

Synthesis and ligand-based reduction chemistry of boron difluoride complexes with redox-active formazanate ligands†

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Mono(formazanate) boron difluoride complexes (LBF₂), which show remarkably facile and reversible ligand-based redox-chemistry, were synthesized by transmetallation of bis(formazanate) zinc complexes with boron trifluoride. The one-electron reduction product [LBF₂]⁻ [Cp₂Co]⁺ and a key intermediate for the transmetallation reaction, the six-coordinate zinc complex (L(BF₃))₂Zn were isolated and fully characterized.

The chemistry of coordination complexes bearing redox-active (or non-innocent) ligands has recently received increasing attention due to its potential application in small molecule activation and catalysis,¹ and its relevance to biological (enzymatic) transformations.² The most studied ligands in this class are dithiolenes/dioxolenes,³ α -diimines⁴ and bis(imino)pyridines.⁵ Formazanates (1,2,4,5-tetraazapentadienyls), which are nitrogen-rich analogues of the well-known β -diketiminates,⁶ have received comparatively little attention as ligands in coordination chemistry.⁷ Unlike β -diketiminates, which have a NCCCN backbone, formazanates feature a NNCNN backbone; the two additional nitrogen atoms provide formazanates with redox-active properties. Specifically, the reduced form of formazanates should be relatively accessible and stable due to delocalization of the SOMO over all 4 N atoms. This is in a way related to the stability of the analogous organic verdazyl radicals, which may be obtained from formazan precursors.⁸ In previous studies, we found that bis(formazanate) zinc complexes such as [PhNNC(*p*-tol)NNPh]₂Zn (**1a**) are capable of storing one or two electrons in the ligand frameworks to form stable singly- and doubly-reduced zinc complexes.⁹ The crystal structures of the reduced complexes show (weak) interactions between the internal nitrogen atoms of formazanate ligands and sodium counter cations. Based on this observation we anticipated that the reduction potential of bis(formazanate) zinc compounds could be altered by coordination to neutral Lewis acids. In the course of testing

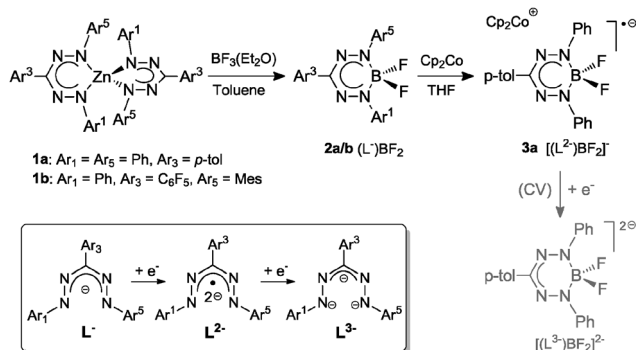
a range of Lewis acids for binding to **1a**, we found that BF₃ reacts cleanly *via* salt metathesis, opening a high-yield synthetic route to obtain mono(formazanate) boron difluoride (LBF₂) complexes which are difficult to access otherwise, either from the parent formazan or formazanate salts (LK or LNa). A related formazanate diacetate compound LB(OAc)₂ was described by Hicks and co-workers,^{7b} and although spectroscopic data suggested ligand-based 1-electron redox-chemistry to occur in these compounds, the 'borataverdazyl' radical anions obtained were too unstable to allow full characterization. Here we report the synthesis and X-ray crystallographic characterization of LBF₂ and the radical anion LBF₂^{•-}, with the formation of a relatively stable 2-electron reduction product LBF₂²⁻ confirmed by cyclic voltammetry. In addition, we provide evidence for the transmetallation pathway by characterization of a likely intermediate.

Mono(formazanate) boron difluoride complexes are readily accessible by transmetallation of bis(formazanate) zinc complexes with BF₃·Et₂O in hot toluene. In the case of (PhNNC(*p*-tol)NNPh)₂Zn (**1a**), a stoichiometric reaction does not go to completion, but full conversion is achieved by performing the reaction with 3 equivalents of BF₃·Et₂O at 70 °C twice. During the reaction, a colour change from deep blue to red and the precipitation of a white solid (presumably ZnF₂) was observed to indicate formation of mono(formazanate) boron difluoride complex (PhNNC(*p*-tol)NNPh)BF₂ (**2a**, Scheme 1), which was isolated as an air-stable, crystalline material in 86% yield. A single crystal X-ray diffraction study (Fig. S1, ESI†) revealed a distorted tetrahedral boron centre, which is displaced out of the (planar) formazanate NNCNN backbone by 0.5 Å. A similar bonding mode was observed for β -diketimate complexes of Sc and attributed to steric interactions.¹⁰ In the absence of significant steric pressure in **2a**, we ascribe the out-of-plane displacement of the B atom to packing effects; the observation of only one ¹⁹F NMR resonance for **2a** even at low temperature is consistent with a low-energy C_{2v} symmetric structure through which the two ¹⁹F environments exchange. As is the case in its parent zinc complex **1a** and the related mono(formazanate) boron diacetate complexes reported by Hicks and co-workers,^{7b} full delocalization within the formazanate framework in **2a** is indicated by the similar N–N and C–N bond lengths in the NNCNN backbone.

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Scheme 1 Synthesis of mono(formazanate) boron difluoride complexes and their reduction products.

The redox-active nature of the formazanate ligand in **2a** was established by cyclic voltammetry (CV) in THF solution with [Bu₄N][PF₆] electrolyte. Upon scanning to negative potentials, the CV shows two quasi-reversible one-electron redox processes (system I/I' and II/II', Fig. 1) that can be assigned to formazanate-based reductions. The first redox-couple of **2a** occurs at more positive potential ($E_{1/2}(I/I') = -0.98$ V vs. Fe^{0/+}) than that in **1a** (-1.31 V vs. Fe^{0/+})⁹ and at similar potential as Hicks *et al.* reported for the analogous mono(formazanate) boron diacetate compound (-0.86 V vs. Fe^{0/+} in CH₃CN).^{7b} A second redox-event is observed at more negative potential ($E_{1/2}(II/II') = -2.06$ V vs. Fe^{0/+}) but also this reduction is reversible. Based on these data, we infer that both one- and two-electron reduction products of **2a** are relatively stable and accessible. Importantly, the second reduction forms the dianion LBF₂²⁻, in which two electrons have been added to a single formazanate ligand to result in a 'L³⁻' fragment coordinated to the boron centre (Scheme 1). Bard *et al.* recently explored the voltammetry of boron dipyrromethenes (BODIPY): in general these show one-electron reductions at more negative potentials compared to **2a**.¹¹ Related β-diketiminato compounds show irreversible reductions at much more negative potential ($E_{p,red} \sim -2.6$ V vs. Fe^{0/+}).¹²

The first redox-couple of **2a** occurs at -0.98 V vs. Fe^{0/+}, which suggests that cobaltocene is a suitable reducing agent to selectively synthesize a singly-reduced product. Upon reaction of **2a** with one equivalent of Cp₂Co in THF, an immediate colour change from red to green is observed to indicate formation of the radical species

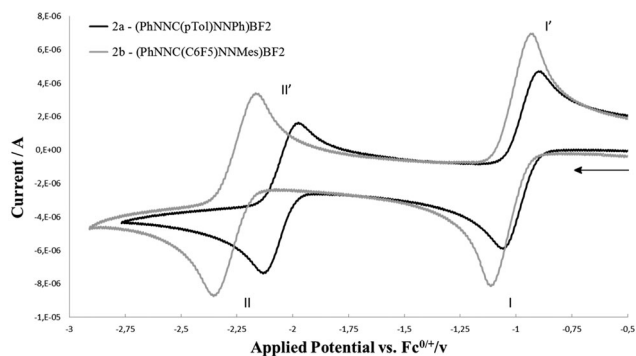


Fig. 1 Cyclic voltammetry of **2a** and **2b** (1.5 mM solution in THF, 0.1 M [Bu₄N][PF₆]) recorded at 100 mV s⁻¹.

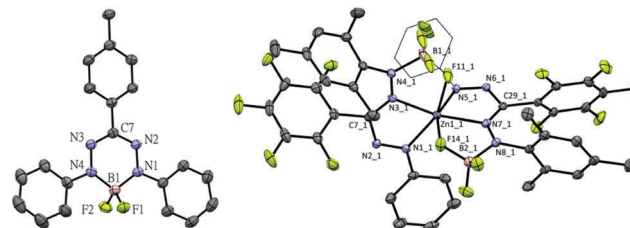


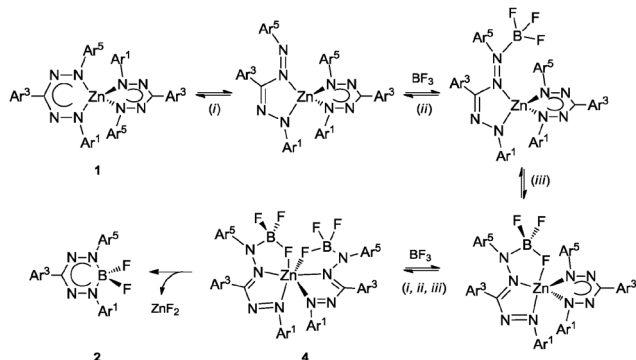
Fig. 2 Molecular structure of **3a** (left) and **4b** (right) showing 50% probability ellipsoids. For **3a**, [Cp₂Co]⁺ cation and THF molecule are omitted; for **4b**, one of the two independent molecules is shown; for both, hydrogen atoms are omitted for clarity.

[Cp₂Co]⁺[(PhNNC(*p*-tol)NNPh)BF₂]⁻ (**3a**). In contrast to the reduction product of the diacetate analogue reported by Hicks, the difluoro complex **3a** is stable in solution under an inert atmosphere for days and can even be boiled in THF–hexane without noticeable decomposition. The surprising stability of **3a** is likely due to the strength of the B–F bonds in comparison to B–OAc. Crystals of **3a** suitable for single-crystal X-ray diffraction analysis were obtained by diffusion of hexane into THF solution at room temperature in quantitative yield (Fig. 2, left). Compared with **2a**, **3a** has shortened B–N (av. 1.554 Å for **2a** vs. av. 1.535 Å for **3a**), elongated N–N (av. 1.309 Å for **2a** vs. av. 1.362 Å for **3a**) and elongated B–F (av. 1.376 Å for **2a** vs. av. 1.410 Å for **3a**) bond lengths. The similar N–N bond lengths in **3a** and the reduced L₂Zn complexes⁹ suggest the ligand of **3a** is a radical dianionic species (L²⁻) in which the unpaired electron occupies a N–N anti-bonding orbital.

UV-Vis absorption spectroscopy of neutral and anionic mono(formazanate) difluoride compounds provides additional evidence for ligand-based reduction and formation of the dianionic ligand radical (L²⁻) (Fig. S3, ESI[†]). The neutral compound **2a** shows a single broad absorption in the visible at 521 nm. In the case of **3a**, absorption is at longer wavelength (716 nm) and at 454 nm with shoulders at 674 and 431 nm, respectively. These absorption bands are in agreement with the presence of reduced formazanate ligands.^{9,13} The EPR spectrum of **3a** shows a broad EPR signal in frozen THF with *g*-value of ~ 2 (Fig. S2, ESI[†]). Attempts to synthesize and characterize the two-electron reduction product have so far been unsuccessful.

In order to expand the scope of transmetalation reactions from bis(formazanate) zinc complexes and boron trifluoride, the reaction of (PhNNC(C₆F₅)NNMes)₂Zn (**1b**) with BF₃ was attempted. The colour of the reaction mixture fades from deep to light orange upon heating **1b** in the presence of 3 eq. BF₃Et₂O at 70 °C overnight, but precipitation of ZnF₂ was not observed. Orange crystals of the product **4b** were obtained by slow diffusion of hexane into a toluene solution at -30 °C in 85% yield (Fig. 2, right). The crystal structure of **4b** shows a distorted octahedral zinc centre. In the structure, there are two tridentate (PhNNC(C₆F₅)NNMes(BF₃)) units coordinated to the Zn centre in a meridional fashion *via* two nitrogens and a fluorine atom to give a [NMF₂]₂Zn compound. This unusual binding motif results from interaction of BF₃ with the terminal nitrogen of the formazanate fragment (the NMe₃ group), which gives rise to 2 five-membered chelate rings upon coordination to the Zn centre. To the best of our knowledge, the structural characterization of this BF₃





Scheme 2 Proposed mechanism of transmetalation from bis(formazanate) zinc complex to mono(formazanate) boron difluoride complex.

binding mode has no precedent in the literature, although the 'frustrated Lewis pair' (tmp)MgCl/BF₃ has been postulated to contain a B–F fragment appended to a Mg–N(tmp) bond.¹⁴ The ¹⁹F-NMR of **4b** shows six distinct resonances with integration ratio of 1:1:3:1:1:1 (Fig. S6, ESI[†]). Five resonances with the same integration (1F) suggest that all F substituents of the C₆F₅ ring are inequivalent due to hindered rotation around the C–C₆F₅ bond. The resonance integrating as 3F shows ¹¹B and ¹⁰B coupling features and can be assigned to the BF₃ unit. The appearance of the BF₃ group in the ¹⁹F NMR does not change upon cooling to –55 °C, which suggests that the barrier to rotation around the N–BF₃ bond is low. Conversely, heating an NMR sample of **4b** to moderate temperature (65 °C for 24 h) does not result in changes in the spectroscopy, confirming that the octahedral [NMF]₂Zn complex is quite stable. Upon heating the NMR tube to 130 °C overnight, full conversion to **2b** is obtained. The ¹⁹F NMR spectrum of the new species shows signals characteristic for a freely rotating C₆F₅ group and a BF₂ unit (¹¹B NMR: –1.34 ppm, triplet with J_{B–F} = 24 Hz). These data are consistent with formation of [PhNNC(C₆F₅)NNMes]BF₂ (**2b**). Cyclic voltammetry of **2b** (Fig. 1) shows two quasi-reversible redox processes similar to **2a** but shifted to more negative potential. This suggests that the electron-rich N-Mes group in **2b** is more important than the electron-withdrawing C–C₆F₅ moiety in modulating the redox-potential of the formazanate fragment.

The sequential transformation **1b** → **4b** → **2b** suggests that a six-coordinate species related to **4b** is likely also involved in the formation of **2a**. Based on these observations, we propose the following mechanism for the transmetalation leading to compounds **4** (Scheme 2): (i) formazanate rearrangement from a 6- to a 5-membered chelate ring liberates the terminal N-atom, (ii) BF₃ binds to this terminal N-atom and brings a B–F group in proximity of the Zn centre, and (iii) the F atom binds to the Lewis acidic Zn(II) centre to form a tridentate [NMF] ligand with two 5-membered chelate rings. Repeating this sequence for the second formazanate ligand results in formation of the [NMF]₂Zn complex **4**. Elimination of ZnF₂ from this complex either occurs rapidly (in case of **1a** → '4a' → **2a**), or requires heating to proceed so that the intermediate can be isolated (**1b** → **4b** → **2b**). A reason for the increased stability of **4b** vs. that of putative intermediate **4a** could be the favorable π-interactions between the electron-rich N-Mes and the

electron-poor C–C₆F₅ substituents,¹⁵ which are present only when the formazanate ligands adopt a 5-membered chelate ring.

In conclusion, transmetalation of bis(formazanate)zinc complexes with BF₃·Et₂O provides a convenient entry into formazanate boron chemistry. The reaction likely occurs *via* initial binding of BF₃ to the formazanate ligand. This pathway is possible through the flexibility of the NNCNN backbone to adopt 5-membered chelate ring isomers, which are inaccessible to their β-diketiminate congeners. One-electron reduction of LBF₂ results in a fully characterized stable ligand-based radical, and cyclic voltammetry confirms a second reduction is possible, allowing access to three oxidation states (LBF₂^{0/–1/–2}) that are all based the redox-chemistry of a single formazanate ligand. The further development of this unique class of stable redox-active ligands towards applications in coordination chemistry and catalysis is the focus of ongoing work in our laboratory.

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