Metallacycles

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σ-Aromaticity in an Unsaturated Ring: Osmapentalene Derivatives Containing a Metallacyclopropene Unit**

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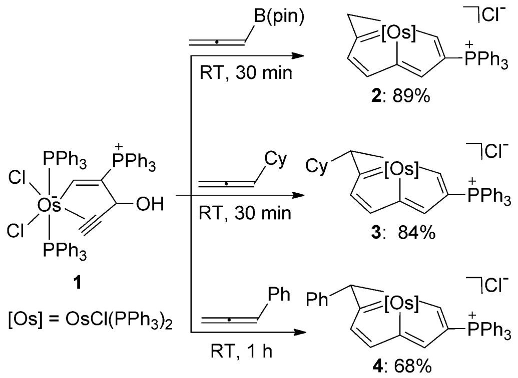
Abstract: *In general, aromaticity can be clarified as π- and σ-aromaticity according to the type of electrons with major contributions. The traditional π-aromaticity generally describes the π-conjugation in fully unsaturated rings whereas σ-aromaticity may stabilize fully saturated rings with delocalization caused by σ-electron conjugation. Reported herein is an example of σ-aromaticity in an unsaturated three-membered ring (3 MR), which is supported by experimental observations and theoretical calculations. Specifically, when the 3 MR in cyclopropaosmapentalene is cleaved by ethane through two isodesmic reactions, both of them are highly endothermic (+29.7 and +35.0 kcal mol^{-1}). These positive values are in sharp contrast to the expected exothermicity, thus indicating aromaticity in the 3 MR. Further nucleus-independent chemical shift and anisotropy of the current-induced density calculations reveal the nature of σ-aromaticity in the unsaturated 3 MR.*

Aromaticity, one of the central topics in chemistry, has attracted lots of experimentalists and theoreticians because of its many fascinating and ever-increasing manifestations.[1] Both σ- and π-aromaticity are possible, depending on the character of the cyclic electron delocalization. The π-aromaticity can be generally assigned to a Hückel system with [4n+2] π electrons[2] or a Möbius one with 4n π electrons.[3] Although it was initially confined to cyclic unsaturated hydrocarbons with delocalized π electrons, now heteroatom-containing cyclic systems have also been reported to be π-aromatic.[4] Specifically, a series of metalla-aromatics, such as metallabenzene,[5,6] metallabenzyne,[7] metallapentalyne,[8] and metallapentalene,[9] have been reported.

The concept of σ-aromaticity was first proposed by Dewar in 1979 to account for the inexplicably small strain in cyclopropane, a fully saturated species.[10] Although σ-aromaticity in cyclopropane has been much disputed,[11] this concept has been extended to other cyclic systems with σ-electron delocalization,[12] such as clusters of hydrogen,[12a,b] of main-group,[12c] and all-metal elements,[12d] as well as the metal–carbonyl clusters.[12e] In addition, "double aromaticity" originally proposed by Chandrasekhar, Jemmis, and Schleyer, describes the stabilization in the 3,5-dehydrophenyl cation, which benefits from six-electron π-aromaticity as well as from its in-plane two-electron three-center σ-aromaticity.[13] Interestingly, later analysis indicated that π-aromaticity was dominating in this cation.[14] Although the concept of double aromaticity was extended to inorganic chemistry (boron clusters) later by Boldyrev, Wang, and co-workers,[15] the dominant σ-aromaticity in an unsaturated system has not been investigated. Herein we report σ-aromaticity in an unsaturated metallacyclopropene unit of cyclopropametallapentalenes.

As shown in Scheme 1, treatment of the complex **1**[6d] with allenylboronic acid pinacol ester at room temperature (RT) led to the formation of the complex **2**, which is persistent both in the solid state and in solution. Specifically, a solid sample of **2** was stable even when heated in air at 180 °C for 3 hours. The complexes **3** and **4** were synthesized similarly by treatment of **1** with cyclohexyl and phenyl allenes. A possible mechanism for the formation of **2**–**4** is proposed in Scheme S1 in the Supporting Information.



Scheme 1. Synthesis of the osmapentalene derivatives **2**–**4** with a metallacyclopropene unit.

The complex **2** has been characterized by X-ray diffraction analysis,[16] nuclear magnetic resonance (NMR) spectroscopy, high-resolution mass spectrometry (HRMS), and elemental analysis. As shown in Figure 1, the nine (Os1, C1–C8) atoms in **2** are approximately coplanar (the mean deviation

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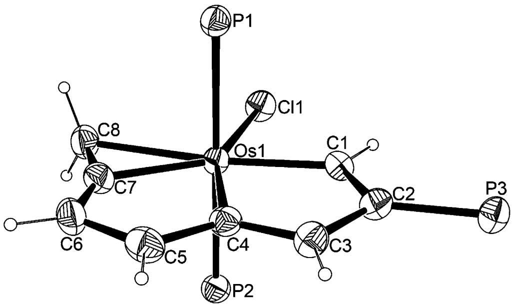
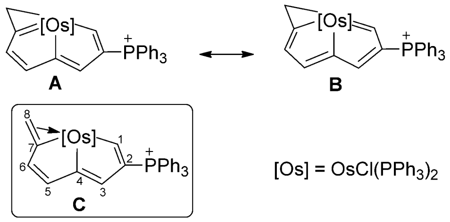


Figure 1. Molecular structure of the cation of **2** (drawn with 50% probability). The phenyl moieties in PPh_3 have been omitted for clarity. Selected bond lengths [Å] and angles [deg]: Os1–C1 2.021(5), Os1–C4 2.076(5), Os1–C7 1.996(5), Os1–C8 2.272(5), C1–C2 1.401(8), C2–C3 1.412(8), C3–C4 1.381(8), C4–C5 1.414(8), C5–C6 1.378(8), C6–C7 1.387(8), C7–C8 1.376(8); Os1-C1-C2 120.0(4), C1-C2-C3 113.0(5), C2-C3-C4 113.0(5), C3-C4-Os1 118.7(4), C4-Os1-C1 75.2(2), Os1-C4-C5 119.3(4), C4-C5-C6 112.5(5), C5-C6-C7 111.0(5), C6-C7-Os1 124.4(4), C7-Os1-C4 72.8(2), Os1-C7-C8 82.5(4), C7-C8-Os1 60.6(3), C8-Os1-C7 36.9(2).

from the least-squares plane is 0.030 Å). Notably, the angle sums in the fused five-membered rings (5MRs, 539.9° and 540.0°) and in the three-membered ring (3MR, 180.0°) are consistent with the ideal values (540° and 180°, respectively). The Os–C bond lengths [Os1-C1 (2.021 Å), Os1-C4 (2.076 Å), and Os1-C7 (1.996 Å)] are all in the range of those in osmapentalene (1.926–2.175 Å).[9] The C–C bond lengths (1.378–1.414 Å) of the fused 5MRs are between those of single and double carbon–carbon bond lengths and are close to those in benzene (1.396 Å). Thus, the fused 5MRs are delocalized. Although the Os1–C8 bond (2.272 Å) is longer than that of other three Os–C bonds in **2**, it is still within the range of Os–C single bonds (1.859–2.360 Å) for Os-C-C structures.[17]

The doublet signal at $\delta = 14.04$ ppm for the H1 proton in the ^1H NMR spectrum of **2**, is slightly downfield from the $\delta = 11.63$–12.46 ppm Os*CH* proton shifts reported in the aromatic osmapentalenes.[9] The other three proton signals on the fused 5 MRs are at $\delta = 8.70$ (H3), 8.68 (H5), and 6.54 ppm (H6). Both of the H8 and C8 signals ($\delta = 3.03$ and 21.8 ppm, respectively) correspond to those observed for osmacyclopropene ($\delta = 3.12$ and 29.19 ppm) as reported previously.[18] The high-field chemical shifts of H8 and C8 in **2** suggest that C8 is an sp^3-hybridized carbon atom.

The crystal and NMR data suggest that **2** contains an osmapentalene unit and an osmacyclopropene unit from the resonance structures of **A** and **B** (Scheme 2). Actually, another probable resonance structure is **C**, which contains a carbon–carbon double bond coordinated to the osmium center. However, significant bonding between the osmium center and the C8 atom is revealed by natural bond orbital (NBO) analysis. The 0.97, 0.82, 0.87, and 0.56 Wiberg bond indices of Os1–C1, Os1–C4, Os1–C7, and Os1–C8, respectively, quantify the distinct interaction between the Os1 and the C8 atoms. In addition, the component of the p orbital on the C8 atom in the Os–C8 bond is 88.08%, thus suggesting it is closer to that (75.00%) of an sp^3 center rather than that (66.67%) of an sp^2 center. Therefore, our experimental observations (crystal and NMR data) and theoretical calculations (NBO analyses) reveal that the C8 atom prefers an sp^3 hybridization, thus indicating an osmacyclopropene moiety in **2**. Thus the resonance the structures of **A** and **B** should be dominant.



Scheme 2. The major resonance structures of the cation of **2**.

The complexes **3** and **4** were also characterized by NMR spectroscopy, HRMS, and elemental analysis. The NMR spectra of **3** and **4** are similar to those of **2**. The structure of **3** was also confirmed by X-ray diffraction analysis (Figure 2); the structural features of **3** are analogous to those of **2**.

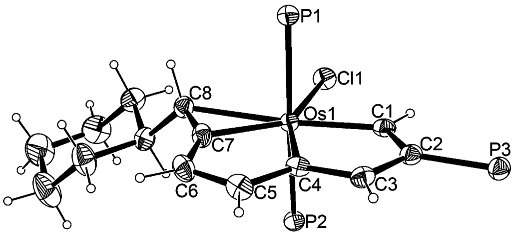
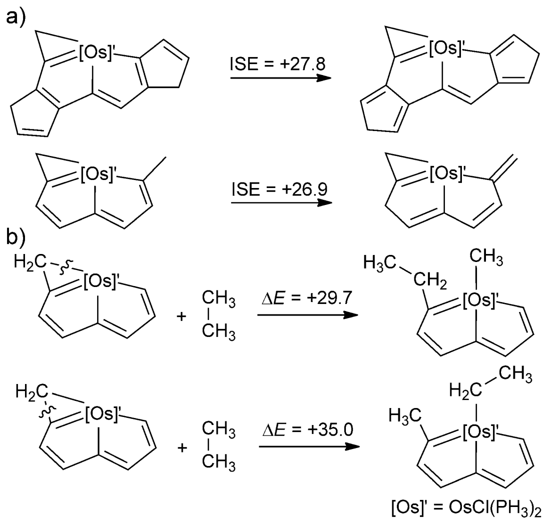


Figure 2. Molecular structure of the cation of **3** (drawn with 50% probability). The phenyl moieties in PPh_3 have been omitted for clarity. Selected bond lengths [Å] and angles [deg]: Os1–C1 2.040(4), Os1–C4 2.080(4), Os1–C7 1.997(4), Os1–C8 2.368(4), C1–C2 1.381(6), C2–C3 1.414(6), C3–C4 1.392(6), C4–C5 1.407(6), C5–C6 1.371(7), C6–C7 1.375(7), C7–C8 1.396(6); Os1-C1-C2 120.0(3), C1-C2-C3 113.6(4), C2-C3-C4 112.8(4), C3-C4-Os1 118.6(3), C4-Os1-C1 74.94(17), Os1-C4-C5 119.5(3), C4-C5-C6 112.7(4), C5-C6-C7 110.3(4), C6-C7-Os1 125.4(3), C7-Os1-C4 71.79(18), Os1-C7-C8 86.6(3), C7-C8-Os1 57.3(2), C8-Os1-C7 36.06(17).

The thermal stability, downfield proton chemical shifts, delocalized carbon–carbon and metal–carbon bonds, and the planarity of the fused 5MRs indicate the complexes **2**–**4** are aromatic. The aromaticity of these complexes was confirmed by the results of density functional theory (DFT) calculations on the unsubstituted model complex of **2′**, where PH_3 replaced the PPh_3 in **2**. Two strain-balanced isomerization stabilization energy (ISE)[19] methods were used to evaluate the aromatic stabilization energy of the fused 5MRs. As shown in Scheme 3a, the ISE values of the fused 5MRs in **2′** (+27.8 and +26.9 $\mathrm{kcal\,mol^{-1}}$), including the zero-point energy corrections, are very close to each other, thus indicating the reliability of the ISE method as well as the aromaticity of the fused 5MRs. The ISEs of **2′** are reduced slightly from the ISE values of the osmapentalenes (+30.7 and +31.4 $\mathrm{kcal\,mol^{-1}}$) as reported previously,[9a] which indicates that appending strained rings could perturb π-electron delocalization in the fused 5MRs.



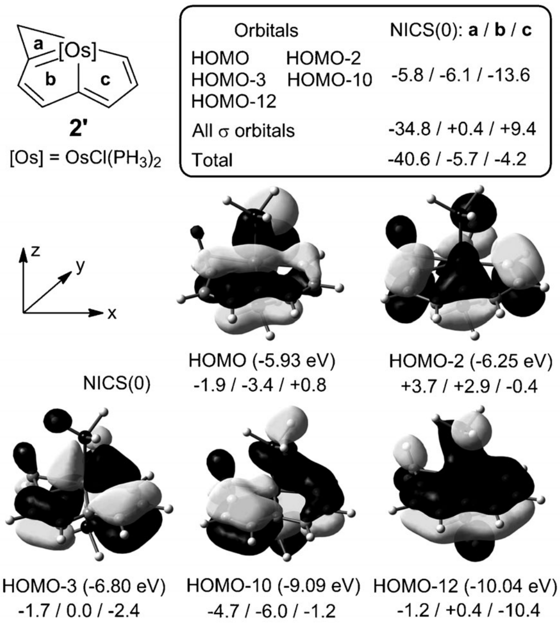
Scheme 3. Theoretical evaluations of the energetics of the model complex **2′**. The values are given in kcal mol^{-1}. a) The aromaticity in the fused 5 MRs is computed by two strain-balanced ISE methods. b) The isodesmic reactions for model complex **2′** by breaking the Os–C and C–C bonds suggest the aromaticity in the 3 MR.

We estimated the energetic effect of the metallacyclopropene in **2′** by means of two isodesmic reactions[20] which involve cleavage of either the Os–C or the C–C bonds in the metallacyclopropene ring (Scheme 3b). In isodesmic reactions, the types and numbers of chemical bonds in the reactants are the same as those in the products.[21] A negative value, computed from their electronic energies, is expected when the ring strain is relieved in these two equations. Thus, similar isodesmic reactions involving 3 MR cleavage by ethane are negative [e.g., in cyclopropane (−26.6 kcal mol^{-1} to pentane), cyclopropene (−55.1 kcal mol^{-1} to cis-2-pentene), and cyclopropabenzene (−66.3 kcal mol^{-1} to 1-ethyl-2-methyl benzene); see Scheme S2].

Astonishingly, the computed electronic energies for the two equations in Scheme 3b are highly positive (+29.7 and +35.0 kcal mol^{-1}). Note that the 5.3 kcal mol^{-1} difference between the reaction energies in Scheme 3b can be attributed to the stronger metal–methyl than metal–ethyl bond as evidenced here by the shorter bond length (2.257 and 2.308 Å) and larger Wiberg bond index (0.76 and 0.73). Since ring strain must be lost (rather than gained) in these isodesmic reactions, what is the origin of the endothermicity of the two equations in Scheme 3b? First, it cannot be attributed to repulsion between the alkyl groups resulting from cleavage of the Os–C or C–C bond since the closest H···H distances between these alkyl groups are 2.032 and 2.084 Å, respectively. Hence, such repulsion is not severe. Then what is it in the end? As aromaticity is one of the largest stabilizing factors in chemistry, could it exist in the metallacyclopropene ring in **2** and be large enough to overwhelm the ring strain? If so, the loss of 3 MR aromaticity could be the key to the origin, with the assumption that there is not much difference of the 5 MRs aromaticity between the reactant and the product of the two equations in Scheme 3b. Indeed, such an assumption is validated by their close ISE values (Scheme S3).

To examine our hypothesis of the aromaticity in the 3 MR, we performed nucleus-independent chemical shift (NICS) calculations[22] on the unsubstituted model **2′**. In general, negative values indicate aromaticity and positive values indicate antiaromaticity. Indeed, the NICS(1)$_{zz}$ value of the 3 MR (−27.4 ppm) is even more negative than those of the fused 5 MRs (left and right: −19.1 and −19.7 ppm), thus indicating that both the 3 MR and 5 MRs in **2′** are aromatic. The switch of antiaromaticity in pentalene to aromaticity in osmapentalene was reported previously and is a result of the introduction of a metal fragment.[9a]

To probe the nature of the aromaticity in the 3 MR, we performed canonical molecular orbital (CMO) NICS calculations. As there is a saturated carbon atom in the metallacyclopropene unit of **2′**, the dissected NICS(0) instead of NICS(1)$_{zz}$ is purposely chosen to gain an insight into the nature of the possible σ-aromaticity in this 3 MR. Computations show that the total contributions of the NICS(0) value for the 3 MR from the five occupied π-molecular orbitals (HOMO, HOMO−2, HOMO−3, HOMO−10, and HOMO−12; see Figure 3) are −5.8 ppm whereas the NICS(0) value from all the σ orbitals (−34.8 ppm) is much more negative, thus indicating σ-aromaticity in the 3 MR. Thus the σ-aromaticity is first determined to be dominating in an unsaturated species. As shown in Scheme S4, the model complex with conjugated fused 5 MRs produces an endothermic isomerization reaction (+12.3 kcal mol^{-1}) whereas that without fused 5 MRs gives a exothermic one (−8.7 kcal mol^{-1}), thus indicating that the conjugated fused 5 MRs in **2′** play an important role in the achievement of strong aromaticity in the metallacyclopropene ring. In a word, CMO-NICS calculations on **2′** reveal the σ-aromaticity is dominating in the



Orbitals	NICS(0): **a** / **b** / **c**
HOMO HOMO-2 HOMO-3 HOMO-10 HOMO-12	-5.8 / -6.1 / -13.6
All σ orbitals	-34.8 / +0.4 / +9.4
Total	-40.6 / -5.7 / -4.2

Figure 3. Key occupied π MOs and their energies together with their contributions to NICS(0) (in ppm) for the model complex **2′**. The eigenvalues of the MOs are given within parentheses in the first line whereas the NICS(0) values of rings a, b, and c are given in the second line.

unsaturated metallacyclopropene unit of cyclopropametallapentalene.

In addition, the σ-aromaticity in the unsaturated 3MR of **2′** is further supported by the anisotropy of the current-induced density (ACID) analysis.[23] As shown in Figure 4, the current density vectors plotted on the ACID isosurface indicate a diatropic ring current in the 3MR only in the σ system whereas the diatropic ring current in the π system is only displayed along the periphery of fused 5MRs in **2′**, thus confirming the σ-aromaticity in the 3MR and π-aromaticity in fused 5MRs of **2′**, respectively (see also Figures S3 and S4).

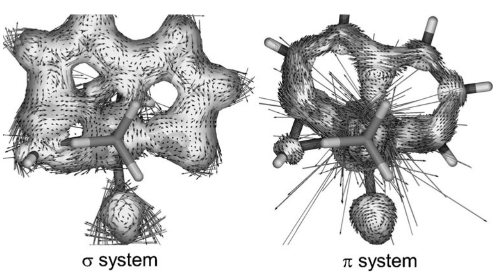


Figure 4. ACID isosurfaces of **2′** separated into the σ and π contribution. Current density vectors are plotted onto the ACID isosurface of 0.035 to indicate dia- and paratropic ring currents. The magnetic field vector is orthogonal with respect to the ring plane and points upward (clockwise currents are diatropic).

In summary, σ-aromaticity has been determined to be dominating in an unsaturated system. The observed thermal stability, delocalized carbon–carbon bonds, and the planarity of these cyclopropa-annulated metallapentalene derivatives could be attributed to the σ- and π-aromaticity in 3MR and 5MRs, respectively. The remarkable stability of these cyclopropametallapentalenes together with their facile preparation will significantly facilitate follow-up studies. Our findings on σ-aromaticity in an unstaturated 3MR will stimulate more efforts to explore the possibility of σ-aromaticity in other unsaturated systems.

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[16] CCDC 991905 (**2**) and 991906 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[17] Based on a search of the Cambridge Structural Database, CSD version 5.35 (November 2013).

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