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Unusual B₄N₂₂ Ligand in a Ruthenium Pseudo-Triple-Decker Sandwich Complex Displaying Three Reversible Electron Transfer Steps

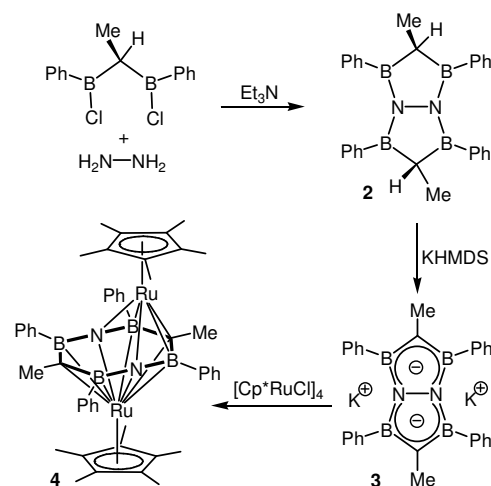
Hanh V. Ly, Heikki M. Tuononen, Masood Parvez, and Roland Roesler*

Dedicated to Prof. Richard J. Puddephatt

Polydecker sandwich complexes are highly desirable synthetic targets because of their potential applications as advanced materials, due to the considerable interactions between their metal centers.¹ Cyclopentadienyl² and benzene³ have demonstrated early on their ability to coordinate bifacially to transition metals and generate triple-decker sandwich complexes. Although larger oligomers have been identified in the gas phase,⁴ the energy of such bridging π interactions involving neutral or singly-charged carbon-based ligands is low and oligomers with more than four decks have not been isolated in the condensed phase. Exceptions are the sandwich compounds of the main group metals that associate forming extended structures in the solid-state.⁵ In order to circumvent the low tendency of organic ligands to bridge metal centers and build stacked sandwich compounds, annelated cyclopentadienyl derivatives such as indacene⁶ and especially pentalene^{6a,7} have been used as building blocks for staggered multidecker sandwich compounds. Although promising, these systems have limitations associated to the narrow choice of substitution patterns available, resulting in low solubility of the higher oligomers or in the formation of complex mixtures of isomers. The recent synthesis of hexamethylpentalene is a promising development in this area.⁸ Heterocyclic rings, particularly those containing boron, have a higher tendency to coordinate bifacially and generate stacked sandwich compounds.⁹ The largest multidecker sandwich compounds known to date contain six decks and feature dianionic cyclic ligands with B₂C₃ and B₃C₂ frameworks.¹⁰ The only family of polydecker complexes reported so far, [Ni(C₃B₂Me₂RR'R'')]_n, displayed conducting properties.¹¹

Within the scope of our investigation on heterocyclic cyclopentadienyl analogues we developed the 1,2-diaza-3,5-diboroly ligands **1**.¹² Herein we report the extension of this project to the pentacenediyl-like dianion in **3**, which is a very promising π -bridging ligand for the assembly of polymeric materials.

The precursor **2** was obtained as a mixture of *cis* and *trans* isomers through condensation of hydrazine and 1,1-bis(phenylchloroboryl)methane^{12b} in the presence of triethylamine (see Supporting Information). The *trans* isomer could be separated



Scheme 1. Synthesis of derivatives **2–4**.

by crystallization and structurally characterized (Fig. 1).¹³ It features a long N-N bond of 1.48 Å, slightly longer than the N-N bonds observed in hydrazine (1.45 Å)¹⁴ and the metal complexes of **1** (1.44 – 1.47 Å).¹² The endocyclic B-C and B-N bonds are, at 1.57 and

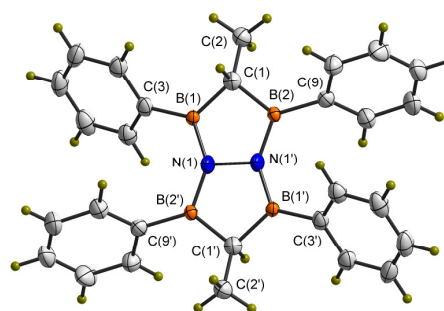


Figure 1. Molecular structure of *trans*-**2**. Selected bond lengths [Å] and angles [°]: N-N 1.480(2), B-N 1.436(2), 1.437(2), B-C(1) 1.571(2), 1.574(2), B-N-B 140.88(14), 109.58(14), N-B-C(1) 109.02(14), B-C-B 101.86(13), B-N-N 109.54(15).

1.44 Å, longer and slightly shorter, respectively, than the corresponding bonds in the alkali metals salts of the monocyclic analogs.^{12b} For comparison, the B-N bonds in borazines measure 1.42 – 1.44 Å.¹⁵

Double deprotonation of **2** with K[N(SiMe₃)₂] could be conducted directly or in two successive steps, yielding the orange dipotassium salt **3**. As expected, both isomers produced the same mono and dianions. The disappearance of the methine protons was noticeable in the ¹H NMR spectrum of **3**, and the deprotonation resulted in a 14 ppm upfield shift of the ¹¹B NMR signal. Despite its very similar geometry, the 8- π -electron heterocyclic ligand in **3** is

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not a direct analogue of the 10- π -electron pentalenediyl.^{7,8}

A crystal structure was determined for **3**(*tmeda*)₂, revealing that the planar B₄N₂C₂ ligand was coordinated by two potassium ions each supporting a TMEDA molecule, in a centrosymmetric arrangement (Fig. 2).¹³ The transition from **2** to **3** involves a shortening of the intraannular N-N and B-C bonds and a slight lengthening of the B-N bonds, resembling the transition from cyclopentadiene to cyclopentadienyl. The separation between the two potassium ions measures 5.52 Å and is comparable to the K \cdots K separation observed in polymeric cyclopentadienyls (5.52 – 5.85 Å)^{12b} and the dimeric potassium pentalenediyl derivative (5.43, 5.48 Å).¹⁶

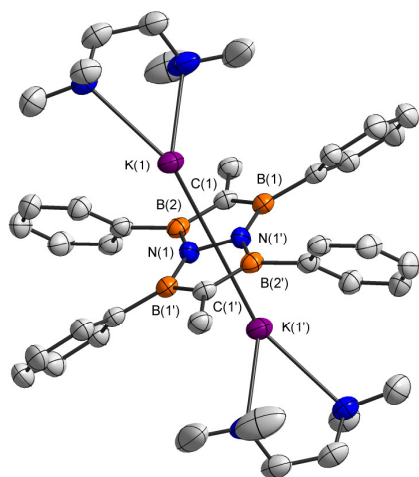


Figure 2. Molecular structure of **3**(*tmeda*)₂. All hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: N-N 1.442(4), B-N 1.474(4), 1.483(4), B-C(1) 1.494(4), 1.502(4), K-N 2.809(3), 2.820(2), K-B 3.268(3) – 3.377(3), B-N-B 143.3(2), N-B-C(1) 108.5(2), 109.6(2), B-C-B 104.7(2), B-N-N 107.9(2), 108.8(2).

Reaction of **3** with [Cp**Ru*Cl]₄ yielded the pseudo-triple-decker sandwich **4**. The Cp* groups, as well as the boron centers and the phenyl and methyl substituents of the π -bridging ligand are equivalent on the NMR time scale, and the corresponding chemical shifts are unremarkable. The compound generated an intense signal corresponding to the molecular ion in the mass spectrum, and its identity was confirmed by a high resolution mass spectrum, as well as elemental analysis. An X-ray diffraction study on a single crystal of **4** validated the pseudo-triple-decker sandwich structure and revealed a few surprising features (Fig. 3).¹³ The N-N bond cleaves upon the formation of **4**, and the 8- π -electron bicyclic ligand transforms into a B₄N₂C₂ ring. Its geometry can be best described as a severely elongated hexagon and it is, to our knowledge, unprecedented for eight-membered rings. The structure is asymmetric, with Ru(1) situated at nearly equal distances from all B atoms (2.488(7) – 2.546(7) Å), while Ru(2) is clearly η^5 -coordinated. The coordination of Ru(1) can be described as η^7 or η^8 , depending on the involvement of C(2) to the bonding (Ru(1)-C(2) 2.548(6) Å vs. Ru(1)-C(1) 2.402(5) Å and Ru(2)-C(2) 2.257(6) Å). The metal atoms are situated close to the B₄N₂C₂ ligand (1.58, 1.62 Å vs. Ru-Cp* 1.82, 1.86 Å) and consequently very close to each other (3.24 Å). For comparison, the separation between the metals measures 3.90 Å in (Cp**Ru*)₂B₈H₁₄.^{17b} Unfortunately, no complete structural data is available for the analogues containing all-carbon ligands, [(Cp**Ru*)₂C₈H₆]^{6a} and *transoid*-[(Cp*Ru*)₂C₈H₈].^{17a}

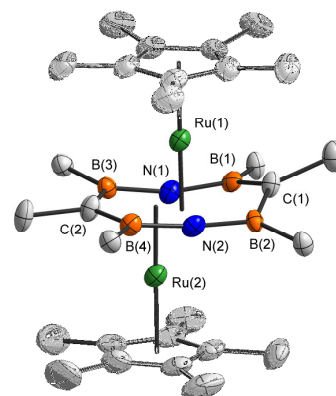


Figure 3. Molecular structure of **4**. For clarity, only the ipso carbon atoms of the phenyl substituents are represented and all hydrogen atoms have been eliminated. Selected bond lengths [Å] and angles [°]: N \cdots N 2.676(11), B(1)-N(1) 1.437(9), B(3)-N(1) 1.440(9), B(2)-N(2) 1.400(9), B(4)-N(2) 1.462(9), B(1)-C(1) 1.542(10), B(2)-C(1) 1.565(9), B(3)-C(2) 1.582(9), B(4)-C(2) 1.558(9), Ru(1) \cdots Ru(2) 3.240(6), Ru-N, 2.118(5) – 2.132(6), Ru-B 2.351(7) – 2.546(7), Ru-C 2.257(6) – 2.548(6), B-N-B 166.4(6), 172.1(6), N-B-C 110.7(6) – 114.2(5), B-C-B 123.8(6), 130.1(5).

A computational analysis at the DFT level (see Supporting Information) performed on the model structure **4a**, featuring a hydrogen substituted B₄N₂C₂H₆ ligand and Cp groups, gave a molecular geometry in reasonable agreement with the X-ray diffraction data. The frontier MO analysis of **4a** shows that substantial mixing of the ligand orbitals with the MOs of the [CpRu]⁺ fragments takes place, resulting in a formal insertion of the metal atoms into the N-N bond. The ruthenium d orbitals interact mainly with the two nitrogen p orbitals which are orientated in the B₄N₂C₂ plane and perpendicular to it, respectively. The similar oxidative addition of hydrazines to transition metals has recently been reported.¹⁸ Energy decomposition analysis conducted for **4a** confirms that the primary, thermodynamic driving force for its formation is the cleavage of the N-N bond, and the subsequent formation of the Ru-N interactions: the total orbital interaction between the formally cationic and anionic fragments of the complex is strong with a calculated value of around -1900 kJ mol⁻¹ (total calculated bond energy is -2400 kJ mol⁻¹). Mayer bond orders obtained for **4a** support the description of Ru(2) as η^5 -coordinated whereas coordination of Ru(1) can be best described as η^8 ; the largest bond orders are calculated for Ru-N interactions, around 0.45. As expected, the bonding analysis shows no sign of N-N interactions. Hence, the computational data indicates that the atypical linear B-N-B moieties in **4** can be described with formally sp-hybridized nitrogen atoms whose unhybridized p orbitals have an important contribution to the ligand-metal bonding.

Cyclic voltammetry of **4** in THF revealed two reversible reduction steps at -1.30 and -1.99 V vs. SCE and one reversible oxidation at 0.42 V. The expansion of the electrochemical window using DME confirmed this behaviour and allowed for the observation of an additional, irreversible oxidation at 1.10 V, while the electrochemical range of CH₂Cl₂ enabled the observation of only one reduction and one oxidation step at -1.45 and 0.18 V. All one-electron transfer steps are well separated, indicating significant electron delocalization over the framework. The reversible oxidation likely involves the Ru²⁺/Ru³⁺ process while the irreversible electron transfer could be attributed to the oxidation of the Cp* ligand, as observed for Cp*₂Ru (0.55 and 1.25 in CH₂Cl₂),¹⁹ (Cp**Ru*)₂C₈H₆ (0.11 and 0.40 V in THF, -0.02 and 0.48 in CH₂Cl₂),^{6a} and

(Cp**Ru*)₂B₈H₁₄ (0.17 and 0.93 V in 8.5:1.5 CH₂Cl₂/toluene).^{17a} The reduction steps have no parallel in the chemistry of related species containing all-carbon and all-boron ligands and are attributed to processes centred mostly on the B₄N₂C₂²⁻ ligand. A theoretical analysis supports this view, as the optimized geometry of [4a]²⁻ is C_{2h} symmetric and contains a planar B₄N₂C₂ framework with no apparent N-N interaction. A two-electron oxidation was reported for the related *transoid*-[(CpRu)₂C₈H₈] complex, resulting in cleavage of a C-C bond in the bridging ligand and formation of a flyover dication.^{17a}

In conclusion, a pentalenediyl-like dianion with B₄N₂C₂ framework was isolated as a dipotassium salt, **3**. Its reaction with [Cp**Ru*Cl]₄ prompted the cleavage of the N-N bond and yielded the pseudo-triple-decker sandwich complex **4**, featuring a highly unusual monocyclic bridging ligand with an elongated-hexagonal B₄N₂C₂ skeleton. A computational analysis showed that this ligand could be considered a distorted form of the bicyclic ligand, brought about by the coordination to the transition metal. The cyclic voltammogram of **4** displayed three reversible, well separated one-electron transfer steps indicating efficient electron delocalization over the framework. Its ligand properties render the highly unusual π -bridging ligand a very promising building block for the design of larger sandwich-like architectures.

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- [13] Crystallographic data. *trans-2*: C₂₈H₂₈B₄N₂, 173 K, 0.20 × 0.20 × 0.08 mm, monoclinic, space group *P2₁/n*, *a* = 14.1990(10), *b* = 6.0800(2), *c* = 14.6470(11) Å, $\alpha = \gamma = 90^\circ$, $\beta = 103.012(3)^\circ$, *V* = 1232.01(13) Å³, *Z* = 2, $\rho_{\text{calcd}} = 1.175 \text{ g cm}^{-3}$, $3.64 \leq \theta \leq 27.42^\circ$, *R*₁ = 0.0502 (*I* > 2 σ (*I*)), *wR*₂ = 0.1296 (all data); residual electron density: 0.203/-0.172 e Å⁻³. **3(tmeda)**: C₂₀H₂₀B₂KN₃, 173 K, 0.16 × 0.08 × 0.06 mm, triclinic, space group *P-1*, *a* = 7.4770(5), *b* = 11.9330(9), *c* = 12.3420(10) Å, $\alpha = 94.030(3)^\circ$, $\gamma = 97.951(4)^\circ$, $\beta = 101.459(5)^\circ$, *V* = 1063.43(14) Å³, *Z* = 2, $\rho_{\text{calcd}} = 1.162 \text{ g cm}^{-3}$, $2.50 \leq \theta \leq 24.9^\circ$, *R*₁ = 0.051 (*I* > 2 σ (*I*)), *wR*₂ = 0.138 (all data); residual electron density: 0.22/-0.26 e Å⁻³. **4**: C₄₈H₅₆B₄N₂Ru₂, 173 K, 0.20 × 0.12 × 0.05 mm, monoclinic, space group *C2*, *a* = 24.955(8), *b* = 19.629(5), *c* = 10.626(3) Å, $\alpha = \gamma = 90^\circ$, $\beta = 114.964(15)^\circ$, *V* = 4719(2) Å³, *Z* = 4, $\rho_{\text{calcd}} = 1.458 \text{ g cm}^{-3}$, $3.24 \leq \theta \leq 27.48^\circ$, *R*₁ = 0.0387 (*I* > 2 σ (*I*)), *wR*₂ = 0.1125 (all data); residual electron density: 0.968/-0.695 e Å⁻³. MoK α radiation ($\lambda = 0.71073$ Å). Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included at geometrically calculated positions and refined using the riding model. CCDC-655685 - 655687 contain the supplementary crystallographic data for compounds **2** - **4**, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
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