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Electronic reason for the stabilization of osmabenzyne

Sheng-Yong Yang *, Xiang-Yuan Li, Yi-Zhi Huang

College of Chemical Engineering, Sichuan University, Chengdu 610065, People's Republic of China

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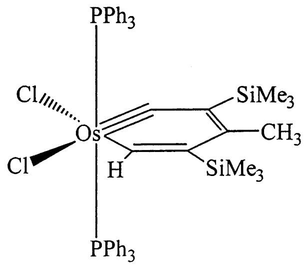
Abstract

The electronic reason for the stabilization of osmabenzyne $\overline{Os[{\equiv}C{-}C(SiMe_3){=}C(CH_3){-}C(SiMe_3){=}C}H]Cl_2(PPh_3)_2$ has been examined with the aid of orbital interaction analysis and density functional theory calculations. The results show that the six-membered metallacycle exhibits somewhat aromatic properties. The filled metal $d_{x^2-y^2}$-orbital interacts with the equatorial p-orbital of the high reactive carbyne carbon ($\equiv$C) in a back-bonding fashion, which can deactivate the carbyne carbon. The chloride ligand *trans* to the carbyne carbon, which is a stronger π-donor, can enhance the d–p interaction. On the other hand, the π-donor ligand *trans* and *cis* to the carbyne carbon benefit the d_{xz}–3π back-bonding interaction between the metal and carbon unit, hence stabilizing the osmabenzyne. And the silyl group on the carbon adjacent to the carbyne carbon can prevent the protonation back to the corresponding osmabenzene through its polarization effect in a way. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Osmabenzyne; Stabilization; Electronic reason

1. Introduction

Benzynes are considered as very important intermediates in organic and organometallic synthesis. They are frequently used in synthesis and mechanism studies [1]. However, it is difficult to isolate free benzynes because of their low thermal stability and high reactivity. Nevertheless, recently a stable and isolable metallabenzyne $\overline{Os[{\equiv}C{-}C(SiMe_3){=}C(CH_3){-}C(SiMe_3){=}C}H]Cl_2(PPh_3)_2$ (**1**) has been synthesized and characterized firstly by Jia and co-workers [2]. The unusual stability of osmabenzyne attracts our attention. Despite the reactivity of **1** will certainly be reduced by the steric protection of the strained Os≡C bond provided by the ligands at the osmium center and the nearby trimethylsilyl group on the adjacent carbon atom [3]. Anyway protonation of osmabenzyne **1** back to its corresponding osmabenzene should be favored because of the smallest size of proton and the good aromaticity of metallacycle in osmabenzene [4–6]. Therefore, an additional electronic reason for the stabilization of the osmabenzyne **1** should be expected. Our purpose, in this work, is to investigate the electronic reason for the stabilization of osmabenzyne **1** by orbital interaction analysis and density functional theory (DFT) calculations.



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2. Qualitative analysis of fragment orbital interaction

Before presenting our results from DFT calculations, we need to briefly summarize the qualitative analysis of fragment orbital interaction between the transition metal and carbon ring.

The C_5R_4 unit in osmabenzyne **1** is perhaps best regarded as a neutral ligand [7,8]. In this view, it possesses eight valence electrons, in addition to backbone σ-electrons. Four of these valence electrons are

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* Corresponding author. Tel.: +86-28-85405233; fax: +86-28-85407797

E-mail address: yangshengyong@yahoo.com (S.-Y. Yang).

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used to form σ-bonds to osmium, while the remaining four are π-electrons and reside in relatively low-lying 1π and 2π orbitals of the carbon unit (see (a) and (b) of Scheme 1). Naturally osmabenzyne **1** can be considered as an octahedral Os(II)≡d^6 complex. The three d orbitals which accommodate the six d electrons are d_{xz}, d_{yz} and $d_{x^2-y^2}$ in our coordinates system. The d_{xz}-orbital will interact in a back-bonding fashion with the empty 3π orbital of the carbon unit (see (c) of Scheme 1). Considering the four π-electrons (1π and 2π), the metallacycle possesses six π-electrons and therefore obeys the Hückel $4n+2$ rule, which is similar with the case in metallabenzenes as Thorn/Hoffmann described [9]. The d_{yz}-orbital keeps nonbonding with the carbon unit [10]. And the remaining $d_{x^2-y^2}$-orbital can be stabilized by the empty equatorial p-orbital (if the two phosphine ligands are considered as being at the apical position) of the carbyne carbon (≡C). This d–p π-back-bonding interaction (metal-to-carbon back-donation) can saturate the electron-deficient carbyne carbon, therefore deactivating the metallabenzyne (see (e) of Scheme 1).

Undoubtedly, what can enhance the two d–p π-back-bonding interactions, i.e. $d_{x^2-y^2}$(Os)–p(carbyne carbon) and d_{xz}(Os)–3π(carbon unit), will play stabilization effect on the osmabenzyne. Clearly, the most important factors may come from the ligands which *trans* and *cis* to the carbyne carbon (*trans*- and *cis*-ligand for short, respectively). Effects of the *trans*- and *cis*-ligand on the d–p π-back-bonding interactions and the stabilization of the osmabenzyne, as well as the subsituent effect of the silyl group on the carbon atom adjacent to the carbyne carbon, will be examined in the following sections with the aid of DFT calculations.

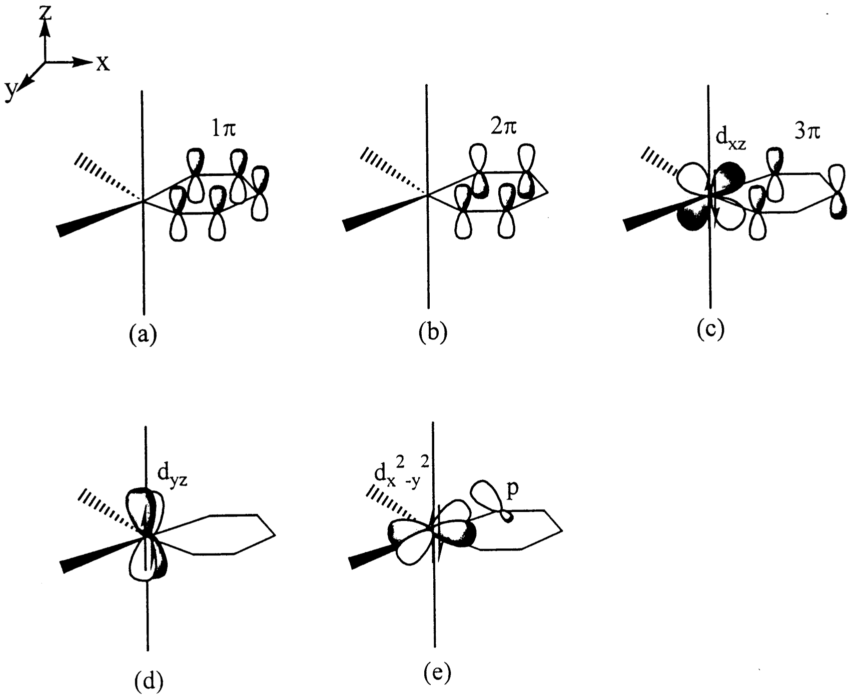
3. Computational method

Molecular geometries of all model complexes used in the following have been fully optimized at the Becke3LYP(B3LYP) level of DFT [11]. The LANL2DZ effective core potentials [12] and basis sets were used to describe Os, Cl and P. While the standard 6-31G** basis set was used for Si, C and H [13]. Polarization functions were also added to Cl and P, i.e. Cl(ξ(d) = 0.514) and P(ξ(d) = 0.34). All the calculations were performed with the GAUSSIAN-98 software package [14]. Natural bond orbital (NBO) analyses were performed using the NBO program [15] as implemented in the GAUSSIAN-98 program.

4. Results and discussion

4.1. Structure aspects of osmabenzyne

Model osmabenzyne $\overline{\mathrm{Os[{\equiv}C{-}C(SiH_3){=}C(CH_3){-}C(SiH_3){=}CH}}\mathrm{]Cl_2(PH_3)_2}$ (**2**) ($SiMe_3$ and PPh_3 ligands were modeled using SiH_3 and PH_3 groups, respectively) have been fully optimized and the important structural parameters are shown in Fig. 1,



Scheme 1.

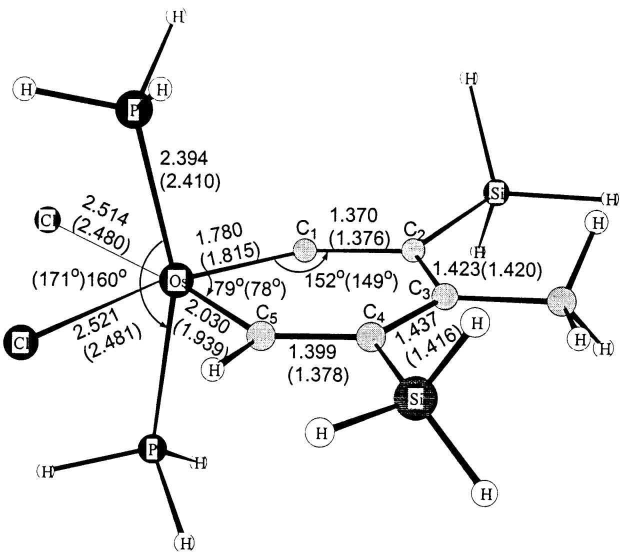


Fig. 1. Optimized structure with selected structure parameters for the model osmabenzyne **2** together with experimental structural parameters of **1** (given in parentheses). Selected bond indices (from NBO analysis): $Os-C_1$, 1.592; $Os-C_5$, 0.786; C_1-C_2, 1.437; C_2-C_3, 1.355; C_3-C_4, 1.298; C_4-C_5, 1.530 (distances are in Å and angles are in °).

together with those (in the parentheses) from the experimentally characterized osmabenzyne **1**. Clearly, the theoretical calculations well reproduce the experimental results except the smaller P–Os–P angle (160 vs. 171°), which will be discussed below.

From Fig. 1, we can see that the planar structure of the metallacycle keeps very well. The dihedral angles within the metallacycle are almost zero for all (i.e. $Os/C_1/C_2/C_3$, $C_1/C_2/C_3/C_4$, $C_2/C_3/C_4/C_5$, $C_3/C_4/C_5/Os$, $C_4/C_5/Os/C_1$ and $C_5/Os/C_1/C_2$). The sum of the internal angles within the ring is 719.8°, very close to the value of 720° required for a planar hexagon. The carbon–carbon distances within the ring are 1.370 Å for C_1-C_2, 1.423 Å for C_2-C_3, 1.437 Å for C_3-C_4 and 1.399 Å for C_4-C_5, which are comparable to those found in osmabenzene (1.39, 1.42, 1.38 and 1.36 Å, respectively) [5] and benzene itself (1.398 Å) [16]. The $Os-C_5$ bond length (2.030 Å) is slightly shorter than that (2.169 Å) for calculated Os–C single bond, and longer than that (1.881 Å) for calculated Os–C double bond. The bond distance of $Os-C_1$ (1.78 Å) is intermediate between normal Os–C double and triple bonds (1.881 and 1.725 Å, respectively) [17]. The bond distance data demonstrate the delocalization of bonding, a typical character of aromatic property.

The bond delocalization can also be found from the calculated bond indices (see the caption of Fig. 1). The C–C bond indices are between 1.298 and 1.530, which are comparable to the calculated those for benzene (1.436). The $Os-C_5$ bond index is 0.786, which is intermediate between calculated Os–C single and double bond indices (0.625 and 1.475, respectively). And $Os-C_1$ bond index is 1.618, which is within the range of those for Os–C double and triple bonds (1.475 and 2.070, respectively) [17].

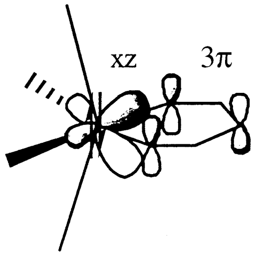
Although the delocalization of bonding within the metallacycle is evident, the differences of C–C distances and bond indices also exist. Especially, one may see that the notable arrangement of the short C_1-C_2, C_4-C_5 distances and concomitant long C_2-C_3, C_3-C_4 distances (see Fig. 1), which has somewhat similarity with the case of quinoid. This may stem from the weak interaction between the metal d_{xz}-orbital and the 3π orbital of carbon unit (see (c) of Scheme 1). The evidence can be found from the charge populations of the carbon atoms. The net charges are −0.184 for C_1, −0.246 for C_2, 0.131 for C_3, −0.144 for C_4 and −0.289 for C_5. The positive charge on C_3 indicates fewer electrons back-donating from occupied metal d_{xz} to the empty 3π orbital of the carbon unit [18].

Here another structure feature should be mentioned, that is the bending of P(phosphine)–Os–P(phosphine). Our calculated P–Os–P angle for model osmabenzyne **2** is 160°. The bending of P–Os–P is expected to enhance the $d_{xz}-3\pi$ back-bonding interaction between the metal and carbon unit (see Scheme 2); therefore benefits the aromaticity of the metallacycle. But the P–Os–P angle for osmabenzyne **1** is 171° experimentally, which is 11° larger than calculated result (for model osmabenzyne **2**). This is due to the steric crowdedness for phenyl groups in **1**, which disfavors the smaller P–Os–P angle.

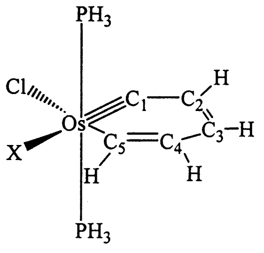
4.2. *Effect of trans- and cis-ligand on the stabilization for osmabenzyne*

Model osmabenzyne **3** with different *trans*-ligand X (X = Cl, CH_3, H, SiH_3) is used to examine the *trans*-ligand effect on the stability of osmabenzyne by DFT calculations. The ligands (X) used here represent different electronic properties, including a π-donor (Cl), σ-donor (CH_3, H) and π-acceptor (SiH_3) [19].

The calculated bond indices and distances of $Os-C_1$ and $Os-C_5$ of model osmabenzyne **3** with different *trans*-ligand X have been given in Table 1. The bond index data show that the different *trans*-ligand X has no significant impact on the $Os-C_5$ bond strength. Nevertheless, the bond index of $Os-C_1$ increases in the order



Scheme 2.



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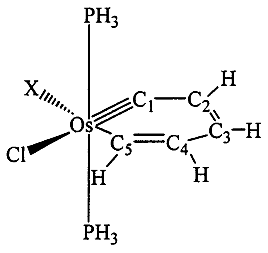

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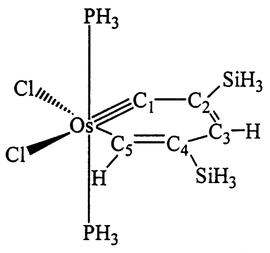

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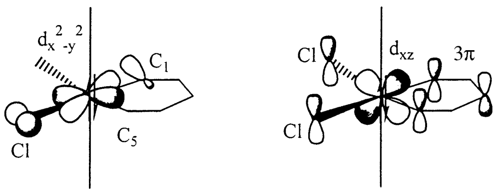
$SiH_3 < H < CH_3 < Cl$, which corresponds exactly to the trend of X from having π-acceptor, σ-donor to having π-donor properties. A reasonable explanation for the trend is that a π-donor ligand *trans* to the carbyne carbon (C_1) benefits the $d_{x^2-y^2}$–p and d_{xz}–3π back-bonding interactions between the metal and carbon unit (see (a) and (b) of Scheme 3), therefore enhancing the Os–C_1 bond. And a π-acceptor ligand will compete against these π-back-bonding interactions, which results in the weakest Os–C_1 bond. The calculated bond distances of Os–C_1 show that chloride ligand indeed corresponds to the shortest Os–C_1 distance (1.782 Å). But the SiH_3 does not give the longest Os–C_1 distance. This exception may be related to the steric effect of the silyl group. Actually, the C_5R_4 carbon unit nears the *trans*-ligand (X) more closer than the *cis*-ligand (Cl) in the studied complexes (the angle is about 80° for X(*trans*)–Os–C_5, and about 110° for Cl(*cis*)–Os–C_1). A bulky ligand X favors long Os–C_5 distance, which may shorten the Os–C_1 distance due to the carbon ring strain, i.e. steric crowded X ligand prefers short Os–C_1 distance. On the other hand, the short Os–C_1 distance is disfavored due to the *trans* influence of the ligand at the *trans* position of the C_1. Therefore, a final compromise is that the Cl ligand gives the shortest Os–C_1 distance due to the weakest *trans* influence of Cl. The hydride ligand corresponds to the longest Os–C_1 distance because of the smallest size and strong *trans* influence of H. Reasonably, the CH_3 and SiH_3 ligand give the intermediate Os–C_1 distance due to the steric crowdedness and the strongest *trans* influence of the two ligands. On the other hand, comparing with CH_3, SiH_3 gives smaller Os–C_1 bond index (1.485 for CH_3 and 1.381 for SiH_3) which further supports that the π-acceptor ligand SiH_3 makes against the d–p π-back-bonding interactions between the metal and carbon unit.

Table 1
Calculated Wiberg bond indices (from NBO) and bond distances (in Å) of Os–C_1 and Os–C_5 in the model osmabenzyne **3** and **4**

X	Wiberg bond index		Bond distance	
	Os–C_1	Os–C_5	Os–C_1	Os–C_5
trans-X	$\mathrm{Os(\equiv C{-}CH{=}CH{-}CH{=}CH)Cl}$(*trans*-X)$\mathrm{(PH_3)_2}$			
Cl	1.624	0.778	1.782	2.039
CH_3	1.485	0.782	1.827	2.048
H	1.382	0.799	1.835	2.045
SiH_3	1.381	0.771	1.828	2.057
cis-X	$\mathrm{Os(\equiv C{-}CH{=}CH{-}CH{=}CH)Cl}$(*cis*-X)$\mathrm{(PH_3)_2}$			
Cl	1.624	0.778	1.782	2.039
CH_3	1.648	0.643	1.777	2.014
H	1.641	0.578	1.777	2.013
SiH_3	1.617	0.573	1.777	2.014

Model osmabenzyne **4** with different ligand X are used to examine the *cis*-ligand effect on the stability of osmabenzyne. The calculated bond indices and distances of Os–C_1 and Os–C_5 have also been shown in Table 1. From Table 1, one can see that the Os–C_1 distances with different *cis*-ligand X are almost the same except X = Cl, and so do the Os–C_5 distances. This can be easily interpreted by the *trans* influence and steric effect of the *cis*-ligand X and the carbon ring strain as discussed before, although the steric effect cannot play significant role here because the carbon ring keeps away from the *cis*-ligand X in the studied complexes. Comparing with H, the SiH_3 and CH_3 ligands prefer shorter Os–C_5 distance due to their steric crowdedness as mentioned above, but their stronger *trans* influence properties eliminate this shortening effect. Finally, the CH_3, H, and SiH_3 give almost the same Os–C_1 and Os–C_5 distances. And chloride ligand gives the shortest Os–C_5 distance and the longest Os–C_1 distance comparing to the other *cis*-ligand X because of the weakest *trans* influence of Cl. From the bond index, we can see that the *cis*-ligand X has not evident influence on the Os–C_1 bond strength. But the Os–C_5 bond index increases with the *cis*-ligand X from having π-acceptor, σ-donor to



(a) (b)

Scheme 3.

having π-donor properties. Reasonably, this should be attributed to that a π-donor ligand can enhance the d_{xz}–3π back-bonding interaction between the metal and carbon unit (see (b) of Scheme 3), but a π-acceptor ligand goes against this π-back-bonding interaction.

From the calculated bond indices and orbital interaction analysis discussed above, we can conclude that a stronger π-donor ligand which *trans* or *cis* to the carbyne carbon can stabilize the osmabenzyne through enhancing the d–p π-back-bonding interactions between the metal fragment and carbon unit. The stabilizing effects of *trans*- and *cis*-ligands can also find support energetically. The estimated binding energies (BE) [20] between the metal fragment and carbon unit for model osmabenzyne **3** and **4** with different *trans*-ligand X and *cis*-ligand X, respectively, which are based on the B3LYP calculation, are given in Table 2. From Table 2, we can see that the chloride corresponds to the largest BE, which is consistent with that a stronger π-donor ligand benefits the binding between the metal fragment and carbon unit. The lower BE when $X = SiH_3$ and CH_3 may mainly arise from their strong *trans*-influencing property, which weaken the binding between the metal fragment and carbon unit.

The energy differences (ΔE) between osmabenzynes and their corresponding osmabenzenes for model osmabenzyne **3** and **4**, which can be considered as estimated values for the protonatation energies of osmabenzynes back to osmabenzenes, are presented in Table 2. From Table 2, we can see that the ΔE values increase with the ligand *trans* (*cis*) to the carbyne carbon from having π-donor, σ-donor to having π-acceptor properties. It denotes that protonation of osmabenzyne with π-donor ligand *trans* (*cis*) to the carbyne carbon back to its corresponding osmabenzene is more difficult comparing with that of osmabenzyne with σ-donor or π-acceptor ligand *trans* (*cis*) to the carbyne carbon.

Table 2
Estimated BE (in atomic unit) and energy difference between osmabenzyne and its corresponding osmabenzene (ΔE, in atomic unit) for model osmabenzyne **3** and **4**

X	BE [a]	ΔE
trans-X	$\overline{\mathrm{Os}(\equiv\mathrm{C{-}CH{=}CH{-}CH{=}C}}\mathrm{H})\mathrm{Cl}(trans\text{-}\mathrm{X})(\mathrm{PH}_3)_2$	
Cl	0.282	0.334
CH_3	0.266	0.380
H	0.270	0.384
SiH_3	0.258	0.385
cis-X	$\overline{\mathrm{Os}(\equiv\mathrm{C{-}CH{=}CH{-}CH{=}C}}\mathrm{H})\mathrm{Cl}(cis\text{-}\mathrm{X})(\mathrm{PH}_3)_2$	
Cl	0.282	0.334
CH_3	0.262	0.364
H	0.274	0.381
SiH_3	0.265	0.397

[a] BE is evaluated as the energy difference between the model complex and its constituent $OsCl(X)(PH_3)_2$ and C_5H_4 moieties. Here the geometry of C_5H_4 is got from $\overline{\mathrm{Os}(\equiv\mathrm{C{-}CH{=}CH{-}CH{=}C}}\mathrm{H})\mathrm{Cl}_2(\mathrm{PH}_3)_2$.

Following the suggestion of one referee, we also examine the metal d_{xz}-, $d_{x^2-y^2}$-orbital populations and Os atomic population. We found no significant dependence of the d_{xz}-, $d_{x^2-y^2}$-orbital populations on the different property of the *trans*- or *cis*-ligand. This may be related to the fact that the d–p π-back-donating interactions between the metal and carbon unit greatly depends on the *trans*- or *cis*-ligand X. In other words, although a π-donor ligand can increase the metal d_{xz}- or $d_{x^2-y^2}$-orbital population, the concomitant enhanced d–p π-back-donating interactions between the metal and carbon unit will reduce this effect. And a π-acceptor ligand cannot donate electron to the metal d_{xz}- or $d_{x^2-y^2}$-orbital, but the weakened metal to carbon back-donating can decrease the metal d-orbitals' electron expenditure. The atomic population of Os in model osmabenzyne **3** is, 0.127 for $X = Cl$, 0.125 for $X = CH_3$, 0.007 for $X = H$ and -0.067 for $X = SiH_3$ (the same case has been found for model osmabenzyne **4**). It seems that the Os atomic population has nothing to do with the π-donor/π-acceptor property of X. A reasonable explanation for this trend is that the osmium atomic population mainly depends on the σ-donating ability or electronegativety of X.

4.3. Substituent effect of silyl group

To examine the substituent effect of silyl group on the carbon adjacent to the carbyne carbon on the stability of osmabenzyne, model osmabenzyne **5** has been calculated. The $Os–C_1$ and $Os–C_5$ bonds indexes are 1.618 and 0.786, respectively. No significant change is found comparing with those (1.624 and 0.778, respectively) of unsubstituent osmabenzyne $\overline{\mathrm{Os}(\equiv\mathrm{C{-}CH{=}CH{-}CH{=}C}}\mathrm{H})\mathrm{Cl}_2(\mathrm{PH}_3)_2$. The most remarkable change is the net charge of C_1 (-0.184) compared with that (-0.196) of the unsubstituent osmabenzyne. The change of charge population is probably due to the very positive charge carried by Si through its σ-polarization. The more positive charge of C_1 makes against the attachment of proton. As a result, we can say that the silyl group can hinder the protonation of osmabenzyne back to its corresponding osmabenzene.

5. Conclusion

In this paper, an attempt has been made to examine the electronic reason for the stabilization of osmabenzyne $\overline{\mathrm{Os}[\equiv\mathrm{C{-}C(SiMe_3){=}C(CH_3){-}C(SiMe_3){=}C}}\mathrm{H}]\mathrm{Cl}_2(\mathrm{PPh}_3)_2$ with the aid of qualitative fragment orbital interaction analysis and density functional theory calculations.

The valence electron analysis shows that the six-membered metallacycle possesses six π-electrons and therefore obeys the Hückel $4n+2$ rule. The planar structure and bond delocalization of the metallacycle also show that the osmabenzyne has somewhat aromatic property. The bending away from the carbon unit of the P(phosphine)–Os–P(phosphine) can enhance this aromaticity.

The filled metal $d_{x^2-y^2}$-orbital can interact with the equatorial p-orbital of the high reactive carbyne carbon in a back-bonding fashion, which can deactivate the carbyne carbon. This d–p π-back-bonding interaction can be enhanced by the ligand *trans* to carbyne carbon if it is a stronger π-donor ligand. And a strong π-donor ligand *trans* or *cis* to the carbyne carbon also benefits the d_{xz}–3π back-bonding interaction between the metal and carbon unit. The calculated bond indices show that a π-donor ligand *trans* to the carbyne carbon indeed corresponds to larger Os–C_1 bond index, and a π-donor ligand *cis* to the carbyne carbon also gives larger Os–C_5 bond index, comparing with σ-donor or π-acceptor ligand. The *trans*- and *cis*-ligand effects are further supported by the calculated BE and energy difference between osmabenzyne and its corresponding osmabenzene.

And the substituent effect of silyl group on the carbon adjacent to the carbyne carbon on the stability of osmabenzyne has been examined. The result show that the silyl group causes the carbyne carbon more positive, which indicates that silyl group can prevent the protonation back to the corresponding osmabenzene through its polarization effect.

Acknowledgements

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[17] The bond distances and indices of Os–C single, double and triple bond are got from the results of calculated model complexes $[OsCl_2(CH_3)(=CH_2)(PH_3)_2]^-$ and $OsCl_2(CH_3)(\equiv CH)(PH_3)_2$ which are optimized at B3LYP level and using the same basis sets as the context.

[18] To eliminate the influence of substituent silyl and methyl groups on the carbon ring, the net charges on carbons of the unsubstituted osmabenzyne are examined. They are -0.196 for C_1, -0.169 for C_2, -0.057 for C_3, -0.08 for C_4 and -0.286 for C_5. Also fewer electrons are distributed on C_3 comparing with C_1, C_2, C_4 and C_5.

[19] A reviewer commented, SiH_3 ligand is strongly electron-donating. But it also has somewhat π-acceptor property. See: (a) F.R. Lemke, K.J. Galat, W.J. Youngs, Organometallics 18 (1999) 1419;
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