

# Sandwich Complexes

## Unusual B<sub>4</sub>N<sub>2</sub>C<sub>2</sub> Ligand in a Ruthenium Pseudo-Triple-Decker Sandwich Complex Displaying Three Reversible Electron-Transfer Steps\*\*

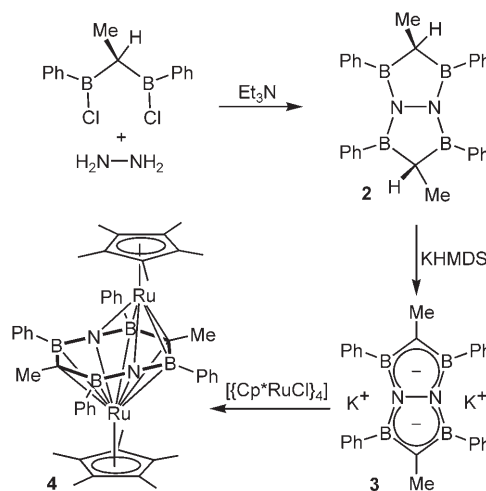
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Dedicated to Professor Richard J. Puddephatt

Polydecker sandwich complexes are highly desirable synthetic targets because of their potential applications as advanced materials, owing to the considerable interactions between their metal centers.<sup>[1]</sup> Cyclopentadienyl<sup>[2]</sup> and benzene<sup>[3]</sup> ligands were demonstrated early on to coordinate bifacially to transition metals and thus generate triple-decker sandwich complexes. Although larger oligomers have been identified in the gas phase,<sup>[4]</sup> the energy of such bridging  $\pi$  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 sandwich compounds of the main-group metals, which form extended structures in the solid state.<sup>[5]</sup> To circumvent the low tendency of organic ligands to bridge metal centers and build stacked sandwich compounds, annelated cyclopentadienyl derivatives such as indacene<sup>[6]</sup> and especially pentalene<sup>[6a,7]</sup> have been used as building blocks for staggered multidecker sandwich compounds. Although promising, these systems have limitations associated with 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.<sup>[8]</sup> Heterocyclic rings, particularly those containing boron, have a higher tendency to coordinate bifacially and generate stacked sandwich compounds.<sup>[9]</sup> The largest multidecker sandwich compounds known to date contain six decks and feature dianionic cyclic ligands with B<sub>2</sub>C<sub>3</sub> and B<sub>3</sub>C<sub>2</sub> frameworks.<sup>[10]</sup> The only family of polydecker

complexes reported so far,  $[\text{Ni}(\text{C}_3\text{B}_2\text{Me}_2\text{RR}'\text{R}'')]_x$  displayed conducting properties.<sup>[11]</sup>

Within the scope of our investigation on heterocyclic cyclopentadienyl analogues, we developed the 1,2-diaza-3,5-diborolyl derivatives **1**.<sup>[12]</sup> Herein, we report the extension of this project to the pentalenediyl-like dianion in **3** (Scheme 1), which is a very promising bridging  $\pi$  ligand for the assembly of polymeric materials.



**Scheme 1.** Synthesis of derivatives **2–4**. KHMDs = K[N(SiMe<sub>3</sub>)<sub>2</sub>], Cp\* = C<sub>5</sub>Me<sub>5</sub>.

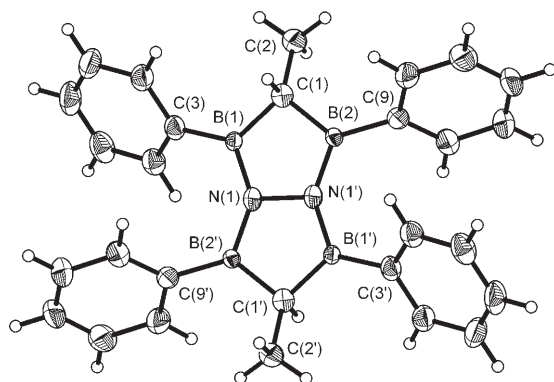
The precursor **2** was obtained as a mixture of *cis* and *trans* isomers through condensation of hydrazine and 1,1-bis(phenylchloroboryl)ethane<sup>[12b]</sup> in the presence of triethylamine (see the Supporting Information). The *trans* isomer could be separated by crystallization and was structurally characterized (Figure 1).<sup>[13]</sup> It features a long N–N bond of 1.48 Å, slightly longer than the N–N bonds in hydrazine (1.45 Å)<sup>[14]</sup> and the metal complexes of **1** (1.44–1.47 Å).<sup>[12]</sup> The endocyclic B–C and B–N bonds (average 1.57 and 1.44 Å) are longer and slightly shorter, respectively, than the corresponding bonds in the alkali-metal salts of the monocyclic analogues.<sup>[12b]</sup> For comparison, the B–N bonds in borazines measure 1.42–1.44 Å.<sup>[15]</sup>

Double deprotonation of **2** with K[N(SiMe<sub>3</sub>)<sub>2</sub>] could be conducted directly or in two successive steps, yielding the orange dipotassium salt **3**. As expected, both isomers

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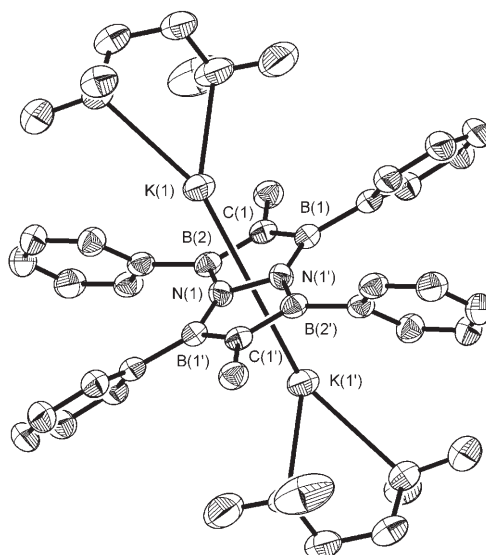


**Figure 1.** Molecular structure of *trans*-**2**. Thermal ellipsoids are set at 50 % probability. Selected bond lengths [Å] and angles [°]: N–N 1.480(2), B–N 1.436(2), 1.437(2), B–C(1) 1.571(2), 1.574(2); B–N–B 140.88(14), N–B–C(1) 108.89(13), 109.02(14), B–C(1)–B 101.86(13), B–N–N 109.54(15), 109.58(14).

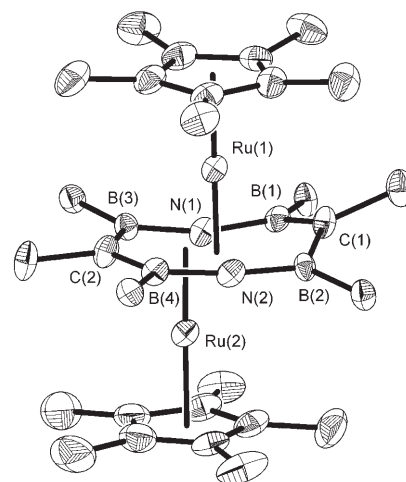
produced the same mono- and dianions. The loss of the methine protons was noticeable in the  $^1\text{H}$  NMR spectrum of **3**, and the deprotonation resulted in a  $\delta = 14$  ppm upfield shift of the  $^{11}\text{B}$  NMR signal. Despite its very similar geometry, the 8- $\pi$ -electron heterocyclic ligand in **3** is not a direct analogue of the 10- $\pi$ -electron pentalenediyl dianion.<sup>[7,8]</sup>

The crystal structure of **3**(*tmeda*)<sub>2</sub> (*tmeda* = *N,N,N',N'*-tetramethylethylenediamine) was determined, revealing that the planar  $\text{B}_4\text{N}_2\text{C}_2$  ligand is coordinated by two potassium ions, each supporting a *tmeda* molecule, in a centrosymmetric arrangement (Figure 2).<sup>[13]</sup> 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 the cyclopentadienyl anion. The separation between the two potassium ions measures 5.52 Å and is comparable to the K⋯K separation observed in polymeric cyclopentadienyl salts (5.52–5.85 Å)<sup>[12b]</sup> and the dimeric potassium pentalenediyl derivative (5.43, 5.48 Å).<sup>[16]</sup>

Reaction of **3** with  $[(\text{Cp}^*\text{RuCl})_4]$  yielded the pseudo-triple-decker sandwich **4**. The  $\text{Cp}^*$  groups, as well as the boron centers and the phenyl and methyl substituents of the bridging  $\pi$  ligand are equivalent on the time scale of NMR spectroscopy, 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 by 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 (Figure 3).<sup>[13]</sup> The N–N bond cleaves upon the formation of **4**, and the 8- $\pi$ -electron bicyclic ligand transforms into a  $\text{B}_4\text{N}_2\text{C}_2$  ring. Its geometry can be best described as a severely elongated hexagon, and is, to our knowledge, unprecedented for eight-membered rings. The structure is asymmetric, with Ru(1) situated within bonding distance from all the B atoms (2.488(7)–2.546(7) Å), while Ru(2) is clearly  $\eta^5$ -coordinated by N(1), B(3), C(2), B(4), and N(2). The coordination of Ru(1) can be described as  $\eta^7$  or  $\eta^8$ , depending on the involvement of C(2) in the bonding (Ru(1)–C(2) 2.548(6) Å



**Figure 2.** Molecular structure of **3**(*tmeda*)<sub>2</sub>. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are set at 50 % probability. 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 2.820(2), 2.889(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).



**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 omitted. Thermal ellipsoids are set at 50 % probability. Selected bond lengths [Å] and angles [°]: N(1)⋯N(2) 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)⋯Ru(2) 3.240(6), Ru–N, 2.118(5)–3.2(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).

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  $\text{B}_4\text{N}_2\text{C}_2$  ligand (1.58, 1.62 Å vs. Ru– $\text{Cp}^*$  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  $[(\text{Cp}^*\text{Ru})_2\text{B}_8\text{H}_{14}]$ .<sup>[17b]</sup> Unfortunately, no complete structural data is available for the

analogues containing all-carbon ligands,  $[(\text{Cp}^*\text{Ru})_2\text{C}_8\text{H}_6]^{[6a]}$  and *transoid*- $[(\text{CpRu})_2\text{C}_8\text{H}_8]$  ( $\text{Cp} = \text{C}_5\text{H}_5$ ).<sup>[17a]</sup>

A computational analysis at the DFT level (see the Supporting Information) performed on the model structure **4a**, which features a hydrogen-substituted  $\text{B}_4\text{N}_2\text{C}_2\text{H}_6$  ligand and Cp groups, gave a molecular geometry in reasonable agreement with the X-ray diffraction data. The frontier molecular orbital (MO) analysis of **4a** shows that substantial mixing of the ligand orbitals with the MOs of the  $\{\text{CpRu}\}^+$  fragments takes place, thus 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 that are orientated parallel and perpendicular to the  $\text{B}_4\text{N}_2\text{C}_2$  plane. The similar oxidative addition of hydrazines to transition metals has recently been reported.<sup>[18]</sup> 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  $-1900 \text{ kJ mol}^{-1}$  (total calculated bond energy is  $-2400 \text{ kJ mol}^{-1}$ ). Mayer bond orders obtained for **4a** support the description of Ru(2) as  $\eta^5$ -coordinated, whereas coordination of Ru(1) can be best described as  $\eta^8$ ; the largest bond orders (around 0.45) are calculated for Ru–N interactions. As expected, the bonding analysis shows no sign of N–N interactions. Hence, the computational data indicate 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  $-1.99 \text{ V}$  vs. standard calomel electrode (SCE) and one reversible oxidation at  $0.42 \text{ V}$ . The expansion of the electrochemical window using dimethoxyethane (DME) confirmed this behavior and allowed for the observation of an additional, irreversible oxidation at  $1.10 \text{ V}$ , while the electrochemical range of  $\text{CH}_2\text{Cl}_2$  enabled the observation of only one reduction and one oxidation step at  $-1.45$  and  $0.18 \text{ V}$ , respectively. All one-electron transfer steps are well-separated, indicating significant electron delocalization over the framework. The reversible oxidation likely involves the  $\text{Ru}^{2+}/\text{Ru}^{3+}$  process, while the irreversible electron transfer could be attributed to the oxidation of the  $\text{Cp}^*$  ligand, as observed for  $[\text{Cp}^*_2\text{Ru}]$  ( $0.55$  and  $1.25 \text{ V}$  in  $\text{CH}_2\text{Cl}_2$ ),<sup>[19]</sup>  $[(\text{Cp}^*\text{Ru})_2\text{C}_8\text{H}_6]$  ( $0.11$  and  $0.40 \text{ V}$  in THF,  $-0.02$  and  $0.48 \text{ V}$  in  $\text{CH}_2\text{Cl}_2$ ),<sup>[6a]</sup> and  $[(\text{Cp}^*\text{Ru})_2\text{B}_8\text{H}_{14}]$  ( $0.17$  and  $0.93 \text{ V}$  in  $8.5:1.5 \text{ CH}_2\text{Cl}_2/\text{toluene}$ ;  $\text{V}$  versus SCE in all cases).<sup>[17b]</sup> The reduction steps have no parallel in the chemistry of related species containing all-carbon and all-boron ligands and are attributed to processes centered mostly on the  $[\text{B}_4\text{N}_2\text{C}_2]^{2-}$  ligand. A theoretical analysis supports this view, as the optimized geometry of  $[\text{4a}]^{2-}$  is  $C_{2h}$ -symmetric and contains a planar  $\text{B}_4\text{N}_2\text{C}_2$  framework with no apparent N–N interaction. A two-electron oxidation was reported for the related *transoid*- $[(\text{CpRu})_2\text{C}_8\text{H}_8]$  complex, resulting in cleavage of a C–C bond in the bridging ligand and formation of a flyover dication.<sup>[17a]</sup>

In conclusion, a pentalenediyl-like dianion with  $\text{B}_4\text{N}_2\text{C}_2$  framework was isolated as a dipotassium salt, **3**. Its reaction

with  $[(\text{Cp}^*\text{RuCl})_4]$  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  $\text{B}_4\text{N}_2\text{C}_2$  skeleton. A computational analysis showed that this ligand could be considered a distorted form of the bicyclic ligand, brought about by 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 bridging  $\pi$  ligand a very promising building block for the design of larger sandwich-like architectures.

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- [13] Crystallographic data: *trans*-**2**: C<sub>28</sub>H<sub>28</sub>B<sub>4</sub>N<sub>2</sub>, 173 K, 0.20 × 0.20 × 0.08 mm, monoclinic, space group *P*2<sub>1</sub>/*n*, *a* = 14.1990(10), *b* = 6.0800(2), *c* = 14.6470(11) Å, β = 103.012(3)°, *V* = 1232.01(13) Å<sup>3</sup>, *Z* = 2, ρ<sub>calcd</sub> = 1.175 g cm<sup>-3</sup>, 3.64 ≤ θ ≤ 27.42°, *R*<sub>1</sub> = 0.0502 (*I* > 2σ(*I*)), *wR*<sub>2</sub> = 0.1296 (all data); residual electron density 0.203/–0.172 e Å<sup>-3</sup>. **3**(tmeda)<sub>2</sub>: C<sub>20</sub>H<sub>29</sub>B<sub>2</sub>KN<sub>3</sub>, 173 K, 0.16 × 0.08 × 0.06 mm, triclinic, space group *P*1̄, *a* = 7.4770(5), *b* = 11.9330(9), *c* = 12.3420(10) Å, α = 94.030(3), γ = 97.951(4), β = 101.459(5)°, *V* = 1063.43(14) Å<sup>3</sup>, *Z* = 2, ρ<sub>calcd</sub> = 1.162 g cm<sup>-3</sup>, 2.50 ≤ θ ≤ 24.9°, *R*<sub>1</sub> = 0.051 (*I* > 2σ(*I*)), *wR*<sub>2</sub> = 0.138 (all data); residual electron density 0.22/–0.26 e Å<sup>-3</sup>. **4**·1.5 C<sub>6</sub>H<sub>14</sub>: C<sub>57</sub>H<sub>77</sub>B<sub>4</sub>N<sub>2</sub>Ru<sub>2</sub>, 173 K, 0.20 × 0.12 × 0.05 mm, monoclinic, space group *C*2, *a* = 24.955(8), *b* = 19.629(5), *c* = 10.626(3) Å, β = 114.964(15)°, *V* = 4719(2) Å<sup>3</sup>, *Z* = 4, ρ<sub>calcd</sub> = 1.458 g cm<sup>-3</sup>, 3.24 ≤ θ ≤ 27.48°, *R*<sub>1</sub> = 0.0387 (*I* > 2σ(*I*)), *wR*<sub>2</sub> = 0.1125 (all data); residual electron density 0.968/–0.695 e Å<sup>-3</sup>. MoK<sub>α</sub> radiation (λ = 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, -655686, and -655687 (**2**, **3**, and **4**, respectively) contain the supplementary crystallographic data for this paper. 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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