

Enhancing Electron Accepting Ability of Triarylboron via π -Conjugation with 2,2'-Bipy and Metal Chelation: 5,5'-Bis(BMes₂)-2,2'-bipy and Its Metal Complexes

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Triarylboron compounds with a high Lewis acidity/electron-accepting ability are highly sought-after materials because of their potential applications in olefin polymerization,¹ nonlinear optics,² organic light emitting diodes (OLEDs),³ and anion sensors.⁴ For applications as effective and competitive electron transport materials in OLEDs, in addition to being chemically and thermally stable, triarylborons are required to have a deep LUMO level with a strong electron-accepting ability. Stable triarylborons with a high Lewis acidity are also desired for use as fluoride sensors in aqueous or alcohol solvents to overcome the competing binding of protons for fluoride ions.⁴ B(C₆F₅)₃ ($E_{1/2}^{\text{red}} = \sim -1.17$ V vs FeCp₂⁺⁰)^{5a} and a number of diboron molecules based on fluorinated phenyl or biphenyl possess the strongest Lewis acidity among triarylborons.^{1,5} However, their general instability toward ambient air renders them unsuitable for applications in OLEDs or sensors. Stable triarylboron compounds usually contain two or three *ortho*-substituted aryl groups such as mesityl to protect the boron center from nucleophiles such as H₂O. This approach, however, sacrifices the Lewis acidity of the boron center due to the electron-donating nature of mesityls, as evidenced by the typical $E_{1/2}^{\text{red}}$ values (-2.0 to -2.8 V vs FeCp₂⁺⁰) of BMes₂(Ar).

One way to enhance the Lewis acidity or the electron-accepting ability of protected triarylboron is to link two or more boron centers to a π -conjugate unit. In fact, Kaim and co-workers have shown nearly two decades ago that, by connecting two BMes₂ groups with a phenyl or a biphenyl, the Lewis acidity of the molecule can be substantially enhanced.^{6a} Yamaguchi and co-workers have demonstrated that the attachment of three BMes₂ groups to a B(9,10-anthryl)₃ core can shift $E_{1/2}^{\text{red}}$ to -1.66 V vs FeCp₂⁺⁰, thus significantly increasing the electron-accepting ability.^{6b} Shirota and Noda have established that 5,5'-bis(BMes₂)-2,2'-bithiophene has a strong electron-accepting capability ($E_{1/2}^{\text{red1}} = -1.76$ V vs Ag/AgNO₃), enabling its successful use as an electron transport material in OLEDs.^{3a} Compared to phenyl, biphenyl, or thiophene, pyridyl or bipyridyl linkers should be more effective in enhancing Lewis acidity of triarylboron due to the electronegative nitrogen atoms. 2,2'-Bipy is especially attractive as a linker because of the possibility of further tuning the electron-accepting ability of the boron center by metal chelation. On the basis of these considerations, we have explored the synthesis of 5,5'-bis(BMes₂)-2,2'-bipy (B2bipy, **1**) and examined the impact of metal chelation on Lewis acidity and photophysical properties of **1**. The preliminary results are presented herein.

The synthesis of **1** was accomplished by the reaction of BMes₂F with 5,5'-(Li)₂-2,2'-bipy in a 2.2:1 ratio at -100 °C in $\sim 58\%$ yield. The two pyridyl rings are coplanar, as revealed by the crystal structure shown in Figure 1. **1** is stable toward ambient air and H₂O in solution and the solid state. Its cyclic voltammetry (CV) diagram in DMF has two reversible and highly reproducible

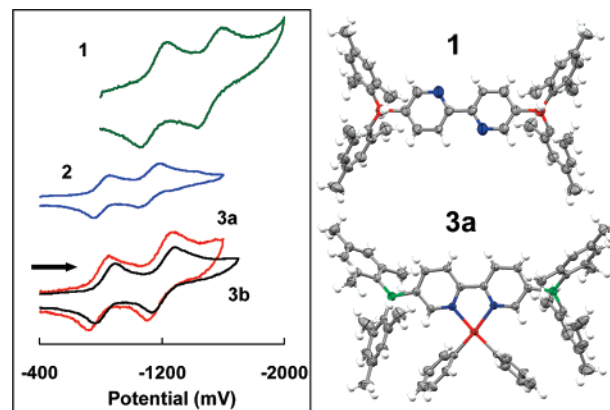


Figure 1. Left: cyclic voltammetry diagrams of **1**, **2**, **3a**, and **3b** versus Ag/AgCl reference electrode ($E_{1/2}^{\text{ox}}$ of FeCp₂ = 0.55 V) in DMF (0.10 M NBu₄PF₆, scan rate = 2 V/s for **1** and **3a** and 0.5 V/s for **2** and **3b**). Right: crystal structures of **1** and **3a**.

reduction peaks ($E_{1/2}^{\text{red1}} = -1.69$ V, $E_{1/2}^{\text{red2}} = -2.07$ V vs FeCp₂⁺⁰), attributable to the consecutive reduction of the two boron centers. The $E_{1/2}^{\text{red1}}$ of **1** is ~ 0.27 V more positive than that of BMes₂-(C₆H₄)₂-BMes₂ (ca. -1.96 V vs FeCp₂⁺⁰),^{6a} thus confirming that bipy is indeed more effective than biphenyl in enhancing the electron-accepting ability of the boron center. The difference between the first and the second reduction potential, $\Delta E_{1/2}^{\text{red}}$ (0.38 V), of **1** is 0.13 V greater than that of BMes₂-(C₆H₄)₂-BMes₂ (0.25 V), indicative of greater electronic communication between the two boron centers in **1**. It is noteworthy that $E_{1/2}^{\text{red1}}$ of **1** is similar to that of BMes(C₆F₅)₂ (-1.72 V vs FeCp₂⁺⁰).^{5a} The electronegative py rings and the coplanarity of the bipy unit that allows effective conjugation of the two boron centers in **1** are clearly responsible for its high Lewis acidity, relative to the biphenyl analogue. MO calculations have in fact confirmed that there is an extensive π -conjugation between the B atoms and the bipy unit (see Supporting Information).

Like 2,2'-bipy, **1** is an effective chelate ligand for metal ions as demonstrated by a Cu(I) complex, [Cu(B2bipy)(PPh₃)₂][BF₄] (**2**), obtained from the reaction of [Cu(CH₃CN)₂(PPh₃)₂][BF₄] with **1**, and two Pt(II) complexes, Pt(B2bipy)R₂, R = Ph, **3a**, R = Me, **3b**, obtained from the reactions of the corresponding [Pt(SMe₂)R₂]_n with **1**. The choice of these two metal ions is based on the fact that they are well-known to display metal-to-ligand (diimine) charge transfer (MLCT) transitions.^{7,8} **2** and **3a** are air stable in solution and the solid state, while **3b** appears to be sensitive to air. The crystal structure of **3a** determined by X-ray diffraction shows that the Pt(II) center has a typical square planar geometry (Figure 1). Like the free ligand **1**, all complexes also display two reversible and highly reproducible reduction peaks in their CV diagrams (Figure

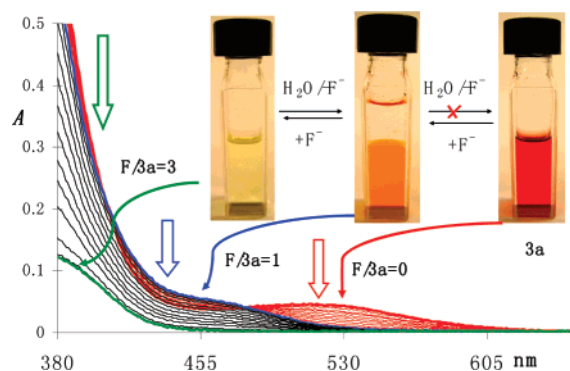


Figure 2. The MLCT region of the UV-vis titration spectra of **3a** (3.2×10^{-5} M) by TBAF in CH_2Cl_2 . The red region corresponds to the spectral change with the addition of 1 equiv of F^- . Inset: visual color change of **3a** (1.0×10^{-3} M) with the addition of 1 equiv of F^- (middle) and 3 equiv of F^- in CH_2Cl_2 and the reverse color switching after addition of H_2O (middle).

1). Most remarkable is that the reduction peaks of the complexes are much more positive than those of **1** (e.g., $E_{1/2}^{\text{red1}}$ is -1.36 V for **2**, -1.34 V for **3a**, and -1.38 V for **3b** vs Fc/Fc^+) and close to that of $\text{B}(\text{C}_6\text{F}_5)_3$ (~ -1.17 V),^{5a} demonstrating that the electron-accepting ability of B2bipy is much further enhanced by metal chelation. Similar change in reduction potential of substituted bipyridines upon coordination has been observed previously.⁹ Also noteworthy is the difference of $E_{1/2}^{\text{red1}}$ and $E_{1/2}^{\text{red2}}$ for the free ligand and the complexes: 0.31 V for **2**, less than that of **1**; 0.40 V for **3a** and 0.38 V for **3b**, similar to that of **1** (0.38 V).

In contrast to the colorless free ligand **1**, the metal complexes are all intensely colored orange for **2**, red for **3a**, and burgundy for **3b** in the solid state and in CH_2Cl_2 due to a broad metal-to-ligand (B2bipy) charge transfer band in the visible region. The MLCT band shifts to higher energy with increasing solvent polarity. Compared to the bipy chelate analogues, the MLCT band of the B2bipy complexes is red-shifted by ~ 100 nm (e.g., in CH_2Cl_2 , $\text{Pt}(\text{bipy})\text{Ph}_2$, $\lambda_{\text{MLCT}} = 438$ nm; **3a**, $\lambda_{\text{MLCT}} = 542$ nm), consistent with a deeper LUMO (π^*) of the B2bipy ligand. Because the MLCT transition involves the π^* orbital of B2bipy with significant contributions from the B atoms, it was anticipated to be sensitive to anion binding to the B centers, thus its possible use as an effective probe for anions. To test this idea, we chose to examine F^- binding to **2** and **3a**, due to the fact that protected triarylborons are known to bind to F^- with a high selectivity.⁴ To our delight, **2** and **3a** were found to change color instantly upon the addition of NBu_4F (TBAF) in organic solvents, and the resulting color is dependent on the ratio of $[\text{F}^-]/[\text{complex}]$.

In non-alcoholic solvents, two stages of color change were observed for both compounds; the addition of ~ 1 equiv of F^- changes the color of **2** from orange to yellow, **3a** from red to orange, and further addition of ~ 1.5 equiv of F^- changes **2** from yellow to colorless, **3a** from orange to light yellow. This two-stage color change can be attributed to the formation of a 1:1 (F^- :complex) adduct and a 2:1 adduct, respectively, and the sequential quenching of the MLCT band of the free complex and the 1:1 intermediate, as illustrated by the UV-vis spectral change and the corresponding color change of **3a** with F^- addition in Figure 2. Interestingly, the addition of H_2O to the solution of the 2:1 adduct reversed the color to that of the 1:1 adduct but not the original complex, an indication that the first F^- is tightly bound to the boron center. This observation was also confirmed by ^1H and ^{19}F NMR titration experiments which showed the nearly quantitative formation of the 1:1 product after the addition of 1 equiv of F^- to the complex, the requirement of

~ 2.5 equiv of F^- to form the 2:1 adduct, and the conversion of the 2:1 adduct to the 1:1 adduct after extraction by D_2O . Using the UV-vis titration data, the F^- binding constants K_1 and K_2 in CH_2Cl_2 were determined to be $\geq 10^9$ and $\sim 10^6$ M^{-1} for **3a**, respectively (see Supporting Information).

Consistent with the strong binding by the first F^- is the observation that **2** and **3a** are able to form the 1:1 adduct with excess F^- in the presence of methanol as established by UV-vis and NMR experiments. In fact, the addition of excess TBAF to **2** in a $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$ solution (1:4) resulted in the quantitative precipitation of the yellow 1:1 adduct $\text{Cu}(\text{B2bipyF})(\text{PPh}_3)_2$, **2F**, which has been fully characterized, further confirming the formation of the 1:1 adduct in methanol. The inability of the complex to bind to the second F^- in the presence of methanol is again due to the decreased Lewis acidity of the 1:1 adduct. The unusual ability of **2** and **3a** to bind to F^- in the presence of methanol confirms unequivocally the exceptionally high Lewis acidity of the boron centers in the complexes. **1** is also capable of binding 1 equiv of F^- in the presence of alcohol ($K \approx 10^4$ M^{-1}) or 2 equiv of F^- in non-alcoholic solvents ($K_1 \geq 10^8$ M^{-1} , $K_2 \approx 10^6$ M^{-1}), which can be monitored by either absorption or fluorescence spectra. The structure of the 2:1 adduct $[\text{NBu}_4]_2[\mathbf{1F}_2]$ was established by X-ray diffraction. Nonetheless, the metal complexes are clearly more attractive for anion binding/sensing applications because of their high Lewis acidity and the distinct visual MLCT-based color change.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada for financial support.

Supporting Information Available: Synthetic and experimental details, full characterization data, CV diagrams, UV-vis spectra, NMR and UV-vis titration data by TBAF, and all crystal data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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JA0725652