

Ortho-, Meta-, and Para-Directing Influence of Transition-Metal Fragments in 12-Vertex *closo*-Cyclopentadienylmetallaheteroboranes: Additive Nature of Structural Increments

Farooq Ahmad Kiani and Matthias Hofmann*

Anorganisch-Chemisches Institut, Ruprecht-Karls-Universität Heidelberg,
Im Neuenheimer Feld 270, D-69120 Heidelberg, Germany

Received September 20, 2005

Cyclopentadienylmetal fragments in 12-vertex *closo*-cyclopentadienylmetallaheteroboranes have a clear preference with respect to the positions relative to heteroatoms in the thermodynamically most stable isomer. Cyclopentadienyl derivatives of group 9 and 10 metals direct a carbon atom to meta and para positions, respectively. CpM fragments of two group 8 metals, i.e., Ru and Os, have the tendency to direct carbon atoms to meta positions, while that of Fe directs carbon atoms to ortho positions. By using increments for two general structural features, i.e., HetHet'_o (two heteroatoms at ortho positions) and HetHet'_m (two heteroatoms at meta positions), the relative stabilities of numerous isomers can be easily predicted. A comparison with DFT-computed relative stabilities of 101 metallaheteroboranes incorporating up to 4 heteroatoms shows good agreement: the average and standard deviations of the values derived from increments are 1.4 and 1.9 kcal mol⁻¹, respectively.

1. Introduction

Transition metals may occupy vertexes in deltahedral boranes and related heteroboranes, as was shown for the first time by Hawthorne et al.¹ in 1965. Typically, units of the type CpM (Cp = cyclopentadienyl; M = transition metal) replace BH or CH moieties. A large number of such structures are experimentally known^{2–5} with various metals, e.g., Fe,^{6–10} Co,^{6,8,11–13} Ni,¹³ Ru,¹⁴ and Rh,¹² in which a CpM fragment itself or its alkyl derivatives simply replace a BH vertex of a deltahedron so that

the cage topology remains the same. However, a systematic theoretical study of icosahedral heteroboranes incorporating various transition metals has never been carried out. This paper comprises a detailed study of diamagnetic 12-vertex *closo*-cyclopentadienylmetallaheteroborane clusters, the topology of which can be directly derived by Wade's well-established electron-counting rules.^{15,16}

Among metal-free 12-vertex *closo*-heteroboranes, usually smaller, more electronegative, formally electron withdrawing heteroatoms occupy nonadjacent vertexes in the thermodynamically most stable isomer according to Williams' heteroatom placement rule.^{17–19} A 12-vertex *closo* cluster with two more electronegative heteroatoms adjacent to each other is highly unfavorable and usually rearranges to more stable meta and para isomers, if enough activation energy is provided. For example, 1,2-PCB₁₀H₁₁ successively rearranges to its 1,7- and 1,12-isomers upon heating.²⁰ Larger, less electronegative, formally electron donating heteroatoms, however, tend to occupy adjacent vertexes in thermodynamically most stable 12-vertex *closo*-diheteroborane isomers.²¹ For example, due to the fact that it has the greatest thermodynamic stability,²¹ the experimentally known ortho (1,2) isomer of 12-vertex *closo*-Bi₂B₁₀H₁₀²² is not expected to rearrange into meta (1,7) or para (1,12) isomers. In the case of cyclopentadienylmetallaheteroboranes (for these

* To whom correspondence should be addressed. E-mail: matthias.hofmann@aci.uni-heidelberg.de.

(1) Hawthorne, M. F.; Pilling, R. L. *J. Am. Chem. Soc.* **1965**, *87*, 3987–3988.

(2) Saxena, A. K.; Hosmane, N. S. *Chem. Rev.* **1993**, *93*, 1081–1124 and references therein.

(3) Jelliss, P. A. *Organomet. Chem.* **2004**, *31*, 112–129 and references therein.

(4) Hosmane, N. S.; Maguire, J. A. *Eur. J. Inorg. Chem.* **2003**, *22*, 3989–3999.

(5) Grimes, R. S. In *Comprehensive Organometallic Chemistry 2*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: New York, 1995; pp 373–430.

(6) Shirokii, V. L.; Knizhnikov, V. A.; Vinokurov, I. I.; Bazhanov, A. A.; Mayer, N. A. *Russ. J. Gen. Chem. (Engl. Transl.)* **1997**, *67*, 1185–1187.

(7) Štíbr, B.; Holub, J.; Teixidor, F.; Viñas, C. *Collect. Czech. Chem. Commun.* **1995**, *60*, 2023–2027.

(8) Cerny, V.; Pavlik, I.; Kustkova-Maxova, E. *Collect. Czech. Chem. Commun.* **1976**, *41*, 3232–3244.

(9) Štíbr, B. *J. Organomet. Chem.* **2005**, *690*, 2857–2859.

(10) Garcia, M. P.; Green, M.; Stone, F. G. A.; Somerville, R. G.; Welch, A. J. *J. Chem. Soc., Chem. Commun.* **1981**, *16*, 871–872.

(11) (a) Evans, W. J.; Hawthorne, M. F. *Inorg. Chem.* **1974**, *13*, 869–874. (b) Evans, W. J.; Dunks, G. B.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1973**, *95*, 4565–4574. (c) Hawthorne, M. F.; Kaloustian, M. K.; Wiersemay, R. J. *J. Am. Chem. Soc.* **1971**, *93*, 4912–4913.

(12) Hanusa, T. P.; Todd, L. J. *Polyhedron* **1985**, *4*, 2063–2066.

(13) Rietz, R. R.; Dustin, D. F.; Hawthorne, M. F. *Inorg. Chem.* **1974**, *13*, 1580–1584.

(14) Kudinov, A. R.; Perekalin, D. S.; Rynin, S. S.; Lyssenko, K. A.; Grintselev-Knyazev, G. V.; Petrovskii, P. V. *Angew. Chem., Int. Ed.* **2002**, *41*, 4112–4114.

(15) Wade, K. *Adv. Inorg. Chem. Radiochem.* **1976**, *18*, 1–66.

(16) Wade, K. In *Metal Interactions with Boron Clusters*; Grimes, R. N., Ed.; Plenum Press: New York, 1982; Chapter 1, pp 1–41.

(17) Williams, R. E. *J. Am. Chem. Soc.* **1965**, *87*, 3513.

(18) Williams, R. E. In *Progress in Boron Chemistry*; Brotherton, R. J., Steinberg, H., Eds.; Pergamon Press: New York, 1970; Vol. 2, Chapter 2, p 57.

(19) Williams, R. E. *Chem. Rev.* **1992**, *92*, 177–207 and references therein.

(20) Štíbr, B. *Collect. Czech. Chem. Commun.* **2002**, *67*, 843–868 and references therein.

(21) Kiani, F. A.; Hofmann, M. *Dalton Trans.*, DOI: 10.1039/b512700a.

(22) Little, J. L.; Whitesell, M. A.; Kester, J. G.; Foltz, K.; Todd, L. J. *Inorg. Chem.* **1990**, *29*, 804–808.

compounds, we use a numbering system, in which the metal vertex bears number 1), however, one encounters both situations: heating of 1,2-CpNiCB₁₀H₁₁ results in cluster rearrangement to a structure with the CpNi and H–C units in meta (1,7) and para (1,12) positions,¹³ thus apparently obeying Williams' heteroatom placement rule.^{17–19} Similarly, 1-Cp-1,2,3-CoC₂B₉H₁₁ also rearranges into the isomers with carbon atoms at vertexes nonadjacent to the cyclopentadienylcobalt fragment.^{11c} In contrast, carbon atoms ortho to the CpFe unit in the experimentally known 1-Cp-[1,2,3-FeC₂B₉H₁₁][–] structure¹ do not rearrange to meta or para positions (at least there are no such experimental reports available). We wanted to rationalize such different behaviors of experimentally known 12-vertex *closo*-cyclopentadienylmetallaheteroboranes on the basis of theory and find rules that allow us to identify the most stable cyclopentadienylmetallaheteroborane isomers.

Such quantitative rules in terms of structural increments or energy penalties were already established for various *nido*- and *closo*-heteroboranes with different numbers, connectivities, and types of heteroatoms.^{21,23–27} These allow us to accurately reproduce the DFT-computed relative stabilities of various 6-,²³ 10-²⁴ and 11-vertex *nido*-heteroboranes^{25–27} and 12-vertex *closo*-heteroboranes.²¹ Here, we apply the structural increment studies to cyclopentadienylmetallaheteroboranes, which despite the large size and quite different nature of the CpM fragment, show structural features and in turn structural increments of very high additive nature. These structural increments allow us not only to reproduce the relative stabilities of a large number of known (for example, [CpFeC₂B₉H₁₁][–],¹ CpFeC₃B₈H₁₁,^{7,28,29} CpFePC₂B₈H₁₀,^{30,31} CpFeP₂CB₈H₉)³² and unknown isomeric 12-vertex *closo*-cyclopentadienylferraheteroboranes but also to estimate the relative stabilities of 12-vertex *closo*-cyclopentadienylmetallaheteroboranes with various other transition metals, e.g., Ru,¹⁴ Os, Co,^{8,11,12,13} Rh,¹² Ir, Ni,¹³ Pd, and Pt, without actually computing them. This study also helped to find out the nature of interaction of two, three, and four heteroatoms in a single 12-vertex *closo*-cyclopentadienylmetallaheteroborane cluster. We find that cyclopentadienylmetal fragments are specific toward directing the heteroatoms to the ortho-, meta-, and para positions in the thermodynamically most stable isomer.

2. Computational Details

Geometry optimizations, frequency calculations, and zero-point energy computations of various 12-vertex *closo*-cyclopentadienylmetallaheteroboranes with M = Fe, Co, Ni were performed at the RB3LYP/6-31G(d) level using Gaussian 03,³³ followed by single-point energy calculations at the RB3LYP/6-311+G(d,p) level. For M = Ru, Os, Rh, Ir, Pd, Pt, the structures were optimized at the

RB3LYP/LANL2DZ level using d-polarization functions for B, C, and P ($\xi = 0.388, 0.600, 0.340$, respectively)³⁴ with frequency and zero-point energy calculations at the same level. Single-point energies were determined at the RB3LYP/SDD level with additional p-type polarization functions for Ru, Os, Rh, Ir, Pd, Pt, and H ($\xi = 0.081, 0.077, 0.086, 0.081, 0.091, 0.086, 1.000$)³⁴ and d-polarization functions for B, C, and P (see above).

3. Results and Discussion

Initially 1,2-, 1,7- and 1,12-isomers of [CpMBC₁₀H₁₁]^{2–} (M = Fe, Ru, Os), those of [CpMBC₁₀H₁₁][–] (M = Co, Rh, Ir), and those of CpMBC₁₀H₁₁ (M = Ni, Pd, Pt) were computed. These isomers differ only with respect to the positions of the CpM fragment and the H–C moiety. The energy differences of ortho and meta isomers with respect to para isomers gave energy penalties for the structural features MC_o and MC_m, respectively (a CpM fragment at ortho and meta positions relative to a carbon atom, respectively) (see section 3.1). The energy penalties for MC_o and MC_m reflect the specific preference of a CpM fragment toward the positions of a CH moiety in the thermodynamically most stable isomer (section 3.2). The increase in the extent of electron localization results in a periodically progressive increase in energy penalties of these structural features along the period (section 3.3). A large number of cyclopentadienyliron-containing 12-vertex *closo*-carborane structures from [CpFeCB₁₀H₁₁]^{2–} to CpFeC₃B₈H₁₁, phosphaborane structures from [CpFePB₁₀H₁₀]^{2–} to CpFeP₃B₈H₈, and phosphacarbaboranes, i.e., [CpFePCB₉H₁₀][–], CpFeP₂CB₈H₉, and CpFePC₂B₈H₁₀, were computed in order to check the additive nature of the structural increments for CpM containing 12-vertex *closo*-metallaheteroboranes (section 3.4). The results help to quickly estimate the relative thermodynamic stabilities of various 12-vertex *closo*-cyclopentadienylmetallacarboranes, where M may be Fe or any other group 8, 9, or 10 metal (section 3.5).

3.1. Structural Features in Metallaheteroboranes. In comparison to *nido*-heteroboranes, the highly symmetrical *closo* clusters require a small number of structural features. Only two general structural features, i.e., HetHet'_o and HetHet'_m (Figure 1), are required for 12-vertex *closo*-heteroboranes.²¹ As it turns out, they behave additively and may be applied to estimate quite accurately the relative stabilities of a large number of cyclopentadienylmetallaheteroborane isomers with up to four heteroatoms.

The structural feature HetHet'_o represents two equal or different heteroatoms adjacent (at ortho positions) to each other. For example, 1,2-P₂B₁₀H₁₀ has the structural feature PP_o for two adjacent phosphorus atoms, whereas [1-Cp-1,2-FeCB₁₀H₁₁]^{2–} has the structural feature FeC_o for a CpFe unit adjacent to a carbon atom. The structural increment (energy penalty) for

(23) Hofmann, M.; Fox, M. A.; Greatrex, R.; Schleyer, P. v. R.; Williams, R. E. *Inorg. Chem.* **2001**, *40*, 1790–1801.

(24) Kiani, F. A.; Hofmann, M. *Eur. J. Inorg. Chem.* **2005**, *12*, 2545–2553.

(25) Kiani, F. A.; Hofmann, M. *Inorg. Chem.* **2004**, *43*, 8561–8571.

(26) Kiani, F. A.; Hofmann, M. *Inorg. Chem.* **2005**, *44*, 3746–3754.

(27) Kiani, F. A.; Hofmann, M. *J. Mol. Model.*, DOI: 10.1007/s00894-005-0037-3.

(28) Grüner, B.; Mikulasek, L.; Císařová, I.; Štíbr, B. *J. Organomet. Chem.* **2005**, *690*, 2853–2856.

(29) Perekalin, D. S.; Holub, J.; Golovanov, D. G.; Lyssenko, K. A.; Petrovskii, P. V.; Štíbr, B.; Kudinov, A. R. *Organometallics* **2005**, *24*, 4387–4392.

(30) Štíbr, B.; Holub, J.; Bakardjiev, M.; Pavlik, I.; Tok, O. L.; Wrackmeyer, B. *Eur. J. Inorg. Chem.* **2003**, 2524–2528.

(31) Štíbr, B.; Holub, J.; Bakardjiev, M.; Pavlik, I.; Tok, O. L.; Císařová, I.; Wrackmeyer, B.; Herberhold, M. *Chem. Eur. J.* **2003**, *9*, 2239–2244.

(32) Bakardjiev, M.; Holub, J.; Carr, M. J.; Kennedy, J. D.; Štíbr, B. *Dalton Trans.* **2005**, 909–913.

(33) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; 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.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Foxall, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, revision C.02; Gaussian, Inc.: Wallingford, CT, 2004.

(34) Huzinaga, S.; Andzelm, J. *Gaussian Basis Sets for Molecular Calculations*; Elsevier: Amsterdam, 1984, pp 23–25.

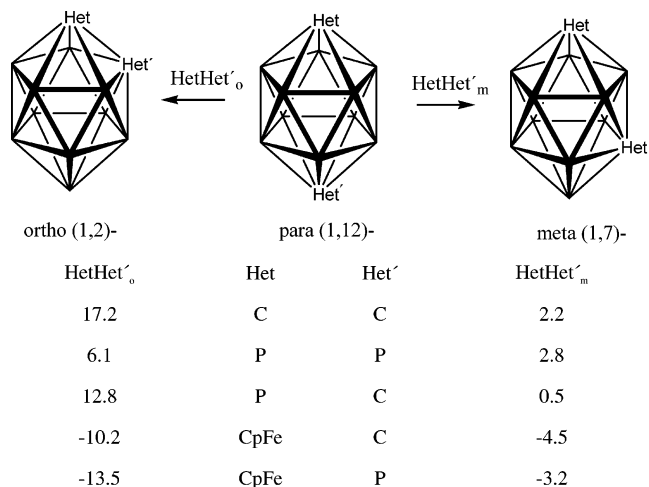


Figure 1. Structural features, HetHet'_o and HetHet'_m, in CpM fragment containing 12-vertex *closo*-metallaheteroboranes. Energy penalties (in kcal mol⁻¹) for HetHet'_o and HetHet'_m are the energy differences of ortho (1,2) and meta (1,7) isomers with respect to the para (1,12) isomer. A negative value for HetHet'_o (or HetHet'_m) means that the ortho (or meta) isomer is thermodynamically more stable than the para isomer.

HetHet'_o in a 12-vertex *closo*-diheteroborane is obtained directly by comparing the relative energies of the ortho and para isomers (Figure 1). HetHet'_m is the structural feature for two heteroatoms at positions meta to each other, and its increment is obtained as the energy difference of a meta and its para isomeric 12-vertex *closo* cluster. The energy penalties for various MC_o and MC_m structural features, where one heteroatom is a CpM fragment (M = group 8, 9, or 10 metal) and the other heteroatom is a H-C moiety, are listed in Chart 1. The statistically fitted energy penalties of 17.2 kcal mol⁻¹ for CC_o (two adjacent carbon atoms), of 2.2 kcal mol⁻¹ for CC_m (two carbon atoms at meta positions to each other), of 12.8 kcal mol⁻¹ for PC_o (a phosphorus and a carbon atoms adjacent to each other), of 0.5 kcal mol⁻¹ for PC_m (a phosphorus and a carbon atom at meta positions to each other), of 6.1 kcal mol⁻¹ for PP_o (two adjacent phosphorus atoms), and of 2.8 kcal mol⁻¹ for PP_m (two phosphorus atoms at meta positions to each other), as used in 12-vertex *closo*-cyclopentadienyl ferraheteroboranes, are listed in Figure 1. Except for cobalt, osmium, and ruthenium, usually the absolute values for the HetHet'_o energy penalties (Chart 1 and Table 1) are larger than those of HetHet'_m. Energy penalties for these structural features can be used to obtain the relative stabilities of various 12-vertex *closo*-cyclopentadienylmetal-containing metallaheteroboranes (section 3.4).

3.2. Ortho-, Meta-, and Para-Directing Influence of Metal Atoms to a Carbon Atom in Metallocarboranes. Williams' heteroatom placement rule¹⁷⁻¹⁹ suggests that heteroatoms occupy vertices as far apart as possible when equivalently connected sites are available. This rule indirectly identifies para-directing influences of two heteroatoms on each other in a 12-vertex *closo*-diheteroborane. In this section, we show that the CpM fragments are also specific but not necessarily always para directing toward the positions of heteroatoms in the metallocarboranes.

Chart 1 lists the energy penalties for the structural features MC_o (for a CpM group adjacent to a carbon atom) and MC_m (for a CpM group at meta position to a carbon atom), where M = group 8, 9, 10 metal. The MC_o and MC_m values are negative for Fe, Ru, and Os, indicating that the ortho and meta isomers are more stable than the para isomer for [CpMCB₁₀H₁₁]²⁻ (where M = Fe, Ru, Os). The more negative FeC_o as compared

Chart 1. Structural Increments for 12-Vertex *closo*-Cyclopentadienylmetallocarboranes

M ^a	χ ^b	C.R. ^c	n(+x) ^d	
MC _o ^e				
MC _m ^f				
Group 8 heteroatoms	Group 9 heteroatoms		Group 10 heteroatoms	
Fe	1.83 125 1(+2)	Co	1.88 126 2(+3)	
-9.0 ^g -3.6		-0.02 -1.2	Ni	1.91 121 3(+4)
8.5 0.9				
Ru	2.2 126 1(+2)	Rh	2.28 135 2(+3)	
-2.9 -3.6		5.1 -1.2	Pd	2.2 131 3(+4)
12.2 0.9				
Os	2.2 128 1(+2)	Ir	2.2 137 2(+3)	
-0.7 -3.4		8.5 -1.4	Pt	2.28 128 3(+4)
17.1 1.2				

^a M denotes the cyclopentadienylmetal derivative of a group 8, 9, or 10 metal. ^b For electronegativity values, see: Pauling, L. *The Nature of the Chemical Bond*; Cornell University Press: Ithaca, NY, 1960. ^c For covalent radii in picometers, see: Huheey, J. E.; Keiter, E. A.; Keiter, R. L. *Inorganic Chemistry: Principles of Structure and Reactivity*, 4th ed.; HarperCollins: New York, 1993. ^d n is the number of electrons formally localized by a given heteroatom (+x values in parentheses indicate the formal positive charge on the metal center of a CpM unit). ^e Structural feature for a CpM fragment at an ortho position relative to a H-C moiety. ^f Structural feature for a CpM fragment at a meta position relative to a H-C moiety. ^g For FeC_o and FeC_m, the estimated energy penalties (-9.0 and -3.6 kcal mol⁻¹) were obtained by direct comparison of two isomers differing with respect to one structural feature, as in all other cases. Statistical fitting to a large number of isomers resulted in slightly different energy penalties of -10.2 and -4.5 kcal mol⁻¹ for FeC_o and FeC_m, respectively.

to the FeC_m energy penalty clearly indicates that the ortho isomer [1-Cp-1,2-FeCB₁₀H₁₁]²⁻ is energetically favored over its meta isomer, i.e. [1-Cp-1,7-FeCB₁₀H₁₁]²⁻, by 5.4 kcal mol⁻¹, which is the numerical difference between -9.0 and -3.6 kcal mol⁻¹ (see Chart 1). For Ru and Os, more negative MC_m energy penalties indicate that the meta isomers are thermodynamically most stable, although this preference of meta over ortho is only slight (0.7 kcal mol⁻¹) for Ru. For cobalt as well, the preference of ortho over para is negligible (-0.02 kcal mol⁻¹) and the meta isomer is thermodynamically most stable. For Rh and Ir, negative MC_m energy penalties also indicate an increased thermodynamic stability of the meta isomers. When group 10 metals, i.e., Ni, Pd, and Pt, are incorporated as CpM fragments, both MC_o and MC_m have positive energy penalties, indicating that the para isomers are thermodynamically more stable.

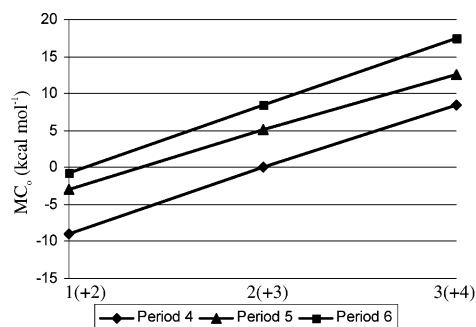
In short, cyclopentadienylmetal fragments of group 9 and 10 metals direct the H-C moiety to meta and para positions in the thermodynamically most stable isomer, respectively. Among group 8 heteroatoms, CpFe directs a H-C moiety to the ortho positions, while CpRu and CpOs direct it to meta positions in the thermodynamically most stable isomers.

3.3. Periodic Trends in MC_o and MC_m Energy Penalties and Their Dependence on the Extent of Electrons Localized

Table 1. Relative Stabilities (kcal mol^{-1}) of $[1\text{-CpFeC}_x\text{B}_{10}\text{H}_{11}]^{(3-x)-}$ Isomers

name	formula	FeC _o −10.2	FeC _m −4.5	CC _o 17.2	CC _m 2.2	ΣE_{inc}^a	$E_{\text{inc}}^{\text{rel } b}$	E_{calc}^c	ΔE^d
AA	$[1\text{-Cp-1,2-FeCB}_{10}\text{H}_{11}]^{2-}$	1				−10.2	0.0	0.0	0.0
AB	$[1\text{-Cp-1,7-FeCB}_{10}\text{H}_{11}]^{2-}$		1			−4.5	5.7	3.6	2.1
AC	$[1\text{-Cp-1,12-FeCB}_{10}\text{H}_{11}]^{2-}$					0.0	10.2	9.0	1.2
BA	$[1\text{-Cp-1,2,4-FeC}_2\text{B}_9\text{H}_{11}]^-$	2			1	−18.2	0.0	0.0	0.0
BB	$[1\text{-Cp-1,2,9-FeC}_2\text{B}_9\text{H}_{11}]^-$	1	1			−14.7	3.5	4.4	−0.9
BC	$[1\text{-Cp-1,2,8-FeC}_2\text{B}_9\text{H}_{11}]^-$	1			1	−8.0	10.2	6.4	3.8
BD	$[1\text{-Cp-1,2,12-FeC}_2\text{B}_9\text{H}_{11}]^-$	1			1	−8.0	10.2	10.8	−0.6
BE	$[1\text{-Cp-1,2,3-FeC}_2\text{B}_9\text{H}_{11}]^-$	2		1		−3.2	15.0	16.0	−1.0
CA	$1\text{-Cp-1,2,4,10-FeC}_3\text{B}_8\text{H}_{11}$	2	1		1	−20.5	0.0	0.0	0.0
CB	$1\text{-Cp-1,2,3,5-FeC}_3\text{B}_8\text{H}_{11}$	3		1	2	−9.0	11.5	8.8	2.7
CC	$1\text{-Cp-1,2,3,9-FeC}_3\text{B}_8\text{H}_{11}$	2	1	1	1	−5.5	15.0	14.2	0.8
CD	$1\text{-Cp-1,2,4,7-FeC}_3\text{B}_8\text{H}_{11}$	2	1	1	2	−3.3	17.2	15.7	1.5
CE	$1\text{-Cp-1,2,7,9-FeC}_3\text{B}_8\text{H}_{11}$	1	2	1	1	0.2	20.7	20.4	0.3
CF	$1\text{-Cp-1,2,3,12-FeC}_3\text{B}_8\text{H}_{11}$	2		1	2	1.2	21.7	22.0	−0.3
CG	$1\text{-Cp-1,2,3,4-FeC}_3\text{B}_8\text{H}_{11}$	3		2	1	6.0	26.5	25.5	1.0
CH	$1\text{-Cp-1,2,3,8-FeC}_3\text{B}_8\text{H}_{11}$	2	1	2	1	11.7	32.2	32.4	−0.2
CI	$1\text{-Cp-1,2,7,8-FeC}_3\text{B}_8\text{H}_{11}$	1	2	2	1	17.4	37.9	38.1	−0.2
CJ	$1\text{-Cp-1,2,7,12-FeC}_3\text{B}_8\text{H}_{11}$	1	1	2	1	21.9	42.4	43.4	−1.0
CK	$1\text{-Cp-1,2,3,7-FeC}_3\text{B}_8\text{H}_{11}$	2	1	3		26.7	47.2	46.7	0.5
CL	$1\text{-Cp-1,2,7,11-FeC}_3\text{B}_8\text{H}_{11}$	1	2	3		32.4	52.9	53.3	−0.4
CM	$1\text{-Cp-1,7,8,12-FeC}_3\text{B}_8\text{H}_{11}$		2	3		42.6	63.1	63.6	−0.5

^a ΣE_{inc} is the sum of energy penalties for all structural features in a given structure. ^b $E_{\text{inc}}^{\text{rel}}$ is the relative stability of a given isomer with respect to the most stable one estimated from increments. ^c E_{calc} is the DFT-computed relative stability of a given isomer. ^d ΔE is the difference of $E_{\text{inc}}^{\text{rel}}$ and E_{calc} .



Number of electrons localized at the metal vertex (Formal charge on the metal center)

Figure 2. Energy penalties for MC_o , i.e., a carbon atom adjacent to a cyclopentadienylmetal fragment, increase with an increase in the number of electrons localized at the metal vertex (or with an increase in the formal positive charge on the metal center) in the CpM unit.

by a CpM Fragment. Both MC_o and MC_m energy penalties increase along the period: i.e., they are largest for group 10 heteroatoms and smallest for group 8 heteroatoms within one period (Chart 1).

It has already been pointed out that the energy penalties of various structural features depend directly on the extent of electron localization by a given heteroatom.²⁶ In cyclopentadienylmetallacarboranes, a H–C moiety formally contributes three skeletal electrons per vertex. The number of electrons contributed by a CpM fragment varies, however. The CpM fragments of group 8, 9, and 10 metals formally contribute one, two, and three electrons, respectively. Thus, the extent of electron localization by the CpM fragments increases along the period. It results in increased energy penalties for the structural feature MC_o (Figure 2) and MC_m (Appendix I, Supporting Information) along the period. CpM fragments of group 8 metals have the smallest MC_o and MC_m energy penalties, while those of group 10 have the largest penalties. The increase in energy penalties along the period can also be viewed in the context of positive charge accumulated on the metal center. Group 8, 9, and 10 metal ions can be considered to have formal charges of +2, +3, and +4, respectively. The increase in the energy penalties along the period can be attributed to the positive charge formally

assigned to the metal center in a 12-vertex CpM fragment containing *closo*-metallaheteroborane (Figure 2).

Energy penalties for HetHet'_o are usually larger as compared to those for HetHet'_m (see also section 3.1). As a result, the trends for increase in the HetHet'_o energy penalties (Figure 2) are much clearer and are on a larger scale as compared to those of HetHet'_m energy penalties (Appendix I, Supporting Information).

3.4. Additive Nature of Structural Increments in Cyclopentadienyliron-Containing 12-Vertex *closo*-Metallaheteroboranes. Energy penalties for the structural features HetHet'_o and HetHet'_m are used to reproduce the relative stabilities of various 12-vertex *closo* cyclopentadienyliron-containing carboranes (section 3.4.1), phosphaboranes (section 3.4.2), and phosphacarbaboranes (section 3.4.3). The energy penalties for the two structural features, i.e., HetHet'_o and HetHet'_m , were first determined empirically by comparing two isomers differing with respect to one structural feature (see Figure 1) and were then refined through a statistical fitting procedure in order to minimize the standard deviation. Out of a total of 101 CpFe fragment containing heteroboranes considered in this study, 14 structures are experimentally known. HetHet'_o and HetHet'_m increments can be used additively to give the relative stability of a large number of metallaheteroborane isomers. Figure 3 shows how the structural increment approach can be applied to reproduce the relative stabilities of selected $\text{FePC}_2\text{B}_8\text{H}_{10}$ isomers as an example. Structural increments quite accurately (mostly within 3 kcal mol^{-1}) reproduce the DFT-computed relative stabilities for 101 structures (Figure 4). The difference (ΔE) of DFT-computed relative energies (E_{calc}) and those derived from increments ($E_{\text{inc}}^{\text{rel}}$) is maximum for **HP** (5.3 kcal mol^{-1} , Table S3, Supporting Information).

3.4.1. $[\text{CpFeC}_x\text{B}_{11-x}\text{H}_{11}]^{(3-x)-}$ ($x = 1\text{--}3$) Isomers. $[1\text{-Cp-1,2-FeCB}_{10}\text{H}_{11}]^{2-}$ (**AA**) is the most stable of the three possible $[\text{CpFeCB}_{10}\text{H}_{11}]^{2-}$ isomers (**AA**, **AB**, and **AC**, Table 1). The meta and para isomers **AB** and $[1\text{-Cp-1,12-FeCB}_{10}\text{H}_{11}]^{2-}$ (**AC**) are less stable than the ortho isomer (**AA**) by 3.6 and 9.0 kcal mol^{-1} , respectively.

Five isomeric $[\text{CpFeC}_2\text{B}_9\text{H}_{11}]^-$ structures, i.e., **BA**–**BE**, were computed, of which $[1\text{-Cp-1,2,4-FeC}_2\text{B}_9\text{H}_{11}]^-$ (**BA**), with both carbon atoms adjacent to iron but at positions nonadjacent (meta)

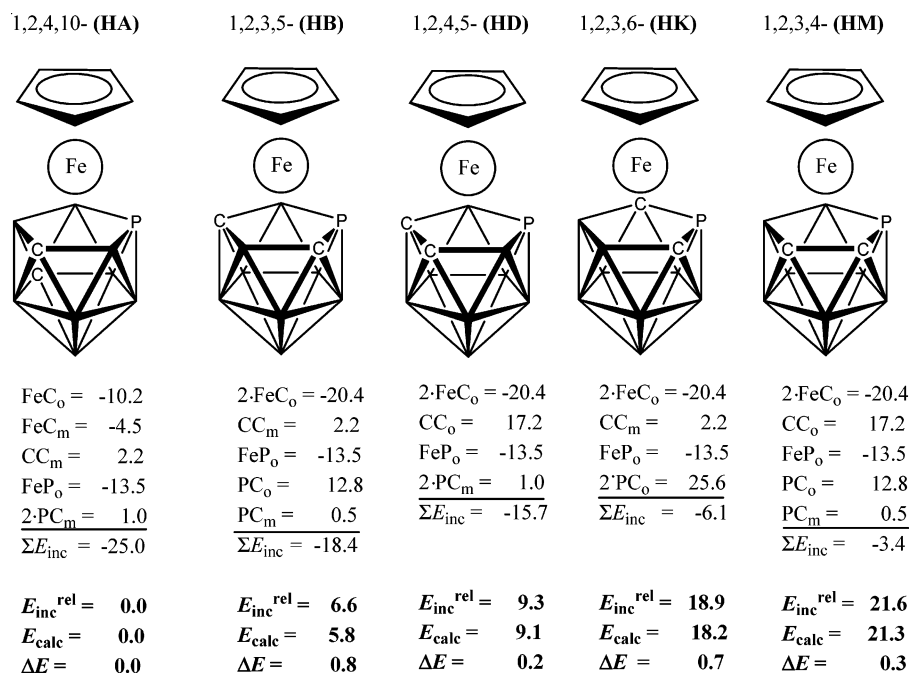


Figure 3. DFT-computed relative stabilities, as well as those from the structural increments of the five selected CpFePC₂B₈H₁₀ isomers. Four possible CpFePC₂B₈H₁₀ isomers (**HB**, **HD**, **HK**, and **HM**) with carbon and phosphorus atoms at positions ortho to the CpFe fragment are thermodynamically less stable as compared with **HA**, which has one carbon atom at the meta position relative to the CpFe unit.

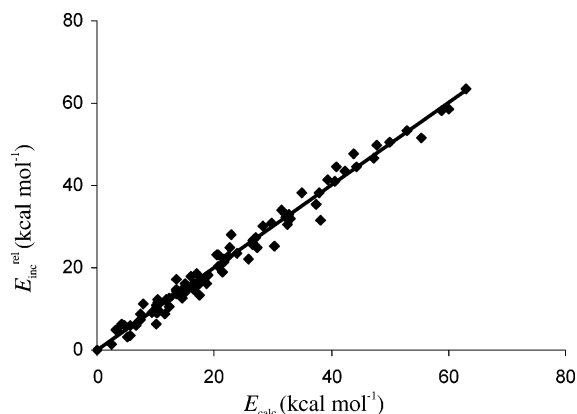


Figure 4. Structural increments accurately reproducing the relative stabilities of cyclopentadienylmetallaboranes computed by DFT methods.

to each other, is the most stable isomer. The CpFe unit prefers ortho relationships with carbon atoms (due to a negative structural increment for FeC_o of -10.2 kcal mol⁻¹), while the two carbon atoms prefer para positions to each other ($E_{inc}[CC_o] = 17.2$ kcal mol⁻¹ and $E_{inc}[CC_m] = 2.2$ kcal mol⁻¹). The ortho Fe–C and meta C–C relationships in the most stable isomer (**BA**) comply with these preferences. The relative stabilities of other [CpFeC₂B₉H₁₁]⁻ isomers are listed in Table 1.

The most stable CpFeC₃B₈H₁₁ isomer (1,2,4,10-CpFeC₃B₈H₁₁, **CA**)²⁹ has two carbon atoms ortho to the CpFe fragment, while the third carbon atom is at a position meta to the CpFe fragment (Table 1). Structural increments predict that 1-Cp-1,7,8,12-FeC₃B₈H₁₁ (**CM**) with all three carbon atoms adjacent to each other but far away from CpFe should result in the highest energy isomer, as is found through computations (see Table 1, **CM**).

3.4.2. [CpFeP_xB_{11-x}H_{11-x}]^{(3-x)-} ($x = 1-3$) Isomers. The FeP_o energy penalty ($E_{inc}[FeP_o] = -13.5$ kcal mol⁻¹) is more negative than that of FeC_o ($E_{inc}[FeC_o] = -10.2$ kcal mol⁻¹), indicating a stronger tendency of phosphorus atoms to be at the ortho position relative to a CpFe unit (see [1-Cp-1,2-

FePB₁₀H₁₀]²⁻ (**DA**) and [1-Cp-1,2,4-FeP₂B₉H₉]⁻ (**EA**); Table S1, Supporting Information). The most stable [CpFePB₁₀H₁₀]²⁻ and [CpFeP₂B₉H₉]⁻ isomers have the same substitution patterns as the carba analogues, i.e., the 1,2- and 1,2,4-positions of heteroatoms, respectively. However, the most stable CpFeP₃B₈H₈ isomer has a different substitution pattern as compared with CpFeC₃B₈H₁₁: 1,2,3,5-positioning of phosphorus atoms (all ortho relative to CpFe), whereas 1,2,4,10-positioning of H–C moieties (one H–C moiety at meta position to the CpFe fragment) constitutes the most stable isomer. This difference can be understood on the basis of more negative FeP_o and less positive PP_o increments as compared with those of FeC_o and CC_o.

The least stable isomers, on the other hand, have the phosphorus atoms at positions adjacent to each other but far apart from the CpFe fragment (see Table S1, Supporting Information).

3.4.3. [CpFePCB₉H₁₀]⁻, CpFePC₂B₈H₁₀, and CpFeP₂CB₈H₁₀ Isomers. Energy penalties for two additional structural features, i.e., PC_o and PC_m (structural features for phosphorus and carbon atoms in ortho and meta arrangements relative to each other, respectively), are required for metallaphosphacarbaboranes. PC_o and PC_m have energy penalties of 12.8 and 0.5 kcal mol⁻¹, respectively. DFT-computed relative stabilities of metallaphosphacarbaborane with three different hetero groups, i.e., CpFe, C, and P, can be reproduced with good accuracy (see Tables S2–S4 in the Supporting Information). The most stable [CpFePCB₉H₁₀]⁻ and CpFeP₂CB₈H₁₀ isomers have the heteroatoms at positions ortho to the CpFe unit. One of the carbon atoms shifts to a meta position in the thermodynamically most stable CpFePC₂B₈H₁₀ isomer: i.e., 1-Cp-1,2,4,10-FePC₂B₈H₁₀. Except for the most stable isomer, i.e., 1,2,4,10, all other FePC₂B₈H₁₀ isomers considered in Figure 3 have carbon and phosphorus atoms at positions ortho to the CpFe fragment. The structural features present in each of the isomers are listed. The relative energy obtained from the structural increment approach (E_{inc}^{rel}) for the five isomers is in excellent agreement with the computed results.

Moreover, from Tables S2–S4 (Supporting Information), it can be concluded that, just as for pure carbon and phosphorus analogues, the $[\text{CpFePCB}_9\text{H}_{10}]^-$, $\text{CpFeP}_2\text{CB}_8\text{H}_9$, and $\text{CpFePC}_2\text{B}_8\text{H}_{10}$ isomers with heteroatoms far apart from the CpFe fragment and adjacent to each other have the least thermodynamic stability.

3.5. Thermodynamically Most Stable 12-Vertex *closo*-Cyclopentadienylmetallacarborane Isomers with Ru, Os, Co, Rh, and Ir Metals. Metallacarboranes with CpM units other than CpFe (e.g., with $M = \text{Co},^{11} \text{Rh},^{12} \text{Ni}^{13}$) and with a Cp*Ru fragment as in $[1\text{-Cp}^*\text{-1,2,3-RuC}_2\text{B}_9\text{H}_{11}]^-$ (where Cp* = pentamethylcyclopentadienyl)¹⁴ or $\text{Cp}^*\text{RuC}_3\text{B}_8\text{H}_{11}$ ³⁵ are also known experimentally. Relative energies for isomeric metallacarboranes with a CpM unit other than CpFe can also be easily estimated by using the energy penalties for the structural features CC_o , CC_m , MC_o , and MC_m . MC_o and MC_m increments for various group 8, 9, and 10 metals are listed in Chart 1. Values of 17.2 and 2.2 kcal mol⁻¹ are used for CC_o and CC_m throughout. They allow us to estimate the relative stabilities of various isomers and in turn to rationalize some interesting facts from experiments. For example, the 1-Cp-1,2-NiCB₁₀H₁₁ isomer upon heating to 450 °C rearranges to 1,7- and 1,12-isomers,¹³ as it is the least stable, in accordance with the positive NiC_o energy penalty ($E_{\text{inc}}[\text{NiC}_o] = 8.5 \text{ kcal mol}^{-1}$). Even larger PdC_o and PtC_o energy penalties allow us to predict the possible thermal rearrangement of experimentally still unknown 1-Cp-1,2-PdCB₁₀H₁₁ and 1-Cp-1,2-PtCB₁₀H₁₁ to 1,7- and 1,12-isomers.

Similarly, 1-Cp-1,2,3-CoC₂B₉H₁₁ rearranges to various isomers with one or both carbon atoms nonadjacent to the CpCo fragment.¹² This is primarily due to the strong para-directing effect of two carbon atoms to each other ($E_{\text{inc}}[\text{CC}_o] = 17.2 \text{ kcal mol}^{-1}$) and secondly to the small meta-directing effect of the CpCo unit ($E_{\text{inc}}[\text{CoC}_m] = -1.2 \text{ kcal mol}^{-1}$) to the carbon atom.

The complex 1-Cp-1,2,3-RhC₂B₉H₁₁ has been reported to rearrange to 1-Cp-1,2,4-RhC₂B₉H₁₁ upon heating.¹² This is because of the high CC_o energy penalty. Our increments suggest that further heating of the 1,2,4-isomer should result in isomeric structures with carbon atoms at positions meta to the CpRh fragment.

No experimental reports are available for 12-vertex *closo*-cyclopentadienyl iridacarboranes so far, however, we predict thermodynamic preference for 1-Cp-1,7,9-IrC₂B₉H₁₁ as compared with Co and Rh analogues.

$[\text{CpFeC}_2\text{B}_9\text{H}_{11}]^-$ structures with only an Fe–C ortho relationship, i.e., $[1\text{-Cp-1,2,3-FeC}_2\text{B}_9\text{H}_{11}]^-$, have been reported,¹ but no meta rearrangements have been reported. This is due to the ortho-directing nature of the CpFe unit to the carbon atoms. However, the known 1-Cp-1,2,3,4-FeC₃B₈H₁₁ structure (with three carbon atoms) rearranges to 1-Cp-1,2,3,5-FeC₃B₈H₁₁ and 1-Cp-1,2,4,10-FeC₃B₈H₁₁.³⁵ The latter is the thermodynamically most stable isomer and has one carbon atom in a meta position in order to counterbalance the strong mutual para-directing effect ($\text{CC}_o = 17.2 \text{ kcal mol}^{-1}$) of three carbon atoms (see section 3.4.1).

3.6. Relative Stabilities of (CO)₃CoCB₁₀H₁₁ Isomers. To determine the effect of the ligands on the metal fragment, we also computed (CO)₃CoCB₁₀H₁₁ isomers for comparison with CpCoCB₁₀H₁₁ isomers. The former has three carbonyl groups, while the latter has a Cp fragment attached to the cobalt atom. Three possible (CO)₃CoCB₁₀H₁₁ isomers, i.e., 1,2, 1,7, and 1,12, were computed and, surprisingly, the energetics of (CO)₃CoCB₁₀H₁₁ were much different from those of CpCoCB₁₀H₁₁. In contrast to the CpCoCB₁₀H₁₁ isomers, where the meta isomer is thermodynamically most stable by 1.2 kcal mol⁻¹ (see Chart 1), the para isomer is the most stable for (CO)₃CoCB₁₀H₁₁. The meta isomer is only slightly more stable (0.5 kcal mol⁻¹) and the ortho isomer is 8.9 kcal mol⁻¹ less stable than the para isomer. Different energy penalties by different substituents can be rationalized: the (CO)₃Co fragment has three carbonyl groups attached to the cobalt atom. A carbonyl ligand, besides being a σ -donor, is also a strong π -acceptor; thus, it takes back electron density from the metal center through back-donation. As a result, the metal withdraws more electron density from the clusters. This increased electron localization at the metal center leads to increased energy penalties, and hence, the para isomer becomes the most stable. We note that the energy penalties of the (CO)₃Co fragment are almost equal to those of the CpNi fragment. The latter also has a higher extent of electron localization as compared with the CpCo fragment.

3.7. Conclusion. To summarize, cyclopentadienylmetal fragments of group 8, 9, and 10 metals in 12-vertex *closo*-cyclopentadienylmetallaheteroboranes have a clear ortho-, meta-, or para-directing influence on heteroatoms. Structural increments increase along one period due to increasing positive charge on the metal center along the period; i.e., as a consequence of an increasing extent of electron localization. The presented structural increments can easily be used to quickly give the relative stabilities of a large number of metallaheteroboranes. These structural increments are substituent specific; a change of the substituent on the metal atom leads to different energy penalties.

Acknowledgment. Financial support by the DFG is gratefully acknowledged.

Supporting Information Available: A comparison of the relative stabilities of various $[1\text{-CpFeP}_x\text{B}_{11-x}\text{H}_{11-x}]^{(3-x)-}$ ($x = 1\text{--}3$), $[1\text{-CpFePCB}_9\text{H}_{10}]^-$, $1\text{-CpFePC}_2\text{B}_8\text{H}_{10}$, and $1\text{-CpFeP}_2\text{CB}_8\text{H}_9$ isomers (Tables S1–S4, respectively) and Cartesian coordinates of the optimized geometries of all cyclopentadienylmetal-containing heteroboranes considered in this study and those of the three isomeric (CO)₃CoCB₁₀H₁₁ structures (Appendix II). This material is available free of charge via the Internet at <http://pubs.acs.org>.

OM050814U

(35) Perekalin, D. S.; Holub, J.; Golovanov, D. G.; Lyssenko, K. A.; Petrovskii, P. V.; Štíbr, B.; Kudinov, A. R. *Organometallics* **2005**, *24*, 4387–4392. See also: Holub, J.; Gruener, B.; Perekalin, D. S.; Golovanov, D. G.; Lyssenko, K. A.; Petrovskii, P. V.; Kudinov, A. R.; Štíbr, B. *Inorg. Chem.* **2005**, *44*, 1655–1659.