Understanding Nonplanarity in Metallabenzene Complexes

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The nonplanarity found in metallabenzene complexes has been investigated theoretically via density functional theory (DFT) calculations. A metallabenzene has four occupied π molecular orbitals (8 π electrons) instead of three that benzene has. Our electronic structure analyses show that the extra occupied π molecular orbital, which is the highest occupied molecular orbital (HOMO) in many metallabenzenes, has antibonding interactions between the metal center and the metal-bonded ring-carbon atoms, providing the electronic driving force toward nonplanarity. Calculations indicate that the electronic driving force toward nonplanarity, however, is relatively small. Therefore, other factors such as steric effects also play important roles in determining the planarity of these metallabenzene complexes. In this paper, how the various electronic and steric factors interplay has been discussed.

Introduction

Metallabenzenes, organometallic compounds formed by formal replacement of a CH group in benzene by an isolobal transition metal fragment, were first considered theoretically by Hoffman et al. in 1979.[1] Since the isolation of the first stable osmabenzenes by Roper's group in 1982,[2] metallabenzene complexes have attracted considerable interest over the last quarter century. Experimentally, research efforts have so far led to the synthesis and characterization of numerous metallabenzene complexes.[3] Examples of structurally characterized metallabenzene complexes are given in Figure 1.[4−16] Theoretically, there are also efforts to understand the chemistry of metallabenzene complexes. For example, the formation mechanism and chemical reactivity of metallabenzene complexes have been extensively studied.[17]

In the studies of metallabenzene complexes, a central issue concerns the π-conjugation of the six-membered metal-containing ring. Indeed, it is true that metallabenzene complexes are highly conjugated in view of the fact that the single−double bond alternation is insignificant in the six-membered metal-containing ring for the majority of the complexes. Although the structures illustrated in Figure 1 show the single−double bond alternation patterns, we hope that readers will not take them literally. The single−double bond alternation patterns are drawn for convenience as we normally do for benzene. While it is generally believed that metallabenzene complexes are highly conjugated systems, it is interesting to note that in many of these complexes the six-membered metal-containing ring deviates appreciably from planarity; that is, the metal center is significantly displaced out of the ring plane (Figure 2). The nonplanarity is quite unexpected because conjugation normally requires planar arrangement. When we use the two dihedral angles (D1 and D2 shown in Figure 1) around the two metal−carbon bonds in the six-membered metal-containing ring as the measure of planarity, we can see that nonplanarity is significant in many of these complexes, although there are still more than half of the complexes with approximately planar six-membered metal-containing rings. In a previous work,[4] we briefly discussed the nonplanarity found in a few osmabenzene complexes and suggested that the nonplanarity is likely due to electronic reasons. In this article, we attempt to analyze the structure and bonding in detail for a wide range of metallabenzene complexes and to understand the nonplanarity with the aid of density

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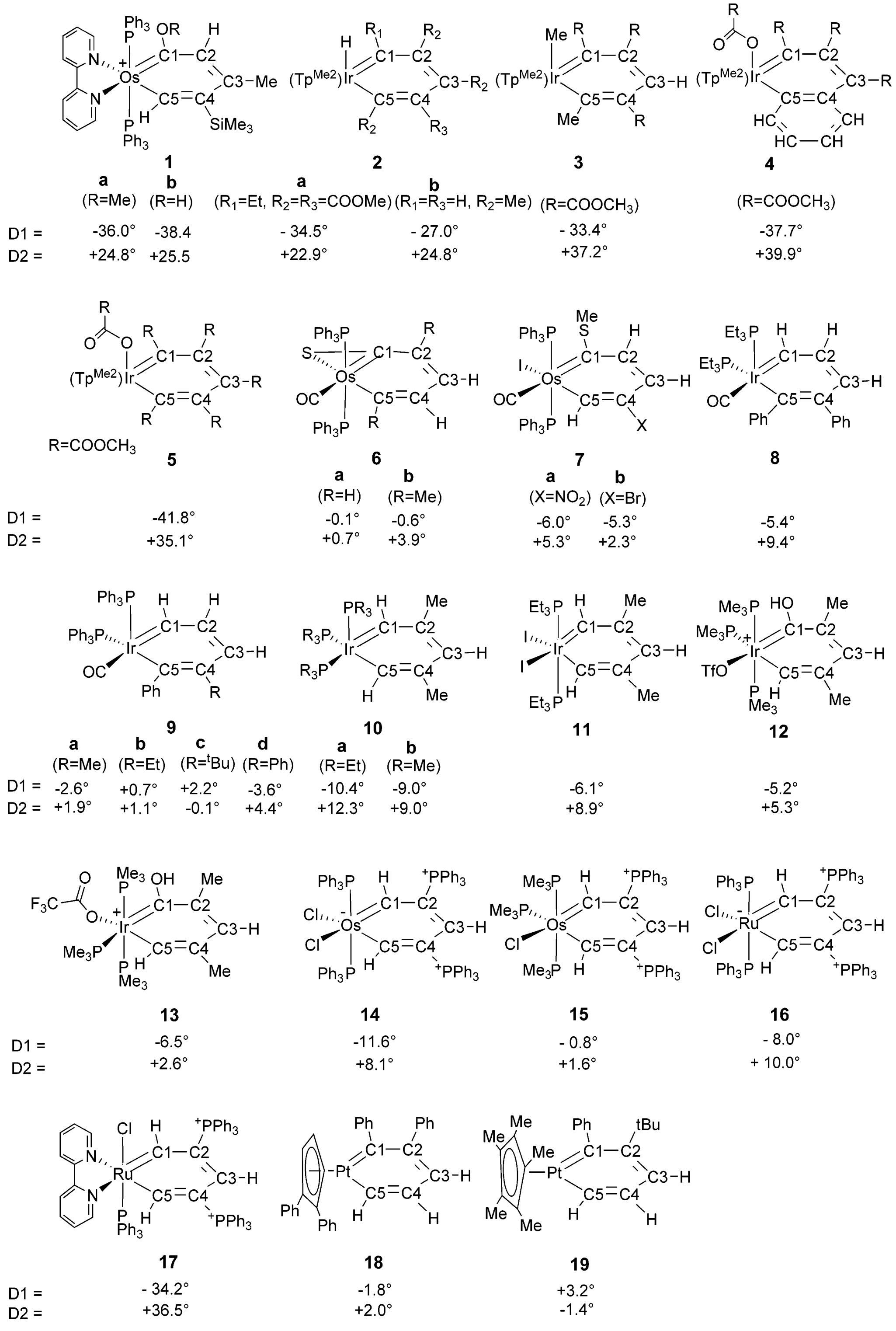

Figure 1. Structurally characterized metallabenzene complexes. D1 and D2 stand for the dihedral angles of C2−C1−M−C5 and C4−C5−M−C1, respectively.

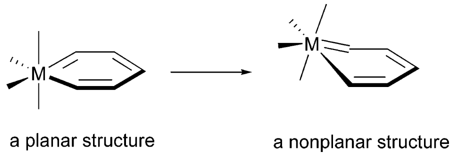

Figure 2. Nonplanarity observed in many metallabenzene complexes given in Figure 1.

functional theory calculations. We hope to answer the following questions. Is there an electronic reason for the nonplanarity in general? How do other forces, such as steric forces, interact with the electronic forces in determining the nonplanarity observed in the class of metal complexes?

Computational Details

All structures of model metallabenzene complexes were optimized at the mPW1K[18] level of density functional theory. The

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mPW1K level of theory has been proved to provide reliable results on the structures and energetics in the calculations of metallabenzene complexes.[17] Frequency calculations at the same level of theory have also been performed to confirm that all stationary points were minima (no imaginary frequencies). The Stuttgart/Dresden effective core potentials[19] were used to describe Pt, Ru, Os, Ir, P, Si, S, I, Br, and Cl atoms, while the standard 6-31G basis set was used for C, N, B, O, and H atoms. Polarization functions were added for Pt (ζ(f) = 0.883), Ru (ζ(f) = 1.072), Os (ζ(f) = 0.707), and Ir (ζ(f) = 0.792) as well as Cl (ζ(d) = 0.514), Br (ζ(d) = 0.389), I (ζ(d) = 0.266), Si (ζ(d) = 0.262), S (ζ(d) = 0.421), N (ζ(d) = 0.8), C (ζ(d) = 0.8), and P (ζ(d) = 0.34) that are directly bonded to the metal center.[17,20] All calculations were performed with the Gaussian 03 software package.[21] Molecular orbitals obtained from the mPW1K calculations were plotted using the Molden 3.7 program written by Schaftenaar.[22] The natural bond orbital (NBO) program,[23] as implemented in Gaussian 03, was also used to obtain Wiberg bond indices (bond orders),[24] which are a measure of bond strength.

Results and Discussion

Calculated Structures versus Experimental Ones. Figure 3 shows selected examples of the calculated model complexes. In the model complexes, PH_3 was used as model phosphines. For easy comparison, the numbering scheme for the model complexes follows closely the one used in Figure 1. We added the symbol "prime" to differentiate them from the experimental complexes. Clearly, the calculated geometries of the model complexes reproduce well most of the experimentally determined complexes. In particular, the planarity and nonplanarity are also well reproduced.

Electronic Structures of Metallabenzenes with an Octahedral Metal Center. All the known metallabenzene complexes have an 18e configuration around the metal centers. Therefore the term "metallabenzenes" discussed below will refer to such species. The majority of the metallabenzene complexes shown in Figure 1 contain an octahedral metal center with an ML_4, ML_3X, or ML_2X_2 metal fragment. Before the discussion of the factors influencing the planarity for metallabenzene complexes, it is necessary to understand how the metal d orbitals interact with the p_π orbitals from the five carbons in the six-membered metal-containing ring. To achieve this understanding, we designed an orbital interaction diagram shown in Figure 4. Instead of following the conventional approach that considers the orbital interaction between an ML_4, ML_3X, or ML_2X_2 metal fragment and a C_5H_5 organic moiety, we derived the molecular orbitals for a metallabenzene complex by first considering the benzene-like π molecular orbitals. In an octahedral metal center, the metal orbitals available for orbital interaction with the p_π orbitals from the five carbons in the six-membered metal-containing ring are the "t_{2g}" orbitals of the metal fragment. Note that the traditional "t_{2g}" orbitals refer to d_{xz}, d_{yz}, and d_{xy}. Here, the "t_{2g}" orbitals refer to d_{xz}, d_{yz}, and $d_{x^2-y^2}$ because of the choice of the axes (Figure 4). For comparison, Figure 4a shows the six π molecular orbitals of benzene. The left column of Figure 4b shows the six benzene-like molecular orbitals for the six-membered metal-containing ring that incorporates the symmetry-adapted d_{yz} orbital, one of the "t_{2g}" orbitals of the metal fragment, from the metal center. The six benzene-like molecular orbitals are derived simply by substituting one of the carbon p_π orbitals with d_{yz} (see the far right of Figure 4 for the Cartesian coordinates). The central column of Figure 4b shows the resulting d and π molecular orbitals of a metallabenzene complex that are derived from the orbital interaction between the six benzene-like molecular orbitals and the remaining two d orbitals (d_{xz} and $d_{x^2-y^2}$) of the "t_{2g}" set. The π_1, π_3, π_5, and π_7 molecular orbitals shown in the central column of Figure 4b are simply from the benzene-like molecular orbitals. The $d_{x^2-y^2}$ orbital remains nonbonding because no symmetry-adapted orbitals can be found from the benzene-like molecular orbitals. The π_2, π_4, and π_6 molecular orbitals are derived from the orbital interactions between two benzene-like molecular orbitals and d_{xz}.

Comparing the π molecular orbitals of a metallabenzene with those of benzene, we can see that a metallabenzene has seven π molecular orbitals. Because the metal fragment has two d orbitals (d_{xz}, d_{yz}) having π symmetry with respect to the ring plane, a metallabenzene has one more π molecular orbital than benzene does. Therefore, different from benzene, a metallabenzene with a metal center of 18 valence electron count has four occupied π molecular orbitals (8 π electrons) instead of three. Among the four occupied π molecular orbitals, three (π_1, π_2, and π_3) have bonding interactions between the metal center and the metal-bonded ring-carbon atoms and one (π_4), which is the highest occupied molecular orbital (HOMO) in many 18e metallabenzene complexes, has an antibonding interaction between the metal center and the metal-bonded ring-carbon atoms. As will be discussed below, it is these different characteristics that make metallabenzene complexes unique; that is, nonplanarity is often found in metallabenzenes but rarely seen in benzene and its derivatives.

Driving Forces toward Nonplanarity. As mentioned above, a metallabenzene has four occupied π molecular orbitals: three (π_1, π_2, π_3) are bonding between the metal center and the metal-bonded ring-carbon atoms and one (π_4) is antibonding. A planar geometry maximizes the bonding interactions in the three π-bonding molecular orbitals (π_1, π_2, π_3) and at the same time maximizes the antibonding interaction in the antibonding orbital (π_4). In contrast, a nonplanar geometry could reduce the antibonding interaction in the π_4 orbital and the bonding interactions in the π_1, π_2, and π_3 orbitals. Therefore, when the π_4 molecular orbital shown in Figure 4b is the HOMO, there will be an electronic driving force toward nonplanarity because the HOMO π_4 should have a greater impact than the other three π orbitals (π_1, π_2, and π_3). In other words, when the HOMO corresponds to the π_4 molecular orbital shown in Figure 4b, a nonplanar geometry could reduce the antibonding interaction in the HOMO between the metal center and the metal-bonded ring-carbon atoms, giving rise to extra stability. However, in consideration of the opposite effects of the three π-bonding molecular orbitals and the antibonding orbital on the planarity, we expect that the electronic driving force toward nonplanarity is not very large.

The electronic driving force toward nonplanarity can be illustrated by calculations of the model complexes **A**−**F** (Scheme 1). The model complexes **A**−**C** are derived from metallabenzene complex **1** (Figure 1), which has a nonplanar structure. Calculations show that the metallacycles of the model

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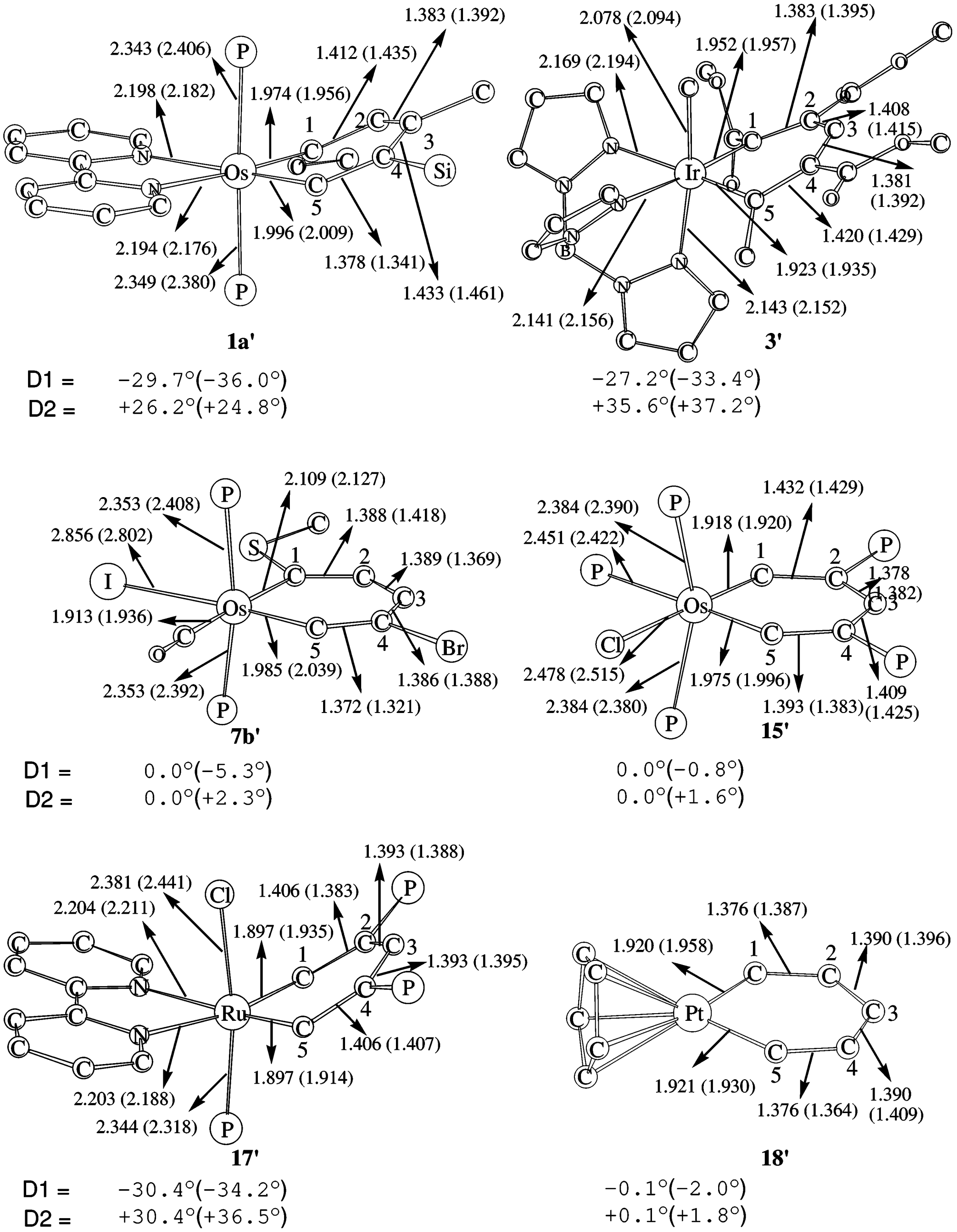


1a'
D1 = −29.7°(−36.0°)
D2 = +26.2°(+24.8°)

3'
−27.2°(−33.4°)
+35.6°(+37.2°)

7b'
D1 = 0.0°(−5.3°)
D2 = 0.0°(+2.3°)

15'
0.0°(−0.8°)
0.0°(+1.6°)

17'
D1 = −30.4°(−34.2°)
D2 = +30.4°(+36.5°)

18'
−0.1°(−2.0°)
+0.1°(+1.8°)

Figure 3. Comparison between calculated and experimental (in parentheses) structural parameters (bond lengths in angstroms). The dihedral angles D1 and D2 were defined in Figure 1. In the model complexes presented here, PH_3 models PR_3 and the symbol "prime" is added in the label of each of the complexes to differentiate the model complexes from the experimental complexes presented in Figure 1. For clarity, all the hydrogen atoms associated with ligands and metallabenzene rings are omitted.

complexes **A**−**C**, which contain pure σ donors (**A**) or a weakly π-accepting ligand (**B**, **C**) or π donor (**F**), deviate significantly from a planar geometry. In contrast, metallacycles of complexes with strong π-accepting ligands (CO, **D**; PF_3, **E**) are almost planar. These results are exactly expected on the basis of the electronic structure analyzed above. As discussed above, the electronic driving force toward nonplanarity comes from the fact that the occupied molecular orbital π_4 has an antibonding interaction between the metal center and the metal-bonded ring-carbon atoms. A strong π-accepting ligand, such as carbonyl or PF_3, should be able to take away electron density from the d_{xz} orbital (Figure 4) that is used to form the orbital π_4, reducing the antibonding interaction between the metal center and the metal-bonded ring-carbon atoms. Therefore, the presence of carbonyl ligand(s) in the metallabenzene complexes could reduce the tendency toward nonplanarity. One might expect that halide ligands, which are π donor ligands, increase the nonplanarity. The dihedral angles in the model osmium complex **F** are only slightly larger than those of model osmium complex **A**, suggesting that the electronic effect of the π donor chloride ligands is quite limited. The σ-withdrawing properties of the halide ligands seem dominant. More examples showing the limited effect of π donor ligands will be further discussed later.

Careful analysis of the calculated structures suggests that the electronic effect is not the only factor contributing to the nonplanarity. The dihedral angles D1 and D2 of the model complex **A** are calculated to be −20.6° and +20.6°, respectively. Calculation of the model complex **B** (a complex closely related to **1**) gives greater nonplanarity with the dihedral angles D1 and D2 of −27.1° and 27.4°, respectively, although bipyridine is a better π acceptor than NH_3. Examining the calculated model complex **B**, we found that there are close contacts between C1-

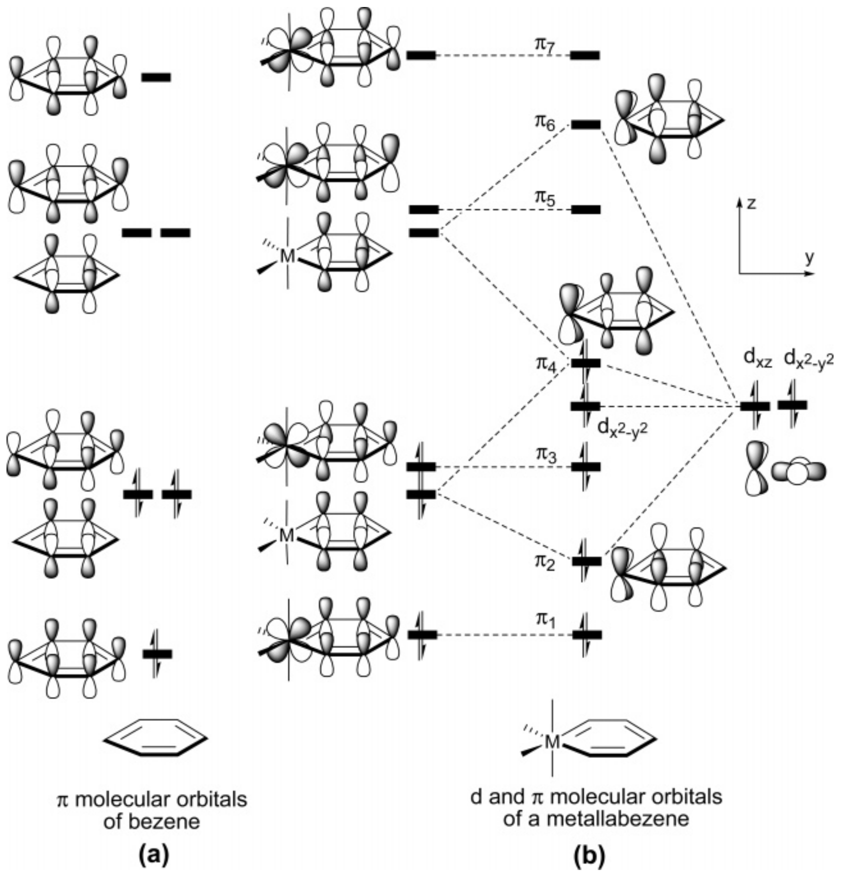
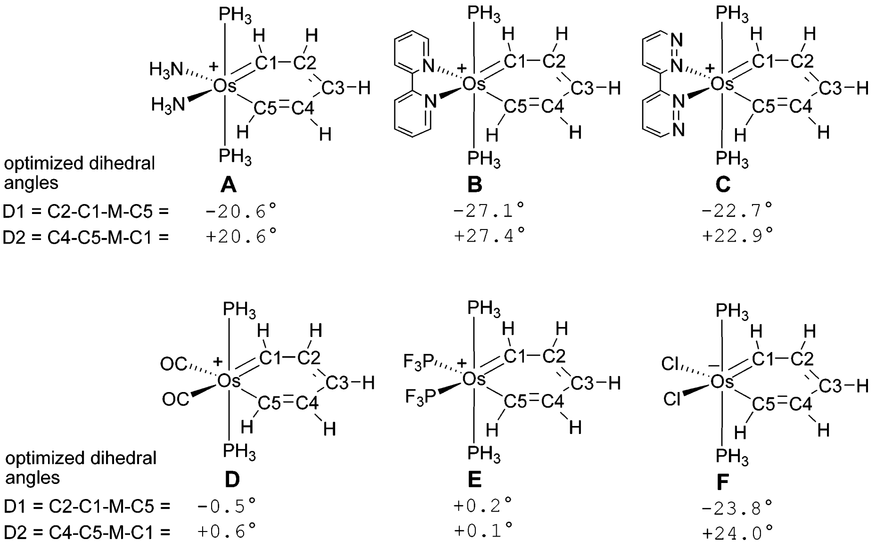


Figure 4. (a) Six π molecular orbitals of benzene. (b) Orbital interaction between the six benzene-like molecular orbitals and the remaining two d orbitals (d_{xz} and $d_{x^2-y^2}$) from the "t_{2g}" set of the metal center for a given metallabenzene complex.

Scheme 1



H/C5-H and the ortho C−H bonds of the bipyridine ligand. Therefore, we believe that the steric repulsive interaction from the close contacts also increases the nonplanarity. The result of the calculations of the model complex **C** supports the steric argument, giving smaller dihedral angles (Scheme 1).

Magnitude of the Driving Force toward Nonplanarity. It is clear that both electronic and steric effects can contribute to the nonplanarity of metallabenzenes. One may wonder what the magnitude of the driving force is. To do this, we calculated the potential energy surface showing the change in the relative energy with respect to the bending of the metal center away from the ring plane for the model complex **A** (Scheme 1), shown in Figure 5a. The fully optimized structure of the model complex **A** corresponds to a nonplanar geometry with the dihedral angles D1 and D2 being −20.6° and +20.6°, respectively (Scheme 1). Although the nonplanarity is quite significant in the model complex **A**, the energy difference between the fully optimized structure and the planar structure, which was obtained with a partial geometry optimization by fixing both D1 and D2 at 0°, is only ca. 0.7 kcal/mol, suggesting that the driving force is not large. For a benzene molecule, a partially optimized nonplanar structure with the corresponding D1 and D2 being fixed at −20.0° and +20.0°, respectively, is calculated to be higher in energy by 4.1 kcal/mol than the fully optimized structure. When

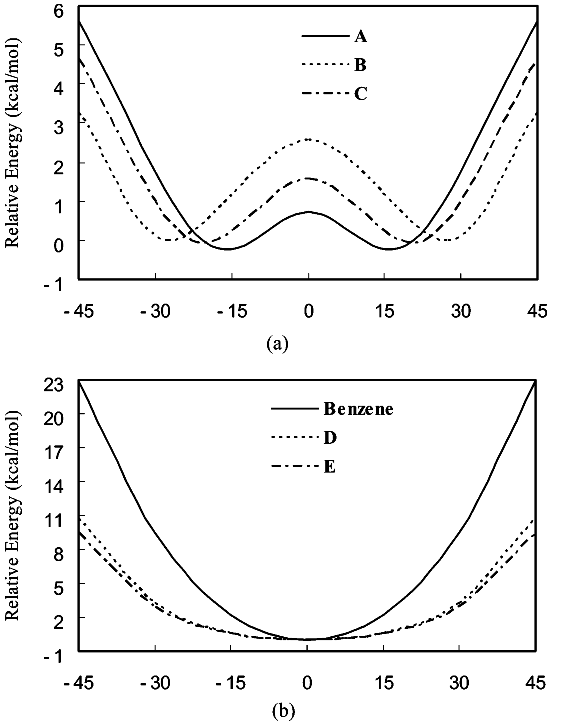


Figure 5. Potential energy surface for the model complexes **A**, **B**, and **C** (a) and **D**, **E**, and benzene (b) shown in Scheme 1, showing the change in the relative energy with respect to the dihedral angle D1 or D2 (deg) defined in Figure 1. In the partial geometry optimizations to obtain energies for structures that do not correspond to the minima, we let D2 = −D1.

the dihedral angles are fixed at −30.0° and +30.0°, the partially optimized structure is higher in energy by 9.5 kcal/mol than the fully optimized structure.

Following the same method as we did for the model complex **A**, we estimated the magnitude of the driving force toward nonplanarity for the model complexes **B** and **C**. We calculated the potential energy surfaces showing the change in the relative energy with respect to the bending of the metal center away from the ring plane for the model complexes **B** and **C**, also shown in Figure 5a. The energy difference between the assumed planar geometry and the fully optimized nonplanar geometry is calculated to be ca. 2.6 kcal/mol for **B** and 1.6 kcal/mol for **C**. As expected, the model complex **B** due to the additional repulsive interaction from closely contacted CH bonds has the greatest driving force toward nonplanarity.

Using the same method, we calculated the energy cost to distort a stable planar geometry to a nonplanar geometry for the model complexes **D** and **E** (Figure 5b). Both the model complexes **D** and **E** have a stable planar geometry (Scheme 1). We can see from Figure 5b that the energy change is also insignificant for both the model complexes **D** and **E** at least in the range of the dihedral angles (D1 or D2) from −30.0° to +30.0°, manifesting the effect of the π_4 antibonding orbital in metallabenzenes. In contrast, benzene shows a drastic change in the energy with respect to distortion toward nonplanarity (Figure 5b).

General Considerations. The results discussed in the preceding subsection suggest that both electronic and steric effects contribute to the nonplanarity of metallabenzenes and that the electronic driving force toward nonplanarity is relatively small.

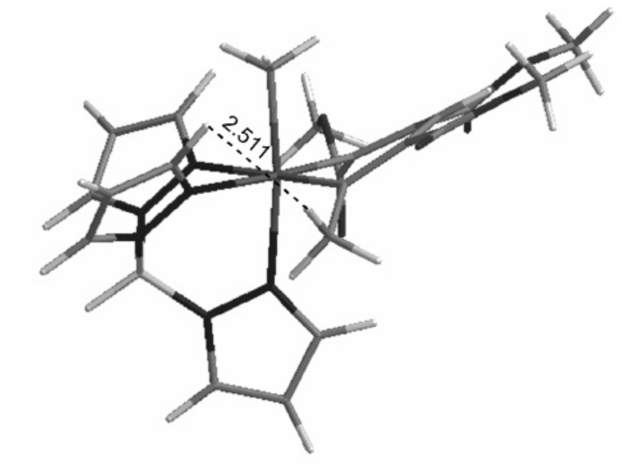
Because the driving force toward nonplanarity is small, we will not be able to see a general picture regarding the nonplanrity for the whole class of metallabenzene complexes given in Figure 1. A minor change in the ligand environment could switch a nonplanar geometry to a planar one or from a planar geometry to a nonplanar one. With this in mind, the observation from the examples shown in Figure 1 becomes readily acceptable that some of the metallabenzene complexes adopt a planar geometry and some do not.

In the following subsections, we will see from our discussion on specific examples that electronic and steric factors could show either the same effect, which increases the nonplanarity, or the opposite effects, which reduce the nonplanarity to give a planar geometry.

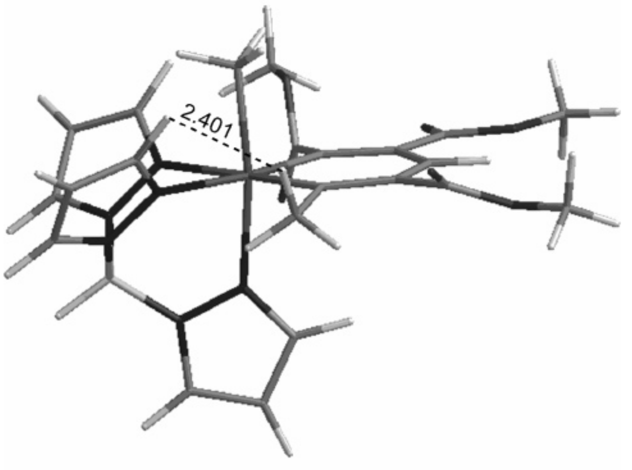
Metallabenzenes Containing Hydrotris(pyrazolyl)borate Ligands. The metallabenzene complexes **2**−**5** contain the hydrotris(3,5-dimethylpyrazolyl)borate ($\mathrm{Tp}^{\mathrm{Me2}}$) ligand, and all have a significant nonplanar metallacycle (Figure 1). In these complexes, the $\mathrm{Tp}^{\mathrm{Me2}}$ ligand, similar to the bipyridine ligand in **1**, is neither a π donor nor a π accepter ligand. The hydride ligand in **2** and the methyl ligand in **3** are also π neutral. The acetate ligand in **4** and **5** is only a weak π donor ligand because of the carbonyl group. Therefore, the bonding characteristics in these complexes should be similar to those in **1**, which were discussed above. We mentioned above that the close contacts between C1-H/C5-H and the ortho C−H bonds of the bipyridine ligand increase nonplanarity in the model complex **B** and the metallabenzene complexes **1**. In the metallabenzene complexes **2**−**5**, there are also similar close contacts. Figure 6 shows the H−H close contact in a perspective view of the calculated (fully optimized) model metallabenzene complex **3′**. It should be noted here that the calculated geometry for the model metallabenzene complex **3′** reproduces well the geometry of the experimental complex **3** as discussed above. From Figure 6, we can see that in a planar geometry the repulsive interaction due to the close contact becomes more severe (see the partially optimized structure).

Different from **1**, these complexes (**2**−**5**) have an unsymmetrical ligand environment above and below the six-membered metal-containing ring, creating an unsymmetrical steric environment and increasing the nonplanarity. The X-ray crystal structures of these complexes indicate that the metal center is displaced out of the ring plane in such a way that the metal-hydride, the metal-methyl, or the metal-acetate moiety moves toward the five ring carbons. Clearly, the direction of the displacement of the metal center is governed by the repulsive interaction due to the close contact.

The above analysis suggests that the deviation from planarity in these complexes is related to both electronic and steric effects. Scheme 2 shows more examples to further illustrate the effects. The model complex **G**, which does not contain non-hydrogen substituents on the Tp ligand and the metallabenzene ring, also shows a nonplanar geometry. The nonplanarity in the model complex **G** is less significant than that in the metallabenzene complex **3** and the model complex **3′**. The result further supports the steric argument given above because the substituents at C(1) and C(5) of the metallabenzene ring in the model complex **G** are hydrogen atoms, which have much less steric effect than the substituents in both the metallabenzene complex **3** and the model complex **3′**. In the model complexes **H** and **I**, we replaced the relevant C−H bond(s) with N. The model complex **H** gives smaller dihedral angles than the model complex **G**, implying the importance of the steric interaction caused by the substituents at those positions of a Tp ligand. The dihedral angles in the model complex **I** are not very different from those in the model complex **G**. These results suggest that the steric effects of the nearest C−H bonds on the three pyrazolyl rings of the Tp



fully optimized structure



partially optimized structure
(fixing the planar metallabenzene ring)

Figure 6. Perspective view of the calculated model complex **3′** showing the close contact (Å) between a C−H bond from the Tp ligand and a C−H bond of the methyl substituent at the C(5) carbon of the metallabenzene ring.

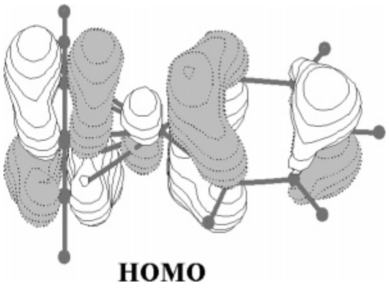


Figure 7. HOMO calculated for the model complex **18′**.

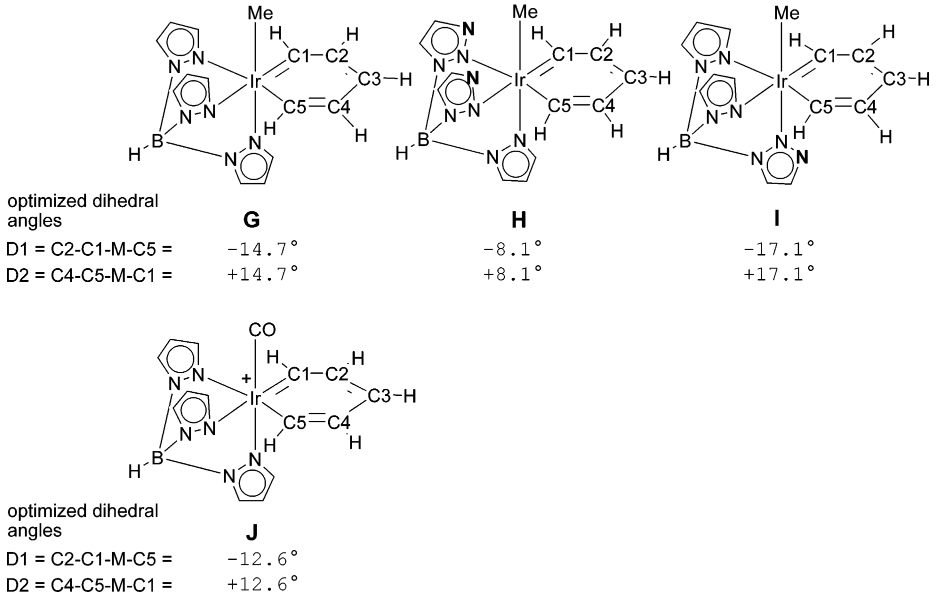
ligands are different. As expected, the dihedral angles in the model complex **J** are smaller than those of model complex **G**. However, the difference is small, suggesting that the electronic effect of the π-accepting carbonyl ligand is quite limited in this case. The results suggest that the effect caused by the Tp ligand, which was discussed above, is much greater than the effect of the π-accepting carbonyl ligand. In the metallabenzene complexes **6**−**9**, Tp and bipyridine ligands, which can significantly increase the nonplanarity, are absent. Therefore, the electronic effect of the π-accepting carbonyl ligand in these complexes dictates.

Metallabenzenes Containing Carbonyl Ligand(s). Each of the metallabenzene complexes **6**−**9** contains a carbonyl ligand. All of these complexes have an approximately planar metallacycle, suggesting that the electronic effect of the π-accepting carbonyl ligand is important in these four complexes. As discussed above, the presence of carbonyl ligand(s) in the metallabenzene complexes (**6**−**9**) reduces the tendency toward nonplanarity. The X-ray crystal structures observed in the metallabenzene complexes **6**−**9** (Figure 1) manifest the importance of the carbonyl ligand in these approximately planar structures. The calculated model complex **7b′** with the SMe substituent at the C1 atom shows a good agreement with the corresponding experimental structure (Figure 3).

Metallabenzene Complex 10. The metallabenzene complex **10** is closely related to complexes **8** and **9**. However, its dihedral angles D1 and D2 are slightly larger, which might be expected since PR_3 is not as good as CO as a π acceptor. The metal center is displaced out of the ring plane in such a way that the axial $Ir-PR_3$ moves away from the five ring carbons to avoid the steric repulsion. Clearly, the unsymmetrical steric environment above and below the metallabenzene ring plane determines the direction of the displacement of the metal center. It should be pointed out that Bleeke, Martin, and their co-workers have also examined the cause of the slight deviation of the metal center from the six-membered ring plane for this complex.[3b,17a] This complex, similar to **8** and **9**, has a square-pyramidal 18e metal center. The metal d_{z^2} orbital is completely filled. Bleeke, Martin, and their co-workers found that a slight deviation of the metal center from the ring plane also allows a bonding interaction between the filled metal d_{z^2} orbital and the empty π orbital of the carbon ligand formed by the five ring carbons. Here, the *z*-axis is defined along the direction perpendicular to the ring plane.

Metallabenzene Complexes 11−**13.** The iridium complex **11** (a formally Ir(III) complex), which has two iodide ligands, is structurally closely related to the osmium model complex **F** (a formally Os(II) complex). While the osmium model complex **F** shows nonplanarity, it is interesting to see that the X-ray crystal structure of the metallabenzene complex **11** shows an approximately planar structure (Figure 1). In an approximate agreement with the experimental structure, the calculation on **K**, a model complex of **11**, gives a perfectly planar structure (Scheme 3). Replacing the two iodide ligands with two chloride ligands gives the model complex **L**. The calculation on **L** also gives a planar structure. In the discussion of the model osmium complex **F**, we have noted that the electronic effect of the π donor ligand is quite limited. Thus, the reason why the metallabenzene complex **11** shows better planarity than the model osmium complex **F** is likely related to the fact that the d orbitals of Ir(III) are relatively more contracted than those of Os(II). The contractedness of the metal d orbitals makes its orbital overlap with ligands small, reducing the antibonding interaction in the π_4 orbital and leading to the planarity observed in these complexes. Indeed, the average bond order of the M−C1 and M−C5 bonds (M: metal) is calculated to be 0.985 and 0.770, respectively, for the model complexes **F** (Scheme 1) and **L** (Scheme 3), supporting the argument above that the Ir(III) d orbitals have smaller orbital overlap with ligands than the Os(II) d orbitals. Moreover, the steric effect exerted by bulky phosphine ligands occupying symmetrically the two ligand coordination sites above and below the ring plane of **11** is expected to provide a counter effect for nonplanarity. More discussion on this counter effect will be given later. The metallabenzene complexes **12** and **13** are cationic species and

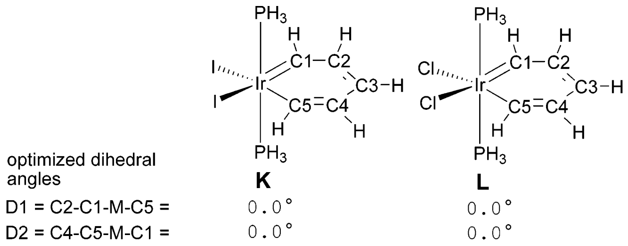
Scheme 2



optimized dihedral angles	G	H	I
D1 = C2-C1-M-C5 =	−14.7°	−8.1°	−17.1°
D2 = C4-C5-M-C1 =	+14.7°	+8.1°	+17.1°

optimized dihedral angles	J
D1 = C2-C1-M-C5 =	−12.6°
D2 = C4-C5-M-C1 =	+12.6°

Scheme 3



optimized dihedral angles	K	L
D1 = C2-C1-M-C5 =	0.0°	0.0°
D2 = C4-C5-M-C1 =	0.0°	0.0°

isoelectronic as well as isostructural with the metallabenzene complex **11**. Therefore, they also show similar planarity to the metallabenzene complex **11**.

Metallabenzenes Containing Phosphonium Substituents on the Six-Membered Metal-Containing Ring. The metallabenzene complexes **14**−**17** all contain phosphonium substituents on the six-membered metal-containing ring. The metallabenzene complex **17**, which displays nonplanarity, will be discussed in the next subsection. The metallabenzene complexes **14**−**16** do not display significant nonplanarity. The observation suggests that phosphonium substituents are capable of reducing the nonplanarity. The electron-deficient phosphonium substituents at C(2) and C(4) in these complexes act as π acceptors, withdraw π electron density from the ring carbons, stabilize the antibonding bonding interaction in the HOMO (Figure 4), and therefore, reduce the nonplanarity. We calculated the model complexes **M**, **N**, and **O** (Scheme 4). Compared with the model complex **A** (Scheme 1), in which the planarity is poor, the model complex **M** shows a planar structure. Similarly, the model complex **N** has a nonplanar structure, while the model complex **O** has a planar structure. Mulliken population analyses[25] provide quantitative support to the argument given here. In the HOMO of the model complex **A**, the percentage contributions of Os, C(1) (or C(5)), and C2 (or C(4)) are 40.1%, 7.0%, and 20.9%, respectively. In the HOMO of the model complex **M**, the percentage contributions of Os, C(1) (or C(5)), and C2 (or C(4)) are 50.1%, 0.9%, and 18.3%, respectively. A similar trend was seen when we compared the percentage contributions for the model complexes **N** and **O**, 40.1%, 7.2%, and 20.8% for **N** versus 51.9%, 1.2%, and 17.9% for **O**. Clearly, the phosphonium substituents at C(2) and C(4) are able to decrease the π electron density on the metal-bonded carbons in the HOMO, reducing the antibonding interactions between the metal center and the metal-bonded carbon atoms.

Nonplanarity in the Metallabenzene Complex 17. Despite that the metallabenzene complex **17** has phosphonium substituents on the ring, it displays significant nonplanarity. The nonplanarity observed in the metallabenzene complex **17** suggests that the effect of phosphonium substituents cannot offset other forces. Calculations on the model complex **P** using two NH_3 ligands for the bipyridine ligand give a nonplanar structure (Scheme 5). The D1 and D2 dihedral angles (in the absolute value) calculated for the model complex **P** are smaller than those experimentally observed in **17**. When the bipyridine ligand is used in the model complex (**17′** in Figure 3), the dihedral angles reproduce very well the experimental values, suggesting that the contacts between C1-H/C5-H and the ortho C−H bonds increase the nonplanarity. Since the model complex **P** also shows nonplanarity, there should be other important reasons, in addition to the contacts between C1-H/C5-H and the ortho C−H bonds, for the nonplanarity of **17**, **17′**, and **P**. We believe that the most important reason is related to the unsymmetric steric environment above and below the metallabenzene ring plane because we have shown that the π-donating effect of the chloride ligand is limited. We calculated the structures of the model complexes **Q** and **R** (Scheme 5). The results of these calculations suggest that the unsymmetric steric environment above and below the metallabenzene ring plane plays the determining role.

The Cp-Containing Metallabenzene Complexes 18 and 19. The two Cp-containing metallabenzene complexes **18** and **19** adopt planar structures (Figure 1). Calculations on the model complex **18′** (Figure 3) reproduce the planarity observed. As discussed above, the driving force toward nonplanarity in metallabenzene complexes is the fact that the π_4 molecular orbital (Figure 4) in most cases corresponds to the HOMO, which has the antibonding interaction between the metal center and the metal-bonded ring carbons. We also know that the driving force is not very large due to the three (bonding) versus one (antibonding) pattern in the four occupied π molecular orbitals. The presence of a substituted Cp ligand in **18** or **19**

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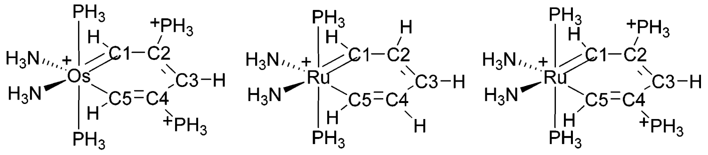
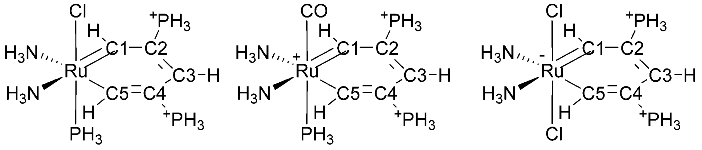
[25] *MullPop*, a program written by Reinoldo Pis Diez at the National University of La Plata, Argentina.

Scheme 4



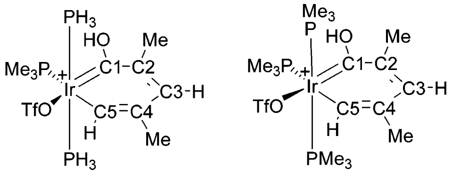
optimized dihedral angles	**M**	**N**	**O**
D1 = C2-C1-M-C5 =	-0.2°	-11.8°	-0.7°
D2 = C4-C5-M-C1 =	-0.1°	+11.8°	+0.6°

Scheme 5

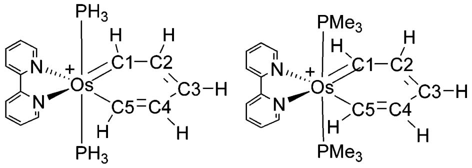


optimized dihedral angles	**P**	**Q**	**R**
D1 = C2-C1-M-C5 =	-26.4°	-17.5°	0.0°
D2 = C4-C5-M-C1 =	+26.4°	+17.5°	0.0°

Scheme 6



optimized dihedral angles	**12'**	**12"**
D1 = C2-C1-M-C5 =	-13.2°	0.1°
D2 = C4-C5-M-C1 =	+10.8°	0.0°



optimized dihedral angles	**B**	**B'**
D1 = C2-C1-M-C5 =	-27.1°	-14.0°
D2 = C4-C5-M-C1 =	+27.4°	+16.0°

disturbs significantly the orbital ordering of the four occupied π molecular orbitals. Carefully examining the frontier molecular orbitals calculated for the model complex **18′**, we found that π_3, not π_4, corresponds to the HOMO (Figure 7). The π_4 orbital, which has an antibonding interaction between the metal center and the metal-bonded ring-carbon atoms, instead corresponds to the second HOMO. The reason for the switch in the orbital ordering can be understood as follows. The metal d orbital contributing to π_3 is d_{yz}, while the metal d orbital contributing to π_4 is d_{xz} (Figure 4). The d_{yz} orbital has greater overlap with the π orbitals of the Cp ring than the d_{xz} orbital does. Therefore, on the basis of the ligand field theory, we expect that as a result of the orbital interaction, the d_{yz} orbital is higher in energy than the d_{xz} orbital, leading to the observation that π_3, not π_4, corresponds to the HOMO in the Cp-containing metallabenzene complexes **18** and **19**. When π_3 is the HOMO, a distortion from planarity will not take place because π_3 has the bonding interaction between the metal center and the metal-bonded ring carbons (Figures 4 and 7).

Steric Effect of Phosphine Ligands. In the model complexes, we used PH_3 to model phosphine ligands. In most cases, the calculated structures reproduce well the experimental structures, especially the nonplanarity, suggesting that the simple model ligand can give good results (see the section Calculated Structures versus Experimental Ones). However, there are complexes in which the planarity is not well reproduced with the model ligand. This is understandable and should be expected because the magnitude of the electronic driving force toward nonplanarity is small. In those metallabenzene complexes having two phosphine ligands occupying the two ligand coordination sites above and below the ring plane, the steric repulsive interactions between the organic moiety in the ring and the alkyl or aryl groups associated with the two phosphine ligands may be able to counterbalance the electronic driving force, giving rise to an approximately planar structure that is not necessarily expected from consideration of electronic factors only. Scheme 6 shows two examples from which we can see that PMe_3 gives smaller dihedral angles.

Summary

In this paper, the nonplanarity displayed by metallabenzene complexes has been theoretically investigated via the density functional theory (DFT) calculations. Different from benzene, a metallabenzene has four occupied π molecular orbitals. The extra occupied π molecular orbital shows antibonding interactions between the metal center and the metal-bonded ring-carbon atoms, providing the electronic driving force toward nonplanarity when it corresponds to the highest occupied molecular orbital (HOMO). Among the four occupied π molecular orbitals, three have bonding interactions between the metal center and the metal-bonded ring-carbon atoms. Therefore, the electronic driving force is relatively small.

Because the electronic driving force is small, other electronic and steric factors also become important in determining the nonplanarity. Among these different electronic and steric factors, some give an enhancing effect, i.e., increasing the nonplanarity, while some provide the counter effect, i.e., decreasing the nonplanarity or offsetting the electronic driving force to give a planar geometry.

Our analyses show that the steric effect exerted by bipyridine and Tp ligands increases the nonplanarity, while the steric effect exerted by bulky phosphine ligands occupying the two ligand coordination sites symmetrically above and below the ring plane reduces the nonplanarity. π electron-withdrawing ligands, such as carbonyls and phosphonium substituents at C(2) and C(4) of the six-membered metal-containing ring also reduce the nonplanarity. For halide ligands, the π electron-donating effect was found to be limited. Instead, the σ-withdrawing properties are important. An unsymmetrical ligand environment above and below the six-membered metal-containing ring is expected to create an unsymmetrical steric environment and increase the nonplanarity.

For the two Cp-containing metallabenzene complexes discussed in this paper, the ligand field created by the Cp ligand makes the extra occupied π molecular orbital no longer the HOMO. Therefore, these two Cp-containing metallabenzene complexes display planarity.

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Supporting Information Available: Complete ref 21 and tables giving Cartesian coordinates and electronic energies for all the calculated structures (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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