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Theoretical Studies on the Stabilities of Metallabenzynes

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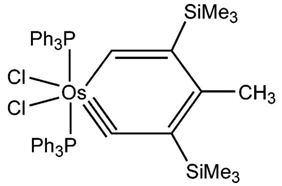
Theoretical calculations at the B3LYP level of density functional theory have been carried out to study the stability of osmabenzyne complexes. Isodesmic reactions have been designed to analyze the ring strain and conjugation energies of the complexes. The ring strain energy was found to be small, primarily because of the relatively small angle of bending at the carbyne carbon. The conjugation energy is comparable to those of benzene and osmabenzene. The effect of substituents at the ring carbons on the stabilities has also been examined. Through molecular orbital analyses, we found that the effect of substituents on the energies of π orbitals in the six-membered ring play important roles in determining the relative stabilities.

Introduction

The chemistry of transition-metal-containing metallabenzenes, which can be considered as species obtained by formally replacing one of the CH groups in benzene by a 15-electron transition-metal fragment, has attracted considerable attention.[1,2] The metallabenzenes were studied theoretically by Hoffmann et al. as early as 1979.[3] The first isolated metallabenzene was reported by Roper et al. in 1982.[4] Over the following 20 years, impressive progress has been made in the synthesis, characterization, and studies of the properties of this interesting class of compounds. A number of metallabenzenes have now been synthesized.[1,2] Interesting properties, including aromatic electrophilic substitution reactions,[2e] have been revealed in recent years.

Closely related to metallabenzenes are metallabenzynes, which can be considered as species obtained by replacing one of the C or CH groups in benzyne by a 14-electron or 15-electron transition-metal fragment. Benzynes are important compounds in organic and organometallic chemistry. Many experimental and theoretical studies have been carried out on benzyne systems.[5] Benzyne has high chemical reactivity and low thermal stability because it has a large ring strain due to the presence of a formal C−C triple bond in the six-membered ring. Indeed, six-membered-ring organic compounds with a triple bond in the six-membered ring such as benzynes and cyclohexyne cannot be isolated in the free state at room temperature, and they can only be detected at low temperature.[6]

In comparison to metallabenzenes, metallabenzynes have been much less studied. At first sight, one might expect that metallabenzynes may be, like benzynes and cyclohexyne, also too unstable to be isolated at room temperature, because the presence of a formal triple bond in the ring is expected to create a considerable ring strain. Contrary to this expectation, the first metallabenzyne (**1**) was recently obtained from the reaction of $OsCl_2(PPh_3)_3$ with $HC{\equiv}CSiMe_3$ in wet dichloromethane.[7] Three new examples of osmabenzynes, including **2**, were also made from the reactions of **1** with acid and Br_2.[8] In the osmabenzynes **1** and **2**, the angles at the carbyne atoms are 148.7(3) and 148.3(6)°, respectively. Since the angles at the carbyne atom in metal−carbyne complexes



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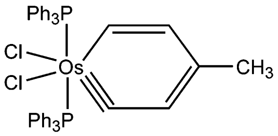

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are usually near 180°,[9] the large angle of bending in the metallabenzyne complexes is expected to cause a considerable ring strain and low thermal stability of osmabenzynes. However, the reported osmabenzynes appear to be thermally much more stable than benzyne and can be conveniently characterized by IR and NMR spectroscopy and X-ray diffraction. There are several possible explanations for the higher thermal stability of osmabenzynes. For example, the ring strain might not be as high as expected, the ring might have substantially large conjugation energy, or the large substituents or ligands might protect the ring from further reactions. The purpose of this work is to investigate the dominant factors responsible for the high thermal stability of metallabenzynes.

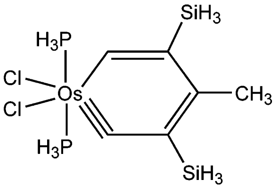
Computational Method

Full geometry optimizations of all the osmabenzyne model complexes were done at the Becke3LYP (B3LYP) level of density functional theory.[10] The effective core potentials (ECPs) of Hay and Wadt with double-ζ valence basis sets (LanL2DZ)[11] were used to describe Os, Cl, P, Br, I, and Si. Polarization functions were also added for Cl ($\zeta_d = 0.514$), P ($\zeta_d = 0.340$), Br ($\zeta_d = 0.389$), I ($\zeta_d = 0.266$), and Si ($\zeta_d = 0.262$).[12] The 6-31G basis set was used for all other atoms.[13] All the calculations were performed with the Gaussian 98[14] software package. Molecular orbitals obtained from the B3LYP calculations were plotted using the Molden v3.5 program written by Schaftenaar.[15]

Results and Discussion

Electronic Structures of Osmabenzyne Complexes. As mentioned in the Introduction, the main purpose of this work is to investigate why metallabenzynes are thermally more stable than benzynes. Before the discussion of the stability of metallabenzynes, it would be useful to briefly describe the electronic structure of metallabenzynes.

Molecular orbital calculations of the model complex (**3**) have been previously reported by Yang et al.[16] The π-donating properties of the chloride ligands have been found to be important in enhancing the Os(d)≡C(p) π bonding interactions. The current paper mainly deals with the questions regarding the ring strain and conjugation energies of the osmabenzyne complexes. For the purpose of this study, we performed calculations on the model complexes $\overline{\mathrm{Os}(\equiv \mathrm{CC(R)}{=}\mathrm{C(R')C(R)}{=}\mathrm{C}}\mathrm{H)Cl_2(PH_3)_2}$. Figure 1 shows the optimized structure of **4**. The calculated structural parameters compare well with those from the experimentally determined X-ray structure of complex **2**.[8] The differences in the bond lengths are within 0.05 Å and those in the bond angles within 1°. For example, the angle at the triply bonded carbon in the crystal structure of **2** is 148.3(6)°, and the calculated angle is 149.3°. The Os≡C bond distance in **2** is 1.805(7) Å, while the calculated distance is 1.793 Å. Clearly, these two important structural parameters are well reproduced in the theoretical calculations. The structural features are also similar to those of **1**.



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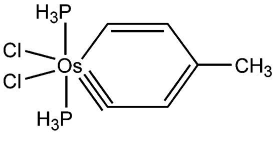

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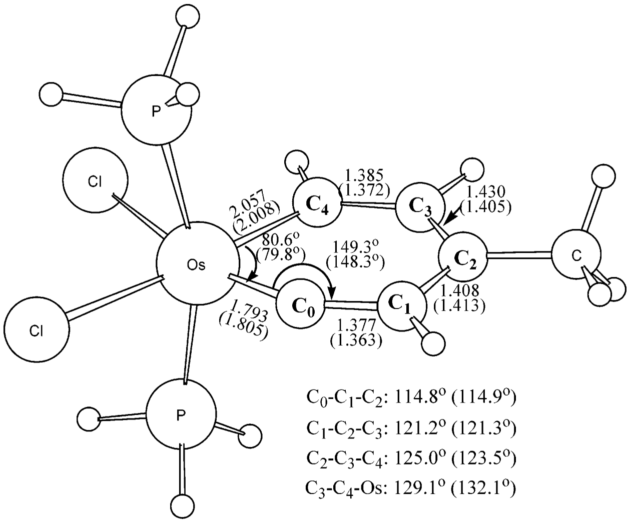

Figure 1. Selected structural parameters for the model complex **4** and its experimental complex **2** (in parentheses). All distances are in Å, and angles are in degrees.

The delocalization of the π-electrons in the osmabenzyne ring can be represented by the resonance contributors **4A** and **4B** or by the resonance hybrid **4C** (Scheme 1). The structural parameters (Figure 1) suggest that the most dominant resonance contributor of the osmabenzyne is **4A**, which has one triple bond and two double bonds in the six-membered ring.

The osmabenzyne complexes considered here can be described as octahedral. It is therefore useful to consider a schematic orbital interaction between the metal fragment $[\mathrm{Os(PH_3)_2Cl_2}]$ and a carbon fragment consisting of five ring-carbon atoms (C_5R_4) (Figure 2). Figure 2 shows an MO diagram for π interactions between the "t_{2g}" orbitals of the metal fragment and the π orbitals of the C_5R_4 unit. The metal−carbon σ bonding MOs are

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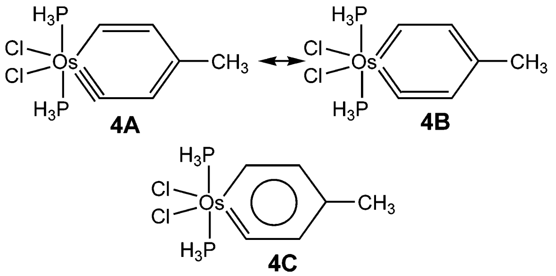
Scheme 1



not shown in the figure for the purpose of clarity. The π orbitals of the C_5R_4 unit (see the right-hand column in Figure 2) are the $\pi_{\mathrm{in-plane}}$ atomic orbital from the triply bonded carbon and the linear combinations of the five p_π atomic orbitals, perpendicular to the six-membered planar ring, from the five carbons in the ring. The central column in the figure gives the resulting molecular orbitals derived from the orbital interactions. The rectangular box shown in the central column represents orbitals which accommodate the lone-pair electrons from the chloride ligands of the metal fragment. For the purpose of clarity, the relevant details are omitted.

In the central column, MO1, MO4, and MO6 (LUMO) are orbitals derived from the orbital interactions among 1π, 3π, and $5\pi^*$ of C_5R_4 and d_{xz} from the “t_{2g}” orbitals.

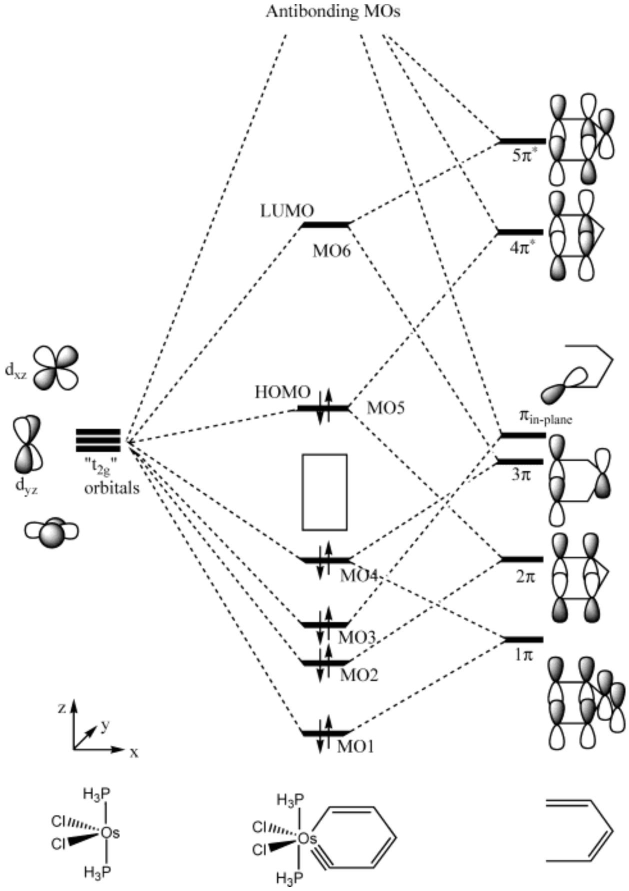


Figure 2. Schematic orbital correlation diagram showing the π interactions between the “t_{2g}” orbitals of the $OsCl_2(PH_3)_2$ metal fragment and the π orbitals of the C_5H_4 unit for $\overline{\mathrm{Os}(\equiv\mathrm{CCH{=}CHCH{=}C}}\mathrm{H})\mathrm{Cl_2(PH_3)_2}$. The rectangular box in the central column represents orbitals that accommodate the Cl lone pair electrons of the metal fragment.

MO2 and MO5 (HOMO) are derived from the interactions among 2π, $4\pi^*$, and d_{yz}. MO3 corresponds to the in-plane π bonding orbital in the Os≡C triple bond. Figure 3 shows the spatial plots of these π molecular orbitals calculated for **4**. The HOMO, similar to that reported previously for **3** in a communication,[8] has significant contribution from the p(π) orbitals at C(1) and C(3), in addition to the contribution from the metal d orbital and the chloride p(π) orbitals. The characteristics of the HOMO have been used to explain the experimental observations that electrophilic substitutions occur preferentially at the two ring carbons.[8]

Stabilities of the Osmabenzyne Complexes. (a) Stability of Osmabenzyne Complex 4 from Isodesmic Reactions. The stability of cyclic compounds can be studied by calculating reaction energies of isodesmic reactions.[17] By consideration of different bonding environments of atoms in a cyclic compound, subclasses of isodesmic reactions, such as homodesmic[18−20] and group equivalent reactions,[21,22] have also been proposed to study ring stability.[23]

On the basis of the definition of homodesmic reactions, reaction 1 shown in Scheme 2 was designed to investigate the stability of the model osmabenzyne complex **4**. In the designed isodesmic reaction, the osmabenzyne complex is broken up into six fragments, including one Os fragment, one sp-carbon fragment, and four sp^2-carbon fragments. The reaction energy of reaction 1 was found to be 34.78 kcal/mol, indicating that a large amount of energy is needed to break the ring. Since the osmabenzyne complex **4** displays extensive π delocalization, the reaction energy of the designed reaction includes both the strain energy and the conjugation energy.

For comparison, we have calculated the reaction energies of similarly designed reactions for some typical molecules, such as benzene, cyclohexane, benzyne, and cyclohexyne. The corresponding designed reactions for the four molecules are given in Scheme 2. The calculated reaction energies are listed in Table 1. Figure 4 shows selected structural parameters calculated for the four molecules.

From Table 1, we can see that benzene has large positive values in the ΔE reaction energy because it is a very stable and highly conjugated compound. A large amount of energy is needed to break the benzene ring. The ΔE value (46.66 kcal/mol) based on reaction 2 can be considered as the conjugation energy, consistent with the previously reported values by George et al. (42.7 ± 3.0 kcal/mol, from a homodesmic reaction using 1,3-butadiene, where the two olefin π bonds are orthogonal to each other as the reference)[24] and Mo et al. (44.48 kcal/mol, based on valence bond theory).[25] The ΔE reaction energies of cyclohexane are close to zero,

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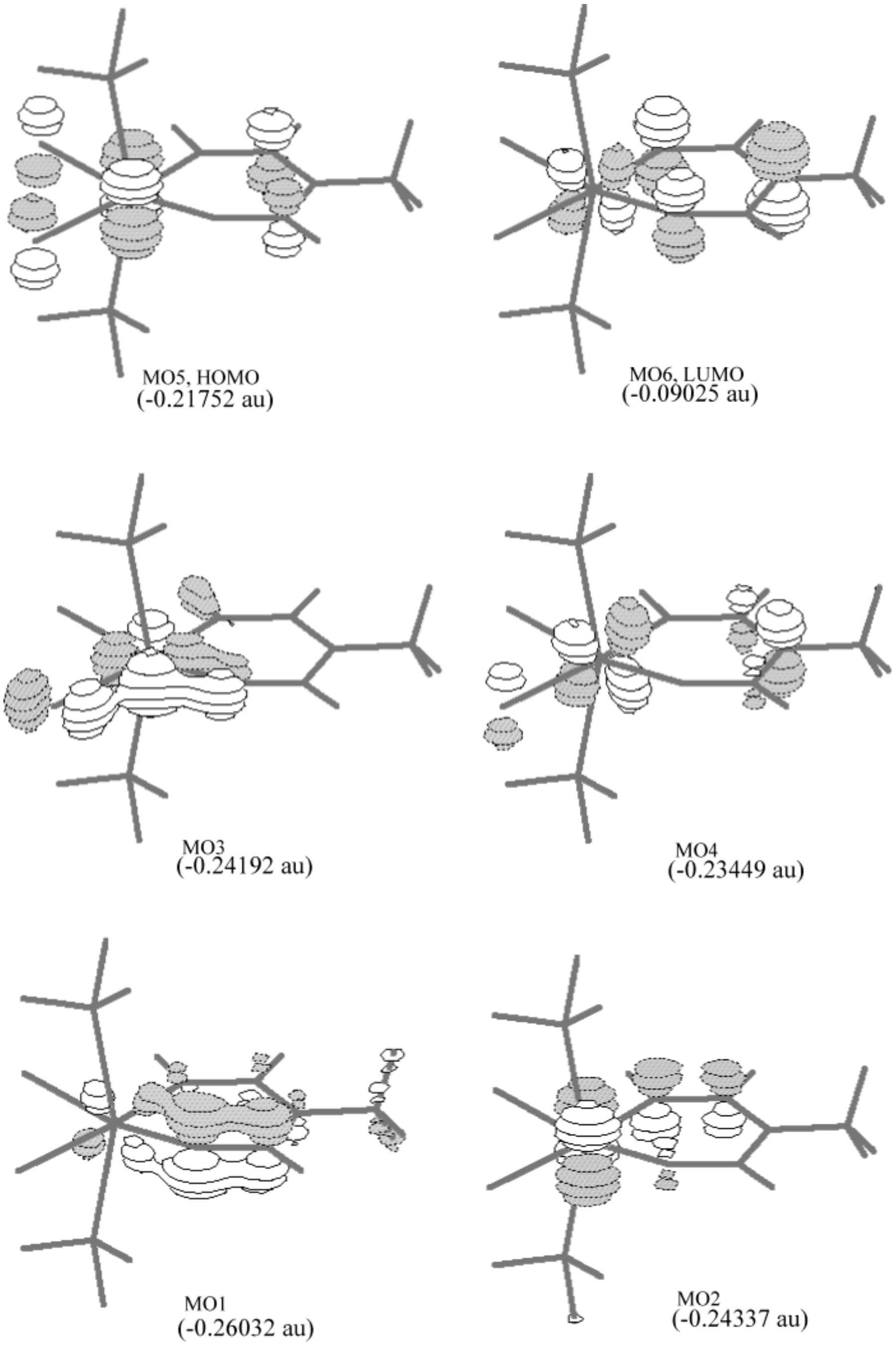

Figure 3. Spatial plots of the HOMO (MO5), LUMO (MO6), and the MO's MO1−MO4 for the model complex **4**. The molecular orbitals were obtained from the B3LYP calculations.

validating the designed reactions, because cyclohexane contains no structural strain and no conjugation energy. Cyclohexyne gives a negative ΔE reaction energy (−45.51 kcal/mol), which can be considered as the angle strain energy. The value is close to the previously reported values by Johnson et al. (−41.2 ± 3.0 kcal/mol).[20] Benzyne also shows a negative but much smaller ΔE reaction energy (−16.13 kcal/mol). This is because the π electrons of benzyne are extensively delocalized and the conjugation energy offsets parts of the considerable ring strain energy. If we employ the reported angle strain energy of benzynes (53.6 kcal/mol),[26] we can easily obtain a conjugation energy of 37.47 kcal/mol (=53.60 kcal/mol − 16.13 kcal/mol) for benzyne.

It should be noted that different values of ΔE can be obtained from different isodesmic reactions. In the isodesmic reactions that we designed, we purposely break the studied cyclic molecules into smaller ones which contain no more conjugate moieties. In the literature, certain isodesmic reactions were designed in such a way that the resulting smaller molecules also contain significant conjugation. Therefore, the calculated values of ΔE based on such isodesmic reactions are expected to be smaller than those we obtained. For example, the conjugate energies of benzene and benzyne with respect to a *trans*-butadiene reference were calcu-

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Scheme 2

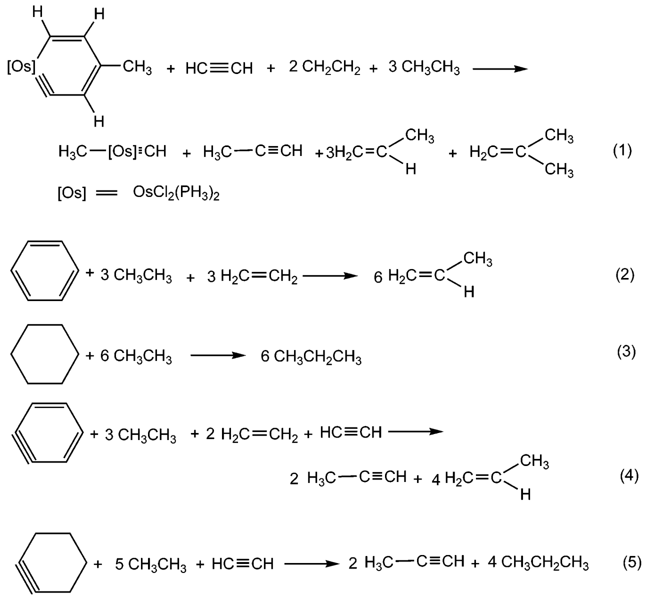
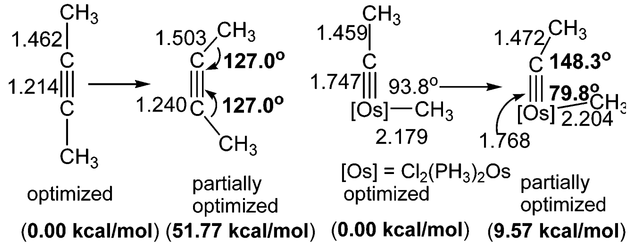


Table 1. Reaction Energies with Zero-Point Energy Corrections, Reaction Energies (in Brackets), and Free Energies (in Parentheses) of Benzene, Cyclohexane, Benzyne, Cyclohexyne, and Osmabenzyne (4)[a]

	Δ*E*
benzene	46.66 [48.14] (54.17)
cyclohexane	0.03 [−1.26] (8.51)
cyclohexyne	−45.51 [−47.30] (−37.98)
benzyne	−16.13 [−15.96] (−9.84)
osmabenzyne (**4**)	34.78 [34.88] (41.36)

[a] The energies are calculated on the basis of the isodesmic reactions shown in Scheme 2. The energies Δ*E* are given in units of kcal/mol.

Scheme 3[a]

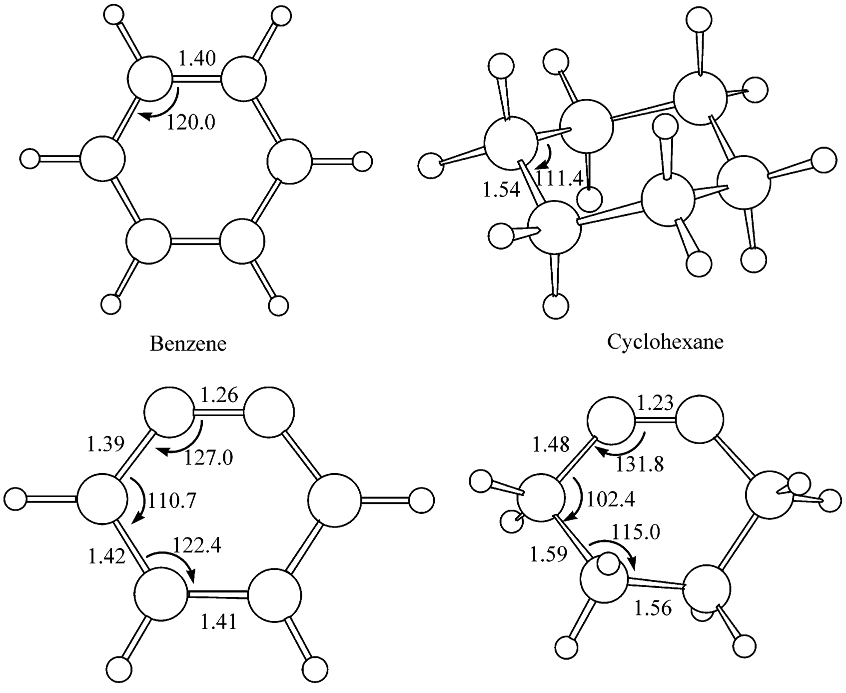


[a] The angles given in boldface are fixed in the partial geometry optimizations.

lated to be 21.80 kcal/mol[18] and 18.60 kcal/mol,[26] respectively.

(b) Angle Strain and Conjugation Energy of Osmabenzyne Complex 4. As mentioned above, the reaction energies of the designed reactions shown in Scheme 2 include both strain energy and conjugation energies. The angle at the carbyne atom of the osmabenzyne **2** is 148.3(6)°. The calculated angles at the two carbyne atoms in benzyne are 127.0°. It is interesting to investigate how this unfavorable angle destabilizes the complex. To estimate the angle bending energies, we performed partial geometry optimizations for $CH_3C{\equiv}CCH_3$ and $Os({\equiv}CCH_3)(CH_3)Cl_2(PH_3)_2$ with predefined angles on the carbyne atoms. The predefined angles, given in boldface and shown in Scheme 3, are based on the X-ray-characterized osmabenzyne **2** and calculated angles of the benzyne molecule. The results of calculations show that the energy needed for the angle bending of $CH_3C{\equiv}CCH_3$ is 51.77 kcal/mol and that for the angle bending of $Os({\equiv}CCH_3)(CH_3)Cl_2(PH_3)_2$ is only 9.57 kcal/mol.

The value of 51.77 kcal/mol is similar to that reported for the ring strain of benzyne calculated from the difference (53.60 kcal/mol) in the energies of optimized and partially optimized $CH_2{=}CHCH{=}CHC{\equiv}CCH{=}CHCH{=}CH_2$.[26] On the basis of the reaction energy

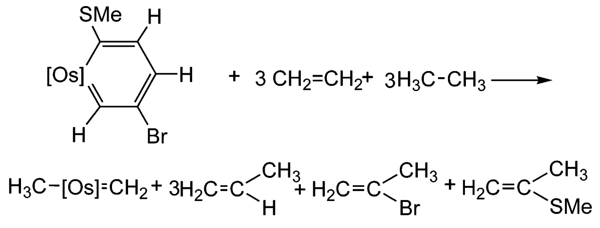


Benzene Cyclohexane

Benzyne Cyclohexyne

Figure 4. Selected structural parameters calculated for benzene, cyclohexane, benzyne, and cyclohexyne. All distances are in Å, and angles are in degrees.

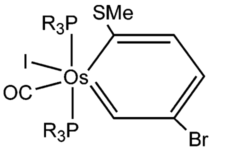
Scheme 4[a]



[a] [Os] = $Os(PH_3)_2(CO)I$.

(−16.13 kcal/mol) calculated for benzyne, we can conveniently derive the conjugation energy (51.77 kcal/mol − 16.13 kcal/mol = 35.64 kcal/mol) for benzyne if we take 51.77 kcal/mol approximately as the angle strain energy. This value is comparable to that (37.47 kcal/mol) mentioned above. Similarly, if the strain energy of osmabenzyne **4** was taken as 9.57 kcal/mol, then the conjugation energy of **4** should be 44.35 kcal/mol (=9.57 kcal/mol + 34.78 kcal/mol), which is very close to that of benzene (46.66 kcal/mol).

For comparison, we also designed the reaction shown in Scheme 4 to get the conjugation energy of **5**, a model complex of Roper's osmabenzene **6**.[2e]



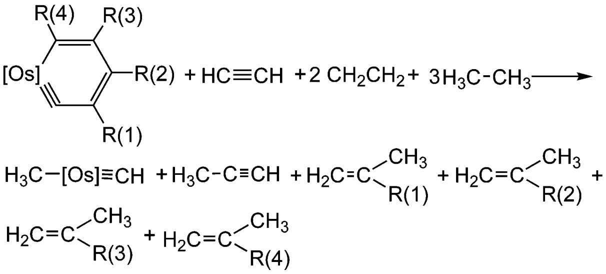
5 (R=H); **6** (R=Ph)

The reaction energy of the reaction shown in Scheme 4 was calculated to be 43.52 kcal/mol. The osmabenzenes are expected to have small ring strain. Therefore, the reaction energy (43.52 kcal/mol) can be considered as the conjugation energy. Interestingly, the conjugation energies calculated for benzene, osmabenzyne (**4**), and osmabenzene (**5**) are close to each other, indicating the extensive delocalization feature in their π systems. In contrast, benzyne has a smaller conjugation energy.

The discussion above indicated that the stability of osmabenzyne is due to the fact that bending of both the $Os{\equiv}C{-}R$ (from 180 to 148.3°) and $Me{-}Os{\equiv}C(R)$ angles (from 93.8 to 79.8°) costs only ca. 10 kcal/mol. In contrast, bending of both of the $C{\equiv}C{-}R$ angles (180°) in 2-butyne to the angles (127°) in benzyne costs as much as 52 kcal/mol in energy. In the literature, several complexes with an $M{\equiv}C{-}R$ angle close to 160° are reported.[27,28] In one case, the angle is as small as 148.7°.[28]

The question of why osmabenzynes have much smaller strain energies than benzyne requires further comment.

Scheme 5[a]



[a] [Os] = $OsCl_2(PH_3)_2$.

Examining the structures of benzyne in Figure 4 and the osmabenzyne in Figure 1, we can see that significant angle bending (from 180°, an optimal angle for an sp-hybridized carbon, to 127° calculated for the two formal triple-bonded carbons) can be found with benzyne, whereas the angles of bending are relatively smaller (from 180 to 148.3° for $Os{\equiv}C{-}R$ and from 93.8 to 79.8° for $CH_3{-}Os{\equiv}CR$) with the osmabenzyne. An angle bending from 180 to 150° at one sp-hybridized carbon of 2-butyne costs approximately 7 kcal/mol on the basis of our calculations. Therefore, most of the total cost in energy associated with bending in the osmabenzyne (9.57 kcal/mol) probably arises from bending at $Os{\equiv}C{-}R$ and the significant difference between the strain energies for benzyne and osmabenzyne can be related to the different magnitudes of the bending angles in the two ring systems. The reasons for the small angle of bending at the carbyne atom in the osmabenzyne ring can be traced back to the naturally longer osmium to carbon bonds compared to the corresponding carbon to carbon bonds and to the small ring angle at the metal center. In metal complexes, ligand−metal−ligand angles of ca. 80° are quite common, and therefore in this case it is expected that reducing the ring angle at osmium from 93.8 to 79.8° will only make a minor contribution to the total strain energy of the osmabenzyne.

One of the reviewers was concerned that angles at the remaining ring sp^2 carbons vary from 115 to 132° (Figure 1). The deviation from the optimal angle (120°) might also contribute significantly to the ring strain energy. We performed calculations on $H_2C{=}CH(Me)$ by varying the C−C−Me angle from 115 to 132°. The maximum energy difference between the lowest energy structure (C−C−Me = 125°) and the highest energy structure (C−C−Me = 115°) is smaller than 2.5 kcal/mol. Clearly, the ±10° deviation from the optimal angle does not cost much energy. The deviation at the remaining ring sp^2 carbons is a result of maximizing the $Os{\equiv}C$ and $Os{-}C$ bonding interactions in the ring.

(c) Substituent Effect on the Stabilities of the Model Complexes. The first experimentally characterized osmabenzyne complex had silyl substituents on C(1) and C(3). There is a question as to whether the silyl substituents have a stabilizing effect on the metallabenzyne. To investigate the stabilizing effect, we calculated model complexes in which the substituents on C(1) and C(3) were varied and the substituents on C(2) and C(4) were the same as the experimental ones, methyl and hydrogen, respectively. The calculated reaction energies (ΔE) based on the general isodesmic reaction shown in Scheme 5 are listed in Table 2.

From Table 2, we can see that the largest ΔE reaction energies are calculated for complexes in which the

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Table 2. Reaction Energies with Zero-Point Energy Corrections, Reaction Energies (in Brackets), Free Energies (in Parentheses), and HOMO−LUMO Gaps of Different Substituted Osmabenzynes in Which R(2) = CH_3 and R(4) = H[a]

R(1), R(3)	ΔE	HOMO−LUMO gap
BH_2	39.17 [39.43] (44.54)	0.1281
SiH_3	38.11 [38.19] (44.36)	0.1242
H	34.78 [34.88] (41.36)	0.1273
CH_3	34.03 [34.18] (41.41)	0.1216
Cl	25.78 [25.13] (30.95)	0.1183
NH_2	21.05 [20.49] (26.83)	0.0954

[a] The energies are calculated on the basis of the isodesmic reactions shown in Scheme 5. The energies are given in units of kcal/mol for ΔE and in units of au for the HOMO−LUMO gaps.

substituents (R(1) and R(3)) on C(1) and C(3) are silyl and boryl groups. Both silyl and boryl groups are considered as strongly σ-donating. The BH_2 group is a also very strongly π-accepting. The silyl group is a relatively weaker π-accepting species. Smaller reaction energies are calculated for complexes in which the substituents (R(1) and R(3)) on C(1) and C(3) are π-donating. For complexes having the substituents H and CH_3, which are strongly σ-donating, the corresponding reaction energies are found to have values in between. If the complex in which R(1) = R(3) = H is taken as the reference, methyl substituents at C(1) and C(3) are found to be slightly destabilizing.

To understand how the substituents in C(1) and C(3) affect the stabilities of the studied osmabenzyne complexes, we have carefully examined how the structural parameters in the six-membered ring varied as a result of the different substituents. The variation was found to be within 0.05 Å in the bond distances and within 6° in the bond angles. We could not observe any correlation between the structural variations and the electronic properties of the R(1) and R(3) substituents. However, the calculated HOMO−LUMO gaps (see Table 2) provide an interesting correlation with the relative stability (ΔE). Larger HOMO−LUMO gaps are calculated for those complexes having larger reaction energies (ΔE). On the basis of the spatial plots of the HOMO's (MO5 in Figure 3), we expected that the π-accepting substituents (silyl and boryl) on C(1) and C(3) are able to stabilize the HOMO (MO5 in Figure 3) and give larger HOMO−LUMO gaps, leading to greater stabilities for the corresponding complexes. For complexes which have π-donating substituents on C(1) and C(3), the HOMOs are expected to be destabilized, giving smaller HOMO−LUMO gaps. The stabilization and destabilization apparently affected the conjugation energy and therefore the stability of the ring.

Conclusion

The electronic structures and stabilities of osmabenzyne complexes have been investigated using density functional calculations. Calculating reaction energies of isodesmic reactions, we have been able to examine the strain energies as well as the conjugation energies of the complexes. In comparison with benzyne, osmabenzyne complexes have much smaller strain energies (ca. 10 kcal/mol), primarily because of the relatively small angle bending at the carbyne carbon. The reason for the small bending angle at the carbyne atom while the ring structure of the osmabenzyne is maintained can be traced back to the small ring angle at the metal center. The deviation from the optimal angle of 120° observed at the four sp^2 carbons does not contribute much to the strain energy and is a result of maximizing the Os≡C and Os−C bonding interactions in the ring. The conjugation energy for the model osmabenzyne (**4**) is estimated to be ca. 44 kcal/mol, almost identical with that estimated for the model osmabenzene (**5**), a model complex of Roper's osmabenzene (**6**).

The relative stabilities of different osmabenzyne complexes with different substituents on the ring are related to the properties of the HOMO and LUMO orbitals. π-Electron accepting groups at C(1) and C(3) are found to increase the HOMO−LUMO gaps and are good stabilizing substituents.

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Supporting Information Available: Tables giving Cartesian coordinates of selected optimized structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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