μ-η^3:η^4-Lithiocene and η^3:η^3-zincocene incorporating 1,2-diaza-3,5-diborolyl, a cyclopentadienyl analog

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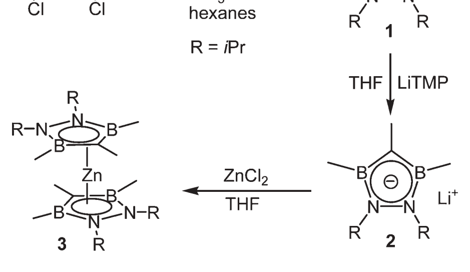
A heterocyclic cyclopentadienyl analog containing only one carbon atom in the ring was prepared and a polymeric lithiocene and a monomeric zincocene containing this novel ligand have been isolated and crystallographically characterized.

The tremendous importance of cyclopentadienyl as a ligand in organometallic chemistry has prompted the design and synthesis of numerous five-membered, heterocyclic analogs involving B, N, P, O, S and Si in addition to C. The reported substitution of two carbon fragments, RC, in cyclopentadienyl with the isolobal pairs (RB^-, RN^+)[1] and (RB^-, O^+)[2] in 1, 2 positions, as well as (RB^-, S^+)[3] in 1, 2 and 1, 3 positions resulted in anionic C_3BN, C_3BO and C_3BS rings. Some of these derivatives proved to be feasible ancillary ligands in catalysts.[4] To our knowledge, not more than two carbon atoms have been replaced by other elements in boron containing heterocyclic analogs of cyclopentadienyl. Anionic phosphorus heterocycles incorporating up to four phosphorus atoms however are extremely versatile ligands that stabilized unusual coordination environments for many transition metals.[5] We investigated and report herein the stability and coordination chemistry of cyclopentadienyl analogs derived from the 1,2-diaza-3,5-diborolidine, **1**. A further incentive for this study was the intriguing coordination chemistry of 1,3-diborolyl, which is to date the only ligand reported to generate polymeric, polydecker sandwich compounds, some of which display semiconductive properties.[6] Theoretical calculations have shown that stable hydrocarbon ligands are not suitable building blocks for conductive polymers with polydecker structure and that the replacement of carbon with selected heteroatoms is a more promising synthetic strategy.[7]

The overall synthetic pathway is outlined in Scheme 1. $MeCH(BCl_2)_2$ was prepared by bubbling acetylene through a mixture of BCl_3 and Me_3SiH dissolved in hexane at −78 °C, using a slight modification of the reported procedure.[8] The product was obtained in low (15–30%) but reproducible yield and could be purified by distillation. Symmetric dimethylation using Me_4Sn yielded $MeCH(MeBCl)_2$[8] which was used further for the synthesis of the ring without the tedious separation of the Me_3SnCl by-product. Ring closure between $MeCH(MeBCl)_2$ and *i*PrNH-NH*i*Pr was easily accomplished in the presence of triethylamine, yielding the novel ring system 1,2-diaza-3,5-diboroline, **1**. The compound was isolated as a colorless, distillable liquid with good solubility in organic solvents, which hydrolyzed rapidly when exposed to the atmosphere. The expected broad quartet corresponding to the methine proton was observed at 0.25 ppm in the ^1H NMR spectrum, while the ^{11}B NMR spectrum of **1** showed a broad singlet at 46.9 ppm.

Deprotonation of **1** using lithium 2,2,6,6-tetramethylpiperidine (LiTMP) proceeded cleanly and in good yield to form the lithium salt **2**, which was obtained after work-up as a solvent-free colorless powder. The air-sensitive material was soluble in THF but insoluble in hydrocarbons. The disappearance of the signal corresponding to the methine proton in the ^1H NMR spectrum, as well as the collapse of the doublet corresponding to the methyl substituent on the ring carbon into a singlet, were clear signs of the successful deprotonation. Singlets were observed in the ^{11}B and ^7Li NMR spectra of **2**, at 38.3 and −2.34 ppm, respectively. The chemical shift of the ^7Li NMR signal suggests the existence of solvent separated ion pairs in THF solution, an observation that is further supported by the equivalence of all four methyl groups in isopropyl on the NMR time scale.

Single crystals suitable for X-ray diffractometry were obtained by slow evaporation of a solution of **2** in a mixture of benzene and tetrahydrofuran. The crystallographic determination revealed a polymeric, polydecker sandwich structure with the rings coordinating bifacially in an η^3:η^4 fashion (Fig. 1). The alternating, planar rings (0.015 Å average deviation out of the mean plane) are staggered at an angle of 180° and tilted with respect to each other at an angle of 21.4°. Two neighboring lithium atoms are separated by a distance of 4.381(8) Å, with the lithium center situated much closer to the ring plane on the η^4 face than on the η^3 face (1.861(5) *vs.* 2.196(5) Å). By comparison, in polymeric lithium cyclopentadienyls neighboring lithium atoms are separated by only 3.9–4.0 Å, with a lithium to ring plane distance of *ca.* 1.95 Å.[9] In these salts the Li–C distances range between 2.22 and 2.37 Å. The C(1)–Li(1′) distance in **2** is situated, with 2.225(6) Å, at the lower end of this



Scheme 1

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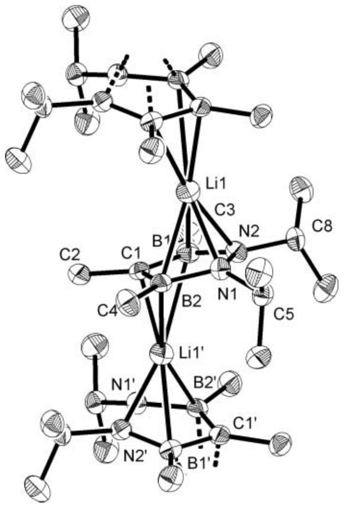

Fig. 1 Molecular structure of **2**. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): N(1)–N(2) 1.466(3), C(1)–B(1) 1.513(4), C(1)–B(2) 1.498(4), N(1)–B(2) 1.479(4), N(2)–B(1) 1.457(4), C(1)–C(2) 1.519(4), C(3)–B(1) 1.589(4), C(4)–B(2) 1.593(4), B(1)–Li(1) 2.369(6), B(2)–Li(1) 2.354(6), N(1)–Li(1) 2.075(5), N(2)–Li(1) 2.112(5), C(1)–Li(1′) 2.225(6), B(1)–Li(1′) 2.543(6), B(2)–Li(1′) 2.751(6); B(2)–C(1)–B(1) 106.9(3), N(2)–B(1)–C(1) 107.5(3), N(1)–B(2)–C(1) 107.6(2), N(2)–N(1)–B(2) 108.3(2), B(1)–N(2)–N(1) 109.6(2).

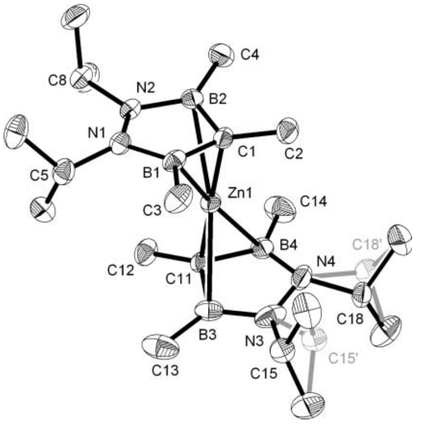

Fig. 2 Molecular structure of **3**. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): C(1)–B(1) 1.532(5), C(1)–B(2) 1.539(5), N(1)–B(1) 1.432(5), N(2)–B(2) 1.442(5), N(1)–N(2) 1.443(4), Zn(1)–C(1) 2.002(3), Zn(1)–B(1) 2.537(4), Zn(1)–B(2) 2.443(4); B(1)–C(1)–B(2) 104.1(3), N(1)–B(1)–C(1) 107.7(3), N(2)–B(2)–C(1) 107.4(3), B(1)–N(1)–N(2) 110.4(3), B(2)–N(2)–N(1) 109.3(2).

range, while the C(1)–Li(1) distance of 2.479(6) Å is clearly outside of the range, indicating an η^4 rather than η^5 coordination mode.

Consistent with the expected electron delocalization, the C–B and the B–N bonds lengths within the ring, with averages of 1.51 and 1.48 Å, are similar to those found in the base stabilized 1,2-azaborolinyl lithium (1.496(6) and 1.503(6) Å, respectively).[10] By comparison, the exocyclic B–C bonds in **2** are *ca.* 8 pm longer than the endocyclic ones. The N–N bond however is, with 1.466(3) Å, comparable in length with an N–N single bond (1.48 Å), and much longer than the N–N bond in pyridazine (1.337(2) Å).[11]

The metathesis reaction of **2** with zinc dichloride in THF yielded the zinc sandwich **3**, which is extremely soluble in hydrocarbons and was crystallized out of a concentrated hexane solution at −35 °C. The diastereotopy observed in the ^{1}H and ^{13}C NMR spectra for the isopropyl substituents indicates that the sandwich structure is maintained in solution. The other parameters of the NMR spectra of **3** are very similar to those observed for **2**. The crystal structure determined for **3** revealed two independent molecules in the unit cell, one centrosymmetric and the other pseudo-centrosymmetric. Due to the similarity between the two molecules, only the latter will be described in detail (Fig. 2). The zinc atom is coordinated η^3 by the nearly parallel rings (dihedral angle 8.9(2)°), with a distance between zinc and the ring plane of *ca.* 2.02 Å. The C–N, B–N, and N–N distances within the rings in **3** are, with 1.53, 1.43 and 1.44 Å, respectively, similar to the values observed for the lithium salt **2**. All three molecular zincocenes previously characterized by X-ray crystallography have asymmetric structures with η^1, η^5 or η^1, η^4 coordinating cyclopentadienyls, while the polymeric Cp_2Zn contains η^1 and η^2 cyclopentadienyls.[12] To our knowledge the η^3 coordination mode has not been observed in zinc dicyclopentadienyl complexes, although it is not uncommon for main group derivatives. Nevertheless, theoretical calculations performed for the symmetric dizinc metallocene [Zn_2(η^5-C_5Me_5)$_2$] found that the energy differences between the optimized structures involving η^5/η^5, η^3/η^3 and η^5/η^1(π) coordination modes were less than 0.1 kcal mol^{-1}.[13] The Zn–C bond distances in **3** average 2.00 Å which is typical for Zn–C covalent bonds[12] and represent the lower end of the range observed in zincocenes (1.99–2.37 Å for η^5 and 2.16–2.22 Å for η^1).[12]

In conclusion, we have developed a synthetic route to a heterocyclic cyclopentadienyl analog containing only one carbon in the ring. Similar to its organic counterparts, this anionic CB_2N_2 ligand forms a polymeric lithiocene involving C, B, and N coordination to the metal, as well as an unprecedented, symmetric zincocene with an η^3 coordination mode of the ligand. The coordination behavior of the new ligand towards various transition metals is being investigated.†

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Notes and references

† All manipulations were conducted under strict exclusion of air and moisture in an atmosphere of dry argon or *in vacuo* using Schlenk line and glove box techniques.

1,2-Diaza-3,5-diborolidine, 1: A solution of 1,1-bis(chloromethylboryl)-ethane (1.20 g, 7.96 mmol) in hexane (20 mL) was added slowly to a solution containing 1,1-diisopropyl hydrazine (0.90 g, 7.96mmol) and triethylamine (1.61 g, 15.93 mmol) in hexane (15 mL). The suspension was stirred at ambient temperature for 30 min and subsequently filtered. The filtrate was concentrated in vacuum and the residual liquid was distilled under reduce pressure. 0.93 g (60%) of product distilled at 78 °C/5 torr as a clear colorless liquid. δ_H(400 MHz, C_6D_6, 25 °C) 0.25 (q, br, 1H, $^3J_{HH}$ = 8.2 Hz, *H*CCH$_3$), 0.64 (s, 6H, BC*H*$_3$), 1.17 (d, 12H, $^3J_{HH}$ = 6.8 Hz, CH(C*H*$_3$)$_2$), 1.19 (d, 3H, $^3J_{HH}$ = 8.2 Hz, HCC*H*$_3$,), 3.67 (sep, 2H, $^3J_{HH}$ = 6.8 Hz, C*H*(CH$_3$)$_2$); δ_C(100 MHz, C_6D_6, 25 °C) 0.17 (s, br, B*C*H$_3$), 9.01 (s, C*C*H$_3$), 22.9 (s, CH(*C*H$_3$)$_2$), 47.2 (s, *C*H(CH$_3$)$_2$); δ_B(128 MHz, C_6D_6, 25 °C) = 46.9 (s, br); *m/z* (%) (EI+) 194.2 (59) (M^+), 179.2 (100) (M^+ − Me); HRMS 194.2131 ($H_{24}C_{10}N_2{}^{11}B_2$ requires 194.2126).

1,2-Diaza-3,5-diborolyllithium, 2: A yellow solution containing lithium 2,2,6,6-tetramethylpiperidide, LiTMP was formed *in situ* from 1.6 M n-butyllithium in hexane (11.06 ml, 17.7 mmol) and 2,2,6,6-tetramethylpiperidine, TMP, (2.50 g, 17.7 mmol) in THF (3 mL). The solutions of **1** (1.14 g, 5.90 mmol) in THF (3 mL) and LiTMP were pre-cooled to −30 °C, mixed and kept at this temperature for another 2 h. The yellow solution was allowed to warm to room temperature overnight. The solvent was removed under vacuum producing an orange solid, which was washed a few times with hexane (30 mL) and dried under vacuum. The product was obtained as a colorless powder (1.07 g, 90.8%). δ_H(400 MHz, THF-d_8, 25 °C) 0.33 (s, 6H, BCH_3), 1.16 (d, 12H, $^3J_{HH} = 6.8$ Hz, $CH(CH_3)_2$), 1.66 (s, 3H, CCH_3), 3.76 (sept, 2H, $^3J_{HH} = 6.8$ Hz, $CH(CH_3)_2$); δ_C(100 MHz, THF-d_8, 25 °C) 0.2 (s, br, BCH_3), 13.6 (s, CCH_3), 23.0 (s, $CH(CH_3)_2$), 48.2 (s, $CH(CH_3)_2$); δ_C(100 MHz, THF-d_8, −50 °C) 1.4 (s, BCH_3), 14.1 (s, CCH_3), 22.9 (s, $CH(CH_3)_2$), 48.4 (s, $CH(CH_3)_2$), 86.7 (s, br, CCH_3); δ_B(128 MHz, THF-d_8, 25 °C) 38.3 (s, br); δ_{Li}(155 MHz, THF-d_8, 25 °C) −2.34 (s); *m/z* (%) (EI) ($M^+ - Li + H$) 194.2 (36), 179.2 (100) ($M^+ - Li - Me + H$). X-Ray quality crystals were obtained by slow evaporation of a solution of **2** in a mixture of THF and benzene.

Bis(1,2-diaza-3,5-diborolyl)zinc, 3: A solution of **2** (0.150 g, 0.750 mmol) and anhydrous $ZnCl_2$ (0.051 g, 0.375 mmol) in THF (30 mL) was stirred for 20 h at ambient temperature. The solvent was removed under vacuum and the residue was extracted with hexane (30 mL). Concentration and cooling of the solution to −35 °C yielded colorless crystals of **3** (110 mg, 65.1%). δ_H(400 MHz, C_6D_6, 25 °C) 0.73 (s, 6H, BCH_3), 1.23 (d, 6H, $^3J_{HH} = 6.9$ Hz, $CH(CH_3)_2$), 1.30 (d, 6H, $^3J_{HH} = 6.9$ Hz, $CH(CH_3)_2$), 1.76 (s, 3H, CCH_3), 3.88 (sep, 2H, $^3J_{HH}$ 6.9 Hz, $CH(CH_3)_2$); δ_C(100 MHz, C_6D_6, 25 °C) −0.3 (s, br, BCH_3), 11.8 (s, CCH_3), 23.5 (s, $CH(CH_3)_2$), 24.2 (s, $CH(CH_3)_2$), 47.9 (s, $CH(CH_3)_2$); δ_C(100 MHz, THF-d_8, −50 °C) 2.1 (s, BCH_3), 13.5 (s, CCH_3), 22.9 (s, $CH(CH_3)_2$), 23.8 (s, $CH(CH_3)_2$), 48.0 (s, $CH(CH_3)_2$), 63.7 (s, br, CCH_3); δ_B(128 MHz, C_6D_6, 25 °C) 37.6 (s, br); *m/z* (%) (EI+) 450.3 (28) (ZnL_2^+) 257.1 (23) $(ZnL)^+$, 194.2 (39) (L^+). HRMS 450.3412 ($H_{46}C_{20}N_4{}^{11}B_4{}^{64}Zn$ requires 450.3386).

X-Ray crystal structure analysis of 2 and 3: Nonius Kappa CCD diffractometer, $Mo_{K\alpha}$ radiation, $\lambda = 0.71073$ Å, scan mode ω and φ, $T = 173(2)$K, Lorentz and polarization correction as well as absorption correction using multi-scan method. The structures were solved by the direct methods and expanded using Fourier techniques; hydrogen atoms were included at geometrically idealized positions and were not refined. SIR-92 was used for structure solution, the method of refinement was full matrix least squares at F^2, and the refinement was performed with SHELXL-97. **2**: Crystal dimensions 0.20 × 0.18 × 0.04 mm, crystal system orthorhombic, space group $P2_12_12_1$, $a = 8.573(5)$, $b = 9.925(6)$, $c = 14.892(9)$ Å, $V = 1267.1(13)$ Å^3, $Z = 4$, $\rho_{calc.} = 1.048$ Mg m^{-3}, $\theta_{max.} = 25.0°$, 2153 measured reflections, 1266 independent intensities ($R_{int} = 0.032$), absorption coefficient 0.058 mm^{-1}, number of free parameters 142, final R ($I > 2\sigma(I)$), $R1 = 0.044$, $wR2 = 0.098$. **3**: Crystal dimensions 0.20 × 0.18 × 0.06 mm, crystal system triclinic, space group P, $a = 10.091(4)$, $b = 14.803(4)$, $c = 15.697(5)$ Å, $\alpha = 114.89(2)$, $\beta = 97.12(2)$, $\gamma = 101.33(2)°$, $V = 2028.6(12)$ Å^3, $Z = 3$, $\rho_{calc.} = 1.108$ Mg m^{-3}, $\theta_{max.} = 25°$, 13417 measured reflections, 7107 independent intensities ($R_{int} = 0.032$), absorption coefficient 0.920 mm^{-1}, number of free parameters 421, final R ($I > 2\sigma(I)$), $R1 = 0.047$, $wR2 = 0.109$. CCDC 266130 (**2**) and 266131 (**3**). See http://dx.doi.org/10.1039/b508152a for crystallographic data in CIF or other electronic format.

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