Formazans as β-diketiminate analogues. Structural characterization of boratatetrazines and their reduction to borataverdazyl radical anions†

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Formazans react with boron triacetate to produce boratatetrazines, which can be reduced to yield borataverdazyl radical anions—the first boron containing verdazyl radicals.

β-Diketimine ligands **1** have rapidly grown into one of the benchmark ancillary ligands in recent years.[1] With specific reference to main group chemistry, derivatives of **1** have been complexed to a substantial portion of s- and p-block elements and have proven to be effective in stabilizing unusual geometries and bonding modes. The popularity of this ligand family stems from their relative ease of synthesis, and the ability to readily tune ligand steric and electronic properties through substitution patterns on the nitrogen and carbon atoms of the ligand backbone.
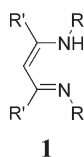
It stands to reason that ligand skeletons similar in structure to **1** could also be useful in main group complex chemistry. For example, the transition metal[2] and main group[3] coordination chemistry of triazapentadienyl ligands **2** is beginning to develop. Formazans **3** are a class of molecules known for well over a century[4] which bear a strong structural resemblance to β-diketimines. However, the coordination chemistry of formazans has only received sporadic attention,[5] and essentially *no* main group chemistry of formazans has been reported, save for some partially characterized boron complexes.[6] Herein we present preliminary forays into boron complex chemistry of derivatives of **3**, thereby demonstrating the potential formazans offer as viable alternatives to the β-diketimines.
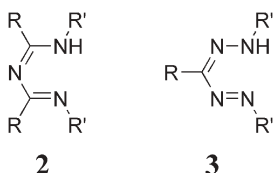
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Two 1,3,5-triaryl formazans **3a** and **3b** (**3a**: R = *p*-tol, R′ = Ph; **3b**: R = Ph , R′ = *p*-tol) were prepared by literature methods, *i.e.* addition of an arenediazonium salt to an *N*-aryl hydrazone.[4] Both derivatives were isolated in high yield as intense red (green to reflected light) crystals. X-Ray crystal structures‡ of both **3a** and **3b** were determined, and both compounds adopt the *syn,s-cis* ("closed") conformation adopted by some other formazans.[7] This structural isomer is required for subsequent η^2 coordination (see below; other structurally characterized trisubstituted formazans have the *anti* geometry with respect to the C=N bond, which would preclude their ability to chelate[7a,8]). In **3a** (Fig. 1), the NH proton (crystallographically located) asymmetrically bridges N2 and N4: the N2–H2N distance is normal at 1.16 Å and the N4–H2N distance is somewhat longer (1.52 Å). The corresponding NH proton in **3b** is even closer to being symmetrically bridging: the two N–H distances are much closer at 1.31 and 1.45 Å. The bond lengths within the formazan skeleton for both **3a** and **3b** show attenuated degrees of bond length alternation, suggesting a delocalized pi framework spanning the formazan frame. The ¹H NMR spectra show characteristic NH at 15.2 and 15.5 ppm for **3a** and **3b**, respectively.

Reactions of formazans **3a** and **3b** with boron trihalides (BX₃; X = F, Cl) gave complex mixtures and were not pursued further. In contrast, reactions with boron triacetate B(OAc)₃ (Scheme 1) afforded boratatetrazines **4a** and **4b** as dark purple solids in good
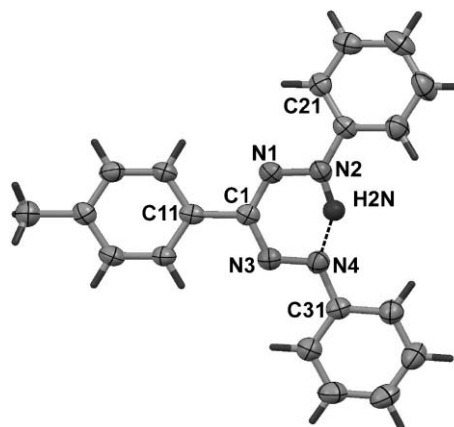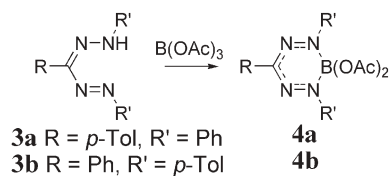

Fig. 1 Molecular structure of **3a**. Thermal ellipsoids at 50% probability. Selected bond lengths N1–N2 1.3123(19), N1–C1 1.338(2), N2–C21 1.398(2), N2–H2N 1.16(2), N3–N4 1.2859(19), N3–C1 1.373(2), N4–C31 1.412(2), N4–H2N 1.52(2), C1–C11 1.474(2) Å. Selected bond lengths for **3b**: N1–N2 1.318(4), N1–C1 1.350(4), N2–C21 1.417(5), N2–H1 1.39(2), N3–N4 1.311(4), N3–C1 1.364(5), N4–C31 1.406(5), N4–H1 1.45(2), C1–C11 1.464(5) Å.

Scheme 1

3a R = p-Tol, R' = Ph
3b R = Ph, R' = p-Tol

yields. The products were purified by recrystallization from hexanes. The ^{11}B NMR of both compounds consists of a singlet at 1.32 ppm. X-Ray structures of **4a** and **4b** were determined and confirm the formazan ligand bound to pseudo-tetrahedral boron in an η^2 fashion. The atoms in the BCN_4 six membered ring are nearly coplanar, with the B atoms in **4b** (Fig. 2) residing 0.14 Å above the CN_4 plane. The near equivalence of bond length pairs that are related by the pseudo-mirror plane are consistent with delocalization within the CN_4 skeleton of the formazan ligand. The average BN bond length in **4b** is 1.561 Å, comparable to the BN bonds found in a number of four coordinate boron complexes of β-diketiminates[9] or dipyrromethane[10]-type ligands.

Electrochemical studies on **4a** and **4b** reveal quasi-reversible reduction waves for each compound at −863 mV and −910 mV respectively vs. Fc/Fc$^+$ (Fig. 3). The reduction product, a radical anion, is formally related to neutral verdazyls which are well-known as a family of stable *neutral radicals*.[11] Three kinds of verdazyl radicals are currently known: partially saturated radicals **6**, carbonyl-based radicals **7**, and phosphorus analogues **8**.[12] In all cases the stability of the radicals is based on the nature of the singly occupied molecular orbital (**9**) which is delocalized over the four nitrogens of the six-membered ring.
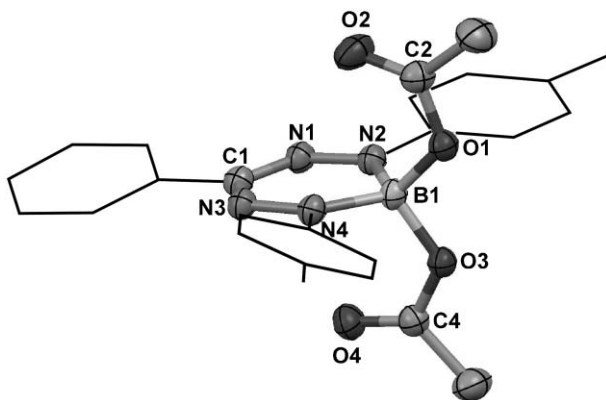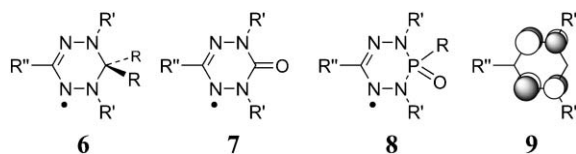

6   **7**   **8**   **9**

Fig. 2 Molecular structure of **4b**. Thermal ellipsoids at 50% probability. Hydrogen atoms are removed for clarity. Selected bond lengths: O1–B1 1.4556(16), O3–B1 1.4683(16), N1–N2 1.2976(14), N1–C1 1.3376(16), N2–B1 1.5623(16), N3–N4 1.3025(14), N3–C1 1.3361(16), N4–B1 1.5601(17) Å. Selected bond angles: N2–N1–C1 119.60(10), N1–N2–B1 123.87(10), N4–N3–C1 118.33(10), N3–N4–B1 125.03(10), N1–C1–N3 126.47(11), O1–B1–O3 103.77(9), N2–B1–N4 105.80(9)°.
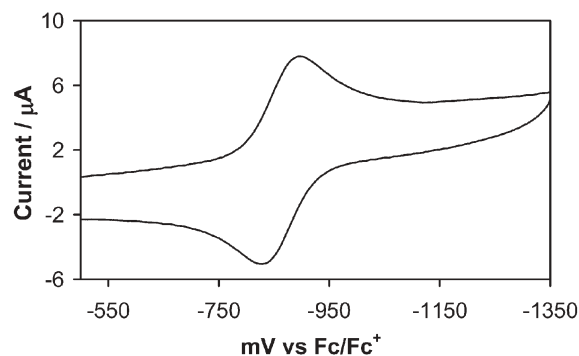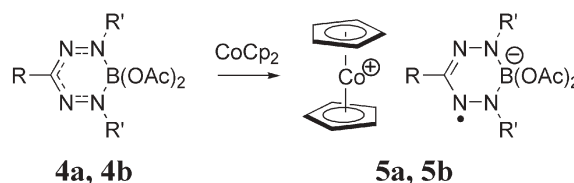

Fig. 3 Cyclic voltammogram of **4a** in CH_3CN (scan rate 100 mV s^{-1}, $Bu_4N^+BF_4^-$ electrolyte).

4a, 4b   **5a, 5b**

Scheme 2

The isolobal relationship between the borataverdazyl radical anion and neutral verdazyl radicals, coupled with the stability of the radical anion suggested by eletrochemical studies, prompted us to attempt a preparative scale reaction of what would be a "borataverdazyl" radical anion. Reactions of **4a** or **4b** with one equivalent of cobaltocene (Scheme 2) immediately produced green precipitates. These compounds are formulated as cobaltocenium salts of the borataverdazyl radical anions **5a** and **5b**.

The salts **5a** and **5b** are extremely air sensitive and decompose in solution even under inert atmosphere, making characterization (and crystallization) a challenge. However, satisfactory elemental analyses were obtained for both compounds and both show strong, featureless EPR signals in the solid state with g-values of ∼2. The most compelling evidence in support of the proposed structure comes from solid state electronic spectroscopy (collected in diffuse reflectance mode) shown in Fig. 4. The spectra of formazan **3a** and boratatetrazine **4a** (red and purple lines, respectively) are consistent with their solution spectra and, in the case of **3a**, with the spectra of other 1,3,5-triarylformazans with the
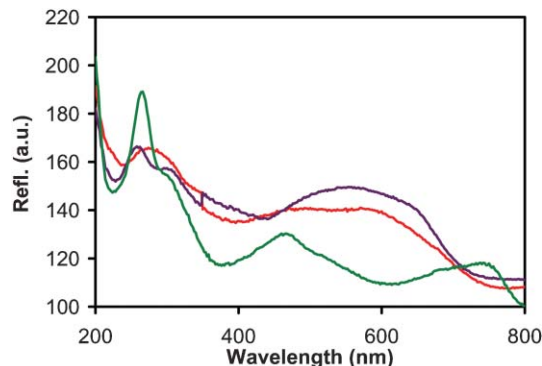

Fig. 4 Diffuse reflectance spectra of formazan **3a** (red line), boratate-trazine **4a** (purple line), and radical anion **5a** (green line).

closed conformation. The spectrum of **5a** has a low energy maximum at 738 nm, which is very close to the longest wavelength absorption maximum of derivatives of 1,3,5-triarylverdazyls **6** (R′ = R″ = Ar). Importantly, the consistency between absorption maxima of **5** is with derivatives of **6**—which can be understood on the basis of the isolobal relationship between *neutral* tetrahedral carbon and *anionic* tetrahedral boron; the electronic spectra of the carbonyl-containing verdazyls **7** are substantially different because of the additional conjugation of the verdazyl chromophore with the carbonyl π manifold.

In summary, we have reported the synthesis and structural characterization of 'boratatetrazines', boron complexes of the formazan ligand. This highlights the potential versatility of formazans for main group chemistry, and in addition we have demonstrated a facet of formazan chemistry that is not, to our knowledge, available to β-diketiminates or other related ligands: the ability to convert inorganic heterocycles to stable radical analogues. Current efforts are devoted to further enhancing the stability of the radical anions *via* substituent effects and exploration of other main group element formazan chemistry.

Notes and references

‡ *Crystal data for* **3a**: $C_{20}H_{18}N_4$, M = 314.38, monoclinic, $P2_1/c$, a = 11.7762(8), b = 13.4272(9), c = 12.0220(8) Å, β = 118.5943(12)°, V = 1669.08(19) Å³, Z = 4, T = 193 K, 3429 independent reflections, $R1$ = 0.0503, $wR2$ = 0.1364. *Crystal data for* **3b**: $C_{21}H_{20}N_4$, M = 328.41, orthorhombic, *Pbca*, a = 7.830(1), b = 21.154(2), c = 22.289(3) Å, V = 3691.9(8)Å³, Z = 8, T = 296 K, 2431 independent reflections, $R1$ = 0.055, $wR2$ = 0.128. *Crystal data for* **4a**: $C_{24}H_{23}BN_4O_4$, M = 442.27, triclinic, $P\bar{1}$, a = 10.3612(15), b = 14.925(2), c = 15.608 (2) Å, α = 103.098(2), β = 97.538(2), γ = 95.549(2), V = 2310.5(6) Å³, Z = 4, T = 193 K, 9430 independent reflections, $R1$ = 0.0514, $wR2$ = 0.1460. *Crystal data for* **4b**: $C_{25}H_{25}BN_4O_4$, M = 456.30, triclinic, $P\bar{1}$, a = 9.8688(13), b = 10.6690(14), c = 12.4677(17) Å, α = 87.363(2), β = 80.634(2), γ = 66.5696(18)°, V = 1188.2(3) Å³, Z = 2, T = 193 K, 4822 independent reflections, $R1$ = 0.0394, $wR2$ = 0.1117. CCDC 613050–613053.

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