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 \((C_nH_n)M(B_6X)(C_nH_n)\) \((M = Fe, Ru, Mn, Re; X = B, C, N; n = 5, 6)\) containing almost perfect planar hexacoordinate carbon atoms and other planar hexacoordinate nonmetals at the centers of the \(B_6X\) middle-deckers. Effective \(d-\pi\) coordination interactions between the partially filled 3d orbitals of the transition-metal center and the delocalized \(\pi\) orbitals of the three parallel ligands maintain the stabilities of these triple-decker complexes. The strong IR absorption peaks of \((C_nH_n)M(B_6X)(C_nH_n)\) 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.

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**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 \(D_4h\) \(Al_4C^2\) \(\neq 5, 6\) containing almost perfect planar hexacoordinate carbon atoms 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 \(M_4H_4C\) \((M = Cu, Ni),[9] ppC in Cu_2H_2X\) \((X = B, C, N, O),[10] planar pentacoordinate silicon (ppSi) in \(M_3H_2X\) \((M = Pd, Pt; X = Si, Ge),[11] and planar hexacoordinate silicon (phSi) in Cu_3H_2X\) \((X = Si, Ge)\) 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 triply-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 \(C_6B_3\) 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 \(C_6H_5\) is a 6π-electron monoanion, to meet the 18-electron requirements of the two FeII centers, the most possible triple-decker structure of a dinuclear neutral \(C_6H_5Fe(B_6C)Fe(C_6H_5)\) would contain a \(B_6C^2\) middle-decker to balance the overall molecular charge of the system, while the two \(C_6H_5\) rings serve as terminal ligands, with the whole complex possessing a \(C_2\) symmetry. But a singlet \(C_2\) \((C_6H_5)Fe(B_6C)Fe(C_6H_5)\) 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,p) 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 C₅H₅⁻ terminal ligands are replaced with two neutral benzene molecules C₆H₆, two Mn⁺ 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 C₉(C₅H₅)Fe(B₆C)Fe(C₅H₅) involving Fe 3d orbitals and the delocalized π orbitals of the three parallel ligands and Figure 3 demonstrates the calculated IR spectra of C₉(C₅H₅)Fe(B₆C)Fe(C₅H₅) and C₉(C₅H₅)Mn(B₆C)Mn(C₅H₅) to facilitate future spectroscopic investigations. All the calculations in this work were performed using the Gaussian 03 program.[18]

Figure 1. Optimized structures of (C₅H₅)M(B₆X)M(C₅H₅) 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 νmin (cm⁻¹) indicated.

Table 1. Averaged bond lengths r [Å], M–phX–M bond angles θ, HOMO energies EHOMO [eV], HOMO–LUMO energy gaps ΔEgap [eV], and natural atomic charges qphX [e], and total Wiberg bond indices WBIphX of the phX centers of typical (C₅H₅)M(B₆X)M(C₅H₅) complexes at DFT-B3LYP level.

<table>
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<tr>
<th>(C₅H₅)M(B₆X)M(C₅H₅)</th>
<th>rM-C</th>
<th>rM-B</th>
<th>rM-phX</th>
<th>rB-B</th>
<th>θ</th>
<th>EHOMO</th>
<th>ΔEgap</th>
<th>qphX</th>
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<td>2.510</td>
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<td>1.624</td>
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<td>3.53</td>
<td>-0.68</td>
<td>3.92</td>
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<tr>
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<td>2.474</td>
<td>1.884</td>
<td>1.603</td>
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<td>2.464</td>
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<td>2.620</td>
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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 C₅H₅ terminal ligands rotating clockwise while the B₆X 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 (C₅H₅)₂Fe and (C₆H₆)₂Cr. But a singlet C₂ (C₅H₅)Fe(B₆N)Fe(C₅H₅)⁺ monocation turned out to be a transition state with one imaginary frequency at 62i cm⁻¹ (an up-and-down movement of the B₆ ring along the Fe–phN–Fe axis). Structural analyses indicate that the three quasiplanar ligands intervened by two Fe atoms in the prototypic C₂ (C₅H₅)Fe(B₆C)Fe(C₅H₅) 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 θFe–phC–Fe = 177.8° and the averaged bond lengths of rFe–C = 2.057 Å, rFe–B = 2.474 Å, rFe–phC = 1.884 Å, and rB–B = 1.603 Å. All the (C₅H₅)M(B₆X)–M(C₅H₅) complexes (M = Fe, Ru; X = B, C, N; n = 5, 6) possess very similar triple-decker structures featured with the B₆X 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 (rB–B ≈ rphX–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 B₆C²⁻.[8] The calculated Fe–C bond lengths of 2.057 Å in (C₅H₅)Fe(B₆C)Fe(C₅H₅) turned out to be very close to the corresponding measured values of 2.064 Å in ferrocene (C₅H₅)Fe(C₅H₅).[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 (B₆C)Fe.[13] This suggests that a triple-decker (C₅H₅)Fe(B₆C)Fe(C₅H₅) complex could be constructed by inserting a half-sandwich-type (B₆C)Fe into a ferrocene molecule (C₅H₅)Fe(C₅H₅). The middle-decker B₆C²⁻ in structure 2 acts as a bridge to link two half-sandwich-type (C₅H₅)Fe together by forming two Fe–phC inter-

Figure 2. Typical MO pictures of C₂ (C₅H₅)Fe(B₆C)Fe(C₅H₅) involving Fe 3d and the delocalized π orbitals of the three parallel ligands. For doubly degenerate orbitals, only one of them is depicted.
actions. Heavy transition-metal complexes \((\text{C}_6\text{H}_6)\text{Cr}\)–\(\text{B}_6\text{C}\)–\(\text{Cr}\text{C}_6\text{H}_6\) with \(\text{C}_2\) symmetries were confirmed to be transition states. With the \(\text{C}_2\) symmetry constraints removed during structural optimization, these structures were slightly distorted to \(\text{C}_1\) symmetries with the lowest frequencies (\(\nu_{\text{min}}\)) of 9 and 16 cm\(^{-1}\) for \(X = \text{C}\) and \(B\), respectively.

A triple-decker \((\text{C}_6\text{H}_6)\text{Mn} (\text{B}_6\text{C}) \text{Mn} (\text{C}_6\text{H}_6)\) (5) with a phC center and two neutral \(\text{C}_6\text{H}_6\) terminal ligands has the averaged bond lengths of \(r_{\text{Mn} - \text{C}} = 2.104\) Å, \(r_{\text{Mn} - \text{phC}} = 1.919\) Å, \(r_{\text{Mn} - \text{B}} = 2.500\) Å, and \(r_{\text{Mn} - \text{B}} = 1.603\) Å. The three ligands are almost perfectly parallel to one another and the \(\text{Mn} - \text{C}\) distances of 2.104 Å are well in line with the measured \(\text{Cr} - \text{C}\) distance of \(r_{\text{Cr} - \text{C}} = 2.15\) Å in \(D_{6h}(\text{C}_6\text{H}_6)_2\text{Cr}\). With two \(\text{C}_6\text{H}_6\) terminal ligands, both phB and phN can be stabilized at the centers of the \(\text{B}_6\text{X}\) middle-deckers, as indicated in Figure 1 for structures 4 and 6, which have bond lengths of \(r_{\text{Mn} - \text{phB}} = 1.956\) Å and \(r_{\text{Mn} - \text{B}} = 1.624\) Å in 4 and \(r_{\text{Mn} - \text{phN}} = 1.871\) Å and \(r_{\text{Mn} - \text{B}} = 1.618\) Å in 6. A triple-decker \((\text{C}_6\text{H}_6)\text{Re} (\text{B}_6\text{C}) \text{Re} (\text{C}_6\text{H}_6)\) also turned out to be a stable singlet species with \(\nu_{\text{min}} = 16\) cm\(^{-1}\).

The stabilities of the phC-containing \(\text{C}_2 (\text{C}_6\text{H}_6)\text{Fe} (\text{B}_6\text{C})\)–\(\text{Fe} (\text{C}_6\text{H}_6)\) and \(\text{C}_2 (\text{C}_6\text{H}_6)\text{Mn} (\text{B}_6\text{C}) \text{Mn} (\text{C}_6\text{H}_6)\) are supported by the negative thermodynamic quantity changes of the following processes starting from stable reactants [Equation (1)].

\[
(\text{C}_6\text{H}_6)_2\text{Fe}(\text{D}_\text{ex}) + (\text{B}_6\text{C})\text{Fe}(\text{C}_\text{ex}) = (\text{C}_6\text{H}_6)\text{Fe}(\text{B}_6\text{C})\text{Fe}(\text{C}_6\text{H}_6)(\text{C}_2) \tag{1}
\]

\[
(\text{C}_6\text{H}_6)_2\text{Mn} (\text{D}_\text{ex}) + (\text{B}_6\text{C})\text{Mn} (\text{C}_\text{ex}) = (\text{C}_6\text{H}_6)\text{Mn}(\text{B}_6\text{C})\text{Mn}(\text{C}_6\text{H}_6)(\text{C}_2) \tag{2}
\]

In Equation (2), the monocation \((\text{C}_6\text{H}_6)_2\text{Mn}^+\) with \(\nu_{\text{min}} = 32\) cm\(^{-1}\) and monooanion \((\text{B}_6\text{C})\text{Mn}^-\) with \(\nu_{\text{min}} = 301\) cm\(^{-1}\) are isoelectronic with \(D_{6h}(\text{C}_6\text{H}_6)_2\text{Cr}\) and \(C_{6v}(\text{B}_6\text{C})\text{Fe}\)[13] respectively. With ZPE corrections included, \(\Delta E (1) = -124.8\), \(\Delta H (1) = -122.8\), \(\Delta G (1) = -87.1\), and \(\Delta E (2) = -396.2\), \(\Delta H (2) = -394.9\), \(\Delta G (2) = -554.0\) 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 \((\text{C}_6\text{H}_6)\text{Fe} (\text{B}_6\text{C})\text{Fe} (\text{C}_6\text{H}_6)\) (1) possess the total Wiberg bond indices (WBI)s of WBIphC = 3.85, WBIphN = 3.96, WBIphB = 3.50, WBIphFe = 2.98, respectively. The middle-decker \(\text{B}_6\text{C}\) in the complex has the bond orders of WBIphB = 1.14 and WIBphFe = 0.56, well in line with the corresponding bond orders of WBIphB = 1.29 and WIBphFe = 0.63 in free \(\text{B}_6\text{C}^2\)–[8]. The slight bond-order difference is well compensated for by two extra phC–Fe interactions in vertical directions with WBIphC=Fe = 0.20 and WBIphFe = 3.85 to satisfy the bonding requirement of the central carbon atom. It is also interesting to notice that the phC centers in \((\text{C}_6\text{H}_6)\text{Fe} (\text{B}_6\text{C})\text{Fe} (\text{C}_6\text{H}_6)\) (2), \((\text{C}_6\text{H}_6)\text{Ru} (\text{B}_6\text{C})\text{Ru} (\text{C}_6\text{H}_6)\) (3), and \((\text{C}_6\text{H}_6)\text{Mn} (\text{B}_6\text{C}) \text{Mn} (\text{C}_6\text{H}_6)\) (5) carry approximately unitary negative charges, with \(\eta_{\text{phC}} = -0.96|e|, -1.02|e|, -0.90|e|\), 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 orbital perpendicular to the \(\text{B}_6\text{C}\) 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 orbital in ptC-containing systems[1,6,4,9].

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 \((\text{C}_6\text{H}_6)\text{Fe}(\text{B}_6\text{C})\text{Fe}(\text{C}_6\text{H}_6)\) mainly involve the contributions from Fe 3d\(\pi\), and 3d\(\sigma\)\(\pi\), while MO-75, MO-70, and MO-64 are mostly composed of different interactions between Fe 3d\(\pi\), and the delocalized \(\sigma\) or \(\sigma\) orbital s of the \(\text{B}_6\text{C}\)––middle-decker. The degenerate MO-74 consists almost purely of the delocalized \(\pi\) orbital of the middle-decker \(\text{B}_6\text{C}^2\). Fe 3d\(\pi\), and 3d\(\sigma\)\(\pi\) 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 \(\pi\) orbitals of the three parallel ligands (MO-51 also involves the in-phase contribution from Fe 3d\(\pi\)). It is these \(\pi\) and \(\sigma\)–\(\pi\) 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\(\pi\) and the delocalized \(\pi\) orbitals of the \(\text{C}_6\text{H}_6\)–ligands.
Frequency analyses indicate that the two strong IR absorptions of \( C_2 (C_6H_7)Fe(B_6C)Fe(C_6H_7) \) 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\(_3\)H\(_3\) 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\(_5\)H\(_5\) 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\(_6\)H\(_7\))Mn(B\(_6\)C)Mn(C\(_6\)H\(_7\)), 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\(_n\)H\(_n\))M(B\(_n\)X)M(C\(_n\)H\(_n\)) (M = Fe, Ru, Mn, Re; X = B, C, N; \( n = 5, 6 \)) in which the hexagonal B\(_n\)X middle-deckers are well maintained, the metal–ligand (M–C\(_n\)H\(_n\)) 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 \( \pi \) 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\(_n\)C\(^2\) [9] this work has introduced phCs and other nonmetal centers phXs at the centers of inorganic B\(_n\)X middle-deckers to transition-metal-triple-decker complexes, providing a possible new approach to synthesize phC-containing systems in future experiments.

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**References**


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