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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$_2$N$_2^-\overline{2}$ skeletons were characterized. Electrochemical measurements supported by computational studies revealed that in combination with larger metal ions such as Ru the CB$_2$N$_2^-\overline{2}$ 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. 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, metal complexes featuring five-membered heterocyclic Cp skeletons were characterized, free or stabilized in the coordination sphere of transition metals. In this context, we reported a family of ligands with CB$_2$N$_2^-\overline{2}$ frameworks and characterized their complexes with group 1 and 12 metals. 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$^2$, 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$_2$N$_2^-\overline{2}$ skeletons that display a classical, η$^{4}$-coordination of the heterocyclic ring.

A new precursor featuring a cyclic, pyrazolidyl backbone was synthesized in a fashion similar to reported procedures, in an attempt to enforce a reduction of the CNCN dihedral angle and hence improve the participation of the nitrogen lone pairs to the π-system of the ligand. 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$_2$] 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'Ru and Cp'Fe, respectively). The $^{13}$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) metallocones incorporating ligands with C$_5$BN$^-\overline{2}$ frameworks.
parallel, (Fig. 1) and ionization energies of Fe and Ru sandwich compounds. The computational investigation was carried out for a set of model compounds, which lack of data for identically substituted ligands. Hence, a direct comparison of the ligand skeletons is hindered by the reduced considerably in comparison to other ligands from this family, to only 2 - 3°. However, the C$_2$N$_2$ planes form dihedral angles of 11 – 15° with the B$_2$N$_3$ 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$_2$N$_2$ ring was 1.67 Å for Fe and 1.84 Å for Ru, nearly identical to the corresponding distances in Cp$_2$M (1.66 Å for Fe and 1.84 Å for Ru) and Cp$_5$M (1.66 Å for Fe and 1.80 Å for Ru). 

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$_2$Cl$_2$. The reported values for Cp$_2$Ru (+0.55 V), Cp$_2$Fe (+0.46 V), and Cp$_5$Fe (-0.11 V) indicate that the diazaborolidine ligands reported herein are comparable to or better electron donors than the parent cyclopentadienyl, 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. 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 Supplementary Information).

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$_2$Fe is 10 kJ mol$^{-1}$ lower than that of its CB$_2$N$_2$ 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$_2$N$_2$ ligand contains a pyrazolylidene backbone. Comparable ionization energies were also calculated for Fe and Ru complexes incorporating methylated ligands based on the C$_2$BN$^-$ 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$_2$N$_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.

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Notes and references

1. (a) A. Togni and R. L. Halterman, Metalloccenes, Wiley VCH, Weinheim 1998, Vol. I, B; (b) N. Long, J. Metallococenes: An Introduction to Sandwich Complexes, Blackwell Science Ltd., London 1998; (c) P. Jutzi and N. Burford, Chem. Rev. 1999, 99, 969.
2. (a) T. J. Kealy and P. L. Pauson, Nature 1951, 168, 1039; (b) G. Wilkinson, M. Rosenblum, M. C. Whiting and R. B. Woodward, J. Am. Chem. Soc. 1952, 74, 2125; (c) R. B. Woodward, M. Rosenblum and M. C. Whiting, J. Am. Chem. Soc. 1952, 74, 3458; (d) E. O. Fischer and W. Pfah, Z. Naturforsch. 1952, 7B, 377; (e) E. Buch and E. O. Fischer, Z. Naturforsch. 1952, 7B, 676; (f) P. F. Eliland and R. Pepinsky, J. Am. Chem. Soc. 1952, 74, 4971.
3. See ref. 10b for a timeline of the reports on the first Cp analogs.
4. (a) O. J. Scherer, Angew. Chem., Int. Ed. Engl. 1990, 29, 1104; (b) M. Scheer and E. Herrmann, Z. Chem. 1990, 30, 41; (c) F. Mathey, Coord. Chem. Rev. 1994, 137, 1; (d) J. F. Nixon, Chem. Soc. Rev. 1995, 24, 319; (e) M. Scheer, S. Deng, O. J. Scherer and M. Sierka, Angew. Chem., Int. Ed. Engl. 2005, 44, 3755.
5. (a) J. Schulze and G. Schmid, Angew. Chem., Int. Ed. Engl. 1980, 19, 54; (b) A. J. Ashe III, X. Fang and J. W. Kampf, Organometallics 1998, 17, 2379; (c) A. J. Ashe III, J. W. Kampf, M. Schiesher, Organometallics 2000, 19, 4681; (d) J. Chen, X. Fang, Z. Bajko, J. W. Kampf and A. J. Ashe III, Organometallics 2004, 23, 5088.
6. V. Y. Lee, R. Kato, A. Sekiguchi, A. Krapp and G. Frenking, J. Am. Chem. Soc. 2007, 129, 10340.
7. H. Nöth and W. Regnet, Z. Anorg. Allg. Chem. 1967, 352, 1.
(a) O. J. Scherer and T. Brück, *Angew. Chem., Int. Ed. Engl.* 1987, 26, 59; (b) E. Urnėžius, W. W. Brennessel, C. J. Cramer, J. E. Ellis, P. v. R. Schleyer, *Science* 2002, 295, 832.

(a) M. J. D. Bodet, W. E. Piers, T. S. Sorensen and M. Parvez, *Angew. Chem. Int. Ed.* 2007, 46, 4940; (b) A. J. V. Marwitz, M. H. Matus, L. N. Zakharov, D. A. Dixon and S.-Y. Liu, *Angew. Chem. Int. Ed.* 2009, 48, 973; (c) T. D. Forster, H. M. Tuononen, M. Parvez and R. Roesler, *J. Am. Chem. Soc.* 2009, 131, 6689; (d) G. Alcaraz, L. Vendier, E. Clot and S. Sabo-Etienne, *Angew. Chem. Int. Ed.* 2010, 49, 918; (e) C. Y. Tang, A. L. Thompson and S. Aldridge, *Angew. Chem. Int. Ed.* 2010, 49, 921; (f) S. R. Daly, B. J. Bellott, D. Y. Kim and G. S. Girolami, *J. Am. Chem. Soc.* 2010, 132, 7254.

(a) Ly, H. V.; Forster, T. D.; Maley, D.; Parvez, M.; Roesler, R. *Chem. Commun.* 2005, 4468-4470. (b) Ly, H. V.; Forster, T. D.; Coerente, A. M.; Eisler, D. J.; Konu, J.; Parvez, M.; Roesler, R. *Organometallics* 2007, 26, 1750-1756. (c) Ly, H. V.; Forster, T. D.; Parvez, M.; McDonald, R.; Roesler, R. *Organometallics* 2007, 26, 3516-3523. (d) Ly, H. V.; Tuononen, H. M.; Parvez, M.; Roesler, R. *Angew. Chem., Int. Ed.* 2008, 47, 361-364. (e) Ly, H. V.; Konu, J.; Parvez, M.; Roesler, R. *Dalton Trans.* 2008, 3454-3460.

(a) Robbins, J. L.; Edelstein, N.; Spencer, B.; Smart, J. C. *J. Am. Chem. Soc.* 1982, 104, 1882-1893. (b) Tilley, T. D.; Grubbs, R. H.; Bercaw, J. E. *Organometallics* 1984, 3, 274-278.

(a) Amirkhalili, S.; Höhner, U.; Schmid, G. *Angew. Chem., Int. Ed. Engl.* 1982, 21, 68. (b) Schmid, G.; Höhner, U.; Kampmann, D.; Zaika, D.; Boese, R. *Chem. Ber.* 1983, 116, 951-959. (c) Schmid, G.; Haske, S.; Zaika, D.; Boese, R.; Blaser, D. *Chem. Ber.* 1994, 127, 73-80. (f) Schmid, G.; Barbenheim, G.; Boese, R. Z. *Naturforsch.* 1985, 40b, 787-793.

(a) Dunitz, J. D.; Orgel, L. E.; Rich, A. *Acta Cryst.* 1956, 9, 373-375. (b) Hardgrove, G. L.; Templeton, D. H. *Acta Cryst.* 1959, 12, 28-32. (c) Freyberg, D. P.; Robbins, J. L.; Raymond, K. N.; Smart, J. C. J. *Am. Chem. Soc.* 1979, 101, 892-897. (d) Zhang, Y.; Kim, C. D.; Coppens, P. *Chem. Commun.* 2000, 2299-2300.

(a) Astruc, D. Electron Transfer and Radical Processes in Transition-Metal Chemistry, VCH, New York 1995. (b) Connelly, N. G.; Geiger, W. E. *Chem. Rev.* 1996, 96, 877-910.

Liu, S.-Y.; Lo, M. M.-C.; Fu, G. C. *Angew. Chem., Int. Ed.* 2002, 41, 174-176.