A Binuclear 1,1′-Bis(boratabenzene) Complex: Unprecedented Intramolecular Metal–Metal Communication through a B−B Bond

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Abstract: *We report the synthesis of the first 1,1′-bis(borata-benzene) species by tetrabromodiborane(4)-induced ring-expansion reactions of cobaltocene. Six equivalents of cobaltocene are required as the species plays the dual role of reagent and reductant to yield $[\{(\eta^5\text{-}C_5H_5)Co\}_2\{\mu:\eta^6,\eta^6\text{-}(BC_5H_5)_2\}]$. The formally dianionic bis(boratabenzene) moiety with a boron–boron single bond can be viewed as a symmetric dimer of the parent boratabenzene anion as well as the first example of a diboron analogue of biphenyl. The solution electrochemistry of the bimetallic complex shows four stepwise redox events, indicating significant intramolecular interaction between the cobalt ions across the 1,1′-bis(boratabenzene) unit. The magnetic properties, as investigated by variable-temperature SQUID magnetometry, reveal weak intramolecular antiferromagnetic interactions. Density functional theory calculations support the experimental results and add insight into the various electronic states of the complex.*

Boratabenzene systems are negatively charged boron-containing 6π-heteroatomic aromatic systems isoelectronic to the cyclopentadienyl anion (Cp).[1] Nomenclature for these systems classifies them based on the nature of the exocyclic substituent's interaction with the boron center.[2] As seen in Figure 1 this interaction is typically conceived as either a) a
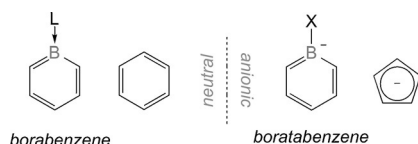

Figure 1. Classification of borabenzenes with their carbon-based analogues; L = neutral Lewis base, X = anionic Lewis base.

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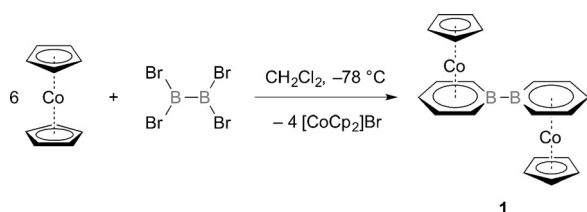http://dx.doi.org/10.1002/anie.201603437.

borabenzene system, coordinating a Lewis base in an effort to stabilize the vacant p orbital on boron,[3] or b) a boratabenzene system, in which a traditional covalent bond between the boron and the exocyclic substituent exists, resulting in a formal negative charge for the aromatic system.[4] While borabenzene species are typically thought to feature full 6π-electron delocalization over all five carbons and the boron atom of the heteroatomic ring, the anionically charged boratabenzene systems feature delocalization primarily across the five carbon atoms of the ring and only partially interact with the boron substituent. Accordingly, borataben-zenes typically feature B-bound substituents which tend to reduce the electron deficiency of the boron atom.[5]

In view of the use of boratabenzene systems as ligands in coordination chemistry, the strength and nature of this exocyclic bond provides a means to vary their electron-donating ability and hence the electronic properties of the metal center.[2b] By the formal coupling of two boratabenzene rings through the boron atoms, we hypothesized that a less electron-donating derivative would be formed that could prove beneficial for mediating electronic communication between redox-active metal centers due to a stronger metal-to-boron interaction. We present herein the synthesis of a dinuclear cobalt complex with the μ-bridging 1,1′-bis(bor-atabenzene) ligand and demonstrate its ability to transmit intramolecular metal–metal interactions.[6–8] To our knowledge, this represents the first instance where an interaction between metal ions is observed across a diborane interme-diary.[9]

An effective method for the preparation of transition-metal boratabenzene complexes is based on a ring-expansion reaction of Cp ligands with functionalized dihaloboranes.[2,10] Changing the boron reagent to a tetrahalodiborane(4) and using cobaltocene as cyclopentadienyl source proved successful in constructing the new metal-bridging diboron ligand. Treatment of six equivalents of cobaltocene with tetrabromodiborane(4) at −78 °C led to the formation of the double-ring-expanded bis(boratabenzene) species (**1**, Scheme 1) in moderate yields (39%). The reaction is unique in that it features cobaltocene playing a dual role in which two equivalents are consumed in the ring expansion and four equivalents are consumed as the reductant. Workup of the product yielded $[\{(\eta^5\text{-}C_5H_5)Co\}_2\{\mu:\eta^6,\eta^6\text{-}(BC_5H_5)_2\}]$ (**1**) as a dark violet crystalline solid featuring a melting point of 145 °C with thermal decomposition in excess of 223 °C. The paramagnetic proton NMR spectrum of **1** exhibits four broad singlet resonances at $\delta = 32$, 28, and −51 ppm for the protons of the boratabenzene rings and a broad singlet at $\delta = −57$ ppm for the cyclopentadienyl ring protons, consistent

Scheme 1. Synthesis of 1,1′-bis(boratabenzene) complex **1**.

with the inversion symmetry of the complex. The ^{11}B-$\{^1$H$\}$ NMR signal is observed at $\delta = 79$ ppm, which is remarkably shifted away from the typical region for transition-metal boratabenzene complexes as a result of the influence of the paramagnetic metal centers.[2] A magnetic susceptibility measurement performed on **1** in solution (Evans method; $\mu_{eff} = 2.3\ \mu_B$)[11] is consistent with the metal centers being in a low-spin d^7 electronic state, each containing an unpaired electron.

Crystals suitable for single crystal X-ray diffraction were grown from a saturated *n*-hexane solution of **1** at low temperature. Analysis of the molecular structure (Figure 2) shows that the bond lengths within the BC_5 ring are closely akin to most known η^6-coordinate boratabenzene transition-
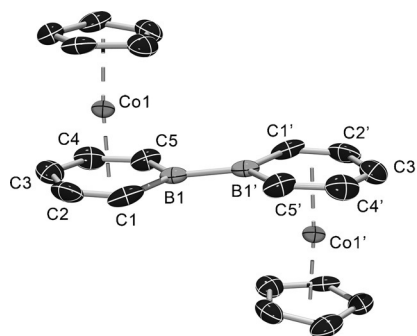

Figure 2. ORTEP projection for the molecular structure of **1**. Ellipsoids are set at 50% probability; hydrogen atoms are omitted for clarity. Selected symmetry-related atoms are labeled with an apostrophe. Selected bond lengths [Å]: B1-B1′ 1.71(1), B1-Co1 2.277(8), C3-Co1 2.09(1), Co1···Co1′ 5.76, B1-C1 1.57 [avg.], C1-C2 1.38 [avg.], C2-C3 1.425 [avg.].

metal systems with average B–C distances of 1.57 Å and average C–C distances of 1.40 Å.[2] The boron–boron bond between the bis(boratabenzene) rings is difficult to discuss with accuracy due to an inversion center lying between the B–B unit, but can be estimated to be 1.71(1) Å, which is in the typical range of B–B single bonds.[12] The cobalt–cobalt separation in the *trans*-configured structure is 5.76 Å and thus slightly longer than in the all-cyclopentadienyl analogue (ca. 5.1 Å for bicobaltocene).[13] Examination of the BC_5H_5 ring shows a bending of the boron atom towards the metal center by approximately 6°, contrary to related boratabenzene complexes in which the boron atom is displaced away from the metal.[2] This can be attributed to the absence of an electron-donating boron substituent and thus a more pronounced electron-deficiency at the boron atom.

The EPR spectrum of **1** was measured in toluene glass at 20 K (see Figure S2 in the Supporting Information). It exhibits a broad resonance centered near $g = 2$, with superimposed ^{59}Co ($I = 7/2$) hyperfine couplings, and a broad downfield signal at $g \approx 4.6$. The resolved lines were simulated with rhombic spin Hamiltonian parameters ($g_1 = 1.863$, $g_2 = 2.022$, and $g_3 = 2.117$; $A_1 = 161$, $A_2 = 84$, and $A_3 = 424$ MHz) that are in line with EPR data of other low-spin boratabenzene cobalt(II) complexes.[6a, 14] The observed broad features, in particular the signal with zero crossing at around $g = 4.5$, suggest that a triplet state ($S = 1$) is populated at this temperature. This interpretation is supported by solid-state SQUID magnetic measurements, which indicate that the individual cobalt ions in **1** have the $S = \frac{1}{2}$ spin state and are only weakly antiferromagnetically coupled with an exchange coupling constant $J = -6.0\ cm^{-1}$ ($\hat{H} = -2J\hat{S}_1 \cdot \hat{S}_2$ Hamiltonian; see Supporting Information for details). The small value for J indicates that the $S = 1$ state lies only slightly above the singlet ground state and is thus appreciably populated at temperatures above 10 K. In contrast, the closely related bis(boratabenzene) complex with a *para*-phenylene spacer shows a stronger antiferromagnetic coupling ($J = -28.0\ cm^{-1}$), despite a longer metal–metal separation.[7] The B–B bond in the bis(boratabenzene) **1** thus seems to be a poor mediator for magnetic exchange, leaving the metal ions largely magnetically isolated. To accurately describe the temperature dependencies of the magnetic moments of **1** in the range of 2–295 K, intermolecular interactions had to be taken into account (Weiss constant $\Theta = -8.3$ K). This may be related to the molecular packing of **1** which shows a perpendicular arrangement of neighboring molecules that is held together by a network of close C-H···B contacts (ca. 3.18 Å).

The redox properties of the dicobalt compound (**1**) were studied using cyclic voltammetry (CV) and differential pulse voltammetry (DPV). Complex **1** displayed two closely spaced oxidation waves and two well-resolved reduction waves, corresponding to the $[\mathbf{1}]^{0/1+}$, $[\mathbf{1}]^{1+/2+}$, $[\mathbf{1}]^{0/1-}$, and $[\mathbf{1}]^{1-/2-}$ redox couples, respectively (see Figure 3). The oxidation processes
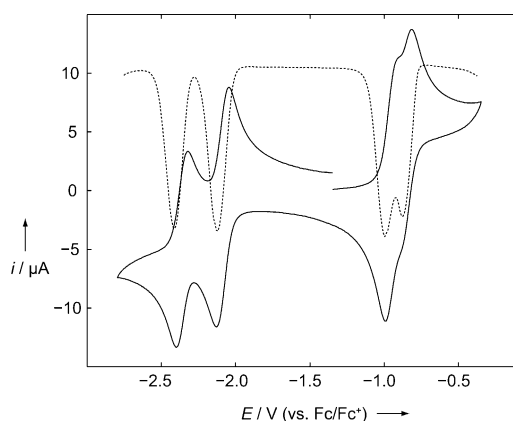

Figure 3. Cyclic voltammogram (——) and differential pulse voltammogram (•••••) of **1** in THF with 0.1 M [nBu$_4$N][PF$_6$] as the supporting electrolyte. Formal potentials: $E_{1/2}(1) = -0.84$ V, $E_{1/2}(2) = -0.94$ V, $E_{1/2}(3) = -2.09$ V, and $E_{1/2}(4) = -2.36$ V (relative to the Fc/Fc$^+$ couple; Fc = [(η^5-C$_5$H$_5$)$_2$Fe]).

are identified as Co^{II}/Co^{III} and the reduction processes as Co^{II}/Co^{I} couples by the similarity of their E values to those of related (η^6-boratabenzene)(η^5-cyclopentadienyl)cobalt complexes.[6,7] The separation of the two oxidation events in the cyclic voltammogram of **1** ($\Delta E = 102$ mV) suggests an approximate comproportionation constant of $K_c = 10^{1.7}$, whereas the second pair of redox couples associated with the two reduction events features a markedly higher comproportionation constant of $K_c = 10^{4.6}$ ($\Delta E = 272$ mV).[15] These findings reveal clear evidence for interaction between the metal centers, with a more pronounced electronic coupling in the mixed-valent monoanion than in the monocation.[16] The electronic interaction is stronger than in the related bimetallic cobalt complex containing a *para*-phenylene bridge, which shows no resolvable separations between the $Co^{III/II}$ and $Co^{II/I}$ redox couples, but considerably weaker than in bicobaltocene ($\Delta E = 395$ mV for the $Co^{III/II}$ couple).[13] As a result of the comparatively electron-deficient boron atoms in **1** the delocalization of positive charge is reduced, leading to a more localized structure.

Using ferrocenium hexafluorophosphate ([Cp_2Fe][PF_6], Cp = cyclopentadienyl) as the oxidant we tried to quantify the voltammetric data by isolation of the singly and doubly oxidized analogues of **1**. Oxidation of the bis(boratabenzene) species was performed with either one or two equivalents of ferrocenium hexafluorophosphate ([Cp_2Fe][PF_6], Cp = cyclopentadienyl) in 1,2-difluorobenzene yielding the mono- and dicationic species, respectively. Both species were found to be poorly soluble in 1,2-difluorobenzene and could only be redissolved in either acetonitrile or nitromethane, however, the mono- and dications are not stable in these solvents and will gradually decompose. The mixed-valent monocation could only be identified by EPR spectroscopy (see Figure S3), whereas the dication allowed characterization by NMR spectroscopy. Characteristic ^{1}H NMR signals for the Cp ($\delta = 5.77$ ppm) and boratabenzene ligands ($\delta = 6.97$, 6.77 and 6.19 ppm) indicate a diamagnetic ground state of the dication $[\mathbf{1}]^{2+}$ with the cobalt ions in a low-spin d^6 configuration and the formation of only one isomer. The ^{11}B NMR chemical shift is at $\delta = 24.5$ ppm, which is in the typical range for η^6-boratabenzene transition metal complexes.[2] Preparative oxidation of **1** supports the voltammetric conclusions of successive one-electron, metal-centered oxidation events leading to a closed-shell dicobalt(III) complex.

To gain further insight into the intricate and diverse electronic states of bis(boratabenzene) complex **1**, energy minimization calculations were conducted within Kohn–Sham density functional theory (DFT) at the OLYP/TZP level. The energetics of the different spin states were investigated so as to have a good characterization of the resulting oxidation and reduction products. The variation of the spin states of the neutral system provide strong corroborating evidence to the experimental data obtained via EPR and solid-state SQUID magnetic measurements. Notably the $S = 1$ state is less stable than the $S = 0$ ground state by a marginal 19 cm^{-1} in line with the $S = 1$ state being appreciably populated at temperatures above 10 K.

The molecular orbital contributions of the valence orbitals yield an explanation for the near identical geometries of both

the $S = 0$ and $S = 1$ spin states. That is, in the HOMO of the $S = 0$ state, both of the electrons are situated in the $d_{x^2-y^2}$ orbital on separate cobalt centers, whereas in the $S = 1$ spin state the electrons are no longer confined to individual metal centers. However, the predominant contributions towards both the HOMO and the HOMO−1 molecular orbitals are still composed of the $d_{x^2-y^2}$ orbitals on both of the cobalt centers. The molecular orbital contributions for the $S = 0$ state also highlight an important characteristic of the $S = 0$ spin state, that is, the confinement of the spin paired α and β electrons to individual cobalt centers indicates that the ground state $S = 0$ spin state is a potential candidate to form a neutral singlet biradical. This apparent spin-pairing between electrons that appear to be nearly entirely situated on separate metal centers suggests a degree of communication between the cobalt metal centers within the $S = 0$ state. Figure 4 displays the HOMO−2 of the $S = 1$ state for both the
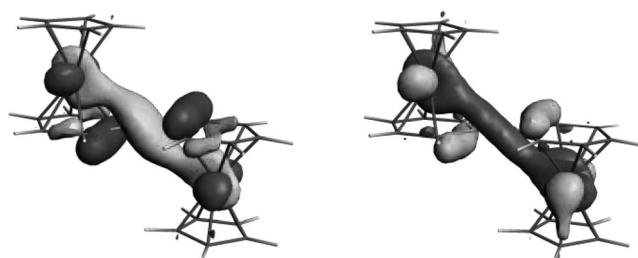

Figure 4. HOMO−2 of the neutral $S=1$ system, both the α (left) and β (right) electrons.

α and β electrons, respectively. It clearly shows that there is significant conjugation between the two cobalt centers mediated via the B−B bond, thus allowing for electronic interaction between them. Thus, whilst the $S = 0$ and $S = 1$ states are both likely to be occupied at temperatures above 10 K, it would appear that both spin states have a viable mechanism available for intramolecular metal–metal communication.

In summary, we have prepared a bimetallic transition-metal complex with a bridging bis(boratabenzene) ligand containing a boron–boron single bond. The dianionic diboron ligand, which can be viewed as an isoelectronic and isostructural analogue of biphenyl, was shown to facilitate electronic coupling between the metal sites, as evidenced by the potential separations between successive one-electron redox events in the cyclic voltammogram. The extent of metal–metal communication thereby depends on the charge of the metal atoms, with the negative charge being more efficiently delocalized across the bis(boratabenzene) unit. Magnetic studies indicate that the cobalt(II) ions are weakly antiferromagnetically coupled across the bridge. Our current efforts are directed at the isolation of the free bis(boratabenzene) ligand by decomplexation of the η^5-cyclopentadienyl cobalt moieties and at the characterization of the mixed-valence analogues.

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[17] CCDC 470487 (**1**), contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif..