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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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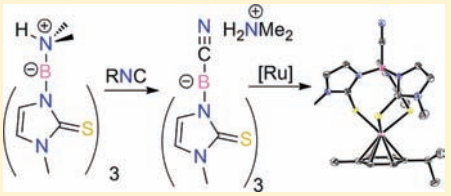
Supporting Information

ABSTRACT: A number of new charge-neutral zwitterionic tris(methimazolyl)-borate ligands have been synthesized, either by substitution of the dimethylamine group in the adduct (dimethylamine)tris(methimazolyl)borane (**1**) or by insertion into its B–N(dimethylamine) bond by an unsaturated Lewis base. Two new anionic ligands, (thiocyanato)tris(methimazolyl)borate and (cyano)tris-(methimazolyl)borate, have also been accessed by this method.



INTRODUCTION

Poly(azolyl)borates, the most common of which is the hydrotris(pyrazolyl)borate (Tp), are some of the most popular polydentate 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 centers.[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).

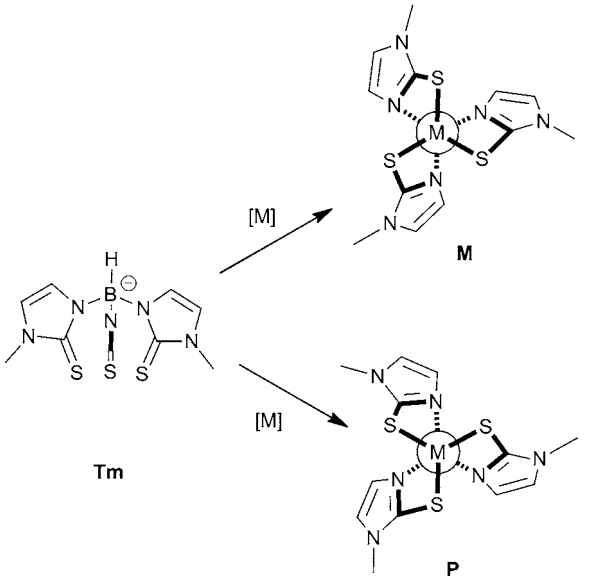
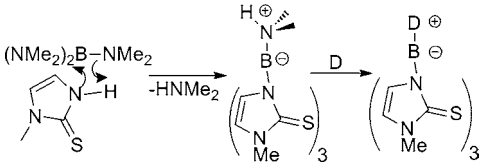


Figure 1. P and M enantiomers of a complex of the Tm ligand.

Hydrotris(azolyl)borates are typically synthesized 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 and Trofimenko reported the synthesis of a charge-neutral zwitterionic analogue of Tp [$(HNMe_2)B(pz)_3$], 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 the tris(pyrazolyl) [ZTp] type.[4] The dimethylamine in $(HNMe_2)$-$B(methimazolyl)_3$ (**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).

Scheme 1. Synthesis and Substitution of [(HMe_2N)ZTm]. (D = Donor)



The substitution is aided by the loss of $HNMe_2$ gas from the reaction mixture which drives the equilibrium toward the product and enables the use of donors considerably less basic than $HNMe_2$ (e.g., pyridine).

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 $B(NMe_2)_3$ as

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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 maximize its interaction with the three methimazolyl groups, and thus to relay chirality to the rest of the ligand. This would leave the choice of methyimazolyl 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 $(HNMe_2)ZTm$ (**1**), and we report here some results from this study. The donors used in this work are shown in Figure 2.

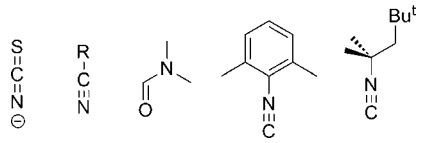


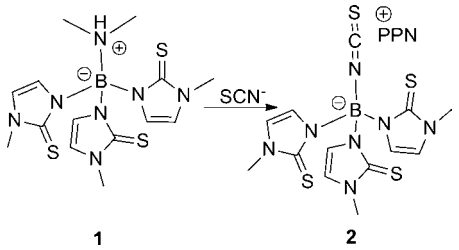
Figure 2. Donors used in this work. R = Me, Ph.

RESULTS AND DISCUSSION

Anionic Tris(methimazolyl)borate Ligands from $(HNMe_2)ZTm$ (1). Having demonstrated the broad scope of the synthesis of charge-neutral ZTm ligands by substitution of the amine in $(HNMe_2)ZTm$ (**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 = N_3, NCS, NCO) with iodine.[6] Thus the pseudohalides N_3^-, NCS^-, and NCO^- were chosen as potential donors in this role. Because of the insolubility of the $[PPN]^+$ and $[PPh_4]^+$ salts of these anions in toluene, the usual solvent for our substitution reactions, acetonitrile was employed as the reaction medium. Reaction with both N_3^- 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 $NaNH_2$ cause degradation of **1** by deprotonation of the dimethylamine functionality leading to the anion $[(Me_2N)B(mt)_3]^-$, which appears to be unstable as only free methimazole is isolated in these reactions. However, N_3^- and NCO^- are not strong Brönsted 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 h (Scheme 2).

The ^1H NMR spectrum of **2** shows no signals due to N−H or NMe_2 groups indicating the loss of $HNMe_2$. The methimazolyl proton signals show small shifts relative to **1** reflecting minor changes in electronic structure between the neutral zwitterionic **1** and anionic **2**. Electrospray ionization 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 (cf. 2058 cm^{-1} in [PPN]SCN), thus indicating a strengthening of this bond upon coordination to the boron center.

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



A complex of ligand **2** was obtained by reaction of [PPN][(SCN)B(mt)$_3$] with $[(p\text{-cymene})RuCl_2]_2$ at room temperature in methanol for 2 h followed by addition of sodium tetraphenylborate. After filtration of the precipitated salts and workup of the solution the salt $[\{(SCN)B(mt)_3\}Ru(p\text{-cymene})]$ $[BPh_4]$ (**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 crystallizes in

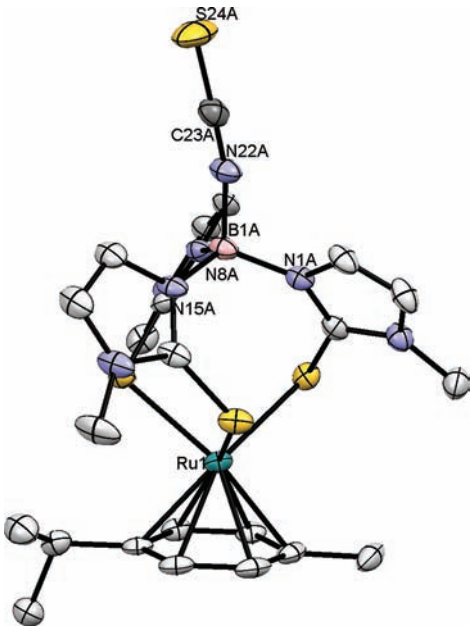


Figure 3. Structure of $[(\kappa^3\text{-}[S,S,S]\text{-(thiocyanate)-B(methimazolyl)}_3)\text{-}Ru(p\text{-cymene})]$ (**3**). Hydrogen atoms and counterion omitted for clarity. Selected bond lengths and angles are provided in Table 1.

space group *I*2/*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

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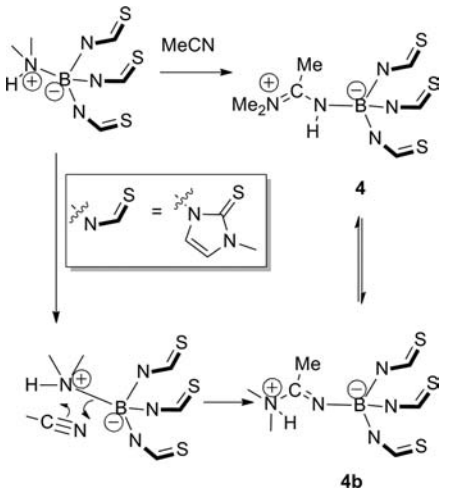
mean N_{mt}−B−Ru−S torsion in this complex is relatively large (θ = −49.1°) compared to the literature value (θ = 45.1°) for [TmRu(*p*-cymene)]Cl.[8] However, the displacement of the metal from the plane of the methimazole ring (ω = 58.6°) compares favorably with reported values (ω = −58.0°).[9,10]

Unexpected Intermediate. Analysis of samples of the reaction mixture during the synthesis of **2** by ^{1}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}H NMR spectrum of the reaction mixture showed no trace of **1** after 3 h and EI-MS of the isolated colorless precipitate of the new species **4** showed a molecular ion at m/z = 436.1. The ^{1}H NMR spectrum displayed three new resonances at 2.06, 3.05, and 3.29 ppm, each integrating as 3H. Similarly, the ^{13}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 dimethylamine 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 tautomerizes to provide a more stable secondary amidino moiety (**4**).

Scheme 3. Proposed Mechanism for the Reaction Between the $(HNMe_2)$ZTm (1) and Acetonitrile



The inequivalence of the NMe_2 methyl groups in the ^{1}H NMR spectrum of **4**, because of the presence of the C═N bond in the *N*,*N*′-dimethylacetamidino group, demonstrates the preference for tautomer **4** over **4b**. Such reactivity of **1** with MeCN, while 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]

A complex (**5**) of the new ligand **4** was obtained by stirring a solution of the ligand in methanol with $[(p\text{-cymene})RuCl_2]_2$ followed by precipitation by addition of $[NH_4][PF_6]$. X-ray crystallography of this complex confirmed the predicted structure of the ligand (Figure 4). The angles around the

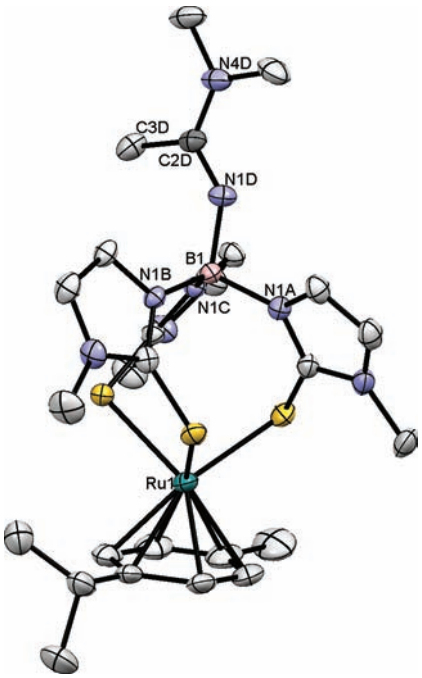


Figure 4. Structure of $[\kappa^3$-[*S*,*S*,*S*]-(*N*,*N*-dimethyl-acetamidine)B-$(mt)_3Ru(p\text{-cymene})][PF_6]_2$ (**5**). Hydrogen atoms and counterions omitted for clarity. Selected bond lengths and angles are provided in Table 1.

NMe_2 group N(4D) (117.0, 120.7, and 122.3°) confirm its hybridization as sp^2, and thus the ligand structure as **4** rather than **4b**. The C(2D)−N(4D) bond length to the NMe_2 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 NMe_2 nitrogen, although it is likely that there is some degree of delocalization. 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 (θ = −48.95°) and the displacement of the metal from the methimazole plane is comparable (ω = 57.85°) to **3** indicating a similar degree of helicity.

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 h at 110 °C. Mass spectrometry (EI) confirmed the expected formulation of **6** with a molecular ion peak at m/z = 498.2. The ^{1}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, because of 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 dimethyamine 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 synthesized and crystals were grown in a similar manner as for

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5. The crystal structure of 7 (Figure 5) shows that the phenyl ring resides between the arms of the ligand, approximately

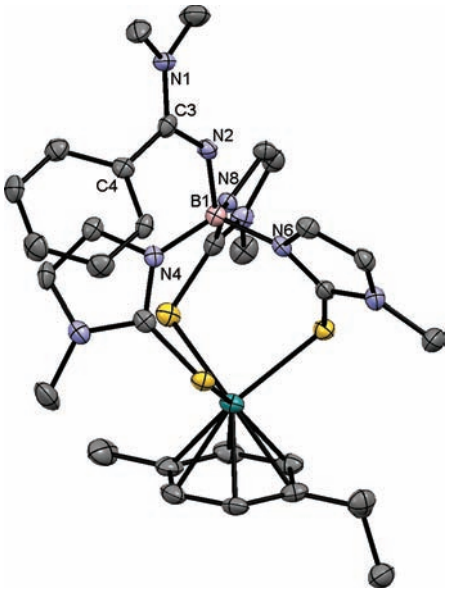
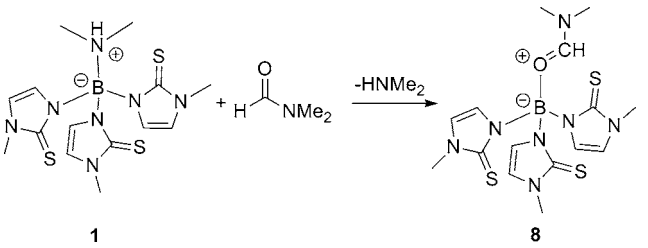


Figure 5. Structure of the dication in [κ^3-[S,S,S]-(*N*,*N*-dimethylbenzamidine)B(methimazolyl)$_3$Ru(*p*-cymene)][PF_6]$_2$ (7). Hydrogen atoms, counterions and MeCN solvent omitted for clarity. Selected bond lengths and angles are provided in Table 1.

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 neighbor 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 NMe_2 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** (θ = −48.54° and ω = 58.35°).

Both ligands **4** and **6** are nitrogen analogues of the ligand characterized 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 dimethylformamide (DMF) to boron and adopting sp^2 hybridization. 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 h provided a colorless precipitate (Scheme 4). The ^{1}H 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

Scheme 4. Direct Route to (DMF)ZTm (8)



nucleophiles which are known to substitute the dimethylamine group in **1** to include oxygen donors.

Isonitriles. Having successfully exploited both nitrogen and oxygen donors it was of interest to investigate the coordination of a carbon donor to the boron center. Thus, 2,6-dimethylphenyl isonitrile was stirred with **1** in toluene under reflux for 4 days providing a colorless precipitate of compound **9** upon workup (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 ^{1}H 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 synthesized by Györi et al.,[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 ^{1}H NMR studies showed three resonances for H_a (Scheme 5) at 223 K indicating inequivalence of the methimazole rings at this temperature. Coalescence of these resonances occurred above 253 K. These data indicate that the isonitrile carbon is stabilized by a fluxional interaction with the methimazole sulfur atoms which equilibrates between the three methimazolyl arms faster than the NMR time scale at room temperature (Scheme 5).

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 et al. (Figure 7).[15] However, Carboni et al.'s system is fused to pyridine rather than an imidazole ring and contains an sp^3-hybridized 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 et al.'s system [1.805 Å], and thus consistent with a weak C−S interaction and the

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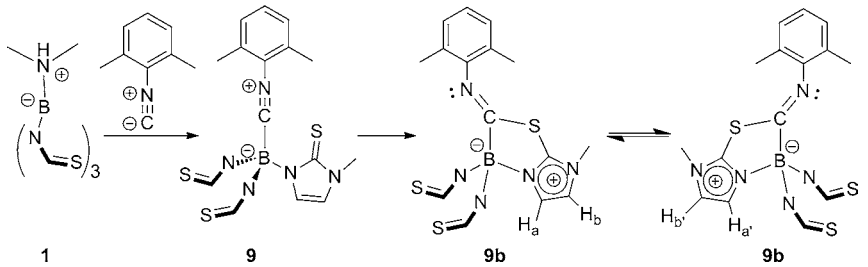
Scheme 5. Reaction of 1 with ArNC Gives (ArNC)ZTm (9) Which Is Stabilized by the Formation of the Fluxional Species 9b



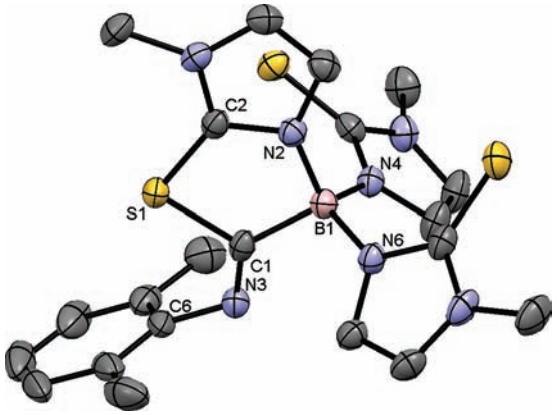


Figure 6. Structure of 3-bis(methimazolyl)-2-(2,6-dimethylphenylimino)-7-methyl-[1,4,3]-thiazaborolo[5,4-*b*]imidazolium (**9b**). Hydrogen atoms omitted for clarity. Selected bond lengths and angles are provided in Table 1.

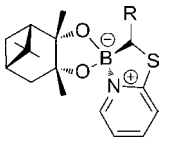


Figure 7. Carboni's thiazaborolo system.

observed fluxionality of this species in solution. Also consistent with this is the rather short 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 et al.'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 hybridization 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.

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 center. 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 center during the synthesis of ligand **9**.

The free ligand **9** was coordinated to Ru(II) by treatment with $[Ru(p\text{-cymene})Cl_2]_2$ in methanol, and the resulting complex (**10**) precipitated after anion exchange with $[NH_4][PF_6]$. The ^1H NMR spectrum of this complex indicated that the ligand in this complex coordinates in a κ^3-[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 $(AB)_2$ system in a κ^3-[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, for ruthenium to adopt the preferred octahedral geometry, the ligand must be coordinated in a κ^3-mode rather than a bidentate κ^2-[S,S] mode. Therefore, upon coordination of the two free methimazolyl arms to a metal center, the fluxional carbon−sulfur interaction observed in **9b** becomes irreversible resulting in an [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 κ^3-[N,S,S] mode to give an achiral complex (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

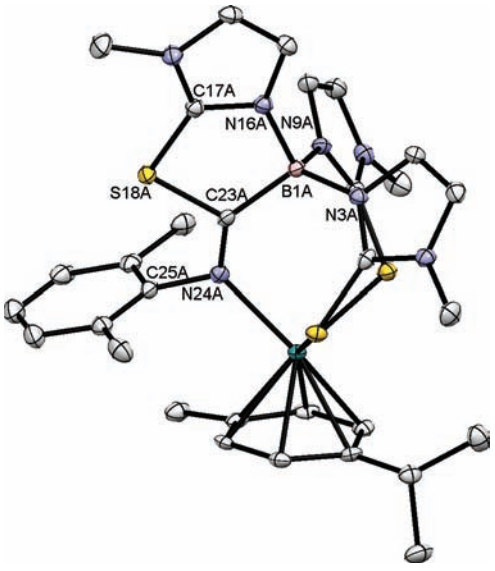


Figure 8. Structure of the dication in [{κ^3[N,S,S]-3-bis(methimazolyl)-2-(2,6-dimethylphenylimino)-7-methyl-[1,4,3]-thiazaborolo[5,4-*b*]imidazolium}Ru(*p*-cymene)] $[PF_6]_2$ (**10**). Hydrogen atoms counterions omitted for clarity. Selected bond lengths and angles are provided in Table 1.

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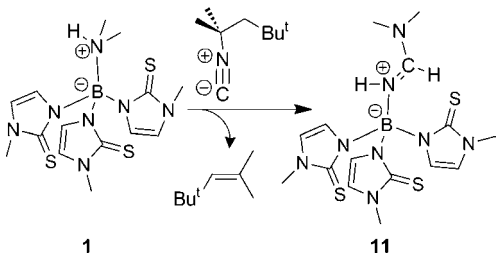
this bond upon complexation. The C(17A)−S(18A) bond [1.731(2) Å] is essentially unchanged from the previous thiazaborole [1.721(3) Å] and the C(17A)−S(18A)−C(23A) angle (90.3°) is only very slightly larger (89.4°). The exocyclic C═N double bond C(23A)−N(24A) [1.283(3) Å] is also lengthened compared to **9b** [1.255(3) Å] because of 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.

This structure allows us to explain the broadening of the *p*-cymene arene resonances observed in the ^{1}H NMR spectrum of this complex as resulting from hindered rotation of the aryl ring because of interaction with the *o*-xylyl group, which is directed toward the *p*-cymene environment. The ^{13}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 center and thus to the formation of ligand **9b** and complex **10**. An aliphatic isonitrile was expected to be a stronger donor for the boron center. To investigate this the readily available branched alkyl-isonitrile (1,1,3,3-tetramethylbutylisonitrile) was stirred with **1** in toluene under reflux for 12 h. The colorless precipitate isolated after workup was found to be an unexpected reaction product **11** (Scheme 6).

Scheme 6. Synthesis of 11

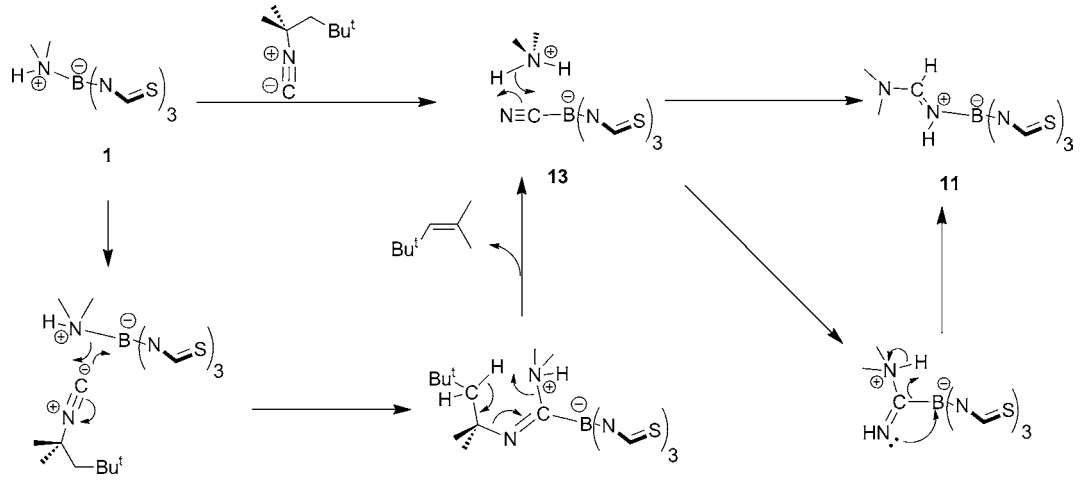


1 **11**

^{1}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}C NMR DEPT experiments showed the presence of a tertiary carbon center 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}C NMR of the free isonitrile showed no evidence for this, even after 48 h in toluene under reflux. On the basis of the spectroscopic evidence, we thus assigned the structure of this ligand as that containing an *N,N′*-dimethylformamidino group attached to the boron (**11**). ^{1}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.

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═NMe_2 double bond as seen in **5**

Scheme 7. Mechanism of Formation of 11 and 13



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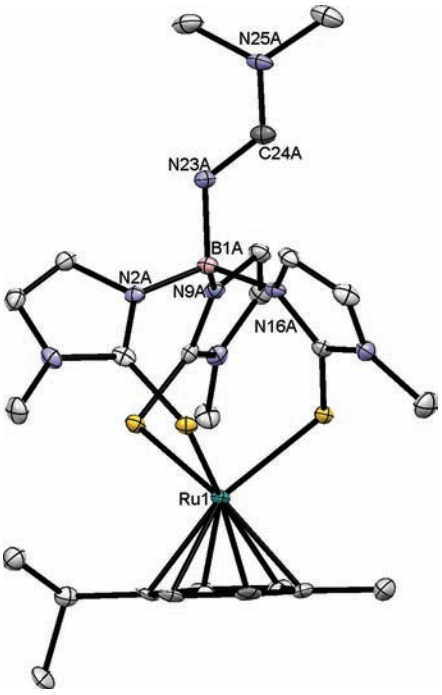


Figure 9. Structure of the dication in $[\kappa^3$-[S,S,S]-(*N*,*N*-dimethylformamidine)B(methimazolyl)$_3$Ru(*p*-cymene)$][PF_6]_2$ (**12**). Hydrogen atoms, counterions and MeCN solvent omitted for clarity. Selected bond lengths and angles are provided in Table 1.

and 7. The mean torsion angle N−B−Ru−S is slightly larger in this complex than in those previously found (θ = 49.49°) however the displacement of the metal from the methimazole plane is smaller in this system (ω = −53.94°).

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 workup of the reaction mixture after only 4 h. 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 ^{1}H NMR spectrum of **13** contained a broadened triplet at 2.69 ppm (6H) and a broad singlet at 8.32 (2H) consistent with $[H_2NMe_2]^+$ as the counterion. The ^{13}C 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**.

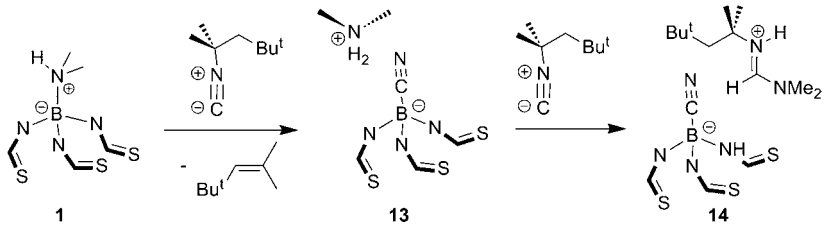
During the course of our mechanistic studies **1** was treated with two molar equivalents of 1,1,3,3-tetramethylbutylisonitrile in toluene under reflux (Scheme 8) which provided a further unanticipated outcome. Initially, after 4 h the intermediate **13** could be detected by ^{1}H NMR spectroscopy.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

In contrast to **11** and **13**, ^{1}H 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 $[(p$-cymene)$RuCl_2]_2$ 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 2218 cm^{-1} which agrees well with literature values of ν(C≡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) Å] than the corresponding B(1A)−N(1A) (NCS) bond in **3** [1.542(4) Å] 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 $[(PhTm)Mn(CO)_3]$ complex [1.634(5) Å].[18] The same bond is only slightly shorter than the

Scheme 8. Reaction of 1 with 2 Molar Equivalents of 1,1,3,3-Tetramethylbutylisonitrile Leading to the Formation of the Salt 14



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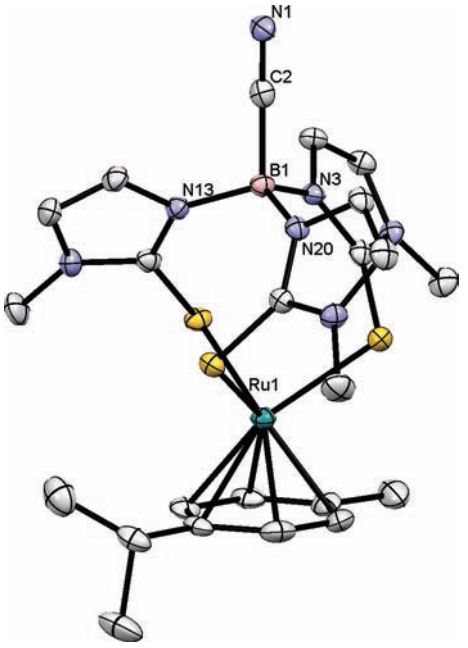


Figure 10. X-ray crystal structure of [κ^3-[S,S,S]-(cyano)B-(methimazolyl)$_3$Ru(*p*-cymene)][PF_6] (**15**). Hydrogen atoms, counterions, and an acetonitrile molecule removed for clarity. Selected bond lengths and angles provided in Table 1.

B−C bond in **10** [1.658(3) Å] 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) Å and does not deviate significantly from linear geometry with a B(1)−C(2)−N(1) angle of 178.5(3)°. The mean torsion angle N−B−Ru−S is somewhat smaller in this complex than in those previously (θ = 41.8°), although the displacement of the metal from the methimazolyl plane is comparable (ω = −59.2°).

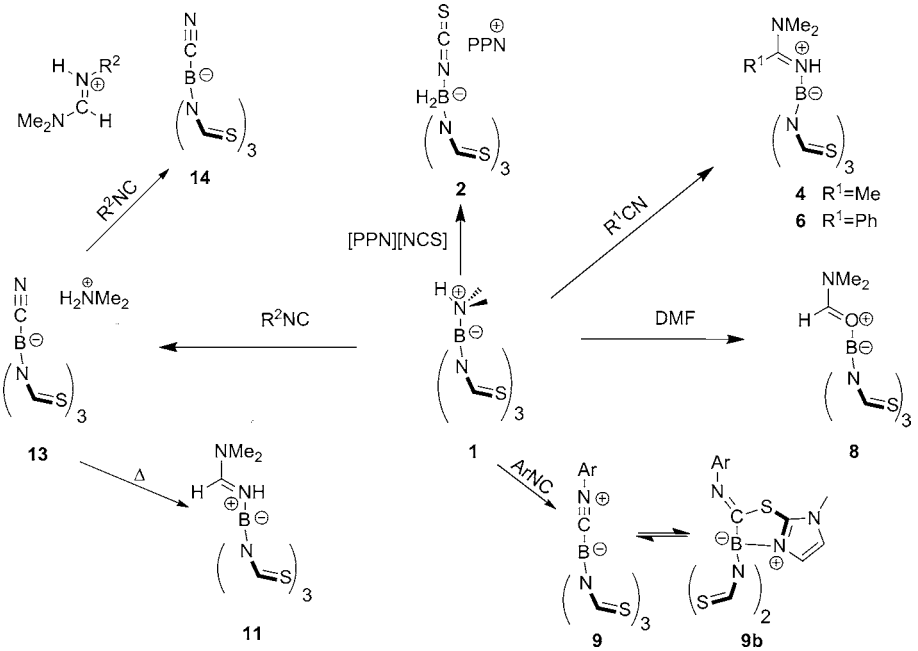
CONCLUSIONS

The work reported in this paper is summarized 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 sulfur 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.

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 600 MHz Bruker Advance III spectrometer. ^{1}H and ^{13}C chemical shifts are reported in ppm relative to $SiMe_4$ (δ = 0) and were referenced internally with respect to the protio solvent impurity or the ^{13}C resonances,

Scheme 9. Reactions of 1 Described in This Work[a]



[a]R^1 = Me, Ph; Ar = 2,6-dimethylphenyl; R^2 = 1,1-3,3-dimethylbutyl.

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Table 1. Selected Bond Lengths (Å) and Angles (deg)

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)−N(23A)	125.0(4)		
C(23A)−N(24A)−Ru(1)	125.60(16)	C(24A)−N(25A)−C(26A)	121.3(4)		
C(25A)−N(24A)−Ru(1)	118.07(14)	C(24A)−N(25A)−C(27A)	120.9(4)		
N(24A)−C(23A)−B(1A)	130.5(2)	C(26A)−N(25A)−C(27A)	117.7(4)		
C23A—N24A—C25A	115.70(19)				
N(19A)−C(17A)−S(18A)	129.07(18)				
C(17A)−(S18A)−C(23A)	90.30(11)				

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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 parts per million (ppm) relative to $BF_3.OEt_2$ (δ = 0). Infrared 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 [$(HMe_2N)B(methimazolyl)_3$] (**1**),[4] [PPN]-[SCN][19] and [(*p*-cymene)$RuCl_2]_2$[20] were synthesized according to the literature procedures. All other chemicals were obtained from Sigma-Aldrich and used as received.

[PPN][(SCN)B(methimazolyl)$_3$] (2). $(HNMe_2)B(methimazolyl)_3$ (**1**) (719.4 mg, 1.8 mmol) was dissolved in acetonitrile (20 cm^3). [PPN][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 × 10 mL) to give the target material as a white powder. (683.3 mg, 51%), MS (ESI$^+$) *m*/*z*: 408 (M^+); ^{1}H NMR (500.1 MHz, $CDCl_3$): δ 7.71−7.63 (m, 6*H*, 6 × C*H*), 7.54−7.40 (m, 24H, 24 × C*H*), 6.84 (br s, 3H, 3 × C*H*), 6.53 (d, *J* = 2.4 Hz, 3H, 3 × C*H*), 3.44 (s, 9H, 3 × NCH_3); ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 164.0 (C═S), 134.0 (3 × CH), 132.1 (6 × CH), 129.7 (6 × CH), 127.0 (d, *J* = 108 Hz, 3 × *C*-P), 122.5 (3 × CH), 116.3 (3 × CH), 34.6 (3 × NCH_3); ^{11}B-NMR ($CDCl_3$, 128.3 MHz): δ −3.50; Elemental analysis: expected for $C_{49}H_{45}BN_8P_2S_4.CHCl_3$ (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).

[(SCN)B(methimazolyl)$_3$Ru(*p*-cymene)] [BPh$_4$] (3). [PPN]-[(SCN)B(methimazolyl)$_3$] (**2**) (100.0 mg, 0.20 mmol) and [Ru(*p*-cymene)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 × 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 × 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 (M^+/2); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.45 (dd, *J* = 5.0, 3.6 Hz, 8H, 8 × C*H*), 7.05 (t, *J* = 7.4 Hz, 8H, 8 × C*H*), 6.98 (d, *J* = 2.0 Hz, 3H, 3 × C*H*), 6.86−6.94 (m, 4H, 4 × C*H*), 6.67 (d, *J* = 2.2 Hz, 3H, 3 × C*H*), 5.12 (t, *J* = 5.8 Hz, 2H, 2 × C*H*), 5.01 (d, *J* = 5.8 Hz, 1H, C*H*), 4.95 (d, *J* = 6.0 Hz, 1H, C*H*), 3.38 (s, 9H, 3 × NCH_3), 2.84 (spt, *J* = 6.9 Hz, 1H, C*H*), 2.04 (s, 3H, CH_3), 1.16 (t, *J* = 7.3 Hz, 6H, 2 × CH_3); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 164.1 (q, *J* = 49 Hz, 4 × *C*-B), 157.2 (C═S), 136.8 (NCS), 136.3 (8 × CH), 125.6 (8 × CH), 121.7 (4 × CH), 121.5 (3 × CH), 121.3 (3 × CH), 107.0 (C_q), 101.0 (C_q), 85.1 (CH), 84.5 (CH), 84.3 (CH), 83.4 (CH), 35.1 (3 × NCH_3) 30.2 (CH), 22.9 (CH_3), 22.1 (CH_3), 18.8 (CH_3); ^{11}B-NMR (128.3 MHz, $CDCl_3$): δ −3.33 (*B*Mt$_3$), −6.48 (*B*Ph$_4$); Elemental analysis: expected for $C_{47}H_{49}B_2Cl_3N_7RuS_4$ (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). $(HNMe_2)B$-(methimazolyl)$_3$ (**1**) (362 mg, 91.6 mmol) was dissolved in acetonitrile (20 cm^3), 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 Et_2O (3 × 10 mL). The target material was isolated as a white powder (288 mg, 72%). MS (EI+) *m*/*z*: 436.1 (M^+); ^{1}H NMR (500.1 MHz, $CDCl_3$): δ 9.87 (s, 1H, 1 × N*H*), 6.66 (d, *J* = 2.3 Hz, 3H, 3 × C*H*), 6.24 (br. s, 3H, 3 × C*H*), 3.58 (s, 9H, 3 × NCH_3), 3.32 (s, 3H, NCH_3), 3.14 (s, 3H, NCH_3), 2.04 (s, 3H, CH_3); ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 167.4 (*C*═N), 164.0 (C═S), 120.4 (CH), 118.1 (CH), 41.3 (CH_3), 40.7 (CH_3), 34.7 (CH_3), 19.1 (CH_3); ^{11}B-NMR (128.3 MHz, $CDCl_3$): δ 0.25; Elemental analysis: expected for $C_{16}H_{25}BN_8S_3$ (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)$_3$Ru(*p*-cymene)] [PF$_6$]$_2$ (5). [(*N*,*N*-dimethylacetamidino)B(methimazolyl)$_3$] (**4**) (101.3 mg, 0.23 mmol) and [Ru(*p*-cymene)$Cl_2]_2$ (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 × 2 mL) and Et_2O (3 × 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^+); ^{1}H NMR (400 MHz, CD_3CN): δ 7.18 (d, *J* = 2.0 Hz, 3H, 3 × C*H*), 6.98 (br. s, 3H, 3 × C*H*), 5.99 (br. s, 1H, N*H*), 5.50 (s, 2H, 2 × C*H*), 5.34−5.43 (m, 2H, 2 × C*H*), 3.67 (s, 9H, 3 × NCH_3), 3.22 (d, *J* = 8.7 Hz, 6H, 2 × NCH_3), 2.94 (spt, *J* = 6.9 Hz, 1H, C*H*), 2.18 (s, 3H, CH_3), 1.96 (br. s, 3H, CH_3), 1.18 (dd, *J* = 6.9, 1.9 Hz, 6H, 2 × CH_3); ^{13}C NMR (125.8 MHz, CD_3CN): δ 168.21 (C_q), 160.1 (*C*═S), 123.4 (3 × CH), 122.0 (3 × CH), 107.9 (C_q), 102.6 (C_q), 86.4 (CH), 86.1 (CH), 85.3 (CH), 84.3 (CH), 42.3 (NCH_3), 37.8 (NCH_3), 36.2 (3 × CH_3), 31.4 (CH), 23.0 (CH_3), 22.6 (CH_3), 20.7 (CH_3), 19.1 (CH_3); ^{11}B-NMR (CD_3CN, 128.3 MHz) δ: −0.71; Elemental analysis: expected for $C_{26}H_{39}BF_{12}N_8P_2RuS_3$ (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). [$HNMe_2$]B[methimazolyl]$_3$ (500 mg, 1.26 mmol) was dissolved in benzonitrile (10 cm^3), 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 × 10 mL) and Et_2O (3 × 10 mL). The target material was isolated as a white powder (336 mg, 53%). MS (EI +) *m*/*z*: 498.2 (M^+); ^{1}H NMR (500.1 MHz, $CDCl_3$): δ 11.12 (s, 1 H, N*H*), 7.51 (m, 5H, 5 × C*H*), 6.82 (s, 3 H, 3 × C*H*), 6.36 (s, 3 H, 3 × C*H*), 3.54, (s, 3H, NCH_3), 3.42 (s, 9 H, 3 × CH_3), 2.79 (s, 3 H, NCH_3); ^{13}C NMR (125.8 MHz, $CDCl_3$): 166.8 (C═S), 132.8 (CH), 132.2 (2 × CH), 131.2 (2 × CH), 127.8 (CH), 116.1 (CH), 41.9 (CH_3), 41.4(CH_3), 34.5 (CH_3); ^{11}B-NMR (128.3 MHz, $CDCl_3$): δ 0.12; Elemental analysis: expected for $C_{21}H_{27}BN_8S_3$ (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)$_3$Ru(*p*-cymene)] [PF$_6$]$_2$ (7). [(*N*,*N*-dimethylbenzamidino)B(methimazolyl)$_3$] (**6**) (101.3 mg, 0.20 mmol, 1 equiv) and [Ru(*p*-cymene)$Cl_2]_2$ (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 × 2 mL) and Et_2O (3 × 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); ^{1}H NMR (500.1 MHz, d^6-DMSO): δ 7.49 (m, 5H, 5 × C*H*), 7.46 (s, 3H, 3 × C*H*), 7.27 (s, 3H, 3 × C*H*), 5.55 (m, 4H, 4 × C*H*) 3.56 (s, 9H, 3 × NCH_3), 2.94 (s, 3H, CH_3), 2.84 (spt, *J* = 6.9 Hz, 1H, C*H*), 2.10 (s, 3H, CH_3), 1.20 (dd, *J* = 6.9 Hz, 6H, 2 × CH_3) (Missing one CH_3 resonance: Under DMSO or H_2O peaks); ^{13}C NMR (101 MHz, DMSO-d$_6$): δ 167.3 (C_q), 157.5 (*C*═S), 132.0 (CH), 128.9 (CH), 127.9 (CH), 122.6 (3 × CH), 121.6 (3 × 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 × NCH_3), 30.0 (CH_3), 22.5 (NCH_3), 21.7 (NCH_3), 18.2 (2 × CH_3); ^{11}B-NMR (128.3 MHz, d^6-DMSO): δ −0.31; Elemental analysis: expected for $C_{31}H_{41}BF_{12}N_8P_2RuS_3$ (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). $(HNMe_2)B(methimazolyl)_3$ (**1**) (501.9 mg, 1.27 mmol) was suspended in toluene (20 cm^3). DMF (105 μL, 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 × 10 mL) and Et_2O (3 × 10 mL). The target material was isolated as a white powder (465 mg, 87%). MS (EI+) *m*/*z*: 423.92 (M^+); ^{1}H NMR (500.1 MHz, $CDCl_3$): δ 8.67 (s, 1H, C(*H*)O), 6.66 (d, *J* = 2.3 Hz, 3H, 3 × C*H*), 6.44 (br. s, 3H, 3 × C*H*), 3.57 (s, 9H, 3 × CH_3), 3.33 (s, 3H, NCH_3), 3.23 (s, 3H, NCH_3); ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 165.0 (−CHO), 164.3 (C═S), 120.7 (CH), 118.3 (CH), 40.3 (CH_3), 36.3 (CH_3), 34.7 (CH_3); ^{11}B-NMR (128.3 MHz, $CDCl_3$): δ 2.29; MS (ESI$^+$) 423.9 ($(M+1)^+$); Elemental analysis: expected for

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$C_{15}H_{22}BN_7OS_3$ (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). $(HNMe_2)B(methimazolyl)_3$ (**1**) (503.2 mg, 1.26 mmol) was suspended in toluene (20 cm^3). 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 × 10 mL) and Et_2O (3 × 10 mL). The resultant white powder was recrystallized from MeCN/Et_2O, 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^+); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.62 (br s, 3H, 3 × C*H*), 6.93−7.11 (m, 3H, 3 × C*H*), 6.77 (d, *J* = 2.3 Hz, 3H, 3 × C*H*), 3.58 (s, 9H, 3 × NCH_3), 2.14 ppm (s, 6H, 2 × CH_3); ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 176.9 (br, C−B), 160.7 (*C*═S), 150.8 (*C*-NC), 128.5 (2 × *C*H), 126.7 (2 × *C*(CH_3)), 125.0 (*C*H), 122.6 (3 × *C*H), 119.3 (3 × *C*H), 34.8 (3 × NCH_3), 18.7 (2 × CH_3); ^{11}B-NMR (128.3 MHz, $CDCl_3$): δ −1.21; Elemental analysis: expected for $C_{21}H_{24}BN_7S_3$ (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)] [PF_6]$_2$ (10). $(HNMe_2)B(methimazolyl)_3$ (**1**) (98.7 mg, 0.20 mmol) and $[Ru(p\text{-cymene})Cl_2]_2$ (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 × 2 mL) and Et_2O (3 × 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). ^{1}H NMR (400 MHz, CD_3CN): δ 7.48 (d, *J* = 2.1 Hz, 1H, C*H*), 7.42 (d, *J* = 2.1 Hz, 1H, C*H*), 6.08−7.38 (m, 7H, 7 × C*H*), 4.78−5.10 (m, 2H, 2 × C*H*), 5.10−5.27 (m, 2H, 2 × C*H*), 3.76 (s, 6H, 2 × NCH_3), 3.55 (s, 3H, NCH_3), 3.03 (spt, *J* = 6.9 Hz, 1H, C*H*), 2.37 (br s, 3H, CH_3), 2.01 (s, 3H, CH_3), 1.26 (d, *J* = 6.9 Hz, 6H, 2 × CH_3), 1.23 (br s, 3H, CH_3); ^{13}C NMR (125.8 MHz, CD_3CN): δ 196.4 (*C*-B), 158.14 (*C*═S), 148.5 (C_q), 131.5 (2 × *C*H), 130.7 (*C*H), 129.7 (C_q), 129.1 (2 × *C*H), 125.1 (*C*H), 123.3 (2 × *C*H), (One CH missing, most likely under H_3CCN resonance), 121.2 (C_q), 113.9 (C_q), 105.3 (C_q), 91.3 (2 × *C*H), 86.5 (2 × *C*H), 48.9 (*C*H), 36.8 (2 × NCH_3), 36.6 (NCH_3), 31.6 (CH_3), 22.9 (CH_3), 18.6 (CH_3), 18.0 (2 × CH_3); ^{11}B-NMR (128.3 MHz, CD_3CN) δ: −2.44; Elemental analysis: expected for $C_{31}H_{38}BF_{12}N_7P_2RuS_3$ (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*-Dimethylaminoformamidine)B(methimazolyl)$_3$ (11). ***Caution!*** *There is a possibility of the formation of HCN in this reaction. Appropriate precautions should be taken when repeating this synthesis.*

$(HNMe_2)B(methimazolyl)_3$ (**1**) (503.5 mg, 1.26 mmol) was suspended in toluene (20 cm^3). 1,1,3,3-tetramethylbutylisonitrile (222 μL, 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 Et_2O (3 × 10 mL). The resultant white powder was recrystallized from MeOH/Et_2O, and the target material was isolated as a white powder (243.5 mg, 46%). MS (EI+) *m*/*z*: 422.1 (M^+); ^{1}H NMR(500.1 MHz, $CDCl_3$): δ 10.02 (d, *J* = 15.5 Hz, 1H, N*H*), 7.94 (d, *J* = 15.5 Hz, 1H, C*H*), 6.68 (d, *J* = 2.1 Hz, 3H, 3 × C*H*), 6.06 (d, *J* = 1.7 Hz, 3H, 3 × C*H*), 3.59 (s, 9H, 3 × NCH_3), 3.18 (s, 3H, NCH_3), 3.07 (s, 3H, NCH_3). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 163.7 (*C*═S), 159.3 (*C*H), 119.8 (3 × *C*H), 118.5 (3 × *C*H), 42.8 (CH_3), 36.1 (CH_3), 34.6 (3 × CH_3); ^{11}B-NMR (128.3 MHz, $CDCl_3$): δ 0.66; Elemental analysis: expected for $C_{15}H_{23}BN_8S_3$ (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)$_3$Ru(*p*-cymene)] [PF_6]$_2$ (12). [(*N*,*N*-dimethylformamidino)B(methimazolyl)$_3$] (**11**) (96.2 mg, 0.23 mmol) and $[Ru(p\text{-cymene})Cl_2]_2$ (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 × 2 mL) and Et_2O (3 × 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); ^{1}H NMR (500 MHz, d^6-DMSO): δ 8.24 (d, *J* = 12.5 Hz, 1H, N*H*), 7.73 (d, *J* = 1.9 Hz, 3H, 3 × C*H*), 7.54 (s, 3H, 3 × C*H*), 6.97 (d, *J* = 13.4 Hz, 1H, C*H*), 6.04 (d, *J* = 6.1 Hz, 2H, 2 × C*H*), 5.94 (dd, *J* = 13.6, 5.3 Hz, 2H, 2 × C*H*), 4.23 (s, 9H, 3 × NCH_3), 3.77 (s, 3H, NCH_3), 3.70 (s, 3H, NCH_3), 3.51 (spt, *J* = 7.0 Hz, 1H, C*H*), 2.22 (s, 3H, CH_3) 1.74 (d, *J* = 6.8 Hz, 6H, 2 × CH_3); ^{13}C NMR (125.8 MHz, CD_3CN) δ 160.4 (*C*H), 158.6 (*C*═S), 123.1 (3 × *C*H), 122.6 (3 × *C*H), 107.9 (C_q), 102.5 (C_q), 86.2 (*C*H), 85.8 (*C*H), 85.2 (*C*H), 84.2 (*C*H), 44.9 (NCH_3), 37.1 (NCH_3), 36.0 (3 × CH_3), 31.4 (CH), 23.0 (CH_3), 22.6 (CH_3), 19.1 (CH_3); ^{11}B-NMR (128.3 MHz, CD_3CN): δ −0.52; Elemental analysis: expected for $C_{25}H_{37}BF_{12}N_8P_2RuS_3$ (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). ***Caution!*** *There is a possibility of the formation of HCN in this reaction. Appropriate precautions should be taken when repeating this synthesis.*

$(HNMe_2)B(methimazolyl)_3$ (**1**) (1.0094 g, 2.55 mmol) was suspended in toluene (20 cm^3). 1,1,3,3-Tetramethylbutyllisonitrile (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 × 10 mL). After cooling the sticky solid was triturated with Et_2O to give a white powder. The resultant white powder could not be recrystallized from CH_2Cl_2/Et_2O, CH_2Cl_2/hexane, MeCN/Et_2O, THF/Et_2O 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 Et_2O (607.0 mg, 56%). MS (ESI-) *m*/*z*: 376.04 (M^-); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.32 (br s, 2H, NH_2), 6.68 (d, *J* = 2.27 Hz, 3H, 3 × C*H*), 6.55 (d, *J* = 1.77 Hz, 3H, 3 × C*H*), 3.58 (s, 9H, 3 × NCH_3), 2.69 (t, *J* = 5.43 Hz, 6H, N(CH_3)$_2$). ^{13}C NMR (126 MHz, $CDCl_3$): δ 162.8 (*C*═S), 130.4 (q, *J* = 80 Hz, *C*-B), 121.0 (3 × *C*H), 118.1 (3 × *C*H), 35.2 (N(CH_3)$_2$), 34.7 (NCH_3); ^{11}B-NMR (128.3 MHz, $CDCl_3$): δ −6.66; Elemental analysis: expected for $C_{15}H_{23}BN_8S_3$ (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). $(HNMe_2)B(methimazolyl)_3$ (**1**) (504.4 mg, 1.26 mmol) was suspended in toluene (20 cm^3). 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 × 10 mL) at 90 °C. After cooling the sticky solid was triturated with Et_2O to give a white powder. The resultant white powder was could not be recrystallized 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 Et_2O (392 mg, 55%). MS (ESI-) *m*/*z*: 376.05 (M^-), (ESI+) 185.05 (M^+); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.52 (br s, 1H, N*H*), 7.58 (d, 1H, C*H*), 6.62 (m, 6H, 6 × C*H*), 3.56 (s, 9H, 3 × CH_3), 3.24 (s, 6H, 2 × NCH_3), 1.73 (s, 2H, CH_2), 1.47 (s, 6H, 2 × CH_3), 0.97 (s, 9H, 3 × CH_3); ^{13}C NMR (126 MHz, $CDCl_3$): δ 163.4 (*C*═S), 152.5 (NC(H)N), 129.3 (q, *J* = 84 Hz, *C*-B), 121.4 (3 × *C*H), 117.4 (3 × *C*H), 59.6 (NCH_3), 54.3 (NCH_3), 37.6 (*C*(CH_3)$_2$), 34.7 (3 × NCH_3), 31.7 (C(CH_3)$_2$), 31.6 (C(CH_3)$_3$), 29.6 (CH_2); ^{11}B-NMR (128.3 MHz, $CDCl_3$): −6.67; Elemental analysis: expected for $C_{24}H_{40}BN_9S_3$ (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)$_3$Ru(*p*-cymene)] [PF_6] (15). [*N*,*N*-dimethyl-*N*′-(1,1,3,3-tetramethylpropyl)formamidinium] [(cyano)B(methimazolyl)$_3$] (**13**) (102.7 mg, 0.18 mmol) and $[Ru(p\text{-cymene})Cl_2]_2$ (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 × 2 mL) and Et_2O (3 × 3

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Table 2. Crystal Data for Compounds 3, 5, 7, 9b, 10, 12, and 15

	3	5	7
chemical formula	$C_{23}H_{29}BN_7RuS_4 \cdot C_{24}H_{20}B \cdot 2(Et2O) \cdot 2(MeOH)$	$C_{26}H_{44}BN_8RuS_3 \cdot 2(F_6P) \cdot C_2H_3N$	$2(C_{31}H_{41}BN_8RuS_3) \cdot 3(C_2H_3N) \cdot 4(F_6P)$
M_r	1159.16	1001.70	2170.60
crystal system, space group	monoclinic, $I2/a$	monoclinic, $P2_1/c$	monoclinic, $P2_1/c$
a, b, c (Å)	16.1020 (4), 25.7120 (7), 27.9161 (9)	16.72141 (12), 12.89427 (8), 20.16553 (14)	17.0566 (3), 13.0618 (2), 19.9834 (3)
β (deg)	105.768 (1)	95.5773 (7)	91.993 (1)
V (Å^3)	11122.8 (5)	4327.31 (5)	4449.41 (12)
Z	8	4	2
μ (mm^{-1})	0.48	0.67	0.66
T_{min}, T_{max}	0.657, 0.746	0.943, 1.000	0.678, 0.745
independent reflections	12310	11145	9083
R_{int}	0.064	0.027	0.074
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.042, 0.096, 1.09	0.042, 0.111, 1.05	0.051, 0.126, 1.04
$\Delta\rangle_{max}$, $\Delta\rangle_{min}$ (e Å^{-3})	0.89, −0.85		1.57, −0.87
	9b		**10**
chemical formula	$C_{21}H_{24}BN_7S_3$		$C_{25}H_{37}BN_8RuS_3 \cdot 2(F_6P)$
M_r	481.46		947.63
crystal system, space group	orthorhombic, $P2_12_12_1$		triclinic, $P\bar{1}$
a, b, c (Å)	10.8256 (2), 13.4721 (3), 16.4802 (3)		12.7200(2), 17.0209(3), 18.7739(3)
α, β, γ (deg)	90, 90, 90		110.562(2), 100.114(1), 97.616 (1)
V (Å^3)	2403.53 (8)		3662.46(10)
Z	4		4
μ (mm^{-1})	3.01		6.75
T_{min}, T_{max}	0.687, 0.900		0.829, 1.000
independent reflections	4854		14453
R_{int}	0.067		0.058
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.039, 0.102, 1.04		0.039, 0.108, 1.06
$\Delta\rangle_{max}$, $\Delta\rangle_{min}$ (e Å^{-3})	0.35, −0.31		1.42, −1.37
	12		**15**
chemical formula	$C_{31}H_{38}BN_7RuS_3 \cdot 2(F_6P)$		$C_{48}H_{61}\ B_2\ F_{12}\ N_{15}\ P2\ Ru2\ S6$
M_r	1006.68		1554.18
crystal system, space group	monoclinic, $P2_1/n$		triclinic, $P\bar{1}$
a, b, c (Å)	13.5789(4), 14.2055(5), 19.7712(8)		10.0598(3), 16.6932(4), 19.9429(5)
α, β, γ (deg)	90, 90, 90		76.356(1), 85.925(1), 75.842(1)
V (Å^3)	3813.7(2)		3155.34(14)
Z	4		2
μ (mm^{-1})	6.53		0.84
T_{min}, T_{max}	0.832, 1.000		0.811, 0.923
independent reflections	7570		12924
R_{int}	0.042		0.045
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.029, 0.080, 1.05		0.040, 0.101, 1.03
$\Delta\rangle_{max}$, $\Delta\rangle_{min}$ (e Å^{-3})	0.58, −0.67		1.44, −0.58

mL). The target material was isolated as a red solid (88.9 mg, 65%). X-ray quality crystals were grown from vapor diffusion of Et_2O into a concentrated solution of the complex in acetonitrile. MS (ESI+) m/z: 611.9 (M^+); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.19 (s, 3H, 3 × C*H*), 6.82 (d, J = 2.1 Hz, 3H, 3 × C*H*), 4.94−5.19 (m, 4H, 4 × C*H*), 3.49 (s, 9H, 3 × NCH_3), 2.87 (dt, J = 13.9, 7.10 Hz, 1H, C*H*), 2.07 (s, 3H, CH_3), 1.19 (t, J = 6.94 Hz, 6H, 2 × CH_3); ^{13}C NMR (126 MHz, $CDCl_3$): δ 158.0, (*C*═S), 128.6 (q, J = 80 Hz, NC-B), 122.7 (3 × CH), 121.6 (3 × 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 × CH_3), 30.3 (0.5 × CH_3), 29.7 (0.5 × CH_3), 22.9 (0.5 × CH_3), 22.1 (0.5 × CH_3), 18.9 (CH_3); Elemental analysis: expected for $C_{47}H_{49}B_2N_7RuS_3$ (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 Table 2. Structures **3** and **7** were collected with with graphite-monochromated Mo−Kα radiation (λ = 0.71073 Å) on a Bruker SMART APEX II CCD diffractometer. Absorption corrections were carried out using the multiscan procedure SADABS.[21] All other data sets were collected on a Agilent Technologies SuperNova diffractometer with Cu−Kα radiation (λ = 1.5418 Å) and X-ray mirror optics. Absorption corrections were carried out using the multiscan procedure CrysAlisPro.[22] All data sets were collected at 100 K. Structure **15** was solved by SIR92[23] and refined by Olex2.[24] All other structures were solved by SHELXS and refined by full-matrix least-squares against F^2 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 Et_2O and 1.5 molecules of MeOH per formula unit. The values of F(000), D, M, and μ are all calculated on this assumption. Structure **15** contained a disordered PF_6 moiety. The occupancies of each component were refined to approximately 0.6:0.4. The largest residual

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electron density peak in **15** is 1.42 e/Å^3 high and resides 3.065 Å from N1AA.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Crystallographic data in CIF format and the variable temperature ^{1}H 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.

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Notes

The authors declare no competing financial interest.

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