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ARTICLES

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

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A theoretical investigation on tetradecker transition metal complexes of Cp−Fe−CB_6−Fe−CB_6−Fe−Cp (**1**) containing double planar hexacoordinate carbons and Cp−Fe−BB_7−Fe−BB_7−Fe−Cp (**2**) containing double planar heptcoordinate 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 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 Å) and phB-centered BB_7^{2-} (r = 1.79 Å) 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} $[BB_7]M[BB_7]$ (M = 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} $[CB_6]_2FeLi_2$.[6] In another recent paper,[7] we presented the first triple-decker transition metal complex of neutral Cp−Fe−CB_6−Fe−Cp, in which two-half-sandwich-type $[CpFe]^+$ 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 $[CB_6Li]^-$ unit[6] 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 tetradecker transition metal complexes of Cp−Fe−CB_6−Fe−CB_6−Fe−Cp (**1**) containing double phCs and Cp−Fe−BB_7−Fe−BB_7−Fe−Cp (**2**) containing double phBs at the two middle deckers. $[CpFe]^+$ monocations prove to effectively stabilize these unusual multidecker 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.

Structural optimizations, frequency analyses, natural bond orbital (NBO) analyses, and stability checks were performed with the Gaussian 03 program[10] 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 method[12] turned out to produce essentially the same results.

When two $[CpFe]^+$ units were attached to a sandwich-type $[CB_6{-}Fe{-}CB_6]^{2-}$ dianion[6] along the molecular axis from opposite ends, the tetradecker 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 Fe′−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 Å 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),

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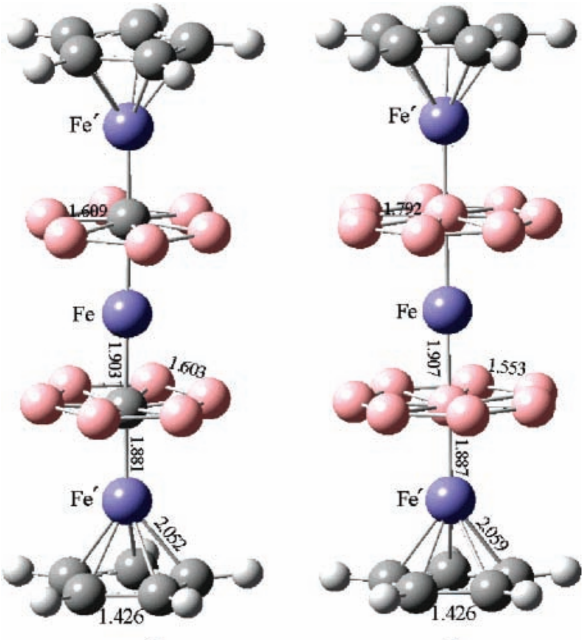

1 **2**

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.

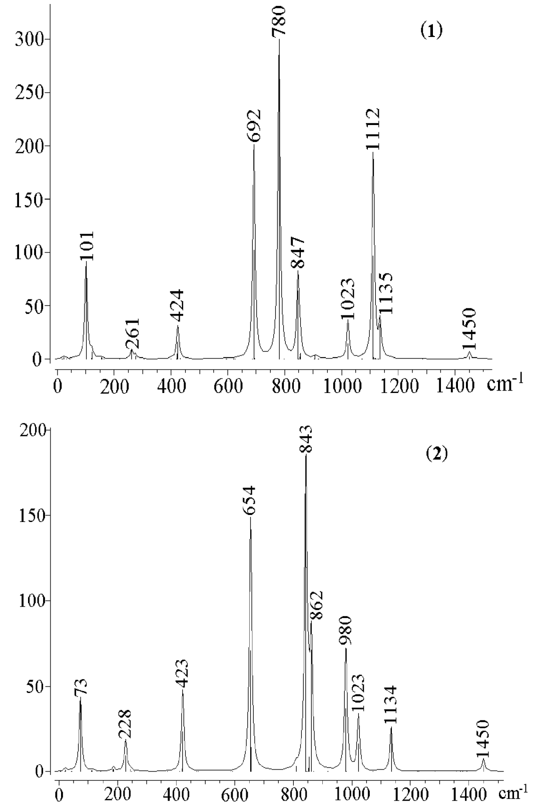

Figure 2. Calculated IR spectra of complexes **1** and **2** at the DFT level.

while the two middle deckers 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 phC centers follow the octet rule with the total Wiberg bond indices of $WBI_{phC} = 3.83$. A phC center forms six phC−B partial 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 π-electrons, the three Fe ($[Ar]4s^2 3d^6$) 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 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.[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]

TABLE 1: Lowest Vibrational Frequencies υ_{min} (cm^{-1}), HOMO Energies E_{HOMO} (eV), HOMO−LUMO Gaps E_{gap} (eV), Natural Atomic Charges of phC and phB Centers q_{phX} (|e|), 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

	structure **1**	structure **2**		structure **1**	structure **2**
υ_{min}	16	5	WBI_{phX}	3.83	3.91
E_{HOMO}	−5.671	−5.880	WBI_{Fe}	2.96	2.95
E_{gap}	2.803	2.992	WBI_B	3.46	3.57
q_{phX}	−0.98	−0.34	VIP	5.94	6.00

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′−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 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.

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.

Molecular orbital (MO) analyses help to understand the bonding pattern of these complexes. Structure **1** possesses the natural atomic electron configurations of phC[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] $4s^{0.15}3d^{7.86}(4s^{0.15}3d_{xy}^{1.11}3d_{x^2-y^2}^{1.81}3d_{xz}^{1.93}3d_{yz}^{1.11}3d_{z^2}^{1.89})$. Obviously, each sp^2 phC 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←π 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 phB[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] $4s^{0.15}3d^{7.80}(4s^{0.15}3d_{xy}^{1.05}$-

$3d_{x^2-y^2}^{1.88}3d_{xz}^{1.92}3d_{yz}^{1.05}3d_{z^2}^{1.91}$). 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 tetradecker 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

$$\mathrm{CpNa}(C_{5v}) + \mathrm{Fe}^{2+} = [\mathrm{CpFe}]^{+}(C_{5v}) + \mathrm{Na}^{+} \qquad (1)$$

$$[\mathrm{CB}_6]^{2-}(D_{6h}) + \mathrm{Na}^{+} = [\mathrm{CB}_6\mathrm{Na}]^{-}(C_{6v}) \qquad (2)$$

$$2[\mathrm{CB}_6\mathrm{Na}]^{-}(C_{6v}) + \mathrm{Fe}^{2+} = [\mathrm{CB}_6{-}\mathrm{Fe}{-}\mathrm{CB}_6]^{2-}(D_{6d}) + 2\mathrm{Na}^{+} \qquad (3)$$

$$2[\mathrm{CpFe}]^{+}(C_{5v}) + [\mathrm{CB}_6{-}\mathrm{Fe}{-}\mathrm{CB}_6]^{2-}(D_{6d}) = \mathrm{Cp}{-}\mathrm{Fe}{-}\mathrm{CB}_6{-}\mathrm{Fe}{-}\mathrm{CB}_6{-}\mathrm{Fe}{-}\mathrm{Cp}(C_2) \qquad (4)$$

$$\text{or } [\mathrm{CB}_6\mathrm{Na}]^{-}(C_{6v}) + \mathrm{Fe}^{2+} = \mathrm{CB}_6\mathrm{Fe}(C_{6v}) + \mathrm{Na}^{+} \qquad (5)$$

$$\mathrm{Cp}_2\mathrm{Fe}(C_5) + 2\mathrm{CB}_6\mathrm{Fe}(C_{6v}) = \mathrm{Cp}{-}\mathrm{Fe}{-}\mathrm{CB}_6{-}\mathrm{Fe}{-}\mathrm{CB}_6{-}\mathrm{Fe}{-}\mathrm{Cp}(C_2) \qquad (6)$$

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 $[\mathrm{CpFe}]^+$ monocations effectively stabilize the $[\mathrm{CB}_6{-}\mathrm{Fe}{-}\mathrm{CB}_6]^{2-}$ dianion which possesses nine occupied MOs with positive energies.[6] Equation 6 shows that two $\mathrm{CB}_6\mathrm{Fe}$ neutrals can also be inserted into a $\mathrm{Cp}_2\mathrm{Fe}$ 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. $[\mathrm{CpFe}]^+$ cations prove to effectively stabilize these unusual complexes which could be expanded to multidecker sandwich-type complexes by insertion of more than two $\mathrm{CB}_6\mathrm{Fe}$ or BB_7-Fe 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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