

ARTICLES

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

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A theoretical investigation on tetradeccker transition metal complexes of $\text{Cp-Fe-CB}_6\text{-Fe-CB}_6\text{-Fe-Cp}$ (**1**) containing double planar hexacoordinate carbons and $\text{Cp-Fe-BB}_7\text{-Fe-BB}_7\text{-Fe-Cp}$ (**2**) containing double planar heptacoordinate borons has been performed in this work at density functional theory level. $[\text{CpFe}]^+$ monocations prove to effectively stabilize these unusual complexes, which are mainly maintained by effective $d-\pi$ 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 CB_6^{2-} hexagon (D_{6h}) was first proposed at density functional theory (DFT) level in 2000,¹ and planar heptacoordinate boron (phB) centered in a slightly distorted B_8^- heptagon (C_{2v}) was initially characterized by a joint photoelectron spectroscopy (PES) and DFT investigation in 2003.^{2,3} Both B_8 neutral and B_8^{2-} dianion (noted as BB_7 and BB_7^{2-} in this work to address their structural features) proved to be perfect D_{7h} heptagons.^{2,3} Bare B_6 and B_8 clusters were confirmed to serve as novel inorganic ligands in the half-sandwich-type LiB_6^- (C_{2v})⁴ and LiB_8^- (C_{7v}),⁵ respectively. Noticing that both the phC-centered CB_6^{2-} ($r = 1.59 \text{ \AA}$) and phB-centered BB_7^{2-} ($r = 1.79 \text{ \AA}$) possess perfect wheellike structures with six delocalized π electrons^{1,2} (similar to the well-known cyclopentadienyl ring of C_5H_5^- (Cp^-)), our group proposed at DFT level the first sandwich-type transition metal complex series of D_{6d} [CB_6] M [CB_6] and D_{7d} [BB_7] M [BB_7] ($\text{M} = \text{Mn, Fe, Co, and Ni}$) and found that alkali-metal counterions like Li^+ could be used to stabilize the systems to form C_{6v} [CB_6Li] $^-$ and D_{2h} [CB_6] $_2\text{FeLi}_2$.⁶ In another recent paper,⁷ we presented the first triple-decker transition metal complex of neutral $\text{Cp-Fe-CB}_6\text{-Fe-Cp}$, in which two-half-sandwich-type $[\text{CpFe}]^+$ units were used to stabilize the phC-containing CB_6^{2-} middle decker. Very recently, the CB_6 unit has been annulated by inserting arenes, olefins, or other one- or two-atom bridging groups into a perimeter B–B bond.⁸ The half-sandwich-type $[\text{CB}_6\text{Li}]^-$ unit⁶ was recently developed at DFT into a new series of alkali-metal and alkaline-earth-metal ferrocene-like complexes mainly stabilized by electrostatic interactions between metal cations and the CB_6^{2-} dianions.⁹ In this work, we expand the investigations at DFT level to tetradeccker transition metal complexes of $\text{Cp-Fe-CB}_6\text{-Fe-CB}_6\text{-Fe-Cp}$ (**1**) containing double phCs and

$\text{Cp-Fe-BB}_7\text{-Fe-BB}_7\text{-Fe-Cp}$ (**2**) containing double phBs at the two middle deckers. $[\text{CpFe}]^+$ monocations prove to effectively stabilize these unusual multidecker complexes, which are mainly maintained by effective $d-\pi$ coordination interactions between the partially filled Fe 3d orbitals and the delocalized π molecular orbitals (MOs) of the four planar deckerlike ligands.

Structural optimizations, frequency analyses, natural bond orbital (NBO) analyses, and stability checks were performed with the Gaussian 03 program¹⁰ at the B3LYP/6-311+G(d,p) level.¹¹ The optimized structures of closed-shell **1** and **2** are depicted in Figure 1 and their calculated IR spectra compared in Figure 2. Table 1 tabulates their electronic properties. Because all the metal centers in these complexes conform to the 18-electron rule (similar to the situation in ferrocene Cp_2Fe), the low-lying states of the systems are expected to be singlet. Unrestricted open-shell calculations on **1** and **2** proved to have the problem of convergence at the same theoretical level. The B3PW91 method¹² turned out to produce essentially the same results.

When two $[\text{CpFe}]^+$ units were attached to a sandwich-type $[\text{CB}_6\text{-Fe-CB}_6]^{2-}$ dianion⁶ along the molecular axis from opposite ends, the tetradeccker complex **1** in C_2 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 $\text{Fe}'\text{-Fe-Fe}'$ angle of 179.3°). The planarity of the CB_6 middle deckers has been well preserved in **1** with the two phC centers lying only $0.10 \text{ \AA}$ above the B_6 plane. The B–B and phC–B bond lengths turned out to be slightly longer than those in the perfect CB_6^{2-} hexagon.¹ 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),

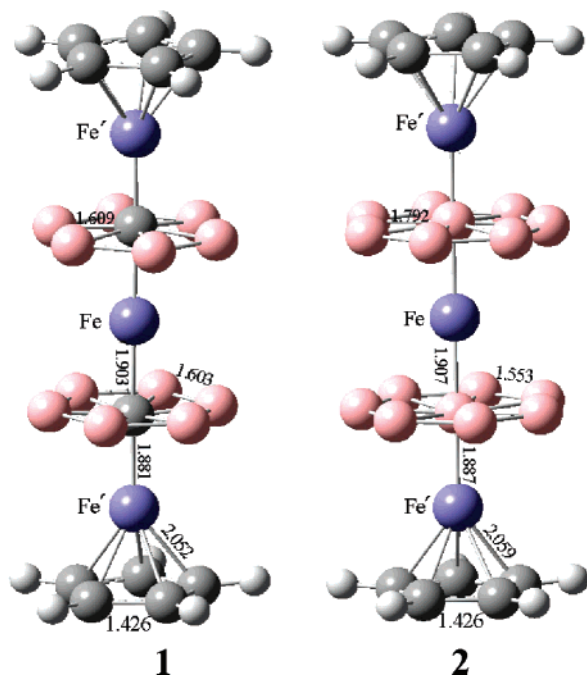


Figure 1. Optimized structures of C_2 Cp-Fe-CB₆-Fe-CB₆-Fe-Cp (**1**) and C_2 Cp-Fe-BB₇-Fe-BB₇-Fe-Cp (**2**) at the DFT level with the necessary averaged bond lengths indicated in angstroms.

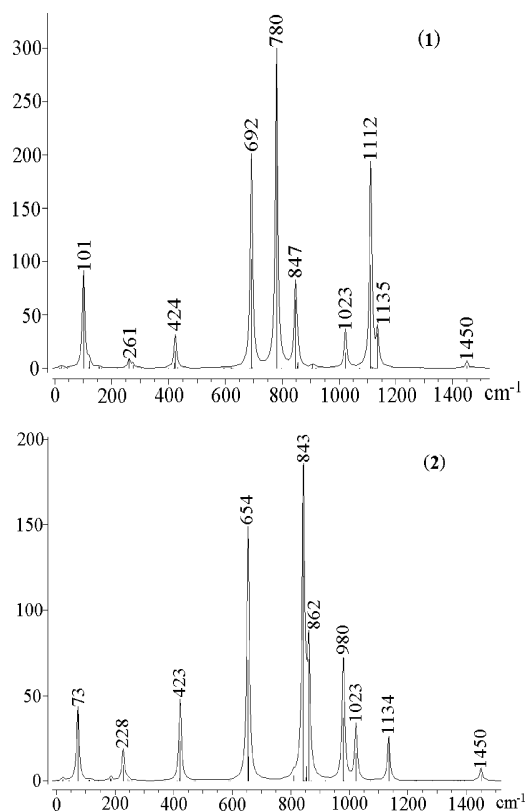


Figure 2. Calculated IR spectra of complexes **1** and **2** at the DFT level.

while the two middle decks remain almost still, similar to the situation in ferrocene Cp_2Fe .^{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 pH₂C centers follow the octet rule with the total Wiberg bond indices of $WBI_{pH_2C} = 3.83$. A pH₂C center forms six pH₂C-B partial bonds within the CB₆ unit it belongs to (with the averaged Wiberg

TABLE 1: Lowest Vibrational Frequencies ν_{min} (cm^{-1}), HOMO Energies E_{HOMO} (eV), HOMO-LUMO Gaps E_{gap} (eV), Natural Atomic Charges of pH₂C and pH₂B Centers q_{pH_2C} ($|e|$), Total Wiberg Bond Orders WBI_{pH_2C} , WBI_{Fe} , and WBI_B , and Vertical Ionization Potentials VIPs (eV) of Complexes **1** and **2** at the DFT Level

	structure 1		structure 2	
ν_{min}	16	5	WBI_{pH_2C}	3.83
E_{HOMO}	-5.671	-5.880	WBI_{Fe}	2.96
E_{gap}	2.803	2.992	WBI_B	3.46
q_{pH_2C}	-0.98	-0.34	VIP	5.94
				6.00

bond order of $WBI_{pH_2C-B} = 0.56$) and two pH₂C-Fe interactions in vertical direction (with $WBI_{pH_2C-Fe} \approx 0.20$). Since each decker has six π -electrons, the three Fe ($[Ar]4s^23d^6$) 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_2Fe). Interestingly, the pH₂C centers in structure **1** carry essentially a unitary negative charge with $q_{pH_2C} = -0.98 |e|$, well in line with the typical feature of planar coordinate carbon which has an extra electron delocalized in its $2p_z$ orbital.^{6,7,13} 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_2Fe .¹⁴

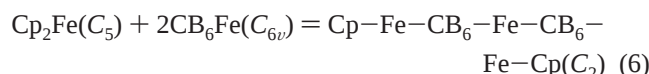
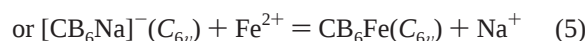
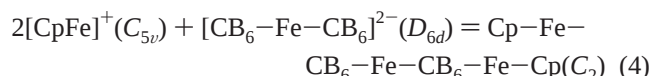
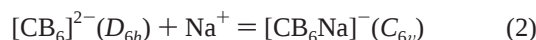
Substituting the two CB₆ middle decks of **1** with planar BB₇ units producing structure **2**, in which both the planarity of the two BB₇ middle decks and the linearity of the Fe'-pH₂B-Fe-pH₂B-Fe' chain are well maintained (with the Fe'-Fe-Fe' angle of 179.9°). As indicated in Table 1, the electronic properties of structure **2** well parallels the results obtained for complex **1**, except the atomic charges of the pH₂B centers: pH₂Bs in **2** carry much lower negative charges ($-0.34 |e|$) than pH₂Cs in **1** due to the fact that B is much less electronegative than C in nature. The periphery B atoms of the CB₆ and BB₇ middle decks 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 CB₆ and BB₇ middle decks, 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.

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 pH₂C 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 cm^{-1} , respectively. Replacement of the CB₆ middle decks in **1** with BB₇ mainly affects the vibrational modes involving the pH₂C centers.

Molecular orbital (MO) analyses help to understand the bonding pattern of these complexes. Structure **1** possesses the natural atomic electron configurations of pH₂C[He] $2s^{0.99}2p^{3.93}(2s^{0.99}2p_x^{1.33}2p_y^{1.33}2p_z^{1.27})$ and Fe[Ar] $4s^{0.15}3d^{7.86}(4s^{0.15}3d_{xy}^{1.11}3d_{x^2-y^2}^{1.81}3d_{xz}^{1.93}3d_{yz}^{1.11}3d_z^{1.89})$. Obviously, each sp^2 pH₂C possesses one extra electron delocalized in its $2p_z$ orbital, while the Fe coordination centers (which lose their $4s^2$ electrons almost completely) gain electrons through the $d-\pi$ coordination interactions between the partially filled Fe $3d$ atomic orbitals and the delocalized π molecular orbitals of CB_6^{2-} and Cp^- ligands, leaving Fe centers in **1** practically neutral. Structure **2** has the atomic electron configurations of pH₂B[He] $2s^{0.56}2p^{2.70}(2s^{0.56}2p_x^{0.86}2p_y^{0.86}2p_z^{0.98})$ and Fe[Ar] $4s^{0.15}3d^{7.80}(4s^{0.15}3d_{xy}^{1.05}2p_z^{0.98})$.

$3d_{x^2-y^2}1.883d_{xz}1.923d_{yz}1.053d_{z^2}1.91$). Here, Fe centers possess almost the same electron configurations as Fe in **1**, but the electron deficient nature of phB centers is clearly demonstrated with the low electron occupations of the phB sp^2 orbitals (compare with that of phC in **1**). It is interesting to notice that, even though the partially delocalized phB $2p_z^{0.98}$ orbital of **2** still possesses an extra electron which is necessary for phB to form effective σ interactions with Fe $3d_z^2$ orbitals in vertical direction. Detailed MO pictures of these tetradeccker complexes prove to be similar to the bonding patterns of the previously reported double- and triple-decker transition metal complexes.^{6,7}

Concerning the thermodynamic stabilities of these complexes, we calculate the energy changes of the following processes by referring to the synthesizing process of ferrocene Cp_2Fe



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 $[CB_6-Fe-CB_6]^{2-}$ dianion which possesses nine occupied MOs with positive energies.⁶ Equation 6 shows that two CB_6Fe neutrals can also be inserted into a Cp_2Fe 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 tetradeccker 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 CB_6Fe or BB_7Fe 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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