Abstract: In general, aromaticity can be clarified as π- and α-aromaticity according to the type of electrons with major contributions. The traditional π-aromaticity generally describes the π-conjugation in fully unsaturated rings whereas α-aromaticity may stabilize fully saturated rings with delocalization caused by α-electron conjugation. Reported herein is an example of α-aromaticity in an unsaturated three-membered ring (3 MR), which is supported by experimental observations and theoretical calculations. Specifically, when the 3 MR in cyclopropane 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 α-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. Both α- 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 or a Möbius one with 4n π electrons. 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. Specifically, a series of metalla-aromatics, such as metallabenzene[5, 6] metallabenzyne,[7] metallapentalyne,[8] and metallapentalene,[9] have been reported.

The concept of α-aromaticity was first proposed by Dewar in 1979 to account for the inexplicably small strain in cyclopropane, a fully saturated species.[10] Although α-aromaticity in cyclopropane has been much disputed[11] this concept has been extended to other cyclic systems with α-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 α-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 prominent α-aromaticity in an unsaturated system has not been investigated. Herein we report α-aromaticity in an unsaturated metallocyclopropene unit of cyclopropametallapentalenes.

As shown in Scheme 1, treatment of the complex 1[6d] with allylenyboric 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.

The complex 2 has been characterized by X-ray diffraction analysis,[20] nuclear magnetic resonance (NMR) spectroscopy, high-resolution mass spectrometry (HRMS), and elemental analysis. As shown in Figure 1, the nine (Os1, Cl–C8) atoms in 2 are approximately coplanar (the mean deviation

Scheme 1. Synthesis of the osmapentalene derivatives 2–4 with a metallocyclopropene unit.
The other three proton signals on the fused H11.63–12.46 ppm OsC delocalized. Although the Os1–C8 bond (2.272 Å) is longer close to those in benzene (1.396 Å), the fused 5MRs are of single and double carbon–carbon bond lengths and are (66.67%) of an sp2 center. Therefore, our experimental observations (crystal and NMR data) and theoretical calculations (NBO analyses) reveal that the C8 atom prefers an sp3 hybridization, thus indicating an osmacyclopropene moiety in 2. Thus the resonance the structures of A and B should be dominant.

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.

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 PH3 replaced the PPh3 in 2. Two strain-balanced isomerization stabilization energy (ISE) 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 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 kcal mol−1) as reported previously, which indicates that appending strained rings could perturb π-electron delocalization in the fused 5MRs.
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 3MR 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 3MR aromaticity could be the key to the origin, with the assumption that there is not much difference of the 5MRs 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 3MR, 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 3MR (−27.4 ppm) is even more negative than those of the fused 5MRs (left and right: −19.1 and −19.7 ppm), thus indicating that both the 3MR and 5MRs in 2' are aromatic. The switch of antiaromaticity in pentalene to aromaticity in osmapentalen was reported previously and is a result of the introduction of a metal fragment.[23]

To probe the nature of the aromaticity in the 3MR, 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 π-aromaticity in this 3MR. Computations show that the total contributions of the NICS(0) value for the 3MR 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 3MR. Thus the π-aromaticity is first determined to be dominating in an unsaturated species. As shown in Scheme S4, the model complex with conjugated fused 5MRs produces an endothermic isomerization reaction (−12.3 kcal mol\(^{-1}\)) whereas that without fused 5MRs gives a exothermic one (−8.7 kcal mol\(^{-1}\)), thus indicating that the conjugated fused 5MRs 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 π-aromaticity is dominating in the

**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 5MRs 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 3MR.

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 metallocyclopentene unit of cyclopropometallapentalene.

In addition, the \( \sigma \)-aromaticity in the unsaturated 3MR of 2' is further supported by the anisotropy of the current-induced density (ACID) analysis. As shown in Figure 4, the current density vectors plotted on 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, \( \sigma \)-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 metallocyclopentene derivatives could be attributed to the \( \sigma \)- and \( \pi \)-aromaticity in 3MR and 5MRs respectively. The remarkable stability of these cyclopropa-annulated metallapentalene derivatives is further supported by the anisotropy of the current-induced density (ACID) analysis.

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Figure 4. ACID iso-surfaces of 2’ separated into the \( \sigma \) and \( \pi \) contribution. Current density vectors are plotted on the ACID iso-surface 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).


[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.


