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Theoretical Investications on Geometric and Electronic Structure, Bonding and Spectral Properties of Dimolybdaboranes $(CpMo)_2B_5H_8X$ (X = H, OH, OC_6H_5)

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Abstract

Density Functional Theory calculations are used to address both the geometrical and electronic structural features, bonding and magnetic properties of the group 6 dimetallaboranes which includes, dimolybedaboranes of the type $(CpMo)_2(B_5H_9)$ (1), and its derivatives $(CpMo)_2(B_4H_8X)$ (X = OH (2), OC_6H_5(3)). Compound $(CpMo)_2B_5H_9$ (1) is experimentally known and compounds 2 and 3 are new molybdenum analogues. DFT (BP86/TZVP) computed metrical parameters and electronic and spectral properties are in good agreement with the experimental values of related clusters and suggest the stability and possible synthesis of new clusters $(CpMo)_2(B_4H_8OH)$ 2 and $CpMo)_2(B_4H_8OPh)$ 3.

Keywords: Metallaborane, Spectroscopy, DFT

1. Introduction

Metallaboranes may be defined as compounds that contain direct metal-boron (M-B) bonding. They are true hybrid clusters of polyhedral boranes and transition metal compounds formed by obeying the cluster electron counting rules and isolobal principle. Metallaborane compounds act as experimental link between transition metal clusters, boranecages. Examples for the metallaborane cluster compounds are $(C_pM)_2B_4H_{12}$ (M = V, Nb, Ta, Cr, Mo, W) $(C_p{*}M)_2B_5H_9$ (M = Cr, Mo, W); (Cp = η^5-C_5H_5 and Cp* = η^5-$C_5(CH_3)_5$). Careful analysis of the geometrical and electronic structure is crucial for these metallaboranes. Computational chemistry tools are in hand to achieve this.

Computational chemistry tools are being used by chemists as a routine procedure for their research, nowadays. Metallaborane chemistry is a fast growing area of research for the past three decades mainly due to their diverse structural features, unique bonding nature and promising applications[1–28]. There are now, a large number of metallaboranes known and both the electron-counting rules and the isolobal principle governing the synthesis of these clusters and defining the scope of this area. Although, experimental metallaborane chemistry is exploring rapidly, theoretical studies on these unique clusters are rather scarce. Infact, many areas of metallaborane chemistry merit theoretical investigations *viz.*, a). Geometric and Electronic Structure, b). Thermal and kinetic stability, c). Isomer preferences, d). Bonding, e). Spectroscopic properties, f). Reactivities, etc.[1–5].

These metallaboranes clusters often possess bridging hydrogens and the number and position of these

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hydrogens is always challenging. The difficulties in finding the number of hydrogen atoms and assigning the correct position of hydrogen atoms which includes both terminal and bridging hydrogens can be analysed and fixed with the help of the computational tools. DFT calculations have already been used to predict the correct assignment of these hydrogen atoms and used for the complete characterization of these metallaborane cluster compounds. Here, we have used computational chemistry tools like DFT calculations to address both the geometrical and electronic structural features, bonding and magnetic properties of the group 6 dimetallaboranes which includes, dimolybedaboranes of the type $(CpMo)_2(B_5H_9)$ (**1**), and its derivatives $(CpMo)_2(B_4H_8X)$ (X = OH,(**2**) OC_6H_5(**3**)) which is similar to the experimentally available molybdenum analogue $(CpMo)_2B_5H_9$ (**1**). The computed results are compared with experimental values when available, or with the related clusters. This will help to find a suitable computational method and appropriate level which is our preliminary aim. Since, metallaborane compounds and metallacarborane compounds find applications in catalysis, material chemistry and medicinal fields, the results of this study could be useful in understanding the geometric, electronic and magnetic properties of already experimentally available metallaborane cluster compounds, for the designing of novel cluster compounds and for their experimental synthesis

2. Computational Details

Computational chemistry tools are becoming important tools in assisting the complete structural charecterization of the compounds and also for the modelling of new compounds[26–30]. All the clusters in this work were studied in the following strategy. 1. Geometry optimization, 2. Frequency calculation. 3. NMR property calculation. 4.Bonding Analysis.

DFT calculation were carried out using the free were ORCA[31]. In ORCA, all geometry optimizations were done with the pure BP86 density functionals with TZVP basis sets[32,33]. In all the calculations, tight SCF convergence criteria were used. Optimized geometries were checked by the following frequency calculations in order to check the obtained geometry is the minima. EPR/NMR module has been used to calculate the NMR chemical shifts of the boron, hydrogen and carbon atoms (F. Neese *et al.*,). Experimental geometry for the cluster **1** was taken as input for geometry optimization. Frequency calculations were performed to confirm the minimum energy structure of the optimized geometry of the clusters 1-3.

NMR chemical shifts were obtained by computing the chemical shielding values of individual atoms by using the BP86/TZVP optimized geometries. Tetramethylsilane ($SiMe_4$) was used as an internal standard for the ^{1}H NMR and ^{13}C NMR. Diborane (B_2H_6) was used as primary reference point for the ^{11}B chemical shielding values and chemical shifts values are calculated. These values then referenced to standard $BF_3.OEt_2$ scale using the experimental value of +16.6 ppm for B_2H_6. Pictures of the optimized geometries are taken using the graphics programme ChemCraft[34].

3. Results and Discussion

Metallaboranes exhibit diverse structural features and applications in the fields like catalysis, biological, and new cluster formations, etc., Here, we have used computational chemistry tools like DFT calculations to address both the geometrical and electronic structural features, bonding and magnetic properties of the group 6 dimetallaboranes which includes, dimolybedaboranes of the type $(CpMo)_2(B_5H_9)$ (**1**), and its derivatives $(CpMo)_2(B_4H_8X)$ (X = OH (**2**), OC_6H_5(**3**)). Compound $(CpMo)_2B_5H_9$ (**1**) is experimentally known and compounds **2** and **3** are new molybdenum analogues. We have optimized the geometries of the compounds **1, 2** and **3** and compared the results with the experimentally available values. The important results obtained are discussed.

4. Geometrical Structure

The DFT optimized geometries at BP86/TZVP level for the clusters studied (1 - 3) are provided in **Figure 1**. The DFT optimized metrical parameters like bond lengths and bond angles are provided in **Table 1**. The synthesis and characterization of the stable B_5 cluster **$(CpMo)_2B_5H_9$** (**1**) is an important beginning of the metallaborane cluster chemistry. From which many metallaborane clusters are drawn and the chemistry of the metallaborane clusters has been explored. The optimized molecular structures of the clusters 1, 2 and 3 resulted in nido-hexagonalbipyramidal geometry with significant M-M bonding interactions.

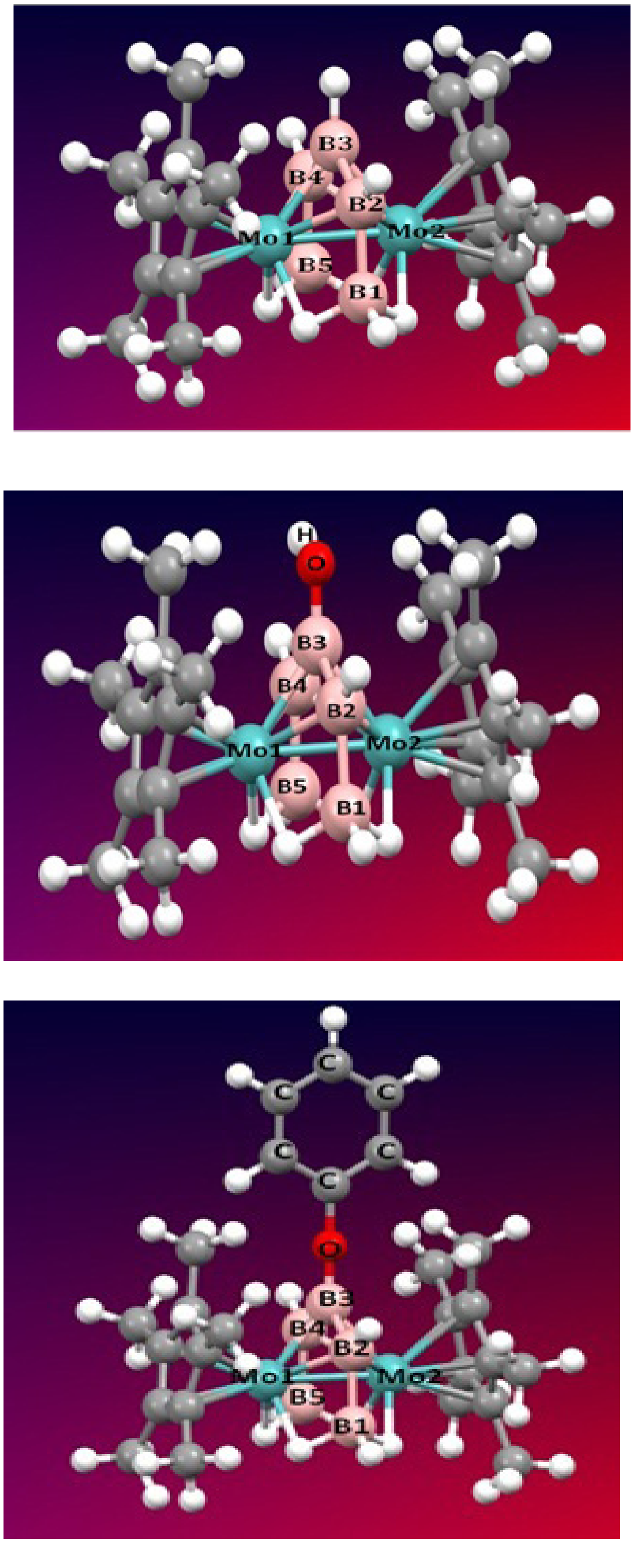

Figure 1. Molecular structure of cluster $(CpMo)_2B_5H_9$ (1), $(CpMo)_2B_5H_8OH$ (2) and $(CpMo)_2B_5H_8OC_6H_5$(3) optimized at DFT (BP86/TZVP) level.

The DFT computed bond parameters for the compound (**1**) are in good agreement with those of the experimental values obtained from X-ray crystallography. The DFT computed values are given in Table 1. The DFT computed Mo-Mo bond distance is 2.817 A^0 which are close to the experimental value of 2.809 A^0. The DFT computed $M\text{-}B_{(average)}$ bond length is 2.267 A^0 which is close to the experimental value of 2.147 A^0. The DFT computed $B\text{-}B_{(average)}$ bond length is 1.673 A^0 which is also close to the experimental value of 1.743 A^0. The DFT computed B-O distance in compound **2** and **3** is 1.360 A^0 which confirm the strong bonding interaction between boron and oxygen atom of the hydroxyl group, and the viability of the proposed hydroxyl substituted and phenoxy substituted dimolybdaborane clusters.

Table 1. Selected bond lengths (Å) for the compounds $(Cp^*Mo)_2B_5H_9$ (1), $(CpMo)_2B_5H_8OH$ (2) and $(CpMo)_2B_5H_8OC_6H_5$(3) optimized at the BP86/TZVP. [Experimental]

Compound	**1 DFT [Exp.]**	**2 DFT**	**3 DFT**
Mo1-Mo2	2.817 [2.809]	2.817	2.817
Mo1-B1	2.357 [2.320]	2.357	2.357
Mo1-B2	2.249 [2.214]	2.249	2.249
Mo1-B3	2.226 [2.181]	2.226	2.226
Mo1-B4	2.253 [2.209]	2.253	2.253
Mo1-B5	2.359 [2.322]	2.359	2.359
Mo2-B1	2.357 [2.322]	2.357	2.357
Mo2-B2	2.252 [2.211]	2.252	2.252
Mo2-B3	2.223 [2.176]	2.223	2.223
Mo2-B4	2.251 [2.216]	2.251	2.251
Mo2-B5	2.356 [2.312]	2.356	2.356
B1-B2	1.776 [1.732]	1.776	1.776
B2-B3	1.736 [1.715]	1.736	1.736
B3-B4	1.735 [1.712]	1.735	1.735
B4-B5	1.775 [1.735]	1.775	1.775
B-B(av)	1.743 [1.673]	1.746	1.746
M-B(av)	2.267 [2.147]	2.267	2.257
B3-OH		1.360	1.360

5. Bonding and Stability

The DFT computed energies of the HOMO, LUMO and the energy gap $E_{LUMO\text{-}HOMO}$ are listed in **Tables 2.**

Table 2. Orbital energies (eV) for the HOMO and LUMO and energy of gap $E_{LUMO-HOMO}$ of the clusters $(Cp^*Mo)_2B_5H_9$ (1), $(Cp^*Mo)_2B_5H_8OH$ (2), $(Cp^*Mo)_2B_5H_8OC_6H_5$ (3), obtained from DFT calculations at BP86/TZVP level using ORCA

Clusters	1	2	3
Homo	-4.9282	-4.8864	-4.7720
Lumo	-2.6126	-2.7016	-2.7701
$E_{LUMO-HOMO}$	2.3158	2.1848	2.0019
Chemical Potential **$(\mu)=E_{LUMO+HOMO}/2$**	-3.7704	-3.7940	-3.7711
Hardness (η) **$E_{LUMO-HOMO}/2$**	1.1579	1.0924	1.0010
Softness **$(S) = 1/\eta$**	0.8636	0.9154	0.9991
Electrophilicity $(\varpi) = M^2/2\eta$	6.1387	6.5884	7.1038

The DFT computed energy gap $E_{LUMO-HOMO}$ value of 2.3 eV for the cluster **1** confirms its highest stability when compared to those of clusters **2** and **3**. The DFT computed $E_{LUMO-HOMO}$ gap value of 2.2 eV and 2.0 eV for the clusters **2** and **3** suggesting the possibility of synthesis of these clusters in the laboratory at room temperature. When comparing the possible stability of hydroxyl substituted dimolybdaborane **2** and phenoxy substituted dimolybdaborane **3,** $E_{LUMO-HOMO}$ gap value confirm the more stable nature of the cluster **2** over **3.**

6. Electronic Structure

The electronic properties like ionization potential, electron affinity, absolute hardness, chemical potential and electrophilicity, of the dimolybdaborane cluster (**1**) and the new clusters **2** and **3** are calculated using DFT method. These electronic properties are calculated from Koopmann's theorem using HOMO and LUMO energies (**Table 2**). The energy required to remove an electron from the outer most orbital of the neutral atom or molecule can termed as Ionization potential. From the energy of the HOMO we can get this value. The energy required to add an electron to the molecule is usually known as electronic affinity which can be calculated from the orbital energy of LUMO. DFT computed E_{HOMO} values of -4.9, -4.9 and -4.8 eV shows the electron donating ability of the compounds **1, 2** and **3** respectively. The reactivity of the clusters can be predicted by energy gap between LUMO and HOMO. The reactivity of the molecule increases when the energy gap $E_{LUMO-HOMO}$ increases and *vice versa*. The stability of the clusters can be assumed from the hardness values. The DFT computed hardness values suggest stability decreases in the order **1** > **2** > **3** for the clusters studied. Hardness values also confirm the more stable nature of the cluster **1** over **2, 3**. (**Table 2**). The most electrophilic nature of the cluster **3** has been revealed from the DFT computed electrophilicity value of 7.1 eV **(Table 2).**

7. Spectroscopic Properties

Spectroscopy is a highly efficient tool for the structural characterization[29–30]. But computational chemistry tools can aid spectral details when there is a problem. DFT methods are already used successfully to characterize the structures of these metallaboranes in a complete manner. The DFT computed ^{11}B, ^{1}H and ^{13}C NMR chemical shift values are provided in the **Table 3.**

Table 3. DFT (BP86/TZVP) computed and experimental NMR chemical shifts δ (ppm) for the compounds $(Cp^*Mo)_2B_5H_9$ (1)

Clusters	**(1) DFT EXP.**	**(2) DFT**	**(3) DFT**
^{11}B NMR			
B1	17.2 [28.4]	13.1	14.0
B2	51.9 [65.6]	54.6	50.0
B3	46.8 [65.6]	57	63.8
B4	50.6 [65.6]	55.2	49.5
B5	16.4 [28.4]	10.1	13.1
^{1}H NMR			
H1	3.7 [5.01]	3.4	2.6
H2	2.9 [5.61]	3.4	3.5
H3	0.5 [3.43]	2.4	4.2
H4	2.6 [5.61]	2.6	4.0
H5	3.1 [5.01]	-5.5	- 7.8
H6	-7.1 [- 6.84]	-5.5	- 8.6
H7	-7.3 [- 6.84]	-7.4	- 5.7
H8	-8.6 [- 6.84]	-7.3	- 5.5
H9	-8.4 [- 6.84]	-	-
^{13}C NMR			
Ccp	113.2	116.1	115.6

In the ^{11}B NMR of the dimolybdaborane cluster **1,** the three of the five boron atoms are resonate at -65.6 ppm and two of the five boron atoms resonate around 28.4 ppm experimentally though there are three different types of borons. DFT calculations at BP86/TZVP level correctly predict the three different types of boron atoms, which are resonate around 17 ppm, 51 ppm and 47 ppm. Interestingly, the peak for the unique boron atom was not observed experimentally and DFT predict that the signal at 47 ppm. In the ^{1}H NMR of the dimolybdaborane **1**, all the bridging hydrogen atoms are resonating around -7.0 ppm from the DFT computations and the corresponding experimentally observed values are around -6.84 ppm. Interestingly the terminal hydrogen atom of the unique boron atom resonates around 3.4 ppm experimentally which is observed at 0.5 ppm computationally. The other terminal hydrogen atoms are resonating around 5 ppm experimentally which are computationally predicted at 2-3 ppm. The more shielded terminal hydrogen atom of the unique boron atom suggests the viability of the substitution at this position. Hence we tried to substitute the -OH group and -OPh group at this position. The DFT computed ^{13}C NMR chemical shift of the carbon atoms of cyclopentadiene ring are around 113 ppm which are also close to the experimental values of the similar clusters.

8. Conclusions

DFT calculations were carried out on the dimolybedaboranes of the type $(CpMo)_2(B_5H_9)$ (**1**), and its derivatives $(CpMo)_2(B_4H_8X)$ (X = OH, (**2**) OC_6H_5(**3**)) to study their geometrical and electronic structural features, stability, isomer preferences and spectroscopic properties. Compound $(CpMo)_2B_5H_9$ (**1**) is experimentally available and compounds **2** and **3** are new molybdenum analogue. The following conclusions were drawn from the present study:

1. DFT calculations using ORCA at BP86/TZVP level predict the structural parameters for the compound dimolybdaborane **1**, are in good agreement with the experimental values.
2. DFT optimized geometries for the OH and OPh substituted dimolybdaborane **2 and 3** are resulted in minima and the bond parameters are in good agreement with the experimental values of the similar cluster compounds and suggesting the possible synthesis of compounds **2 and 3.**
3. DFT (BP86/TZVP) computed $E_{LUMO\text{-}HOMO}$ gap values around 2.0 eV confirm the possible stability of the modelled clusters **2** and **3**. Thus providing the guidance for the viable synthesis of the hydroxyl substituted and phenoxy substituted dimolybdaboranes **2** and **3.**
4. DFT (BP86/TZVP) computed values of conceptual density functional terms like chemical potential (M), electron affinity (EA), ionization potential (IP), hardness (η), and electrophilicity (ω) also confirm the stable nature of cluster **1, 2, 3** and viable synthesis of clusters **2, 3** in the laboratory.
5. The ^{1}H, ^{13}C and ^{11}B NMR chemical shifts computed at DFT (BP86/TZVP) level are in close agreement with the experimentally observed values for the clusters **1.**
6. DFT also compute the ^{11}B NMR chemical shifts which are not observed experimentally, for example the unique boron of the cluster **1**, resonate at 46.8 ppm, which is not observed experimentally.
7. DFT optimized geometries and the computed ^{1}H, ^{13}C and ^{11}B NMR chemical shift values are very useful in successfully assigning the number and position of the bridging and terminal hydrogens of the clusters **1.**

9. References

1. Fehlner TP, Halet J-F, Saillard J-Y. Molecular clusters. A bridge to solid-state chemistry, Cambridge University Press, New York; 2007. https://doi.org/10.1017/CBO9780511628887. PMid:17319670
2. Nishihara Y, Deck KJ, Shang M, Fehlner TP, Haggerty BS, Rheingold AL. Synthesis of cobaltaborane clusters from $[Cp^*CoCl]_2$ and monoboranes. New structures and mechanistic implications. Organometallics.1994; 13:4510–22 https://doi.org/10.1021/om00023a062
3. King RB. Cyclopentadienyl ruthenium, rhodium, and iridium vertices in metallaboranes: Geometry and chemical Bonding Inorganic Chemistry. 2004; 43:4241–7. https://doi.org/10.1021/ic030279v. PMid:15236536
4. Fehlner TP. Systematic metallaborane chemistry. Organometallics. 2000; 19:2643–51. https://doi.org/10.1021/om000355r
5. Fehlner TP. Systematic metallaborane chemistry. Organometallics. 2000; 19:2643–51. https://doi.org/10.1021/om000355r
6. X. Lei, M. Shang, T. P. Fehlner. Search for a general route to metallaboranes via the reaction of monocyclopentadienyl metal chlorides with monoborane. synthesis and reactivity of the rhodaborane nido-1-Cl-2,3-$\{(\eta_5\text{-}C_5Me_5)Rh\}_2B_3H_6$.

Journal of the American Chemical Society. 1998; 120:2686–7. https://doi.org/10.1021/ja974268a

7. H. Yan, A. M. Beatty, T. P. Fehlner. Metallaborane reaction chemistry. nido-Dirhodapentaborane isomer structures and stabilities and utilization of dirhodaboranes as catalysts for alkyne cyclotrimerization. Organometallics. 2002; 21:5029–37. https://doi.org/10.1021/om0205694
8. Lei X, Shang M, Fehlner TP. Chem. Eur. J., 2000, 62, 653-2664.
9. Ghosh S, Noll BC, Fehlner TP. Expansion of iridaborane clusters by addition of monoborane. Novel metallaboranes and mechanistic detail. Dalton Transactions. 2008:371–8. https://doi.org/10.1039/B715040G. PMid:18411847
10. Geetharani K, Bose SK, Pramanik G, Saha TK, Ramkumar V, Ghosh S. An efficient route to group 6 and 8 metallaborane compounds: Synthesis of arachno-[Cp*Fe(CO)B_3H_8] and closo-[$(Cp^*M)_2B_5H_9$] (M = Mo, W). European Journal of Inorganic Chemistry. 2009:1483–7. https://doi.org/10.1002/ejic.200801137
11. Lei X, Shang M, Fehlner TP. Chemistry of dimetallaboranes derived from the reaction of $[Cp^*MCl_2]_2$ with monoboranes (M = Ru, Rh; Cp* = η^5-C_5Me_5). Journal of the American Chemical Society. 1999; 121:1275–87. https://doi.org/10.1021/ja982954j
12. Weller AS, Shang M, Fehlner TP. Chem. Commun. 1998; 1787–8.
13. Le Guennic B, Jiao H, Kahlal S, Saillard J-Y, Halet J-F, Ghosh S, Shang M, et al., Synthesis and characterization of hypoelectronic rhenaboranes. Analysis of the geometric and electronic structures of species following neither borane nor metal cluster electron-counting paradigms. Journal of the American Chemical Society. 2004; 126:3203–17. https://doi.org/10.1021/ja039770b. PMid:15012150
14. Ho J, Deck KJ, Nishihara Y, Shang M, Fehlner TP. J. Am. Chem. Soc. 1995; 117:10292–9.
15. Aldridge S, Hashimoto H, Kawamura K, Shang M, Fehlner TP. Inorg. Chem., 1998, 37, 928-940.
16. Bullick HJ, Grebenik PD, Green MLH, Hughes AK, Leach JB, McGowan PC. Synthesis of η-cyclopentadienyl-polyborane derivatives of molybdenum and tungsten. Journal of the Chemical Society, Dalton Transactions. 1995:67–75. https://doi.org/10.1039/DT9950000067
17. Aldridge S, Shang M, Fehlner TP. Synthesis of novel molybdaboranes from (η^5-C_5R_5)MoCln precursors (R = H, Me; n = 1, 2, 4) Journal of the American Chemical Society. 1998; 120:2586–98. https://doi.org/10.1021/ja973720n
18. Sahoo S, Dhayal RS, Varghese B, Ghosh S. Unusual open eight-vertex oxamolybdaboranes: Structural characterizations of $(\eta^5\text{-}C_5Me_5Mo)_2B_5(\mu^3\text{-OEt})H_6R$ (R = H and n-BuO). Organometallics. 2009; 28:1586–9. https://doi.org/10.1021/om801065r
19. Bose SK, Geetharani K, Varghese B, Mobin SM, Ghosh S. Chem. Eur. J., 2008, 14, 9058-9064.
20. Weller AS, Shang M, Fehlner TP. Synthesis of mono- and ditungstaboranes from reaction of Cp*WCl_4 and $[Cp^*WCl_2]_2$ with BH3·thf or LiBH4 (Cp* = η^5-C_5Me_5). Control of reaction pathway by choice of monoboron reagent and oxidation state of metal center organometallics. 1999; 18:53–64. https://doi.org/10.1021/om980743h
21. Bose SK, Ghosh S, Noll BC, Halet J-F, Saillard J-Y, Vega A. Organometallics. 2007; 26:5377–85.
22. Ting C, Messerle L. Borohydride boron-hydrogen activation and dimerization by a doubly bonded, early-transition-metal organodimetallic complex. Ditantalladiborane syntheses as models for dehydrodimerization of methane to ethane. Journal of the American Chemical Society. 1989; 111:3449–50. https://doi.org/10.1021/ja00191a063
23. Aldridge S, Hashimoto H, Shang M, Fehlner TP. $Cp^*TaCl_2B_4H_8$: synthesis, crystal structure and spectroscopic characterization of an air-stable, electronically unsaturated, chiral tantalaborane. Journal of the Chemical Society, Chemical Communications. 1998:207–8. https://doi.org/10.1039/a706483g
24. Geetharani K, Krishnamoorthy BS, Kahlal S, Mobin SM, Halet J-F, Ghosh S. Synthesis and characterization of hypoelectronic tantalaboranes: comparison of the geometric and electronic structures of [$(Cp^*TaX)_2B_5H_{11}$] (X = Cl, Br, and I). Inorganic Chemistry. 2012; 51:10176–84. https://doi.org/10.1021/ic300848f. PMid:22963332
25. Krishnamoorthy BS, Thakur A, Chakrahari K, Bose S, Hamon P, Roisnel T, et al. Inorganic Chemistry. 2012; 51:10375–83. https://doi.org/10.1021/ic301571e. PMid:22985463
26. Krishnamoorthy BS, Kahlal S, Ghosh S, Halet J-F. Electronic, geometrical, and thermochemical studies on group-14 element-diruthenaborane cluster compounds: a theoretical investigation. Theoretical Chemistry Accounts. 2013; 132:1356–66. https://doi.org/10.1007/s00214-013-1356-6
27. Krishnamoorthy BS, Kahlal S, Le Guennic B, Saillard J-Y, Ghosh S, Halet Sol J-F. Molecular transition-metal boron compounds. Any interest? Solid State Sciences. 2012; 14:1617–23. https://doi.org/10.1016/j.solidstatesciences.2012.03.026
28. Geetharani K, Bose SK, Sahoo S, Ghosh S. A Family of Heterometallic Cubane-Type Clusters with an exo-Fe(CO)3 Fragment Anchored to the Cubane. Angewandte Chemie International Edition. 2011; 50:3908. https://doi.org/10.1002/anie.201008101. PMid:21425424
29. Bose SK, Geetharani K, Ghosh S. C–H activation of arenes and heteroarenes by early transition metallaborane,

[(Cp*Ta)2B5H11] (Cp* = η^5-C_5Me_5). Chemical Communications. 2011; 47:11996. https://doi.org/10.1039/c1cc15394c. PMid:21975826

30. Campagna S, Giannetto A, Serroni S, Denti G, Micali N. Journal of the American Chemical Society. 1995; 1175:1754. https://doi.org/10.1021/ja00111a012
31. Neese F. The ORCA program system. Wiley Interdisciplinary Reviews: Computational Molecular Science. 2012; 2:73–8. https://doi.org/10.1002/wcms.81
32. Vosko SH, Wilk L, Nusair M. Accurate spin-dependent electron liquid correlation energies for local spin density calculations: a critical analysis. Canadian Journal of Physics. 1980; 58:1200–11. https://doi.org/10.1139/p80-159
33. Becke AD. J. Chem. Phys. 1986, 84, 4524-4529. Becke, A. D.; Phys. Rev. A, 1986 38, 3098-3100. Perdew, J. P.; Phys. Rev. B, 1986, 33, 8822-8824. https://doi.org/10.1103/PhysRevB.33.8822 PMid:9938299
34. Chemcraft - graphical software for visualization of quantum chemistry computations [Internet]. Available from: https://www.chemcraftprog.com