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Electrophilic and Nucleophilic Displacement Reactions at the Bridgehead Borons of Tris(pyridyl)borate Scorpionate Complexes

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Although a wide variety of boron-based “scorpionate” ligands have been implemented, a modular route that offers facile access to different substitution patterns at boron has yet to be developed. Here, we demonstrate new reactivity patterns at the bridgehead positions of a ruthenium tris(pyrid-2-yl)borate complex that allow for facile tuning of steric and electronic properties.

Metal complexes derived from tripodal ligands are highly attractive in small molecule activation and catalysis, as enzyme mimics, magnetic materials, photosensitizer, and in light-harvesting applications.¹ The first generation of tris(2-pyrazolyl)borates (Tp) ligands, also referred to as “scorpionate” ligands, was introduced by Trofimenko as early as 1966.² To tune the electronic and steric features of the Tp ligand, 2nd and 3rd generations of ligands that contain functional groups either at the pyrazolyl moieties or as pendent groups attached to boron have since been introduced.³ In recent years, tripodal ligands with pyridyl in place of pyrazolyl groups have attracted significant interest, and tris(2-pyridyl) derivatives with many different bridge atoms have been explored.⁴ In 2012, our group reported the attachment of 2-pyridyl groups at boron to form tris(2-pyridyl)borate ligands (**A**, Fig 1), which will be referred to as Tpyb ligands.⁵ We have extensively explored the coordination behavior of this new ligand class and introduced redox-active complexes with metals such as Fe(II), Cu(II), Mn(II), and Ru(II).⁶ Recently, Comito studied Tpyb vanadium(V) complexes as olefin polymerization catalysts.⁷ We have also developed polymeric Tpyb ligand systems that are derived from styrene or norbornene complexes.⁸ Such polyligands are not only attractive as catalyst supports but also potentially useful in metal ion remediation, as building blocks for magnetic materials, and in ion-selective membranes.⁹

The attachment of specific functional groups to tripodal borate ligands is desirable as it would offer a means to tune the properties of the metal complexes, as well as open up versatile

pathways to integrate them with more complex molecular and polymeric scaffolds. One possible approach is to utilize different aryl groups during creation of the pyridylborate ligand architecture.¹⁰ However, the scope of this method is limited as the high reactivity of the reagents (Grignard species, strongly Lewis acidic boranes) severely restricts the type of functional group that can be attached. Another possibility is to perform a post-functionalization¹¹ after assembly of the metal complexes. In this respect, bridgehead substitution reactions are attractive but largely unexplored because the electrophilic or nucleophilic attack is hindered due to the rigid environment. Very recent studies by Berionni *et al.* show that boratriptycene derivatives (**B**, Fig 1) can be elaborated through electrophilic substitution of aryl or allyl groups on boron, followed by nucleophilic displacement of weakly bound counterions.¹² Given the similar environment at boron we anticipated that such an approach may allow for further elaboration of boron-based Tpyb ligands **A** that are strongly bound to a transition metal.

Herein, we explore the reactivity of Ru-bound scorpionate-type tris(pyrid-2-yl)borate ligands towards strong Lewis acids and Brønsted acids. We find that the treatment of bis(*t*-butylphenyl)-tris(pyrid-yl)borate ruthenium(II) [Ru(Tpyb-*t*BuPh)₂] with Lewis acids BX₃ (X = Br, Cl) results in clean electrophilic displacement of the phenyl groups to give complexes [Ru(Tpyb-X)₂] (X = Br, Cl), without affecting the metal

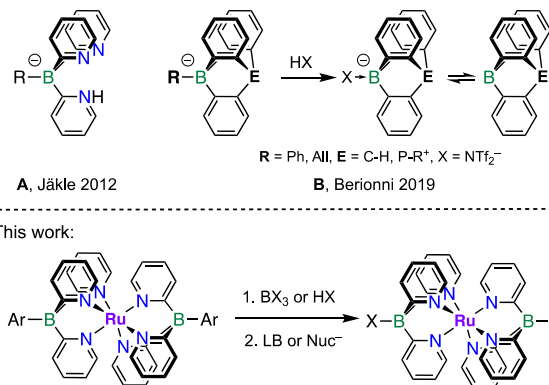
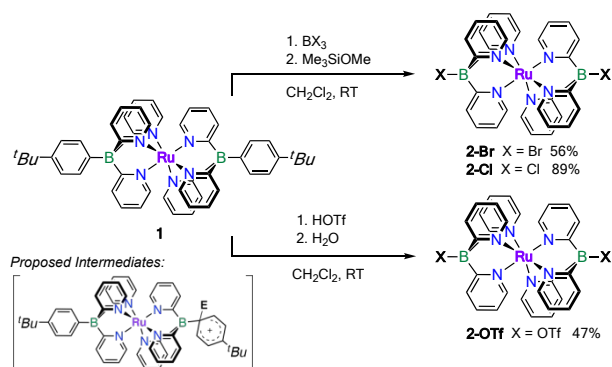


Figure 1. Tris(pyrid-2-yl)borate ligand platform and Berionni’s boratriptycenes; proposed bridgehead substitutions at metal-bound Tpyb ligands.

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Scheme 1. Electrophilic displacement of aryl groups in **1** with strong Lewis acids and Brønsted acids and plausible intermediates (E = H or BX_2)

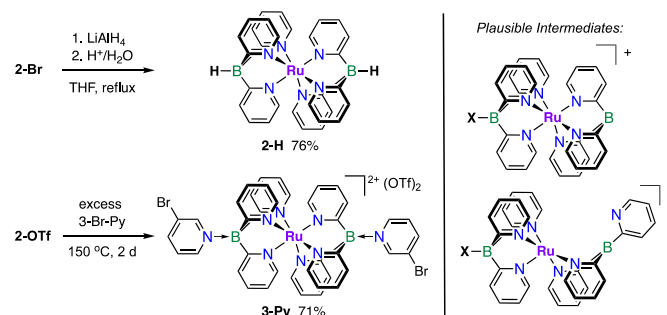
coordination sites, while reaction with Brønsted acids HX produces complexes $[\text{Ru}(\text{Tpyb-X})_2]$ (X = Br, OSO_2CF_3). Subsequent nucleophilic substituent displacement is demonstrated in the conversion of the bromo derivative to the previously unknown parent hydrogen-substituted complex $[\text{Ru}(\text{Tpyb-H})_2]$. In addition, a dicationic species is generated by displacement of the triflates in $[\text{Ru}(\text{Tpyb-OTf})_2]$ with 3-bromopyridine as a neutral nucleophile. UV-vis and cyclic voltammetry studies reveal a pronounced electronic effect of the boron substituent (X = H, Br, Cl, OSO_2CF_3). Thus, we not only present a fundamentally new approach to the diversification of scorpionate ligands, but also a powerful method to tune the electronic structure and properties of these metal complexes.

The bis(*t*-butylphenyl)tris(pyridyl)borate ruthenium(II) (**1**) was chosen for its inert low-spin d_6 -configuration and the wide application scope of Ru polypyridyl complexes. It was prepared in analogy to literature procedures for the synthesis of other Ru scorpionate complexes (ESI).^{5a, 6, 10} Complex **1** was isolated as an air-stable yellow solid and structurally characterized by multinuclear NMR spectroscopy and high-resolution mass spectrometry (Figs S1-S7). To explore the propensity for electrophilic functionalization of the Ru-bound ligands at the boron centers, we reacted **1** with boron halides (BBr_3 , BCl_3) in anhydrous degassed dichloromethane at RT and then added Me_3SiOMe to quench the excess boron halide (Scheme 1). The reaction proceeded to completion within 12 h with BBr_3 but took additional time (4 d) with BCl_3 , presumably because of its weaker Lewis acidity. In each case, a yellow precipitate formed which was collected by filtration, washed first with CH_2Cl_2 and then hexanes, and dried under high vacuum. The products (**2-X**, X = Br, Cl) were characterized by multinuclear NMR, IR and high-resolution mass spectrometry. The solubility of these complexes in most common organic solvents is low, with dichloromethane and chloroform offering the highest solubility, while moderate solubility is achieved in hot benzene or toluene. As expected, we observed two doublets and two pseudo-triplets in the ^1H NMR spectra, corresponding to four different protons at the pyridyl rings (Figs S9, S13). Importantly, the signals for the phenyl and *t*-butyl groups of the precursor (**1**) are completely absent. The ^{11}B NMR signals for **2-Br** (0.0 ppm) and **2-Cl** (-0.7 ppm) are shifted downfield from that of **1** (-6.8 ppm) (Figs S11, S15). This is

consistent with a decrease in electron density at boron as the phenyl groups are replaced by the electronegative Cl and Br substituents. High-resolution MALDI-TOF/ESI-MS data showed the expected molecular ion peaks, thereby further confirming that the halogenated products had formed (Figs S12, S16). It is important to emphasize that there are very few precedents for B-X (X = halide) substituted Tp derivatives, typically obtained as unexpected (by)products in reactions of hydrotris(pyrazolyl)borate transition metal complexes in chlorinated solvents.¹³

We next explored the displacement of the phenyl groups in **1** by reaction with $\text{CF}_3\text{SO}_3\text{H}$ as a strong Brønsted acid in deoxygenated CH_2Cl_2 (Scheme 1). Two divergent reaction pathways may be envisioned: (1) the strong acid may either attack at the aryl group to generate a Wheland-type intermediate with subsequent protodeborylation of the arene and recombination of boron with the triflate counterion, in a manner similar to the borylation reactions discussed above; (2) alternatively, the acid may lead to protonation of one of the pyridyl groups, a process for which there is some precedent in the chemistry of tris(pyrazolyl)borate and related metal complexes.¹⁴ Reaction of **1** with $\text{CF}_3\text{SO}_3\text{H}$ led to a bright yellow solution that was quenched with degassed water. **2-OTf** was isolated as a yellow solid in 47% yield.¹⁵ ^1H NMR analysis showed the expected set of four different aromatic proton signals, the ^{11}B NMR signal shifted downfield to +5.9 ppm, and a singlet was observed in the ^{19}F NMR spectrum at -76.2 ppm that is slightly shifted from that of free OTf^- (Figs S17-21). High-res MALDI-TOF MS analysis further confirmed the generation of the bis-triflate product (Fig S22). Complex **2-Br** can be prepared in a similar manner using HBr as the Brønsted acid (ESI).

Having the new B-X (X = Cl, Br, OTf) derivatives in hand, we next explored the possibility of further nucleophilic displacement of the halogen or triflate ions with anionic and neutral nucleophiles (Scheme 2). Precedents for such nucleophilic bridgehead substitutions are also rare. A related example is the nucleophilic displacement of chlorine in boron subphthalocyanines using silylated reagents $\text{Me}_3\text{Si-Nu}$ (Nu = CN, N_3 , OR) or aluminum hydrides.¹⁶ Bridgehead substitutions with neutral Lewis bases have been reported by Berionni *et al.* for triflimide-substituted, geometrically constrained boratriptycenes.¹² We note that the putative boratriptycene free Lewis acid intermediate in an $\text{S}_{\text{N}}1$ -type reaction is neutral, but in our case dissociation of the anionic substituent X results



Scheme 2. Synthesis of the parent complex **2-H** and dicationic complex **3-Py** via nucleophilic substitution and plausible intermediates.

in a destabilized cationic intermediate. On the other hand, the formation of such a cationic tricoordinate boron species may be promoted by intermittent dissociation of one of the pyridyl ligand from Ru, facilitating the planarization at boron.

Of particular interest was the reaction with a hydride source to access the hitherto unknown parent B-H derivative **2-H**. Reaction of **2-Br** with an excess of LiAlH₄ in anhydrous THF at 80 °C over a period of 5 d resulted in almost quantitative conversion to **2-H** according to ¹H and ¹¹B NMR analysis of the crude mixture. The product was isolated as a light-yellow solid in 76% yield after aqueous workup and column chromatography on silica gel with a mixture of toluene and pentane (1:1) containing 1% of NEt₃. The presence of the B-H functionality is reflected in both the ¹H (quartet at 4.71 ppm) and ¹¹B (doublet at -6.7 ppm) NMR spectra with ¹J(¹¹B, H) = 89 Hz) and further evidenced by a characteristic IR band at 2313 cm⁻¹ (Fig S37-S38, Table S1), which is significantly shifted relative to that of Tp₂Ru (2480 cm⁻¹).¹⁷ To explore the substitution with a neutral nucleophile, **2-OTf** was heated to 150 °C in neat 3-bromopyridine for 2 days, resulting in displacement of OTf anions with pyridyl groups to generate the dicationic complex **3-Py** in 71% yield.

The crystal structures (Fig 2) confirm that substitution reaction sequences at the bridgehead boron atoms proceed without affecting the coordination environment at Ru. The Ru-N distances for **1** of 2.049(2), 2.075(2), and 2.080(2) Å are in the typical range and consistent with the expected low spin configuration;¹⁰ both the Ru-N distances and N-Ru-N angles remain almost unchanged after substitution (Table S2). One exception is that one of the Ru-N distances is slightly shorter than the other two for compounds **1** and **3-Py**, but this is not seen for the other substituted species. Similarly, one of the C_{py}-B-C_{py} and C_{py}-B-C_{ph} angles is relatively smaller for **1** and **3-Py** but not for the other substituted derivatives. The B-C(py) distances of **1** and **3-Py** are also relatively longer, suggesting that steric effects of the phenyl / pyridyl substituent lead to distortions (see Fig S40). These structural features are well reproduced by density functional theory (DFT) studies at the B3LYP/LanL2DZ [Ru, Br] + 6-311G++(d,p) level of theory (Fig S41, Table S3). For **2-OTf**, which appears to be the first example of a structurally characterized triorganoboron triflate complex, the B-O bond distances of 1.579(8) Å [DFT, 1.563 Å] are on the longer side in comparison to other tetracoordinate boron triflate complexes, suggesting that the counterion is relatively weakly bound.^{16a, 18} Conversely, the B-N(py) distance of 1.608(6) Å [DFT, 1.637 Å] for **3-Py** is relatively short and indicative of strong binding of pyridine to a highly Lewis acidic boron center (cf. Py-B(C₆F₅)₃ 1.628(2) Å¹⁹). Finally, we note that compound **1** forms a peculiar extended structure with large solvent-filled cylindrical pores along the crystallographic *c*-axis (Fig S39). Similar supramolecular structures have been observed for *t*-butylphenyl Tpyb complexes of Mg(II), Fe(II) and Mn(II).⁶ None of the substituted complexes show channel-like supramolecular structures, thus the presence of *t*-butylphenyl groups on boron appears to be a prerequisite.

The absorption spectra of the Ru complexes were recorded in CH₂Cl₂ at RT (Fig 3a, Table 1). Strong bands were observed in

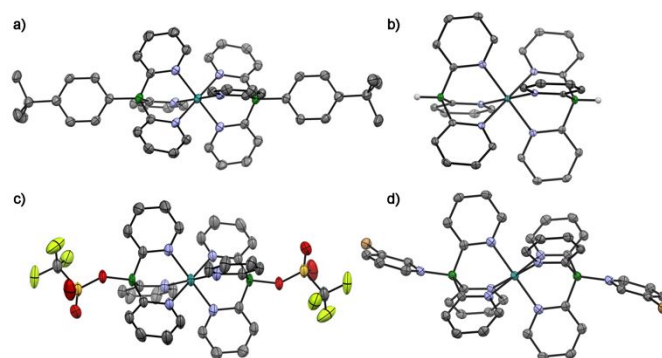


Figure 2. Plots of the X-ray structures of a) **1**, b) **2-H**, c) **2-OTf**, d) **3-Py** (thermal ellipsoids at 50%; all hydrogens except for B-H, benzene solvent molecules for **2-H**, and a water molecule for **3-Py** omitted for clarity. C (grey), H (white), B (dark green), N (blue), O (red), S (orange), F (yellow), Ru (turquoise).

the range of ca. 256 to 261 nm, which are due to π - π^* transitions of the ligands. Almost no effect of the substituents at boron on the position of these π - π^* transition is found. The lower energy absorptions with maxima in the range of 419 to 441 nm originate from metal-to-ligand charge transfer (MLCT; Ru^{II} \rightarrow π /Tpyb) as confirmed by TD-DFT calculations (Fig S42-S47), and they are responsible for the characteristic yellow color¹⁰ of the polypyridyl ruthenium complexes. Notably, replacement of the phenyl groups in **1** ($\lambda_{\text{max}} = 441$ nm) with H, Cl, Br, OTf, or Py⁺ leads to a distinct blue shift of the longest wavelength absorption, which is most pronounced for **2-OTf** ($\lambda_{\text{max}} = 419$ nm). Replacement of triflate with 3-bromopyridine results in a blue-shift back to 428 nm. This suggests a direct correlation of λ_{max} with the electron withdrawing character of the substituent and further indicates a high degree of ionic character of the B-O bond in **2-OTf**. The direct attachment of the substituent to boron is critical as similar effects are not observed when placing electron withdrawing substituents in *para*-position of the phenyl rings of **1**.¹⁰

The redox properties were studied by cyclic voltammetry in CH₂Cl₂. All complexes undergo a single reversible oxidation that is attributed to the Ru^{II}/Ru^{III} redox couple (Fig 3b). The Ru^{II}/Ru^{III} redox potential of **1** ($E_{1/2} = -128$ mV vs. Cp₂Fe⁺⁰) is consistent with those of the structurally similar complexes Ru(Tpyb-X)₂ (X = *p*-C₆H₄SiMe₃, *p*-C₆H₄),¹⁰ and that of **2-H** ($E_{1/2} = -138$ mV) is only modestly shifted to higher potential. In contrast, the oxidation of complexes **2-Cl** ($E_{1/2} = +110$ mV), **2-Br** ($E_{1/2} = +149$ mV) and **2-OTf** ($E_{1/2} = +292$ mV) occurs at much higher potential because of the electron-withdrawing effect of the electronegative substituents on boron, and that of **3-Py** is shifted even further due to the ionic charges. The redox potential increases in the order of **1** ~ **2-H** << **2-Cl** ~ **2-Br** < **2-OTf** < **3-Py**, indicating a gradual lowering of the metal-centered HOMO orbitals. The pronounced decrease in HOMO energy is largely consistent with computational data (Table S4) and coincides with the slight hypsochromic shift of the low energy MLCT transition in the UV-visible spectra discussed earlier. This in turn suggests a strong effect of the substitution pattern at boron on the electron density at the ligands and at Ru.

In conclusion, to explore the functionalization of tripodal tris(pyrid-2-yl)borate ligands at the bridgehead boron center,

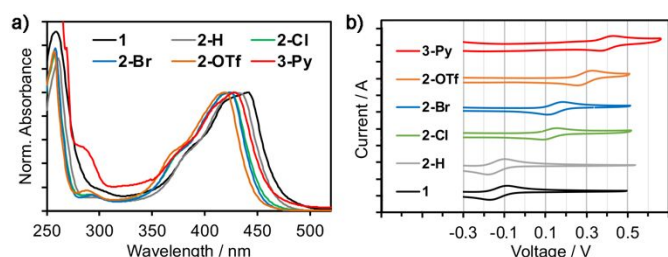


Figure 3. a) Comparison of normalized UV-vis absorption spectra in CH_2Cl_2 solution; b) cyclic voltammograms in CH_2Cl_2 containing 0.1 M $\text{Bu}_4\text{N}[\text{PF}_6]$ at 100 mV/s (referenced internally to $\text{Cp}^*\text{Fe}/\text{Cp}^*\text{Fe}^+$ at -560 mV vs $\text{Cp}_2\text{Fe}/\text{Cp}_2\text{Fe}^+$).

Table 1. Comparison of Spectroscopic and Electrochemical Data of Complexes **1**, **2-H**, **2-Cl**, **2-Br**, **2-OTf**, and **3-Py** in CH_2Cl_2 Solution

Compound	$\lambda_{\text{max}}^{\text{Abs}} / \text{nm}$ [a]	$E_{\text{gap, opt}} / \text{eV}$	$E_{1/2} / \text{mV}$ [b]	$\Delta E_p / \text{mV}$ [b]
1	441, 259	2.81	-128	87
2-H	428, 261	2.90	-138	83
2-Cl	424, 258	2.91	+110	70
2-Br	424, 258	2.92	+149	70
2-OTf	419, 257	2.96	+292	70
3-Py	428, 256	2.90	+396	80

[a] In CH_2Cl_2 solution. [b] From CV data in CH_2Cl_2 with 0.1 M $\text{Bu}_4\text{N}[\text{PF}_6]$ at 100 mV/s.

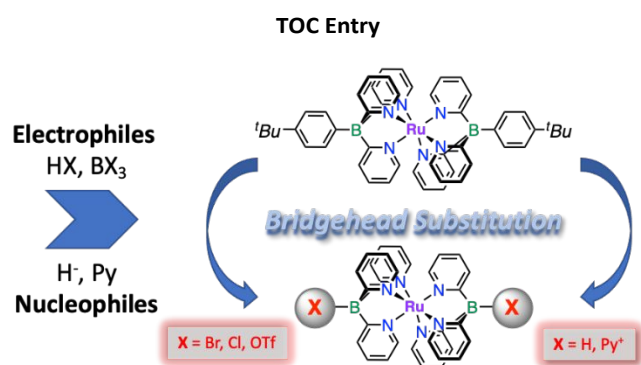
we prepared the octahedral low-spin Ru(II) complex **1** and examined its reactivity with strong Lewis and Brønsted acids. Remarkably, with $\text{BBr}_3/\text{BCl}_3$ selective bromination/chlorination at boron was achieved, suggesting that the boranes preferentially attack (and displace) the pendent *t*-butylphenyl groups without affecting the metal-ligand coordination sites. Treatment of **1** with the strong Brønsted acid $\text{CF}_3\text{SO}_3\text{H}$ resulted in formation of an OTf-substituted complex. Subsequent reactions with nucleophiles provided access to the parent hydride, **2-H**, and a dicationic pyridine complex, **3-Py**. The pronounced electronic effect of the substituents is reflected in the UV-vis and cyclic voltammetry data of the complexes. Our results pose interesting mechanistic questions that will be the subject of future investigations. The new bridgehead substitution approach opens up new routes for attaching these ligands to different molecular and polymeric scaffolds.

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A ruthenium tris(pyridyl)borate complex is subjected to electrophilic and nucleophilic reactions at the bridgehead boron atoms. These transformations allow for facile tuning of steric and electronic properties and open up new pathways to functional scorpionate complexes.