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Stable, crystalline boron complexes with mono-, di- and trianionic formazanate ligands

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Redox-active formazanate ligands are emerging as tunable electron-reservoirs in coordination chemistry. Here we show that boron diphenyl complexes with formazanate ligands, despite their (formal) negative charge, can be further reduced by up to two electrons. A combined crystallographic, spectroscopic and computational study establishes that formazanate ligands are stable in mono-, di- and trianionic form.

Coordination complexes containing ligand systems that are accessible in several oxidation states ('redox-active' ligands) are attractive for catalysis¹ as well as materials applications.² Several classes of redox-active ligands are known but those that combine a modular, straightforward synthesis with excellent chemical stability across two (or more) different redox-states remain scarce. Lappert and co-workers have reported ligand-based reduction chemistry of the popular class of β -diketiminates,³ but these compounds are accessible only at very negative potentials (using strong reducing agents). Taking inspiration from the work by Hicks and co-workers,⁴ our group has started to investigate the (redox-)chemistry of formazanate ligands in coordination compounds. In recent years, we⁵ as well as others^{6,7,8} have taken advantage of the unusual chemistry and photophysics that formazanate ligands provide. In attempts to characterize in more detail the structures that result from ligand-based redox reactions in formazanate compounds, we reported previously that cyclic voltammograms of boron difluoride complexes indicate two sequential reductions take place to form the redox-series $[\text{LBF}_2]^{0/-1/-2}$.^{5b} Attempts to isolate the most reduced member of this series, the dianion $[\text{LBF}_2]^{2-}$, resulted in elimination of fluoride (as NaF) and formation of BN-heterocyclic products that derive from a putative boron carbenoid intermediate.⁹ Here we report (formazanate)boron diphenyl complexes that lead to stable 2-electron reduction products which are characterized by spectroscopic and crystallographic methods.

Scheme 1. Synthesis of (formazanate)boron diphenyl compounds and their reduction products.

The (formazanate)boron diphenyl complexes $(\text{PhNNC}(p\text{-tolyl})\text{NNCAr})\text{BPh}_2$ (Ar = Ph (**2a**); Ar = Mes (**2b**)) are obtained upon refluxing a toluene solution containing equimolar amounts of formazan (**1a** or **1b**) and BPh_3 for 3 days. Purification by column chromatography and recrystallization from hexane gave the products in 63% (**2a**) and 74% (**2b**) isolated yield. The ^{11}B NMR spectrum shows a broad singlet at 1.74 ppm (**2a**) and 2.27 ppm (**2b**), which is similar to the reported (formazanate)boron difluoride analogues^{5b} and suggests a four-coordinated boron centre. Single crystals of **2a** suitable for X-ray crystallography were obtained by recrystallization from hexane solution at -30°C (Figure S1 and Table S1).[†] Overall, the distorted tetrahedral geometry around boron is similar to that in the difluoride analogue, with the B atom displaced out of the plane defined by the 4 N atoms by 0.685 Å giving rise to crystallographically distinct B-Ph groups. However, exchange is fast on the NMR timescale and only one set of resonances is observed for the B-Ph groups in the ^1H and ^{13}C NMR spectra at room temperature. The intraligand N-N and N-C bonds are unremarkable, but the B-N bonds (1.5990(15)/1.5955(15) Å) in **2a** are significantly longer than in the corresponding boron difluoride (1.5589(16)/1.5520(16) Å) due to a decrease in Lewis acidity of the boron centre. Similar to the difluoride analogue, **2a** is weakly emissive in solution (THF: $\lambda_{\text{max}} = 505\text{ nm}$, $\lambda_{\text{em}} = 687\text{ nm}$; Stokes shift = 5246 cm^{-1}).

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

The electrochemical properties of compound **2a** were established by cyclic voltammetry in THF solution (Figure 1), which shows two quasi-reversible 1-electron redox-events at -1.35 and -2.26 V vs. Fc^{0/+}. In comparison with the boron difluoride analogues, the reduction potentials for **2a** are shifted to more negative potentials due to the presence of less electron-withdrawing B-substituents (Ph vs F). As anticipated, replacing an N-Ph substituent for N-Mes on the formazanate backbone (**2b**) results in a shift of the redox-potentials to more negative values. Moreover, the second reduction is clearly less reversible for **2b** and a new oxidation wave is observed at $E_{p,a} = -1.26$ V that likely results from a chemical transformation of the initial 2-electron reduction product.

Chemical synthesis and subsequent characterization of the reduction products of **2** was attempted. The radical anions **3a/b** were generated via treatment with 1 equiv of Cp^{*}₂Co and could be isolated as green crystalline material in good yield (structure of **3b** shown in Fig. 2). More surprisingly, the reaction of compounds **2** with 2 equiv of Na/C₁₀H₈ as reducing agent resulted in the clean formation of the dianions [(formazanate)BPh₂]²⁻, which were obtained in moderate yield as orange crystals of their disodium salts (**4a/b**) upon precipitation from THF/hexane (Scheme 1). While the 2-electron reduction of formazanate boron fluoride results in facile cleavage of both B-F bonds to form 2 equiv of NaF and a (transient) boron carbenoid species,⁹ the B-Ph bond in **4a/b** is thermally stable: when kept in THF solution at room temperature under an inert atmosphere no decomposition is noticeable over several days.

Figure 2. Molecular structures of **3b** (left), **4a** (middle) and **4b**₂ (right). Structures are showing 50% probability ellipsoids. Hydrogen atoms and THF molecules (except for the O atoms bonded to Na) are omitted, and Mes groups in **4b**₂ are shown as wireframe for clarity.

Single-crystal X-ray diffraction studies for compounds **3** and **4** show distorted tetrahedral geometries around the boron centre, with the ligands bound via the terminal N atoms to give 6-membered chelate rings (Figure 2). In comparison to the neutral precursor **2a**, compounds **3** and **4** show progressive elongation of the N-N bonds (e.g., **2a**: 1.3060(13)/1.3090(13) Å; **3a**: 1.369(4)/1.373(4) Å; **4a**: 1.428(3)/1.433(3) Å), consistent with ligand-based reduction which populates the ligand N-N π*-orbitals. At the same time, the N-C(Ar) distances shorten upon reduction, which is consistent with delocalization of electron-density into the N-Ar rings (*vide infra*). The crystal structure of compound **4a** (figure 2, middle) shows that in the solid state, the two Na⁺ ions are coordinated to the dianionic boron complex *via* the internal N atoms of the formazanate ligand (closest contacts are Na-N distances of 2.351(2) and 2.390(2) Å). In contrast to **4a**, the solid state structure of **4b** (figure 2, right) reveals a dimeric structure: the asymmetric unit contains two [(formazanate)BPh₂]²⁻ moieties that are bridged by two Na⁺ cations. Both of these sit in a coordination pocket formed by formazanate N-atoms and aromatic groups, so that no (for Na(1)) or only one additional THF molecule (for Na(2)) is bound to the cation. Interaction of alkali metal cations with the C(π) atoms of aromatic rings is increasingly recognized as an important structural element.^{10,11} Several relatively close contacts (<2.9 Å) between Na⁺ cations and aromatic carbon atoms are observed, but this does not lead to significant distortions within the aromatic rings. Thus, individual Na⁺-C(π) interactions are likely weak, but collectively they are sufficiently stabilizing to successfully compete with the more common O-donors of the THF solvent. The Mes-substituted N(4) and N(5) atoms in **4b** are significantly pyramidalized ($\Sigma\angle(N) = 346.1$ and 345.0°), but those substituted with a Ph group are not (av. 357.5°). This distortion is likely due to steric hindrance forcing the Mes group to rotate out of the plane of the ligand backbone, which prevents delocalization of π-electron density from the electron-rich formazanate backbone into the Mes ring. This is also borne out by the large difference between the N-C(Ph) and N-C(Mes) bond lengths (1.379(4)/1.377(3) and 1.435(4)/1.429(4) Å, respectively) that is in agreement with substantial double bond character for the N-C(Ph) groups.

In comparison to the neutral compounds **2**, the ^{11}B NMR resonances in (diamagnetic) dianions **4** are shifted upfield by ca. 3 ppm, in agreement with more electron-rich compounds. The NMR resonances for the *p*-CH of the N-Ph groups in dianion **4a** are found at δ 5.85 (^1H) and 109.7 ppm (^{13}C) due to significant charge-delocalization into the aromatic N-substituents of the formazanate ligand. For compound **4b**, the ^1H NMR spectrum at room temperature (400 MHz, $\text{THF-}d_8$ solution) shows exchange broadening of the N-Ph group while the other resonances are sharp. Upon decreasing the temperature, decoalescence occurs at ca. 15 °C to reveal 5 inequivalent ^1H environments for the N-Ph group due to restricted rotation around the N-C(Ph) bond. In contrast to **4b**, the N-Ph resonances in **4a** do not show this behaviour and exchange-averaged (albeit somewhat broadened) ^1H NMR resonances are observed down to -60 °C. We attribute this difference to the fact that in **4a**, resonance delocalization from the electron-rich, reduced formazanate backbone occurs into two aromatic groups (N-Ph), whereas in **4b** the perpendicular orientation of the N-Mes group does not allow this and only one N-Ph is involved. As a consequence, in **4b** there is more substantial N=C(Ph) double bond character which results in the restricted rotation observed experimentally. NMR lineshape analysis¹² for compound **4b** in the temperature range between -30 and + 65 °C allowed determination of the activation parameters for the exchange process as $\Delta H^\ddagger = 57.4 \pm 1.8 \text{ kJ}\cdot\text{mol}^{-1}$ and $\Delta S^\ddagger = 1 \pm 6 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ (see SI for details). Thus, the barrier to rotation is much higher than measured for the N-Ar bond in anilines ($\Delta G^\ddagger = 25.5 \text{ kJ}\cdot\text{mol}^{-1}$ for *N*-methylaniline).¹³ Although it is not as high as that in amides (70 – 95 $\text{kJ}\cdot\text{mol}^{-1}$),¹⁴ it indicates significant N-C(Ph) π -bonding due to the highly reduced nature of the formazanate ligand in **4**.

The solution EPR spectra of compounds **3** are more complex than the nine-line signals usually observed for organic verdazyl radicals,¹⁵ and show a multitude of hyperfine interactions. Simulation of the spectrum gave a satisfactory fit with inclusion of two pairs of (inequivalent) N atoms as well as the *ortho/para* phenyl-H and B atoms (Fig. 3 and S2).

Figure 3. Experimental and simulated EPR spectrum of **3b**. Simulation parameters: $g_{\text{iso}} = 2.0040$, $a(\text{N}_{1,4}) = 5.04 \text{ G}$, $a(\text{N}_{2,3}) = 5.17 \text{ G}$, $a(\text{H}_1) = 1.35 \text{ G}$, $a(\text{B}) = 0.98 \text{ G}$.

Gas phase DFT (B3LYP/6-311+G(d,p)) calculations were performed on the $[(\text{formazanate})\text{BPh}_2]^{0/-1/-2}$ compounds in the absence of the cations. The optimized geometries are in good agreement with the structures determined by crystallography.

The N-N bonds in **4a_{calc}** and **4b_{calc}** (1.402 – 1.417 Å) are significantly elongated in comparison to the neutral compounds **2** or radical anions **3**, but somewhat shorter than the crystallographically determined values. The pyramidalization of the N-Mes moiety observed in the dimer $\{\text{4b}\}_2$ is not reproduced in **4b_{calc}**, suggesting that this is due to interaction with the bridging Na^+ cations. Analysis of the molecular orbitals shows that the frontier orbitals (LUMO in **2**, SOMO in **3** and HOMO in **4**) are essentially identical, and are primarily of N-parentage with anti-bonding character between N atoms. An additional contribution comes from the adjacent aromatic rings, which show delocalization on the *ortho*- and *para*-positions and have π -bonding character between the N and $\text{Ph-C}_{\text{ipso}}$ atoms (shown for the HOMO in **4a_{calc}** in Figure 4, N-C(Ph) = 1.372 Å). This is also reflected by the calculated hyperfine interactions in the radicals **3**, with coupling constants of 1.2–1.5 G to the *o*- and *p*-H atoms. For compound **4a_{calc}**, a scan of the torsion angle between the N-Ph group and the ligand backbone, followed by transition-state calculations, gave a DFT-computed barrier for rotation around the N-Ph bond of $\Delta G^\ddagger = 52.9$ and $63.9 \text{ kJ}\cdot\text{mol}^{-1}$ for **4a_{calc}** and **4b_{calc}**, respectively. In the transition state for Ph rotation in **4a_{calc}** (Ph/NNCNN dihedral angle of 94°), the N-C bond to the perpendicular Ph group is elongated to 1.418 Å, whereas it is contracted to 1.367 Å for the Ph that is coplanar. The transition state for rotation around the N-C(Ph) bond in **4b** has both the N-Ph and N-Mes groups perpendicular, effectively preventing conjugation with the aromatic substituents and localizing the HOMO on the NNCCN backbone.

Figure 4. DFT calculated HOMO of **4a_{calc}** (left) and transition state of **4a_{calc}** (right).

In summary, we have shown that in boron diphenyl compounds, the monoanionic formazanate ligand can be cleanly converted to the corresponding dianionic (radical) and trianionic forms. The highly electron-rich ligand backbone in the latter complexes is stabilized by π -conjugation with the N-Ar substituents, leading to partial double bond character and restricted rotation of the N-C(Ph) bond. We are currently exploring the (ligand-based) reactivity of these highly reduced main group complexes toward small-molecule activation.

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Notes and references

† CCDC 1508653-1508657 contain the crystallographic information for compounds **2a**, **3a**, **3b**, **4a**, and **[4b]₂** in CIF format.

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