Sandwich Compounds of Transition Metals with Cyclopolyenes and Isolobal Boron Analogues


Abstract: A series of sandwich compounds of transition metals (M = Ni, Fe, Cr) with cyclic hydrocarbon (M(CH)_n) and borane (M(BH)_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 molecular electronics and pharmacology.[1] Metallocones 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 metallocone 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).

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-boronokane (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.[9]
Metalloccenes and related metal–π complexes attached to carboxation, radical and carbanion centers have also received considerable interest.\textsuperscript{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)\textsubscript{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).\textsuperscript{10a} 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 metallasubstituted cyclobutadiene rings. Interconversion of the staggered and eclipsed conformations (10\textit{a} and \textit{b}, respectively) can occur through \(D_s\)-symmetric transition structure 10\textit{c} (Figure 1, Table 1). Upon ZPE correction, 10\textit{c} is only 0.13 kcalmol\textsuperscript{−1} higher in energy than 10\textit{b} and is actually lower in energy then 10\textit{a} by 0.05 kcalmol\textsuperscript{−1}. Thus, \((\text{η}^5\text{C}_6\text{H}_5)_2\text{Ni}\) 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\textsuperscript{18,19} and previous quantum chemical calculations,\textsuperscript{20,21} our computations show \(D_{5h}\)-symmetric ferrocene (11\textit{b}; Figure 1, Table 1) to be a local minimum. Rotation of the basal cycles through a \(D_s\)-symmetric transition structure (11\textit{a}) involves a barrier of 0.41 kcalmol\textsuperscript{−1}. Numerous experimental studies\textsuperscript{18,19,22,23} have examined the fluxionality of ferrocene, and the experimental estimate of 0.9 ± 0.3 kcalmol\textsuperscript{−1} 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 11\textit{b} is again consistent with significant aromatic character.

In agreement with studies using various experimental techniques (X-ray, IR spectroscopy, gas-phase electron diffraction)\textsuperscript{24,25} as well as previous quantum-chemical calculations\textsuperscript{20,26,27} our calculations predict a \(D_{5h}\)-symmetric structure for \((\text{η}^5\text{C}_6\text{H}_5)_2\text{Cr}\) (12\textit{b}; Figure 1, Table 1). In 12\textit{b}, the distance between the metal atom and the center of each

**Computational Methods**

DFT calculations were carried out using Gaussian03\textsuperscript{22} with the Becke-3 parameter exchange and the Lee–Yang–Parr correlation functional (B3LYP) paired with the 6-311+G(df,p) basis set.\textsuperscript{15} 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 kcalmol\textsuperscript{−1}. In most cases, the structures corresponding to energy minima (\(λ=0\); 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)\textsuperscript{25} from the first-order saddle point (transition state). Molecular structure images were generated with Chemcraft.\textsuperscript{15}

**Results and Discussion**

**Metallocenes with only hydrocarbon ligands:** Both staggered (10\textit{a}, \(D_{5h}\) symmetry) and eclipsed (10\textit{b}, \(D_s\) symmetry) conformations of \((\text{η}^5\text{C}_6\text{H}_5)_2\text{Ni}\) were found to correspond to energy minima (Figure 1, Table 1), with the eclipsed conformation (10\textit{b}) slightly preferred (by 0.18 kcalmol\textsuperscript{−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).\textsuperscript{25} 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 \(D_{5h}\) symmetry). The C–H bonds are bent by \(≈ 20°\) away from the metal center. A NICS value of −25.6 ppm in the center of each hydrocarbon fragment of 10\textit{b} is consistent with aromatic character for the complexed cyclobutadiene rings. Interconversion of the staggered and eclipsed conformations (10\textit{a} and \textit{b}, respectively) can occur through \(D_s\)-symmetric transition structure 10\textit{c} (Figure 1, Table 1). Upon ZPE correction, 10\textit{c} is only 0.13 kcalmol\textsuperscript{−1} higher in energy than 10\textit{b} and is actually lower in energy then 10\textit{a} by 0.05 kcalmol\textsuperscript{−1}. Thus, \((\text{η}^5\text{C}_6\text{H}_5)_2\text{Ni}\) 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\textsuperscript{18,19} and previous quantum chemical calculations\textsuperscript{20,21} our computations show \(D_{5h}\)-symmetric ferrocene (11\textit{b}; Figure 1, Table 1) to be a local minimum. Rotation of the basal cycles through a \(D_s\)-symmetric transition structure (11\textit{a}) involves a barrier of 0.41 kcalmol\textsuperscript{−1}. Numerous experimental studies\textsuperscript{18,19,22,23} have examined the fluxionality of ferrocene, and the experimental estimate of 0.9 ± 0.3 kcalmol\textsuperscript{−1} 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 11\textit{b} is again consistent with significant aromatic character.
Metallocenes with appended carbocations, radicals and carbanions: Derivatives of structures 10–12 with attached CH$_{1^*}$ (* = +, *, –) 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$_4$H$_3$CH$_2$ fragment in this structure is too great, so the metalene group remains essentially coplanar with the cyclobutadiene fragment.

Boron-based metalocene analogues: Replacement of the C$_4$H$_4$ rings of 10 with isolobal B$_4$H$_4$ borane fragments results

basal cycle (1.646 Å) is the shortest among the metalloccenes 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 $D_{4h}$-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 metalloccenes 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.

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.

<table>
<thead>
<tr>
<th>Structure</th>
<th>$\Delta E$</th>
<th>$\Delta E_{ZPE}$</th>
<th>$\lambda$</th>
<th>$\omega_{iso}$</th>
<th>$q_{M}$</th>
<th>NICS</th>
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<tr>
<td>10a, $D_{4h}$</td>
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<td>11.8</td>
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<td>–</td>
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<td>10b, $D_{4h}$</td>
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<td>0</td>
<td>0</td>
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<td>0.801</td>
<td>−25.6</td>
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<td>10c, $D_{4}$</td>
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<td>1</td>
<td>39.7</td>
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<td>–</td>
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<td>11a, $D_{4h}$</td>
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<td>0.41</td>
<td>1</td>
<td>51.5</td>
<td>–</td>
<td>–</td>
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<tr>
<td>11b, $D_{4h}$</td>
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<td>−46.6</td>
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<td>12a, $D_{4h}$</td>
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<td>0.71</td>
<td>1</td>
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<td>–</td>
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<tr>
<td>12b, $D_{4h}$</td>
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<tr>
<td>7a, $D_{4h}$</td>
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<td>1.27</td>
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<td>8a, $D_{4h}$</td>
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<td>−37.7</td>
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<td>8b, $D_{4h}$</td>
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<td>–</td>
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<td>9a, $D_{4h}$</td>
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<td>0</td>
<td>83.1</td>
<td>−1.123</td>
<td>−44.8</td>
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<td>9b, $D_{4h}$</td>
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<td>5.57</td>
<td>1</td>
<td>81.0</td>
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<td>–</td>
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<td>19a, $C_{6h}$</td>
<td>0</td>
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<td>0</td>
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<td>0.656</td>
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<tr>
<td>19b, $C_{6h}$</td>
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<td>0.70</td>
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<td>–</td>
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<td>–</td>
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<td>0</td>
<td>0</td>
<td>34.3</td>
<td>−0.146</td>
<td>−34.8$^{[b]}$</td>
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<tr>
<td>20a, $C_{6h}$</td>
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<td>0</td>
<td>10.7</td>
<td>−0.431</td>
<td>−35.1$^{[b]}$</td>
</tr>
<tr>
<td>20b, $C_{6h}$</td>
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<td>0.94</td>
<td>1</td>
<td>41.8</td>
<td>–</td>
<td>–</td>
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</table>

$^a$ Relative energy: $\Delta E$ [kcal mol$^{-1}$], relative energy with ZPE correction $\Delta E_{ZPE}$ [kcal mol$^{-1}$]: $\lambda$: number of negative hessian eigenvalues; $\omega_{iso}$ (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.

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$^{[b]}$) and chromocene (12b$^{[b]}$) are given in italics.
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). 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 $D_{4h}$-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 $D_{5h}$-symmetric conformer 8a is an energy minimum while the $D_{5d}$-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) and the B–H bonds bend slightly towards the metal atom, here by $\approx$3.5°. The NICS value at the center of the B$_5$ rings in 8a (−37.7 ppm) is again substantial.

Replacement of the benzene rings of 12 by B$_6$H$_{12}$ fragments leads to 9 (Figure 3, Table 1), the lowest energy conformation of which is $D_{6h}$-symmetric 9a. $D_{6h}$-Symmetric 9b is the transition-state structure for rotation of the basal...
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 \(\sigma\) 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 \(\approx 2°\) away from the metal, while the B–H bonds bend by \(\approx 1°\) 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 [(\(\eta^5\)-B\(_{10}\)H\(_{10}\))Fe(\(\eta^5\)-C\(_5\)H\(_5\))] (6) has been synthesized and characterized by NMR.\[39\] 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...
transition-state structures, while C₅-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 B₅ 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 ppm 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 (C₆v-symmetric 20a) over an eclipsed conformation (20b, also of C₆v 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 C₆ and B₆ 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 B₆H₁₂, respectively) are again observed.
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 B₄ rings in the basal B₄H₈ 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 4p-electron cyclobutadiene, B₄H₈ exists only as a short lived species without metal complexation. B₄H₈ has been observed in the pyrolysis of B₄H₁₀ [28] and B₅H₁₁ [29] but our calculations suggest that four isomers (21–24) of free B₄H₈ 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 kcalmol⁻¹, respectively. Three Ni(21)₂ complexes were also located (25–27) in which 21 is bound
to the metal by B–H···M and/or Bₘ···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 B₆H₁₀⁻ 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.

The structure of free B₆H₁₂[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 B₆H₁₂ that we find is C₂-symmetric arachno 30. A D₃h-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 Bₘ 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).

A similar approach may be used to design stable metallo-boranes 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.

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Figure 6. Geometries of minima 33–37 calculated at the B3LYP/6-311+G(d,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 BN 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 metalloboranes provide greater stabilization of appended carbocations and radicals than do metallocaranes, 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.

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