



Synthesis and structure of heterometallic clusters of early transition metals†

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Manuscript received online 15 September 2019, accepted 19 September 2019

In continuation of our recent studies on the reactivity of $[(Cp^*Nb)_2B_4H_{10}O]$, **1** with metal carbonyls, we have carried out its reactivity with $[Fe_2(CO)_9]$ that led to the formation of $[(Cp^*Nb)_2B_2H_4O\{H_2Fe_2(CO)_6BH\}]$, **1**. Compound **1** is a heterometallic boride cluster in which $[Nb_2Fe_2]$ core describes a butterfly framework with one boron atom lying in a semi-interstitial position. Further, in an attempt to isolate the heterometallic metallaboranes of group 4, we have performed the thermolysis reaction of $[Cp_2Hf(BH_4)_2]$ with $[Cp^*IrB_3H_9]$ that led to the formation of *arachno*- $[(Cp_2Hf)(Cp^*Ir)B_3H_9]$, **2**, analogous to $[(Cp_2Zr)(Cp^*Ir)B_3H_9]$. Compounds **1** and **2** have been characterized by mass spectrometry, 1H , ^{11}B and ^{13}C NMR spectroscopy and the structural types were unequivocally established by crystallographic analysis.

Keywords: Boron, niobium, hafnium, iridium, heterometallic.

Introduction

Synthesis of higher vertex clusters are of continuing importance due to their fascinating geometry¹⁻³ as well as their applications in various fields^{4,5}. Main group elements⁶, transition metals⁷ or the combination of both⁸ are known to make large cage geometries. Boron is not an exception to this. In particular, boranes and metallaboranes of higher nuclearity, even beyond icosahedron, are reported^{9,10}. They are either a single cage cluster¹¹ or a fused geometry, where two or more polyhedral clusters are fused either through vertex, edge or face¹².

In metallaborane chemistry, there are many ways to obtain cluster expansion¹³. Two of the main approaches are insertion of metal carbonyl fragments into a preformed metallaborane or the reaction of two preformed metallaboranes^{14,15}. Cluster electron counting rules along with isolobal principle can back the formation of these clusters^{16,17}. Hence, having in hand a wide range of metallaboranes containing group 4 to 9 transition metals¹⁸⁻²⁰, we have tried their reactivity with various metal carbonyls²¹⁻²³. Not all, but many of them resulted in the formation of fused clusters^{22,23}. In this course, we have recently reported the synthesis of face

fused clusters from the reactivity of $[(Cp^*M)_2B_4H_{10}O]$ ($M = Nb$ and Ta) with $[Ru_3(CO)_{12}]^{23b}$. Herein, we report the reactivity of $[(Cp^*Nb)_2B_4H_{10}O]$ with $[Fe_2(CO)_9]$ as an extension of the earlier work. In addition, we report the synthesis and structure of hetero-dimetallaborane having groups 4 and 9 transition metals.

Experimental

General procedures and instrumentation

General procedures and the instrumentation of all the experiments were conducted under an argon atmosphere using standard Schlenk techniques. Solvents were distilled prior to use under argon. $[Fe_2(CO)_9]$, $[Cp_2HfCl_2]$ and $[LiBH_4]$ of 2 M in THF were purchased from Aldrich chemicals and used as received. $[(Cp^*Nb)_2B_4H_{10}O]^{23b}$, $[Cp_2Hf(BH_4)_2]^{24}$, $[Cp^*IrCl_2]^{25}$, $[Cp^*IrB_3H_9]^{26}$ and $BH_3 \cdot THF^{27}$ were synthesized as per the literature. Thin-layer chromatography was performed on a 250 mm dia aluminium-supported silica gel plates (Merck TLC plates). The NMR spectra were recorded on 400 or 500 MHz Bruker FT-NMR spectrometer. The residual solvent protons were used as reference (δ , ppm, $CDCl_3$: 7.26; C_6D_6 : 7.16). Infrared spectra were obtained on a Jasco FT/IR-1400 spectrometer. Mass spectra were recorded on a

†Professor Priyadarajan Ray Memorial Lecture (2018).

Bruker Micro TOF-II mass spectrometer in ESI ionization mode.

Synthesis of 1

In a flame-dried Schlenk tube, $[(Cp^*Nb)_2B_4H_{10}O]$, (0.1 g, 0.19 mmol) was dissolved in hexane (20 mL). To this $[Fe_2(CO)_9]$ (0.03 g, 0.08 mmol) was added and stirred for 18 h at room temperature. The solvent was removed *in vacuo* and the residue was extracted through celite using a *n*-hexane/ CH_2Cl_2 mixture (90:10 (v/v)). After removal of solvent, the residue was subjected to chromatographic purification using silica gel TLC plates. Elution with *n*-hexane/ CH_2Cl_2 (80:20 (v/v)) yielded brown solid $[(Cp^*Nb)_2B_2H_4O\{H_2Fe_2(CO)_6BH\}]$, **1** (0.015 g, 10%).

1: MS (ESI⁺): *m/z* Calcd. for $[C_{26}H_{37}B_3Nb_2Fe_2O_7]^+$: 792.97. Found: 792.56; $^{11}B\{^1H\}$ NMR (160 MHz, $CDCl_3$, 22°C): δ = 148.5 (s, 1B), 31.3 (s, 1B), -4.3 (s, 1B) ppm; 1H NMR (500 MHz, $CDCl_3$, 22°C): δ = 5.25 (br, 2BH_t), 2.16 (s, 15H, Cp*), 1.97 (s, 15H, Cp*), -2.73 (s, 1H, Nb-H-B), -6.65 (s, 1H, Nb-H-B), -9.48 (s, 1H, Nb-H-B), -14.37 (s, 1H, Nb-H-Fe), -18.08 (s, 1H, Nb-H-Fe) ppm; $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, 22°C): δ = 213.9 (CO), 115.5, 114.7 (s, C_5Me_5), 12.7, 12.2 (s, C_5Me_5) ppm; IR (CH_2Cl_2 , cm^{-1}): $\bar{\nu}$ = 2359 (B-H_t), 2059, 2012, 2001 (CO), 1382 (B-O).

Synthesis of 2

A toluene solution of $[Cp^*IrB_3H_9]^{26b}$ (0.082 g, 0.22 mmol) was added to a flame-dried Schlenk tube. To this, freshly prepared $[Cp_2Hf(BH_4)_2]$ (0.17 g, 0.50 mmol) was added at 0°C. The reaction mixture was heated at 80°C for 24 h in presence of excess $BH_3 \cdot THF$. The solvent was evaporated under vacuum, and the residue was extracted with *n*-hexane/ CH_2Cl_2 and the extract was filtered through celite. After removal of the solvent, the residue was subjected to chromatography on silica gel TLC plates. Elution with a *n*-hexane/ CH_2Cl_2 (70:30, v/v) mixture yielded pale yellow solid $[(Cp_2Hf)(Cp^*Ir)B_3H_9]$, **2** (0.031 g, 9%) along with *arachno*- $[(Cp_2Hf)(Cp^*Ir)B_4H_{10}]$ (0.086 g, 25%).

2: HR-MS (ESI⁺): Calcd. for $[C_{20}H_{34}B_3HfIr+Na]^+$: 703.1932. Found: 703.1943. $^{11}B\{^1H\}$ NMR (160 MHz, C_6D_6 , 22°C): δ = 6.6 (s, 1B), -5.4 (s, 1B), -15.4 (s, 1B) ppm; 1H NMR (500 MHz, C_6D_6 , 22°C): δ = 5.41 (s, 5H, Cp), 5.21 (s, 5H, Cp), 4.62 (br, 2BH_t), 4.27 (br, 2BH_t), 3.47 (br, BH_t), 1.72 (s, 15H, Cp*), -0.03 (br, 1H, B-H-B), -4.58 (br, 1H, Hf-H-B), -7.91 (br, 1H, Hf-H-B), -14.92 (s, 1H, Ir-H) ppm; $^{13}C\{^1H\}$ NMR (125 MHz, C_6D_6 , 22°C): δ = 106.0, 103.9 (s, C_5H_5), 99.5 (s,

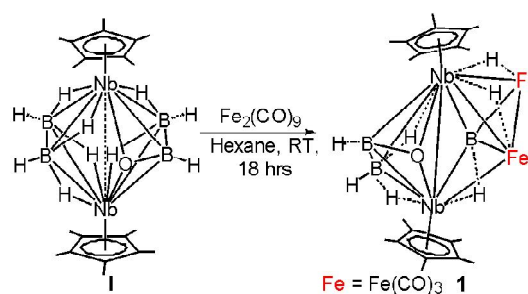
C_5Me_5), 9.6 (s, C_5Me_5) ppm; IR (CH_2Cl_2 , cm^{-1}): $\bar{\nu}$ = 2440, 2468 (B-H_t) cm^{-1} .

X-Ray structure determination

Crystallographic information for compounds **1** and **2** is provided in Table S1 (ESI). The crystal data for **1** was collected and integrated using a Bruker APEX-II CCD diffractometer at 296 K and **2** using D8 VENTURE Bruker AXS at 150 K with graphite-monochromated MoK_{α} radiation (λ = 0.71073 Å). The structures were solved by heavy atom methods using SHELXS-97 for **1** and SHELXT-2015 for **2**²⁸ and refined using SHELXL-2014 for **1** and SHELXL-2016 for **2**²⁹. Molecular structures were drawn using Olex2³⁰. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre.

Results and discussion

*Reactivity of $[(Cp^*Nb)_2B_4H_{10}O]$ with $[Fe_2(CO)_9]$* : Recently, we have developed a new approach for the synthesis of oxametallaboranes of group 5 metals, $[(Cp^*M)_2B_4H_{10}O]$ (M = Nb and Ta)^{23b}. These oxametallaboranes were found to be very reactive towards metallocarbonyls to form highly complex fused higher vertex clusters²³. In our earlier study, we have performed the reactivity of $[(Cp^*Ta)_2B_4H_{10}O]$ with $[Fe_2(CO)_9]$ to form a edge fused cluster $[(Cp^*Ta)_2B_2H_4O\{H_2Fe_2(CO)_6BH\}]$ ^{23a}. Also, the pyrolysis of $[(Cp^*M)_2B_4H_{10}O]$, (M = Nb or Ta) with $[Ru_3(CO)_{12}]$ yielded heterometallic face-fused clusters^{23b}. We now extend this work and carried out the reactivity of $[(Cp^*Nb)_2B_4H_{10}O]$, **1** with $[Fe_2(CO)_9]$ that yielded $[(Cp^*Nb)_2B_2H_4O\{H_2Fe_2(CO)_6BH\}]$, **1** (Scheme 1). Cluster **1** was isolated as a brown solid by preparative thin-layer chromatography (TLC) in 10% yield. It was characterized spectroscopically as well as by single crystal X-ray diffraction analysis.



Scheme 1. Synthesis of **1**.

The ^{11}B NMR spectrum of **1** shows three resonances at δ = -4.3, 31.3 and 148.5 ppm with equal intensity. The reso-

nances at $\delta = 148.5$ ppm is highly downfield indicating more number of connectivity with metals. The remaining peaks are comparable to two of the chemical shifts observed in the starting material, **I**^{23b}. The ¹H NMR spectrum indicated the presence of two Cp* environments at $\delta = 2.16$ and 1.97 ppm. The ¹³C NMR further confirms the presence of both Cp* as well as CO ligands. The IR spectrum also exhibited intense bands characteristic of terminal carbonyl groups at 2059, 2012 and 2001 cm⁻¹. All these spectroscopic data are in good agreement with earlier reported, [(Cp*Ta)₂B₂H₄O{H₂Fe₂(CO)₆BH}]^{23a}. Further, mass spectrometric analysis of **1** also indicates the composition of **1** as [C₂₆H₃₇B₃Nb₂Fe₂O₇]⁺.

In order to confirm the spectroscopic assignments, the solid state X-ray diffraction analysis was performed that shows the structure of **1** as shown in Fig. 1. As per the expectation compound **1** turn to be the Nb analogue of the reported Ta-Fe boride cluster^{23a}. The molecular structure of **1** can be

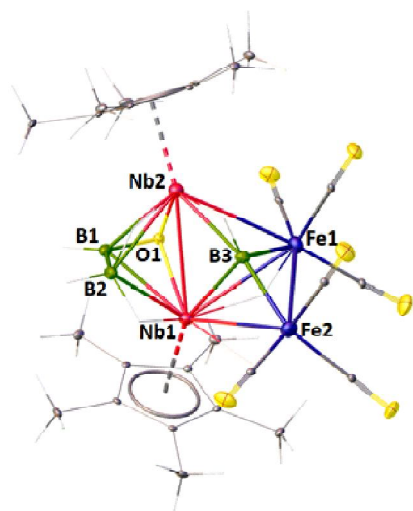
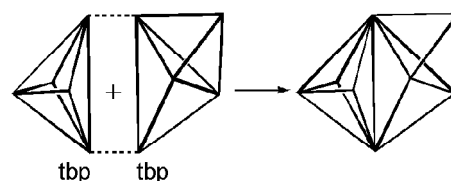


Fig. 1. Molecular structure and labeling diagram of **1**. Selected bond lengths [Å] and angles [°]: Nb1-Nb2 2.9290(4), Nb1-Fe1 2.9769(5), Nb1-Fe2 2.9196(5), Nb2-Fe2 3.0359(5), Fe1-Fe2 2.7248(7), B1-O1 1.417(4), Nb1-O1 2.108(2), Nb1-B3 2.398(4), Nb2-B3 2.213(4), Fe1-B3 1.921(4), B1-B2 1.718(6); Nb1-B1-Nb2 78.34(12), Nb1-O1-Nb2 88.23(8), Fe1-B3-Fe2 87.19(16), Nb2-B3-Fe1 165.1(2), Nb2-B3-Fe2 91.28(15), Fe2-Nb1-Nb2 62.541(12).

considered as a fusion of two trigonal bipyramidal (tbp) units; [Nb₂B₂O] tbp which is retained as such from the reactant, **I** fused through the Nb-Nb edge to [Nb₂Fe₂B] tbp which replaced the [B₂H₆]²⁻ unit in **I** (Scheme 2). The fused structure of **1** can be validated by Mingos's fusion formalism¹⁷. The



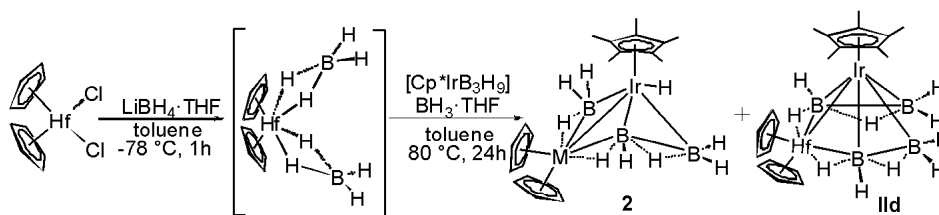
Scheme 2. Cluster fusion of **1**.

total cluster valence electron of **1** is 70 [2Cp*Nb (2×10 = 20 e) + 3B (3×3 = 9 e) + 7H (7 e) + O (6 e) + 2Fe (2×8 = 16 e) + 6 CO (6×2 = 12 e) = 70 cve] which is in exact match with the electron count by fusion formalism of Mingos [tbp [Nb₂B₂O] (42 e) + tbp [Nb₂Fe₂B] (62 e) – edge [Nb₂] (34 e) = 70 cve].

The [Nb₂Fe₂B] tbp unit can be also considered as a butterfly boride where the unique boron atom (B3) resides at the semi-interstitial position of [Nb₂Fe₂] butterfly geometry in which Nb2 and Fe2 occupies the wing tip and Nb1 and Fe1 occupies the hinge position. The boride boron connects the wingtip metal atoms with an angle of 165.14° where the boron atoms project outwards from the plane containing Nb2-Fe2. The internal dihedral angle for [Nb₂Fe₂] butterfly core is 108°, which is similar to its Ta-analogue, [(Cp*Ta)₂B₂H₄O{H₂Fe₂(CO)₆BH}] (108°) and agrees well with the ideal dihedral angle 109° for a four atom *arachno*-butterfly cluster derived from a *closo*-octahedron³¹.

The observed bond parameters in **1** are quiet similar to the reported Ta-analogue. The Nb-Nb bond distance of 2.9290(4) Å is comparable to the distance in [(Cp*Nb)₂(B₂H₄O){Ru(CO)₂}(B₂H₄){Ru(CO)₃}(μ-H)₄] (2.9373(10) Å) formed from the reaction of **I** with Ru₃(CO)₁₂^{23b}. In both these cases, Nb-Nb bond is significantly longer than that of **I** (2.7458(8) Å) and . This elongation of bond length might be due to electron pulling from the other parts of the cluster which is fused through the Nb-Nb bond. In addition, the boron-oxygen bond length of 1.417(4) Å, is comparable to that in **I** (1.454(17) Å) and shorter than the other reported oxametallaborane clusters^{23b,32}. The Fe-Fe bond distance of 2.7248(7) Å falls in the range associated with a M-M single bond³³.

*Synthesis and characterization of arachno-[(Cp₂Hf)-(Cp*Ir)B₃H₉] 2:* After having success with the isolation and characterization of a series of hybrid clusters, [(Cp₂M)-(Cp*M')B₄H₁₀], **Ila-d** (**Ila**, M = Zr, M' = Rh; **Ilb**, M = Zr, M' = Ir; **Ilc**, M = Hf, M' = Rh and **Ild**, M = Hf, M' = Ir) and [(Cp₂M)(Cp*M')B₃H₉], **III** (M = Zr, M' = Ir)³⁴, we were inter-

Scheme 3. Synthesis of **2**.

ested to synthesise the Ir-Hf pentaborane(11) analogue. Hence, we have carried out the pyrolysis of the intermediate obtained from the metathesis of $[\text{Cp}_2\text{HfCl}_2]$ and $\text{LiBH}_4 \cdot \text{THF}$ with $[\text{Cp}^*\text{IrB}_3\text{H}_9]$ in presence of borane at slightly higher temperature and longer time than the earlier report. This led to the formation of *arachno*- $[(\text{Cp}_2\text{Hf})(\text{Cp}^*\text{Ir})\text{B}_3\text{H}_9]$, **2** along with *arachno*- $[(\text{Cp}_2\text{Hf})(\text{Cp}^*\text{Ir})\text{B}_4\text{H}_{10}]$, **II d** (Scheme 3). Compound **2** was separated using thin layer chromatographic method which enabled us to characterize **2** spectroscopically and structurally in pure form. The details of characterization of compounds **2** is discussed below.

Compound **2** was isolated as yellow solid in 9% yield. The ^{11}B NMR peaks at $\delta = -15.4, -5.4$ and 6.6 ppm in 1:1:1 ratio confirm the presence of three boron environments. Further, the ^1H NMR spectrum of **2** shows one type of Cp^* proton at $\delta = 1.72$ ppm and two kinds of Cp protons at $\delta = 5.41$ and 5.21 ppm with equal intensity. In addition, the ^1H NMR shows resonances at upfield region at $\delta = -0.03, -4.58$ and -7.91 ppm along with a sharp peak at $\delta = -14.92$ ppm. The ^{13}C NMR spectra further supports the presence of one kind of Cp^* and two types of Cp protons. The $^{11}\text{B}\{^1\text{H}\}$ and ^1H NMR spectra are having very similar pattern to that of reported $[(\text{Cp}_2\text{Zr})(\text{Cp}^*\text{Ir})\text{B}_3\text{H}_9]$ which suggests **2** as an analogous compound in which Zr atom is replaced by a Hf. The mass spectrometric analysis of compound **2** confirms its composition as $\text{C}_{20}\text{H}_{34}\text{B}_3\text{HfIr}$.

In order to confirm the spectroscopic assignments and elucidate the crystal structure of compound **2**, an X-ray dif-

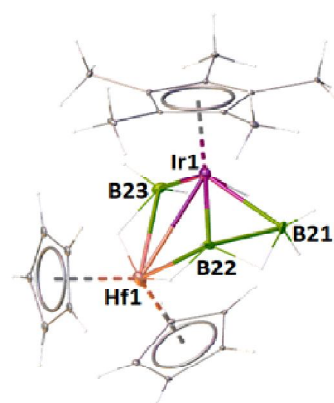
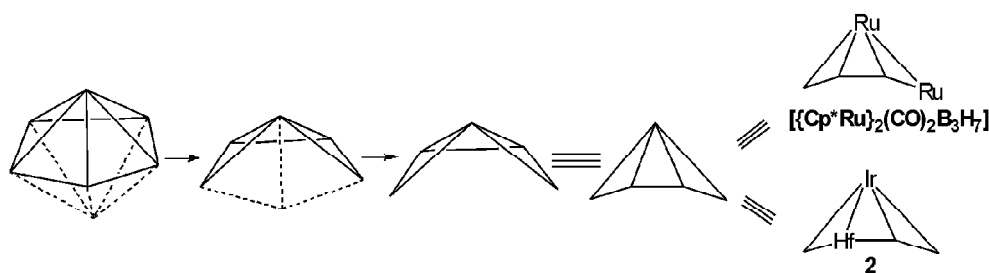
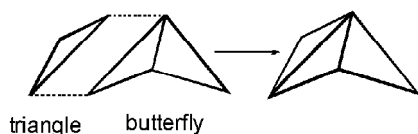


Fig. 2. Molecular structure and labeling diagram for **2**. Selected bond lengths (Å) and angles ($^\circ$): Ir1-Hf1 2.9317(5), Ir1-B21 2.205(10), Ir1-B22 2.145(8), Ir1-B23 2.228(10), Hf1-B22 2.581(9), Hf1-B23 2.590(10), B21-B22 1.852(14); Ir1-B23-Hf1 74.5(3), Ir1-B22-Hf1 76.1(3), Ir1-B21-B22 63.1(4).

fraction analysis was undertaken. Light yellow block-shaped crystals suitable for X-ray diffraction analysis were grown by cooling a concentrated hexane solution of **2** to 0°C . Compound **2** crystallizes in the triclinic space group $P-1$ and contains four molecules in the unit cell. The solid-state X-ray structure revealed that compound **2** is the first metal analogue of *arachno*- B_5H_{11} with an incorporated Hf atom. As shown in Fig. 2, the molecular structure of **2** can be viewed as an *arachno* structure which can be derived from two vertex removal from its parent *closo*-pentagonal bipyramid geometry as shown in Scheme 4. Compound **2** have eight skel-

Scheme 4. Schematic generation of observed geometry of **2** from a pentagonal bipyramid.

Scheme 5. Cluster fusion of **2**.

eton electron pairs (sep) as $\{\text{Cp}^*\text{Ir}\}$ and $\{\text{Cp}_2\text{Hf}\}$ are two-electron fragments, hence consistent with the Wade's skeleton electron count of *arachno*- $[\text{B}_5\text{H}_{11}] (n+3)^{16}$. On the basis of the Mingos fusion formalism¹⁷, cluster **2** can be seen as a fusion of $[\text{IrHfB}_2]$ butterfly (42 e) and $[\text{IrHfB}]$ triangle (38 e) through an edge of $[\text{IrHf}]$ (34 e) as shown in Scheme 5 to afford cve of 46 ($42 + 38 - 34 = 46$ cve) which corroborates with the electron count for the formula $[(\text{Cp}^*\text{Hf})(\text{Cp}^*\text{Ir})\text{B}_3\text{H}_9]$ $[\text{Cp}_2\text{Hf} (14 \text{ e}) + \text{Cp}^*\text{Ir} (14 \text{ e}) + 3\text{B} (3 \times 3 = 9 \text{ e}) + 9\text{H} (9 \text{ e}) = 46 \text{ cve}]$.

Comparing the structures of the reactant, $[(\text{Cp}^*\text{Ir})\text{B}_3\text{H}_9]$ and **2**; the only difference observed among them is the presence of Cp^*Hf unit which is inserted into the B-B bond of the earlier. The observed framework structure of **2** is comparable with that of $\{[\text{Cp}^*\text{Ru}]_2(\text{CO})_2\text{B}_3\text{H}_7\}^{35}$ (Scheme 4). The locations of the BH_2 units and the positions of the metal centers make these structures different. In compound **2**, the metal centers are four and three-connected; however, in $\{[\text{Cp}^*\text{Ru}]_2(\text{CO})_2\text{B}_3\text{H}_7\}$ they are four and two-connected. The bond parameters of **2** is in agreement with its Zr analogue, **III**. In addition the Ir-Hf distance of 2.9317(5) Å in **2** is similar to that in **IId**.

Conclusions

In this article, we have described the synthesis of two heterometallic metallaborane clusters **1** and **2** employing two different strategies. Compound **1** is derived from the reaction of an oxametallaborane with $[\text{Fe}_2(\text{CO})_9]$, while compound **2** was an *arachno*-pentaborane(11) analogue synthesized from reaction of two preformed metallaboranes of group 4 and 9. Both the compounds **1** and **2** are edge fused clusters which obey Mingos's fusion formalism.

Acknowledgements

This project was supported by the Council of Scientific and Industrial Research (CSIR; No. 01(2939)/18/emr-II), New Delhi, India. DST-FIST, India, is gratefully acknowledged for the HRMS facility. RP, AH and AD are grateful to IIT Madras, CSIR and UGC, respectively, for fellowships. The authors thank Mr. V. Ramkumar for X-ray structure analysis.

References

- (a) N. S. Hosmane and J. A. Maguire, *Phosphorus, Sulfur Silicon Relat. Elem.*, 1997, **124**, 263; (b) R. E. P. Winpenny, *Comment. Inorg. Chem.*, 1991, **20**, 233.
- (a) A. Burke, D. Ellis, B. T. Giles, B. E. Hodson, S. A. Macgregor, G. M. Rosair and A. J. Welch, *Angew. Chem. Int. Ed.*, 2003, **42**, 225; (b) R. N. Grimes, *Coord. Chem. Rev.*, 2000, **200**, 773; (c) A. K. Saxena and N. S. Hosmane, *Chem. Rev.*, 1993, **93**, 1081.
- (a) R. N. Grimes. in: 'Comprehensive Organometallic Chemistry II', eds. E. W. Abel, F. G. A. Stone and G. Wilkinson, Pergamon, Oxford, UK, 1995, **9**, 373; (b) C. E. Housecroft, *Polyhedron*, 1987, **6**, 1935; (c) C. E. Housecroft, *Adv. Organomet. Chem.*, 1991, **33**, 1.
- L. F. Tietze, U. Griesbach, U. Bothe, H. Nakamura and Y. Yamamoto, *ChemBioChem*, 2002, **3**, 219; (b) A. H. Soloway, W. Tjarks, B. A. Barnum, F. G. Rong, R. F. Barth, I. M. Codogni and J. G. Wilson, *Chem. Rev.*, 1998, **98**, 1515; (c) I. B. Sivaev and V. V. Bregadze, *Eur. J. Inorg. Chem.*, 2009, 1433.
- G. G. Hlatky, R. R. Eckman and H. W. Turner, *Organometallics*, 1992, **11**, 1413; (b) T. J. Carter, R. Mohtadi, T. S. Arthur, F. Mizuno, R. Zhang, S. Shirai and J. W. Kampf, *Angew. Chem. Int. Ed.*, 2014, **53**, 3173; (c) R. Núñez, I. Romero, F. Teixidor and C. Viñas, *Chem. Soc. Rev.*, 2016, **45**, 5147.
- (a) M. Driess and H. Nöth (Eds.), "Molecular Clusters of the Main Group Elements", Wiley VCH, Weinheim, 2004; (b) E. Bernhardt, D. J. Brauer, M. Finze and H. Willner, *Angew. Chem. Int. Ed.*, 2007, **46**, 2927.
- (a) M. D. Morse, *Chem. Rev.*, 1986, **86**, 1049; (b) L. G. Perla and S. C. Sevov, *Angew. Chem. Int. Ed.*, 2016, **55**, 6721.
- (a) L. G. Perla and S. C. Sevov, *J. Am. Chem. Soc.*, 2016, **138**, 9795; (b) L. G. Perla and S. C. Sevov, *Inorg. Chem.*, 2015, **54**, 8401; (c) K. Tatsumi, Y. Inoue, H. Kawaguchi, M. Kohsaka, A. Nakamura, R. E. Cramer, W. VanDooorne, G. J. Taogoshi and P. N. Richmann, *Organometallics*, 1993, **12**, 352.
- (a) D. K. Roy, S. K. Bose, R. S. Anju, B. Mondal, V. Ramkumar and S. Ghosh, *Angew. Chem. Int. Ed.*, 2013, **52**, 3222; (b) D. K. Roy, B. Mondal, P. Shankhari, R. S. Anju, K. Geetharani, S. M. Mobin and S. Ghosh, *Inorg. Chem.*, 2013, **52**, 6705.
- (a) L. Deng, J. Zhang, H.-S. Chan and Z. Xie, *Angew. Chem. Int. Ed.*, 2006, **45**, 4309; (b) L. Deng, H.-S. Chan and Z. Xie, *Angew. Chem. Int. Ed.*, 2005, **44**, 2128.
- (a) W. J. Evans and M. F. Hawthorne, *J. Chem. Soc., Chem. Commun.*, 1974, 38; (b) D. K. Roy, S. Ghosh and J.-F. Halet, *J. Clust. Sci.*, 2014, **25**, 225.
- (a) Md. Zafar, S. Kar, C. Nandi, R. Ramalakshmi and S. Ghosh, *Inorg. Chem.*, 2019, **58**, 47; (b) S. K. Bose, S. Ghosh, B. C. Noll, J.-F. Halet, J.-Y. Saillard and A. Vega, *Organometallics*, 2007, **26**, 5377; (c) F. P. Olsen, R. C. Vasavada and M. F. Hawthorne, *J. Am. Chem. Soc.*, 1968, **95**, 3946; (d) R. S. Dhayal, S. Sahoo, K. H. K. Reddy, S. M. Mobin, E. D. Jemmis and S. Ghosh, *Inorg. Chem.*, 2010, **49**, 900.
- (a) J. D. Kennedy, *Prog. Inorg. Chem.*, 1984, **32**, 519; (b) J. D. Kennedy *Prog. Inorg. Chem.*, 1986, **36**, 211; (c) K. B.

- Gilbert, S. K. Boocock and S. G. Shore, in: 'Comprehensive Organometallic Chemistry', eds. G. Wilkinson, E. W. Abel and F. G. A. Stone, Pergamon, New York, 1982, **41**, 879; (d) S. Ghosh, B. C. Noll and T. P. Fehlner, *Dalton Trans.*, 2008, 371.
14. (a) A. Thakur, S. Sahoo, V. Ramkumar and S. Ghosh, *Inorg. Chem.*, 2012, **51**, 8322; (b) R. S. Anju, K. Saha, B. Mondal, V. Dorcet, T. Roisnel, J.-F. Halet and S. Ghosh, *Inorg. Chem.*, 2014, **53**, 10527; (c) A. Thakur, K. K. V. Chakrahari, B. Mondal and S. Ghosh, *Inorg. Chem.*, 2013, **52**, 2262.
 15. (a) J. Bould, U. Dörfler, N. P. Rath, L. Barton, C. A. Kilner, M. G. S. Londesborough, D. L. Ormsby and J. D. Kennedy, *Dalton Trans.*, 2006, 3752; (b) J. Bould, C. William, J. D. Kennedy and J. T. Simon, *J. Chem. Soc., Dalton Trans.*, 1998, 2777.
 16. (a) K. Wade, *J. Chem. Soc., Chem. Commun.*, 1971, **15**, 792; (b) K. Wade, *Adv. Inorg. Chem. Radiochem.*, 1976, **18**, 1; (c) K. Wade, in: 'Electron Deficient Compounds', Nelson, London, 1971; (d) K. Wade, *Inorg. Nucl. Chem. Lett.*, 1972, **8**, 559.
 17. (a) D. M. P. Mingos, *Acc. Chem. Res.*, 1984, **17**, 311; (b) D. M. P. Mingos, *J. Chem. Soc., Chem. Commun.*, 1983, 706; (c) D. M. P. Mingos and R. L. Johnston, *Struct. Bonding (Berlin)*, 1987, **68**, 29; (d) D. M. P. Mingos and D. J. Wales, "Introduction to Cluster Chemistry", Prentice Hall, New York, 1990.
 18. (a) S. Ghosh, M. Shang, Y. Li and T. P. Fehlner, *Angew. Chem. Int. Ed.*, 2001, **40**, 1125; (b) K. Yuvaraj, D. K. Roy, K. Geetharani, B. Mondal, V. P. Anju, P. Shankhari, V. Ramkumar and S. Ghosh, *Organometallics*, 2013, **32**, 2705; (c) S. Ghosh, B. C. Noll and T. P. Fehlner, *Angew. Chem. Int. Ed.*, 2005, **44**, 6568; (d) S. Sahoo, K. H. K. Reddy, R. S. Dhayal, S. M. Mobin, V. Ramkumar, E. D. Jemmis and S. Ghosh, *Inorg. Chem.*, 2009, **48**, 6509.
 19. (a) K. Geetharani, S. K. Bose, G. Pramanik, T. K. Saha, V. Ramkumar and S. Ghosh, *Eur. J. Inorg. Chem.*, 2009, 1483; (b) S. K. Bose, K. Geetharani, B. Varghese, S. M. Mobin and S. Ghosh, *Chem. Eur. J.*, 2008, **14**, 9058; (c) D. K. Roy, R. Borthakur, R. Prakash, S. Bhattacharya, R. Jagan and S. Ghosh, *Inorg. Chem.*, 2016, **55**, 4764; (d) S. Ghosh, A. M. Beatty and T. P. Fehlner, *Collect. Czech. Chem. Commun.*, 2002, **67**, 808.
 20. (a) S. Sahoo, R. S. Dhayal, B. Varghese and S. Ghosh, *Organometallics*, 2009, **28**, 1586; (b) R. S. Dhayal, S. Sahoo, V. Ramkumar and S. Ghosh, *J. Organomet. Chem.*, 2009, **694**, 237; (c) K. K. Chakrahari, D. Sharmila, S. K. Barik, B. Mondal, B. Varghese and S. Ghosh, *J. Organomet. Chem.*, 2014, **749**, 188.
 21. (a) K. Geetharani, S. K. Bose, S. Sahoo, B. Varghese, S. M. Mobin and S. Ghosh, *Inorg. Chem.*, 2011, **50**, 5824; (b) K. Yuvaraj, D. K. Roy, B. Mondal, B. Varghese and S. Ghosh, *Inorg. Chem.*, 2015, **54**, 8673; (c) S. Ghosh, M. Shang and T. P. Fehlner, *J. Am. Chem. Soc.*, 1999, **121**, 7451; (d) B. S. Krishnamoorthy, A. Thakur, K. K. V. Chakrahari, S. K. Bose, P. Hamon, T. Roisnel, S. Kahlal, S. Ghosh and J.-F. Halet, *Inorg. Chem.*, 2012, **51**, 10375; (e) D. Sharmila, B. Mondal, R. Ramalakshmi, S. Kundu, B. Varghese and S. Ghosh, *Chem. Eur. J.*, 2015, **21**, 5074.
 22. (a) S. K. Bose, K. Geetharani, B. Varghese and S. Ghosh, *Inorg. Chem.*, 2011, **50**, 2445; (b) D. K. Roy, R. Jagan and S. Ghosh, *J. Organomet. Chem.*, 2014, **772**, 242; (c) K. Geetharani, S. K. Bose and S. Ghosh, *Organometallics*, 2011, **30**, 191; (d) D. Sharmila, K. Yuvaraj, S. K. Barik, D. K. Roy, K. K. V. Chakrahari, R. Ramalakshmi, B. Mondal, B. Varghese and S. Ghosh, *Chem. Eur. J.*, 2013, **19**, 15219.
 23. (a) S. K. Bose, K. Geetharani, S. Sahoo, K. H. K. Reddy, B. Varghese, E. D. Jemmis and S. Ghosh, *Inorg. Chem.*, 2011, **50**, 9414; (b) R. Prakash, A. De, K. Bakthavachalam and S. Ghosh, *Inorg. Chem.*, 2018, **57**, 14748.
 24. (a) T. J. Marks and J. R. Kolb, *Chem. Rev.*, 1977, **77**, 263; (b) N. Davies, B. D. James and M. G. H. Wallbridge, *J. Chem. Soc. A*, 1969, 2601.
 25. C. White, A. Yates and P. M. Maitlis, *Inorg. Synth.*, 1992, **29**, 228.
 26. (a) X. Lie, M. Shang and T. P. Fehlner, *Chem. Eur. J.*, 2000, **6**, 2653; (b) [Cp*IrB₃H₉] was not isolated from the reaction mixture in pure form. [Cp*IrH₄] was present along with it.
 27. R. C. Moore, S. S. White (Jr.) and H. C. Kelly, *Inorg. Synth.*, 1970, **12**, 109.
 28. (a) G. M. Sheldrick, SHELXS97 and SHELXL97. Program for Crystal Structure Solution and Refinement, University of Göttingen, Germany, 1997; (b) G. M. Sheldrick, *Acta Cryst.*, 2015, **A71**, 3.
 29. G. M. Sheldrick, *Acta Cryst.*, 2015, **C71**, 3.
 30. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Crystallogr.*, 2009, **42**, 339.
 31. F.-E. Hong, D. A. McCarthy, J. P. White III, C. E. Cottrell and S. G. Shore, *Inorg. Chem.*, 1990, **29**, 2874.
 32. (a) X. L. R. Fontaine, H. Fowkes, N. N. Greenwood, J. D. Kennedy and M. Thornton-Pett, *J. Chem. Soc., Chem. Commun.*, 1985, 1722; (b) E. J. Ditzel, X. L. R. Fontaine, H. Fowkes, N. N. Greenwood, J. D. Kennedy, P. MacKinnon, Z. Sisan and M. Thornton-Pett, *J. Chem. Soc., Chem. Commun.*, 1990, 1692; (c) Y.-H. Kim, A. Brownless, P. A. Cooke, R. Greatrex, J. D. Kennedy and M. Thornton-Pett, *Inorg. Chem. Commun.*, 1998, **1**, 19; (d) D. K. Roy, S. K. Bose, K. Geetharani, K. K. V. Chakrahari, S. M. Mobin and S. Ghosh, *Chem. Eur. J.*, 2012, **18**, 9983.
 33. A. Bandyopadhyay, M. Shang, C. S. Jun and T. P. Fehlner, *Inorg. Chem.*, 1994, **33**, 3677.
 34. (a) R. S. Anju, D. K. Roy, B. Mondal, V. Ramkumar and S. Ghosh, *Organometallics*, 2013, **32**, 4618; (b) D. K. Roy, A. De, R. Prakash, S. K. Barik and S. Ghosh, *Eur. J. Inorg. Chem.*, 2017, 4452.
 35. A. DiPasquale, X. Lei and T. P. Fehlner, *Organometallics*, 2001, **20**, 5044.