An investigation of the aromaticity of transition metal heterocyclic complexes by conventional criteria and indices of aromaticity

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Received 22 July 2003; accepted 15 January 2004

Abstract

Conventional criteria and indices of aromaticity, including electronic, geometric, energetic and magnetic aspects have been applied to examine the aromaticity of five typical transition metal heterocyclic complexes, i.e. six-membered osmabezene **1** and iridabenzene **2**, five-membered cobaltacyclopentadiene **3** and iridacyclopentadiene **4**, and four-membered tungstacyclobutadiene **5**. The results show that the cyclic, planar, conjugated and Hückel $4n + 2$ rule's criteria in the transition-metal-containing heterocycles of the five complexes studied are all met. Five quantitative aromaticity indices, including Bird aromatic index (I_n), homodesmotic reaction aromatic stabilization energy (HASE), absolute hardness (η), diamagnetic susceptibility exaltation (Λ) and NMR chemical shift (δH), qualitatively lead to a consistent and affirmative conclusion that all of them are aromatic. However, they fail to draw a common conclusion for their relative magnitudes of aromaticity, which proves once again the multidimensional character of aromaticity.
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Keywords: Transition metal heterocyclic complex; Aromaticity; Aromaticity index

1. Introduction

Traditionally, the term "aromaticity" has been associated with some specific organic compounds, which common characteristics are planar, cyclic and possessing delocalized π-electrons, for examples, benzene, furan, pyridine, thiophene and phosphabenzene. A significant feature of these systems is that the conjugated π orbitals are composed by the p orbitals of carbon or heteroatoms. Here we call them as traditional or conventional p–p π conjugated systems. The electronic structure and aromaticity, including quantitative criterion and index of aromaticity, of these p–p π conjugated systems have been well studied [1,2]. However, very little has been known about the transition metal heterocyclic compound, in which a CH group has been formally replaced by a transition metal
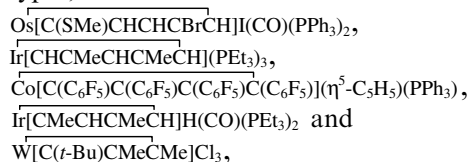
and its associated ligands [3–5]. A typical feature of these compounds is that the transition metal d orbital participates the π-conjugation. By contrast with p–p π conjugated systems, here we call them as d–p π conjugated systems. In 1979, Thorn and Hoffmann [6] predicted that metallabenzenes were aromatic. However, as far as we know, it is not exactly clear that how to judge whether a transition metal heterocyclic compound is aromatic and estimate its magnitude of aromaticity. And this is the objective of our investigations. In this paper, we will just focus on examining the aromaticity of five typical transition metal heterocyclic complexes by the conventional criteria and indices of aromaticity, such as Hückel $4n + 2$ rule, Bird aromaticity index, homodesmotic reaction aromatic stabilization energy (HASE), absolute hardness, diamagnetic susceptibility exaltation and NMR chemical shift, which have been applied successfully to the traditional p–p π conjugated systems. And further studies on new criteria and indices of aromaticity for transition-metal-containing complexes will be conducted in the future.

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2. Models and computational details

For the purpose of our investigation, five typical transition metal heterocyclic complexes have been chosen, i.e. six-membered osmabezene $Os[CHCHCHCHCH]I(CO)(PH_3)_2$ **1** and iridabenzene $Ir[CHCHCHCHCH](PH_3)_3$ **2**, five-membered cobaltacyclopentadiene $Co[CHCHCHCH](\eta^5\text{-}C_5H_5)(PH_3)$ **3** and iridacyclopentadiene $Ir[CHCHCHCH]H(CO)(PH_3)_2$ **4** and four-membered tungstacyclobutadiene $W[CHCHCH]Cl_3$ **5**. These model compounds came from their experimental prototypes, i.e.

$Os[C(SMe)CHCHCBrCH]I(CO)(PPh_3)_2$,

$Ir[CHCMeCHCMeCH](PEt_3)_3$,

$Co[C(C_6F_5)C(C_6F_5)C(C_6F_5)C(C_6F_5)](\eta^5\text{-}C_5H_5)(PPh_3)$,

$Ir[CMeCHCMeCH]H(CO)(PEt_3)_2$ and

$W[C(t\text{-}Bu)CMeCMe]Cl_3$,

respectively, with all PPh$_3$ and PEt$_3$ ligands were modeled using PH$_3$ groups and all substituents on their carbon units were replaced by hydrogen [3,7–9].

1   **3**   **5**

2   **4**
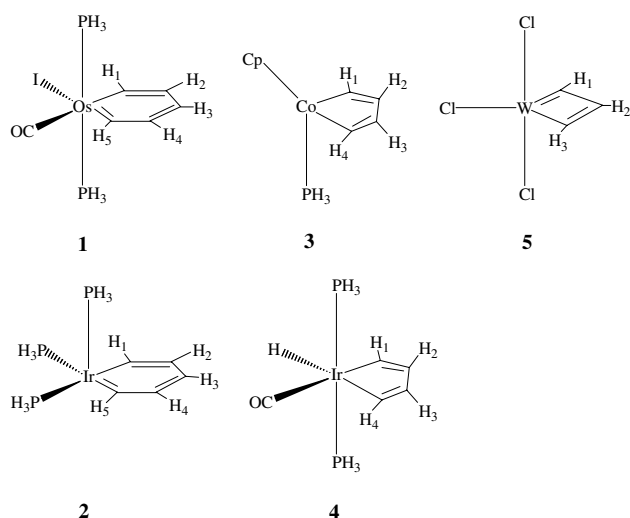
Molecular geometries of all model complexes used in the follows have been fully optimized at the B3LYP level of DFT [10]. The LANL2DZ effective core potentials [11] and basis sets were used to describe Os, Ir, Co, W, P, I and Cl, while the standard 6-31G** basis set was used for C, H, O and N [12]. Polarization functions were also added to P, I and Cl, i.e. P ($\xi(d) = 0.34$), I ($\xi(d) = 0.266$) and Cl ($\xi(d) = 0.514$). Moreover, one reviewer concerned that DFT method might overestimate the conjugation in general, and then aromaticity in this paper. This is true in general. To check the possible method problem, we followed the reviewer's suggestion, MP2 method (the same basis sets as the above) was used to calculate complex **1**. The optimized structure parameters have no significant changes comparing with the ones by the method of B3LYP. But compared with the

experimental structure parameters, it seems that the DFT method gave a better agreement with the experiments than MP2 (the biggest discrepancy is 0.106 Å for MP2, 0.085 Å for DFT). Natural bond orbital (NBO) analyses were performed using the NBO program as implemented in the GAUSSIAN-98 program [13]. Molecular magnetic susceptibilities and NMR chemical shifts were calculated at the B3LYP level using the continuous set of gauge transformations (CSGT) [14] and the gauge-independent atomic orbital (GIAO) [15] methods, respectively. All the calculations were performed with the GAUSSIAN-98 software package [16].

3. Results and discussion

In traditional aromaticity chemistry, we assert a compound is aromatic based on four basic criteria, namely, cyclic, planar, conjugated and Hückel $4n + 2$ rule, which should be met at the same time. There are also many quantitative indices of aromaticity, including Bird index, HASE, absolute hardness, diamagnetic susceptibility exaltation and NMR chemical shift, with which one can compare the relative magnitude of different aromatic compound. We here apply these conventional criteria and quantitative indices of aromaticity to our model transition metal heterocyclic compounds in order to assess their aromaticities in detail.

3.1. Geometric criteria

Model osmabenzene **1**, iridabenzene **2**, cobaltacyclopentadiene **3**, iridacyclopentadiene **4** and tungstacyclobutadiene **5** have been fully optimized. The optimized structures and some important structural parameters are shown in Fig. 1, together with those parameters from their experimentally characterized prototypes (no for the prototype of **4**). Clearly, the theoretical calculations may be said to well reproduce the experimental results when the differences between the models and their experimental prototypes are considered.

Our calculations show three wonderfully planar metallacycles: the dihedral angles C$_3$–C$_2$–C$_1$–Os, C$_4$–C$_3$–C$_2$–C$_1$ and C$_5$–C$_4$–C$_3$–C$_2$ in **1**, C$_3$–C$_2$–C$_1$–Ir and C$_4$–C$_3$–C$_2$–C$_1$ in **4**, and C$_3$–C$_2$–C$_1$–W in **5** are nearly zero, and the sums of the internal angles within the rings are 720°, 540° and 360°, respectively, which are the values exactly required for planar hexagon, pentagon and quadrangle, respectively. By comparison, the atoms of Ir in **2** and Co in **3** are slightly departed from the planes of their carbon portions, 5° in **2** and 3° in **3**.

From the bond distance data listed in Fig. 1, we can see that the C–C bond distances in the five metallacycles are obviously averaged since the largest deviation is 0.042 Å in **1**, 0.010 Å in **2**, 0.108 Å in **3**, 0.110 Å in **4** and even zero in **5**, and all can be comparable to those found
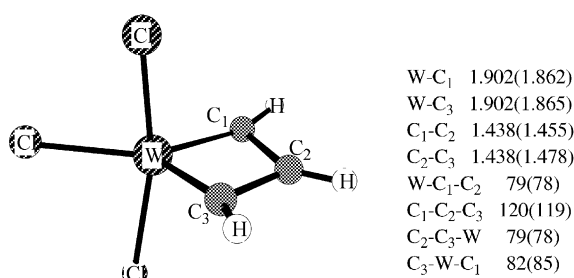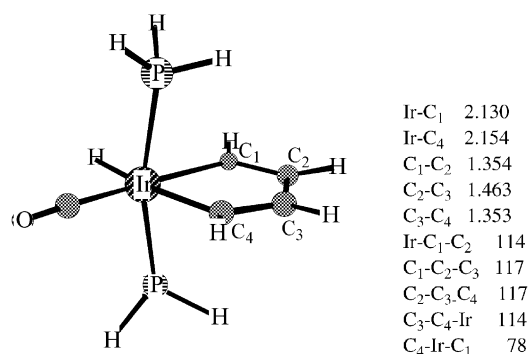
Os-C$_1$ 2.096(2.128)
Os-C$_5$ 1.998(2.039)
C$_1$-C$_2$ 1.375(1.418)
C$_2$-C$_3$ 1.417(1.367)
C$_3$-C$_4$ 1.389(1.390)
C$_4$-C$_5$ 1.405(1.320)
Os-C$_1$-C$_2$ 129(126)
C$_1$-C$_2$-C$_3$ 123(123)
C$_2$-C$_3$-C$_4$ 126(127)
C$_3$-C$_4$-C$_5$ 125(126)
C$_4$-C$_5$-Os 130(129)
C$_5$-Os-C$_1$ 87(87)

Ir-C$_1$ 1.998(2.024)
Ir-C$_5$ 1.998(1.985)
C$_1$-C$_2$ 1.389(1.369)
C$_2$-C$_3$ 1.399(1.402)
C$_3$-C$_4$ 1.399(1.370)
C$_4$-C$_5$ 1.389(1.392)
Ir-C$_1$-C$_2$ 130(131)
C$_1$-C$_2$-C$_3$ 124(123)
C$_2$-C$_3$-C$_4$ 123(125)
C$_3$-C$_4$-C$_5$ 124(122)
C$_4$-C$_5$-Ir 130(133)
C$_5$-Ir-C$_1$ 87(85)

Co-C$_1$ 1.934(1.995)
Co-C$_4$ 1.934(1.993)
C$_1$-C$_2$ 1.352(1.326)
C$_2$-C$_3$ 1.460(1.467)
C$_3$-C$_4$ 1.352(1.335)
Co-C$_1$-C$_2$ 113(112)
C$_1$-C$_2$-C$_3$ 115(117)
C$_2$-C$_3$-C$_4$ 115(115)
C$_3$-C$_4$-Co 113(113)
C$_4$-Co-C$_1$ 84(82)

Ir-C$_1$ 2.130
Ir-C$_4$ 2.154
C$_1$-C$_2$ 1.354
C$_2$-C$_3$ 1.463
C$_3$-C$_4$ 1.353
Ir-C$_1$-C$_2$ 114
C$_1$-C$_2$-C$_3$ 117
C$_2$-C$_3$-C$_4$ 117
C$_3$-C$_4$-Ir 114
C$_4$-Ir-C$_1$ 78

W-C$_1$ 1.902(1.862)
W-C$_3$ 1.902(1.865)
C$_1$-C$_2$ 1.438(1.455)
C$_2$-C$_3$ 1.438(1.478)
W-C$_1$-C$_2$ 79(78)
C$_1$-C$_2$-C$_3$ 120(119)
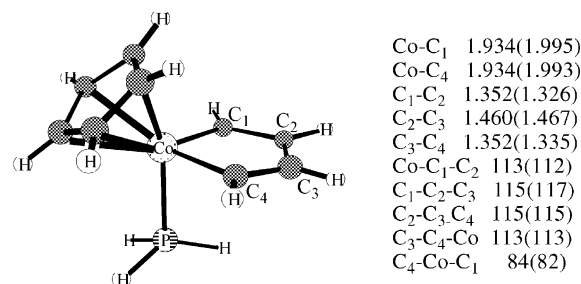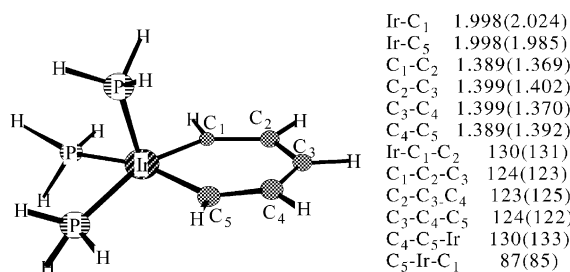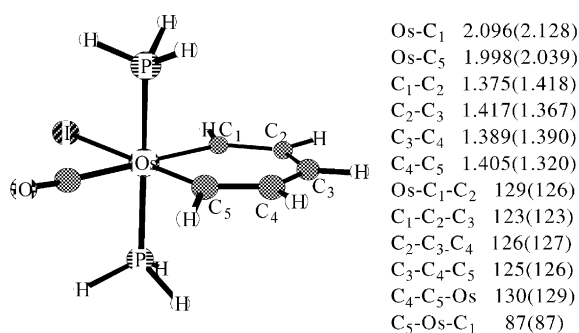C$_2$-C$_3$-W 79(78)
C$_3$-W-C$_1$ 82(85)

Fig. 1. Optimized structures with selected structure parameters for the model 1–5 together with experimental structural parameters of their prototypes (given in the parentheses). Distances are in Å and angles are in degrees.

in benzene (1.398 Å) [17]. Such evenness can also be seen among M–C (M = Os, Ir, Co, W) bonds, which are all between normal M–C single and double bonds since the normal distances are 2.148 and 1.943 Å for Os–C single and double bonds, 2.160 and 1.897 Å for Ir–C bonds, 1.966 and 1.737 Å for Co–C bonds, 2.139 and 1.862 Å for W–C bonds [18].

In a word, these systems studied here show good planarity and conjugation properties in the transition-metal-containing heterocycles.

3.2. The Hückel $4n + 2$ rule

In the six-membered model complexes 1 and 2, the carbon unit is perhaps best regarded as a monoanionic ligand $C_5H_5^-$ [19]. In this view, it possesses eight valence electrons in addition to back-bone σ-electrons. Four of these valence electrons are used to form σ-bonds to osmium or iridium, while the remaining four are π-electrons and reside in comparatively low-lying 1π and 2π orbitals of the carbon unit (see (a) and (b) of Scheme 1). Naturally 1 can be considered as a distorted octahedral Os(II)≡d^6 complex and 2, a distorted trigonal bipyramidal Ir(I)≡d^8 complex. The filled d_{xz} orbital of Os(II) and hybrid d_{xz}/d_z^2 orbital of Ir(I) in our coordinates system will interact in a back-bonding fashion with the empty 3π orbital of the carbon unit (see (c) and (d) of Scheme 1). Considering the four π-electrons of the carbon unit, both 1 and 2 therefore obey the Hückel $4n + 2$ rule as Thorn/Hoffmann predicted [6].

In the two five-membered metallacycles 3 and 4, the carbon unit is obviously a dianion ligand ($C_4H_4^{2-}$) and possesses the similar four π-electrons residing 1π and 2π orbitals (see (a) and (b) of Scheme 2) as the above $C_5H_5^-$. Then 3 is a sexadentate Co(III)≡d^{10} complex and 4 is a sexadentate Ir(III)≡d^6 complex. They have filled hybrid d_{xz}/d_z^2 orbital and d_{xz} orbital in our coordinates system, respectively, which can interact with the empty 3π orbital of the carbon unit in back-bonding fashion (see (c) and (d) of Scheme 2) and donate two π-electrons so that both of them have six π-electrons and obey the Hückel $4n + 2$ rule.
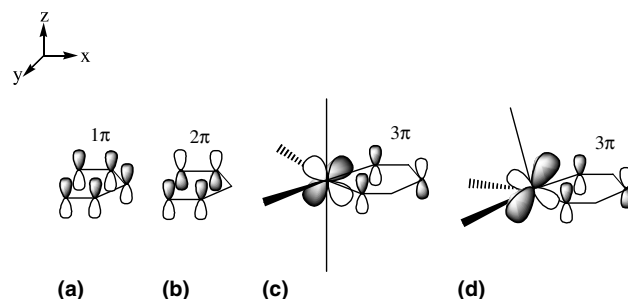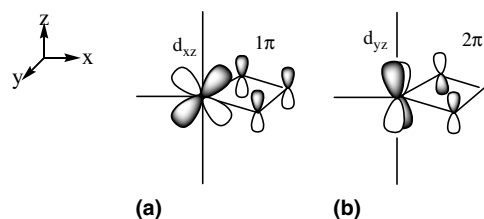

Scheme 1.
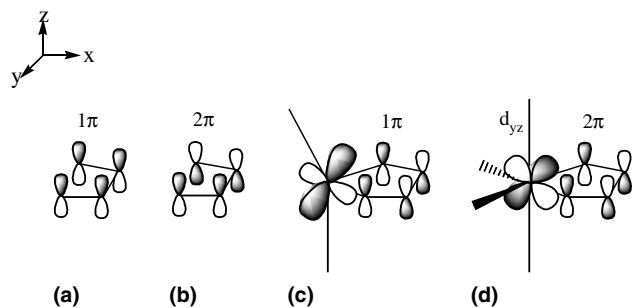
Scheme 2.

In the four-membered **5**, the carbon unit C_3H_3 can be considered as monoanion $C_3H_3^-$ ligand. It possesses 16 valence electrons totally. Besides the ten back-bone σ-electrons and the four electrons which are used to form σ-bonds to metal center, there are two π-electrons residing in its 1π orbital. This orbital can interact with the empty metal d_{xz} orbital in a back-bonding fashion (see (a) of Scheme 3). And the only two d electrons of the metal center reside in its d_{yz} orbital, which keeps nonbonding with the carbon unit (at most a rather weak δ interaction between it and the 2π orbital (see (b) of Scheme 3), which can be ignored) [3]. In this consideration, the four-membered metallacycle has only two formal π electrons, but still obeys the $4n + 2$ rule ($n = 0$).

The above qualitative fragment orbital interaction analysis demonstrates that the five metallacycles studied all possess the electronic property of aromatic species, conforming to the Hückel $4n + 2$ rule, though the

Scheme 3.

numbers of atoms in these metallacycles are not the same.

3.3. Bird aromaticity index I_n

The equalization of bond lengths has been generally recognized as the property of delocalized bonds. I_n, introduced by Bird, was used to demonstrate whether a traditional heterocyclic compound possesses such property [20]. It is based upon the statistical evaluation of the extent of variation of ring bond orders as given by the expression

$$I_n = 100(1 - V/V_K), \quad \text{where } V = \frac{100}{\bar{N}} \sqrt{\frac{\sum (N - \bar{N})^2}{n}},$$

$\bar{N}$ is the arithmetic mean of the n various ring bond orders, N, which we here get directly from NBO analysis instead of the original method $N = a/R^2 - b$. V_K is the value of V for the corresponding non-delocalised Kekulé form with alternating single and double bonds. Bird gave unified $V_K = 33.3$ for six-membered heterocycles and $V_K = 35$ for five-membered herterocycles, but no for four-membered ones.

We here consider that different hetero-atoms impact the value of V_K as strongly as the different ring sizes do. So we have calculated V_K for every studied system following its original define, i.e. V for an partially optimized system with the bond lengths in the ring being fixed, where the single and double C–C bonds equal with ones in cyclobutadiene, the single and double M–C bonds equal with ones coming from the corresponding $MR_n(CH_2)(CH_3)$ (for six- and four-membered cycles) or $MR_n(CH_3)_2$ (for five-membered cycles). The data of I_n for five metallacycles in this method have been listed in Table 1. The positive I_n data demonstrate that the electrons in the rings are delocalized, and therefore they are aromatic. We can also see that the I_n decreases from six-membered **1** (18) and **2** (26) to five-membered **3** (7) and **4** (6) as well as from six-membered benzene (100) and pyridine (99) to five-membered pyrrole (39), while I_4 for four-membered **5**, 78, is the greatest among the five metallacycles. It is, I_n predicts

Table 1
Calculated $I_6/I_5/I_4$, HASE, absolute hardness (η) and diamagnetic susceptibility exaltation (Λ)

Compound	$I_6/I_5/I_4$	HASE[a]/(kJ mol^{-1})	η/eV	Λ/cgs-ppm
Osmabenzene **1**	18	−79.3	4.43	−7.0
Iridabenzene **2**	26	−61.7	4.22	−10.2
Cobaltacyclopentadiene **3**	7	−17.9	4.62	−2.2
Iridacyclopentadiene **4**	6	−23.1	4.81	−1.5
Tungstacyclobutadiene **5**	78	−11.3	4.78	−11.0
Benzene	100	−163.0	6.47	−10.9
Pyridine	99	−134.7	6.32	−10.6
Pyrrole	39	−90.0	6.65	−9.7

[a] Scaled by zero-point vibrational energy.

the relative aromaticity for the five model complexes studied as five-membered **3** and **4** < six-membered **1** and **2** < four-membered **5**.

3.4. Homodesmotic reaction aromatic stabilization energy

Homodesmotic reaction aromatic stabilization energy (HASE) is a measure calculating the delocalized energy of π-electrons in a conjugated system on the basis of a model homodesmotic reaction, where there are the same number of bonds between given atoms in each state of hybridization both in products and reactants [21,22]. We designed Eqs. (1)–(5) for the five metallacycles and (6)–(8) for the other traditional cycles, where the conjugated rings with multiple bonds were converted to the corresponding cyclic monoenes, which is expected to cancel strain effects more effectively than when they are converted to some alkenes [22,23]. The calculated data of HASEs for the eight cycles have been shown in Table 1. They are all negative, which demonstrates that all of the five model metallacycles, as well as benzene, pyridine and pyrrole, are aromatic. And the negative HASEs for the five objects decrease in such sequence as six-membered **1** (79.3 kJ mol^{-1}) and **2** (61.7 kJ mol^{-1}) > five-membered **3** (17.9 kJ mol^{-1}) and **4** (23.1 kJ mol^{-1}) > four-membered **5** (11.3 kJ mol^{-1}), which predicts their aromaticities decrease with decreasing ring size. It is in part due to that any increment scheme cannot completely cancel planar cyclic strain.

$$(1)$$

$$(2)$$

$$(3)$$

$$(4)$$

$$(5)$$

$$(6)$$

$$(7)$$

$$(8)$$
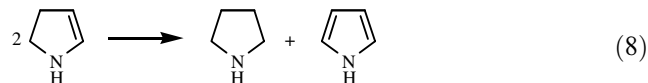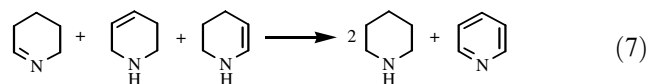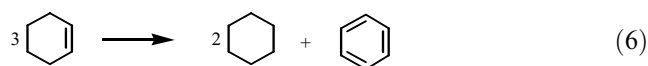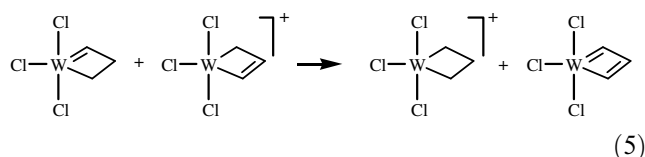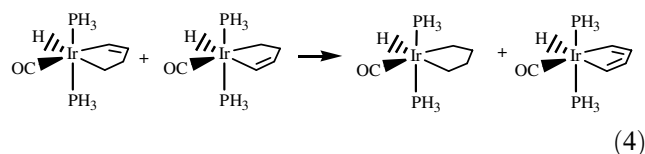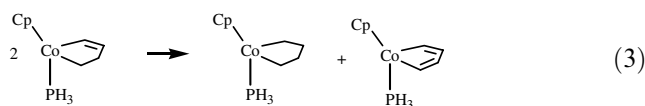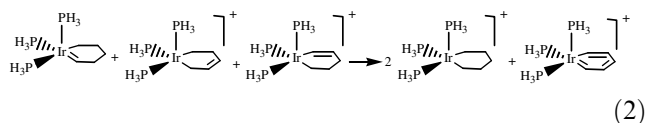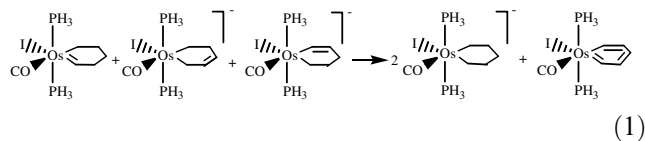
3.5. Absolute hardness (η)

Absolute hardness is an important criteria to value the stabilization and reactivity of a molecule [24], which has been defined as half the HOMO–LUMO gap for Hartree–Fock (HF) or Hückel theory, i.e. $\eta = (\varepsilon_{LUMO} - \varepsilon_{HOMO})/2$, by Pearson according to Koopman's theorem of frontier orbital [25]. Recently Zhou and Parr have developed it as a quantitative aromaticity measure and defined the dividing line between aromatic and antiaromatic species as $0.2\eta_B$ (η_B = the absolute hardness of benzene) on the ground of a great deal of calculations and comparison [26]. And they have also inferred in light of the principle of maximum hardness that the larger the η is, the more aromatic the molecule is.

η data listed in Table 1 are HF absolute hardness, and for the consistency in the discussion the HF calculations were performed on the single points of the above structures optimized with DFT method. The hardness values for the model complexes **1**–**5** are 4.43, 4.22, 4.62, 4.81 and 4.78 eV, respectively, which are all larger than twenty percent of benzene's 6.47 eV. Then according to Zhou and Parr, all the five metallacycles are aromatic, and the five- and four-membered metallacycles are more aromatic than the six-membered ones.

3.6. Diamagnetic susceptibility exaltation (Λ)

In the 60s of twentieth century, Dauben et al. [27] reported an experimental criterion of aromatic character based on global susceptibilities of compounds, which recently has been improved in computing by Kutzelnigg [28] and Schleyer etc. [29]. The diamagnetic susceptibility exaltation (Λ) of a conjugated system is the difference between the calculated susceptibility of itself (χ_M) and that of corresponding localized system (χ'_M): $\Lambda = \chi_M - \chi'_M$ (χ'_M is estimated with the method of bond separation, i.e. homodesmotic reaction equations in our work). A negative diamagnetic susceptibility exaltation exhibits aromaticity, whereas antiaromaticity. From the computed data of Λ listed in Table 1, we can see that the exaltations of all the five metallacyles are negative, which demonstrates the diamagnetic cyclic current in the rings and therefore they are aromatic. The negative

Table 2
The calculated NMR chemical shift data of out-ring protons

	H_1	H_2	H_3	H_4	H_5
Osmabenzene **1**	11.45	7.54	7.21	7.14	13.19
Iridabenzene **2**[a]	10.75	7.32	7.01		
Cobaltacyclopentadiene **3**	7.86	6.81			
Iridacyclopentadiene **4**	8.59	6.75	6.91	6.17	
Tungstacyclobutadiene **5**	9.82	12.14			
Benzene	7.39				
Pyridine	8.78	7.20	7.55		
Pyrrole	6.53	6.18			

[a] H_1 is the hydrogen atom on the carbon adjacent to hetero-atom, namely α hydrogen; H_2 is the β hydrogen and H_3 is the γ hydrogen.

exaltations for five-membered **3** and **4** (2.2 and 1.5 cgs-ppm) are obviously less than those for six-membered **1** and **2** (7.0 and 10.2 cgs-ppm), while that for four-membered **5** (11.0 cgs-ppm) is larger than all of them. That is, the six-membered metallacycles are more aromatic than the five-membered ones, but the four-membered is the most aromatic among them, which is agreed with I_n.

3.7. NMR chemical shift of out-ring proton (δH)

It has long been recognized that the conjugated system of π electrons under an applied field supports a ring current, which exerts a deshielding effect on atoms outside the ring [30]. As a result, the out-ring protons of an aromatic cycle are shifted downfield in their ^{1}H NMR spectrum. So we can determine the aromaticity of a cycle according to the computed NMR chemical shifts of its out-ring protons. The computed δH data for the eight cycles are presented in Table 2. The protons around the five metallacycles are obviously shifted downfield as that in benzene, pyridine and pyrrole. Among them, the α-Hs' shifts should be partly attributed to the magnetic anisotropic influences from the adjacent large metal atoms [3], while the others' shifts primarily come from the aromatic cyclic current. We can also see that those non-α-Hs in six-membered **1** and **2** are shifted more than those in five-membered **3** and **4**, while that in the four-membered **5** is shifted most among them. Then the relative aromaticity order, five-membered **3** and **4** < six-membered **1** and **2** < four-membered **5**, having been predicted by both I_n and Λ, can be reproduced.

4. Conclusion

In this paper, an attempt has been made to investigate aromaticities of five typical d–p π conjugated model organometallic complexes, i.e. six-membered osmabezene **1** and iridabenzene **2**, five-membered cobaltacyclopentadiene **3** and iridacyclobutadiene **4** and four-membered tungstacyclobutadiene **5**, with the aid of qualitative fragment orbital interaction analysis and quantitative density functional theory calculations.

The optimized structures show that each of the five metallacycles keeps very good coplanarity no matter it is six-, five- or four-membered, and also the average of bond lengths has been observed. The valence electron analysis denotes that the six- and five-membered metallacycles (**1**, **2**, **3**, **4**) possess six delocalized π-electrons due to the back-bonding interaction between the filled metal d_{xz} orbital or hybrid d_{xz}/d_z^2 orbital and the empty 3π orbital of the carbon unit, and four-membered **5** has two delocalized π-electrons due to the interaction between its empty metal d_{xz} orbital and the filled 1π orbital of its carbon unit. That is, the conventional criteria of cyclic, planar, conjugated and Hückel $4n + 2$ rule in the transition-metal-containing heterocycles of the five complexes studied are all met.

The aromaticities of these five models have also been quantitatively probed with diverse aromaticity indicators, i.e. Bird aromatic index (I_n), homodesmotic reaction aromatic stabilization energy (HASE), absolute hardness (η), diamagnetic susceptibility exaltation (Λ) and NMR chemical shift (δH), which covers their aspects of geometry, energetic and magnetic properties. Although these traditional methods qualitatively lead to a consistent and affirmative conclusion that all of them exist aromaticity, they fail to draw a common conclusion for their relative magnitudes of aromaticity, which is found to differ depending on the aromaticity criterion used. It proves once again the multidimensional character of aromaticity that has been widely accepted recently [1,31–34]. Three among the indices, I_n, diamagnetic susceptibility and NMR chemical shift, point to the relative ordering **3** and **4** < **1** and **2** < **5**, that is, the six-membered metallacycles are more aromatic than the five-membered ones and the four-membered one is the most aromatic among them. Whereas the other two energy indices, HASE and absolute hardness, almost get to each other's reverse: HASE predicts their aromaticities decrease with decreasing ring size, while absolute hardness predicts the smaller five- and four-membered metallacycles are more aromatic than the six-membered ones.

Acknowledgements

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