(1)-N(6)	117.0(3)	S1—C1—N3	120.39 (18)
N1A-B1A-N15A	110.2 (2)	N(1D)-B(1)-N(1B)	108.94(19)	N(2)-B(1)-N(6)	106.1(3)	S1—C1—B1	112.56 (17)
C23A-N22A-B1A	167.2 (3)	N(1A)-B(1)-N(1B)	108.35(18)	N(8)-B(1)-N(6)	107.3(3)	N3—C1—B1	126.8 (2)
N22A-C23A-S24A	178.2(3)	C(2D)-N(1D)-B(1)	132.9(2)	C(3)-N(2)-B(1)	135.4(3)	S1—C2—N1	129.47 (19)
		N(1D)-C(2D)-C(3D)	121.5(2)	N(1)-C(3)-N(2)	118.6(4)	S1—C2—N2	120.32 (19)
		N(4D)-C(2D)-N(1D)	119.7(2)	N(1)-C(3)-C(4)	118.1(4)	N2—B1—C1	101.23 (19)
		N(4D)-C(2D)-C(3D)	118.9(2)			N4—B1—C1	108.1 (2)
		C(2D)-N(4D)-C(6D)	120.7(2)			N6—B1—C1	111.36 (19)
		C(2D)-N(4D)-C(5D)	122.3(3)				
		C(6D)-N(4D)-C(5D)	117.0(2)				
10		12		15			
Ru(1)-N(24A)	2.1127(19)	Ru(1)-S(11A)	2.4224(10)	Ru(1) – S(12)	2.4331 (9)		
Ru(1)-S(4A)	2.4147(6)	Ru(1)-S(18A)	2.4296(11)	Ru(1) – S(19)	2.4356 (9)		
Ru(1)-S(11A)	2.4156(6)	Ru(1)-S(4A)	2.4351(11)	Ru(1) – S(26)	2.4340 (9)		
B(1A)-N(9A)	1.533(3)	B(1A)-N(16A)	1.536(6)	B(1)-C(2)	1.624 (5)		
B(1A)-N(3A)	1.535(3)	B(1A)-N(2A)	1.546(6)	B(1)-N(3)	1.535 (4)		
B(1A)-N(16A)	1.561(3)	B(1A)-N(23A)	1.549(6)	B(1)-N(13)	1.540 (4)		
B(1A)-C(23A)	1.658(3)	B(1A)-N(9A)	1.556(6)	B(1)-N(20)	1.551 (4)		
N(16A)-C(17A)	1.325(3)	N(23A)-C(24A)	1.323(6)	N(1)-C(2)	1.143 (4)		
C(17A)-S(18A)	1.731(2)	C(24A)-N(25A)	1.306(6)				
S(18A)-C(23A)	1.791(2)	N(25A)-C(26A)	1.463(6)				
C(17A)-N(19A)	1.322(3)	N(25A)-C(27A)	1.466(6)				
C(23A)-N(24A)	1.283(3)						
N(24A)-C(25A)	1.452(3)						
N(24A)-Ru(1)-S(4A)	83.15(6)	S(11A)-Ru(1)-S(18A)	92.18(4)	S(12)-Ru(1)-S(26)	91.85 (3)		
N(24A)-Ru(1)-S(11A)	95.17(5)	S(11A)-Ru(1)-S(4A)	89.53(4)	S(26)-Ru(1)-S(19)	91.88 (3)		
S(4A)-Ru(1)-S(11A)	95.15(2)	S(18A)-Ru(1)-S(4A)	91.28(4)	S(12)-Ru(1)-S(19)	91.08 (3)		
N(9A)-B(1A)-N(3A)	109.67(18)	N(16A)-B(1A)-N(2A)	110.5(4)	N(3)-B(1)-N(13)	111.3 (3)		
N(9A)-B(1A)-N(16A)	109.42(19)	N(16A)-B(1A)-N(23A)	107.2(3)	N(3)-B(1)-N(20)	111.9 (3)		
N(3A)-B(1A)-N(16A)	109.57(19)	N(2A)-B(1A)-N(23A)	107.5(4)	N(13)-B(1)-N(20)	113.0 (3)		
N(9A)-B(1A)-C(23A)	105.43(19)	N(16A)-B(1A)-N(9A)	112.2(4)	N(3)-B(1)-C(2)	106.3 (3)		
N(3A)-B(1A)-C(23A)	120.62(19)	N(2A)-B(1A)-N(9A)	110.8(3)	N(13)-B(1)-C(2)	107.1 (3)		
N(16A)-B(1A)-C(23A)	101.54(17)	N(23A)-B(1A)-N(9A)	108.4(3)	N(20)-B(1)-C(2)	106.8 (3)		
C(17A)-N(16A)-B(1A)	115.40(19)	C(24A)-N(23A)-B(1A)	125.5(4)	N(1)-C(2)-B(1)	178.5 (3)		
C17A-N16A-C22A	106.77(19)	N(25A)-C(24A)-	125.0(4)				
C(23A)-N(24A)-Ru(1)	125.60(16)	C(24A)-N(25A)-	121.3(4)				
C(25A)-N(24A)-Ru(1)	118.07(14)	C(24A)-N(25A)-	120.9(4)				
N(24A)-C(23A)-B(1A)	130.5(2)	C(26A)-N(25A)-	117.7(4)				
C23A-N24A-C25A	115.70(19)						
N(19A)-C(17A)-S(18A)	129.07(18)						
C(17A) – (S18A) –	90.30(11)						

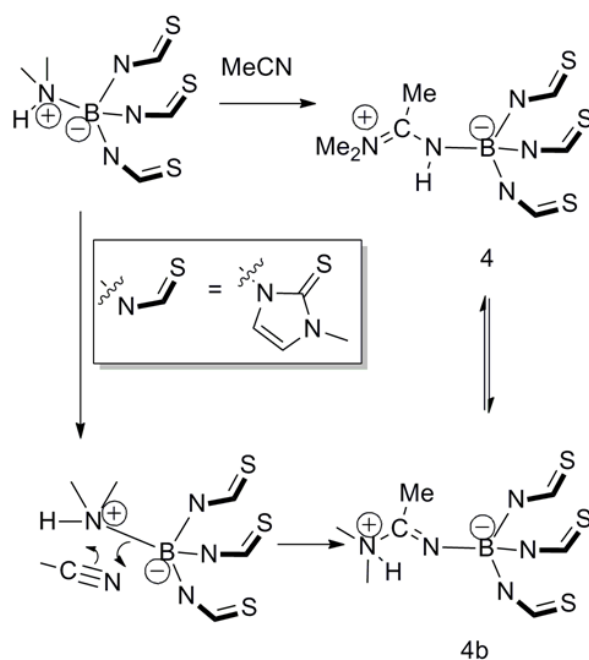
Table 1: Selected bond lengths (Å) and angles (°).

An unexpected intermediate

Analysis of samples of the reaction mixture during the synthesis of **2** by $^1\text{H-NMR}$ indicated the presence of an intermediate in the reaction. The origin of this species as a product of the reaction of **1** with the acetonitrile solvent was confirmed by heating a solution of **1** in acetonitrile to reflux which cleanly provided the same species (**4**). The $^1\text{H NMR}$ spectrum of the reaction mixture showed no trace of **1** after 3 hours and EI-MS of the isolated colorless precipitate of the new species **4** showed a molecular ion at $m/z = 436.1$. The $^1\text{H-NMR}$ spectrum displayed three new resonances at 2.06, 3.05 and 3.29 ppm, each integrating as 3H. Similarly, the $^{13}\text{C-NMR}$ spectrum showed three new resonances in the alkyl region at 19.1, 40.6 and 41.2 ppm. An additional quaternary carbon resonance was also apparent at 167.3 ppm.

The spectra of **4** clearly indicate the retention of the dimethylamino group and the addition of a molecule of acetonitrile to **1**. Thus the acetonitrile does not substitute the HNMe_2 as observed with all other donors previously employed, but rather adds to the species, most likely through insertion into the B-N bond (**Scheme 3**). The 1,2-insertion of the nitrile into the B-N bond provides a species (**4b**) which tautomerises to provide a more stable secondary amidino moiety (**4**).

The inequivalence of the NMe_2 methyl groups in the $^1\text{H-NMR}$ spectrum of **4**, due to the presence of the $\text{C}=\text{N}$ bond in the N, N'-dimethylacetamido group, demonstrates the preference for tautomer **4** over **4b**. Such reactivity of **1** with MeCN, whilst somewhat unexpected, is not altogether unprecedented. Burger et al. have described a similar reaction between a boron analogue of cyclopropane with hydrogen cyanide or trimethylsilyl cyanide in the presence of acetonitrile which undergoes a ring expansion reaction via a similar mechanism.¹¹



Scheme 3. Proposed mechanism for the reaction between the $(\text{HNMe}_2)\text{ZTm}$ (**1**) and acetonitrile.

A complex (**5**) of the new ligand **4** was obtained by stirring a solution of the ligand in methanol with [(*p*-cymene)RuCl₂]₂ followed by precipitation by addition of [NH₄][PF₆]. X-ray crystallography of this complex confirmed the predicted structure of the ligand (Figure 4). The angles around the NMe₂ group N(4D) (117.0, 120.7 and 122.3°) confirm its hybridisation as *sp*², and thus the ligand structure as **4** rather than **4b**. The C(2D)-N(4D) bond length to the NMe₂ group is shorter [1.315(3) Å] than the C(2D)-N(1D) bond [1.337(3) Å] pointing to the same conclusion and suggesting that the positive charge resides on the NMe₂ nitrogen, although it is likely that there is some degree of delocalisation. The N-B bond length was found to be 1.545(3) Å which is concordant with typical B-N(*sp*²) coordinate bonds. The mean torsion angle N-B-Ru-S ($\theta = -48.95^\circ$) and the displacement of the metal from the methimazole plane is comparable ($\omega = 57.85^\circ$) to **3** indicating a similar degree of helicity.

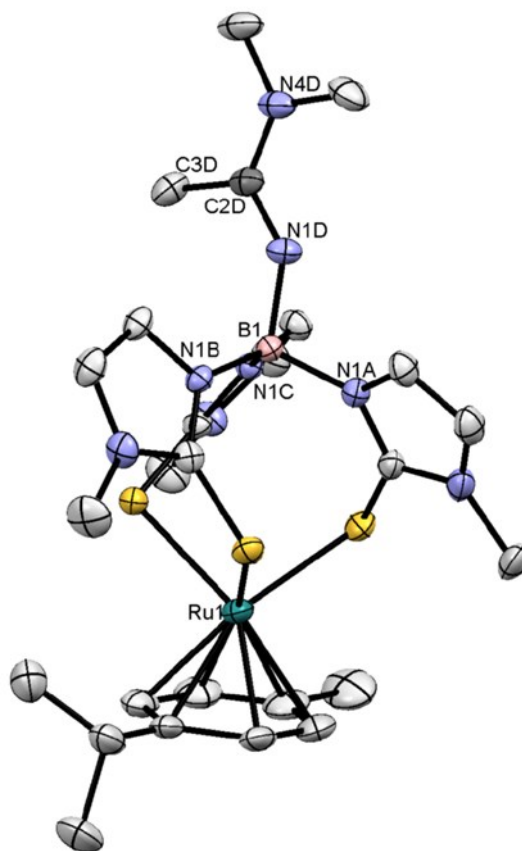


Figure 4. Structure of [κ^3 -[S,S,S]-(N,N-dimethyl-acetamidine)B(mt)₃Ru(*p*-cymene)][PF₆]₂ (**5**). Hydrogen atoms and counter-ions omitted for clarity. Selected bond lengths and angles are provided in **Table 1**.

This unexpected result led us to investigate whether other nitriles displayed similar reactivity with **1**. Despite its lower Lewis basicity, benzonitrile was also shown to insert into the B-N coordinate bond. This conversion proceeded more slowly than that with acetonitrile, despite the higher reflux temperature, providing the target

species (**6**) after 8 hours at 110°C. Mass spectrometry (EI) confirmed the expected formulation of **6** with a molecular ion peak at $m/z = 498.2$. The $^1\text{H-NMR}$ spectrum showed unusually broadened resonances for the methimazolyl protons at (6.39 and 6.84 ppm) which suggested possible restricted rotation about the B-N bond to the amidino group, due to steric interaction between the phenyl and methimazole rings, and consequent inequivalence of the methimazolyl rings. Additionally **6** displays a larger difference in the chemical shifts for the dimethylamine derived methyl groups (2.83 and 3.57 ppm) which we attribute to ring-current effects of the phenyl ring which are absent in the methyl derivative **4**. A ruthenium complex of this ligand (**7**) was synthesised and crystals were grown in a similar manner as for **5**. The crystal structure of **7** (Figure 5) shows that the phenyl ring resides between the arms of the ligand, approximately parallel to one of the methimazolyl rings which may indicate some π -stacking interactions. The distance between the centroid of the phenyl ring and that of its nearest methimazolyl neighbour is 3.419 Å, and the angle between the two ring planes is 24.5°. The B-N(2) bond distance [1.544(5) Å] in this ligand is essentially the same as the corresponding bond in **5**, as is the N(2)-C(3) bond to the NMe₂ group [1.340(5) Å]. The C(3)-N(1) bond, however, is slightly longer than in **5** [1.326(5) Å] indicating the effect of the phenyl ring on the resonance structure within the N-C-N unit. This observation is confirmed by the lower energy of the C=N bond stretching vibration in the IR spectrum which appears at 1608 cm⁻¹ and compares with 1632 cm⁻¹ in **5**. The helicity values for this complex also compare well with those for **3** and **5** ($\theta = -48.54^\circ$ and $\omega = 58.35^\circ$).

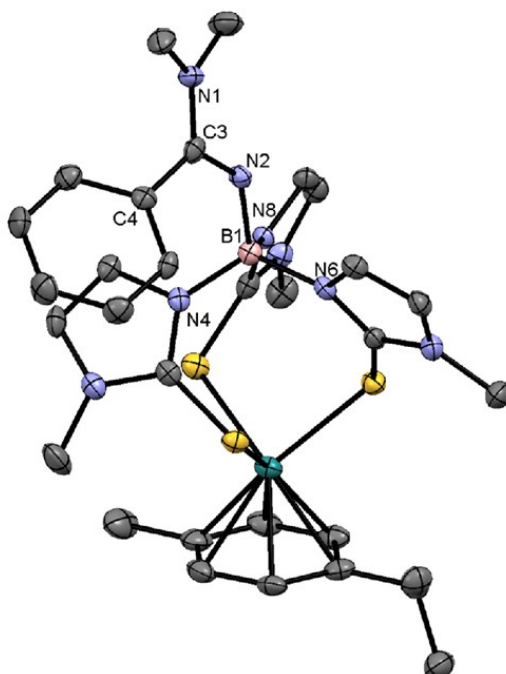
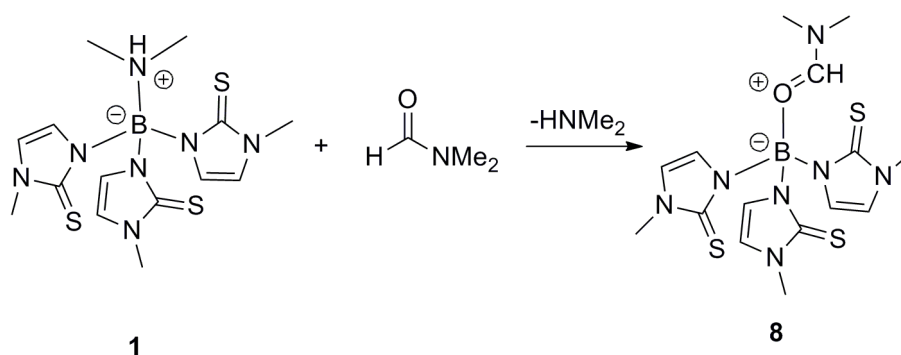


Figure 5. Structure of the dication in [κ^3 -[S,S,S]-(N,N-dimethylbenzamidine)B(methimazolyl)₃Ru(*p*-cymene)]²⁺[PF₆]₂ (**7**). Hydrogen atoms, counter-ions and MeCN solvent omitted for clarity. Selected bond lengths and angles are provided in Table 1.

Both ligands **4** and **6** are nitrogen analogues of the ligand characterised by Reglinski et al. in which a dimethylformamide molecule was found to coordinate to the boron fourth position, (DMF)ZTm.¹² The crystal structure of this ligand shows the expected oxygen coordination of the DMF to boron and adopting sp^2 hybridisation. We therefore expected that reaction of **1** with DMF would yield the same ligand by substitution of the dimethylamine moiety. Reaction of **1** with one molar equivalent of DMF under reflux in toluene for 6 hours provided a colorless precipitate (Scheme 4). The ¹H-NMR spectrum of this material confirmed it to be (DMF)ZTm (**8**) with two resonances at 3.25 and 3.31 ppm each integrating as 3H, as well as a singlet at 8.69 ppm (1H) due to the formyl proton. Mass spectrometry (ESI) displayed a molecular ion peak at $m/z = 423.9$ consistent with this formulation. Finally, the IR spectrum also agreed with reported data and displayed an absorbance at 1679 cm^{-1} assigned to the DMF C=O stretch. This reaction expands the range of available nucleophiles which are known to substitute the dimethylamine group in **1** to include oxygen donors.



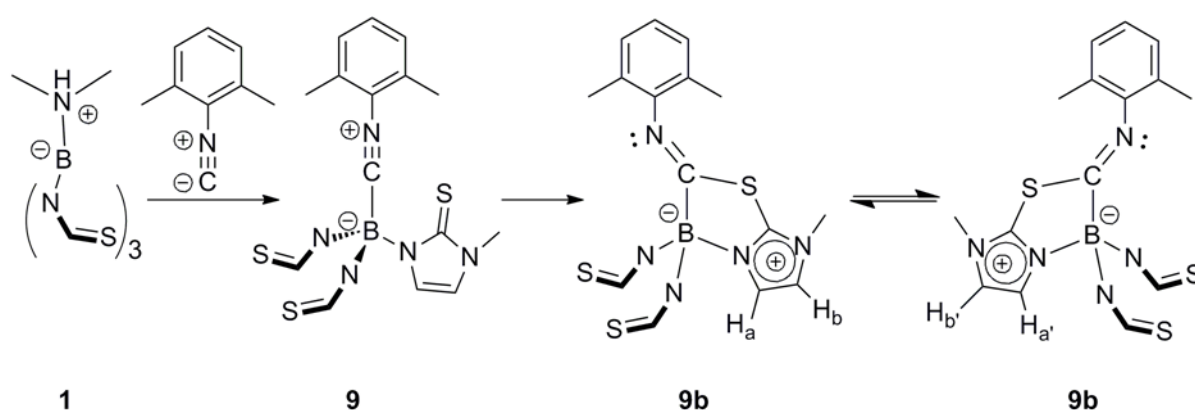
Scheme 4. Direct route to (DMF)ZTm (**8**).

Isonitriles

Having successfully exploited both nitrogen and oxygen donors it was of interest to investigate the coordination of a carbon donor to the boron centre. Thus, 2,6-dimethylphenyl isonitrile was stirred with **1** in toluene under reflux for 4 days providing a colorless precipitate of compound **9** upon work-up (Scheme 5).

The mass spectrum (EI) of **9** showed a peak at $m/z = 481.1$ indicating its formulation as the species formed from substitution of HNMe_2 by the isonitrile, (ArNC)ZTm. Its ¹H-NMR spectrum showed no resonances which could be assigned to an NMe_2 group indicating its substitution during the reaction. However, a broad singlet at 2.14 ppm (6H), along with a multiplet (3H) in the aromatic region, confirmed the presence of the isonitrile aryl group. It should be noted that the three methimazolyl arms in the free ligand **9** appear equivalent by NMR spectroscopy at ambient temperature. However, IR spectroscopy of **9** showed no absorption corresponding to a CN triple bond, but an absorption was observed at 1660 cm^{-1} corresponding to a C=N

stretch. Very weak and missing nitrile bands have been reported previously by Kitson and Griffith when the nitrile is bonded to electronegative groups.¹³ Despite this fact, a similar boron compound, Na[(cyano)B(pyrrolyl)₃], previously synthesised by Gyóri,¹⁴ displayed the expected nitrile stretching frequency at around 2217 cm⁻¹, however no information was provided on the intensity of this band. Variable temperature ¹H-NMR studies showed three resonances for H_a (Scheme 5) at 223K indicating inequivalence of the methimazole rings at this temperature. Coalescence of these resonances occurred above 253K. These data indicate that the isonitrile carbon is stabilized by a fluxional interaction with the methimazole sulphur atoms which equilibrates between the three methimazolyl arms faster than the NMR timescale at room temperature (Scheme 5).



Scheme 5. Reaction of **1** with ArNC gives (ArNC)ZTm (**9**) which is stabilised by the formation of the fluxional species **9b**.

The X-ray crystal structure of this compound confirmed the presence of a C-S interaction (Figure 6) and the resulting [1.4.3]-thiazaborolo-[5,4-b]-imidazolium ring formed by attack of the methimazole sulfur at the isonitrile carbon, thus confirming the structure of the ligand as **9b**. There are few reports of thiazaborole rings in the literature; the only structurally characterized compound in the CCDC was reported by Carboni (Figure 7).¹⁵ However, Carboni's system is fused to pyridine rather than an imidazole ring and contains a *sp*³-hybridised carbon in the 2-position resulting in a partially unsaturated ring. These differences may contribute to a tighter thiazaborole ring in **9b** demonstrated by the shorter bond lengths and smaller angles found in this complex. The thiazaborole S(1)-C(1) bond length [1.835(2) Å] is indicative of a relatively long C-S single bond, slightly longer than in Carboni's system [1.805 Å], and thus consistent with a weak C-S interaction and the observed fluxionality of this species in solution. Also consistent with this is the rather short the C(2)-S(1) bond [1.721(3) Å] (*cf.* 1.700(3) and 1.686(3) for the C=S bonds in the other two methimazolyl groups) indicating some residual double bond character in this bond. The corresponding C-S bond in Carboni's thiazaborole is 1.743 Å. The C(1)-S(1)-C(2) angle in **9b** (89.4°) is surprisingly acute (*cf.* 94.9° in the Carboni

system). The B(1)-C(1)-S(1) angle in **9b** is 112.6° (*cf.* 108.5° in the Carboni system) which is indicative of sp^2 hybridisation of the carbon in this position. The presence of an exocyclic C=N double bond is confirmed by the short C(1)-N(3) bond length of 1.255(3) Å.

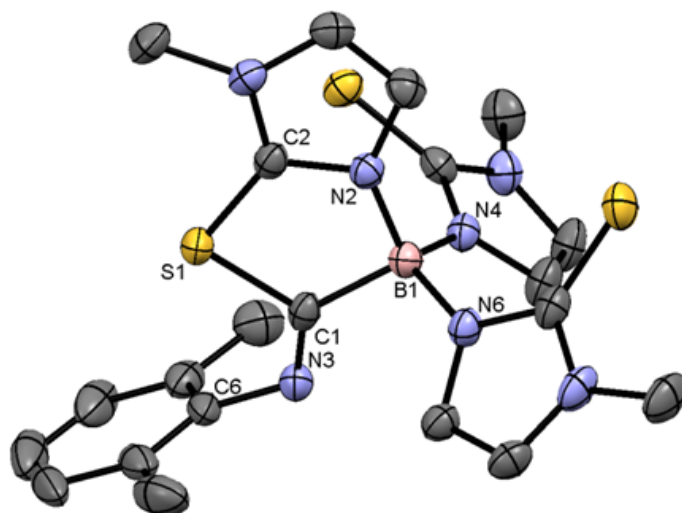


Figure 6. Structure of 3-bis(methimazolyl)-2-(2,6-dimethylphenylimino)-7-methyl-[1,4,3]-thiazaborolo[5,4-b]imidazolium (**9b**). Hydrogen atoms omitted for clarity. Selected bond lengths and angles are provided in **Table 1**.

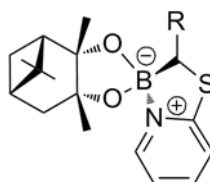
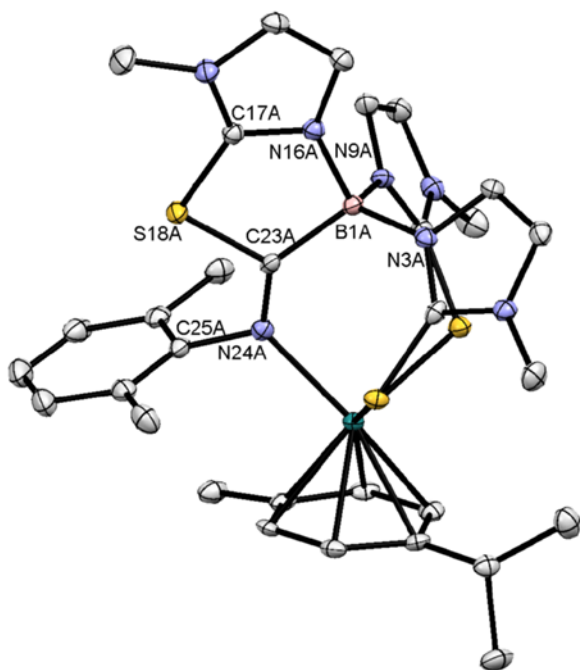


Figure 7. Carboni's thiazaborolo system.

It may be surmised that **9b** arises because the donor properties of the sp -hybridized carbon donor of the isonitrile are insufficient to stabilize the electron-deficient boron centre. The formation of this species illustrates the nucleophilic character of the methimazolyl sulfur atoms, something we have previously observed to be responsible for the formation of ring-opened products on attempted coordination of oxazolines to the boron in **1**.⁵ The structure of **9b** confirms the presence of a B-C bond in the ligand, and thus by implication that substitution of the HNMe_2 moiety in **1** occurs by attack of the isonitrile carbon at the boron centre during the synthesis of ligand **9**.

The free ligand **9** was coordinated to Ru(II) by treatment with $[\text{Ru}(p\text{-cymene})\text{Cl}_2]_2$ in methanol and the resulting complex (**10**) precipitated after anion exchange with $[\text{NH}_4][\text{PF}_6]$. The $^1\text{H-NMR}$ spectrum of this complex indicated that the ligand in this complex coordinates in a $\kappa^3\text{-[N,S,S]}$ mode and that the thiazaborole ring is thus retained in the coordinated ligand. The aromatic region showed two different methimazolyl environments in a ratio of 2:1. Two broad resonances also appeared at 5.15 and 4.97 ppm representing the *p*-cymene aryl protons which generally appear as a sharp $(\text{AB})_2$ system in a $\kappa^3\text{-[S,S,S]}$ coordinated ligand. The Mass spectrum (ESI) shows a molecular ion peak at $m/z = 358.3$ corresponding to $M^+/2$ and confirms the formulation of the complex. The lack of a ruthenium-bound chloride in the molecular ion peak indicates that, in order for ruthenium to adopt the preferred octahedral geometry, the ligand must be coordinated in a κ^3 -mode rather than a bidentate $\kappa^2\text{-[S,S]}$ mode. Therefore, upon coordination of the two free methimazolyl arms to a metal centre the fluxional carbon-sulfur interaction observed in **9b** becomes irreversible resulting in an $[\text{N,S,S}]$ donor ligand.

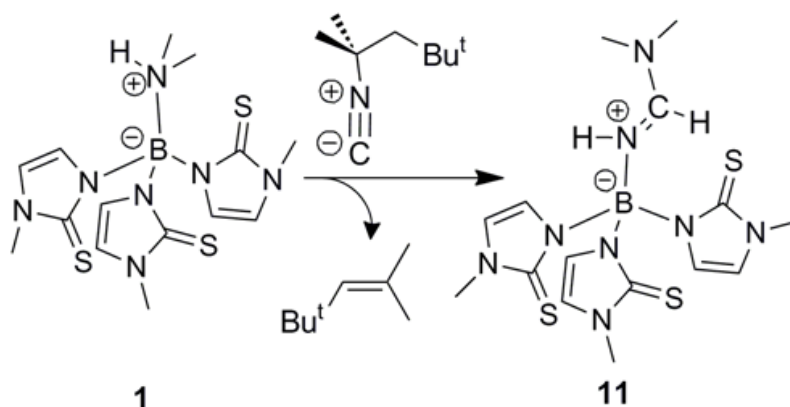
The X-ray crystal structure of **10** confirms our interpretation of the spectroscopic data and shows the ligand coordinating in a $\kappa^3\text{-[N,S,S]}$ mode to give an achiral complex (\leftarrow Figure **8**). The thiazaborole S(18A)-C(23A) bond length [1.791(2) Å] is shorter than in **9b** [1.835(2) Å] reflecting a strengthening of this bond upon complexation. The C(17A)-S(18A) bond [1.731(2) Å] is essentially unchanged from the previous thiazaborole [1.721(3) Å] and the C(17A)-S(18A)-C(23A) angle (90.3°) is only very slightly larger (89.4°). The exocyclic C=N double bond C(23A)-N(24A) [1.283(3) Å] is also lengthened compared to **9b** [1.255(3) Å] due to the coordination of the imine nitrogen to ruthenium. The B(1A)-N(16A) bond [1.561(3) Å] is lengthened relative to the other two B-N bonds [1.535(3) and 1.533(3) Å] in **10** and to the same bond in the free ligand **9b** [1.544(5) Å] meaning that it is more comparable with a Lewis adduct type bond.



\leftarrow **Figure 1.** Structure of the dication in $[\{\kappa^3\text{[N,S,S]}\text{-3-bis(methimazolyl)\text{-}2\text{-}(2,6\text{-dimethylphenylimino)\text{-}7\text{-methyl}\text{-}[1,4,3]\text{-thiazaborolo[5,4-}b\text{]imidazolium}\}\text{Ru}(p\text{-cymene})] [\text{PF}_6]_2$ (**10**). Hydrogen atoms counter-ions omitted for clarity. Selected bond lengths and angles are provided in **Table 1**.

This structure allows us to explain the broadening of the *p*-cymene arene resonances observed in the $^1\text{H-NMR}$ spectrum of this complex as resulting from hindered rotation of the aryl ring due to interaction with the *o*-xylyl group, which is directed towards the *p*-cymene environment. The $^{13}\text{C-NMR}$ spectrum of the complex shows a resonance for the C-B carbon at 196.4 ppm which is comparable to the signal for the analogous carbon in another M-N=C(S)-B compound (210 ppm)¹⁶ but significantly higher than the corresponding carbon in **9** at 177.2 ppm.

The electron withdrawing nature of the aryl group in the isonitrile may contribute to the poor donor ability of the carbon centre and thus to the formation of ligand **9b** and complex **10**. An aliphatic isonitrile was expected to be a stronger donor for the boron centre. To investigate this the readily available branched alkyl-isonitrile (1,1,3,3-tetramethylbutylisonitrile) was stirred with **1** in toluene under reflux for 12 hours. The colorless precipitate isolated after work-up was found to be an unexpected reaction product **11** (Scheme 6).

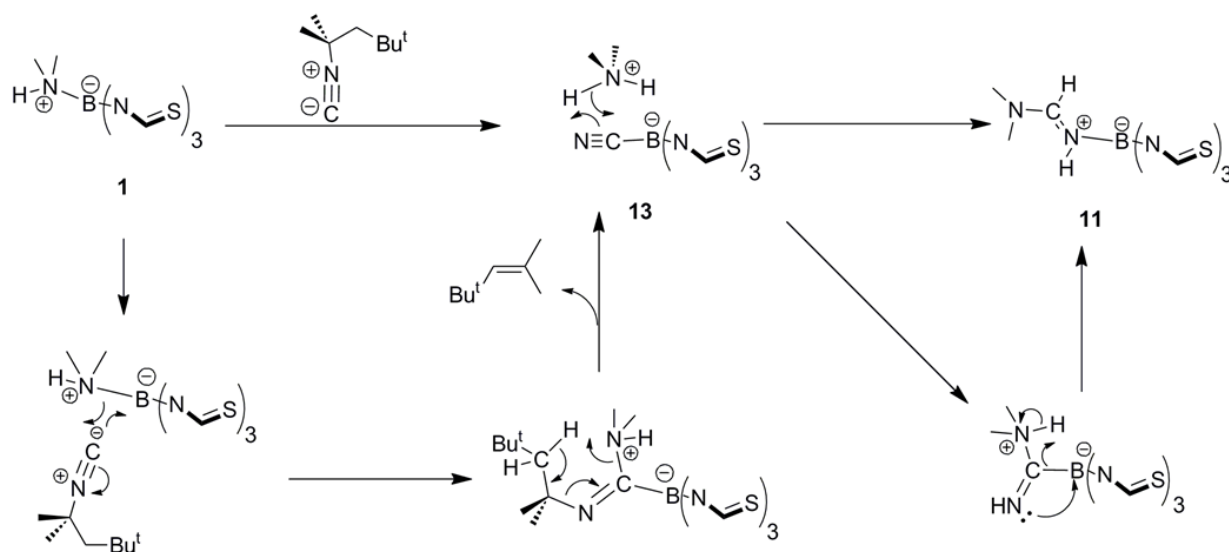


Scheme 6. Synthesis of **11**.

$^1\text{H-NMR}$ spectroscopy of **11** showed no resonances corresponding to the isonitrile alkyl group, however two sharp singlets at 3.05 and 3.15 ppm which each integrate as 3H were present in the spectrum. Given our experience with nitriles this suggested that the NMe_2 group had been retained. Instead of the expected alkyl multiplets, two new doublets are present at 7.93 and 10.01 ppm which each integrate to 1H and display a coupling constant of 15.6 Hz indicative of a *trans*-relationship. $^{13}\text{C-NMR}$ DEPT experiments showed the presence of a tertiary carbon centre at 159.0 ppm, however this carbon showed no C-B coupling indicating nitrogen-boron coordination. Isomerism of isonitriles to nitriles is known to occur over time at room temperature,¹⁷ however, $^{13}\text{C-NMR}$ of the free isonitrile showed no evidence for this, even after 48 hours in toluene under reflux. Based on the spectroscopic evidence the structure of this ligand was thus assigned as that containing an N,N'-dimethylformamidino group attached to the boron (**11**). $^1\text{H-NMR}$ studies in deuterated

toluene confirmed the formation of 2,4,4-trimethylpent-2-ene resulting from the intramolecular removal of the β -proton in the alkyl moiety with concomitant elimination of the dimethylammonium cation (

Scheme 7). The inherent stability of the trisubstituted alkene may contribute to its elimination in this process, and isonitriles not susceptible to this proton abstraction would necessarily provide a different product.



Scheme 7. Mechanism of formation of **11** and **13**.

Ligand **11** was complexed to Ru(II) as previously described for complexes of the related ligands. X-ray crystallography of this complex confirmed that the ligand contains a formamidino group bound to boron as indicated by the spectroscopic data (Figure 9), and this unexpected result indicates that this reaction does not proceed through the type of mechanism shown in **Scheme 3**. It is interesting to note, however, that the ligand **11**, formed by this elimination of the alkyl group from the alkylisonitrile, is the formamidino (CH) analogue of the acetamidino (CMe) and benzamidino (CPh) containing ligands (**4** and **6**), formed by treatment of ZTm (**1**) with acetonitrile and benzonitrile respectively. The B-N(formamidino) bond length in **12** [1.5210(16) Å] is rather shorter than that found in complexes **5** and **7** of the acetamidino and benzamidino analogues **4** and **6**. The N(23A)-C(24A) (formamidino) bond length [1.323(6) Å] is slightly longer than the C(24A)-N(25A) bond length [1.306(6) Å] indicating a C=NMe₂ double bond as seen in **5** and **7**. The mean torsion angle N-B-Ru-S is slightly larger in this complex than in those previously found ($\theta = 49.49^\circ$) however the displacement of the metal from the methimazole plane is smaller in this system ($\omega = -53.94^\circ$).

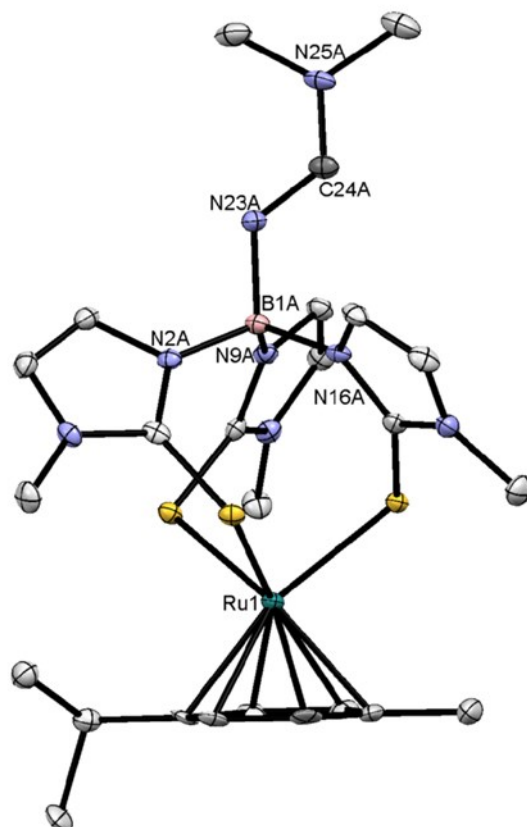


Figure 9: Structure of the dication in [κ^3 -[S,S,S]- (N,N-dimethylformamidine)B(methimazolyl)₃Ru(p-cymene)]][PF₆]₂ (**11**). Hydrogen atoms, counter-ions and MeCN solvent omitted for clarity. Selected bond lengths and angles are provided in **Table 1**.

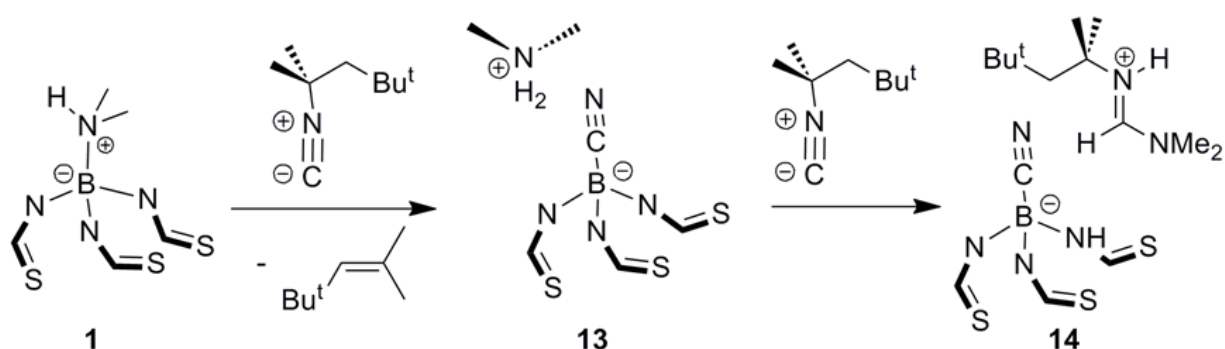
Further NMR investigation of the synthesis of **11** established the presence of an intermediate (**13**) in the reaction (

Scheme 7). This cyano species could be isolated upon work-up of the reaction mixture after only 4 hours. Negative ion ESI-MS showed a molecular ion peak at $m/z = 376.04$ indicating that the ligand was no longer a charge-neutral zwitterion but instead an anionic species leading us to assign the structure as (NC)Tm. The ¹H-NMR spectrum of **13** contained a broadened triplet at 2.69 ppm (6H) and a broad singlet at 8.32 (2H) consistent with [H₂NMe₂]⁺ as the counter ion. The ¹³C-NMR spectrum of **13** contains a four-line signal at 130.4 ppm confirming the presence of a quaternary C-B bond in this intermediate, in contrast to the corresponding singlet at 159.3 ppm in the spectrum of **11**. However, the expected IR absorption band for the nitrile functionality was not observed in the expected 2200-2260 cm⁻¹ region of the spectrum. Elemental analysis confirmed the assigned formula of **11**, it is therefore assumed that in this instance, as with **9**, the absorption due to C-N stretching is too weak to be detected.

A plausible mechanism for the formation of both **11** and **13** is shown in

Scheme 7. Initial insertion of the isonitrile carbon into the B-N coordinate bond gives an intermediate species which may undergo 1,6-sigmatropic rearrangement with loss 2,4,4-trimethyl-2-pentene to give **13**. Upon extended heating conversion of the salt **13** into the neutral zwitterionic ligand **11** occurs by insertion of the nitrile group into a dimethylammonium N-H bond, and subsequent isomerization provides **11**.

During the course of our mechanistic studies **1** was treated with two molar equivalents of 1,1,3,3-tetramethylbutylisonitrile in toluene under reflux (Scheme 8) which provided a further unanticipated outcome. Initially, after 4h the intermediate **13** could be detected by ¹H-NMR spectroscopy. However, after further heating no resonances corresponding to **11** were detected, instead the salt **14** was isolated as a colorless powder after work-up (Scheme 8).



Scheme 8. Reaction of **1** with 2 molar equivalents of 1,1,3,3-tetramethylbutylisonitrile leading to the formation of the salt **14**.

In contrast to **11** and **13**, ¹H-NMR spectroscopy of **14** showed three resonances at 0.97 (9H), 1.47 (6H) and 1.73 (2H) ppm corresponding to the 1,1,3,3-tetramethylbutyl group. Additionally, a resonance at 3.24 ppm (6H) indicated the presence of the dimethylamine group in the product. Finally, resonances at 8.52 and 7.52 ppm indicated the presence of amidinium NH and CH protons respectively. Although these resonances were too broad to determine the relationship between these protons, it was expected, based on the steric bulk of the other substituents, that the protons would exhibit a *trans*-relationship. Negative ion ESI-MS showed a molecular ion peak at $m/z = 376.05$, whereas the positive ion spectrum showed a molecular ion peak for the cation at $m/z = 185.05$. Thus it is clear that the dimethylammonium cation of the salt **13** reacts preferentially with excess isonitrile in preference to the boron-bound nitrile function which occurs in the absence of a second equivalent of the isonitrile.

Ligand **14** was coordinated to Ru(II) by treatment with $[(p\text{-cymene})\text{RuCl}_2]_2$ in methanol, and the resulting complex (**15**) precipitated after anion exchange with ammonium hexafluorophosphate. As expected this complex showed no resonances for the 1,1,3,3-tetramethylbutyl group or the dimethylamine fragment. The

mass spectrum (positive ion EI) contained a peak at $m/z = 611.9$ confirming the assigned formula of **15**. A very weak IR absorption band was present in the spectrum of this complex at 2218cm^{-1} which agrees well with literature values of $\nu(\text{C}\equiv\text{N})$ for similar compounds.¹⁴

The X-ray crystal structure of **15** (Figure 10) confirms the presence of the predicted B-CN moiety inferring its presence in the free ligand **14**. The B(1)-C(2) bond length is significantly longer [$1.624(5)\text{ \AA}$] than the corresponding B(1A)-N(1A) (NCS) bond in **3** [$1.542(4)\text{ \AA}$] which supports the assignment as a C-bound cyano group in **15**, and by implication also in the free ligand **14**. This B-C bond length is comparable with that found in the previously reported $[(\text{PhTm})\text{Mn}(\text{CO})_3]$ complex [$1.634(5)\text{ \AA}$].¹⁸ The same bond is only slightly shorter than the B-C bond in **10** [$1.658(3)\text{ \AA}$] which was stabilized by attack of the methimazolyl sulfur. The C(2)-N(1) bond displays a typical nitrile bond length of $1.144(5)\text{ \AA}$ and does not deviate significantly from linear geometry with a B(1)-C(2)-N(1) angle of $178.5(3)^\circ$. The mean torsion angle N-B-Ru-S is somewhat smaller in this complex than in those previously ($\theta = 41.8^\circ$), although the displacement of the metal from the methimazolyl plane is comparable ($\omega = -59.2^\circ$).

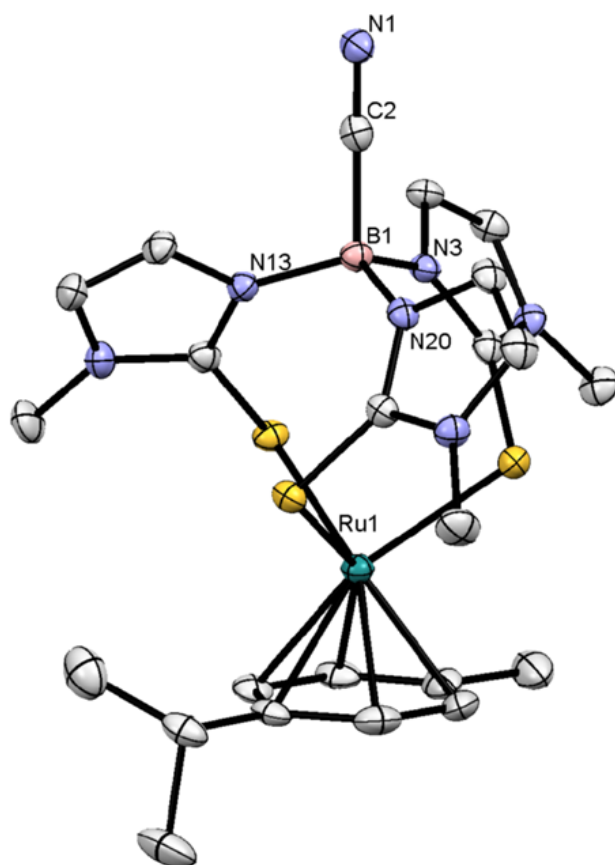
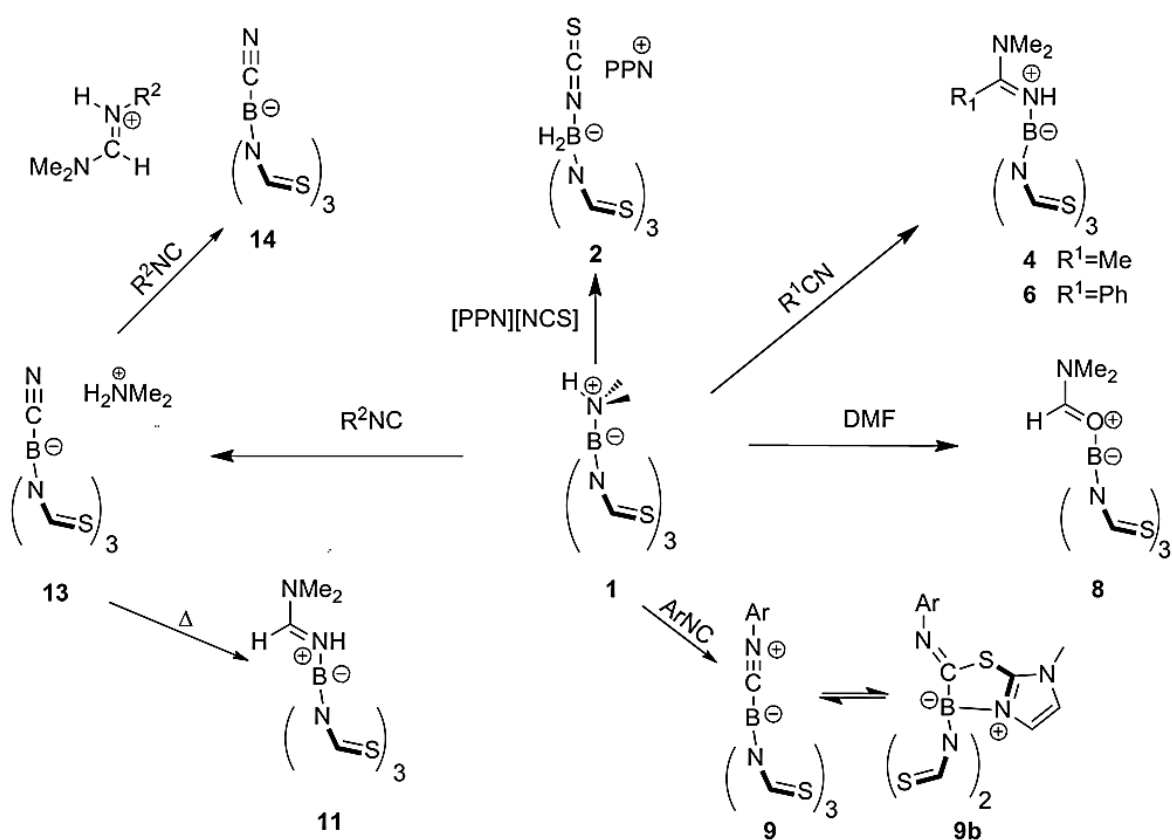


Figure 10: X-ray crystal structure of $[\kappa^3\text{-[S,S,S]-(cyano)B(methimazolyl)}_3\text{Ru}(p\text{-cymene})][\text{PF}_6]$ (**15**).

Hydrogen atoms, counter-ions and an acetonitrile molecule removed for clarity. Selected bond lengths and angles provided in **Table 1**.

Conclusions

The work reported in this paper is summarised in Scheme 9. We have reported the synthesis of a variety of new charge-neutral zwitterionic tris(methimazolyl)borate ligands from reaction of (dimethylamine)tris(methimazolyl)borane (**1**) with nitriles, isonitriles and N,N-dimethylformamide, these reactions resulting in charge-neutral ZTm species containing C-B, N-B, and O-B coordinate bonds. Reaction of **1** with 2,6-dimethylphenylisonitrile gives ligand **9** which, in solution, exhibits a fluxional interaction between the isonitrile carbon and the methimazolyl sulphur atoms resulting in a [1,4,3]-thiazaborolo-[5,4-b]imidazolium ring which is retained upon ligand complexation, the resulting complex containing a κ^3 -[N,S,S] coordinated ligand. In addition, anionic ligands have been accessed by substitution of the dimethylamine moiety in **1** with the thiocyanate anion and via the fragmentation of an alkylisonitrile to provide the cyano-substituted ligand system. The common theme of the formation of boron-bound amidinato groups from the reaction with acetonitrile (to give acetamidinato), benzonitrile (to give benzamidinato) and an alkylisonitrile (to give fomamidinato) is striking and illustrates the stability of this particular functionality coordinated to boron in these systems. The use of the chemistry reported in the elaboration of this ligand system to incorporate further functionality at this boron fourth position may be envisaged.



Scheme 9. Reactions of **1** described in this work. $\text{R}^1 = \text{Me, Ph}$; $\text{Ar} = 2,6\text{-dimethylphenyl}$; $\text{R}^2 = 1,1\text{-}3,3\text{-dimethylbutyl}$.

Experimental Section

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. Mass spectra were recorded on a MAT 900 XP (EI) or Thermo-Fisher LCQ Classic (ESI). NMR spectra were recorded either on a 400 MHz, 500 MHz or 600MHz Bruker Advance III spectrometer. ^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; quartet, q, septet, spt; multiplet, m; broad, br. ^{11}B chemical shifts are reported in ppm relative to $\text{BF}_3 \cdot \text{OEt}_2$ ($\delta = 0$). Infra red spectra were recorded from either in solution or a nujol mull using cells with CaF_2 windows on a Jasco FT-IR 410 spectrometer, or as neat solids using a Perkin-Elmer Spectrum 65. The compounds $[(\text{HMe}_2\text{N})\text{B}(\text{methimazolyl})_3]$ (**1**),⁴ $[\text{PPN}][\text{SCN}]$ ¹⁹ and $[(p\text{-cymene})\text{RuCl}_2]_2$ ²⁰ were synthesised according to the literature procedures. All other chemicals were obtained from Sigma-Aldrich and used as received.

$[\text{PPN}][(\text{SCN})\text{B}(\text{methimazolyl})_3]$ (2**):** $(\text{HNMe}_2)\text{B}(\text{methimazolyl})_3$ (**1**) (719.4 mg, 1.8 mmol) was dissolved in acetonitrile (20 cm^3). $[\text{PPN}][\text{SCN}]$ (1.074 g, 1.8 mmol) was added and the solution was heated to reflux for 24 h. After this time the solvent was half removed *in vacuo* and Et_2O was added (30 cm^3). The precipitate which formed was filtered by cannula and washed with Et_2O (3 x 10 mL) to give the target material as a white powder. (683.3 mg, 51%), MS (ESI⁺) *m/z*: 408 (M^+); ^1H -NMR (500.1 MHz, CDCl_3): δ 7.71-7.63 (m, 6H, 6 x CH), 7.54-7.40 (m, 24H, 24 x CH), 6.84 (br s, 3H, 3 x CH), 6.53 (d, $J = 2.4$ Hz, 3H, 3 x CH), 3.44 (s, 9H, 3 x NCH_3); ^{13}C -NMR (125.8 MHz, CDCl_3): δ 164.0 (C=S), 134.0 (3 x CH), 132.1 (6 x CH), 129.7 (6 x CH), 127.0 (d, $J = 108$ Hz, 3 x C-P), 122.5 (3 x CH), 116.3 (3 x CH), 34.6 (3 x NCH_3); ^{11}B -NMR (CDCl_3 , 128.3 MHz): δ -3.50; Elemental analysis: expected for $\text{C}_{49}\text{H}_{45}\text{BN}_8\text{P}_2\text{S}_4 \cdot \text{CHCl}_3$ (1066.33): C, 56.32; H, 4.35; N, 10.51; found: C, 55.84; H, 4.55; N, 10.91 %; IR (CHCl_3): 2153 cm^{-1} (N=C=S).

$[(\text{SCN})\text{B}(\text{methimazolyl})_3\text{Ru}(p\text{-cymene})]$ [BPh₄**] (**3**):** $[\text{PPN}][(\text{SCN})\text{B}(\text{methimazolyl})_3]$ (**2**) (100.0 mg, 0.20 mmol) and $[\text{Ru}(p\text{-cymene})\text{Cl}_2]$ (41.8 mg, 0.10 mmol) were dissolved in MeOH (5 cm^3) and stirred for 1 h. Sodium tetraphenylborate (91.5 mg, 0.40 mmol) was then added and a precipitate formed immediately. The precipitate was filtered and washed with MeOH (3 x 2 cm^3). The solvent was then half removed from the filtrate and ether added (*ca.* 5 cm^3). Red crystals precipitated and these were filtered and washed with ether (3 x 5 cm^3). The target material was isolated as a red solid (57.8 mg, 30%). X-ray quality crystals were grown by slow diffusion of ether into a concentrated solution of the complex in chloroform. MS (ESI⁺) *m/z*: 643.9 ($\text{M}^+/2$); ^1H -NMR (500 MHz, CDCl_3): δ 7.45 (dd, $J = 5.0, 3.6$ Hz, 8H, 8 x CH), 7.05 (t, $J = 7.4$ Hz, 8H, 8 x CH), 6.98 (d, $J = 2.0$ Hz, 3H, 3 x CH), 6.86 - 6.94 (m, 4H, 4 x CH), 6.67 (d, $J = 2.2$ Hz, 3H, 3 x CH), 5.12 (t, $J = 5.8$ Hz, 2H, 2 x CH), 5.01 (d, $J = 5.8$ Hz, 1H, CH), 4.95 (d, $J = 6.0$ Hz, 1H, CH), 3.38 (s, 9H, 3 x NCH_3), 2.84 (spt, $J = 6.9$ Hz, 1H, CH), 2.04 (s, 3H, CH_3), 1.16 (t, $J = 7.3$ Hz, 6H, 2 x CH_3); ^{13}C -NMR (125.8 MHz, CDCl_3) δ 164.1 (q, $J = 49$ Hz, 4 x C-B), 157.2 (C=S), 136.8 (NCS), 136.3 (8 x CH), 125.6 (8 x CH), 121.7 (4

x CH), 121.5 (3 x CH), 121.3 (3 x CH), 107.0 (C_q), 101.0 (C_q), 85.1 (CH), 84.5 (CH), 84.3 (CH), 83.4 (CH), 35.1 (3 x NCH₃) 30.2 (CH), 22.9 (CH₃), 22.1 (CH₃), 18.8 (CH₃); ¹¹B-NMR (128.3 MHz, CDCl₃): δ -3.33 (BMt₃), -6.48 (BPh₄); Elemental analysis: expected for C₄₇H₄₉B₂Cl₃N₇RuS₄ (1082.27): C, 58.63; H, 5.13; N, 10.18; found: C, 58.68; H, 5.23; N, 10.16 %; IR 2095 cm⁻¹ (N=C=S).

(*N,N*-dimethylacetamidino)B(methimazolyl)₃ (4): (HNMe₂)B(methimazolyl)₃ (**1**) (362 mg, 91.6 mmol) was dissolved in acetonitrile (20 cm³) and the solution was heated to reflux for 3 h becoming cloudy after 1 h. The precipitate which formed upon cooling was filtered by cannula and washed with Et₂O (3 x 10 mL). The target material was isolated as a white powder (288 mg, 72%). MS (EI+) m/z: 436.1 (M⁺); ¹H-NMR (500.1 MHz, CDCl₃): δ 9.87 (s, 1H, 1 x NH), 6.66 (d, *J* = 2.3 Hz, 3H, 3 x CH), 6.24 (br. s, 3H, 3 x CH), 3.58 (s, 9H, 3 x NCH₃), 3.32 (s, 3H, NCH₃), 3.14 (s, 3H, NCH₃), 2.04 (s, 3H, CH₃); ¹³C-NMR (125.8 MHz, CDCl₃): δ 167.4 (C=N), 164.0 (C=S), 120.4 (CH), 118.1 (CH), 41.3 (CH₃), 40.7 (CH₃), 34.7 (CH₃), 19.1 (CH₃); ¹¹B-NMR (128.3 MHz, CDCl₃): δ 0.25; Elemental analysis: expected for C₁₆H₂₅BN₈S₃ (436.15): C, 44.03; H, 5.77; N, 25.68; found: C, 44.14; H, 5.67; N, 25.73 %; IR (KBr) 1618 cm⁻¹ (C=N).

[(*N,N*-dimethylacetamidino)B(methimazolyl)₃Ru(*p*-cymene)] [PF₆]₂ (5): [(*N,N*-dimethylacetamidino)B(methimazolyl)₃] (**4**) (101.3 mg, 0.23 mmol) and [Ru(*p*-cymene)Cl₂]₂ (71.8 mg, 0.12 mmol) were dissolved in MeOH and stirred overnight. Ammonium hexafluorophosphate (75.5 mg, 0.46 mmol) was then added and a precipitate formed immediately. After stirring the precipitate was filtered and washed with MeOH (3 x 2 mL) and Et₂O (3 x 3 mL). The target material was isolated as a red solid (133.3 mg, 60%). X-ray quality crystals were grown by slow diffusion of ether into a concentrated solution of the complex in acetonitrile. MS (ESI+) m/z: 335.86 (M⁺); ¹H-NMR (400 MHz, CD₃CN): δ 7.18 (d, *J* = 2.0 Hz, 3H, 3 x CH), 6.98 (br. s, 3H, 3 x CH), 5.99 (br. s, 1H, NH), 5.50 (s, 2H, 2 x CH), 5.34 - 5.43 (m, 2H, 2 x CH), 3.67 (s, 9H, 3 x NCH₃), 3.22 (d, *J* = 8.7 Hz, 6H, 2 x NCH₃), 2.94 (spt, *J* = 6.9 Hz, 1H, CH), 2.18 (s, 3H, CH₃), 1.96 (br. s, 3H, CH₃), 1.18 (dd, *J* = 6.9, 1.9 Hz, 6H, 2 x CH₃); ¹³C-NMR (125.8 MHz, CD₃CN): δ 168.21 (C_q), 160.1 (C=S), 123.4 (3 x CH), 122.0 (3 x CH), 107.9 (C_q), 102.6 (C_q), 86.4 (CH), 86.1 (CH), 85.3 (CH), 84.3 (CH), 42.3 (NCH₃), 37.8 (NCH₃), 36.2 (3 x CH₃), 31.4 (CH), 23.0 (CH₃), 22.6 (CH₃), 20.7 (CH₃), 19.1 (CH₃); ¹¹B-NMR (CD₃CN, 128.3 MHz) δ: -0.71; Elemental analysis: expected for C₂₆H₃₉BF₁₂N₈P₂RuS₃ (1046.58): C, 32.63; H, 4.26; N, 11.28 found: C, 32.57; H, 4.05 ; N, 11.58 %; IR (Nujol) 1632 cm⁻¹.

(*N,N*-dimethyl-Benzimidamide)B(methimazolyl)₃ (6): [HNMe₂]B[methimazolyl]₃ (500 mg, 1.26 mmol) was dissolved in benzonitrile (10 cm³) and the solution was heated to 110°C for 8 h. The precipitate which formed upon cooling was filtered by cannula and washed with toluene (3 x 10 mL) and Et₂O (3 x 10 mL). The target material was isolated as a white powder (336 mg, 53%). MS (EI+) m/z: 498.2 (M⁺); ¹H-NMR (500.1 MHz, CDCl₃): δ 11.12 (s, 1 H, NH), 7.51 (m, 5H, 5 x CH), 6.82 (s, 3 H, 3 x CH), 6.36 (s, 3 H, 3 x CH), 3.54, (s, 3H, NCH₃), 3.42 (s, 9 H, 3 x CH₃), 2.79 (s, 3 H, NCH₃); ¹³C-NMR (125.8 MHz, CDCl₃): 166.8 (C=S), 132.8 (CH), 132.2 (2 x CH), 131.2 (2 x CH), 127.8 (CH), 116.1 (CH), 41.9 (CH₃), 41.4(CH₃), 34.5 (CH₃); ¹¹B-NMR

(128.3 MHz, CDCl₃): δ 0.12; Elemental analysis: expected for C₂₁H₂₇BN₈S₃ (498.2): C, 50.60; H, 5.46; N, 22.48; found: C, 50.44; H, 5.37; N, 22.34 %; IR 1602 cm⁻¹ (C=N).

[(N,N-dimethylbenzamidino)B(methimazolyl)₃Ru(p-cymene)] [PF₆]₂ (7): [(N,N-dimethylbenzamidino)B(methimazolyl)₃] (6) (101.3 mg, 0.20 mmol, 1 eq) and [Ru(p-cymene)Cl₂]₂ (63.4 mg, 0.10 mmol) were dissolved in MeOH and stirred overnight. Ammonium hexafluorophosphate (65.4 mg, 0.40 mmol) was then added and a precipitate formed immediately. The precipitate was filtered and washed with MeOH (3 x 2 mL) and Et₂O (3 x 3 mL). The target material was isolated as a red solid (153.2 mg, 74%). X-ray quality crystals were grown by slow diffusion of ether into a concentrated solution of the complex in acetonitrile. MS (ESI⁺) m/z: 367.23 (M⁺/2); ¹H-NMR (500.1 MHz, d⁶-DMSO): δ 7.49 (m, 5H, 5 x CH), 7.46 (s, 3H, 3 x CH), 7.27 (s, 3H, 3 x CH), 5.55 (m, 4H, 4 x CH) 3.56 (s, 9H, 3 x NCH₃), 2.94 (s, 3H, CH₃), 2.84 (spt, J = 6.9 Hz, 1H, CH), 2.10 (s, 3H, CH₃), 1.20 (dd, J = 6.9 Hz, 6H, 2 x CH₃) (Missing one CH₃ resonance: Under DMSO or H₂O peaks); ¹³C-NMR (101 MHz, DMSO-d₆): δ 167.3 (C_q), 157.5 (C=S), 132.0 (CH), 128.9 (CH), 127.9 (CH), 122.6 (3 x CH), 121.6 (3 x CH), 105.8 (C_q), 100.9 (C_q), 85.1 (CH), 84.4 (CH), 83.7 (CH), 82.9 (CH), 44.0 (CH), 34.8 (3 x NCH₃), 30.0 (CH₃), 22.5 (NCH₃), 21.7 (NCH₃), 18.2 (2 x CH₃); ¹¹B-NMR (128.3 MHz, d⁶-DMSO): δ -0.31; Elemental analysis: expected for C₃₁H₄₁BF₁₂N₈P₂RuS₃ (1023.72) C, 36.37; H, 4.04; N, 10.95; found C, 36.55; H, 3.90; N, 11.27 %; IR (Nujol) 1608 cm⁻¹.

(DMF)B(methimazolyl)₃ (8): (HNMe₂)B(methimazolyl)₃ (1) (501.9 mg, 1.27 mmol) was suspended in toluene (20 cm³). DMF (105 μ L, 1.35 mmol) was added and the solution was heated to reflux for 6 h becoming cloudy after 1 h. After cooling the precipitate was filtered by cannula and washed with toluene (3 x 10 mL) and Et₂O (3 x 10 mL). The target material was isolated as a white powder (465 mg, 87%). MS (EI⁺) m/z: 423.92 (M⁺); ¹H-NMR (500.1 MHz, CDCl₃): δ 8.67 (s, 1H, C(H)O), 6.66 (d, J = 2.3 Hz, 3H, 3 x CH), 6.44 (br. s, 3H, 3 x CH), 3.57 (s, 9H, 3 x CH₃), 3.33 (s, 3H, NCH₃), 3.23 (s, 3H, NCH₃); ¹³C-NMR (125.8 MHz, CDCl₃): δ 165.0 (-CHO), 164.3 (C=S), 120.7 (CH), 118.3 (CH), 40.3 (CH₃), 36.3 (CH₃), 34.7 (CH₃); ¹¹B-NMR (128.3 MHz, CDCl₃): δ 2.29; MS (ESI⁺) 423.9 ((M+1)⁺); Elemental analysis: expected for C₁₅H₂₂BN₇OS₃ (423.4): C, 42.55; H, 5.24; N, 23.16; found: C, 42.63; H, 5.16; N, 23.12 %; IR (MeCN): 1678 cm⁻¹ (s, C=O).

3-bis(methimazolyl)-2-(2,6-dimethylphenylimino)-7-methyl-[1,4,3]-thiazaborolo-[5,4-b]-imidazolium (9/9b): (HNMe₂)B(methimazolyl)₃ (1) (503.2 mg, 1.26 mmol) was suspended in toluene (20 cm³). 2,6-dimethylphenylisonitrile (167 mg, 1.27 mmol) was added and the solution was heated to reflux for 4 days. After cooling the solvent was half removed in vacuo and the precipitate which formed was filtered by cannula and washed with toluene (3 x 10 mL) and Et₂O (3 x 10 mL). The resultant white powder was recrystallised from MeCN/Et₂O and the target material was isolated as a white powder (541.2 mg, 89%). X-ray quality crystals were grown from slow diffusion of diethyl ether into a concentrated solution of 9 in DCM. MS (EI⁺) m/z: 481.2 (M⁺); ¹H-NMR (CDCl₃, 400MHz): δ 7.62 (br s, 3H, 3 x CH), 6.93 - 7.11 (m, 3H, 3 x CH), 6.77 (d, J = 2.3 Hz, 3H, 3 x CH), 3.58 (s, 9H, 3 x NCH₃), 2.14 ppm (s, 6H, 2 x CH₃); ¹³C-NMR (125.8 MHz, CDCl₃):

δ 176.9 (br, C-B), 160.7 (C=S), 150.8 (C-NC), 128.5 (2 x CH), 126.7 (2 x C(CH₃)), 125.0 (CH), 122.6 (3 x CH), 119.3 (3 x CH), 34.8 (3 x NCH₃), 18.7 (2 x CH₃); ¹¹B-NMR (128.3 MHz, CDCl₃): δ -1.21; Elemental analysis: expected for C₂₁H₂₄BN₇S₃ (481.47): C, 52.39; H, 5.02; N, 20.36; found: C, 52.25; H, 5.09; N, 20.43 %; IR (Nujol) 1660 cm⁻¹ (CN).

[κ^3 -[N,S,S]-3-bis(methimazolyl)-2-(2,6-dimethylphenylimino)-7-methyl-[1,4,3]-thiazaborolo-[5,4-b]-imidazolium)Ru(p-cymene)] [PF₆]₂ (10): (HNMe₂)B(methimazolyl)₃ (**1**) (98.7 mg, 0.20 mmol) and [Ru(p-cymene)Cl₂]₂ (65.4 mg, 0.11 mmol) were dissolved in MeOH and stirred for 2 h. Ammonium hexafluorophosphate (67.7 mg, 0.42 mmol) was then added and an orange-red precipitate formed immediately. The precipitate was filtered and washed with MeOH (3 x 2 mL) and Et₂O (3 x 3 mL). The target material was isolated as a red solid (132.6 mg, 65%). X-ray quality crystals were grown by slow diffusion of ether into a concentrated solution of the complex in acetonitrile. MS (ESI+) m/z: 358.3 (M⁺/2). ¹H-NMR (400 MHz, CD₃CN): δ 7.48 (d, *J* = 2.1 Hz, 1H, CH), 7.42 (d, *J* = 2.1 Hz, 1H, CH), 6.08 - 7.38 (m, 7H, 7 x CH), 4.78 - 5.10 (m, 2H, 2 x CH), 5.10-5.27 (m, 2H, 2 x CH), 3.76 (s, 6H, 2 x NCH₃), 3.55 (s, 3H, NCH₃), 3.03 (spt, *J* = 6.9 Hz, 1H, CH), 2.37 (br s, 3H, CH₃), 2.01 (s, 3H, CH₃), 1.26 (d, *J* = 6.9 Hz, 6H, 2 x CH₃), 1.23 (br s, 3H, CH₃); ¹³C-NMR (125.8 MHz, CD₃CN): δ 196.4 (C-B), 158.14 (C=S), 148.5 (C_q), 131.5 (2 x CH), 130.7 (CH), 129.7 (C_q), 129.1 (2 x CH), 125.1 (CH), 123.3 (2 x CH), (One CH missing, most likely under H₃CCN resonance), 121.2 (C_q), 113.9 (C_q), 105.3 (C_q), 91.3 (2 x CH), 86.5 (2 x CH), 48.9 (CH), 36.8 (2 x NCH₃), 36.6 (NCH₃), 31.6 (CH₃), 22.9 (CH₃), 18.6 (CH₃), 18.0 (2 x CH₃); ¹¹B-NMR (128.3 MHz, CD₃CN) δ : -2.44; Elemental analysis: expected for C₃₁H₃₈BF₁₂N₇P₂RuS₃ (1006.68) C, 36.99; H, 3.80; N, 9.74; found C, 37.14; H, 3.72; N, 9.73; IR (Nujol) 1567 cm⁻¹.

(N,N-dimethylaminoformamidino)B(methimazolyl)₃ (11): SAFETY NOTE: There is a possibility of the formation of HCN in this reaction. Appropriate precautions should be taken when repeating this synthesis. (HNMe₂)B(methimazolyl)₃ (**1**) (503.5 mg, 1.26 mmol) was suspended in toluene (20 cm³). 1,1,3,3-tetramethylbutylisonitrile (222 μ L, 1.26 mmol) was added and the solution was heated to reflux for 12 h. After cooling the solvent was half removed in vacuo and the precipitate which formed was filtered by cannula and washed with Et₂O (3 x 10 mL). The resultant white powder was recrystallised from MeOH/Et₂O and the target material was isolated as a white powder (243.5 mg, 46%). MS (EI+) m/z: 422.1 (M⁺); ¹H-NMR (500.1 MHz, CDCl₃): δ 10.02 (d, *J* = 15.5 Hz, 1H, NH), 7.94 (d, *J* = 15.5 Hz, 1H, CH), 6.68 (d, *J* = 2.1 Hz, 3H, 3 x CH), 6.06 (d, *J* = 1.7 Hz, 3H, 3 x CH), 3.59, (s, 9H, 3 x NCH₃), 3.18 (s, 3H, NCH₃), 3.07 (s, 3H, NCH₃). ¹³C-NMR (125.8 MHz, CDCl₃): δ 163.7 (C=S), 159.3 (CH), 119.8 (3 x CH), 118.5 (3 x CH), 42.8 (CH₃), 36.1 (CH₃), 34.6 (3 x CH₃); ¹¹B-NMR (128.3 MHz, CDCl₃): δ 0.66; Elemental analysis: expected for C₁₅H₂₃BN₈S₃ (422.40): C, 42.65; H, 5.49; N, 26.53; found: C, 42.72; H, 5.39; N, 26.43 %; IR (KBr) 1683 cm⁻¹ (C=N).

[(N,N-dimethylformamidino)B(methimazolyl)₃Ru(p-cymene)] [PF₆]₂ (12): [(N,N-dimethylformamidino)B(methimazolyl)₃] (**11**) (96.2 mg, 0.23 mmol) and [Ru(p-cymene)Cl₂]₂ (72.5 mg, 0.12 mmol) were dissolved in MeOH and stirred overnight. Ammonium hexafluorophosphate (74.2 mg, 0.46

mmol) was then added and a precipitate formed immediately. The precipitate was filtered and washed with MeOH (3 x 2 mL) and Et₂O (3 x 3 mL). The target material was isolated as a red solid (114.7 mg, 53 %). X-ray quality crystals were grown by slow diffusion of ether into a concentrated solution of the complex in acetonitrile. MS (ESI+) m/z: 328.8 (M⁺/2); ¹H-NMR (500 MHz, d⁶-DMSO): δ 8.24 (d, *J* = 12.5 Hz, 1H, NH), 7.73 (d, *J* = 1.9 Hz, 3H, 3 x CH), 7.54 (s, 3H, 3 x CH), 6.97 (d, *J* = 13.4 Hz, 1H, CH), 6.04 (d, *J* = 6.1 Hz, 2H, 2 x CH), 5.94 (dd, *J* = 13.6, 5.3 Hz, 2H, 2 x CH), 4.23 (s, 9H, 3 x NCH₃), 3.77 (s, 3H, NCH₃), 3.70 (s, 3H, NCH₃), 3.51 (spt, *J* = 7.0 Hz, 1H, CH), 2.22 (s, 3H, CH₃) 1.74 (d, *J* = 6.8 Hz, 6H, 2 x CH₃); ¹³C-NMR (125.8 MHz, CD₃CN) δ 160.4 (CH), 158.6 (C=S), 123.1 (3 x CH), 122.6 (3 x CH), 107.9 (C_q), 102.5 (C_q), 86.2 (CH), 85.8 (CH), 85.2 (CH), 84.2 (CH), 44.9 (NCH₃), 37.1 (NCH₃), 36.0 (3 x CH₃), 31.4 (CH), 23.0 (CH₃), 22.6 (CH₃), 19.1 (CH₃); ¹¹B-NMR (128.3 MHz, CD₃CN): δ -0.52; Elemental analysis: expected for C₂₅H₃₇BF₁₂N₈P₂RuS₃ (947.62) C, 31.69; H, 3.94; N, 11.82; found C, 32.11; H, 3.38; N, 11.83 %; IR (Nujol) 1688 cm⁻¹.

[Dimethylammonium] [(cyanato)B(methimazolyl)₃] (13): SAFETY NOTE: There is a possibility of the formation of HCN in this reaction. Appropriate precautions should be taken when repeating this synthesis.

(HNMe₂)B(methimazolyl)₃ (**1**) (1.0094 g, 2.55 mmol) was suspended in toluene (20 cm³).

1,1,3,3,-tetramethylbutylisonitrile (435 μL, 2.55 mmol) was added and the solution was heated to reflux for 4 h. After cooling, the resulting sticky solid was filtered and washed with toluene at 90°C (2 x 10 mL). After cooling the sticky solid was triturated with Et₂O to give a white powder. The resultant white powder could not be recrystallised from CH₂Cl₂/Et₂O, CH₂Cl₂/hexane, MeCN/Et₂O, THF/Et₂O or by cooling of solutions of the material. In each instance the product precipitated as a sticky solid or oil which could be converted back into a powder by trituration with Et₂O (607.0 mg, 56%). MS (ESI-) m/z: 376.04 (M⁻); ¹H-NMR (400 MHz, CDCl₃): δ 8.32 (br s, 2H, NH₂), 6.68 (d, *J* = 2.27 Hz, 3H, 3 x CH), 6.55 (d, *J* = 1.77 Hz, 3H, 3 x CH), 3.58 (s, 9H, 3 x NCH₃), 2.69 (t, *J* = 5.43 Hz, 6H, N(CH₃)₂). ¹³C-NMR (126 MHz, CDCl₃): δ 162.8 (C=S), 130.4 (q, *J* = 80 Hz, C-B), 121.0 (3 x CH), 118.1 (3 x CH), 35.2 (N(CH₃)₂), 34.7 (NCH₃); ¹¹B-NMR (128.3 MHz, CDCl₃): δ -6.66; Elemental analysis: expected for C₁₅H₂₃BN₈S₃ (422.40): C, 42.65; H, 5.49; N, 26.53; found: C, 42.75; H, 5.36; N, 26.36 %.

[N,N-dimethyl-N'-(1,1,3,3-tetramethylpropyl)formamidinium] [(cyanato)B(methimazolyl)₃] (14):

(HNMe₂)B(methimazolyl)₃ (**1**) (504.4 mg, 1.26 mmol) was suspended in toluene (20 cm³).

1,1,3,3,-tetramethylbutylisonitrile (434 μL, 2.55 mmol) was added and the solution was heated to reflux for 12 h. After cooling the resulting sticky solid was filtered and washed with toluene (2 x 10 mL) at 90°C. After cooling the sticky solid was triturated with Et₂O to give a white powder. The resultant white powder was could not be recrystallised by the methods described above for **13**. In each instance the product was obtained as a sticky solid or oil which could be converted back into a powder by trituration with Et₂O (392 mg, 55%). MS (ESI-) m/z: 376.05 (M⁻), (ESI+) 185.05 (M⁺); ¹H-NMR (400 MHz, CDCl₃): δ 8.52 (br s, 1H, NH), 7.58 (d, 1H, CH), 6.62 (m, 6H, 6 x CH), 3.56 (s, 9H, 3 x CH₃), 3.24 (s, 6H, 2 x NCH₃), 1.73 (s, 2H, CH₂), 1.47 (s,

6H, 2 x CH₃), 0.97 (s, 9H, 3 x CH₃); ¹³C-NMR (126 MHz, CDCl₃): δ 163.4 (C=S), 152.5 (NC(H)N), 129.3 (q, J = 84 Hz, C-B), 121.4 (3 x CH), 117.4 (3 x CH), 59.6 (NCH₃), 54.3 (NCH₃), 37.6 (C(CH₃)₂), 34.7 (3 x NCH₃), 31.7 (C(CH₃)₂), 31.6 (C(CH₃)₃), 29.6 (CH₂); ¹¹B-NMR (128.3 MHz, CDCl₃): -6.67; Elemental analysis: expected for C₂₄H₄₀BN₉S₃ (561.64): C, 51.32; H, 7.18; N, 22.45; found: C, 51.18; H, 7.06; N, 22.61 %; IR 1694 cm⁻¹ (C=N).

[(Cyano)B(methimazole)₃Ru(p-cymene)] [PF₆] (15): [N,N-dimethyl-N'-(1,1,3,3-tetramethylpropyl)formamidinium] [(cyano)B(methimazolyl)₃] (**13**) (102.7 mg, 0.18 mmol) and [Ru(p-cymene)Cl₂]₂ (54.2 mg, 0.09 mmol) were dissolved in MeOH and stirred overnight. Ammonium hexafluorophosphate (29.4 mg, 0.18 mmol) was then added and a precipitate formed immediately. The precipitate was filtered and washed with MeOH (3 x 2 mL) and Et₂O (3 x 3 mL). The target material was isolated as a red solid (88.9 mg, 65%). X-ray quality crystals were grown from vapour diffusion of Et₂O into a concentrated solution of the complex in acetonitrile. MS (ESI+) m/z: 611.9 (M⁺); ¹H-NMR (400 MHz, CDCl₃): δ 7.19 (s, 3H, 3 x CH), 6.82 (d, J = 2.1 Hz, 3H, 3 x CH), 4.94 - 5.19 (m, 4H, 4 x CH), 3.49 (s, 9H, 3 x NCH₃), 2.87 (dt, J = 13.9, 7.10 Hz, 1H, CH), 2.07 (s, 3H, CH₃), 1.19 (t, J = 6.94 Hz, 6H, 2 x CH₃); ¹³C-NMR (126 MHz, CDCl₃): δ 158.0, (C=S), 128.6 (q, J = 80 Hz, NC-B), 122.7 (3 x CH), 121.6 (3 x CH), 107.2 (C_q), 101.3 (C_q), 85.2 (CH), 84.6 (CH), 84.5 (CH), 83.6 (CH), 53.5 (CH), 35.2 (3 x CH₃), 30.3 (0.5 x CH₃), 29.7 (0.5 x CH₃), 22.9 (0.5 x CH₃), 22.1 (0.5 x CH₃), 18.9 (CH₃); Elemental analysis: expected for C₄₇H₄₉B₂N₇RuS₃ (930.83): C, 60.65; H, 5.31; N, 10.53, found: C, 60.78; H, 5.39; N, 10.54 %; IR 2218 cm⁻¹.

X-ray crystallography: Crystal data for **3**, **5**, **7**, **9b**, **10**, **12** and **15** are presented in **Error! Reference source not found.** Structures **3** and **7** were collected with with graphite-monochromated Mo-K α radiation (λ = 0.71073 Å) on a Bruker SMART APEX II CCD diffractometer. Absorption corrections were carried out using the multi-scan procedure *SADABS*.²¹ All other data sets were collected on a Agilent Technologies SuperNova diffractometer with Cu-K α radiation (λ = 1.5418 Å) and X-ray mirror optics. Absorption corrections were carried out using the multi-scan procedure CrysAlisPro.²² All datasets were collected at 100 K. Structure **15** was solved by SIR92²³ and refined by Olex2.²⁴ All other structures were solved by SHELXS and refined by full-matrix least squares against F² using SHELXL.²⁵ All non-hydrogen atoms were refined anisotropically, while hydrogen atoms were placed in calculated positions, constrained to ride on their parent atom with group U_{iso} values assigned [U_{iso}(H)= 1.2U_{iso} for aromatic carbons and 1.5U_{iso} for methyl atoms]. Structure **5** contains MeCN disordered over two sites. The occupancies of each component were fixed at 0.5 after competitive refinement. Structures **7** and **10** contained disordered solvent regions which were treated using the SQUEEZE routine of PLATON.²⁶ In **7** the number of electrons treated equates to 1 MeCN per formula unit. In **10** the number equates to 2 molecules of Et₂O and 1.5 molecules of MeOH per formula unit. The values of F(000), D, M and mu are all calculated on this assumption. Structure **15** contained a disordered PF₆ moiety. The occupancies of each

component were refined to approximately 0.6:0.4. The largest residual electron density peak in **15** is 1.42 e/Å³ high and resides 3.065 Å from N1AA.

	9b	10
Chemical formula	C ₂₁ H ₂₄ BN ₇ S ₃	C ₂₅ H ₃₇ BN ₈ RuS ₃ ·2(F ₆ P)
<i>M_r</i>	481.46	947.63
Crystal system, space group	Orthorhombic, <i>P</i> 2 ₁ 2 ₁ 2 ₁	Triclinic, <i>P</i> -1
<i>a</i> , <i>b</i> , <i>c</i> (Å)	120	12.7200(2), 17.0209(3), 18.7739(3)
α, β, γ (°)	10.8256 (2), 13.4721 (3), 16.4802 (3)	110.562(2), 100.114(1), 97.616 (1)
<i>V</i> (Å ³)	2403.53 (8)	3662.46(10)
<i>Z</i>	4	4
μ (mm ⁻¹)	3.01	6.75
<i>T_{min}</i> , <i>T_{max}</i>	0.687, 0.900	0.829, 1.000
Independent reflections	4854	14453
<i>R_{int}</i>	0.067	0.058
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.039, 0.102, 1.04	0.039, 0.108, 1.06
Δ _{max} , Δ _{min} (e Å ⁻³)	0.35, -0.31	1.42, -1.37

	12	15
Chemical formula	C ₃₁ H ₃₈ BN ₇ RuS ₃ ·2(F ₆ P)	C ₄₈ H ₆₁ B ₂ F ₁₂ N ₁₅ P ₂ Ru ₂ S ₆
<i>M_r</i>	1006.68	1554.18
Crystal system, space group	Monoclinic, <i>P</i> 2 ₁ / <i>n</i>	Triclinic, <i>P</i> -1
<i>a</i> , <i>b</i> , <i>c</i> (Å)	13.5789(4), 14.2055(5), 19.7712(8)	10.0598(3), 16.6932(4), 19.9429(5)
α, β, γ (°)	90, 90, 90	76.356(1), 85.925(1), 75.842(1)
<i>V</i> (Å ³)	3813.7(2)	3155.34(14)
<i>Z</i>	4	2
μ (mm ⁻¹)	6.53	0.84
<i>T_{min}</i> , <i>T_{max}</i>	0.832, 1.000	0.811, 0.923
Independent reflections	7570	12924
<i>R_{int}</i>	0.042	0.045
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.029, 0.080, 1.05	0.040, 0.101, 1.03
Δ _{max} , Δ _{min} (e Å ⁻³)	0.58, -0.67	1.44, -0.58

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