Tetradecaker Transition Metal Complexes Containing Double Planar Hexacoordinate Carbons and Double Planar Heptacoordinate Borons

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A theoretical investigation on tetradecaker transition metal complexes of Cp–Fe–CB6–Fe–CB6–Fe–Cp (1) containing double planar hexacoordinate carbons and Cp–Fe–BB7–Fe–BB7–Fe–Cp (2) containing double planar heptacoordinate borons has been performed in this work at density functional theory level. [CpFe]⁺ monocations prove to effectively stabilize these unusual complexes, which are mainly maintained by effective d–π coordination interactions between the partially filled Fe 3d orbitals and the delocalized π molecular orbitals (MOs) of the four planar deckerlike ligands. The results obtained in these model computations expand the domain of ferrocene chemistry and could provide a new approach for synthesizing planar hyper-coordinate carbons and borons in transition metal complexes.

As first-row neighbors in the periodic table, carbon and boron possess rich chemistries which continuously expand human imaginations. The exciting planar hexacoordinate carbon (phC) at the center of a perfect CB6²⁻ hexagon (D6h) was first proposed at density functional theory (DFT) level in 2000, and planar heptacoordinate boron (phB) centered in a slightly distorted B6⁻ heptagon (C2v) was initially characterized by a joint photoelectron spectroscopy (PES) and DFT investigation in 2003. Both B6⁻ neutral and B6²⁻ dianion (noted as BB7⁻ and BB7²⁻ in this work to address their structural features) proved to be perfect D7h heptagons. Bare B6 and B6 clusters were confirmed to serve as novel inorganic ligands in the half-sandwich-type LiB6⁻ (C2v)² and LiB6⁻ (C7v)² respectively. Noticing that both the phC-centered CB6²⁻ (r = 1.59 Å) and phB-centered BB7²⁻ (r = 1.79 Å) possess perfect wheellike structures with six delocalized π electrons (similar to the well-known cyclopentadienyl ring of C5H5⁻ (Cp⁻)), our group proposed at DFT level the first sandwich-type transition metal complex series of D6h [CB6]M[X] and D2h [BB7]M[BB7] (M = Mn, Fe, Co, and Ni) and found that alkali-metal counterions like Li⁺ could be used to stabilize the systems to form CB6[M][Li]⁻ and D2[M][BB7]Li2. When two [CpFe]⁺ units were attached to a sandwich-type [CB6⁻Fe–CB6⁻Fe]²⁻ dianion along the molecular axis from opposite ends, the tetradecaker complex 1 in C2 symmetry was produced, with the four deckers being almost perfectly parallel to one another and the Fe–phC–Fe–phC–Fe chain being practically linear (with the Fe–Fe–Fe angle of 179.3°). The planarity of the CB6 middle deckers has been well preserved in 1 with the two phC centers lying only 0.10 Å above the B6 plane. The B–B and phC–B bond lengths turned out to be slightly longer than those in the perfect CB6²⁻ hexagon. Structure 1 proves to be a true minimum on the potential energy surface of the complex with the lowest vibrational frequency of 16 cm⁻¹ which originates from the rotation of the two Cp⁻ rings in opposite directions around the molecular axis (A mode).
while the two middle deckers remain almost still, similar to the situation in ferrocene Cp$_2$Fe.$^6,^{14}$ The energy of the highest occupied molecular orbital (HOMO) of 1 proves to be highly negative ($-5.671$ eV) and the HOMO–LUMO energy gap is greater than 2.80 eV. NBO analysis indicates that the two phC centers follow the octet rule with the total Wiberg bond indices of WBI$_{phC} = 3.83$. A phC center forms six phC-$\pi$ bonds within the CB$_6$ unit it belongs to (with the averaged Wiberg bond order of WBI$_{phC-B} = 0.56$) and two phC–Fe interactions in vertical direction (with WBI$_{phC-Fe} \approx 0.20$). Since each decker has six $\pi$-electrons, the three Fe ([Ar]$4s^24d^6$) coordination centers all fully conform with the 18-electron rule with the averaged total Wiberg bond index of WBI$_{Fe} = 2.96$ (in line with WBI$_{Fe} = 2.99$ in Cp$_2$Fe). Interestingly, the phC centers in structure 1 carry essentially a unitary negative charge with $q_{phC} = -0.98$ [e], well in line with the typical feature of planar coordinate carbon which has an extra electron delocalized in its 2p$_z$ orbital.$^5,^7,^{13}$ The calculated Fe–C bond lengths of $R_{Fe-C} \approx 2.054$ Å in 1 agree well with the corresponding measured value of $R_{Fe-C} = 2.064$ Å in Cp$_2$Fe.$^{14}$

Substituting the two CB$_6$ middle deckers of 1 with planar BB$_7$ units producing structure 2, in which both the planarity of the two BB$_7$ middle deckers and the linearity of the Fe–phB–Fe–phB–Fe chain are well maintained (with the Fe–C–Fe angle of 179.9$^\circ$). As indicated in Table 1, the electronic properties of structure 2 well parallels the results obtained for complex 1, except the atomic charges of the phB centers: phBs in 2 carry much lower negative charges ($-0.34$ [e]) than phCs in 1 due to the fact that B is much less electronegative than C in nature. The periphery B atoms of the CB$_6$ and BB$_7$ middle deckers in 1 and 2 possess the averaged total Wiberg bond indexes of WBI$_B = 3.46$–3.57. Multicenter bonding plays an important role within the CB$_6$ and BB$_7$ middle deckers, and the Fe–B weak coordination interactions (with WBI$_{Fe-B} = 0.11$–0.18) help to stabilize these unusual complexes. As shown in Table 1, the calculated vertical ionization potentials (VIP = 5.94–6.00 eV) of 1 and 2 well parallel (but slightly higher than) their HOMO energies, in line with Koopmans theorem.

The frequency analyses may facilitate future IR measurements. Figure 2 indicates that 1 and 2 possess similar calculated IR spectra. For 1, the most intensive IR absorption at 780 cm$^{-1}$ (unscaled) originates from the out-of-plane asymmetric vibration (B mode) of the two phC centers (with a symmetric off-planed IR inactive A mode at 799 cm$^{-1}$), while the two peaks at 692 and 1112 cm$^{-1}$ come from their in-plane vibrations. For 2, the corresponding vibrational frequencies are calculated to be 862, 871, 654, and 980 am$^{-1}$, respectively. Replacement of the CB$_6$ middle deckers in 1 with BB$_7$ mainly affects the vibrational modes involving the phC centers.

**Table 1:** Lowest Vibrational Frequencies $v_{min}$ (cm$^{-1}$), HOMO Energies $E_{HOMO}$ (eV), HOMO–LUMO Gaps $E_{gap}$ (eV), Natural Atomic Charges of phC and phB Centers $q_{phX}$ (eV), Total Wiberg Bond Orders WBI$_{phX}$, WBI$_{Fe}$, and WBI$_{B}$, and Vertical Ionization Potentials VIPs (eV) of Complexes 1 and 2 at the DFT Level

<table>
<thead>
<tr>
<th>Structure</th>
<th>$v_{min}$</th>
<th>$E_{HOMO}$</th>
<th>$E_{gap}$</th>
<th>$q_{phX}$</th>
<th>WBI$_{phX}$</th>
<th>WBI$_{Fe}$</th>
<th>WBI$_{B}$</th>
<th>VIP</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>16</td>
<td>-5.671</td>
<td>-5.880</td>
<td>-0.98</td>
<td>3.83</td>
<td>2.96</td>
<td>3.46</td>
<td>5.94</td>
</tr>
<tr>
<td>2</td>
<td>5</td>
<td>2.803</td>
<td>2.992</td>
<td>-0.34</td>
<td>3.57</td>
<td>2.96</td>
<td>3.46</td>
<td>6.00</td>
</tr>
</tbody>
</table>

**Figure 1.** Optimized structures of $C_2$ Cp–Fe–CB$_6$–Fe–CB$_6$–Fe–Cp (1) and $C_2$ Cp–Fe–BB$_7$–Fe–BB$_7$–Fe–Cp (2) at the DFT level with the necessary averaged bond lengths indicated in angstroms.

**Figure 2.** Calculated IR spectra of complexes 1 and 2 at the DFT level.
Cp₂Fe(C)₆ deficient nature of phB centers is clearly demonstrated with the low electron occupations of the phB sp² orbitals (compare with that of phC in 1). It is interesting to notice that, even though the partially delocalized phB 2pₓ orbital of 2 still possesses an extra electron which is necessary for phB to form effective σ interactions with Fe 3dₓ orbital in vertical direction. Detailed MO pictures of these tetradecker complexes prove to be similar to the bonding patterns of the previously reported double- and triple-decker transition metal complexes.⁵,⁶

Concerning the thermodynamic stabilities of these complexes, we calculate the energy changes of the following processes by referring to the synthesizing process of ferrocene Cp₃Fe

\[
\text{CpNa(C}_5\text{)} + \text{Fe}^{2+} = [\text{CpFe}]^+(C_5) + \text{Na}^+ \quad (1)
\]

\[
[\text{CB}_6]^2-(D_{9h}) + \text{Na}^+ = [\text{CB}_6\text{Na}]^-(C_{6h}) \quad (2)
\]

\[
2[\text{CB}_6\text{Na}]^-(C_{6h}) + \text{Fe}^{2+} = [\text{CB}_6^2-\text{Fe}^2-\text{CB}_6^2]^{2-}(D_{9h}) + 2\text{Na}^+ \quad (3)
\]

\[
2[\text{CpFe}]^+(C_5) + [\text{CB}_6^2-\text{Fe}^2-\text{CB}_6^2]^{2-}(D_{9h}) = \text{Cp}^-\text{Fe}-\text{Cp}^-\text{Fe}-\text{Cp}^-\text{Fe} \quad (4)
\]

or \([\text{CB}_6\text{Na}]^-(C_{6h}) + \text{Fe}^{2+} = \text{Cp}_2\text{Fe}(C_{6h}) + \text{Na}^+ \quad (5)
\]

\[
\text{Cp}_2\text{Fe}(C_3) + 2\text{Cp}_2\text{Fe}(C_{6h}) = \text{Cp}^-\text{Fe}-\text{Cp}^-\text{Fe}-\text{Cp}^-\text{Fe} - \text{Fe}^-\text{Cp}^-\text{Fe}(C_3) \quad (6)
\]

With zero point corrections included, these reactions all prove to be strongly favored in energies, with \(\Delta E_1 = -1.078 \times 10^3\) kJ/mol, \(\Delta E_2 = -0.904 \times 10^3\) kJ/mol, \(\Delta E_3 = -1.299 \times 10^3\) kJ/mol, \(\Delta E_4 = -1.443 \times 10^3\) kJ/mol, \(\Delta E_5 = -1.631 \times 10^3\) kJ/mol, and \(\Delta E_6 = -0.217 \times 10^3\) kJ/mol. Equation 4 clearly indicates that two [CpFe]⁺ monocations effectively stabilize the [Cp₂Fe⁻·CB₂]⁻ dianion which possesses nine occupied MOs with positive energies.⁶ Equation 6 shows that two CB₆Fe neutrals can also be inserted into a Cp₂Fe sandwich structure to form the target complex 1, but the energy release of this process is much smaller than eq 4.

In summary, a DFT investigation on a new class of tetradecker transition metal complexes containing double phCs and phBs has been presented in this work. The Fe centers in these complexes may be replaced by Ru, Os, or other transition metals. [CpFe]⁺ cations prove to effectively stabilize these unusual complexes which could be expanded to multidecker sandwich-type complexes by insertion of more than two CB₆Fe or BB₇Fe units. Our model computations introduce double phC centers into sandwich-type structures and shed new insights into syntheses of planar hyper-coordinate carbons and borons in transition metal complexes in the future.

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References and Notes