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All-Boron Analogue of Planar Benzene on an Osmium Template

Ketaki Kar,^a Gaurav Joshi,^b Eluvathingal D. Jemmis,^{*b} and Sundargopal Ghosh^{*a}Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

The synthesis of planar hexaborane B₆ ring remains a long-standing and elusive ambition in boron chemistry, defying boron's intrinsic electron deficiency that drives it to favour polyhedral three-dimensional geometries rather than chains and rings. Owing to this domination, earlier attempts to stabilize the planar B₆ ring in a monometallic template encountered no success. Herein, we report the synthesis and structure of *bis-nido*-[Cp*Os(η⁶-B₆H₁₁)] (Cp* = η⁵-C₅Me₅) (**1**), the first planar [B₆H₁₁] ring stabilized by monometallic late transition metal (TM) fragment, [Cp*Os]. The fluxionality due to rapid exchange between the bridging hydrogens in **1** led to considerable structural intrigue, resembling the dynamic behaviour seen in *nido*-[B₆H₁₀]. Furthermore, we have successfully isolated the intermediate boron chains, *nido-arachno*-[Cp*Os(η⁵-B₅H₁₂)] (**2**) and *nido-arachno*-[Cp*Os(η⁴-B₄H₉)] (**3**). The B₅ chain in **2** and the B₄ chain in **3** are isoelectronic with the pentadienyl radical (C₅H₅) and the 1,3-butadiene radical cation (C₄H₆)⁺, respectively. Extensive multicenter bonding interactions are demonstrated to stabilize the unique flat ring as well as boron chains within monocapped scaffolds.

Introduction

The influence of planar organic aromatic molecules in chemistry is overwhelming; in contrast, the chemistry of aromatic molecules from neighbouring main group elements is only beginning. Interest in the chemistry of the *cyclo*-P_{*n*} ring, isoelectronic to *cyclo*-(CH)_{*n*}, is coming of age.^{1–5} There are now several examples of aromatic systems among heavier elements in the nitrogen group.^{6–11} The boron group presents a different scenario due to electron deficiency.^{12–18} The classical *closo*-polyhedral boranes (B_{*n*}H_{*n*})^{2–} follow Wade's Rule and the Rudolph diagram exemplify the *nido*- or *arachno*-structures with an increasing number of electrons.¹² Planar rings are rarely in the reckoning. Interestingly, the early synthesis and structural assignment of a dication of hexamethylbenzene, (C₆(CH₃)₆)²⁺ (**I**), which is isoelectronic to *nido*-[B₆H₁₀] (**II**), have been a reminder of the lineage to planar rings (Chart 1).^{19–22} Over the past few decades, there have been several reports on planar B_{*n*} rings (*n* = 3–5) stabilized either by main group or transition metal (TM) fragments. For example, B₃ rings in Na₄[B₃(NCy₂)₃]₂·2DME (**III**) (Chart 1), B₄ ring in [(CO)₃Fe(B₄H₈)], B₅ ring in [CpFe(B₅H₁₀)] and others.^{24–30} Although numerous theoretical studies have shown the stabilization of the planar B₆ ring isoelectronic with benzene,^{31–35} only a very few experimental reports have demonstrated its stabilization within a triple-decker sandwich-type scaffold using early transition metals.^{36–39} Recently, we

have compiled these significant experimental and theoretical advances and proposed a modified Rudolph diagram with emphasis on planar boron rings.³⁰ Despite several significant efforts and occasional breakthroughs in the chemistry of hexagonal planar boron rings, the isolation of the flat parent B₆ ring, isoelectronic to benzene, in a monometallic template remains enigmatic.

Although some reports on planar B_{*n*} (*n* = 4 and 5) rings stabilized in monometallic templates are available, all attempts to isolate a hexagonal planar B₆ ring in a monometallic template have not met with success. In this article, we report the first planar B₆ ring stabilized by a monometallic {Cp*Os} in *bis-nido*-arrangement, [Cp*Os(η⁶-B₆H₁₁)] (**1**), utilizing an optimized new synthetic strategy involving controlled pyrolysis (Scheme 1). The [B₆H₁₁] ring with five B–H–B-bridging hydrogens is isoelectronic to benzenyl cation radical [C₆H₆]⁺. In pursuit of elucidating the intermediates from monoborane precursor to complex **1**

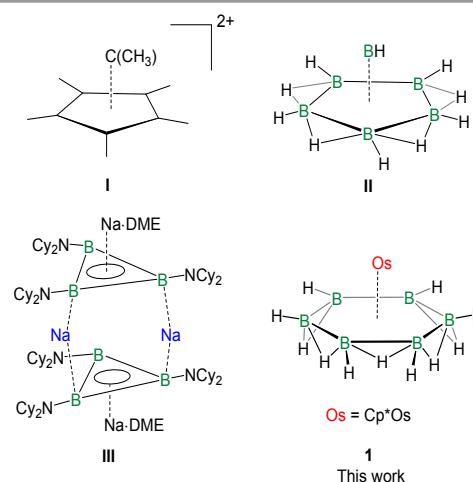


Chart 1. The occurrence of pyramidal geometry in (C₆(CH₃)₆)²⁺ (**I**), isoelectronic to *nido*-B₆H₁₀ (**II**), planar B₃ rings in Na₄[B₃(NCy₂)₃]₂·2DME (**III**).

^a Department of Chemistry, Indian Institute of Technology Madras Chennai 600036, India E-mail: sghosh@iitm.ac.in.

^b Inorganic and Physical Chemistry Department, Indian Institute of Science Bangalore 560012, India E-mail: jemmis@iisc.ac.in.

† Footnotes relating to the title and/or authors should appear here.

Supplementary Information available: CCDC 2438685 (for **1**), 2438887 (for **2**), 2438789 (for **3**).

For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/x0xx00000x



featuring a flat B₆ ring, we have also isolated key intermediates *nido-arachno*-[Cp*Os(η^5 -B₅H₁₂)] (**2**) and *nido-arachno*-[Cp*Os(η^4 -B₄H₉)] (**3**). The [B₅H₁₂] in **2** and [B₄H₉] in **3** are isoelectronic to pentadienyl radical [C₅H₇], and 1,3-butadiene radical cation [C₄H₆]⁺ respectively, using less obvious analogies (*vide infra*). Although attempts to isolate the B₂ and B₃ intermediates have not been successful, this is the first synthetic attempt to follow reactions starting from B₁ species to the planar B₆ ring, isolating and characterizing the intermediate B₄ and B₅ chains along the way. Complexes **1**, **2**, and **3** have been well-characterized through various spectroscopic techniques and single-crystal X-ray diffraction analysis.

Results and discussion

Synthesis and Characterization

The thermolysis reaction of [Cp*OsBr₂]₂ with an excess of [BH₃-SMe₂] at 95 °C resulted in the formation of [Cp*Os(η^6 -B₆H₁₁)] (**1**) as a colourless solid along with some unidentified air and moisture-sensitive products. The ¹H NMR spectrum of **1** shows a peak at δ = 1.58 ppm for Cp* that was confirmed by ¹³C{¹H} NMR. The ¹H chemical shift at δ = -3.56 ppm indicates B-H-B protons. The room-temperature ¹¹B{¹H} NMR spectrum of **1** exhibits a single peak at δ = 8.6 ppm. The ¹H{¹¹B} chemical shift at δ = 3.56 ppm can be assigned to six terminal B-H_t protons. The mass spectrum of **1** shows isotopic distribution patterns at *m/z* 402.2301, corresponding to the molecular formula [C₁₀H₂₇B₆O_s].

To corroborate the spectroscopic data, a single-crystal X-ray diffraction analysis was carried out on a suitable crystal of **1**. The molecular structure of **1**, shown in Figure 1, shows a planar six-membered B₆ ring stabilized by a monometallic {Cp*Os} unit. There are six terminal B-H bonds and an additional six hydrogens are positioned to bridge the six B-B bonds forming a [B₆H₁₂] motif with a symmetrical environment. The average Os-B bond distance (2.187 Å) is comparable with the previously reported osmaboranes.⁴⁰ The average B-B bond distance of 1.753 Å in **1** is comparable with reported triple-decker sandwich complex, *nido-closo-nido*-[(Cp*Re)(μ - η^6 : η^6 -1,2-B₆H₄Cl₂)(Cp*Re)]³⁶ (1.726 Å) but slightly shorter than *nido-closo-nido*-[(Cp*Ti)(μ - η^6 : η^6 -B₆H₆)(μ -H)₆(Cp*Ti)]³⁷ (1.80 Å). The average $\angle$ B-B-B angle in the six-membered ring is 119.98°, similar to that of a planar hexagon (120°). The molecular formula deduced from the crystal structure, i.e., [Cp*Os(η^6 -B₆H₁₂)] leads to an electron count around the metal of 19 (1×{Cp*Os} = 13, {B₆H₁₂}

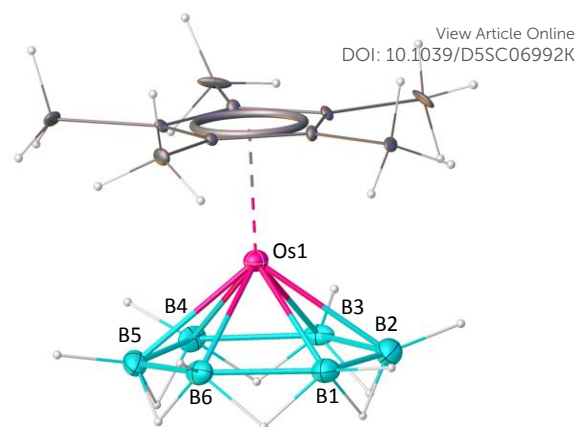
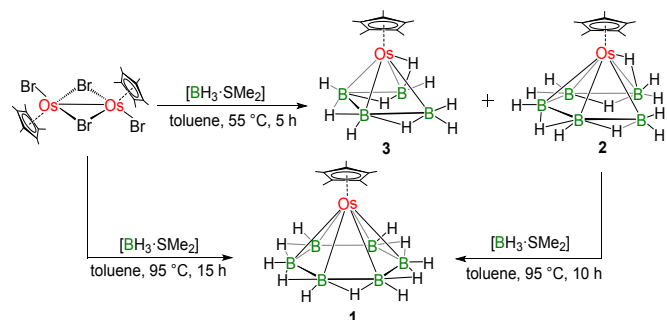


Figure 1. Molecular structure and labelling diagram of **1**. Selected bond lengths (Å) and angles (deg): B1-B2 1.754(17), B2-B3 1.74(3), B3-B4 1.75(2), B4-B5 1.762(14), B5-B6 1.74(2), Os1-B1 2.26(3), Os1-B3 2.20(2), Os1-B5 2.16(3); B4-B5-B6 117(2), B3-B4-B5 123(2). The standard refinement of the X-ray diffraction data for this 18-electron complex **1** indicates the presence of six bridging hydrogens (B-H-B). However, for a neutral 18-electron complex, only 5 bridging hydrogens are expected. Closer analysis of the X-ray diffraction data, supported by theoretical calculations, confirms a structure featuring five bridging hydrogens, as discussed in the text.

= 6), suggesting the presence of an odd electron. However, no paramagnetic behaviour was observed in the EPR spectrum of **1**. Also, computational studies of the structure [Cp*Os(η^6 -B₆H₁₂)] at the B3LYP-D3/Def2-SVP level of theory, with the odd electron, led to a non-planar B₆ ring (Figure S29). Further, there is no evidence of the presence of an anion in the unit cell of **1**. We examined the X-ray diffraction data further. The terminal B-H and bridging B-H-B protons were identified from difference electron density maps, and their positions were refined using single-crystal X-ray analysis. It was found that all the bridging hydrogen sites are partially occupied with equal occupancy. This partial occupancy indirectly suggests the presence of five bridging hydrogen atoms in **1**. Therefore, it is reasonable to assume that the correct formula for **1** is [Cp*Os(η^6 -B₆H₁₁)], which results in an 18-electron count around the osmium center (13 electrons from {Cp*Os} and 5 from the {B₆H₁₁}). [B₆H₁₁] is isoelectronic to benzenyl cation radical [C₆H₆]⁺, a 5 π ligand. The five additional hydrogens bridge the five out of six B-B bonds and contribute the necessary five electrons. As expected, the non-bridged 2center-2electron (2c-2e) B-B bond is computed to be shorter (1.635 Å at B3LYP-D3/Def2-SVP level) than the bridged 3c-2e B-H-B bond (1.761-1.808 Å, Figure S30a, Table S1). The distribution of molecules in the crystal structure is such that the position of the B-B bond without bridging hydrogen in the crystal structure, is random, resulting in diffraction data supporting nearly equal B-B bond distances. The sixth 2c-2e B-B bond is also capable of forming a similar bridged B-H-B 3c-2e bond. Therefore, to check the fluxionality of complex **1**, variable temperature ¹H and ¹¹B{¹H} NMR experiments were performed (Figures 2a and 2b), enabling the possibility of slowing down the exchange of five bridged hydrogen atoms. But this experiment revealed no splitting of the single ¹¹B peak except broadening at lower temperatures. This broadening may be due to the lessening of spin-lattice relaxation time, a common phenomenon for boron-containing complexes. Probably, a rapid hydrogen exchange among the bridging hydrogens in



Scheme 1. Synthesis of **1** [Cp*Os(η^6 -B₆H₁₁)], **2** [Cp*Os(η^5 -B₅H₁₂)], and **3** [Cp*Os(η^4 -B₄H₉)].



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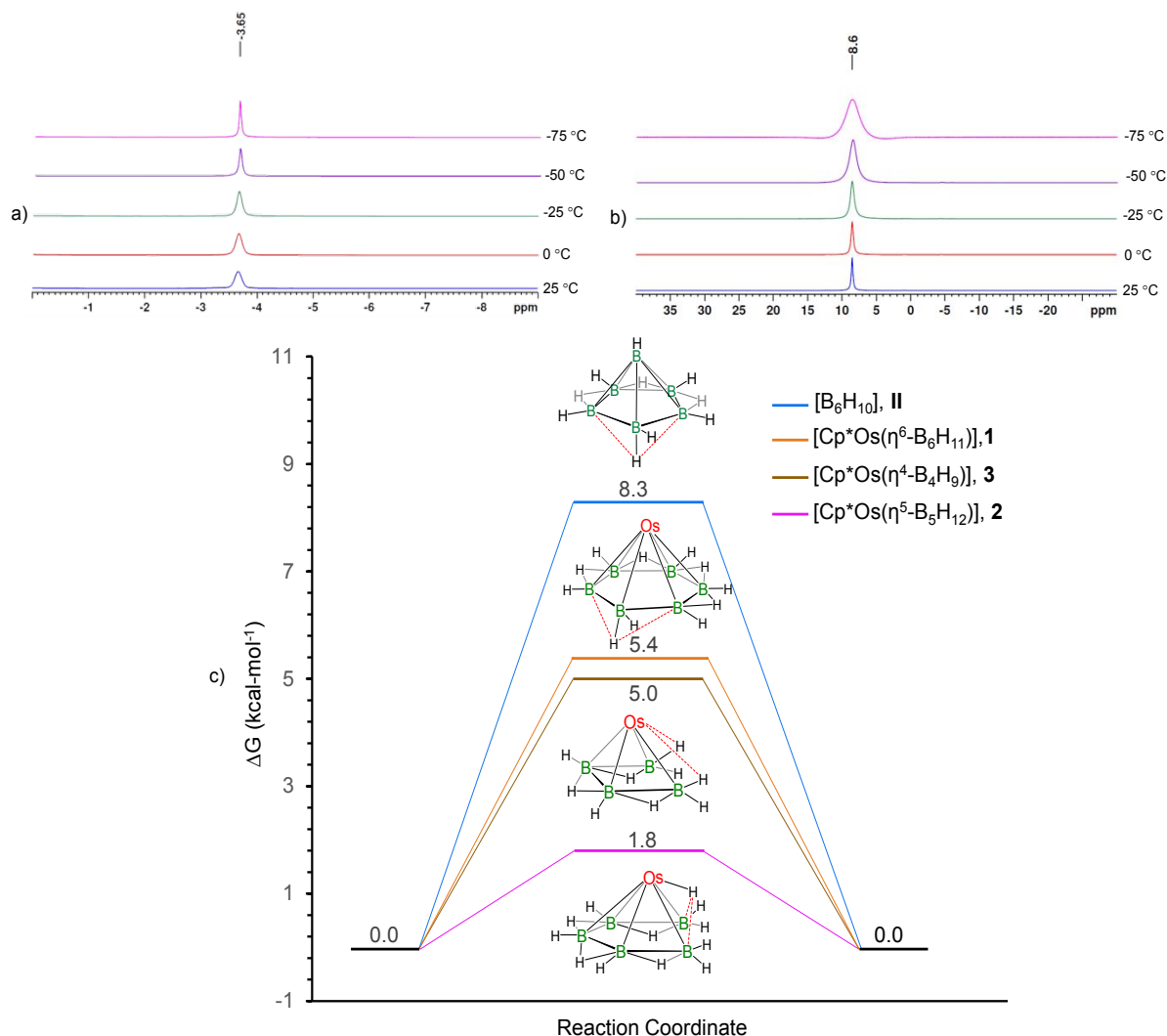


Figure 2. a) Variable-temperature $^1\text{H}\{^{11}\text{B}\}$ NMR spectrum of **1** in the hydride region showing no splitting; b) Variable-temperature $^{11}\text{B}\{^1\text{H}\}$ NMR spectra of **1** showing no splitting except broadening at lower temperatures. c) Free energy surface for the terminal and bridging hydrogen exchange in $[\text{B}_6\text{H}_{10}]$ (**II**) and $[\text{Cp}^*\text{Os}(\eta^6\text{-B}_6\text{H}_{11})]$ (**1**), the switching of B-H-Os bridge from one boron to another in $[\text{Cp}^*\text{Os}(\eta^5\text{-B}_5\text{H}_{12})]$ (**2**), and the switching of agostic interaction in $[\text{Cp}^*\text{Os}(\eta^4\text{-B}_4\text{H}_9)]$ (**3**) at the B3LYP-D3/Def2-SVP level of theory with implicit solvation at 298K. For easy comparison of the variation in the barrier for hydrogen shift, the relative energies of the ground states of all compounds are brought to zero in the Figure.

solution led to the equivalence of five bridging hydrogens. Such a type of rapid exchange of bridging hydrogens has been reported in $[\text{nido-B}_6\text{H}_{10}]$ (**II**), producing similar ambiguities.²¹ The barrier for exchange of bridging hydrogens in **1** is calculated to be 5.4 kcal/mol, much lower than the corresponding barrier for **II** $[\text{nido-B}_6\text{H}_{10}]$ (8.3 kcal/mol) at the same level of theory (Figure 2c). Therefore, due to the very high fluxionality of the bridging hydrogen atoms, the expected splitting in the variable-temperature ^{11}B and ^1H NMR experiments was not observed, even at very low temperatures. It is due to the difficulty in locating the light H atom among a cluster of heavier atoms,

together with the possibility of random positioning of the five bridging H-atoms in the B_6 ring in the crystal structure, leading to the diffraction data that gave six bridging hydrogens instead of five.

Intermediates

To gain insights into the formation of **1**, the reaction of $[\text{Cp}^*\text{OsBr}_2]_2$ with $[\text{BH}_3\cdot\text{SMe}_2]$ was monitored under various reaction conditions. We observed that at milder reaction conditions, we could isolate the lower boron congeners $[\text{Cp}^*\text{Os}(\eta^5\text{-B}_5\text{H}_{12})]$ (**2**) and $[(\text{Cp}^*\text{Os})(\eta^4\text{-B}_4\text{H}_9)]$ (**3**). Further thermolysis of the mixture of **2** and **3** in the presence of



[BH₃-SMe₂] at 95 °C for 10 h resulted in the formation of **1**. The ¹H NMR spectrum showed peaks at δ = 1.48 ppm (**2**) and 1.56 ppm (**3**) for Cp* protons. Peaks in ¹H{¹¹B} NMR at δ = -3.36 and -3.89 ppm in 2:2 ratio (for **2**) and δ = -3.79 and -4.16 ppm in 1:2 ratio (for **3**) correspond to different B-H-B protons. The upfield ¹H chemical shifts at δ = -12.55 and -15.60 ppm may correspond to terminal Os-H or Os-H-B protons, which were further confirmed by ¹H-¹¹B HSQC as Os-H-B protons (Figures S14 and S24). The room-temperature ¹¹B{¹H} NMR spectrum of **2** exhibited peaks at δ = 2.9, 0.8 and -6.5 ppm in 2:1:2 ratio, while **3** exhibited peaks at δ = -2.5 and -12.1 ppm in 2:2 ratio. The mass spectra of **2** and **3** demonstrated isotopic distribution patterns at m/z 390.2105 and 419.2204, respectively.

The solid-state X-ray structure of **2** confirmed that a B₅ chain is stabilized in the coordination sphere of {Cp*Os} unit and this is best described as *nido-arachno* arrangement (Figure 3). The average B-B bond distance of 1.822 Å is considerably longer than the average B-B bond distance of 1.713 Å in the triple-decker sandwich complex [(Cp*W)₂B₅H₉].⁴¹ Unfortunately, due to the presence of two-fold disorder, it was not possible to locate or freely refine any of the 12 hydrogens associated with Os-H-B, B-H-B and B-H. Thus, the hydrogen positions were inferred based on various NMR experiments (Figures S10, S13 and S14) and computational studies (Figure S30b). Interestingly, the [B₅H₁₂] chain in **2** is isoelectronic to pentadienyl radical, [C₅H₇], a 5π ligand. This isoelectronic equivalence is most easily demonstrated by assuming [C₅H₇] as an anion [C₅H₇]⁻ with 6π electrons as in [Cp]⁻. Replacement of five carbon atoms in [C₅H₇]⁻ by five isoelectronic [B]⁻ units results in the formula [B₅H₇]⁶⁻. The four B-B sigma bonds can be protonated so that the charge is reduced to -2 in [B₅H₁₁]²⁻. If one of the end [BH₂] groups (say B1) is also protonated, the resulting [B₅H₁₂]⁻ will have the end boron as an equivalent of [BH₄]⁻. Thus, there are four π electrons from B2 to B5 and two electrons from one of the B-H bond pairs of B1 to constitute the 6 electrons equivalent of [Cp]⁻. The computed structure clearly indicates a stretched B1-H-Os1 interaction, where the B1-H bond is long (1.482 Å at B3LYP-

D3/Def2-SVP) and the Os1-H distance of 1.657 Å is comparable to the metal-hydride bond distance of 1.661 Å in [Os(PPh₃)₂H₂(η⁴-B₄H₈)].²⁹ The distance between the hydrogen of the B5-H-Os1 3c-2e bond and the terminal B5 atom, i.e., B5-H, is 1.966 Å. If the protonation is assumed to take place at that end (B5), there will be an equivalent structure with B5-H-Os1 3c-2e bond. The barrier for the interconversion between these two equivalent structures is calculated to be only 1.8 kcal/mol (Figure 2c). A similar phenomenon was observed with *arachno*-[B₅H₁₁].²² Due to this very fast exchange, the expected change in the variable-temperature ¹¹B and ¹H NMR experiments was not observed, even at very low temperatures (Figures S16 and S17). The crystal structure presents a more complex picture. The structure has a two-fold disorder in the ratio 38:62. With the disorder and a very heavy osmium atom present, it is impossible to locate the hydrogen atoms belonging to borons from the difference Fourier map and these hydrogens cannot be fixed geometrically. This explains the unusual differences in B-B bond lengths from the X-ray and computational data (Table S1). Although an analogous C₅ chain was observed in [Cp*Ru(η⁵-C₅H₇(CH₃))] +,⁴² **2** is the first example of boron catenation resulting in the formation of a B₅ chain in the coordination sphere of a monometallic {Cp*Os} unit.

The solid-state X-ray structure of **3** showed a B₄ chain stabilized in the coordination sphere of a monometallic {Cp*Os} unit and can be described as *nido-arachno* arrangement (Figure 3). The average B-B bond distance is 1.841 Å is comparable to the average B-B bond distance in [W(IMes)(η⁴-BH₂Mes-BMes-BMes-BH₂Mes)] (1.82 Å)⁴³. This molecule contains nine hydrogens which are linked as Os-H-B, B-H-B, and terminal B-H bonds. Among these, five are terminal, three bridge the B1-B2, B2-B3, and B3-B4 bonds and one bridges the Os1-B1 bond (Figure 3). Though Fehner and co-workers previously characterized an iridium-stabilized B₄ chain [(Cp*Ir)B₄H₁₀], only by NMR experiments,⁴⁴ **3** is the first example of a structurally characterized osmium-stabilized B₄ chain. The coordinated [B₄H₉] chain in **3** is isoelectronic to 1,3-butadiene radical cation

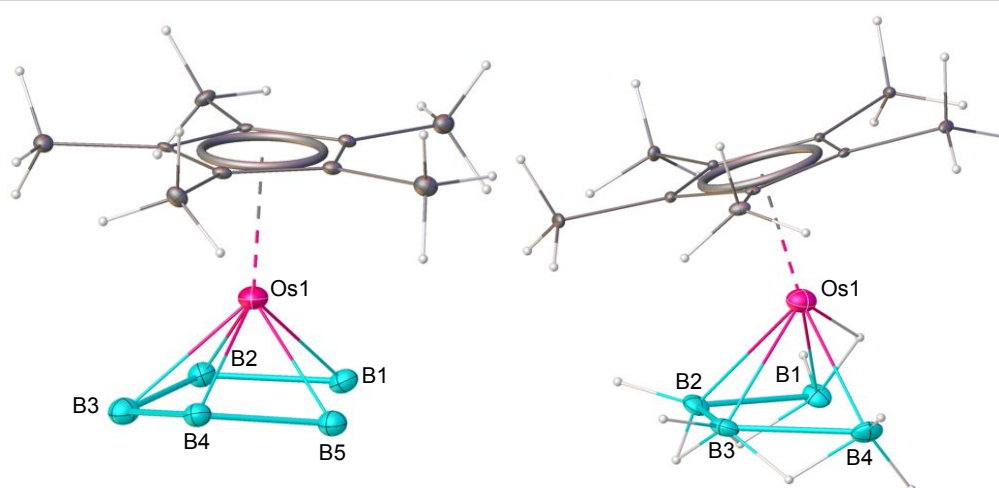


Figure 3. Molecular structures of (**2**) Cp*Os(η⁵-B₅H₁₂) (left) and (**3**) Cp*Os(η⁴-B₄H₉) (right). Hydrogen positions in **2** could not be located crystallographically due to disorder. They were confirmed by different NMR experiments and computational analysis. Selected bond lengths [Å] and angles (deg) (**2**): Os1-B2 2.02(3), Os1-B3 2.15(3), Os1-B5 2.16(3), Os1-B4 2.23(3), Os1-B1 2.24(3), B1-B2 1.77(4), B3-B4 1.77(4); B2-Os1-B3 57.0(12), B3-Os1-B5 81.9(17), B1-B2-B3 118(3), B4-B3-B2 107(3). (**3**): B1-B2 1.846(11), B2-B3 1.826(12), B3-B4 1.851(13), Os1-B1 2.305(7), Os1-B2 2.146(7), Os1-B3 2.150(7), Os1-B4 2.300(7); B3-B2-B1 111.7(6), B2-B3-B4 112.4(5).



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$[\text{C}_4\text{H}_6]^+$, a 3π ligand which, in addition, may donate two electrons through an agostic B-H-Os bond. Replacement of four carbon atoms by four isoelectronic $[\text{B}]^-$ units results in the formula $[\text{B}_4\text{H}_6]^{3-}$. Protonation of the three B-B sigma bonds results in the neutral $[\text{B}_4\text{H}_9]$. The three bridging hydrogens provide three electrons. A terminal B-H bond from one of the two end $[\text{BH}_2]$ groups (say B1) of the B_4 -chain provides an additional two electrons through the agostic B1-H-Os1 interaction (B1-H = 1.338 Å, Os1-H = 1.797 Å, Os1-B1 = 2.015 Å, Figure S33). The other $[\text{BH}_2]$ group (say B4) is similarly capable of this interaction, resulting in a degenerate exchange between the terminal boron atoms with an energy barrier of 5.0 kcal/mol (Figure 2c). Due to this rapid exchange of Os-H-B bridging hydrogen, no change was observed in the variable-temperature ^{11}B and ^1H NMR (Figures S26 and S27), similar to that of complexes **1** and **2**. While catenation and chain structures serve as the foundation of organic chemistry, homonuclear chains in the chemistry of boron are very limited.⁴³ Instead, the formation of hypervalent clusters and cages is the norm. Thus,

the π -type complexes featuring B_5 and B_4 chain units are very novel.

Our attempts to isolate intermediates with two and three boron atoms (B_2 and B_3) were not successful in this reaction pathway. Generally, in most of the metathesis reactions between pentamethylcyclopentadienyl metal polychlorides and borane/borate reagents, such as $[\text{BH}_3\cdot\text{THF}]$, $[\text{BH}_3\cdot\text{SMe}_2]$, $[\text{LiBH}_4]$, $[\text{Li}[\text{BH}_3(\text{EPh})]]$, (E = S, Se or Te) etc., the typical by-products are $[\text{BH}_3]$, $[\text{BHCl}_2]$, $[\text{BH}_2\text{Cl}]$ etc. All these reagents underwent salt-elimination reactions leading to the formation of metal polyborohydride complexes that successively yielded metallaborane by hydrogen elimination.^{45,46} So, in this case, the metathesis reactions between pentamethylcyclopentadienyl metal polybromides and $[\text{BH}_3\cdot\text{SMe}_2]$ may have primarily yielded $[\text{BH}_3]$, $[\text{BHBr}_2]$, $[\text{BH}_2\text{Br}]$ etc., along with osmium polyborohydride complexes, which may have undergone hydrogen elimination to form these complexes **2**, **3**, and subsequently, **1**. In addition,

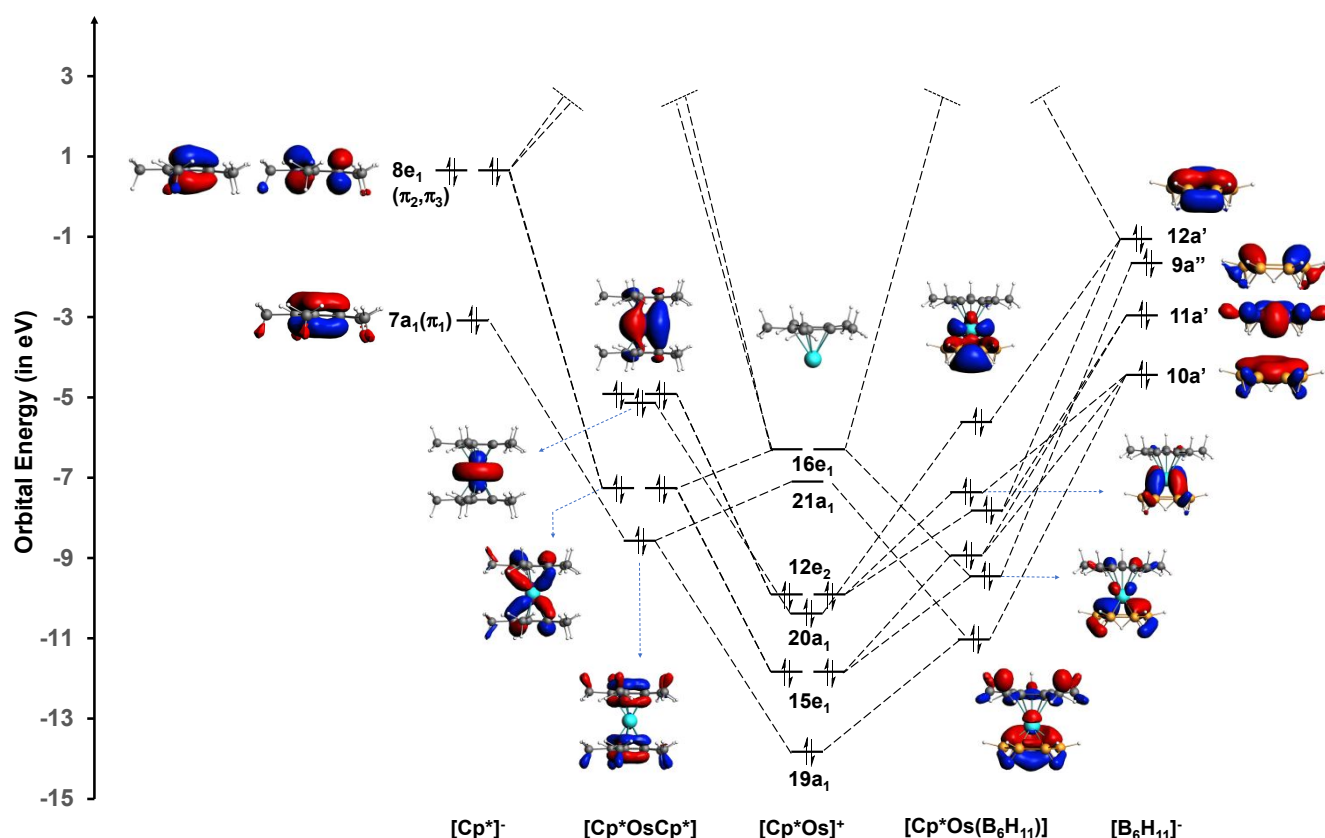


Figure 4. Orbital interaction diagram of $[\text{Cp}^*\text{Os}]^+$ with $[\text{Cp}^*]^-$ and $[\text{B}_6\text{H}_{11}]^-$ ligands in complex $[\text{Cp}^*\text{OsCp}^*]$ and **1**, $[\text{Cp}^*\text{OsB}_6\text{H}_{11}]$ in C_{5v} and C_s symmetry respectively computed at B3LYP-D3/TZP level of theory using ADF software.^{49,50} The well-known frontier orbitals of the fragment $[\text{Cp}^*\text{Os}]$ are given in the middle of the diagram. Only the occupied π MOs of Cp^* are



given on the left. The top four frontier MOs are given for $[B_6H_{11}]$ on the extreme right and there is extensive σ - π mixing in $[B_6H_{11}]$. C_{5v} point group nomenclature is used for (Cp^*) and $(CpOs)^+$ and C_s nomenclature for $[B_6H_{11}]$. In **1**, the σ - π mixing makes the distinction between σ and π orbitals difficult, unlike $[Cp^*OsCp^*]$. DOI: 10.1039/D5SC06992K

these reactions also yielded several air and moisture-sensitive by-products. Although we have tried to isolate other sensitive by-products by fractional crystallization, we were unsuccessful mainly due to their poor yields. We could isolate only those compounds that are stable during chromatography work-up. This prevents us from formulating an acceptable reaction mechanism currently.

Electronic Structures and Bonding

While the electron requirement of **1** is understood in comparison to ferrocene, these structures, especially **2** and **3**, are better understood using the mno rule, an extension of Wade's Rule.⁴⁷ According to this, the electron count required for the stability of a condensed polyhedral structure is given by $(m + n + o)$ skeletal electron pairs, where m is the number of polyhedra, n is the number of vertices, and o is the number of polyhedra connected through a single bridging atom. For *nido* and *arachno* arrangements, two additional variables, p and q ,

are added, with values of 1 and 2 electron pairs, respectively. Thus, ferrocene requires 16 ($m = 2$, $n = 11$, $o = 1$, $p = 2$) skeletal electron pairs. What is available is 16 (30 electrons from ten $[CH]$, and 2 electrons from Fe), so that ferrocene is electron sufficient. Application of the mno rule demands 17 electron pairs in **1** ($m = 2$, $n = 12$, $o = 1$ and $p = 2$). What is available is also 17 (15e from five $[CH]$, 12e from $[B_6H_6]$, 5e from five bridging H, and 2e from Os). It is instructive to relate the bonding in **1** to the known triple-decker sandwich *nido-closo-nido*- $[(Cp^*Re)(\mu-\eta^6-\eta^6-1,2-B_6H_4Cl_2)(Cp^*Re)]$. While an mno electron count of 25 electron pairs ($m = 3$, $n = 18$, $o = 2$ and $p = 2$) is obtained for a model compound *nido-closo-nido*- $[(Cp^*Re)(\mu-\eta^6-\eta^6-B_6H_6)(Cp^*Re)]$, the available electron pairs are only 22 (15 from two Cp^* , 6 from the $[B_6H_6]$ ring and one from the Re atoms together assuming a pseudo octahedral complex with d^6 Re atoms). However, the number of electrons required for stability in triple-decker complexes depends on many factors such as the size of the middle ring, the size of the metal atom, substituents

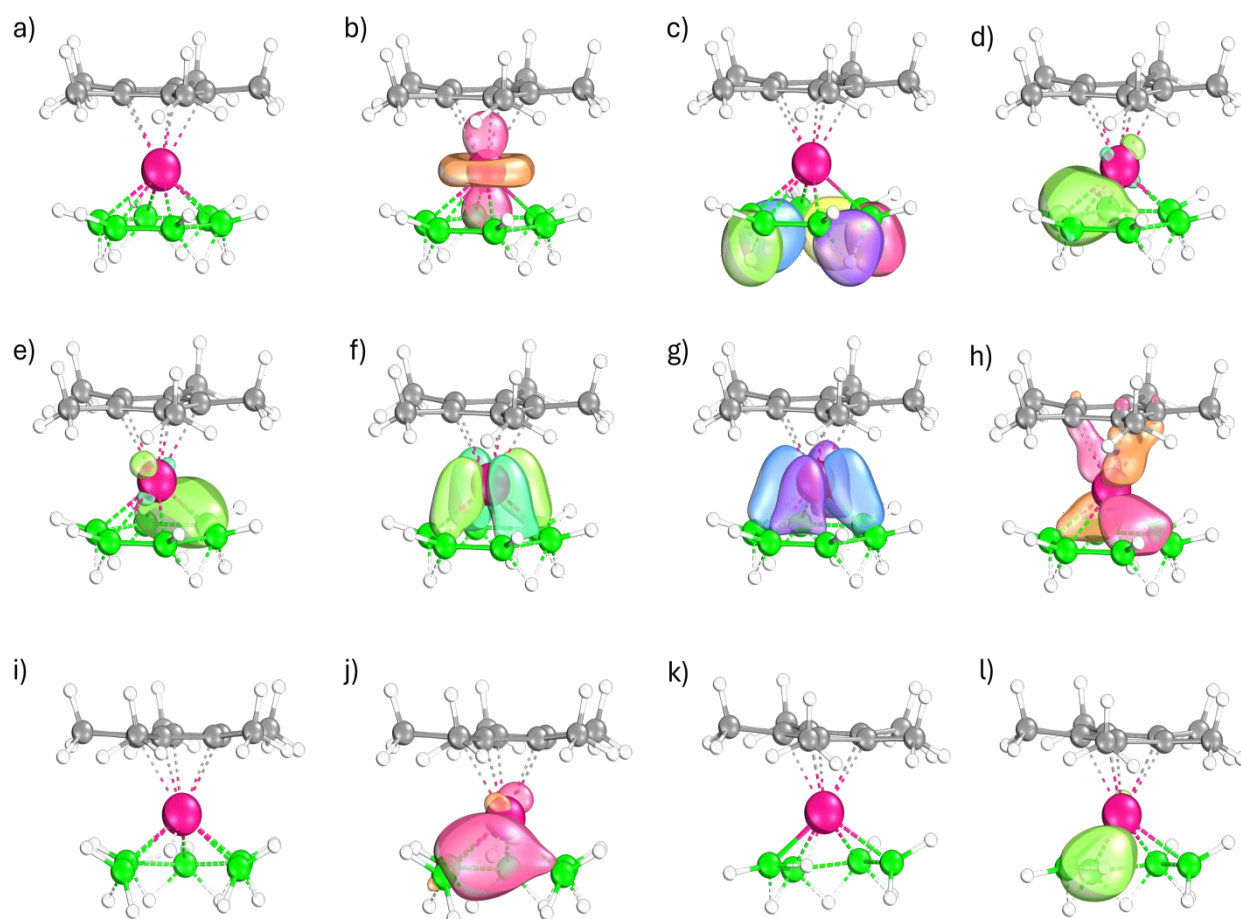


Figure 5. Selected localized orbitals of **1** (a) computed using IBOview: (b) a 1c-2e lone pair on osmium; (c) five 3c-2e bond orbitals; and (d-h) five multicenter osmium-boron bond orbitals. Complex **2** (i) and **3** (k) display similar localized orbitals, with the exception that in each case one of the five osmium-boron multicenter orbitals include contribution from a terminal hydrogen (j and l, respectively). For clarity, the 2c-2e bond orbitals, and three metal- Cp^* multicenter orbitals are omitted (see text).

on the rings, metal-metal bond, spin multiplicity of the complex etc.⁴⁸ These variables disappear when one of the $[Cp^*Re]$ groups is removed, leading to the equivalent of **1**.

The osmaborane **2** has a *nido*- $[Cp^*Os]$ and an *arachno*- $[OsB_5H_{12}]$ condensed through Os, so that the mno rule gives 17e pairs ($m = 2$, $n = 11$, $o = 1$, $p = 1$, $q = 2$). The number of skeletal



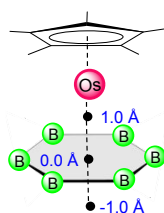
electron pairs available is also 17 (15 electrons from five [CH], 10 electrons from [B₅H₅], 4 electrons from four bridging H, 2 electrons from the two additional H on the terminal B atoms, 1 electron from the additional H atom forming the Os-H-B 3c-2e bridge and 2 electrons from Os). The mno count for **3**, (Cp*Os)(η^4 -B₄H₉), is 16 skeletal pairs (m = 2, n = 10, o = 1, p = 1, and q = 2). What is available appears to be only 15 (15 electrons from five [CH], 8 electrons from [B₄H₄], 3 electrons from three bridging H, 2 electrons from two additional H on the terminal B atoms and 2 electrons from Os). However, a closer look at the structure indicates that one of the terminal B-H bonds of the *arachno*-[OsB₄H₉] unit bends towards the metal, making it an agostic-B-H-Os interaction. This completes the required electronic requirement.

While this qualitative electron counting brings equivalence between the electronic structure of permethylferrocene and that of [Cp*Os(η^6 -B₆H₁₁)] **1**, there are many differences in detail. The high stability of the C-C σ bond in Cp* and the high symmetry keep a large difference in the π and σ bond orbitals in Cp*. In contrast, the five B-B bridging hydrogens in [B₆H₁₁] force the terminal hydrogens on the opposite side of the B₆ ring. This leads to σ - π mixing and the distinction between π and σ MOs vanishes. The consequences are seen in Figure 4, where fragment interaction diagrams for the formation of permethylferrocene and structure **1** are compared. While it is still possible to trace the MOs with dominant contribution of π MOs of Cp* in permethylferrocene, it is not easily possible to make the distinction between orbitals with predominant σ or π interaction in structure **1**, [Cp*Os(η^6 -B₆H₁₁)].

The bonding of **1**, **2**, and **3** is further examined using Intrinsic Bond Orbitals (IBOs).^{51,52} These are obtained from Intrinsic Atomic Orbitals (IAOs), a minimal set of atomic orbitals on atoms in molecules, polarised to depict the molecular environment. The IBOs obtained from IAOs represent chemical bonding, as commonly understood, even in difficult-to-

understand molecules. These localized bond orbitals are generated using IBOview and represented for selected bond orbitals of **1**, **2** and **3** (Figure 5). The localization identifies several obvious two-centre, two-electron bond orbitals and multicentre bond orbitals (Figures S31-33). Notably, the metal lone pair (Figure 5b), the three centre-two electron orbitals corresponding to bridging of B-B bonds with hydrogens (Figure 5c), and three multicentre orbitals connecting the Cp* ring to the metal, remain consistent across all three complexes (Figures S31-33). Most intriguing variation is the nature of osmium-boron multicenter bond orbitals as we go from B₆ ring in **1** to B₅ and B₄ chains in **2** (Figure 5i), and **3** (Figure 5k), respectively. There are five multicenter bond orbitals involving the osmium and boron atoms (Figures 5d-h for **1**, Figures S32 and S33 for **2** and **3**). In **2** and **3**, one of the multicenter bond orbitals has contributions from osmium, terminal boron and the hydrogen bridging them (Figures 5j and 5l). In **2**, the terminal boron is bonded to four hydrogen atoms; two of these are terminal hydrogens, one forms a bridging bond with another boron, and one bridges between osmium and boron. This bonding environment classifies it as a [BH₄]⁻ fragment. Notably, the B-H bond that interacts with osmium is considerably lengthened, and the osmium's interaction with this terminal boron is relatively weak (with B-H, Os-H and Os-B bond distances of 1.482 Å, 1.657 Å, and 2.324 Å, and corresponding bond orders of 0.36, 0.35 and 0.32, respectively). This weakened bond facilitates an easier transfer of hydrogen to another terminal boron (Figure 3). In contrast, in **3**, the terminal boron is attached to three hydrogens; a single terminal hydrogen, one bridging bond with another boron, and one bridging between the osmium and boron-thus assigned as a [BH₃]⁻ fragment. Here, the interacting B-H bond shows only minor elongation, and the osmium has a more pronounced interaction with both the boron and the hydrogen (with bond distances for B-H, Os-H, and Os-B being 1.339 Å, 1.797 Å, and 2.015 Å, and bond orders of

Table 1. Comparison of NICS values for [Cp*Os(η^6 -B₆H₁₁)] (**1**) and bis(benzene)chromium [(C₆H₆)Cr(C₆H₆)] and [Cp*OsCp*], computed at the B3LYP-D3/Def2-SVP level of theory. Negative NICS values imply aromaticity. In double-decker sandwich complexes, NICS(1.0) and NICS(-1.0) are measurements towards and away from the metal, respectively; see drawing on the left.



Complexes	NICS _{iso} (0.0)	NICS _{zz} (0.0)	NICS _{iso} (1.0)	NICS _{zz} (1.0)	NICS _{iso} (-1.0)	NICS _{zz} (-1.0)
[Cp*Os(η^6 -B ₆ H ₁₁)] 1	-37.6	-55.4	-49.5	-166.7	-11.4	-22.1
[(C ₆ H ₆)Cr(C ₆ H ₆)] ⁵³	-48.9	-58.3	-180.0	-229.7	-19.8	-34.0
[Cp*OsCp*] ⁵⁵	-25.9	-30.3	-73.2	-88.2	-12.9	-29.0

0.58, 0.26, and 0.73, respectively). This arrangement characterizes the interaction of a [BH₃]⁻ fragment with an intact B-H bond as an agostic interaction, as described before.

Aromaticity Comparison

We have further compared the aromaticity of the stabilized planar B₆ ring in the monometallic template (**1**) with that of the benzene ring in bis(benzene)chromium, [(C₆H₆)Cr(C₆H₆)]⁵³ (Table 1) using NICS values. While the absolute NICS values as indicators of aromaticity fail in metal complexes, a comparison

can be made between a series of related complexes.⁵⁴ NICS values follow similar trends for **1** and bis(benzene)chromium. It remains negative at the center and at positions 1 Å above (towards the metal) and below (opposite to the metal) the plane (see picture). The negative values away from the metal suggest **1** to be aromatic. Therefore, the planar B₆ ring follows a similar aromaticity pattern of the benzene ring stabilized in double-decker sandwich complexes. The orbital interaction diagram (Figure 4, above) shows that despite the σ - π mixing arising from bridging hydrogens in [B₆H₁₁], the frontier MOs of



[Cp*OsB₆H₁₁] (**1**) have much resemblance to those in [Cp*OsCp*]⁵⁵, further highlighting that aromaticity in **1** should be comparable to [Cp*OsCp*] (Table 1).

Conclusions

Synthesis of mixed metallocene, [Cp*Os-(η^6 -B₆H₁₁)] (**1**), *nido-arachno*-[Cp*Os(η^5 -B₅H₁₂)] (**2**) and *nido-arachno*-[(Cp*Os)(η^4 -B₄H₉)] (**3**) from B₁ precursor [BH₃·SMe₂] presents novel possibilities in boron chemistry. In complex **1**, five bridging hydrogens contribute to an 18-electron count configuration. In complex **2**, four bridging hydrogens, along with an additional hydrogen bridging the Os–B bond, achieve the same 18-electron count. In complex **3**, although only three bridging hydrogens are present, a B–H bond donates two electrons to osmium in a manner similar to agostic sigma-complex formation, fulfilling the 18e configuration. These complexes also follow the mno rule. These novel ways in which [B₆H₁₁], [B₅H₁₂] and [B₄H₉] provide five electrons lead to dynamic degenerate rearrangements involving H-migrations that cannot be frozen even at low temperatures. Detailed analysis of aromaticity using NICS values shows that [Cp*Os(η^6 -B₆H₁₁)] is nearly as aromatic as bis(benzene)chromium, [(C₆H₆)Cr(C₆H₆)]. These findings emphasize the intricate bonding environments in all the complexes, with multicentre interactions playing a pivotal role in stabilizing the structures and opening up new approaches in organometallic chemistry without carbon.

Author contributions

K. K. has executed the experimental synthesis, characterisation and analysed the data. G. J. has carried out theoretical calculations. All authors have contributed to the preparation of the manuscript. S. G. and E. D. J. have supervised the experimental and theoretical studies.

Conflicts of interest

There are no conflicts to declare.

Data availability

The data that support the findings of this study are available in the ESI† of this article.

Acknowledgements

The generous support of SERB, New Delhi, India (grant no. CRG/2023/000189) is gratefully acknowledged. K. K thanks DST-INSPIRE, and G. J. thanks IISc for research fellowships. EDJ thanks ANRF for research funding through National Science Chair. We thank Dr. P. K. Sudhadevi Antharjanam and Dr. Babu Varghese, IIT Madras, for the single crystal X-ray diffraction data collection, structure refinement and discussion. The computational facility of SERC-IISc is gratefully acknowledged.

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DOI: 10.1039/D5SC06992K

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DOI: 10.1039/D5SC06992K



- Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no CCDC- 2438685 (1), 2438887 (2), 2438789 (3). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
- The data supporting this article have been included as part of the SI. Supplementary information: Experimental procedures and characterization of all species and reaction products.

