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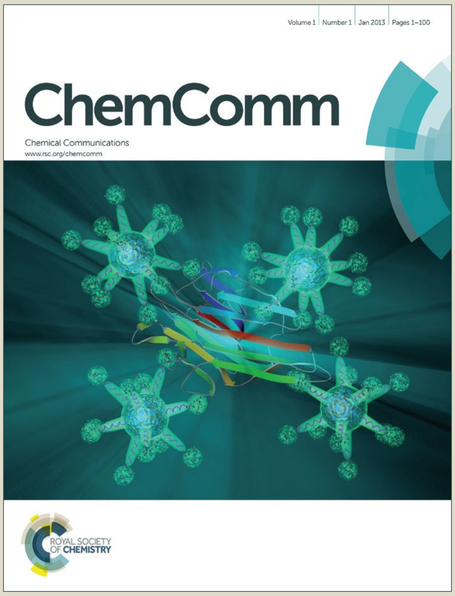

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Unexpected Higher Stabilisation of Two Classical Antiaromatic Frameworks with a Ruthenium Fragment over Osmium Counterpart: Origin Probed by DFT Calculations

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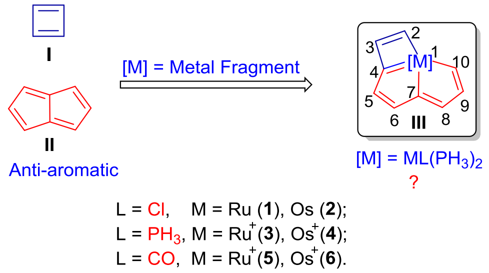
Density functional theory (DFT) calculations were carried out to investigate the stability and aromaticity of metallapentalocyclobutadienes. The results reveal unexpected higher stabilisation with a 3*d* ruthenium fragment over 4*d* osmium counterpart. Moreover, direct 1–3 metal–carbon bonding in the metallabutadiene unit of these two complexes is negligible.

Aromaticity, one of the most important concepts in chemistry, has long attracted considerable interest of both experimentalists and theoreticians due to its ever increasing diversity.[1] Many aromatics, including benzene and its derivatives, porphyrins, fullerenes, carbon nanotubes, and graphene, have numerous applications in many fields, such as materials science, energy science, and environmental science. In general, monocyclic conjugated compounds with [4*n* + 2] π electrons[2] are aromatic in their ground state whereas those with [4*n*] π electrons are antiaromatic. Syntheses of antiaromatic species are particularly challenging because usually they are unstable and reactive. For example (Scheme 1), cyclobutadiene[3,4] (CBD, **I**) and pentalene[5,6] (**II**) are highly unstable as two typical representatives of antiaromatic compounds for monocyclic and bicyclic systems with [4*n*] π-electrons.

Among various approaches to reduce antiaromaticity, introduction of a metal fragment[7] is particularly popular. Recently, Zhu, Xia and co-workers[8] reported stabilisation of two typically antiaromatic frameworks, CBD and pentalene by introducing an osmium fragment. Complexes **2** ([Os] = $OsCl(PH_3)_2$ in Scheme 1) has a pentagonal bipyramidal structure with the seven coordination sites occupied by four carbon atoms (C2, C4, C7, and C10), one chlorine atom, and two phosphorus atoms. Theoretical and experimental studies reveal that the osmium fragment reduces the antiaromaticity in both CBD and pentalene simultaneously. An interesting question is raised: could other late transition-metal such as ruthenium stabilise these two antiaromatic frameworks, too? If so, weaker stabilisation is expected because syntheses of second-row metallaaromatics have proven to be more difficult than third-row transition metal counterpart.[9] For instance, the first metallabenzene, metallanaphthalene, metallapentalyne and metallapentalene are all osmium complexes. Our ongoing interest in aromaticity[7a-7c,8,10] has led us to examine this hypothesis. Here we report a DFT study on the stability and aromaticity of metallapentalocyclobutadienes (Scheme 1). Interestingly, unexpected higher stabilisation of these two classical antiaromatic CBD and pentalene with ruthenium over osmium is identified. The ligand effect on the stabilisation is investigated in detail.



Scheme 1 Proposed metallapentalocyclobutadienes with different metal centers and ligands.

To probe the aromaticity of metallapentalocyclobutadienes, we employed the "isomerization stabilisation energy" (ISE)[11] method, which is quite effective to evaluate the aromaticity, especially for highly strained systems. The indene-isoindene approach is homodesmotic and has the advantage that all carbon atoms in the ring are *sp*^{2}-hybridized in both the reactants and products. As shown in Fig. 1 and Table 1, the positive ISE values (+30.8 and +16.5 kcal mol^{-1}) of CBD and pentalene confirm the antiaromaticity of these two typical antiaromatic species,[8] whereas the large negative ISE values of complexes **1** and **2** reflect their global aromaticity. The results indicate that the introduction of ruthenium fragment could also

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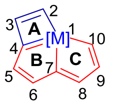
considerably reduce the antiaromaticity of CBD and pentalene. Unexpectedly, the complex **1** (-29.5 kcal mol^{-1}) have more negative ISE value than **2** (-26.8 kcal mol^{-1}), indicating that the stabilisation caused by a ruthenium fragment is higher than the osmium counterpart.

Table 1 The ISE and NICS(1)$_{zz}$ values (ppm) for three rings of metallapentalocyclobutadienes

	ISE	NICS(1)$_{zz}$ A	B	C
1	-29.5	21.3	-4.2	4.4
2	-26.8	28.5	-6.3	5.9
3	-22.3	20.6	-7.0	1.1
4	-21.1	27.3	-9.8	2.2
5	-22.8	18.8	-6.6	1.0
6	-21.1	25.1	-9.1	1.8

To probe the origin of higher stabilisation of ruthenium over osmium, we examined the local aromaticity of three rings in metallapentalocyclobutadienes by dissecting the ISE value of complexes **1** and **2** (Fig. 1). Interestingly, the ISE values for the three local rings (rings **A**-**C**) for complexes **1** and **2** were computed to be -6.3, -18.3, -5.8 kcal mol^{-1} and -3.4, -17.8, and -6.8 kcal mol^{-1}, respectively. Thus the origin of higher stabilisation caused by ruthenium could be attributed to the higher stabilisation of the CBD ring.

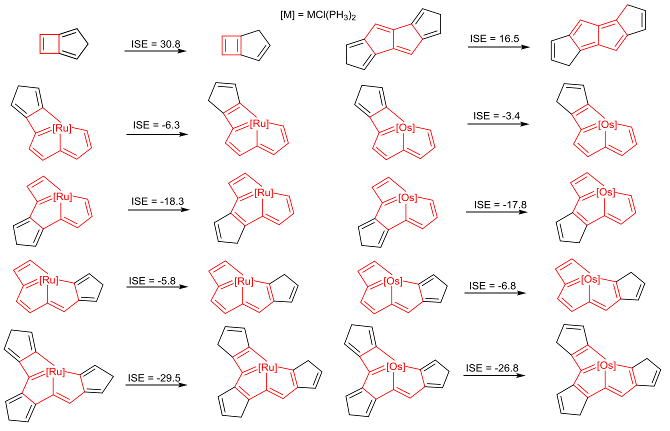


Fig. 1 The Indene-isoindene ISE evaluations of the antiaromaticity of CBD and pentalene and the aromaticity of **1** and **2** complexes. The energies (kcal mol^{-1}) include the zero-point energy corrections. The ISE values of CBD, pentalene and complex **2** are taken from ref.8 for comparison.

Note that the sum of these ISE values (-30.4 and -28.0 kcal mol^{-1}) for three rings are very close to those overall ISE values (-29.5 and -26.8 kcal mol^{-1}) of complexes **1** and **2**, indicating the reliability of this method. In addition, more negative ISE values (-18.3 and -17.8 kcal mol^{-1}) of the central five-membered ring are both found in complexes **1** and **2** than those (-5.8 and -6.8 kcal mol^{-1}) of the terminal five-membered ring, suggesting higher aromaticity over the terminal five-membered rings. One of the reasons could be attributed to an anticlockwise current of CBD unit, which could enhance the ring current of the central ring as these two ring currents have the same direction along the M-C4 bond. Note that previous study by Islas, Solà and co-workers shows that some metallacyclopentadienes could be aromatic or antiaromatic, depending on the metal fragments.[0]

NICS calculations were performed to further examine the aromaticity in metallapentalocyclobutadienes. In general, negative values indicate aromaticity and positive values antiaromaticity. As shown in Table 1, the computed NICS(1)$_{zz}$ are consistent with those ISE values qualitatively. Specifically, the NICS(1)$_{zz}$ values of rings **A**, **B**, and **C** in **1** are +21.3, -4.2 and +4.4 ppm, respectively, which are significantly reduced in comparison with those of the parent CBD (+55.9 ppm) and pentalene (+56.5 ppm),[7a] confirming the stabilisation of the metal center. Note that higher stabilisation of CBD by ruthenium over osmium is also supported by the NICS calculations. For instance, complex **2** has less positive NICS(1)$_{zz}$ value of ring **A** than complex **1** (21.3 vs 28.5 ppm).

To gain an insight into the origin of higher stabilisation of CBD by ruthenium over osmium in complexes **1** and **2**, we employed the electron localisation function (ELF)[12] analysis to these two species. ELF is one of the most powerful methods to understand chemical bonding because it enables the localisation of regions in the molecular space at which electrons concentrate, thus chemically significant regions, such as bonds or lone pairs, can be identified. Fig. 2C depicts the bifurcation values of the ELF$_\pi$ basins of the C3−C4 in complexes **1** and **2**. The bifurcation value of the C3−C4 bond in complex **1** (0.579) is slightly larger than that in complex **2** (0.531), indicating a reduced localised structure and leading to higher stabilisation of CBD framework. In addition, the C3−C4 bond length (1.431 Å) in complex **2** (Fig. 2B) is longer than that (1.421 Å) in complex **1**, in line with higher stabilisation of the CBD ring of ruthenium. The reduced localisation could be mainly attributed to the less diffused d orbitals of ruthenium over osmium, leading to a smaller Wiberg bond index difference between the M-C$_2$ and M-C$_4$ bonds.

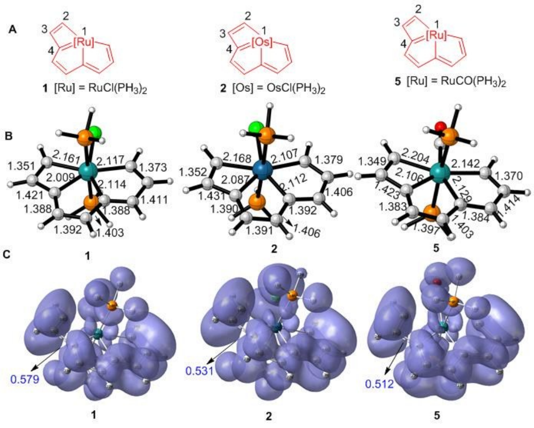


Fig. 2 (**A**) Structures of **1**, **2**, and **5**. (**B**) Selected bond distances (Å) of metal−carbon and carbon−carbon bonds. (**C**) The bifurcation values of the ELFπ basins for the C3−C4 bond in complexes **1**, **2**, and **5**.

In order to gain an insight into aromaticity in metallapentalocyclobutadienes, CMO–NICS calculations were carried out. As shown in Fig. 3, the six occupied π molecular orbitals (MOs) of complexes **1** and **2** are derived from the orbital interactions between the $p_{z\pi}$ atomic orbitals of the C_9H_7 unit (perpendicular to the tricycle plane) and two 5*d* orbitals (5d_{xz} and 5d_{yz}) of the metal center, reflecting the π delocalisation along the perimeter of the tricyclic system. Again, the less positive NICS(1)$_{\pi zz}$ value (+23.3 vs +31.6 ppm) for the CBD ring confirms the higher stabilisation of the ruthenium over osmium and reduced antiaromaticity. All in all, the ISE values together with the NICS calculations unambiguously confirm the stabilisation of the metal fragment in the CBD and pentalene frameworks, which could be mainly attributed to participation of three electrons from metal *d* orbitals into π conjugation as five *d* electrons from the metal have been used to form σ bonds.

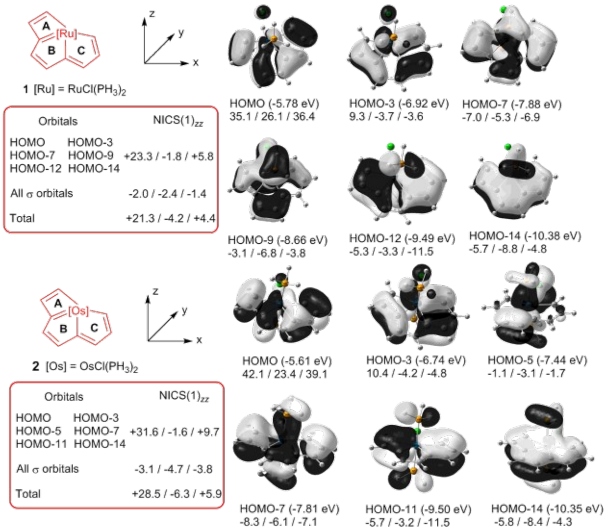


Fig. 3 Six key occupied π MOs and their energies together with their contributions to NICS(1)$_{zz}$ (ppm) for complex **1** and **2**. The eigenvalues of the MOs are given in parentheses on the first line, and the NICS(1)$_{zz}$ values of rings **A**, **B**, and **C** are given on the second line.

The ligand effect was examined by changing the Cl ligand to PH_3 and CO and the computed ISE, NICS and Wiberg bond indices are shown in Tables 1 and 2 (**3**–**6**). In addition, the data in Table 2 show that there is a negligible interaction between the metal center and the C_3 carbon atom, evidenced by the weaker Wiberg bond indices (0.04), in sharp contrast to the direct 1–3 metal–carbon bonding (with bond orders of 0.26–0.43) of previously reported groups 4–6 metallacyclobutadienes.[13] In addition, metallapentalocyclobutadienes (**1**–**2**) have relative larger Wiberg bond indices of metal–carbon in comparison with **3**–**6** with PH_3 and CO ligands, possibly due to the π donor character of the chloride ligand.

The computed ISE values and NICS(1)$_{zz}$ for metallapentalocyclobutadienes suggest that the PH_3 and CO ligands have a slight effect on the aromaticity in comparison with the ligand Cl. According to the ISE values the stabilisation of two antiaromatic frameworks caused by the transition metals are reduced. For example, when the ligand Cl is replaced by the ligand PH_3, complexes **3** and **4** have less negative ISE values (-22.3 and -21.1 kcal mol^{-1} in Table 1) than complexes **1** and **2** (-29.5 and -26.8 kcal mol^{-1} in Table 1). Again, we found ruthenium has higher stabilisation of CBD than osmium, evidenced by more negative ISE values (-4.4 vs -1.7 kcal mol^{-1}, see Fig. S1 in the Supplementary Information) and less positive NICS(1)$_{zz}$ value of ring **A** (20.6 vs 27.3 ppm).

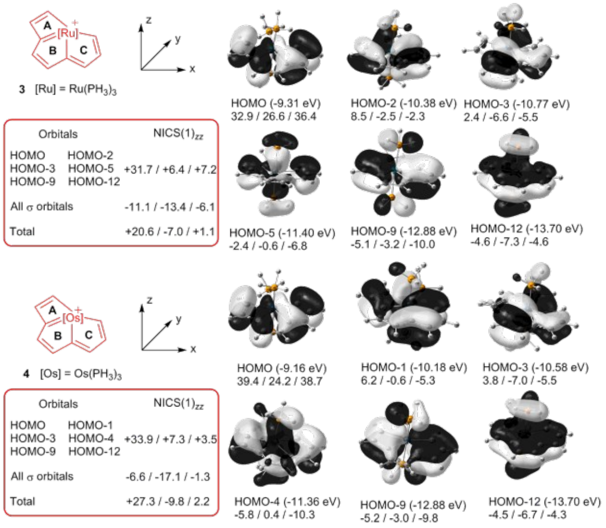


Fig. 4 Six key occupied π MOs and their energies together with their contributions to NICS(1)$_{zz}$ (ppm) for **3** and **4** complexes. The eigenvalues of the MOs are given in parentheses on the first line, and the NICS(1)$_{zz}$ values of rings **A**, **B**, and **C** are given on the second line.

When the CO ligand is introduced to replace the Cl ligand, the stabilisation is very similar to those with the PH_3 ligand (Table 1 and Fig. S2). It could be understandable as the positive charge has already made the metal centre electron poor. Thus the strong π-acceptor ability of CO can't be fully exhibited. The reduced stabilisation of CBD are also supported by the smaller bifurcation value (0.512) of the ELF$_\pi$ basins of the C3–C4 in complex **5** (Fig. 2C). Again, the CMO–NICS calculations in Figs. 4 and 5 show that the central five-membered ring is more aromatic than the terminal five-membered ring.

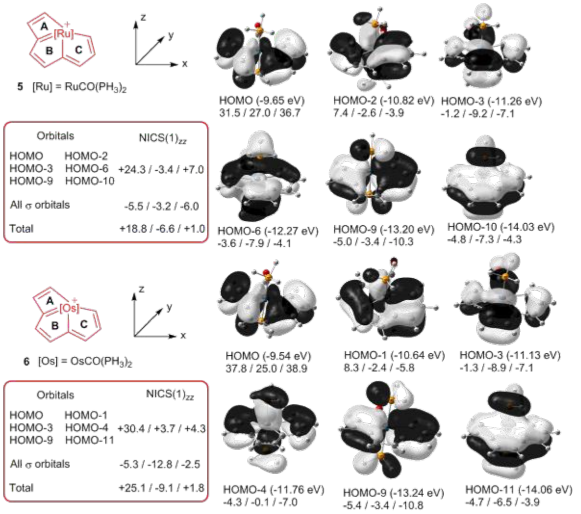
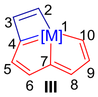


Fig. 5 Six key occupied π MOs and their energies together with their contributions to NICS(1)$_{zz}$ (in ppm) for **5** and **6** complexes. The eigenvalues of the MOs are given in parentheses on the first line, and the NICS(1)$_{zz}$ values of rings **A**, **B**, and **C** are given on the second line.

Table 2 The computed Wiberg bond indices of metal–carbon bonds in metallapentalocyclobutadienes.

	$M_1–C_2$	$M_1–C_3$	$M_1–C_4$	$M_1–C_7$	$M_1–C_{10}$
1	0.71	0.04	0.75	0.74	0.77
2	0.79	0.04	0.86	0.81	0.88
3	0.70	0.04	0.74	0.71	0.77
4	0.77	0.04	0.83	0.78	0.88
5	0.68	0.04	0.71	0.70	0.75
6	0.73	0.04	0.79	0.76	0.86

In conclusion, DFT calculations reveal unexpected higher stabilisation of second row transition metals ruthenium over the third row osmium, which could mainly attributed to higher stabilisation of CBD arising from the reduced localisation of M-C and C-C bonds. Compared with PH_3 and CO ligands, the chloride ligand has higher stabilisation of these two antiaromatic frameworks, evidenced by relatively larger Wiberg bond indices of metal–carbon bonds caused by relatively electron-rich metal centres. In addition, the direct 1–3 metal–carbon bonding in the metallabutadiene unit of these late transition metal complexes is negligible, in sharp contrast to that of early transition metal complexes.

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