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## COMMUNICATION

# An Electron-poor Di-Molybdenum Triple-decker with a Puckered [B<sub>4</sub>Ru<sub>2</sub>] Bridging Ring is an *oblato-closo* Cluster $\ddagger$

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An unprecedented, 22-valence-electron triple-decker sandwich complex [(Cp\*Mo)<sub>2</sub>{μ-η<sup>6</sup>:η<sup>6</sup>-B<sub>4</sub>H<sub>4</sub>Ru<sub>2</sub>(CO)<sub>6</sub>}], **2** has been prepared. In an effort to generate analogous triple-deckers with group 6 metal carbonyl fragments in the middle deck, we have isolated [(Cp\*MoCO)<sub>2</sub>(μ-H)<sub>2</sub>B<sub>4</sub>H<sub>4</sub>], **3** that provides the first direct evidence for the missing link between [(Cp\*MoCl)<sub>2</sub>B<sub>3</sub>H<sub>7</sub>] and [(Cp\*Mo)<sub>2</sub>B<sub>5</sub>H<sub>9</sub>] clusters.

Discovery of ferrocene,<sup>1</sup> which played a key role in the emerging field of organometallic chemistry, opened up an interesting aspect of compounds with sandwich structure.<sup>2</sup> As a result, due to their unique structural features<sup>3</sup> and useful applications in catalysis, supramolecular chemistry and molecular electronics<sup>4</sup> a considerable interest has been shown in the area of multimetallic complexes containing π-conjugated ligands.<sup>5-7</sup> Two decades later, the landmark synthesis of the first triple-decker sandwich complex tris(η<sup>5</sup>-cyclopentadienyl) dinickelation, [Cp<sub>3</sub>Ni<sub>2</sub>]<sup>+</sup>,<sup>8</sup> indeed augmented the field of multi-decker sandwich complexes. Although, the formation of [Cp<sub>3</sub>Ni<sub>2</sub>]<sup>+</sup> was first observed by the mass spectrum analysis of nickelocene,<sup>9</sup> Grimes reported the first neutral and air stable triple decker compounds [(CpCo)<sub>2</sub>RC<sub>2</sub>B<sub>3</sub>H<sub>4</sub>] (R = Me/H), containing a central [RC<sub>2</sub>B<sub>3</sub>H<sub>4</sub>]<sup>4-</sup> ring (formally isoelectronic with C<sub>5</sub>H<sub>5</sub>).<sup>10</sup> Nearly after this (1974), Salzer established the X-ray structure of [Cp<sub>3</sub>Ni<sub>2</sub>]<sup>+</sup> as [Cp<sub>3</sub>Ni<sub>2</sub><sup>+</sup>BF<sub>4</sub><sup>-</sup>].<sup>11</sup>

Planar rings built up by one element have been the focus of experimental and theoretical work in the molecular and inorganic solid-state chemistry.<sup>12, 13</sup> As a result, triple-decker compounds containing *cyclo*-(η<sup>n</sup>-E<sub>n</sub>) as middle deck (E = C, P, As, Sb etc.; n = 5 or 6)<sup>14-16</sup> experienced the most proliferation. Having one valence

electron less than carbon, boron is known to build mainly cage sub-structures.<sup>12a, 13, 17</sup> Thus, compounds containing planar boron ring are almost non-existent and only a handful of such compounds are known (Chart 1). The first structurally characterized compounds containing planar boron clusters as ligands were the triple-deckers [(Cp\*ReH)<sub>2</sub>B<sub>5</sub>Cl<sub>5</sub>]<sup>18</sup> and [(Cp\*Re)<sub>2</sub>B<sub>6</sub>H<sub>4</sub>Cl<sub>2</sub>], **I**,<sup>19</sup> in which the B<sub>n</sub>X<sub>n</sub> (n = 5, 6; X = H or Cl) unit was found to be perfectly planar pentagonal or hexagonal motif trapped with two Cp\*Re fragments. Himmel and co-workers have recently reported the doubly base-stabilized B<sub>3</sub>H<sub>6</sub><sup>+</sup> analogue accommodating a planar boron triangle.<sup>20</sup>

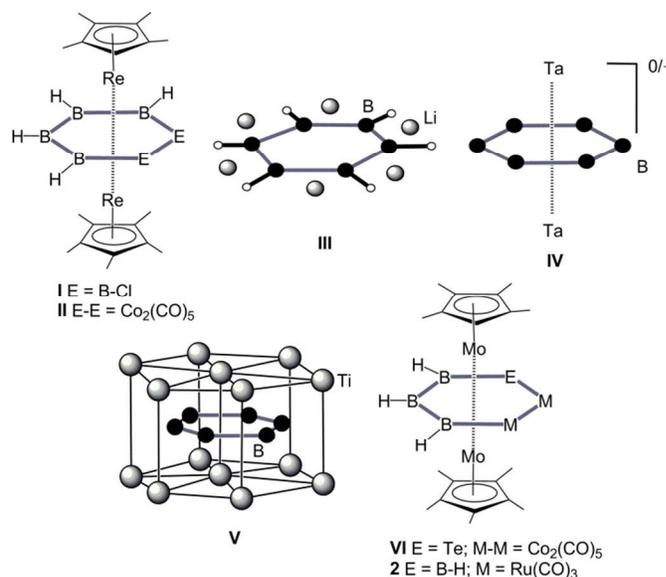


Chart 1. Different species containing six-member ring composed of B atom.

However, the only bare planar B<sub>6</sub> ring as a structural motif was discovered recently in the solid compound [Ti<sub>7</sub>Rh<sub>4</sub>Ir<sub>2</sub>B<sub>8</sub>], **V** in which the B<sub>6</sub> ring is sandwiched between two metal atoms in a bipyramidal fashion.<sup>21</sup>

Several theoretical studies have been appeared that explains the bonding situation of the triple decker sandwich complexes.<sup>22</sup> Wade's rules predict maximal stability for an electron count of 30.<sup>23</sup> A

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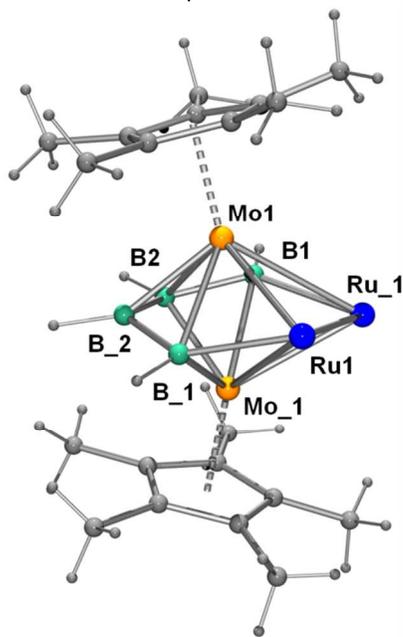
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‡ Dedicated to Professor Russell N Grimes on the occasion of his 80th birthday in recognition of his outstanding contributions to the area of boron chemistry.

† Electronic Supplementary Information (ESI) available: CCDC-1036041-1036043 and 1036888, For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b000000x/

detailed account by Hoffmann and co-workers predicted that complex with 30 or 34 valence electrons would show stable closed shell species.<sup>24</sup> In 2003 Boldyrev and co-workers<sup>25</sup> theoretically predicted the new family of planar aromatic highly charged boranes, such as  $[B_6H_6]^{6-}$ , **III** stabilized by six  $Li^+$  cation surrounding the species. A recent theoretical investigation has shown the possibility of the formation of  $[Ta_2B_6]^{0-}$ , **IV** in which the planar  $B_6$  ring is sandwiched by two Ta atoms.<sup>26</sup>

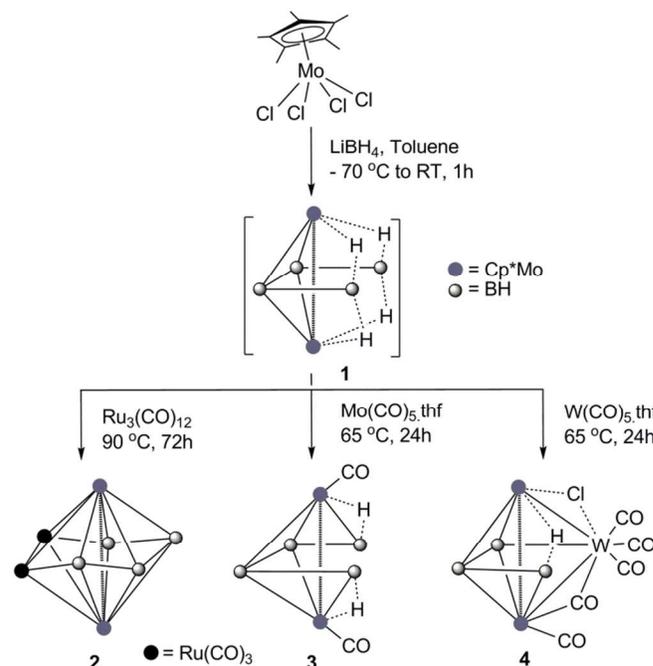
After developing a good route for  $[(Cp^*Re)_2B_4H_8]^{27}$ , Fehlner and co-workers tried to close the central open ring with the main group and transition metal fragments. As a result, two novel triple-decker compounds  $[(Cp^*Re)_2\{\mu-\eta^6:\eta^6-B_6H_4Cl_2\}]$ ,<sup>19</sup> **I** and  $[(Cp^*Re)_2\{\mu-\eta^6:\eta^6-B_4H_4Co_2(CO)_5\}]$ ,<sup>28</sup> **II** were isolated with the successful ring closure. During the course of our studies on novel triple-decker complex, we have recently isolated and structurally characterized a triple-decker complex  $[(Cp^*Mo)_2\{\mu-\eta^6:\eta^6-B_3H_3TeCo_2(CO)_5\}]$ ,<sup>29</sup> **VI** where the middle deck is composed of B, Co, and a heavy Te atom. Therefore, in an attempt to close the central open ring of  $[(Cp^*Mo)_2B_4H_8]$ , **1**<sup>30</sup> a proposed intermediate obtained from metathesis reaction of  $[Cp^*MoCl_4]$  with  $LiBH_4 \cdot thf$  at low temperature, we carried out the reaction with  $[Ru_3(CO)_{12}]$  that yielded triple-decker  $[(Cp^*Mo)_2\{\mu-\eta^6:\eta^6-B_4H_4Ru_2(CO)_6\}]$ , **2** (4%). The  $^{11}B\{^1H\}$  NMR spectrum shows one broad peak at  $\delta = 91.3$  ppm and the mass spectrometric data of **2** confirms the composition of  $C_{26}H_{34}B_4O_6Mo_2Ru_2$ .  $^1H$  NMR spectrum reveals equivalent  $Cp^*$  ligand and no metal hydrides or bridging hydride were observed. The presence of CO ligands was confirmed by  $^{13}C$  NMR spectrum and IR spectroscopy. However, identity of the molecule was unambiguous and definitive structural characterization was determined by X-ray diffraction analysis on a suitable crystal obtained from a solution of compound **2** in hexane at  $-5^\circ C$ .



**Fig. 1** Molecular structure of **2**. The CO groups in  $Ru_2(CO)_6$  and Mo-Mo bond are omitted for clarity. Selected bond lengths (Å): Mo1–Mo<sub>1</sub> 2.7510(5), Mo1–Ru1 2.6625(4), Mo<sub>1</sub>–Ru<sub>1</sub> 2.9529(4), Ru<sub>1</sub>–Ru<sub>1</sub> 2.8822(5), B1–B2 1.622(5), B2–B<sub>2</sub> 1.679(7), B1–Ru1 2.180(4), B1–H1 1.080(19), B2–H2 1.224(19).

The molecular structure of **2**, shown in Fig. 1, can be seen as  $[(Cp^*Mo)_2\{\mu-\eta^6:\eta^6-B_4H_4Ru_2(CO)_6\}]$ , fully consistent with the solution spectroscopic data. The molecule possess a puckered six-member hexahapto  $[B_4H_4Ru_2(CO)_6]$  ring, sandwiched between two

$Cp^*Mo$  fragments (mean plane standard deviation 0.18133 Å and sum of internal angles 698.2°; Fig. S4†). The six CO ligands of the two Ru atoms are oriented in eclipsed fashion around the Ru-Ru bond, which causes dis-rotatory bent in  $Cp^*$  ligands (dihedral angle 28.07°). The methyl groups of the  $Cp^*$  ligands are nearly in eclipsed orientations. The Mo-Mo bond length of 2.751 Å is comparable with reported molybdaboranes. Although the Mo-B, B-Ru and Ru-Ru distances are in the range found for other molybda/ruthenaboranes,<sup>31</sup> the average B-B distance of 1.650(6) Å is comparably shorter.<sup>32</sup> The structure of **2** contains a  $[(Cp^*Mo)_2B_4H_4]$  fragment, qualitatively similar to that of  $[(CpMo)_2B_4H_8]$  with the four hydrogen atoms replaced by  $[Ru_2(CO)_6]$  fragment. Therefore, the observed structure of **2** is consistent with the description of triple-decker complex and highly significant because it extends the generality of *oblato-closo*<sup>33</sup> designation of the  $[(Cp^*Re)_2(B_nH_n)]$  species.

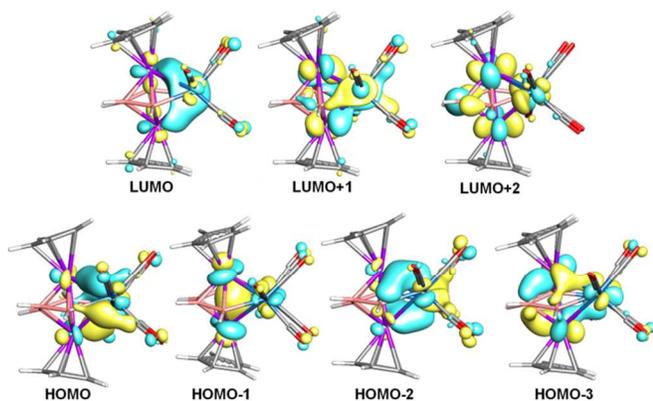


**Scheme 1** Synthesis of **2-4**†

The very low formal electron count of 22<sup>34</sup> is particularly notable and to the best of our knowledge, to date, **2** is the second example with lowest recorded electron count among triple-decker complexes.<sup>35</sup> Compound **2** contains 5 skeletal electron pairs (sep), thus it does not obey Wade-Mingos rule<sup>36</sup> to be called a *closo*-hexagonal bipyramidal. This led us to perform a detailed electronic structure and bonding analysis of **2** in the context of 34-ve  $[Cp_3Ni_2]^+$ . The MO correlation diagrams are shown in Fig. S6†. The Extended-Hueckel MO calculations, carried out by Hoffmann and co-workers,<sup>24</sup> showed that the HOMO of  $[Cp_3Ni_2]^+$  ( $e_1'$ ) is made up of  $d_{xz}$  and  $d_{yz}$  orbitals of CpNi fragments. Six of the low lying occupied molecular orbitals; often designated as “ $t_{2g}$ ” ( $d_{xy}$ ,  $d_{x^2-y^2}$  and  $d_{z^2}$ ) remain non-bonding. An oblate middle ring as well as a short M-M distance causes the  $a_1'$  ( $d_z^2$ , M-M bonding) and  $a_2''$  orbitals (M-M antibonding) to be strongly separated. As a result, the M-M antibonding orbital lies very high and stayed unoccupied. Therefore, a 24-ve complex (**I**) can be attained by strengthening the interactions between the metal centres and metal-ring.<sup>18</sup>

The existence of a puckered middle ring in **2** may be due to the mismatch of energy of  $\{Cp^*Mo\}$  fragment orbitals and the  $[B_4H_4Ru_2(CO)_6]$  ring. The high metal based orbital energies of Mo, low energy central ring orbitals and the non-planar orientation of

Cp\* ligands lower the orbital symmetry and hence, make the bonding situation very complex. The existence of a short Mo-Mo distance of 2.7510(5) Å in **2**, splits the bonding ( $a_1'$ ) and the antibonding ( $a_2''$ ) orbitals by 11.23 eV. The HOMO-1 of **2** is  $a_1'$  i.e., Mo-Mo bonding, whereas the HOMO and LUMO largely localized over two Ru atoms. The LUMO+1 orbitals are Mo-Mo bonding with



**Fig. 2** Frontier molecular orbitals of **2** as obtained from calculation. Contour values:  $\pm 0.04$  (e/bohr<sup>3</sup>)<sup>1/2</sup>.

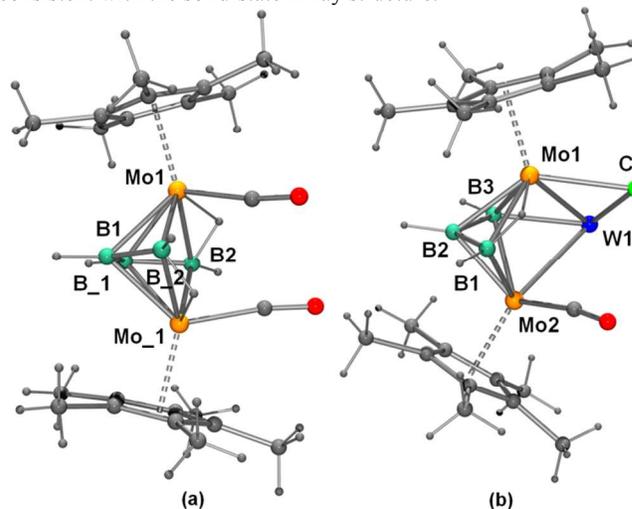
$\delta$  symmetry, which are strongly destabilised by the antibonding interaction with the  $\sigma$ -bonding orbitals of middle  $[B_4Ru_2]$  ring (Fig. 2). However, the corresponding bonding combinations with  $\delta$  symmetry are filled and stabilised. As a result, participation of the “ $t_{2g}$ ” orbitals of Mo and Ru provide four pairs of electrons to satisfy the skeletal electron counting. Although a good HOMO-LUMO gap of ca. 3.75 eV observed for **1**, only ca. 0.86 eV has been computed for **2** that describes its less thermodynamic stability.

The main group-transition metal clusters mimic structural aspects of metal clusters, metal hydroborate complexes, and metal-hydrocarbon  $\pi$  complexes.<sup>12a,b,37</sup> Both isolobal analogies and cluster electron-counting protocols are now strongly established as conceptual and practical tools to modern chemists.<sup>38</sup> Hence, the synthesis of main group analogues provides an experimental platform for developing and understanding the role of element variation both in structure and reactivity.<sup>38</sup> As, “conical”  $\{Ru(CO)_3\}$  and “ $C_{4v}$ ”  $\{M(CO)_4\}$  ( $M = Mo$  and  $W$ ) fragments are isolobal to  $\{BH\}$ <sup>38,39</sup>, we performed the reaction of **1** with group 6 mono-metal carbonyl fragments,  $[M(CO)_5.thf]$  ( $M = Mo$  and  $W$ ; Scheme 1). Although the objective of generating triple-decker complexes was not achieved, we have isolated  $[(Cp^*MoCO)_2(\mu-H)_2B_4H_4]$ , **3** in good yield (40%). The <sup>11</sup>B NMR shows two resonances in 1:1 ratio and the <sup>1</sup>H NMR shows one up-field chemical shift with a broad signal at  $\delta = -9.81$  ppm. The presence of terminal CO ligands has been confirmed by IR and <sup>13</sup>C NMR spectroscopy.

The solid state X-ray structure of **3**, shown in Fig. 3a, can be viewed as  $\{Mo_2B_2\}$  tetrahedron, in which two boron atoms (B2 and B<sub>2</sub>) capped the  $Mo_2B$  triangular faces. Geometry of **3** can also be visualized as *oblate-arachno* polyhedra with the removal of two vertices from *oblate closo* hexagonal bipyramid. The CO ligands are oriented towards the open face of the cluster along with two Mo-H-B bonds. Isolation of **3** provides for the first time, the direct evidence of the existence of saturated molybdaborane compound  $[(Cp^*Mo)_2B_4H_{10}]$ , in which four hydrogen atoms are replaced by two CO ligands.

With a view to further investigating the scope of this chemistry in the synthesis of analogous triple-decker, we perform the reaction of **1** with  $[W(CO)_5.thf]$  under analogous conditions to those employed for **3**. However, the product  $[(Cp^*MoCO)(Cp^*MoCl)(\mu-H)B_3H_3W(CO)_4]$  **4**, so formed is a derivative of **3**. Compound **4** was isolated

in 10% yield along with the formation of **3** (6%) and characterized by standard spectroscopic and crystallographic methods. Note that, the presence of chloride in **4** might have come from the excess of LiCl, generated during the metathesis reaction of  $[Cp^*MoCl_4]$  with  $LiBH_4.thf$ . The solid state X-ray structure of **4**, shown in Fig. 3b, is analogous to **3** and **1**<sup>29</sup> and one of the differences between these two is the presence of a  $[W(CO)_4]$  fragment in **4** instead of a BH fragment. The solution state spectroscopic data of **4** are fully consistent with the solid-state X-ray structure.



**Fig. 3** Molecular structure of (a) **3** and (b) **4**. The Mo-Mo bond and CO groups of  $W(CO)_4$  are omitted for clarity. Selected bond lengths (Å): **3**: B1-B2 1.63(3), B1-B<sub>1</sub> 1.73(6), Mo1-Mo<sub>1</sub> 2.9262(11), B1-H1 1.13(2), B2-H2 1.150(11), B2-H2A 1.156(11), **4**: Mo1-Mo2 2.9611(7), B1-B2 1.719(12), B2-B3 1.736(10), B3-W1 2.340(7), Mo1-W1 3.0004(6), Mo2-Cl1 2.4246(15), W1-Cl1 2.5203(16), B3-H3 1.15(2), B1-H1D 1.13(2), B1-H1E 1.15(2), Mo2-H1E 1.77(7), B2-H2 1.15(2).

The existence of  $[(Cp^*Mo)_2B_4H_4]$  fragment both in **2** and **3** directed us to find out a probable mechanism for the formation of **2**. As a result, we carried out the reaction of **3** with  $[Ru_3(CO)_{12}]$ . To our surprise, both thermolytic and photolytic reactions failed to generate **2**, instead a heterometallic boride  $[(Cp^*Mo)_2(CO)_4(\mu_4-B)Ru_2(CO)_6(\mu-H)]$ , **5** (8%) was isolated in less yield (Fig. S5†, see supporting information).

In conclusion, this work describes the isolation of the first 22 valence electron triple-decker complex containing a  $[B_4Ru_2]$  ring. Further, in an effort to generate analogous triple-deckers with group 6 metal carbonyl fragments in the middle deck, we have isolated  $[(Cp^*MoCO)_2B_4H_6]$  that offers a direct evidence for the missing link between the  $[M_2B_3]$  and  $[M_2B_5]$  clusters ( $M = Mo$ ). The bonding of these novel complexes have been studied computationally by DFT methods. The results described here find a new foray towards the search of group 6 triple-decker complexes. Such studies are in progress.

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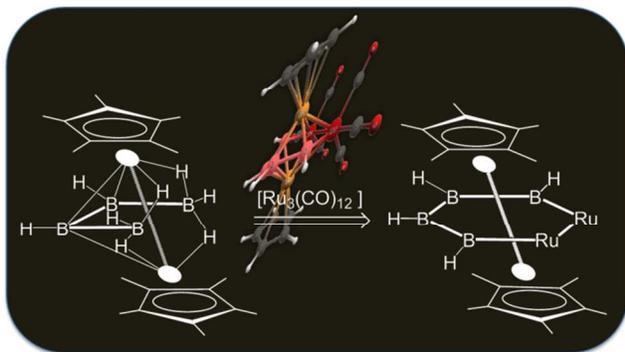
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## COMMUNICATION

Table of contents

**An Electron-poor Di-Molybdenum Triple-decker with a Puckered [B<sub>4</sub>Ru<sub>2</sub>] Bridging Ring is an *oblato-closo* Cluster<sup>‡†</sup>**Bijan Mondal<sup>a</sup>, Bijnaneswar Mondal<sup>a</sup>,  
Koushik Pal<sup>a</sup>, Babu Varghese<sup>b</sup> and  
Sundargopal Ghosh<sup>a\*</sup>

An unprecedented, 22 valence-electron triple-decker sandwich complex [(Cp\*Mo)<sub>2</sub>{μ-η<sup>6</sup>:η<sup>6</sup>-B<sub>4</sub>H<sub>4</sub>Ru<sub>2</sub>(CO)<sub>6</sub>}] has been prepared, which is the second example with lowest recorded electron count among the triple-decker complexes.



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**Keywords:** boron, triple-decker, metallaborane, molybdenum.