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Published in:
Chemical Communications

DOI:
10.1039/c4cc03244f

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Document Version
Publisher's PDF, also known as Version of record

Publication date:
2014

Link to publication in University of Groningen/UMCG research database

Citation for published version (APA):

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

M.-C. Chang and E. Otten*

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 (LBF₂)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 dihioles/dioxolenes,³ β-dimines⁴ and bis(imino)pyridines.⁵ Formazanates (1,2,4,5-tetraazapentadienyls), which are nitrogen-rich analogues of the well-known β-diketiminate,⁶ have received comparatively little attention as ligands in coordination chemistry.¹⁷ Unlike β-diketiminate, 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 framework 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 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,⁷⁷ and although spectroscopic data suggested ligand-based 1-electron redox-chemistry to occur in these compounds, the ‘bonavetardzy’ 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-diketiminate 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 C₂v 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,⁷⁷ 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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‡ Electronic supplementary information (ESI) available: Synthesis and characterization data for compounds 2a, b, 3a and 4b. CCDC 995403–995405. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c4cc03244f

DOI: 10.1039/c4cc03244f
Importantly, the second reduction forms the dianion $LBF_2$ equivalent of $Cp_2Co$ in THF, an immediate colour change from red suggests that cobaltocene is a suitable reducing agent to selectively reduce the formazanate ligand to result in a ‘$L^3-$’ fragment coordinated to the boron centre (Scheme 1). Bard et al. recently explored the voltammetry of $L^2Zn$ complexes and boron trifluoride, the reaction of (PhNNCN(C6F5)NNMes)2Zn with 3 eq. BF3 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 (PhNNCN(C6F5)NNMes(BF3)) units coordinated to the Zn centre in a meridional fashion via two nitrogens and a fluorine atom to give a [NNF$_2$]Zn compound. This unusual binding motif results from interaction of BF3 with the terminal nitrogen of the formazanate fragment (the NMes group), which gives rise to 2 five-membered chelate rings upon coordination to the Zn centre.

In order to expand the scope of transmetallation reactions from bis(formazanate) zinc complexes and boron trifluoride, the reaction of (PhNNNC(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 (PhNNNC(C6F5)NNMes(BF3)) units coordinated to the Zn centre in a meridional fashion via two nitrogens and a fluorine atom to give a [NNF$_2$]Zn compound. This unusual binding motif results from interaction of BF3 with the terminal nitrogen of the formazanate fragment (the NMes 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...
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. The 19F-NMR of 4b shows six distinct resonances with integration ratio of 1:1:3:1:1:1 (Fig. S6, ESIF). 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 11Ba n d10B coupling features and can be assigned to a B–F fragment appended to a Mg–N(tmp) bond. The 19F-NMR of [NNF]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 BF3 unit ([11F NMR: --1.34 ppm, triplet with JBF = 24 Hz). These data are consistent with formation of PhN[C(N)C6F5]2NNMebF3 (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 transmetallation 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 2n centre, and (iii) the F atom binds to the Lewis acidic Zn(n) centre to form a tridentate [NNF] ligand with two 5-membered chelate rings. Repeating this sequence for the second formazanate ligand results in formation of the [NNF]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, which are present only when the formazanate ligands adopt a 5-membered chelate ring.

In conclusion, transmetallation of bis(formazanate)zinc complexes with BF3Et2O 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-diketiminato 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 (LBF20→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.

Notes and references