DOI: 10.1002/ejic.200600118

Triple-Decker Transition-Metal Complexes $(C_nH_n)M(B_6C)M(C_nH_n)$ (M = Fe, Ru, Mn, Re; *n* = 5, 6) Containing Planar Hexacoordinate Carbon Atoms

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Keywords: Planar hexacoordinate carbon / Triple-decker transition-metal complexes / Density functional theory / Geometric structures / Electronic structure / IR spectroscopy

A density functional theory investigation is presented in this work on a new class of triple-decker complexes (C_nH_n)-$M(B_6X)M(C_nH_n)$ (M = Fe, Ru, Mn, Re; X = B, C, N; *n* = 5, 6) containing almost perfect planar hexacoordinate carbon atoms and other planar hexacoordinate nonmetals at the centers of the B_6X middle-deckers. Effective d–π coordination interactions between the partially filled 3d orbitals of the transition-metal center and the delocalized π orbitals of the three parallel ligands maintain the stabilities of these triple-decker complexes. The strong IR absorption peaks of (C_nH_n)-$M(B_6X)M(C_nH_n)$ complexes mainly originate from the in-plane and off-plane vibrations of their planar hexacoordinate nonmetal centers. The results obtained in this work provide a possible new approach to characterize planar hexacoordinate carbon-containing systems in future experiments and expand the structural domain of transition-metal complexes by introducing inorganic B_6X middle-deckers into traditional sandwich-type structures.

Introduction

As a challenge to tetrahedral carbon, which has dominated organic chemistry and biochemistry for over 130 years, planar tetracoordinate carbon (ptC) was first proposed by Hoffmann et al.[1] about 30 years ago and was recently observed in gas phases in D_{4h} Al_4C^-,[2] C_{2v} Al_3XC, Al_3XC^- (X = Si, Ge),[3,4] and $[CAl_4]^{2-}$.[5] The smallest anion with a ptC at its center is D_{2h} C_5^{2-}, which has been incorporated in various neutral molecules.[6] Theoretical studies on planar coordinate carbon atoms also include planar pentacoordinate carbon atoms (ppCs) in $B_3C_2H_2C$ and extended systems[7] and planar hexacoordinate carbon atoms (phCs) in the B_6C^{2-} dianion.[8] Designing and characterizing new forms of planar coordinate C atoms remains a huge challenge in chemistry. In a series of recent works at density functional theory (DFT) level, our group developed a strategy to incorporate planar coordinate group IV elements at the centers of various hydrometal polygons, including ptC in M_4H_4C (M = Cu, Ni),[9] ppC in Cu_5H_5X (X = B, C, N, O),[10] planar pentacoordinate silicon (ppSi) in M_5H_5X (M = Pd, Pt; X = Si, Ge),[11] and planar hexacoordinate silicon (phSi) in Cu_6H_6X (X = Si, Ge) complexes.[12] Employing B_6C^{2-} as an aromatic ligand, in a recent communication,[13] we incorporated quasi-phCs in a new class of sandwich-type complexes $(B_6C)_2M$ (M = Mn, Fe, Co, Ni). In this work at DFT level, we introduce B_6C^{2-} to a novel class of triple-decker complexes $(C_nH_n)M(B_6C)M(C_nH_n)$ (M = Fe, Ru, Mn, Re; *n* = 5, 6) that contain almost perfect phCs at the centers of the B_6C middle-deckers. Similar results are also obtained for their isoelectronic complexes with planar hexacoordinate boron (phB) or planar hexacoordinate nitrogen (phN) centers. In the triple-decker[14] and multi-decker[15] complexes reported before, the hexanuclear benzene-centered tris(alkynyl triple-decker) complex[14] is particularly interesting, in which the three ligands around the benzene core are typical triple-decker complexes with a C_2B_3 ring as the middle-decker. However, to the best of our knowledge, there have been no triple-decker complexes with phCs, phBs, or phNs reported to date in the literature.

Theoretical Method

As the phC-containing B_6C^{2-} unit[8] is a 6π-electron aromatic dianion, while $C_5H_5^-$ is a 6π-electron monoanion, to meet the 18-electron requirements of the two Fe^{II} centers, the most possible triple-decker structure of a dinuclear neutral $(C_5H_5)Fe(B_6C)Fe(C_5H_5)$ would contain a B_6C^{2-} middle-decker to balance the overall molecular charge of the system, while the two $C_5H_5^-$ rings serve as terminal ligands, with the whole complex possessing a C_{2v} symmetry. But a singlet C_{2v} $(C_5H_5)Fe(B_6C)Fe(C_5H_5)$ turned out to be a transition state with one imaginary frequency. Relaxing the system in the imaginary vibrational mode leads to a slightly distorted C_2 structure that is a true minimum. The initially optimized structures with C_2 symmetries obtained at the hybrid DFT-B3LYP/6-31+G(d) level were refined comparatively with the bigger bases of 6-311+G(d,p) and 6-

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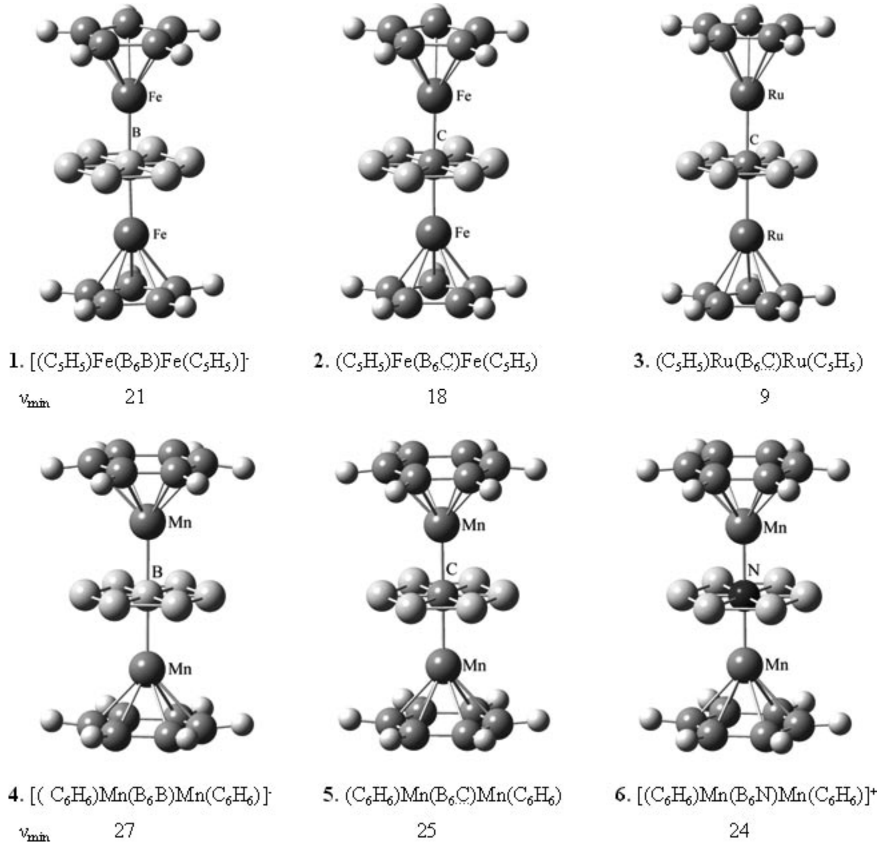
311+G(3df,p) and the optimized results turned out to be quite insensitive to the bases employed. When $C_5H_5^-$ terminal ligands are replaced with two neutral benzene molecules C_6H_6, two Mn^I centers are required to replace Fe^{II} to follow the 18-electron rule. Natural bond orbital (NBO) analyses[16] and zero-point energy (ZPE) corrections were performed in the frequency analyzing processes. Results obtained at B3LYP/6-311+G(d,p) level are presented in this work hereafter for the first-row transition-metal complexes. For heavy transition-metal complexes, we choose the basis of 6-31+G(d,p) for nonmetal atoms and Lanl2dz[17] (which contains an effective core potential for transition metals) for the second- and third-row transition metals. Figure 1 depicts the optimized structures that are true minima on their potential energy surfaces and Table 1 tabulates their geometrical and electronic properties. Figure 2 shows the typical molecular orbitals (MOs) of C_2 $(C_5H_5)Fe(B_6C)Fe(C_5H_5)$ involving Fe 3d orbitals and the delocalized π orbitals of the three parallel ligands and Figure 3 demonstrates the calculated IR spectra of C_2 $(C_5H_5)Fe(B_6C)Fe(C_5H_5)$ and C_2 $(C_6H_6)Mn(B_6C)Mn(C_6H_6)$ to facilitate future spectroscopic investigations. All the calculations in this work were performed using the Gaussian 03 program.[18]



1. $[(C_5H_5)Fe(B_6B)Fe(C_5H_5)]^-$ **2.** $(C_5H_5)Fe(B_6C)Fe(C_5H_5)$ **3.** $(C_5H_5)Ru(B_6C)Ru(C_5H_5)$

$\tilde{\nu}_{min}$ 21 18 9

4. $[(C_6H_6)Mn(B_6B)Mn(C_6H_6)]^-$ **5.** $(C_6H_6)Mn(B_6C)Mn(C_6H_6)$ **6.** $[(C_6H_6)Mn(B_6N)Mn(C_6H_6)]^+$

$\tilde{\nu}_{min}$ 27 25 24

Figure 1. Optimized structures of $(C_nH_n)M(B_6X)M(C_nH_n)$ triple-decker complexes (M = Fe, Ru, Mn, Re; X = B, C, N; n = 5, 6) containing planar hexacoordinate nonmetal centers, with the lowest vibrational frequencies $\tilde{\nu}_{min}$ (cm^{-1}) indicated.

Table 1. Averaged bond lengths r [Å], M–phX–M bond angles θ, HOMO energies E_{HOMO} [eV], HOMO–LUMO energy gaps ΔE_{gap} [eV], and natural atomic charges q_{phX} (|e|), and total Wiberg bond indices WBI_{phX} of the phX centers of typical $(C_nH_n)M(B_6X)M(C_nH_n)$ complexes at DFT-B3LYP level.

$(C_nH_n)M(B_6X)M(C_nH_n)$	$r_{M–C}$	$r_{M–B}$	$r_{M–phX}$	$r_{B–B}$	θ	E_{HOMO}	ΔE_{gap}	q_{phX}	WBI_{phX}
$(C_5H_5)Fe(B_6B)Fe(C_5H_5)^-$	2.059	2.510	1.913	1.624	177.2°	–1.82	3.53	–0.68	3.92
$(C_5H_5)Fe(B_6C)Fe(C_5H_5)$	2.057	2.474	1.884	1.603	177.8°	–5.70	3.52	–0.96	3.85
$(C_5H_5)Fe(B_6N)Fe(C_5H_5)^+$	2.064	2.464	1.845	1.619	177.9°	–9.68	3.47	–1.12	3.01
$(C_5H_5)Ru(B_6C)Ru(C_5H_5)$	2.190	2.606	2.047	1.612	179.1°	–5.76	3.59	–1.02	3.73
$(C_5H_5)Ru(B_6B)Ru(C_5H_5)^-$	2.197	2.620	2.046	1.638	178.7°	–1.88	3.45	–0.73	3.91
$(C_6H_6)Mn(B_6B)Mn(C_6H_6)^-$	2.092	2.542	1.956	1.624	180.0°	–1.76	3.73	–0.57	3.92
$(C_6H_6)Mn(B_6C)Mn(C_6H_6)$	2.104	2.500	1.919	1.603	180.0°	–5.36	3.72	–0.90	3.89
$(C_6H_6)Mn(B_6N)Mn(C_6H_6)^+$	2.124	2.472	1.871	1.618	180.0°	–9.12	3.50	–1.08	3.05
$(C_6H_6)Re(B_6C)Re(C_6H_6)$	2.217	2.587	2.012	1.626	180.0°	–4.83	3.25	–1.02	3.75

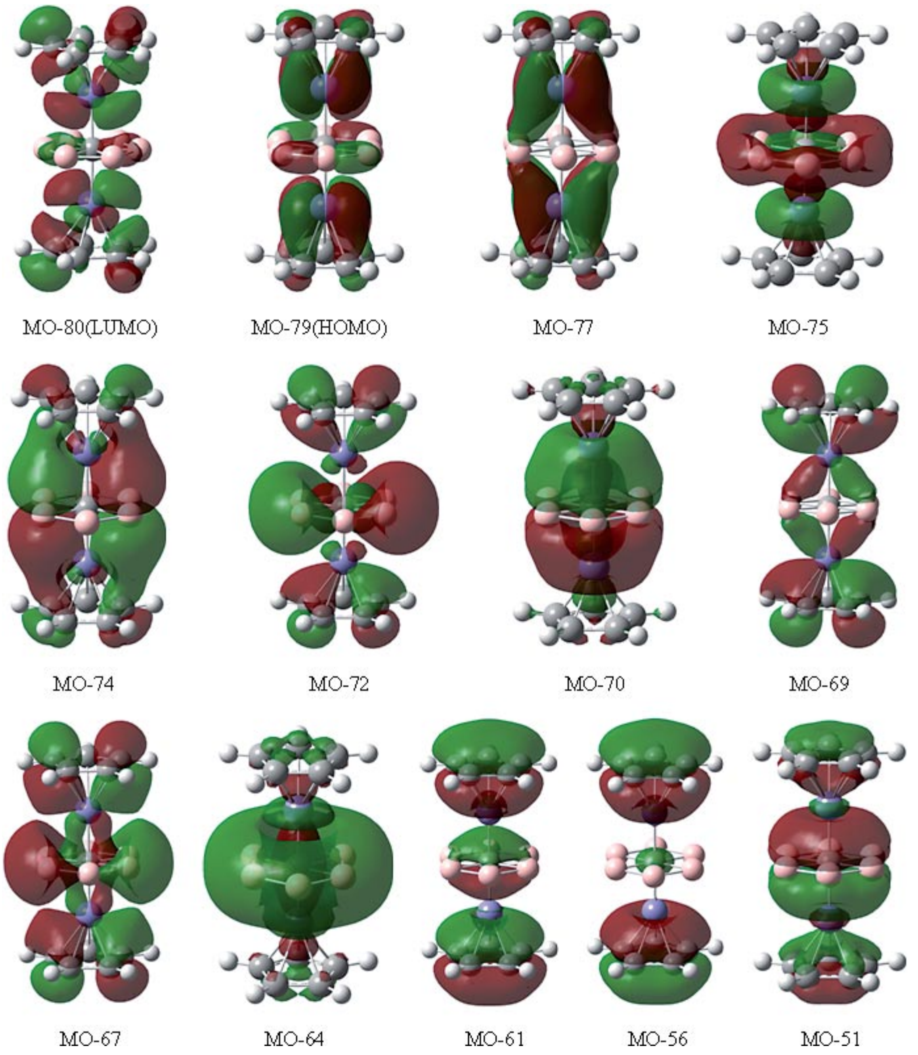


Figure 2. Typical MO pictures of C_2 $(C_5H_5)Fe$ $(B_6C)Fe(C_5H_5)$ involving Fe 3d and the delocalized π orbitals of the three parallel ligands. For doubly degenerate orbitals, only one of them is depicted.

Results and Discussion

As shown in Figure 1, all the triple-decker structures possess a real lowest vibrational frequency corresponding to rotations of the three parallel ligands about the M–phX–M molecular axis (with the two C_nH_n terminal ligands rotating clockwise while the B_6X middle-decker rotates anticlockwise) with a small energy barrier of about 2 kcal/mol, similar to the lowest-energy rotary vibrational modes of the well-known sandwich-type $(C_5H_5)_2Fe$ and $(C_6H_6)_2Cr$. But a singlet C_2 $(C_5H_5)Fe(B_6N)Fe(C_5H_5)^+$ monocation turned out to be a transition state with one imaginary frequency at 62i cm^{-1} (an up-and-down movement of the B_6 ring along the Fe–phN–Fe axis). Structural analyses indicate that the three quasiplanar ligands intervened by two Fe atoms in the prototypic C_2 $(C_5H_5)Fe(B_6C)Fe(C_5H_5)$ are almost perfectly parallel to one another, with the three axial atoms of Fe, phC, and Fe being nearly collinear with the bond angle of $\theta_{Fe\text{–}phC\text{–}Fe} = 177.8°$ and the averaged bond lengths of $r_{Fe\text{–}C} = 2.057$ Å, $r_{Fe\text{–}B} = 2.474$ Å, $r_{Fe\text{–}phC} = 1.884$ Å, and $r_{B\text{–}B} = 1.603$ Å. All the $(C_nH_n)M(B_6X)$-$M(C_nH_n)$ complexes (M = Fe, Ru; X = B, C, N; n = 5, 6) possess very similar triple-decker structures featured with the B_6X middle-deckers, which are almost perfect hexagons with phX atoms located at their geometrical centers and approximately equal B–B and phX–B bond lengths ($r_{B\text{–}B} \approx r_{phX\text{–}B}$). The B–B bond lengths in the middle-deckers of these complexes (see Table 1 for details) are slightly longer than the corresponding B–B distance of 1.594 Å in free B_6C^{2-}.[8] The calculated Fe–C bond lengths of 2.057 Å in $(C_5H_5)Fe(B_6C)Fe(C_5H_5)$ turned out to be very close to the corresponding measured values of 2.064 Å in ferrocene $(C_5H_5)Fe(C_5H_5)$,[19] while the Fe–phC distances of 1.884 Å are 0.224 Å longer than the corresponding Fe–phC distance in half-sandwich-type $(B_6C)Fe$.[13] This suggests that a triple-decker $(C_5H_5)Fe(B_6C)Fe(C_5H_5)$ complex could be constructed by inserting a half-sandwich-type $(B_6C)Fe$ into a ferrocene molecule $(C_5H_5)Fe(C_5H_5)$. The middle-decker B_6C^{2-} in structure **2** acts as a bridge to link two half-sandwich-type $(C_5H_5)Fe$ together by forming two Fe–phC inter-

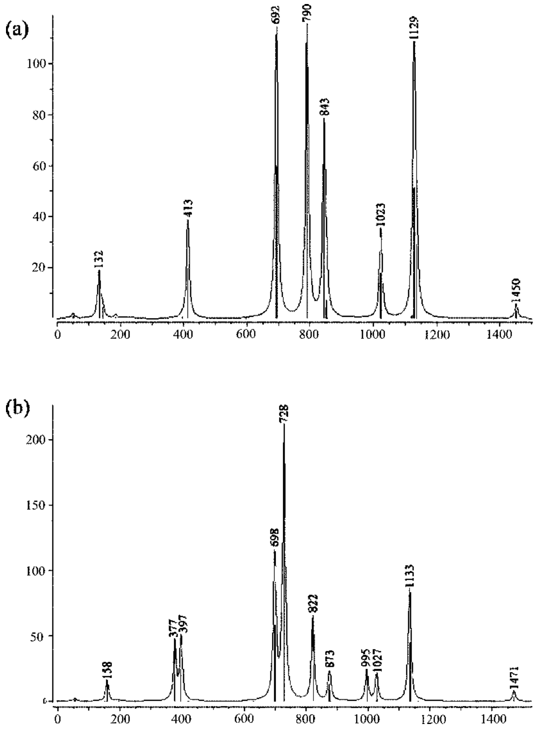


Figure 3. Calculated IR spectra (in cm^{-1}) of C_2 $(C_5H_5)Fe(B_6C)Fe(C_5H_5)$ (a) and C_2 $(C_6H_6)Mn(B_6C)Mn(C_6H_6)$ (b).

actions. Heavy transition-metal complexes $(C_5H_5)Ru(B_6X)Ru(C_5H_5)$ (X = C, B) with C_2 symmetries were confirmed to be transition states. With the C_2 symmetry constraints removed during structural optimization, these structures were slightly distorted to C_1 symmetries with the lowest frequencies ($\tilde{\nu}_{min}$) of 9 and 16 cm^{-1} for X = C and B, respectively.

A triple-decker $(C_6H_6)Mn(B_6C)Mn(C_6H_6)$ (**5**) with a phC center and two neutral C_6H_6 terminal ligands has the averaged bond lengths of $r_{Mn-C} = 2.104$ Å, $r_{Mn-phC} = 1.919$ Å, $r_{Mn-B} = 2.500$ Å, and $r_{B-B} = 1.603$ Å. The three ligands are almost perfectly parallel to one another and the Mn–C distances of 2.104 Å are well in line with the measured Cr–C distance of $r_{Cr-C} = 2.15$ Å in D_{6h} $(C_6H_6)_2Cr$. With two C_6H_6 terminal ligands, both phB and phN can be stabilized at the centers of the B_6X middle-deckers, as indicated in Figure 1 for structures **4** and **6**, which have bond lengths of $r_{Mn-phB} = 1.956$ Å and $r_{B-B} = 1.624$ Å in **4** and $r_{Mn-phN} = 1.871$ Å and $r_{B-B} = 1.618$ Å in **6**. A triple-decker $(C_6H_6)Re(B_6C)Re(C_6H_6)$ also turned out to be a stable singlet species with $\tilde{\nu}_{min} = 16$ cm^{-1}.

The stabilities of the phC-containing C_2 $(C_5H_5)Fe(B_6C)Fe(C_5H_5)$ and C_2 $(C_6H_6)Mn(B_6C)Mn(C_6H_6)$ are supported by the negative thermodynamic quantity changes of the following processes starting from stable reactants [Equation (1)].

$$(C_5H_5)_2Fe(D_5) + (B_6C)Fe(C_{6v}) = (C_5H_5)Fe(B_6C)Fe(C_5H_5)(C_2) \quad (1)$$

$$(C_6H_6)_2Mn^+(D_{6h}) + (B_6C)Mn^-(C_{6v}) = (C_6H_6)Mn(B_6C)Mn(C_6H_6)(C_2) \quad (2)$$

In Equation (2), the monocation $(C_6H_6)_2Mn^+$ with $\tilde{\nu}_{min} = 32$ cm^{-1} and monoanion $(B_6C)Mn^-$ with $\tilde{\nu}_{min} = 301$ cm^{-1} are isoelectronic with D_{6h} $(C_6H_6)_2Cr$ and C_{6v} $(B_6C)Fe$,[13] respectively. With ZPE corrections included, $\Delta E(1) = -124.8$, $\Delta H(1) = -122.8$, $\Delta G(1) = -87.1$, and $\Delta E(2) = -596.2$, $\Delta H(2) = -594.9$, $\Delta G(2) = -554.0$ kJ/mol. These negative values indicate that the desired products are favored in thermodynamics relative to the corresponding reactants. Detailed kinetic studies are beyond the reach of available computing resources at this stage.

NBO analyses indicate that all the component atoms in these complexes follow the octet rule. For example, atoms in $(C_5H_5)Fe(B_6C)Fe(C_5H_5)$ (**1**) possess the total Wiberg bond indices (WBIs) of $WBI_{phC} = 3.85$, $WBI_C = 3.96$, $WBI_B = 3.50$, $WBI_H = 0.94$, and $WBI_{Fe} = 2.98$, respectively. The middle-decker B_6C in the complex has the bond orders of $WBI_{B-B} = 1.14$ and $WIB_{B-phC} = 0.56$, well in line with the corresponding bond orders of $WBI_{B-B} = 1.29$ and $WIB_{B-phC} = 0.63$ in free B_6C^{2-}.[8] The slight bond-order difference is well compensated for by two extra phC–Fe interactions in vertical directions with $WBI_{phC-Fe} = 0.20$ and $WBI_{phC} = 3.85$ to satisfy the bonding requirement of the central carbon atom. It is also interesting to notice that the phC centers in $(C_5H_5)Fe(B_6C)Fe(C_5H_5)$ (**2**), $(C_5H_5)Ru(B_6C)Ru(C_5H_5)$ (**3**), and $(C_6H_6)Mn(B_6C)Mn(C_6H_6)$ (**5**) carry approximately unitary negative charges, with $q_{phC} = -0.96|e|$, $-1.02|e|$, and $-0.90|e|$, respectively. This implies that the phC centers possess approximately an extra electron in triple-decker complexes. It is this extra electron, which occupies the delocalized phC $2p_z$ orbital perpendicular to the B_6C middle-decker, that helps to stabilize the phC center in the complex (see Figure 2), similar to the situation of three sp^2 hybrids plus a doubly occupied $2p_z$ orbital in ptC-containing systems.[1,6d,9]

NBO analyses help to understand the bonding nature of these triple-decker structures. As indicated in Table 1, all these complexes possess negative HOMO energies and their HOMO–LUMO energy gaps are greater than 3.25 eV. Orbital coefficients and the MO pictures shown in Figure 2 indicate that both the degenerate HOMO(MO-79) and MO-77 of $(C_5H_5)Fe(B_6C)Fe(C_5H_5)$ mainly involve the contributions from Fe $3d_{xy}$ and $3d_{x^2-y^2}$, while MO-75, MO-70, and MO-64 are mostly composed of different interactions between Fe $3d_{z^2}$ and the delocalized π or σ orbitals of the B_6C^{2-} middle-decker. The degenerate MO-74 consists almost purely of the delocalized π orbital of the middle-decker B_6C^{2-}. Fe $3d_{xz}$ and $3d_{yz}$ orbitals mainly participate in the formations of the degenerate MO-72, MO-69, and MO-67, while MO-61, MO-56, and MO-51 originate almost purely from the out-of-phase or in-phase interactions between the totally delocalized π orbitals of the three parallel ligands (MO-51 also involves the in-phase contribution from Fe $3d_{z^2}$). It is these d–π and π–π interactions that work together to maintain the stabilities of these triple-decker structures. MO-80, the lowest unoccupied molecular orbital with a negative orbital energy of –2.18 eV, is mainly composed of the out-of-phase overlap between Fe $3d_{yz}$ and the delocalized π orbitals of the $C_5H_5^-$ ligands.

Frequency analyses indicate that the two strong IR absorptions of C_2 $(C_5H_5)Fe(B_6C)Fe(C_5H_5)$ at 692 cm^{-1} and 1129 cm^{-1} in Figure 3 (a) mainly originate from two in-plane vibrations of the phC center within the B_6 ring, while the other strong peak at 790 cm^{-1} corresponds to an off-plane movement of the phC center perpendicular to its B_6 ligand. The unsymmetrical off-plane swings of the 10 H atoms in C_5H_5 ligands produce the IR absorption at 843 cm^{-1} and their in-plane movements result in the absorption peak at 1023 cm^{-1}. The weak peak at 132 cm^{-1} is the result of the up-and-down movements of the B_6 ring along the molecular axis; meanwhile, the peak at 413 cm^{-1} corresponds to unsymmetrical swings of the two C_5H_5 ligands and the weakest peak at 1450 cm^{-1} originates from their in-plane twisting vibrations. As shown in Figure 3 (b), similar vibrational modes exist for C_2 $(C_6H_6)Mn(B_6C)Mn(C_6H_6)$, with the off-plane vibrational mode of the phC center shifted to 728 cm^{-1} while all the other absorption bands are basically maintained. The obvious correspondence in IR spectra between Figure 3a and Figure 3 (b) indicates that these complexes vibrate in similar vibrational modes that are closely related with the triple-decker geometries they possess.

Summary

In summary, planar hexacoordinate nonmetal centers following the octet rule have been stabilized in triple-decker complexes $(C_nH_n)M(B_6X)M(C_nH_n)$ (M = Fe, Ru, Mn, Re; X = B, C, N; n = 5, 6) in which the hexagonal B_6X middle-deckers are well maintained, the metal–ligand $(M–C_nH_n)$ distances possess normal M–C coordination bond lengths, and phX centers carry approximately unitary natural charges. It is the effective coordination interactions between the partially filled 3d orbitals of the transition-metal centers and the delocalized π orbitals of the three parallel ligands that help to stabilize these triple-decker structures. The strong IR absorptions of these complexes mainly originate from the in-plane and off-plane vibrational modes of their phX centers. As a complement to the initial proposal of B_6C^{2-},[8] this work has introduced phCs and other nonmetal centers phXs at the centers of inorganic B_6X middle-deckers to transition-metal triple-decker complexes, providing a possible new approach to synthesize phC-containing systems in future experiments.

Acknowledgments

This work was jointly supported by the Natural Science Foundation of China (No. 20573088) and Shanxi Natural Science Foundation (No. 20021029).

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Received: February 9, 2006