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Sandwich Compounds of Transition Metals with Cyclopolyenes and Isolobal Boron Analogues

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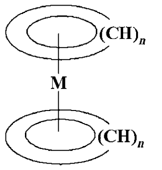
Abstract: A series of sandwich compounds of transition metals (M = Ni, Fe, Cr) with cyclic hydrocarbon ($M(CH)_n$) and borane ($M(BH_2)_n$), ligands (including mixed hydrocarbon/borane sandwiches) has been studied using density functional theory (B3LYP/6-311+G(df,p)). Multicenter bonding between the central metal atom and basal cycloborane rings provides stabilization to planar cycloborane species. Large negative NICS values allude to aromatic character in the cycloboranes similar to the analogous cyclic hydrocarbons. The ability of cycloborane sandwiches to stabilize attached carbocations, radicals and carbanions is also assessed.

Keywords: arenes · boranes · density functional calculations · metallocenes · sandwich complexes

Introduction

Sandwich compounds of transition metals with cyclopolyenes (metallocenes; **1**) comprise a vast and well studied area of organometallic chemistry.[1] Since the discovery of the first sandwich compound, ferrocene (**1**, M = Fe, $n = 5$),[2] metallocenes have received considerable attention because of their unusual structures, multicenter bonding arrays, and widespread applications in fields such as metallocomplex catalysis, molecular electronics and pharmacology.[1] Metallocenes constructed from many of the d and f elements have been synthesized and their molecular structures determined.[1]

A key feature ascribed to many isolable metallocene systems is an induced metallaromaticity.[3] For example, interactions between orbitals on the metal center and the inherently antiaromatic (if planar and delocalized) cyclooctatetraene and cyclobutadiene moieties in complexes such as uranocene **2**[4] and cobaltocene **3**[5] lead to equalization of their C−C bonds and stabilization (based on various criteria).



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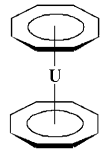

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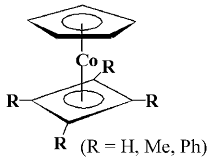

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A new direction in the field of organometallic sandwich chemistry is the use of "electron-deficient" borane and carborane fragments as π-donor basal ligands.[6–9] An example of such a system is given by π-cyclopentadienyl-π-(1)-2,3-dicarbollyliron **4**, in which a metal atom occupies one of the apical positions of the polyhedral carborane cage.[7] An equally interesting group of metalloboranes consists of structures featuring an apical metal atom that induces planarization of *nido*-boronocycles (e.g., cobaltaborane **5**[8] and ferraborane **6**[9]). Investigation into the synthesis, properties and structural peculiarities of such compounds has been a focus of experimental and theoretical studies alike, opening new avenues for the discovery of compounds with unique architectures and physical/chemical properties.[6]

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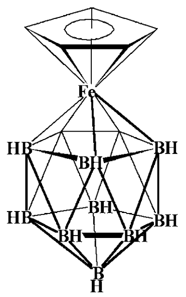
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.200902004: Total energies, harmonic zero-point corrections, frequencies, and atomic coordinates of optimized structures **6**–**20** and **33**–**47** calculated using the B3LYP/6-311+G(df,p) method, as well as additional details on relative binding energies.



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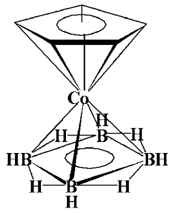

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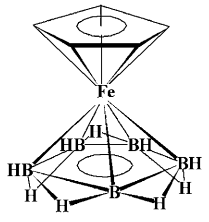

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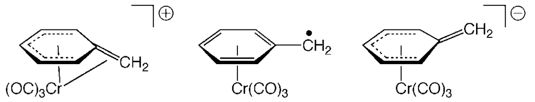
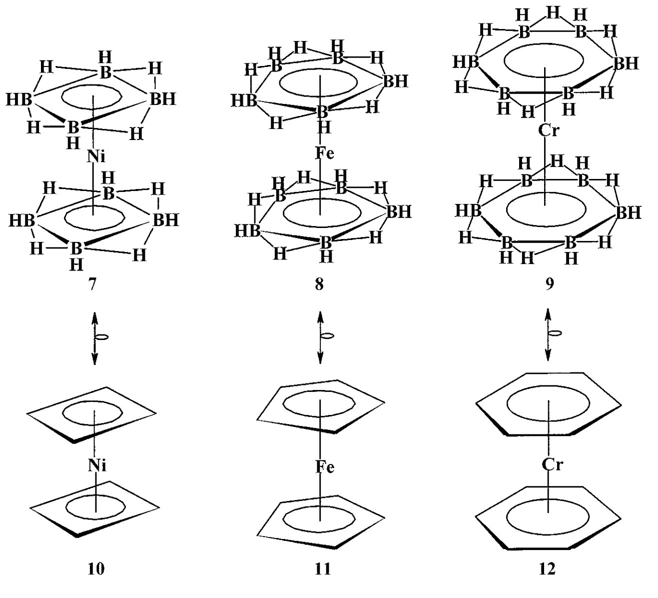
Metallocenes and related metal–π complexes attached to carbocation, radical and carbanion centers have also received considerable interest.[10,11] The geometries of such structures tend to vary dramatically depending on the oxidation state of the attached reactive center. For example, $Cr(CO)_3$-complexed benzyl cation/radical/anion has been shown to undergo hapticity and large geometric changes upon changing the number of electrons at the benzylic position (see below).[10] To our knowledge, analogous boron-based sandwiches have not yet been examined.



In the work described herein, the electronic and geometric structures of the 18-electron sandwich metalloboranes **7**–**9**, as well as their conformational flexibility, has been studied using density functional theory (DFT). The isolobal metallocarbocycles **10**–**12**, as well as mixed complexes such as **6** were also examined. In addition, the ability of boron-based metallocenes to interact with appended cations, radicals and anions was compared to that of carbon-based analogues.



Computational Methods

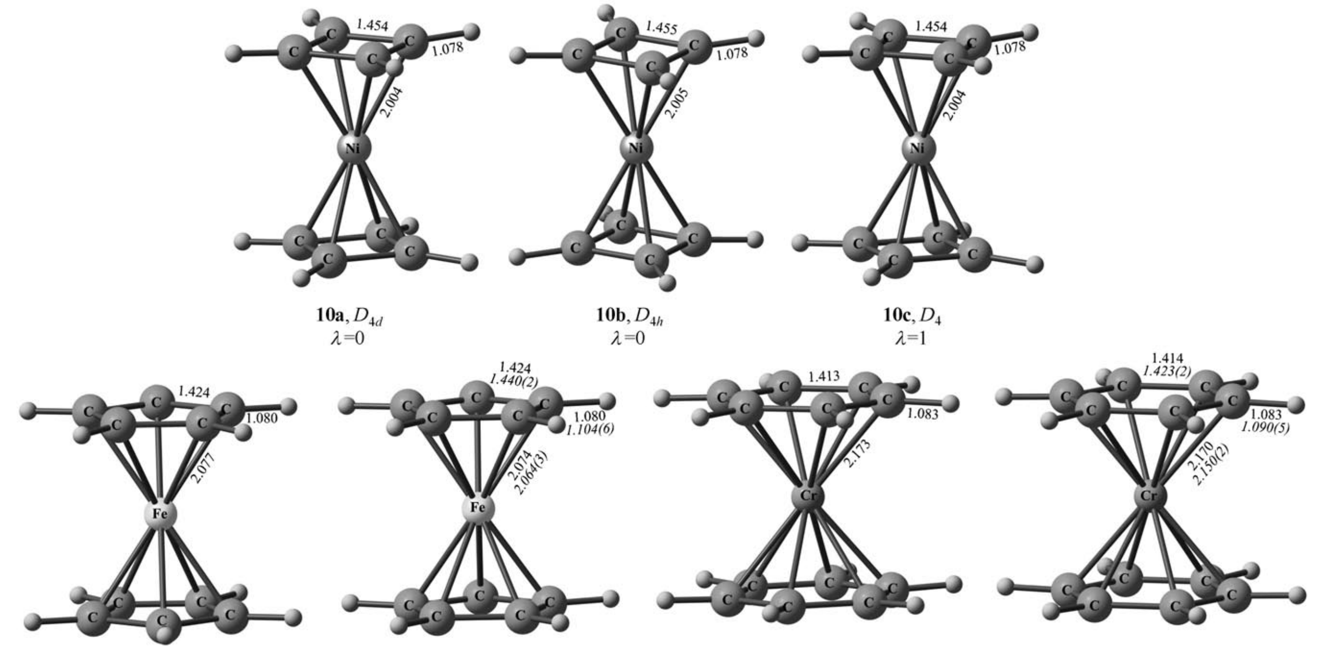
DFT calculations were carried out using Gaussian03[12] with the Becke-3 parameter exchange and the Lee–Yang–Parr correlation functional (B3LYP) paired with the 6-311+G(df,p) basis set.[13] Analytic harmonic frequencies at the same level of theory were used to characterize and evaluate zero-point energy (ZPE) corrections for structures studied herein. ZPE corrected electronic energies are provided throughout in kcal mol^{-1}. In most cases, the structures corresponding to energy minima ($\lambda=0$; where λ is the number of negative eigenvalues of the Hessian matrix for a given stationary point) on the potential energy surface were found by the method of steepest descent (movement along the gradient line[14]) from the first-order saddle point (transition state). Molecular structure images were generated with Chemcraft.[15]

Results and Discussion

Metallocenes with only hydrocarbon ligands: Both staggered (**10a**, D_{4d} symmetry) and eclipsed (**10b**, D_{4h} symmetry) conformations of $(\eta^4\text{-}C_4H_4)_2Ni$ were found to correspond to energy minima (Figure 1, Table 1), with the eclipsed conformation (**10b**) slightly preferred (by 0.18 kcal mol^{-1} with ZPE taken into account). The Ni–C bonds (2.005 Å) are slightly longer than the sum of carbon and nickel covalent radii (1.92 Å).[16] The C–C bonds of the cyclobutadiene fragment are all 1.455 Å, which is intermediate between the long and short bonds of uncomplexed cyclobutadiene (the geometry of the lowest singlet has D_{2h} symmetry). The C–H bonds are bent by ≈2° away from the metal center. A NICS[17] value of −25.6 ppm in the center of each hydrocarbon fragment of **10b** is consistent with aromatic character for the complexed cyclobutadiene rings. Interconversion of the staggered and eclipsed conformations (**10a** and **b**, respectively) can occur through D_4-symmetric transition structure **10c** (Figure 1, Table 1). Upon ZPE correction, **10c** is only 0.13 kcal mol^{-1} higher in energy than **10b** and is actually lower in energy then **10a** by 0.05 kcal mol^{-1}. Thus, $(\eta^4\text{-}C_4H_4)_2Ni$ is conformationally fluxional, residing on a flat potential energy surface (PES) for the rotation of the bound cyclobutadiene rings relative to each other.

In accord with experimental gas-phase electron diffraction studies[18,19] and previous quantum chemical calculations,[20,21] our computations show D_{5h}-symmetric ferrocene (**11b**; Figure 1, Table 1) to be a local minimum. Rotation of the basal cycles through a D_{5d}-symmetric transition structure (**11a**) involves a barrier of 0.41 kcal mol^{-1}. Numerous experimental studies[18,19,22,23] have examined the fluxionality of ferrocene, and the experimental estimate of 0.9 ± 0.3 kcal mol^{-1}[19,23] for the rotation barrier is similar to that from our computations. A NICS value of −46.6 ppm at the center of each cyclopentadienyl ring in **11b** is again consistent with significant aromatic character.

In agreement with studies using various experimental techniques (X-ray, IR spectroscopy, gas-phase electron diffraction)[24–26] as well as previous quantum-chemical calculations,[21,26,27] our calculations predict a D_{6h}-symmetric structure for $(\eta^6\text{-}C_6H_6)_2Cr$ (**12b**; Figure 1, Table 1). In **12b**, the distance between the metal atom and the center of each



10a, D_{4d}
λ=0

10b, D_{4h}
λ=0

10c, D_4
λ=1

11a, D_{5d}
λ=1

11b, D_{5h}
λ=0

12a, D_{6d}
λ=1

12b, D_{6h}
λ=0

Figure 1. Geometries of minima, **10a**, **10b**, **11b**, and **12b**, and transition states for internal rotation of the basal cycles, **10c**, **11a**, and **12a**, calculated at the B3LYP/6-311+G(df,p) level of theory with bond lengths displayed in angstroms [Å]. The experimental gas-phase electron diffraction data for ferrocene (**11b**)[19] and chromocene (**12b**)[25] are given in italics.

Table 1. Energy parameters[a] of the systems **6**–**12**, **19**, and **20** calculated at the B3LYP/6-311+G(df,p) level of theory.

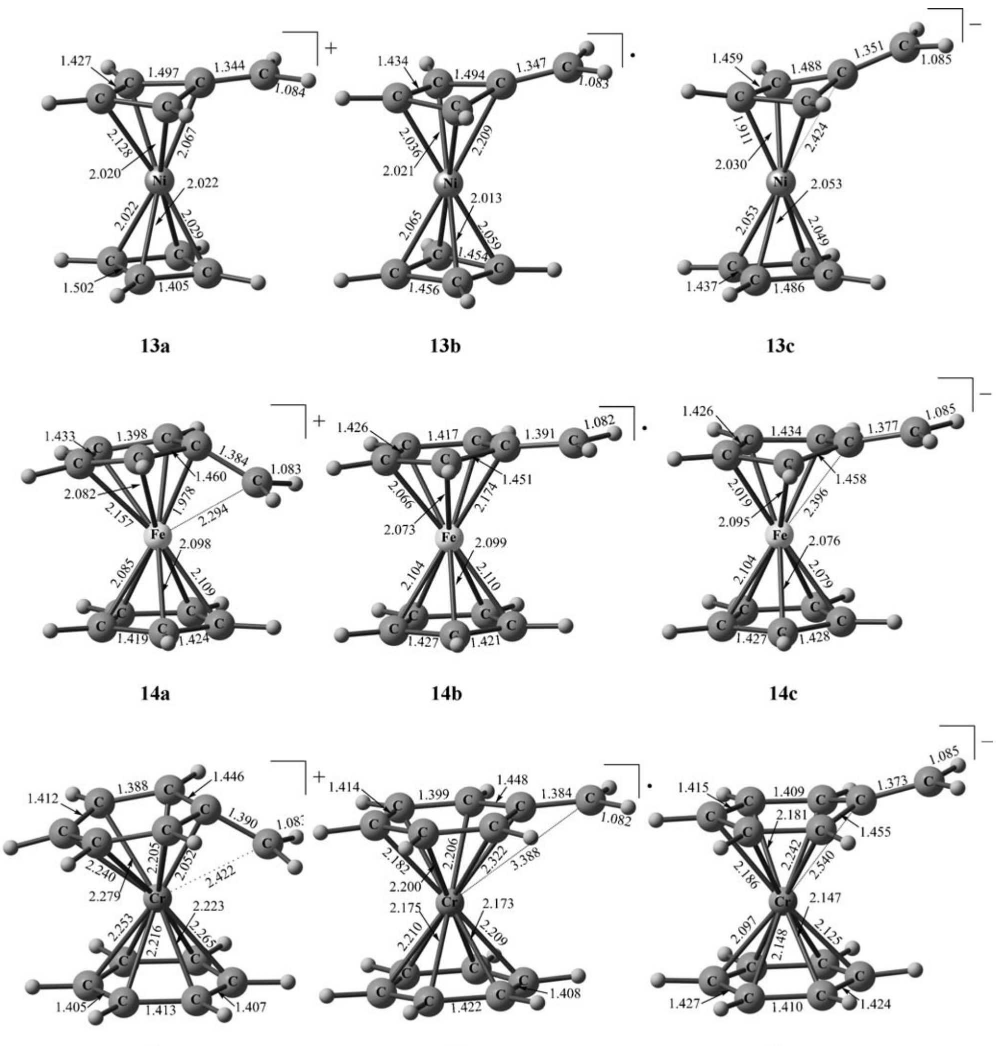
Structure	ΔE	ΔE_{ZPE}	λ	$\omega_1/i\omega$	q_M	NICS
10a, D_{4d}	0.29	0.18	0	11.8	–	–
10b, D_{4h}	0	0	0	51.3	0.801	−25.6
10c, D_4	0.30	0.13	1	*i*29.7	–	–
11a, D_{5d}	0.50	0.41	1	*i*51.5	–	–
11b, D_{5h}	0	0	0	42.2	0.279	−46.6
12a, D_{6d}	0.81	0.71	1	*i*46.3	–	–
12b, D_{6h}	0	0	0	42.9	−0.025	−49.4
7a, D_{4d}	0	0	0	100.7	0.442	−26.8
7b, D_{4h}	1.14	1.27	0	43.0	–	–
7c, D_4	1.15	0.90	1	*i*52.9	–	–
8a, D_{5d}	0	0	0	22.3	−0.648	−37.7
8b, D_{5h}	2.25	2.45	1	*i*48.1	–	–
9a, D_{6d}	0	0	0	83.1	−1.123	−44.8
9b, D_{6h}	5.01	5.57	1	*i*81.0	–	–
19a, C_{4v}	0	0	0	53.8	0.656	−23.8,[b] −28.3[c]
19b, C_{4v}	0.68	0.70	1	*i*27.1	–	–
6a, C_{5v}	0.07	−0.05	1	*i*51.9	–	–
6b, C_{5v}	0.15	0.08	1	*i*47.4	–	–
6c, C_5	0	0	0	34.3	−0.146	−34.8,[b] −51.2[c]
20a, C_{6v}	0	0	0	10.7	−0.431	−35.1,[b] −67.9[c]
20b, C_{6v}	0.62	0.94	1	*i*41.8	–	–

[a] Relative energy: ΔE [kcal mol^{-1}], relative energy with ZPE correction ΔE_{ZPE} [kcal mol^{-1}]; λ: number of negative hessian eigenvalues; $\omega_1/i\omega$ (in cm^{-1}): value of the lowest or imaginary harmonic vibration frequencies; q_M: (NBO) natural charge of metal atom M. [b] NICS at center of hydrocarbon ring. [c] NICS at center of B_n ring.

basal cycle (1.646 Å) is the shortest among the metallocenes considered thus far (1.721 Å for **10b** and 1.684 Å for **11b**) and the HOMO–LUMO energy gap (3.99 eV) is smaller than that for either **10b** (4.23 eV) or **11b** (5.14 eV). The bending of the C−H bonds towards the metal atom is 0.8° and the NICS value at the center of each complexed benzene ring is −49.4 ppm. The benzene rings in **12b** can rotate through a D_{6d}-symmetric transition-state structure (**12a**, Figure 1, Table 1), which again is very close in energy to the minimum (0.71 kcal mol^{-1}). Thus, all of the metallocenes studied herein were found to slightly prefer eclipsed orientations of their basal cycles, but to exist on flat PESs for rotation of their bound hydrocarbon rings.

Metallocenes with appended carbocations, radicals and carbanions: Derivatives of structures **10**–**12** with attached CH_2* (*=+, $^{\bullet}$, −) groups (**13**, **14** and **15**; Figure 2) were also examined. We expected (as for the $Cr(CO)_3$-complexed benzylic species described above) that the cationic structures would bend their CH_2 groups towards the metal, radical structures would exhibit little deviation from planarity, and anionic structures would bend their CH_2 groups away from the metal. These expectations were borne out for the larger systems (**14** and **15**), but cation **13a** did not behave as expected. Apparently the strain associated with distorting the small $C_4H_3CH_2$ fragment in this structure is too great, so the methylene group remains essentially coplanar with the cyclobutadiene fragment.

Boron-based metallocene analogues: Replacement of the C_4H_4 rings of **10** with isolobal B_4H_8 borane fragments results



13a **13b** **13c**

14a **14b** **14c**

15a **15b** **15c**

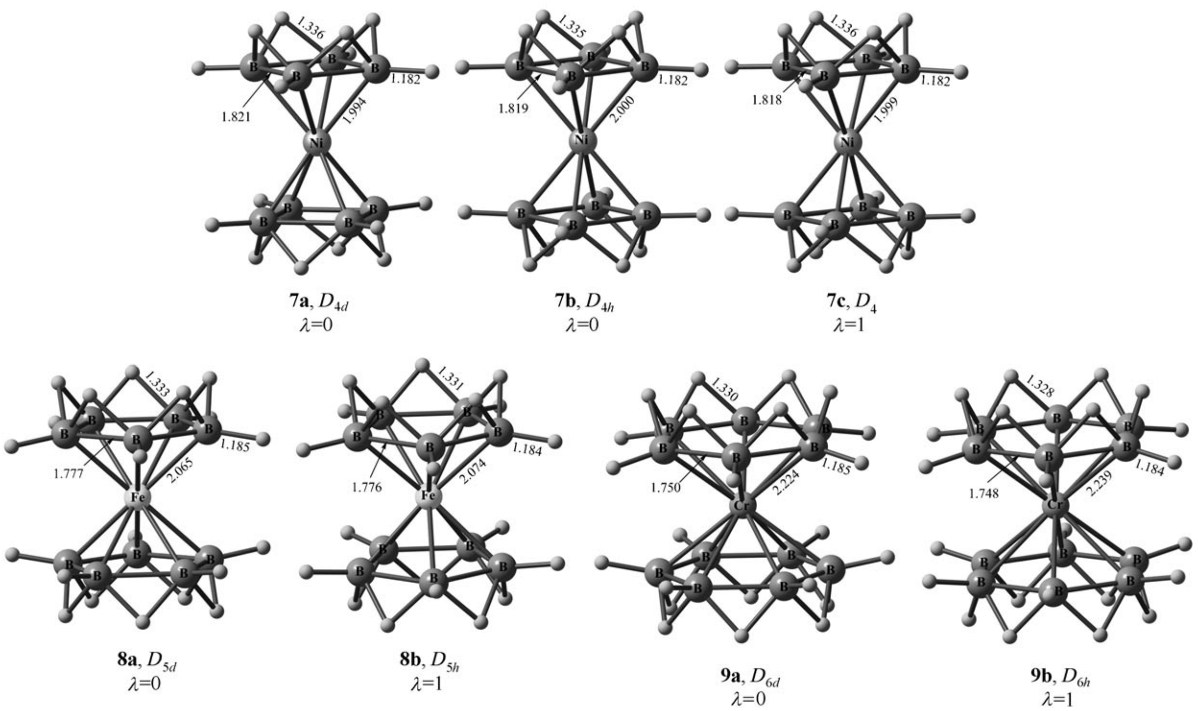
Figure 2. Geometries of minima **13**–**15** calculated at the B3LYP/6-311+G(df,p) level of theory with bond lengths displayed in angstroms [Å].

in sandwich **7** (Figure 3, Table 1). As was the case for the hydrocarbon system, both staggered (**7a**, D_{4d} symmetry) and eclipsed (**7b**, D_{4h} symmetry) conformations are found to be minima. The staggered structure (**7a**) is 1.27 kcal mol^{-1} lower in energy than the eclipsed form (**7b**). In **7a**, the distance between the metal atom and the center of each basal cycle is 1.523 Å, considerably shorter than the analogous distance in **10a** (1.721 Å), and consistent with increased overlap between the frontier molecular orbitals of the basal cycles and the metal d orbitals in **7**. This contention is corroborated by the substantially larger HOMO–LUMO energy gap for **7a** (5.49 eV) as compared with that for **10a** (4.23 eV) or **10b** (4.23 eV).

The Ni–B distances in **7a** (1.994 Å) are slightly shorter than the sum of the respective covalent radii (2.03 Å).[16] The NICS value calculated in the center of each complexed borane in **7a** (−26.8 ppm) points to similar aromatic character as in **10**. Staggered and eclipsed **7a** and **b** can interconvert via a D_4-symmetric transition structure (**7c**), which is, upon inclusion of the ZPE correction, 0.37 kcal mol^{-1} lower in energy than eclipsed minimum **7b**; thus, like its hydrocarbon cousin, **7** is conformationally fluxional.

Replacement of the cyclopentadienyl rings in **11** by isolobal boranes leads to **8** (Figure 3, Table 1). For this system, the D_{5d}-symmetric conformer **8a** is an energy minimum while the D_{5h}-symmetric conformer **8b** is the transition-state structure for rotation (with a barrier of 2.45 kcal mol^{-1}). In **8a**, the distance between the metal atom and the center of each B_5 ring (1.407 Å) is considerably shorter than the corresponding distance in **11** (1.684 Å) and the HOMO–LUMO energy gap for **8a** (5.89 eV) is larger than that for **11b** (5.14 eV). The Fe–B distances (2.065 Å) slightly exceed the sum of boron and iron covalent radii (2.045 Å)[16] and the B−H bonds bend slightly towards the metal atom, here by ≈3.5°. The NICS value at the center of the B_5 rings in **8a** (−37.7 ppm) is again substantial.

Replacement of the benzene rings of **12** by B_6H_{12} fragments leads to **9** (Figure 3, Table 1), the lowest energy conformation of which is D_{6d}-symmetric **9a**. D_{6h}-Symmetric **9b** is the transition-state structure for rotation of the basal



7a, D_{4d}
$\lambda=0$

7b, D_{4h}
$\lambda=0$

7c, D_4
$\lambda=1$

8a, D_{5d}
$\lambda=0$

8b, D_{5h}
$\lambda=1$

9a, D_{6d}
$\lambda=0$

9b, D_{6h}
$\lambda=1$

Figure 3. Geometries of minima, **7a**, **7b**, **8a** and **9a**, and transition states for internal rotation of the basal cycles, **7c**, **8b** and **9b**, calculated at the B3LYP/6-311+G(df,p) level of theory with bond lengths displayed in angstroms [Å].

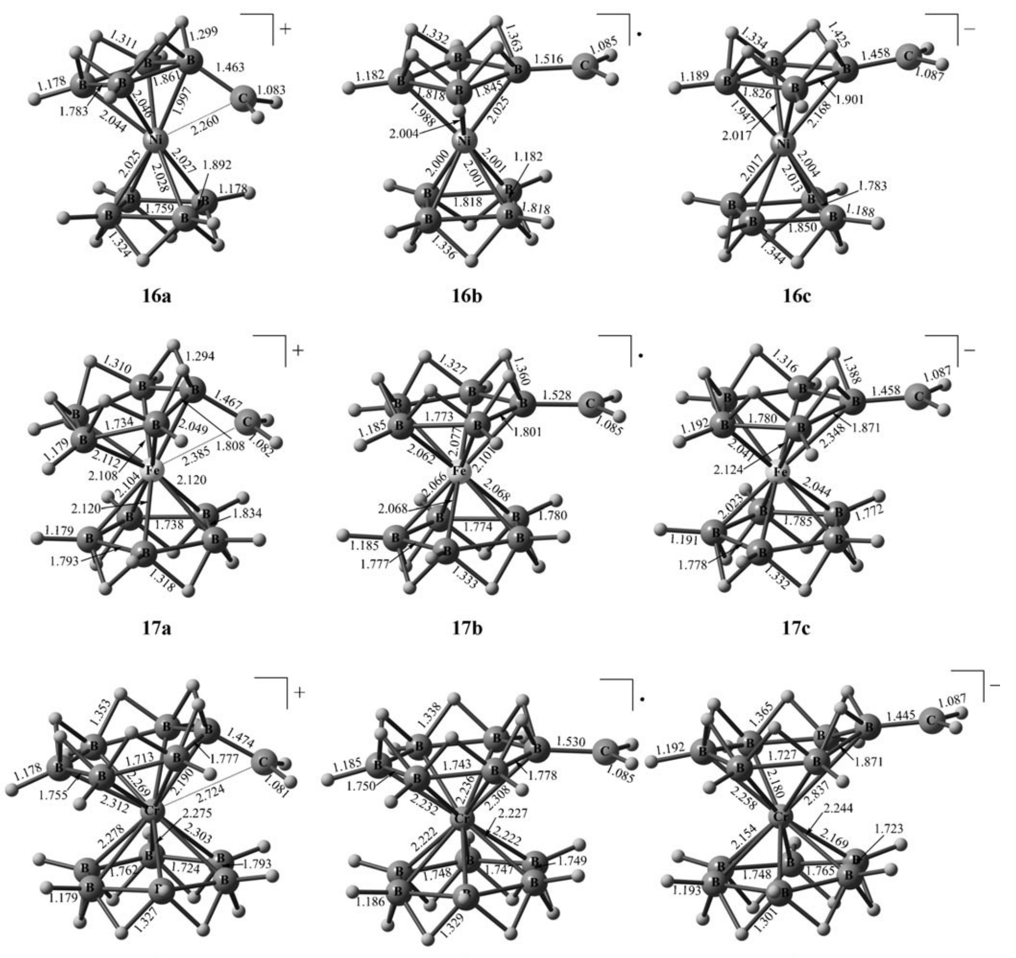
rings. The energy barrier for this process (5.57 kcal mol^{-1}) is somewhat larger than for the metallocenes and other metalloboranes described above. The shortest ring-center to metal-atom distance encountered thus far (1.372 Å) is found in **9a**, which also has the smallest HOMO–LUMO gap (3.38 eV) and the calculated Cr–B distances (2.224 Å) markedly exceed the sum of the Cr and B covalent radii (2.06 Å).[16] The B_6 rings in **9a** are planar and their B−H bonds are considerably (≈4.6°) bent towards the metal center. A large NICS value (−44.8 ppm) is observed for **9a** as well.

Boron-based metallocene analogues with appended carbocations, radicals and carbanions: Boron-based analogues of **13**–**15**, structures **16**–**18** (Figure 4), were also investigated. Like **14a**–**15a**, the cationic species (**16a**–**18a**) all delocalize their positive charge via a strong M···CH_2 interaction. Radicals **16b**–**18b**, like their metallocene counterparts, do not bend the radical center towards the metal by any significant amount. In contrast to their metallocene analogues, anions **16c**–**18c** appear to accommodate their negative charge by direct donation from the CH_2 group to the attached boranes, which significantly perturbs their σ frameworks by elongating some of the B−B bonds; only slight bending of the CH_2 groups away from the metals is observed.

A series of isodesmic reactions (Scheme 1) were constructed in an attempt to assess which sandwich frameworks—hydrocarbon- or borane-based—interact more strongly with appended reactive centers. The energetic data (Table 2) suggest that cationic character is best accommodated by the metallocene. Radicals, which on the whole again favor the metallocene, show significantly smaller preferences in the larger (M = Fe and Cr) systems as compared to their cationic analogues. The anionic structures are quite interesting, with the smaller (M = Ni) case favoring the metallocene and the larger (M = Fe and Cr) cases favoring the metalloboranes, whose somewhat flexible borane frameworks allow for delocalization through distortion, as mentioned above.

Mixed sandwich compounds: Mixed sandwich **19** (Figure 5, Table 1) contains both hydrocarbon and borane basal cycles. This system prefers a staggered conformation (**19a**) of C_{4v} symmetry. In **19a**, the Ni–C distances (2.010 Å) and the Ni–cyclobutadiene center distance (1.727 Å) are slightly longer than those in **10**. In contrast, the Ni–B and Ni–borane center distances (1.986 and 1.512 Å, respectively) are shorter than those in **7**. As was the case in sandwich compounds **10** and **7**, the C−H bonds bend by ≈2° away from the metal, while the B−H bonds bend by ≈1° towards the metal. Large negative NICS values were found in the centers of both the C_4 and B_4 rings (−23.8 and −28.3 ppm, respectively). The barrier for rotation of the basal cycles in **19** is intermediate between those for **10** and **7**, with the C_{4v}-symmetric transition-state structure (**19b**) lying 0.70 kcal mol^{-1} above its minimum (Figure 5, Table 1).

The mixed sandwich complex [(η^5-B_5H_{10})Fe(η^5-C_5H_5)] (**6**) has been synthesized and characterized by NMR.[9] The topology of the PES for **6** differs from those for **11** and **8**. Both C_{5v}-symmetric structures **6a** and **6b** (Figure 5) correspond to

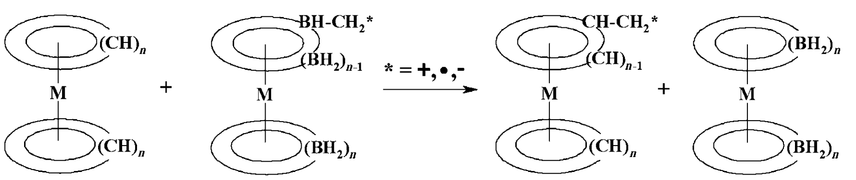


16a **16b** **16c**

17a **17b** **17c**

18a **18b** **18c**

Figure 4. Geometries of minima **16**–**18** calculated at the B3LYP/6-311+G(df,p) level of theory with bond lengths displayed in angstroms [Å].



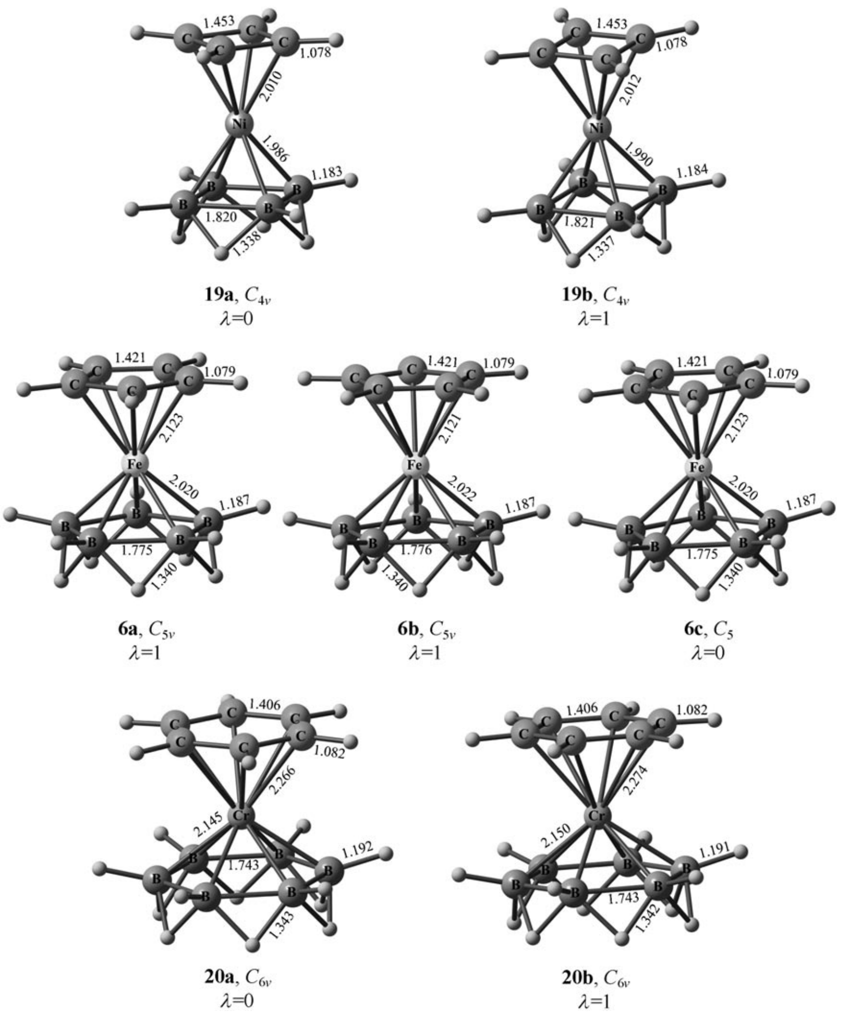
Scheme 1.

Table 2. ΔE_{rxn} [kcal mol^{-1}] for isodesmic reactions (Scheme 1) calculated at the B3LYP/6-311+G(df,p) level of theory.

M	Cationic	Radical	Anionic
Ni	−17.0	−14.7	−9.4
Fe	−14.9	−4.3	9.7
Cr	−30.4	−6.4	15.7

transition-state structures, while C_5-symmetric **6c** is found to be the minimum, however, all three structures are within only 0.15 kcal mol^{-1} of each other (Table 1). In **6a** the distance between the metal atom and the center of the cyclopentadienyl ring (1.745 Å) is elongated relative to that in **11**, while the distance between the metal atom and the center of the B_5 ring (1.343 Å) is considerably shorter than that in **8**. The C–H and B–H bonds of the cyclopentadienyl and cycloborane rings are bent towards the metal atom by 0.4 and 4.4°, respectively. Large NICS values (−34.8 and −51.2 ppm for the hydrocarbon and cycloborane rings, respectively) are again observed.

The mixed ligand sandwich complex **20** (Figure 5, Table 1) prefers a staggered conformation (C_{6v}-symmetric **20a**) over an eclipsed conformation (**20b**, also of C_{6v} symmetry) by 0.94 kcal mol^{-1}. The Cr–B distances (2.145 Å) in **20a** are markedly shorter than those in **9**, while the Cr–C distances (2.266 Å) are longer than those in **12**. In **20a**, the metal atom is again shifted closer to the borane (distances between the chromium atom and the centers of the C_6 and B_6 rings are 1.777 and 1.251 Å, respectively) and the C–H and B–H bonds are bent towards the metal atom by 0.8 and 6.0°, respectively. Large negative NICS values (−35.1 and −67.9 ppm for complexed benzene and B_6H_{12}, respectively) are again observed.



19a, C_{4v} λ=0

19b, C_{4v} λ=1

6a, C_{5v} λ=1

6b, C_{5v} λ=1

6c, C_5 λ=0

20a, C_{6v} λ=0

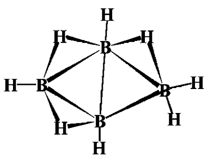
20b, C_{6v} λ=1

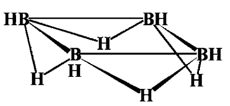
Figure 5. Geometries of minima, **19a**, **6c**, and **20a**, and transition states for internal rotation of the basal cycles, **19b**, **6a**, **6b** and **20b**, calculated at the B3LYP/6-311+G(df,p) level of theory with bond lengths displayed in angstroms [Å].

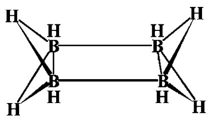
Overall, the geometries of these mixed sandwich compounds provide some insight into the relative strength of the metal–hydrocarbon and metal–borane interactions. In each of the mixed sandwich compounds, the metal–borane distances were significantly shorter than in the bis-borane sandwich compounds and the metal-hydrocarbon distances were longer than in the simple metallocenes. These geometric distortions allude to stronger M–B than M–C interactions. Note also that while NICS values for the hydrocarbons decreased in magnitude for the mixed sandwich compounds relative to the simple metallocenes, those for the boranes increased in magnitude relative to the bis-borane sandwich compounds (Table 1).

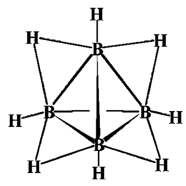
Free boranes: The B_4 rings in the basal B_4H_8 cycles in **7** are planar with their C–H bonds bent only slightly (not more than 1.0°) towards the metal center. Similar to its hydrocarbon analogue, antiaromatic 4π-electron cyclobutadiene, B_4H_8 exists only as a short lived species without metal complexation. B_4H_8 has been observed in the pyrolysis of B_4H_{10}[28] and B_5H_{11},[29] but our calculations suggest that four isomers (**21**–**24**) of free B_4H_8 are possible, with structure **21** being the lowest in energy, and all of them significantly different than the form bound in **7** and **19** (**22** is closest, but like cyclobutadiene, it prefers a rectangular rather than square form when uncomplexed).

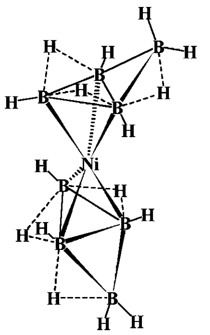
Structures **22**, **23** and **24** are higher in energy than **21** by 50.2, 22.8 and 10.6 kcal mol^{-1}, respectively. Three Ni(**21**)$_2$ complexes were also located (**25**–**27**) in which **21** is bound

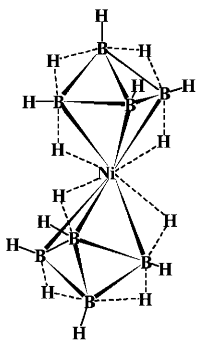

21, C_1

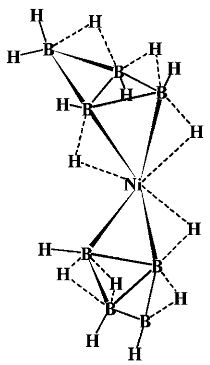

22, C_{2v}


23, D_{2h}


24, D_{2d}

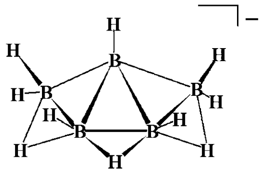

25, C_1


26, C_1

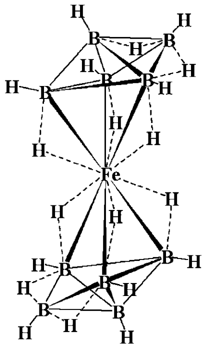

27, C_1

to the metal by B−H···M and/or B_n···M interactions. Complexes **25**–**27** are higher in energy than **7** by 9.77, 0.66 and 18.72 kcal mol^{-1}, respectively.

The lowest energy form of uncomplexed $B_5H_{10}^-$ was found to be *arachno* **28**. Iron complexation of **28** results in **29**, which is 44.71 kcal mol^{-1} higher in energy than **8a**.



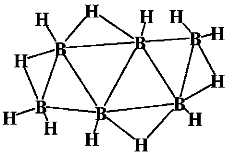
28, C_s



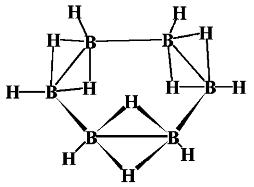
29, C_1

The structure of free B_6H_{12}[30,31] has been determined based on NMR and described as an "open icosahedral belt."[31] In agreement with the experimental results, the lowest energy form of B_6H_{12} that we find is C_2-symmetric *arachno* **30**. A D_{3h}-symmetric minimum (**31**) is approximately 20 kcal mol^{-1} higher in energy. Bis-**30** sandwich compound **32** is found to be 24.0 kcal mol^{-1} higher in energy than **9**. This, and the other examples mentioned above, suggest that metal complexation generally favors boranes with planar B_n rings that are not favored in the absence of the metal.

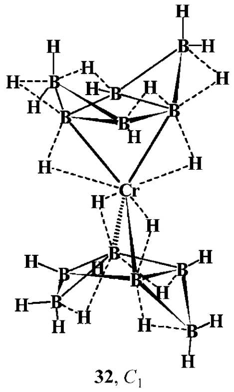
Bridging hydrogens as electronic modulators: Manipulation of the number of bridging hydrogen atoms of the complexed boranes provides an avenue for modulation of the electron count (as was recently discussed for sandwich compounds of non-transition-metal elements).[32] If, for example, a single H-atom is removed from compounds **8** and **6**, then Fe must be replaced by Co to retain a stable 18e$^-$ species (**33** and **34**, Figure 6). Similarly, two H-atoms may be removed and Ni substituted for Fe to arrive at **35**–**37** (Figure 6). In removing two H-atoms, it is preferable (by 8.77 kcal mol^{-1}) to remove one from each borane (e.g., **37**) rather than to remove them both from a single ring (e.g., **35**).



30, C_2

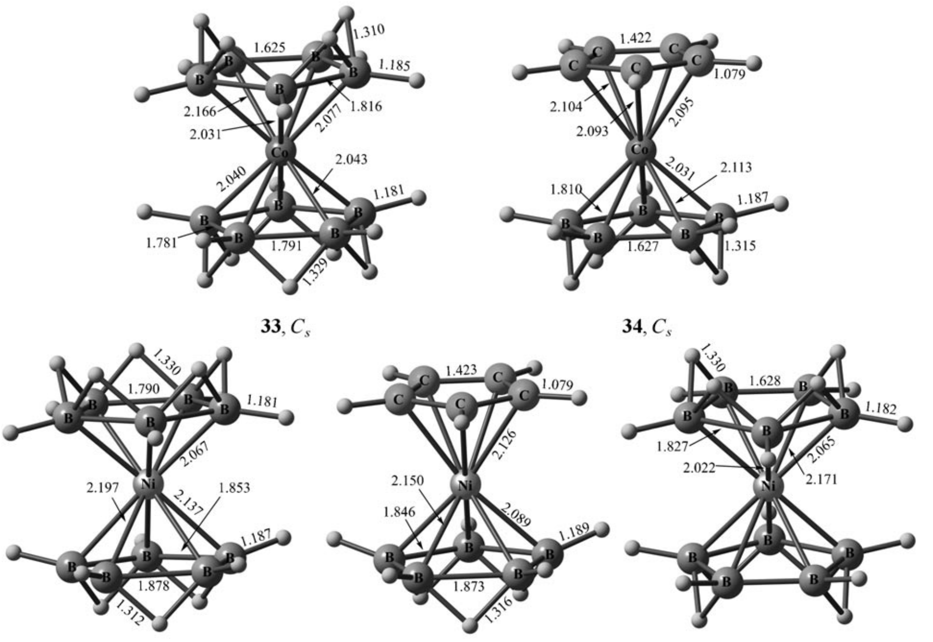


31, D_{3h}



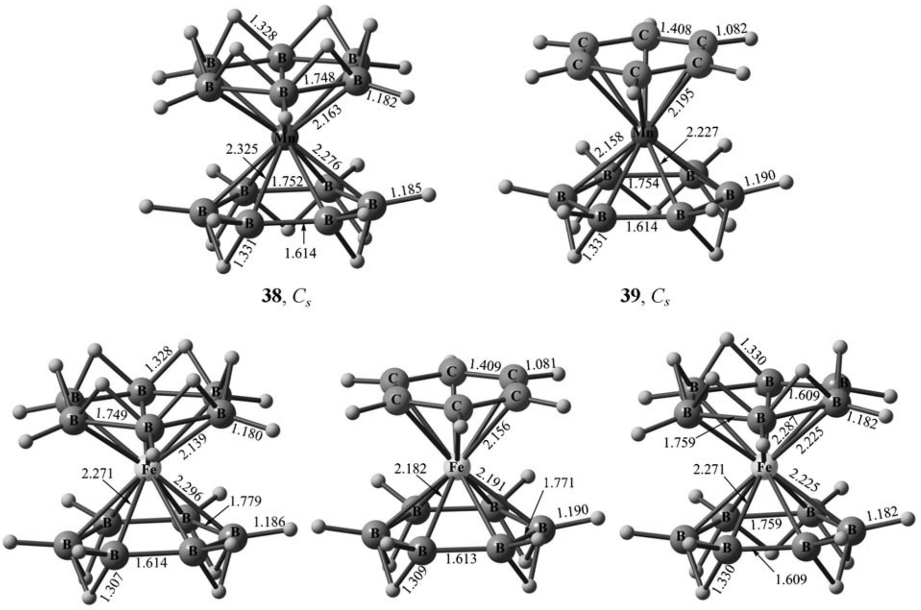
32, C_1

A similar approach may be used to design stable metalloboranes with six-membered basal cycles. Consecutive removal of one, two, three or four bridging hydrogen atoms from **9** and **20** with concomitant substitution of Cr by Mn, Fe, Co and Ni, respectively, generates a series of stable 18e$^-$ sandwich derivatives (Figures 7 and 8). As was the case with five-membered basal cycles, those with six-membered basal cycles prefer arrangements in which H-atoms are evenly distributed over the two boranes.



33, C_s **34**, C_s **35**, C_s **36**, C_s **37**, C_{2h}

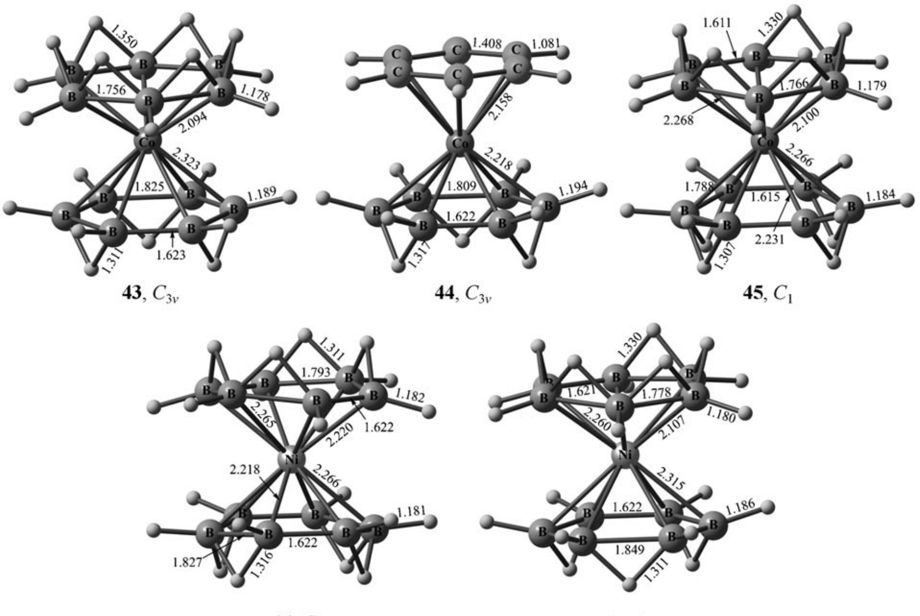
Figure 6. Geometries of minima **33**–**37** calculated at the B3LYP/6-311+G(df,p) level of theory with bond lengths displayed in angstroms [Å].



38, C_s **39**, C_s

40, C_{2v} **41**, C_{2v} **42**, C_1

Figure 7. Geometries of minima **38**–**42** calculated at the B3LYP/6-311+G(df,p) level of theory with bond lengths displayed in angstroms [Å].



43, C_{3v} **44**, C_{3v} **45**, C_1

46, C_2 **47**, C_1

Figure 8. Geometries of minima **43**–**47** calculated at the B3LYP/6-311+G(df,p) level of theory with bond lengths displayed in angstroms [Å].

Conclusion

Our calculations provide insight into a series of sandwich metalloborane compounds in which a transition-metal atom provides stabilization of borane ligands with planar B_n rings, a geometry that is not preferred in the absence of metal complexation. While metallocenes formed from hydrocarbons generally prefer eclipsed conformations, those formed from boranes, as well as mixed ligand complexes, prefer staggered conformations.[33] In sandwiches with borane rings, interaction between the metal center and basal fragments is strengthened relative to that for hydrocarbon analogues, as evidenced by metal–ligand distances and HOMO–LUMO gaps.[34] While metallocenes provide greater stabilization of appended carbocations and radicals than do metalloboranes, boron-based systems provide greater stabilization to carbanions. We hope that the variety of structures described herein will prompt new experiments in the field of metal sandwich chemistry.

Acknowledgements

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[34] a) Equations comparing the binding strengths of hydrocarbons and boranes can be found in the Supporting Information; b) Note also that replacing hydrocarbon cycles by more electropositive borane cycles leads to an increase of electron density on the metal atoms, as indicated by the partial charges shown in Table 1.

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