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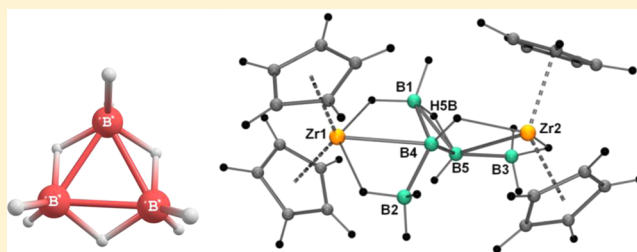
Novel Neutral Zirconaborane $[(\text{Cp}_2\text{Zr})_2\text{B}_5\text{H}_{11}]$: An *arachno*- B_3H_9 Analogue ($\text{Cp} = \eta^5\text{-C}_5\text{H}_5$)

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S Supporting Information

ABSTRACT: The first example of a homometallic neutral zirconaborane, $[(\text{Cp}_2\text{Zr})_2\text{B}_5\text{H}_{11}]$, **1**, has been prepared through the thermolysis of $[\text{Cp}_2\text{Zr}(\text{BH}_4)_2]$, generated from the fast metathesis reaction of $[\text{Cp}_2\text{ZrCl}_2]$ and $\text{LiBH}_4\cdot\text{thf}$ with $\text{BH}_3\cdot\text{thf}$. The solid-state structure of **1** shows an open geometry with a planar B_3 ring. The bonding between the Zr center and the central B_3 ring was studied computationally by DFT methods, and based on the combined experimental and computational results compound **1** can be defined as a metal-stabilized *arachno*- B_3H_9 . Further, in an attempt to synthesize a hybrid analogue of **1** by introducing two electron fragments into *arachno*- $[(\text{Cp}_2\text{Zr})(\text{Cp}^*\text{Ir})\text{B}_4\text{H}_{10}]$, **2**, we have performed the reaction of **2** with $[\text{Ru}_3(\text{CO})_{12}]$. However, the reaction led to the formation of a hybrid metallaborane, $[(\text{Cp}^*\text{Ir})\{\text{Ru}_3(\text{CO})_8\}\text{B}_4\text{H}_{10}]$, **3**.



INTRODUCTION

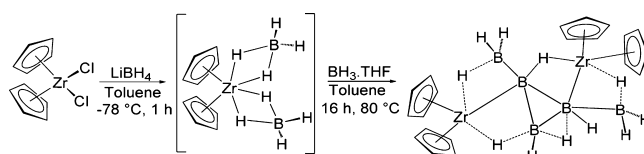
Metallaborane cage chemistry is an interesting and increasingly developing field from both the structure/bonding and reactivity perspectives.^{1–3} In its steady progress, mostly the group 5–9 transition metal metallaborane compounds are explored;^{4–10} however, metallaboranes of early transition metals, in particular, group 4 transition metals, are still scarce.^{11,12} With the exception of tetrahydroborate complexes, few metallapolyboranes containing group 4 transition metals are known.¹¹ Apart from the efforts made by Barton and co-workers to obtain group 4 metallaboranes by the reaction of anionic boranes with metal halides, all other ventures remained unproductive.¹¹ The development of better methods to synthesize these novel metallaboranes remains a constant goal, especially as not many examples of such clusters are known. In a quest to synthesize group 4 metallaboranes, we have recently reported a new hybrid metallaborane, *arachno*- $[(\text{Cp}_2\text{Zr})(\text{Cp}^*\text{Ir})\text{B}_4\text{H}_{10}]$, **2**.¹² As a result, to accomplish a general synthetic route to group 4 metallaborane compounds, we set out to explore the reaction of group 4 cyclopentadienyl-metal chloride complexes with various monoborane reagents ($\text{LiBH}_4\cdot\text{thf}$, $\text{BH}_3\cdot\text{thf}$, $\text{BHCl}_2\cdot\text{SMe}_2$, etc.). Herein, we report the preparation, structural characterization, and bonding situation of a homometallic neutral zirconaborane, $[(\text{Cp}_2\text{Zr})_2\text{B}_5\text{H}_{11}]$, **1**.

RESULTS AND DISCUSSION

Synthesis and Characterization of $[(\text{Cp}_2\text{Zr})_2\text{B}_5\text{H}_{11}]$, **1**.

As shown in Scheme 1, thermolysis of $[\text{Cp}_2\text{Zr}(\text{BH}_4)_2]$, obtained from the reaction of $[\text{Cp}_2\text{ZrCl}_2]$ and LiBH_4 at -70°C , with $[\text{BH}_3\cdot\text{thf}]$ yielded a yellow solid in 26% yield. Compound **1** is identified unequivocally from NMR and IR spectra, elemental analysis, mass spectrometry, and an X-ray crystallographic study as $[(\text{Cp}_2\text{Zr})_2\text{B}_5\text{H}_{11}]$. The $^{11}\text{B}\{^1\text{H}\}$ NMR

Scheme 1. Formation of Homometallic Neutral Zirconaborane $[(\text{Cp}_2\text{Zr})_2\text{B}_5\text{H}_{11}]$, **1**



spectrum of **1** reveals three resonances, whereas the ^1H NMR spectrum shows three types of Cp protons in 2:1:1 ratio. This may be due to the different orientation of the BH_2 units toward the Cp ligands. In addition to the Cp protons, ^1H NMR reveals the presence of one B–H–B at $\delta -1.31$ ppm and a broad resonance centered at $\delta -4.30$ for four Zr–H–B protons. The ^{11}B and ^1H NMR spectra combined with mass spectrometry data suggest that species **1** contains two Cp_2Zr moieties and a B_5H_{11} group. The ^{11}B and ^1H chemical shifts of **1**, calculated using the gauge including atomic orbital (GIAO) and B3LYP functional, agreed well with the experimental values (Tables S1 and S2). This provides a firm test of the validity of the calculated electronic structure of **1**.

Crystals of **1** suitable for an X-ray diffraction study were grown by slow evaporation of CH_2Cl_2 /hexane solution. The structure, shown in Figure 1, is consistent with all the spectroscopic data. The arrangement of the boron atoms resembles that of a disubstituted cyclopropane molecule. All the positions for hydrogen atoms are found in the crystal structure of compound **1**. Each boron atom except B4 (Figure 1) bears a terminal hydrogen atom, and there are four Zr–H–B bridge

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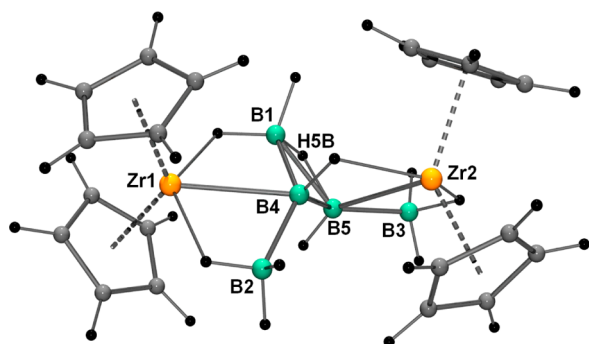
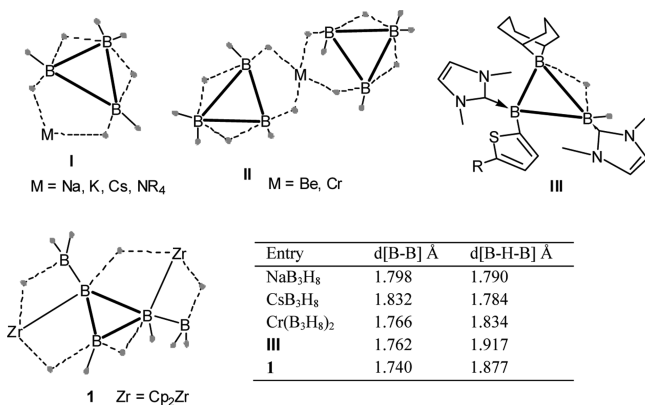


Figure 1. Molecular structure and labeling diagram for **1** (the bridged Zr–B bonds are deleted for clarity). Selected bond lengths (Å): Zr1–B1 2.518(8), Zr1–B4 2.495(8), Zr2–B5 2.517(8), B2–B4 1.783(11), B3–B5 1.802(12), B1–B4 1.722(10), B4–B5 1.758(12), B1–B5 1.877(13), B1–H5B 1.16(8), B5–H5B 1.33(9).

bonds. The B–B distances in **1** vary from 1.721 Å to 1.877 Å; however, the average nonbridged Zr–B distance of 2.506 Å is longer than the corresponding distance of 2.485 Å in ionic zirconaborane species $[(\text{Cp}_2\text{Zr})_2\text{B}_5\text{H}_8][\text{B}_{11}\text{H}_{14}]$.^{11a} The Zr–B distances for Zr–H–B bridge bonds range from 2.518 Å to 2.568 Å, which are shorter as compared to other zirconium–boron complexes, signifying a strong bonding interaction of the $\{\text{Cp}_2\text{Zr}\}$ unit with the borane cage.¹³

One of the interesting features of **1** is the presence of a B_3 triangle that allowed us to relate its structural matrices with different $[\text{B}_3\text{H}_8]^-$ species (**I** and **II**)^{14,15} and a base-stabilized *arachno*- B_3H_9 analogue (**III**)¹⁶ (Chart 1). Generally, the

Chart 1. Different B_3H_8 Species (**I** and **II**), Base-Stabilized *arachno*- B_3H_9 Analogue (**III**), and **1**



hydrogen-bridged B–B bond distances, observed in open boranes, are comparatively longer than the nonbridged ones. The $[\text{B}_3\text{H}_8]^-$ species (**I** and **II**), listed in Chart 1, however, show a reverse trend. Interestingly, the hydrogen-bridged B–B distance of 1.917(3) Å in **III** is significantly longer compared to those observed in species **I**, **II**, and **1**. The B1–B5 edge is bridged by a hydrogen atom in an unsymmetrical fashion, similar to NaB_3H_8 or **III**, with B1–H5B = 1.160(8) Å and B5–H5B = 1.330(9) Å. On the other hand, the angles of the triangular B_3 unit in **1** ranging from 56.4° to 65.2° are comparable with those of **III** (55.4–65.8°) and NaB_3H_8 (59.8–60.3°).

The presence of a planar B_3 ring in **1** draws our attention to carry out theoretical analyses with respect to *arachno*- B_3H_9 and the recently reported X-ray structure of *arachno*- NaB_3H_8 .^{14b}

The natural bond orbital (NBO) analysis shows a charge of ca. 0.40e on each of the boron atoms of the B_3 ring, and the Wiberg bond analysis returned an index of ca. 0.60 for the B–B bond in **1** (Tables S2 and S3). The NBO analysis provides similar results for NaB_3H_8 and B_3H_9 (Figure S1). The bonding situation of **1** is very similar to that of NaB_3H_8 and B_3H_9 , in which two of the B–H–B bonds are considered to be replaced by a three-center two-electron (3c-2e) bond. The NBO analysis further supports the involvement of a Zr–metal in the 3c-2e B–Zr–B bond (Figure S2) in **1**. The charge density distribution of **1**, NaB_3H_8 , and B_3H_9 , shown in Figure 2 and

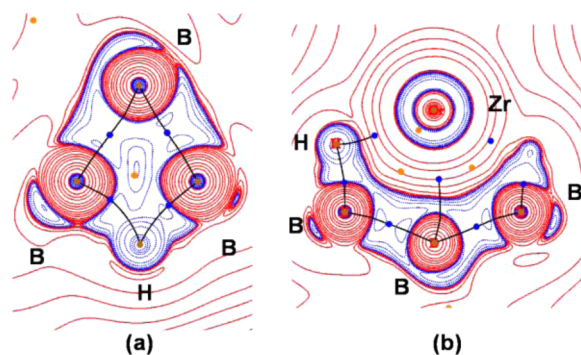


Figure 2. Topology of the Laplacian of electron density ($-\nabla^2\rho$) of **1** in the (a) B_3 plane and (b) ZrB_2 plane.

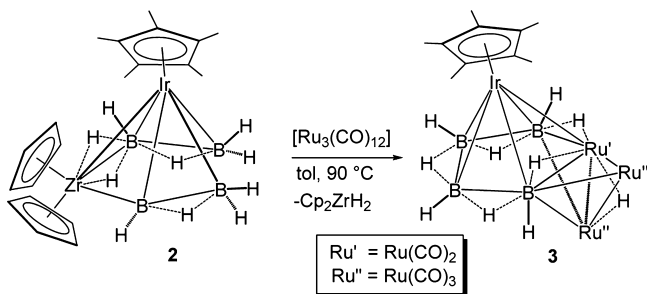
Figure S1, illustrates comparable topological features. As shown in Figure 2a, two curved bond paths are located between the atom critical points of the boron atoms along with one polar B–H–B bond that shows the existence of different types of 3c-2e bonding interactions. Further, the NICS(0) calculation⁷ supports two-dimensional aromatic stabilization of the B_3 ring in **1** (NICS(0) for **1**: −36.16; NaB_3H_8 : −38.48; B_3H_9 : −27.99 ppm). Considering the Zr atoms and the external boron groups as ligands in **1**, both compounds **1** and *arachno*- B_3H_9 possess the same skeleton electron pair count of 5-sep. Thus, based on both the experimental and computational results as described above, compound **1** can be considered a derivative of *arachno*- B_3H_9 .

Alternatively, compound **1** can be considered as a fused cluster, and according to Mingos's formalism,¹⁷ the total cluster valence electron (cve) of such clusters is equal to the sum of the cve for the parent polyhedra minus the electron count of the shared unit (atom, pair of atoms, etc.). As shown in Scheme S1, **1** can be described as fusion of two *arachno*- ZrB_3 ($2\{(14 + 12) + 6\} = 64e$) moieties through the B_3 ($6 \times 3 = 18e$) triangular face. Further, the resulting structure is fused with two triangles ZrB_2 ($2 \times 28 = 56e$) through the Zr–B edge ($24e$). This arrangement of **1** generates an electron count of 54e, which is equal to its total cluster valence electron count.

As part of our present research program on the chemistry of early transition metallaboranes,⁴ we have recently isolated and structurally characterized *arachno*- $[(\text{Cp}_2\text{Zr})(\text{Cp}^*\text{Ir})\text{B}_4\text{H}_{10}]$, **2**, comprising both $\{\text{Cp}^*\text{Ir}\}$ and $\{\text{Cp}_2\text{Zr}\}$ fragments ($\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$).¹² The skeleton electron count of **1** and *arachno*-**2** reveals that the latter possesses two electrons less than **1**. Therefore, in an attempt to synthesize a hybrid analogue of **1** by introducing a two-electron fragment into **2**, we performed the reaction of *arachno*-**2** with $[\text{Ru}_3(\text{CO})_{12}]$. Interestingly, thermolysis of *arachno*-**2** in the presence of $[\text{Ru}_3(\text{CO})_{12}]$ yielded a hybrid metallaborane, $[(\text{Cp}^*\text{Ir})\{\text{Ru}_3(\text{CO})_8\}\text{B}_4\text{H}_{10}]$, **3**,

that does not have a $\{\text{Cp}_2\text{Zr}\}$ moiety (Scheme 2).¹⁸ The ^{11}B NMR shows three resonances in 1:1:2 ratio, and the ^1H NMR

Scheme 2. Synthesis of Cluster 3



shows five upfield chemical shifts with a sharp signal at δ -20.67 ppm. The presence of terminal CO ligands has been confirmed by IR and ^{13}C NMR spectroscopy.

CONCLUSION

In this article we have described the isolation of the first homometallic neutral zirconaborane from the borane condensation method. The structural findings and computational study nicely established a close link between **1** and other *arachno*- B_3 compounds. The results described here find a new foray toward the search for group 4 metallaboranes, and we believe that these species may find applications in metal-mediated catalysis and functionalization reactions. Such studies are in progress.

EXPERIMENTAL SECTION

General Procedures and Instrumentation. All the manipulations were conducted under an Ar/N_2 atmosphere using standard Schlenk techniques or a glovebox. Solvents were distilled prior to use under argon. $[\text{Cp}_2\text{ZrCl}_2]$, LiBH_4 2.0 M in thf, $\text{BH}_3\cdot\text{thf}$, and $[\text{Ru}_3(\text{CO})_{12}]$ (Aldrich) were used as received. Compounds $[\text{Cp}_2\text{Zr}(\text{BH}_4)_2]$ ¹⁹ and **2**¹² were prepared according to a literature method. The external reference, $[\text{Bu}_4\text{N}][\text{B}_3\text{H}_8]$,²⁰ for the ^{11}B NMR was synthesized with the literature method. Preparative thin-layer chromatography was performed with Merck 105554 TLC silica gel 60 F_{254} , layer thickness 250 μm , on aluminum sheets (20×20 cm). NMR spectra were recorded on a 400 and 500 MHz Bruker FT-NMR spectrometer. Residual solvent protons were used as reference (δ , ppm, CDCl_3 , 7.26; C_6D_6 , 7.16), while a sealed tube containing $[\text{Bu}_4\text{N}][\text{B}_3\text{H}_8]$ in $[\text{d}_6]$ -benzene (δ_{B} , ppm, -30.07) was used as an external reference for the ^{11}B NMR. Infrared spectra were recorded on a Nicolet is10 spectrometer. Mass spectra were recorded on a Bruker MicroTOF-II mass spectrometer. Microanalyses for C and H were performed on a PerkinElmer Instruments series II model 2400.

Synthesis of 1. To the solution of $[\text{Cp}_2\text{Zr}(\text{BH}_4)_2]$ (0.12 g, 0.32 mmol) in toluene, an excess amount of $\text{BH}_3\cdot\text{thf}$ was added at ice-cold temperature and left stirring for 1 h. The resulting mixture was then thermolyzed at 80°C for 16 h. The reaction mixture was filtered through Celite. The filtrate was concentrated, and the residue was chromatographed on silica gel TLC plates. Elution with a hexane/ CH_2Cl_2 (30:70 v/v) mixture yielded pale yellow **1** (0.063 g, 26%) based on the amount of $[\text{Cp}_2\text{Zr}(\text{BH}_4)_2]$. **1**: MS (ESI⁺): calculated mass for $^{12}\text{C}_{40}^{1}\text{H}_{51}^{11}\text{B}_5^{90}\text{Zr}_2$, 766.2550, obsd, 766.3512. ^{11}B NMR (22 $^\circ\text{C}$, 128 MHz, CDCl_3): δ 8.1 (br, 2B), 2.5 (br, 2B), -4.1 (br, 1B). ^1H NMR (22 $^\circ\text{C}$, 400 MHz, CDCl_3): δ 6.01 (s, 10H; 2Cp), 5.98 (s, 5H; 1Cp), 5.95 (s, 5H; 1Cp), 3.26 (partially collapsed quartet (pcq), 2H; BH), 2.91 (pcq, 2H; BH), 2.22 (pcq, 2H; BH), -1.31 (br, 1H; B–H–B), -4.31 (br, 4H; Zr–H–B). ^{13}C NMR (22 $^\circ\text{C}$, 100 MHz, CDCl_3): δ 92.4, 89.6 (C_5H_5). IR $\bar{\nu}/\text{cm}^{-1}$: 2512, 2456 (B–H). Anal. (%) Calcd for $\text{C}_{40}\text{H}_{51}\text{B}_5\text{Zr}_2$: C, 62.52; H, 6.69. Found: C, 62.61; H, 6.65.

Synthesis of 3. $[\text{Cp}_2\text{Zr}(\text{Cp}^*\text{Ir})\text{B}_4\text{H}_{10}]$, **2** (0.070 g, 0.11 mmol), was dissolved in toluene (10 cm^3), and the resulting solution was thermolyzed at 90°C for 8 h after the addition of $[\text{Ru}_3(\text{CO})_{12}]$. The solvent was removed, and the residue was extracted in hexane. The filtrate was concentrated and subjected to chromatographic separation. An elution with a mixture of hexane/ CH_2Cl_2 (90:10) gave brown **3** (0.012 g, 11%). MS (ESI⁺): calculated mass for $^{12}\text{C}_{18}^{1}\text{H}_{25}^{16}\text{O}_8^{11}\text{B}_4^{101}\text{Ru}_3^{192}\text{Ir}_1$, 910.8603, obsd 910.7405. ^{11}B NMR (22 $^\circ\text{C}$, 160 MHz, CDCl_3): δ 116.8 (br, 1B), 21.8 (br, 1B), 5.2 (s, 2B). ^1H NMR (22 $^\circ\text{C}$, 500 MHz, CDCl_3): δ 6.02 (pcq, 2H; BH), 4.11 (br, 1H; BH), 3.95 (br, 2H; BH), 1.89 (s, 15H; Cp*), -2.48 (br, 1H; B–H–B), -3.55 (br, 1H; B–H–B), -5.21 (br, 1H; B–HB), -5.73 (br, 1H; Ru–H–B), -8.62 (br, 1H; Ru–H–B), -20.67 (s, 1H; Ru–H–Ru). ^{13}C NMR (22 $^\circ\text{C}$, 125 MHz, CDCl_3): δ 193, 182 (CO), 100.1 (C_5Me_5), 11.2 (C_5Me_5). IR $\bar{\nu}/\text{cm}^{-1}$: 2023, 1999 (CO), 2423 (B–H). Anal. (%) Calcd for $\text{C}_{18}\text{H}_{25}\text{B}_4\text{O}_8\text{IrRu}_3$: C, 23.81; H, 2.77. Found: C, 23.76; H, 2.81.

X-ray Structure Determination. The crystal data for **1** and **3** were collected and integrated using a Bruker Axs kappa apex2 CCD diffractometer, with graphite-monochromated Mo $\text{K}\alpha$ ($\lambda = 0.71073$ Å) radiation at 296 K. The structures were solved by heavy atom methods using SHELXS-97 or SIR92 and refined using SHELXL-97.²¹

Crystal data for 1: $\text{C}_{20}\text{H}_{31}\text{B}_5\text{Zr}_2$, $M_r = 507.94$ g/mol, monoclinic, space group Pc , $a = 9.3091(7)$ Å, $b = 7.9329(6)$ Å, $c = 15.0168(11)$ Å, $\beta = 100.583(3)^\circ$, $V = 1090.10(14)$ Å³, $Z = 2$, $\rho_{\text{calcd}} = 1.547$ g/ cm^3 , final R indices [$I > 2\sigma(I)$] $R_1 = 0.0419$, $wR_2 = 0.0943$, index ranges $-12 \leq h \leq 12$, $-10 \leq k \leq 10$, $-17 \leq l \leq 20$, θ range for data collection 2.226° to 28.589° , crystal size $0.25 \times 0.15 \times 0.10$ mm³, reflections collected 19 304, independent reflections 4312, goodness-of-fit on F^2 1.038.

Computational Details. Geometries of all the complexes were optimized using the density functional theory (DFT)²² method in conjunction with the BP86²³ functional and def2-SVP or Def2-TZVP basis set.²⁴ The model compounds were fully optimized in the gaseous state (no solvent effect) without any symmetry constraints. The optimized geometries were characterized as true minima via analytical frequency calculations. Both combinations (BP86/Def2-TZVP and BP86/Def2-SVP) returned similar structures close to those determined experimentally. Therefore, calculations were carried out with the BP86/Def2-SVP combination, which gives a good description of the geometry determined by X-ray diffraction and are computationally the least expensive. A comparison of the experimental and theoretical structural parameters is given in Table S2. The NMR chemical shifts were calculated using the hybrid Becke–Lee–Yang–Parr (B3LYP) functional²⁵ and aforementioned basis set on the BP86/def2-SVP-optimized geometries. Computation of the NMR shielding tensors employed GIAOs^{26–28} using the implementation of Schreckenbach, Wolff, Ziegler, and co-workers.^{29–33} The ^{11}B NMR chemical shifts were calculated relative to B_2H_6 (B3LYP B shielding constant 84.23 ppm) and converted to the usual $[\text{BF}_3\cdot\text{OEt}_2]$ scale using the experimental δ (^{11}B) value of B_2H_6 , 16.6 ppm.³⁴ NBO analysis was carried out using the NBO routine within the Gaussian09³⁵ package. Wiberg bond indexes (WBIs)³⁶ are obtained on NBO analysis.^{37,38} Multiwfn V. 3.1³⁹ was used for the topological analyses of the electron densities. Atom critical points (acp's) are represented by brown circles; bond critical points (bcp's) by blue circles; and bond paths by black lines. The aromaticity of the compounds being investigated was evaluated by calculating nucleus-independent chemical shift (NICS)^{40,41} indices on the optimized geometry at the same level of theory by using the GIAO method. As a normal routine, we placed a ghost atom at the ring critical point, the point of lowest density of each system, to calculate the magnetic shielding tensor and measure aromaticity from the magnetic point of view. These values are denoted as NICS(0), as suggested by Schleyer et al.⁴⁰

ASSOCIATED CONTENT

Supporting Information

Supplementary crystallographic data, experimental details, computational details, and X-ray crystallographic file for **1**.

This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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REFERENCES

- (1) (a) Kennedy, J. D. *Prog. Inorg. Chem.* **1984**, 32, 519. (b) Kennedy, J. D. *Prog. Inorg. Chem.* **1986**, 36, 211. (c) Gilbert, K. B.; Boocock, S. K.; Shore, S. G. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Abel, E. W., Stone, F. G. A., Eds.; Pergamon: New York, 1982; Part 6, Chapter 41, p 879. (d) Grimes, R. N. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Abel, E. W., Stone, F. G. A., Eds.; Pergamon: New York, 1982; Part 1, Chapter 5.5, p 459.
- (2) (a) Barton, L.; Srivastava, S. K. In *Comprehensive Organometallic Chemistry II*; Wilkinson, G., Abel, E. W., Stone, F. G. A., Eds.; Pergamon: New York, 1995; Vol. 1, Chapter 8, p 275. (b) Grimes, R. N. In *Comprehensive Organometallic Chemistry II*; Wilkinson, G., Abel, E. W., Stone, F. G. A., Eds.; Pergamon: New York, 1995; Vol. 1, Chapter 9, p 374. (c) Grimes, R. N. *Chem. Rev.* **1992**, 92, 251. (d) Saxena, A. K.; Hosmane, N. S. *Chem. Rev.* **1993**, 93, 1081. (e) Geetharani, K.; Tussupbayev, S.; Borowka, J.; Holthausen, M. C.; Ghosh, S. *Chem.—Eur. J.* **2012**, 18, 8482.
- (3) (a) Fehlner, T. P.; Halet, J.-F.; Saillard, J.-Y. *Molecular Clusters: A Bridge to Solid-State Chemistry*; University Press: New York, 2007. (b) Housecroft, C. E.; Fehlner, T. P., Eds. *Inorganometallic Chemistry, Modern Inorganic Chemistry Series*; Plenum: New York, 1992; Chapter 10, p 237. (c) Greenwood, N. N.; Ward, I. M. *Chem. Soc. Rev.* **1974**, 3, 231. (d) Bose, S. K.; Roy, D. K.; Shankari, P.; Yuvaraj, K.; Mondal, B.; Sikder, A.; Ghosh, S. *Chem.—Eur. J.* **2013**, 19, 2337. (e) Anju, R. S.; Roy, D. K.; Geetharani, K.; Mondal, B.; Varghese, B.; Ghosh, S. *Dalton Trans.* **2013**, 42, 12828.
- (4) (a) Roy, D. K.; Bose, S. K.; Geetharani, K.; Chakraborty, K. K. V.; Mobin, S. M.; Ghosh, S. *Chem.—Eur. J.* **2012**, 18, 9983. (b) Bose, S. K.; Geetharani, K.; Varghese, B.; Mobin, S. M.; Ghosh, S. *Chem.—Eur. J.* **2008**, 14, 9058. (c) Bose, S. K.; Geetharani, K.; Ramkumar, V.; Mobin, S. M.; Ghosh, S. *Chem.—Eur. J.* **2009**, 15, 13483. (d) Bose, S. K.; Geetharani, K.; Ghosh, S. *Chem. Commun.* **2011**, 47, 11996.
- (5) (a) Aldridge, S.; Hashimoto, H.; Kawamura, K.; Shang, M.; Fehlner, T. P. *Inorg. Chem.* **1998**, 37, 928. (b) Weller, A. S.; Fehlner, T. P. *Organometallics* **1999**, 18, 447. (c) Aldridge, S.; Shang, M.; Fehlner, T. P. *J. Am. Chem. Soc.* **1998**, 120, 2586.
- (6) (a) Guennic, B. L.; Jiao, H.; Kahlal, S.; Saillard, J.-Y.; Halet, J.-F.; Ghosh, S.; Beatty, A. M.; Rheingold, A. L.; Fehlner, T. P. *J. Am. Chem. Soc.* **2004**, 126, 3203. (b) Ghosh, S.; Rheingold, A. L.; Fehlner, T. P. *Chem. Commun.* **2001**, 895.
- (7) (a) Ghosh, S.; Beatty, A. M.; Fehlner, T. P. *Angew. Chem., Int. Ed.* **2003**, 42, 4678. (b) Ghosh, S.; Noll, B. C.; Fehlner, T. P. *Angew. Chem., Int. Ed.* **2005**, 44, 2916.
- (8) (a) Ghosh, S.; Noll, B. C.; Fehlner, T. P. *Dalton Trans.* **2008**, 371. (b) Roy, D. K.; Bose, S. K.; Anju, R. S.; Mondal, B.; Ramkumar, V.; Ghosh, S. *Angew. Chem., Int. Ed.* **2013**, 52, 3222.
- (9) (a) Venable, T. L.; Grimes, R. N. *Inorg. Chem.* **1982**, 21, 887. (b) Kim, D. Y.; Girolami, G. S. *J. Am. Chem. Soc.* **2006**, 128, 10969.
- (10) (a) Pipal, J. R.; Grimes, R. N. *Inorg. Chem.* **1977**, 16, 3251. (b) Nishihara, Y.; Deck, K. J.; Shang, M.; Fehlner, T. P. *Organometallics* **1994**, 13, 4510.
- (11) (a) Thomas, R. L.; Rath, N. P.; Barton, L. J. *Am. Chem. Soc.* **1997**, 119, 12358. (b) Thomas, R. L.; Rath, N. P.; Barton, L. *Inorg. Chem.* **2002**, 41, 67. (c) Denton, D. L.; Godfroid, R. A.; Barton, L.; Shore, S. G. *Inorg. Chem.* **1996**, 35, 791.
- (12) Anju, R. S.; Roy, D. K.; Mondal, B.; Ramkumar, V.; Ghosh, S. *Organometallics* **2013**, 32, 4618.
- (13) (a) Jordan, G. T.; Shore, S. G. *Inorg. Chem.* **1996**, 35, 1087. (b) Hlatky, G. G.; Turner, H. W.; Eckman, R. R. *J. Am. Chem. Soc.* **1989**, 111, 2728.
- (14) (a) Hill, T. G.; Godfroid, R. A.; White, J. P.; Shore, S. G. *Inorg. Chem.* **1991**, 30, 2952. (b) Dunbar, A. C.; Macor, J. A.; Girolami, G. S. *Inorg. Chem.* **2014**, 53, 822. (c) Bykova, A. Y.; Razgonyayeva, G. A.; Mal'tseva, N. N.; Zhizhin, K. Y.; Kuznetsov, N. T. *Russ. J. Inorg. Chem.* **2012**, 57, 471. (d) Amberger, E.; Gut, E. *Chem. Ber.* **1968**, 101, 1200. (e) Graybill, B. M.; Ruff, J. K.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1961**, 83, 2669.
- (15) (a) Goedde, D. M.; Windler, G. K.; Girolami, G. S. *Inorg. Chem.* **2007**, 46, 2814. (b) Deiseroth, H. J.; Sommer, O.; Binder, H.; Wolfer, K.; Frei, B. Z. *Anorg. Allg. Chem.* **1989**, 571, 21. (c) Gaines, D. F.; Morris, J. H. *J. Chem. Soc., Chem. Commun.* **1975**, 626.
- (16) Braunschweig, H.; Horl, C. *Chem. Commun.* **2014**, 50, 10983.
- (17) (a) Mingos, D. M. P. *Nature (London)* *Phys. Sci.* **1972**, 236, 99. (b) Mingos, D. M. P. *Acc. Chem. Res.* **1984**, 17, 311.
- (18) The solid-state structure of **3**, obtained from a poor-quality X-ray diffraction study, reveals that the core geometry is a pentagonal pyramid. The iridium center is at the pyramidal position, and the base is made of B1–B2–B3–B4–Ru1 (Figure S7).
- (19) (a) Marks, T. J.; Kolb, J. R. *Chem. Rev.* **1977**, 77, 265. (b) Noth, H.; Hartwimmer, R. *Chem. Ber.* **1960**, 93, 2238. (c) Nanda, R. K.; Wallbridge, M. G. H. *Inorg. Chem.* **1964**, 3, 1978. (d) Davies, N.; James, B. D.; Wallbridge, M. G. H. *J. Chem. Soc. A* **1969**, 2601.
- (20) Ryschewitsch, G. E.; Nainan, K. C. *Inorg. Synth.* **1974**, 15, 113.
- (21) (a) SIR92: Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A. *J. Appl. Crystallogr.* **1993**, 26, 343. (b) Sheldrick, G. M. *SHELXS-97*; University of Göttingen: Germany, 1997. (c) Sheldrick, G. M. *SHELXL-97*; University of Göttingen: Germany, 1997.
- (22) Koch, W.; Holthausen, M. C. *A Chemist's Guide to Density Functional Theory*; Wiley-VCH: Weinheim, Germany, 2000.
- (23) (a) Schmider, H. L.; Becke, A. D. *J. Chem. Phys.* **1998**, 108, 9624. (b) Perdew, J. P. *Phys. Rev. B* **1986**, 33, 8822.
- (24) Weigend, F.; Ahlrichs, R. *Phys. Chem. Chem. Phys.* **2005**, 7, 3297.
- (25) (a) Becke, A. D. *Phys. Rev. A* **1988**, 38, 3098. (b) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, 37, 785. (c) Becke, A. D. *J. Chem. Phys.* **1993**, 98, 5648.
- (26) London, F. J. *J. Phys. Radium* **1937**, 27, 397.
- (27) Ditchfield, R. *Mol. Phys.* **1974**, 27, 789.
- (28) Wolinski, K.; Hinton, J. F.; Pulay, P. *J. Am. Chem. Soc.* **1990**, 112, 8251.
- (29) Schreckenbach, G.; Ziegler, T. *J. Phys. Chem.* **1995**, 99, 606.
- (30) Schreckenbach, G.; Ziegler, T. *Int. J. Quantum Chem.* **1997**, 61, 899.
- (31) Schreckenbach, G.; Ziegler, T. *Int. J. Quantum Chem.* **1996**, 60, 753.
- (32) Wolff, S. K.; Ziegler, T. *J. Chem. Phys.* **1998**, 109, 895.
- (33) Wolff, S. K.; Ziegler, T.; van Lenthe, E.; Baerends, E. J. *J. Chem. Phys.* **1999**, 110, 7689.
- (34) Onak, T. P.; Landesman, H. L.; Williams, R. E.; Shapiro, I. J. *Phys. Chem.* **1959**, 63, 1533.
- (35) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.

Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Keith, T.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. *Gaussian 09*, Revision C.01; Gaussian, Inc.: Wallingford, CT, 2010.

(36) Wiberg, K. *Tetrahedron* **1968**, *24*, 1083.

(37) Weinhold, F.; Landis, C. R. *Valency and Bonding: A Natural Bond Orbital Donor-Acceptor Perspective*; Cambridge University Press: Cambridge, U.K, 2005.

(38) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899.

(39) Lu, T.; Chen, F. *J. Comput. Chem.* **2012**, *33*, 580.

(40) Schleyer, P. v. R.; Maerker, C.; Dransfeld, A.; Jiao, H.; Hommes, N. J. R. v. E. *J. Am. Chem. Soc.* **1996**, *118*, 6317.

(41) Chen, Z.; Wannere, C. S.; Cominboeuf, C.; Puchta, R.; Schleyer, P. v. R. *Chem. Rev.* **2005**, *105*, 3842.