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COMMUNICATION

More electron rich than cyclopentadienyl: 1,2-diaza-3,5-diborolyl as a ligand in ferrocene and ruthenocene analogs†

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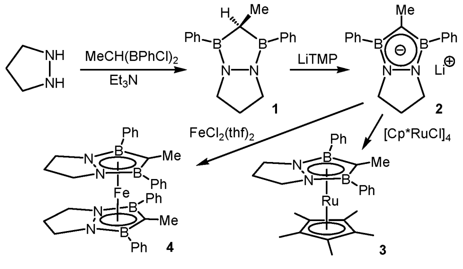
Ruthenium and iron sandwich complexes incorporating cyclopentadienyl analogs with $CB_2N_2^-$ skeletons were characterized. Electrochemical measurements supported by computational studies revealed that in combination with larger metal ions such as Ru the $CB_2N_2^-$ ligand can be more electron-rich than its organic counterpart.

The search for heterocyclic cyclopentadienyl analogs was motivated by the exceptional coordinative properties and numerous applications of the parent compound in organometallic chemistry and catalysis.[1] The incorporation of heteroelements in the ring skeleton aimed to tune the electronic properties of the π-ligand and expand the knowledge of main group elements. In the decades following the discovery and elucidation of the bonding in ferrocene,[2] metal complexes featuring five-membered heterocyclic Cp analogs containing various main group elements were reported.[3] The majority of these ligands contain only one heteroelement in the ring skeleton. Notable exceptions include ligands containing up to five substituent-free group 15 elements in the ring framework, which display a rich coordination chemistry.[4] Most boron-containing Cp analogs include the B,N,[5a] B,S[5b,c] or B,O[5d] pairs that are isolobal with the C_2 fragment. Sandwich complexes incorporating boron-rich bis(dicarbollide) ligands showed promise as tumor imaging reagents.[6] A cyclopentadienyl analog with a $GeSi_2C_2^-$ framework, stabilized in a ferrocene-type complex, remains so far the only ligand in this category containing more than one heavier group 14 element.[7]

A truly "inorganic" ferrocene containing no carbon atoms in the ligand skeleton is still unknown, and early claims regarding the synthesis of a ferrocene featuring $B_2N_3^-$ ligands have not yet been substantiated by a crystal structure.[8] The closest analogs to an "inorganic" ferrocene are compounds featuring phosphorus ligands, such as $[Cp^*Fe(\eta^5\text{-}P_5)]$,[4,9a] and the fully inorganic titanocene $[Ti(\eta^5\text{-}P_5)_2]^{2-}$.[9b] Computational studies identified $Fe(N_5)_2$ as a promising target for synthesis, however, this exotic complex has yet to be isolated.[10] In fact, prior to our work, all reported sandwich complexes that contained five-membered cyclopentadienyl analogs featuring more than three heteroelements in the ring skeleton have been pnictogen derivatives.

The formal replacement of C_2 fragments with isoelectronic BN moieties in simple organic entities has received considerable interest recently, resulting in the isolation of several remarkable molecules with exquisite properties. Analogs of pyrene,[11a] benzene,[11b] ethyl,[11c] ethylene,[11d,e] and propane[11f] incorporating the BN fragment have been characterized, free or stabilized in the coordination sphere of transition metals. In this context, we reported a family of ligands with $CB_2N_2^-$ frameworks and characterized their complexes with group 1 and 12 metals.[12] The coordination chemistry of these ligands was similar to that of Cp, although substantial differences were observed as well. The ring carbon atom proved to play a central role in the binding of the ligand to metals and only η^1, η^2, η^3 and η^4-coordination modes were observed, with the ring nitrogen atoms displaying considerable pyramidalization (CNNC torsion angles of 17–44°). Reported herein are the first transition metal sandwich compounds employing ligands with $CB_2N_2^-$ skeletons that display a classical, η^5-coordination of the heterocyclic ring.

A new precursor **1** featuring a cyclic, pyrazolidyl backbone was synthesized (Scheme 1) in a fashion similar to reported procedures,[12] in an attempt to enforce a reduction of the CNNC dihedral angle and hence improve the participation of the nitrogen lone pairs to the π-system of the ligand.



Scheme 1 Synthesis of derivatives **1–4**.

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† Electronic supplementary information (ESI) available: Complete experimental details for compounds **1–4**, including NMR spectra and CV data, crystallographic data for complexes **3** and **4**, as well as computational details. CCDC 697078 and 697079. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c1cc12281a

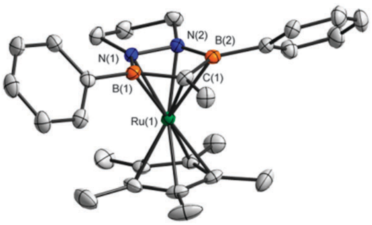

Fig. 1 Molecular structure of **3** with 50% probability level thermal ellipsoids. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å): B–C(1) 1.511(4), 1.522(4), B–N 1.479(3), 1.487(3), N–N 1.431(3), Ru–C(1) 2.296(2), Ru–B 2.322(3), 2.323(3), Ru–N 2.126(2), 2.127(2), Ru–C_{Cp^*} 2.154(2)–2.194(2).

The deprotonation of **1** with formation of **2** was easily accomplished using LiTMP and the corresponding change in molecular symmetry from C_s to C_{2v} was obvious in the NMR spectra. The reaction of **2** with $[Cp^*RuCl]_4$ and $[FeCl_2(thf)_2]$ yielded complexes **3** and **4**, respectively, in good yields. The chemical shifts for the heterocyclic ring carbon (22.4, 91.6, 80.0 and 65.5 ppm in **1**, **2**, **3** and **4**, respectively) mirror the shift of the corresponding carbon resonances in Cp^* (52.2, 105.2, 82.9 and 78.4 ppm in Cp^*H, Cp^*Na, Cp^*_2Ru and Cp^*_2Fe, respectively).[12b,13] The ^{11}B resonances (39.3, 31.5, 14.7 and 13.6 ppm in **1**, **2**, **3** and **4**, respectively) fall in the range observed for Ru (14–18 ppm) and Fe (3–22 ppm) metallocenes incorporating ligands with C_3BN^- frameworks.[14]

Single crystal X-ray diffraction analysis revealed for both **3** (Fig. 1) and **4** (Fig. 2) typical sandwich structures with parallel, η^5-coordinating π-ligands (Fig. 3). The CB_2N_2 rings are reasonably planar (sum of the intraannular angles 538.8–539.4°) but their geometry is best described as an envelope conformation with a dihedral angle along the B···B axis of 8–11°, which allows for a larger separation between the metal and the larger boron atoms. The CNNC torsion angles were reduced considerably in comparison to other ligands from this family, to only 2–3°. However, the C_2N_2 planes form dihedral angles of 11–15° with the B_2N_2 planes and hence the nitrogen atoms remain slightly pyramidal. The intraannular C–B and B–N bonds display distinct multiple bond character, while the N–N distances are typical of single bonds. The distance between the metal and the best plane of the CB_2N_2 ring was 1.67 Å for Fe and 1.84 Å for Ru, nearly identical to the corresponding distances in Cp_2M (1.66 Å for Fe and 1.84 Å for Ru) and Cp^*_2M (1.66 Å for Fe and 1.80 Å for Ru).[15]

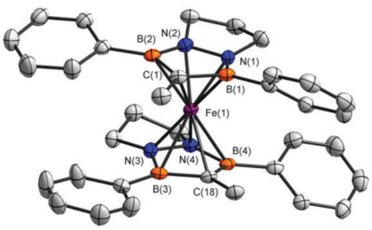

Fig. 2 Molecular structure of **4** with 50% probability level thermal ellipsoids. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å): B–C(1) and B–C(18) 1.510(4)–1.521(4), B–N 1.472(3)–1.489(4), N–N 1.436(3), 1.439(3), Fe–C(1) and Fe–C(18) 2.177(2), 2.192(2), Fe–B 2.198(3)–2.217(3), Fe–N 1.971(2)–1.997(2).

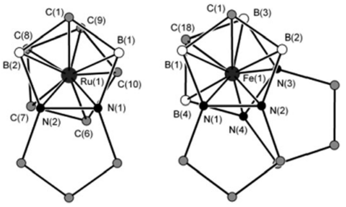

Fig. 3 Perpendicular projection onto the CB_2N_2 planes of **3** (left) and **4** (right) revealing the hapticity of the ligand. Ring substituents have been omitted for clarity.

A cyclovoltammetric study showed that both **3** and **4** display reversible oxidation steps at +0.45 and −0.04 V, respectively, *vs.* SCE in CH_2Cl_2. The reported values for Cp^*_2Ru (+0.55 V), Cp_2Fe (+0.46 V), and Cp^*_2Fe (−0.11 V) indicate that the diazadiborolidine ligands reported herein are comparable to or better electron donors than the parent cyclopentadienyl,[16] confirming the results of a previous study showing that the presence of a BN fragment in the cyclopentadienyl framework generates ligands with superior electron donating capability.[17] However, in the case of **3** and **4** a direct comparison of the ligand skeletons is hindered by the lack of data for identically substituted ligands. Hence, a computational investigation was carried out for a set of model systems (see the ESI†).

Density functional theory was employed to calculate the first ionization energies of Fe and Ru sandwich compounds. The results show that the ionization energy of Cp^*_2Fe is 10 kJ mol^{-1} lower than that of its $CB_2N_2^-$ analog, whereas the trend is reversed for Ru complexes, in which case the difference is also slightly bigger, 16 kJ mol^{-1}. In addition, the calculated ionization energies decrease consistently by *ca.* 10 kJ mol^{-1} if the $CB_2N_2^-$ ligand contains a pyrazolidyl backbone. Comparable ionization energies were also calculated for Fe and Ru complexes incorporating methylated ligands based on a C_3BN^- framework. These data correlate well with the experimental results and confirm the importance of the bicyclic ligand design. They indicate that, for an identical substitution pattern, the larger $CB_2N_2^-$ ring (av. intraannular bond length 1.49 Å in **3**) is a better electron donor than cyclopentadienyl (av. intraannular bond length 1.43 Å in **3**) for the larger Ru and a poorer electron donor for the smaller Fe, likely due to differences in orbital overlap.

Derivatives **3** and **4** prove that the BN pair provides a viable platform for the design of heteroatom-rich cyclopentadienyl analogs. Unlike other systems we investigated,[12] these efficient ligands display a classical η^5 coordination mode towards Fe and Ru and are comparable to or, in the case of the latter metal, even more electron rich than the parent carbon ring, generating complexes with increased reducing ability.

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