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Communication

Triple-Decker Iron and Cobalt Complexes Featuring a Bridging 1,2-Diboratabenzene Ligand

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ABSTRACT: Neutral triple-decker iron and cobalt complexes with a bridging 1,2-diboratabenzene ligand were accessed by reactions of a dilithium 1,2-diboratabenzene reagent with $[Cp^*FeCl]_2$ and $[Cp^*CoCl]_2$, respectively. While 1,2-diboratabenzene metal complexes are known, these represent the first examples of the ligand bridging two metals.

Organometallic sandwich complexes have rich chemistry that has been leveraged in olefin polymerization,[1] materials science,[2] single-molecule magnets,[3] redox probes,[4] and many other applications.[5] The most commonly studied sandwich complexes are metallocenes, species comprised of two unsaturated polycyclic carbon-based ligands bound to a metal center.[6] Within this class, ferrocene and cobaltocene are archetypical examples that have gained attention for their redox chemistry and feature the five membered anionic cyclopentadienide ligand (Cp).[7] The robust 18 electron ferrocene is a useful redox probe while the 19 electron cobaltocene is a potent reducing agent, in both cases leveraging one-electron redox chemistry.[7b,8]

The anionic charge of cyclopentadienide results in strong binding to electropositive metal centers (Figure 1).[7c,9]

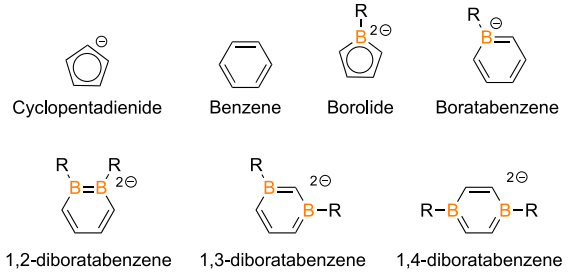

Figure 1. Selected carbon-based and boracyclic aromatic ligands.

Borolide ligands are dianionic variants of Cp that have one boron in the ring (BC_4) and can drastically impact the redox properties of metal centers, recently exemplified with nickel.[10] In six membered systems, a boron atom can be substituted into benzene resulting in anionic boratabenzene ligands that are stronger donors than benzene and comparable to Cp.[11] Incorporating a second boron atom into benzene, a diboratabenzene, increases the charge to dianionic, which has not been widely explored.[12] Three possible isomers of diboratabenzene exist, with boron atoms in the 1,2-, the 1,3-, or the 1,4-positions. The 1,2-diboratabenzene species has been isolated as a dilithio salt and in transition metal complexes, but only the mixed sandwich rhodium complex, Cp*Rh-($C_4H_4B_2Cl_2$), was structurally characterized.[12a,13] There have been no reports on the 1,3-diboratabenzene dianion, and the 1,4-diboratabenzene has a reported transition metal complex.[14]

In sandwich complexes, arenes and heteroarenes can bridge metals to make multidecker complexes.[4c,15] In regard to six membered boron systems, Herberich and co-workers reported a boratabenzene (C_5B) ligand bridged triple-decker sandwich complex between two RuCp* or FeCp* fragments (Cp* = pentamethylcyclopentadienide, Figure 2).[16] The only reported

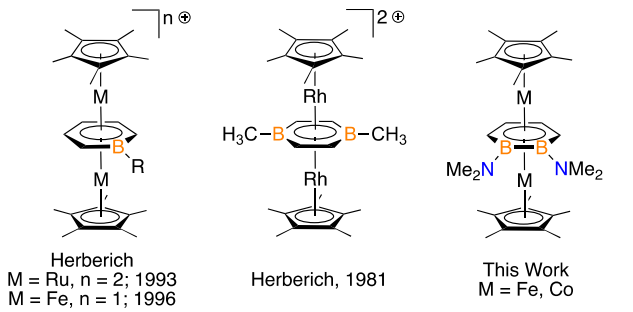

Figure 2. Triple-decker complexes of boratabenzene, 1,4-diboratabenzene, and targeted diboratabenzene complexes.

diboratabenzene triple-decker complex is from the same team, a dirhodium complex with 1,4-diboratabenzene bridging two RhCp* units.[14] The 18-electron valence electron count rule is reliable for predicting stability in mononuclear organometallic complexes, while a total electron count of 30 valence electrons is the standard for stable bimetallic triple-decker complexes.[15e,17] Herein, we target neutral Fe and Co triple-decker complexes and examine their electrochemical properties.

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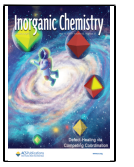

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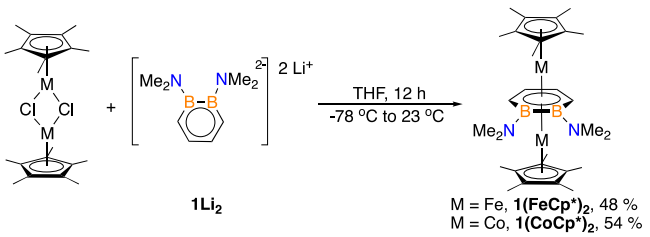
Treatment of pentamethylcyclopentadienyl iron(II) and cobalt(II) chloride dimer reagents [$(MCp^*\text{-}\mu\text{-}Cl)_2$] with one equivalent of dilithiodiboratabenzene with dimethylamino groups on boron ($\mathbf{1Li_2}$) at −78 °C resulted in brown/red and green solutions, respectively (Scheme 1). Growing single

Scheme 1. Synthesis of Iron and Cobalt Complexes, $\mathbf{1(FeCp^*)_2}$ and $\mathbf{1(CoCp^*)_2}$



crystals and conducting X-ray diffraction experiments revealed the products as the iron and cobalt triple-decker complexes featuring the diboratabenzene ligand bridging both metals in an η^6 coordination mode [$\mathbf{1(FeCp^*)_2}$ and $\mathbf{1(CoCp^*)_2}$, Figure 3]. The products were isolated as brown and green solids in

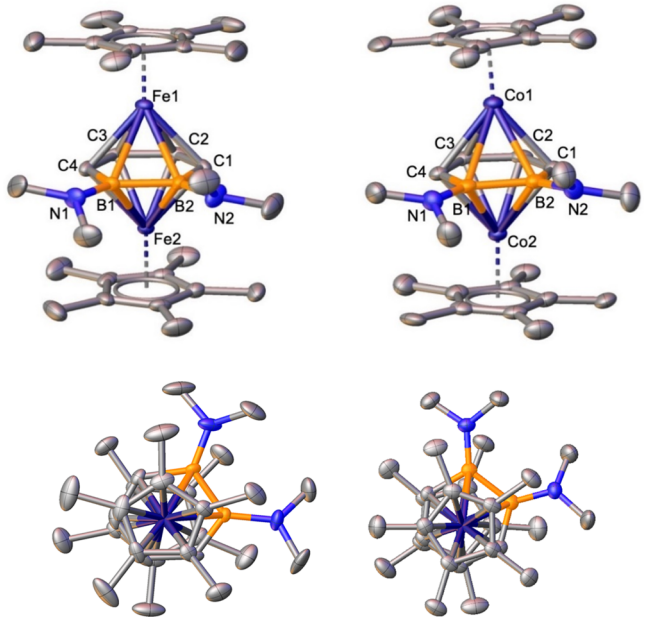


Figure 3. Solid-state structures of $\mathbf{1(FeCp^*)_2}$ (left) and $\mathbf{1(CoCp^*)_2}$ (right). Hydrogen atoms are omitted for clarity, and thermal ellipsoids are drawn at the 50% probability level.

48% and 54% yields, respectively. A ^{11}B NMR spectroscopic resonance at 8.4 ppm was detected for $\mathbf{1(FeCp^*)_2}$ (*cf.* 37.0 ppm for $\mathbf{1Li_2}$) and a diamagnetic ^1H NMR spectrum, consistent with the stable 30 valence electron count [FeCp* = 12 e$^-$; μ^6,η^6-$B_2C_4(NMe_2)_2H_4$ = 6 e$^-$; therefore (2 × Cp*Fe) + μ^6,η^6-$B_2C_4(NMe_2)_2H_4$ = 30]. No signals were observed in the ^{11}B or ^1H NMR spectra for $\mathbf{1(CoCp^*)_2}$ due to its paramagnetic nature. Notable for $\mathbf{1(FeCp^*)_2}$, the $^{13}C\{^1H\}$ NMR signals for the diboratabenzene ring carbons are markedly shifted upfield [$\mathbf{1(FeCp^*)_2}$: 53.5 and 44.1 ppm; cf. $\mathbf{1Li_2}$: 108.5 and 104.6 ppm]. The protons on the diboratabenzene carbons of **1** are also shifted upfield [$\mathbf{1(FeCp^*)_2}$: 4.46 and 1.98 ppm; cf. $\mathbf{1Li_2}$: 6.05 and 5.34 ppm].

Triple-decker complexes with aromatic boron bridging ligands have been structurally characterized for $C_3B_2R_5$, C_4BR_5, C_5BR_6, and B_6R_6 systems,[15b,16a,18] but $\mathbf{1(FeCp^*)_2}$ and $\mathbf{1(CoCp^*)_2}$ represent the first structurally characterized 1,2-diboratabenzene bridged triple-decker complexes. In the solid-state structures of $\mathbf{1(FeCp^*)_2}$ and $\mathbf{1(CoCp^*)_2}$, all three rings are planar (maximum deviation from planarity for Cp* range = 0.001−0.009 Å, **1** = 0.004 and 0.025 Å) and coplanar with respect to each other (range of interplanar angles between Cp* and **1** planes = 2.5−3.9°). A view along the metal−metal vector of $\mathbf{1(FeCp^*)_2}$ and $\mathbf{1(CoCp^*)_2}$ reveals that the Cp* rings are staggered with respect to each other. The angle between the three ring centroids approaches linear axiality [Cp*-**1**-Cp*; $\mathbf{1(FeCp^*)_2}$: = 170.6° and $\mathbf{1(CoCp^*)_2}$: 170.5°].

The intermetal distance (M−M) is shorter in $\mathbf{1(FeCp^*)_2}$ than in $\mathbf{1(CoCp^*)_2}$ [3.2124(6) Å, cf. 3.334(2) Å], and the metal−boracycle centroid distances follow the same trend [$\mathbf{1(FeCp^*)_2}$: 1.622 and 1.606 Å and $\mathbf{1(CoCp^*)_2}$: 1.680 and 1.677 Å]. The Fe−B bonds [avg. 2.351(4) Å] and Fe−C(C_4B_2 ring) bonds [avg. 2.126(4) Å] in $\mathbf{1(FeCp^*)_2}$ are shorter than the corresponding $\mathbf{1(CoCp^*)_2}$ Co−B bonds [avg. 2.425(17) Å] and Co−C(C_4B_2 ring) bonds [avg. 2.166(16) Å]. The B−N bonds in the transition metal complexes are shorter than in $\mathbf{1Li_2}$ [Table 1; $\mathbf{1(FeCp^*)_2}$ avg. = 1.465(4) Å, $\mathbf{1(CoCp^*)_2}$ avg. = 1.456(17) Å, $\mathbf{1Li_2}$ avg. = 1.495(5) Å].

Table 1. Selected Metrical Parameters (Å) in $\mathbf{1(FeCp^*)_2}$ and $\mathbf{1(CoCp^*)_2}$[a]

	$\mathbf{1Li_2}$	$\mathbf{1(FeCp^*)_2}$	$\mathbf{1(CoCp^*)_2}$
B(1)−B(2)	1.706(8)	1.661(4)	1.69(2)
C(1)−B(2)	1.505(6)	1.534(4)	1.517(18)
C(2)−C(1)	1.413(6)	1.411(4)	1.445(17)
C(3)−C(2)	1.417(8)	1.443(4)	1.439(17)
C(4)−C(3)	1.413(6)	1.431(4)	1.428(16)
B(2)−C(4)	1.505(7)	1.528(4)	1.532(18)
B(1)−M1	2.553(9)	2.348(4)	2.426(17)
B(2)−M1	2.471(10)	2.345(4)	2.404(18)
C(1)−M1	2.351(9)	2.156(4)	2.240(16)
C(2)−M1	2.289(10)	2.089(4)	2.132(16)
C(3)−M1	2.265(9)	2.080(5)	2.097(16)
C(4)−M1	2.367(8)	2.152(4)	2.222(16)
B(1)−M2	2.471(10)	2.346(4)	2.413(17)
B(2)−M2	2.553(9)	2.363(5)	2.456(18)
C(1)−M2	2.367(8)	2.182(4)	2.185(16)
C(2)−M2	2.265(9)	2.098(5)	2.140(16)
C(3)−M2	2.289(10)	2.096(5)	2.126(17)
C(4)−M2	2.351(9)	2.152(4)	2.183(16)
B−N (avg)	1.495(5)	1.465(4)	1.456(17)
M-**1** centroid (avg)	1.861	1.614	1.679
RMSD of **1**	0.029	0.004	0.025

[a]RMSD = root-mean-square deviation from planarity of the B_2C_4 ring.

Wiberg bond indices (WBI) were calculated for $\mathbf{1(FeCp^*)_2}$ and $\mathbf{1(CoCp^*)_2}$ as well as the free dianionic ligand, $\mathbf{1}^{2-}$ (Table S-2). Within the central ring, all values are very close between the metal complexes and considerably lower than $\mathbf{1}^{2-}$ [For $\mathbf{1(FeCp^*)_2}$ and $\mathbf{1(CoCp^*)_2}$ ranges listed: B−B (0.87−0.88), C−B (0.97−1.02), C−C (1.16−1.23) cf. $\mathbf{1}^{2-}$ B−B (1.13), C−B (1.31 for both), C−C (1.33−1.49)]. The decreased WBI upon aromatic ligand coordination to metals has been noted in

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the literature and is rationalized by back-donation from the two metal atoms to the central ligand.[15c,19]

Cyclic voltammograms of the two metal complexes were measured in THF (1 mM, 0.1 M $[Bu_4N][PF_6]$ as electrolyte) under a nitrogen atmosphere (Figure 4). The iron complex

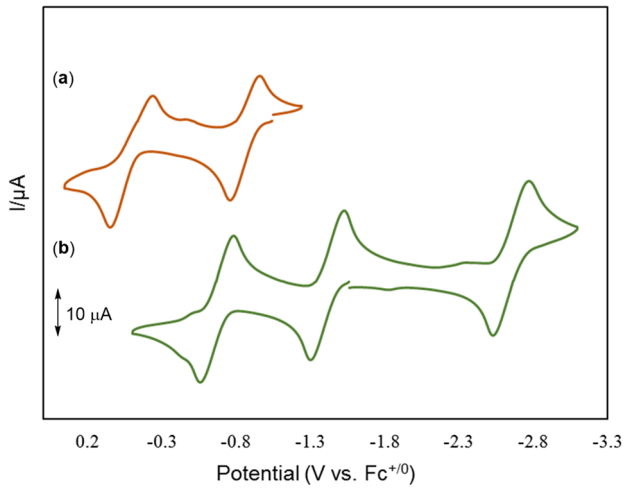

Figure 4. Cyclic voltammograms of (a) **1(FeCp*)$_2$** and (b) **1(CoCp*)$_2$**. Recorded with a glassy-carbon electrode at 1 mM concentrations in THF solutions with 100 mM $[Bu_4N][PF_6]$ as the supporting electrolyte at a scan rate of 0.1 V s^{-1}.

1(FeCp*)$_2$ shows two reversible oxidations at $E_{1/2}$ = −0.87 and −0.10 V vs $Fc^{0/+}$. The two oxidation features of **1(FeCp*)$_2$** are tentatively assigned as $Fe^{II}{}_2 \rightarrow [Fe^{II}Fe^{III}]^+$ and $[Fe^{II}Fe^{III}]^+ \rightarrow [Fe^{III}{}_2]^{2+}$, respectively. Assuming metal-centered redox processes, the large gap between these two oxidation potentials ($\Delta E'$) of 0.77 V affords a comproportionation constant (K_{com}) on the order of 10^{13}, indicating a completely delocalized class III mixed-valent complex for the $Fe^{II}Fe^{III}$ cation by the Robin−Day classification.[20]

As for cobalt complex **1(CoCp*)$_2$**, it also displays two reversible oxidations ($E_{1/2}$ = −1.42 and −0.68) along with a reversible reduction at −2.66 V. We have assigned the oxidations as $Co^{II}{}_2 \rightarrow [Co^{II}Co^{III}]^+$ and $[Co^{II}Co^{III}]^+ \rightarrow [Co^{III}{}_2]^{2+}$, analogous to the iron complex, and the reduction process as $Co^{II}{}_2 \rightarrow [Co^{II}Co^{I}]^-$. The cathodic shift of ∼0.55 V for each of the oxidations relative to the corresponding diiron oxidations is expected for Co^{II} vs Fe^{II}. The separation between the two cobalt oxidations ($\Delta E'$ = 0.74 V) is comparable to **1(FeCp*)$_2$** and again, indicates a class III mixed-valent complex for $[Co^{II}Co^{III}]^+$ ($K_{com} \approx 10^{12}$).

In summary, we have synthesized neutral iron and cobalt triple-decker complexes featuring the 1,2-diboratabenzene dianion as a bridging ligand by salt metathesis. Such neutral triple-decker complexes are rare in organometallic chemistry. Single-crystal X-ray crystallographic analysis of **1(FeCp*)$_2$** and **1(CoCp*)$_2$** reveals that the C_4B_2 units are planar and coordinate to two Cp*M units via an η^6 coordination mode. Electrochemical studies of these complexes reveal two reversible oxidations in both and for the cobalt complex, a reversible reduction event. In these studies, we unearth the 1,2-diboratabenzene ligand that had been neglected for 35 years and reveal its ability to act as a bridging η^6 ligand for bimetallic triple-decker complexes.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.3c00558.

Experimental details, multinuclear NMR spectra, FT-IR spectra, UV−vis spectra, computational details, and X-ray crystallographic details (PDF)

Accession Codes

CCDC 2221482−2221483 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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