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σ-Aromaticity in a Fully Unsaturated Ring

Jingjing Wu,[a] Xin Liu,[a] Yulei Hao,[a] Hongjiang Chen,[a] Peifeng Su,[a] Wei Wu,[a] and Jun Zhu*[a]

Abstract: Aromaticity is one of the most fundamental and fascinating chemical topics, attracting both experimental and theoretical chemists due to its many manifestations. Both σ- and π-aromaticity can be classified, depending on the character of the cyclic electron delocalization. In general, σ-aromaticity stabilizes fully saturated rings with σ-electron delocalization whereas the traditional π-aromaticity describes the π-conjugation in fully unsaturated rings. Here we demonstrate a strong correlation between nucleus-independent chemical shift (NICS) values and extra cyclic resonance energies (ECREs) used to evaluate the σ-aromaticity in an unsaturated three-membered ring (3MR) of cyclopropene, which were computed by molecular orbital (MO) theory and valence bond (VB) theory, respectively. Further study shows that a fully unsaturated ring in methylenecyclopropene and its metallic analogy is σ-aromatic. Our findings revolutionize the fundamental knowledge of the concept of σ-aromaticity, thus opening an avenue to design of σ-aromaticity in other fully unsaturated systems, which are traditionally reserved for the domain of π-aromaticity.

Introduction

Aromaticity, an important concept in chemistry, has attracted lots of experimentalists and theoreticians due to its many fascinating and ever-increasing manifestations.[1] In general, it can be classified as π- and σ-aromaticity according to the type of electrons with major contributions. The π-aromaticity could be found in either 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,[1a,1b] now it has been extended to the heteroatom-containing cyclic systems.[4]

On the other hand, Dewar first proposed the concept of σ-aromaticity[5] to account for the unusual small strain in cyclopropane, a fully saturated species.[6] Although the σ-aromatic stabilization energy of the original cyclopropane was reported to be, at most, 3.5 kcal mol⁻¹ relative to propane,[7] the concept of σ-aromaticity has been reported in other cyclic systems, such as clusters of hydrogen,[8] clusters of main-group,[9] all-metal elements,[10] and the metal-carbonyl clusters.[11] In addition, Chandrasekhar, Jemmis, and Schleyer proposed "double aromaticity" to describe the stabilization in the 3,5-dehydrophenyl

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cation, benefitting from six-electron π-aromaticity as well as from its in-plane two-electron three-center σ-aromaticity.[12] Interestingly, detailed analysis revealed that π-aromaticity was dominating in this cation.[13] Later, Wang, Boldyrev and co-workers extended the concept of double aromaticity to inorganic chemistry (boron clusters).[14] Recently, we reported σ-aromaticity in three-membered metallacycles.[15] However, the σ-aromaticity dominating in a fully unsaturated organic species has not been achieved so far. Now we demonstrate that σ-aromaticity can be dominant in a completely unsaturated three-membered ring of methylenecyclopropene.

Results and Discussion

Aromaticity in the 3MR of cyclopropene. Recently, we reported that σ-aromaticity could be dominant in a partially unsaturated 3MR of cyclopropaosmapentalene.[15a] To probe the origin of σ-aromaticity in the 3MR of cyclopropaosmapentalene, we first investigated the nature of aromaticity in the parent organic species, cyclopropene (C_3H_4) and compared it with the saturated one, cyclopropane (C_3H_6) (see Figure S1). We employed the "extra cyclic resonance energy" (ECRE), defined as the difference between the resonance energies (REs) of a cyclic conjugated compound and its appropriate acyclic model. This method especially emphasizes the importance of ring formation to aromaticity and also considers the hyperconjugative interactions in acyclic systems. The same method has been used to evaluate the σ-aromaticity in cyclopropane.[7] The acyclic reference for cyclopropene can either have the same number of carbon atoms (propene, C_3H_6) which gives ECRE1 or the same number of C-C bonds (**2-butene**, **cis-C_4H_8** and **trans-C_4H_8**) which gives ECRE2 (Figure 1). Both of these two ECREs have been employed here. Thus, a positive ECRE indicates aromaticity whereas a negative one corresponds to an antiaromatic system. The ECREs of nonaromatic systems will be close to zero.

The calculated resonance energies of cyclopropene (C_3H_4) and its acyclic models separated into σ and π components were given in Table 1. The RE^σ of cyclopropene (15.7 kcal mol⁻¹) is slightly larger than that of cyclopropane (12.7 kcal mol⁻¹)[7] whereas RE^σ for C_3H_6 (9.8 kcal mol⁻¹), **cis-C_4H_8** (13.3 kcal mol⁻¹) and **trans-C_4H_8** (13.1 kcal mol⁻¹) are larger than those in C_3H_8 (7.9 kcal mol⁻¹) and C_4H_{10} (11.6 kcal mol⁻¹) reported in our previous study.[7] In addition, the similar trend could be also found in RE^π.
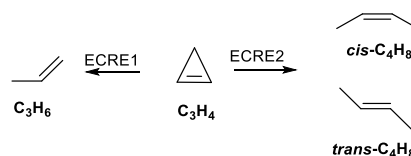

Figure 1. Different acyclic models for the calculation of ECREs of cyclopropene.

In terms of the ECREs, both σ and π components of cyclopropene and cyclopropane are computed (Table 2). The calculated ECRE1$^\sigma$ of cyclopropene (5.9 kcal mol⁻¹) is larger in

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comparison with that of cyclopropane (4.8 kcal mol^{-1}).[7] And the ECRE1$^\pi$ for cyclopropene (6.2 kcal mol^{-1}) is much larger than that in cyclopropane (1.8 kcal mol^{-1}).

Table 1. Resonance energies (RE) including σ and π components for cyclopropene and referred acyclic models (kcal mol^{-1}). All data were computed at the VBSCF/6-31G* level.

Species	C_3H_4	C_3H_6	*cis*-C_4H_8	*trans*-C_4H_8
RE$^\sigma$	15.7	9.8	13.3	13.1
RE$^\pi$	11.4	5.2	10.3	10.4

Table 2. Extra cyclic resonance energies (ECRE) including σ and π contributions for cyclopropene and cyclopropane (kcal mol^{-1}) at the VBSCF/6-31G* level.

Species	cyclopropene	cyclopropane
ECRE1$^\sigma$	5.9	4.8
ECRE1$^\pi$	6.2	1.8
ECRE2$_c^\sigma$	2.4	1.1
ECRE2$_c^\pi$	1.1	1.1
ECRE2$_t^\sigma$	2.6	-1.8
ECRE2$_t^\pi$	1.0	-1.8

The aromaticity of cyclopropene is further investigated by nucleus-independent chemical shift (NICS) calculation based on MO theory.[16] NICS is a key magnetic aromaticity index introduced by Schleyer and co-workers. NICS(0) is defined as the negative magnetic shielding computed at the ring center and NICS(0)$_{zz}$ describes the *zz* component. In general, negative values indicate aromaticity and positive values anti-aromaticity. Canonical molecular orbital (CMO) NICS calculations were performed to identify the σ and π orbital contributions separately. The structure of cyclopropene in Figure 2a was optimized at B3LYP/6-311++G(d,p) level. And the CMO-NICS calculations were performed at the same level. Two occupied π orbitals (HOMO and HOMO-3) of cyclopropene were considered and the calculated NICS(0)$_\sigma$ and NICS(0)$_\pi$ are -18.2 and -10.3 ppm, respectively, indicating higher σ-aromaticity over π-aromaticity. The NICS(0)$_{\sigma zz}$ value (-20.2 ppm) addressing the *zz* component further proves the dominant σ-aromaticity. Thus, the σ-aromaticity in the metallacyclopropene ring[15a] could be rooted in the σ-aromaticity in cyclopropene.
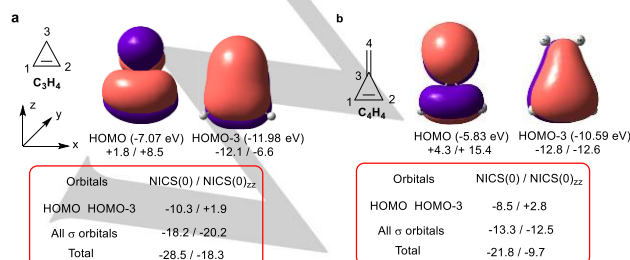
Figure 2. Occupied π MOs and their eigenvalues (in eV) together with their contributions to NICS(0) and NICS(0)$_{zz}$ (in ppm) for cyclopropene ($\mathbf{C_3H_4}$) (a), and methylenecyclopropene ($\mathbf{C_4H_4}$) (b). The eigenvalues of the MOs are given in parentheses on the first line, and the NICS values are given on the second line.
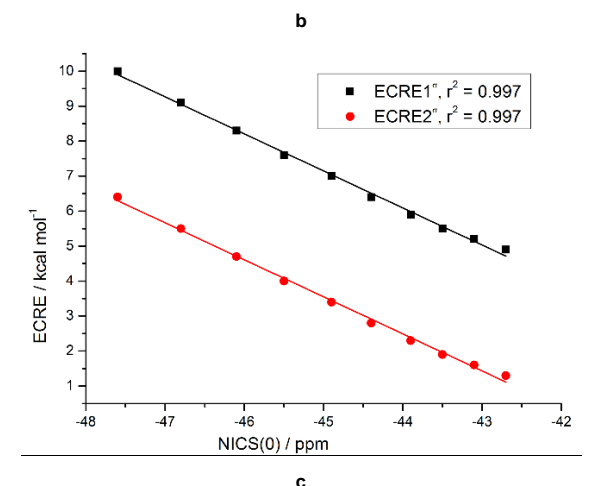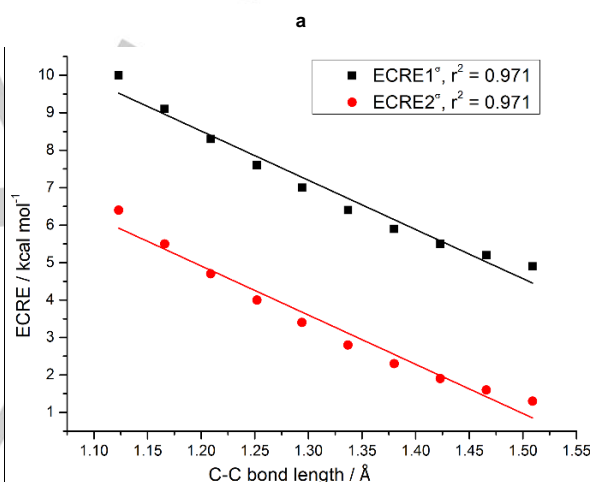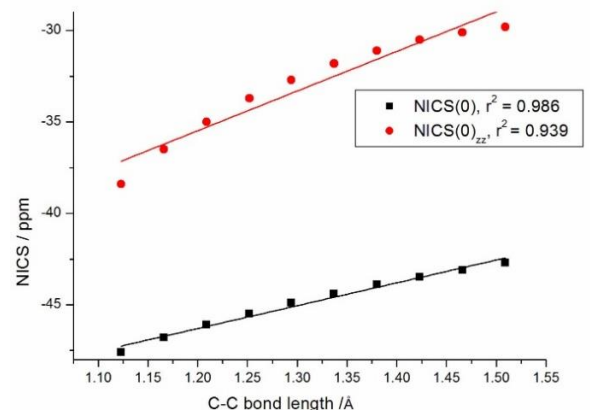
Figure 3. Plots of correlations among NICS values, bond lengths, and ECREs in cyclopropene. (a) NICS values vs bond lengths. (b) ECREs vs bond lengths. (c) ECREs vs NICS(0) values.

3
1 △ 2
C_3H_4

z
↑
↗ y
→ x

HOMO (-7.07 eV)   HOMO-3 (-11.98 eV)
+1.8 / +8.5   -12.1 / -6.6

Orbitals	NICS(0) / NICS(0)$_{zz}$
HOMO HOMO-3	-10.3 / +1.9
All σ orbitals	-18.2 / -20.2
Total	-28.5 / -18.3

4
3
1 △ 2
C_4H_4

HOMO (-5.83 eV)   HOMO-3 (-10.59 eV)
+4.3 /+ 15.4   -12.8 / -12.6

Orbitals	NICS(0) / NICS(0)$_{zz}$
HOMO HOMO-3	-8.5 / +2.8
All σ orbitals	-13.3 / -12.5
Total	-21.8 / -9.7

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A more refined analysis, "dissected NICS" was carried out to probe the origin of σ-aromaticity in cyclopropene. This method reveals the individual contributions of bonds, lone-pairs, and core electrons to the total shielding of cyclopropene. As the major difference between cyclopropene and cyclopropane (Figure S1) is the C1-C2 bond length (e.g., 1.291 Å in the former and 1.509 Å in the latter), we elongated the C1-C2 bond of cyclopropene to 1.509 Å and obtained a significantly distorted cyclopropene (C_3H_4-L, L denotes an elongated bond length), and compared their dissected NICS values (Table 3). The NICS calculations for the fully relaxed cyclopropene C_3H_4 show that the C-C σ and C-C π bonds mainly contribute to the total NICS(0) and NICS(0)$_{zz}$ values. When the C1-C2 was fixed to 1.509 Å, the contribution from the C-C σ bond was reduced sharply whereas other contributions remain almost unchanged. Thus, it could be concluded that the C-C σ bonds play a key role in the achievement of σ-aromaticity in cyclopropene. The shorter C-C σ bond suggests higher σ-aromaticity in cyclopropene.

To further probe the effect of the C-C bond length on σ-aromaticity, one of the C-C bond lengths of cyclopropane was set to a range of distances between 1.123 Å and 1.509 Å while the other two C-C bonds were kept constant at 1.509 Å. Note that a shorter C-C bond length than 1.123 Å will produce an imaginary frequency. Table 4 lists the bond lengths, ECREs and NICS values of cyclopropane. The NICS(0) and NICS(0)$_{zz}$ value becomes more negative when the bond length becomes shorter. Meanwhile, the ECRE1 and ECRE2 become larger, both indicating enhanced σ-aromaticity.

Strong correlations between the C-C bond lengths, NICS values, and ECREs were identified in Figure 3, indicating the reliability of our calculations. Especially, an excellent correlation ($r^2 = 0.997$, Figure 3c) is achieved between two aromatic indices, NICS(0) and ECRE1$^\sigma$ / ECRE2$^\sigma$, indicating that the NICS indices (NICS(0) and NICS(0)$_{zz}$) should be suitable to evaluate the aromaticity in the 3MR of cyclopropane and cyclopropene.

Previous study showed that the π-aromaticity of planar cyclopolyenes can be tuned by the hyperconjugation of the electropositive SiH_3 and electronegative F substituents.[17] Recently, we reported that the σ-aromaticity in a metallacyclopropene ring could also be significantly affected by the substituents.[18] Now we examine the substituent effect of F and SiH_3 ($C_3H_2R_2$, R = F, SiH_3) on the σ-aromaticity in cyclopropene by the CMO-NICS calculations. As shown in Table 5, the NICS(0)$_\sigma$ values for C_3H_4, $C_3H_2F_2$ and $C_3H_2(SiH_3)_2$ are -18.2, -14.0 and -42.2 ppm, respectively, indicating that σ-aromaticity in the 3MR of cyclopropene is reduced by the F substituent and strengthened by the SiH_3 group. The opposite effect was found for π-aromaticity in cyclopropene. Specifically, the NICS(0)$_\pi$ value of $C_3H_2(SiH_3)_2$ is positive (14.9 ppm), indicating antiaromaticity. The NICS(0)$_{zz}$ values produce a similar trend as the NICS(0) values. The hyperconjugation and the electronic effect on π and σ-aromaticity could be combined together to rationalize the significant difference caused by the F and SiH_3 substituents. The CF_2 group acts like a partially vacant p orbital, resulting in $4n + 2$ π-electron in the 3MR[17] whereas the electron withdrawing character reduces the σ-electron density,[18] leading to weaker σ-aromaticity. Inversely, the $C(SiH_3)_2$ group supplies two "pseudo"

π electrons, resulting in $4n$ π-antiaromaticity and its electron donating character makes the 3MR σ-electron rich, leading to stronger σ-aromaticity.

Table 3. Dissected NICS (in ppm) of cyclopropene and its elongated one at ring center.

Structures	NICS	Total NICS	CC(σ)	CC(π)	CH	Core
C_3H_4	NICS(0)	-28.5	-12.4	-13.6	-5.9	+2.9
	NICS(0)$_{zz}$	-18.3	-15.0	-2.7	-5.7	+4.3
C_3H_4-L	NICS(0)	-22.8	-8.7	-13.6	-3.1	+2.6
	NICS(0)$_{zz}$	-7.9	-8.9	-0.9	-1.8	+3.8

Table 4. Bond lengths (Å), NICS (ppm) and ECRE$^\sigma$ (kcal mol^{-1}) values of cyclopropane.

Bond length	ECRE1$^\sigma$	ECRE2$^\sigma$	NICS(0)	NICS(0)$_{zz}$
1.509	4.9	1.3	-42.7	-29.8
1.466	5.2	1.6	-43.1	-30.1
1.423	5.5	1.9	-43.5	-30.5
1.380	5.9	2.3	-43.9	-31.1
1.337	6.4	2.8	-44.4	-31.8
1.294	7.0	3.4	-44.9	-32.7
1.252	7.6	4.0	-45.5	-33.7
1.209	8.3	4.7	-46.1	-35.0
1.166	9.1	5.5	-46.8	-36.5
1.123	10.0	6.4	-47.6	-38.4

Table 5 The NICS(0) and NICS(0)$_{zz}$ values (ppm) with their σ and π contributions for species C_3H_4, $C_3H_2F_2$ and $C_3H_2(SiH_3)_2$.

NICS	C_3H_4	$C_3H_2F_2$	$C_3H_2(SiH_3)_2$
NICS(0)$_\sigma$	-18.2	-14.0	-42.2
NICS(0)$_\pi$	-10.3	-13.5	+14.9
NICS(0)$_{\sigma zz}$	-20.2	-17.0	-32.5
NICS(0)$_{\pi zz}$	+1.9	-3.9	+16.0

σ-Aromaticity dominating in a fully unsaturated ring. Could σ-aromaticity be dominant in a completely unsaturated ring? To address this issue, we investigated the aromaticity in methylenecyclopropene (C_4H_4). This molecule was studied by several groups.[19] However, most studies are limited to global aromaticity or π-aromaticity and its σ-aromaticity remains unclear. Here, we report that its σ-aromaticity rather than π-aromaticity is dominating in the 3MR. As shown in Figure 2b, both the NICS(0)$_\sigma$ and NICS(0)$_{\sigma zz}$ values in methylenecyclopropene are more negative than the NICS(0)$_\pi$ and NICS(0)$_{\pi zz}$, respectively, indicating that σ-aromaticity is dominant in the 3MR of methylenecyclopropene. The slightly reduced σ-aromaticity in

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methylenecyclopropene in comparison with cyclopropene could be attributed to the slightly elongated C=C double bond (e.g., 1.318 Å in the former and 1.291 Å in the latter, shown in Figure S1).
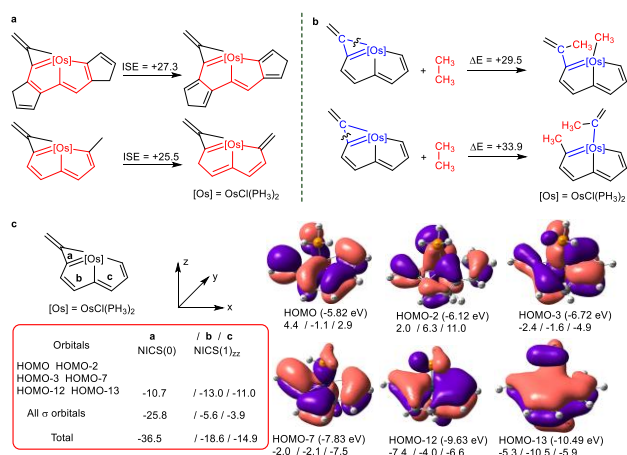

Figure 4. (a) The aromaticity in the fused 5MRs is computed by two strain-balanced ISE methods. The values (in kcal mol^{-1}) include the zero-point energy corrections. (b) The isodesmic reactions for model complex **C$_4$H$_4$-Os** by breaking the Os-C and C-C bonds suggest the aromaticity in the 3MR. Electronic energies (ΔE) are given in kcal mol^{-1} including the zero-point energy corrections. (c) Key occupied π MOs and their energies together with their contributions to NICS(0) and NICS(1)$_{zz}$ (in ppm) for the model complex **C$_4$H$_4$-Os**. The eigenvalues of the MO's are given in parentheses in the first line whereas the NICS(0) and NICS(1)$_{zz}$ values of rings a, b, and c are given in the second line.

Our previous study showed that σ-aromaticity could be dominant in the 3MR of cyclopropaosmapentalene[15a] and osmapentaloselenirene.[15b] So, could σ-aromaticity be dominating in the fully unsaturated 3MR of methylenecyclopropeosmapentalene (**C$_4$H$_4$-Os**)? We therefore examined the aromaticity in complex **C$_4$H$_4$-Os** by DFT calculations. Two strain-balanced "isomerization stabilization energy" (ISE) methods,[20] were used to evaluate the aromatic stabilization energy of the fused 5MRs. As shown in Figure 4a, the ISE values of the fused 5MRs in **C$_4$H$_4$-Os** (+27.3 and +25.5 kcal mol^{-1}) are very close to each other, indicating the reliability of the ISE method as well as the aromaticity of the fused five-membered rings (5MRs). The ISEs of **C$_4$H$_4$-Os** are similar to those of the cyclopropaosmapentalene (+27.8 and +26.9 kcal mol^{-1}) reported previously,[15a] which indicates that switching the hybridisation of the carbon in the 3MR from sp^3-hybridisation to sp^2-hybridisation does not affect π-electron delocalization in the fused 5MRs significantly.

The aromaticity in the 3MR of complex **C$_4$H$_4$-Os** is supported by means of two isodesmic reactions[21] which involve cleavage of either the Os–C or the C–C bonds in the 3MR (Figure 4b). In the isodesmic reactions, the types and numbers of chemical bonds in the reactants are the same as those in the products.[22] A negative value is expected when the ring strain is relieved in these two equations. Thus, similar isodesmic reactions involving 3MR cleavages by ethane are all negative (e.g., in cyclopropane (-26.6 kcal mol^{-1} to pentane), cyclopropene (-55.1 kcal mol^{-1} to *trans*-2-

pentene), and cyclopropabenzene (-66.3 kcal mol^{-1} to 1-ethyl-2-methyl benzene)).[15a] On the contrary, the computed energies for the two equations in Figure 4b (+29.5 and +33.9 kcal mol^{-1}) are very close to those of cyclopropaosmapentalene (+29.7 and +35.0 kcal mol^{-1}).[15a] Since ring strain must be lost (rather than gained) in these isodesmic reactions, the origin of the endothermicity of the two equations in Figure 4b could only attributed to the loss of aromaticity in the 3MR in complex **C$_4$H$_4$-Os**.

To examine our hypothesis of the aromaticity in the 3MR, we performed CMO-NICS calculations on complex **C$_4$H$_4$-Os**. 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 the 3MR. Indeed, computations show that the total contributions of the NICS(0) value for the 3MR from the six occupied π molecular orbitals (HOMO, HOMO-2, HOMO-3, HOMO-7, HOMO-12 and HOMO-13, shown in Figure 4c) are -10.7 ppm whereas the NICS(0) value from all the σ orbitals (-25.8 ppm) is much more negative, indicating that σ-aromaticity is dominating in the 3MR. Note that the negative NICS(1)$_{zz}$ values of the fused 5MRs (-18.6 and -14.9 ppm) suggest π-aromaticity in the 5MRs of complex **C$_4$H$_4$-Os**. As reported previously, the switch of antiaromatcity in pentalene to aromaticity in 5MRs in osmapentalenes was due to the introduction of a metal fragment.[4p]
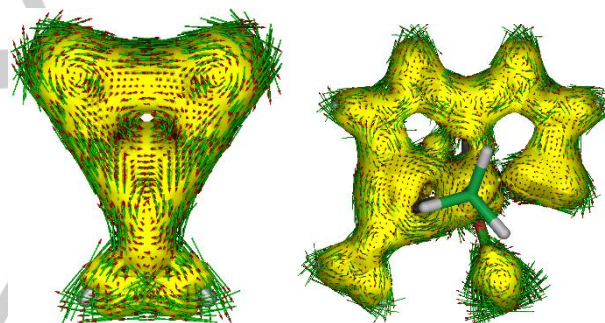

Figure 5. ACID isosurfaces of methylenecyclopropene and complex **C$_4$H$_4$-Os** separated into the σ contributions. Current density vectors are plotted onto the ACID isosurface of 0.040 a.u. to indicate dia- and paratropic ring currents. The magnetic field vector is orthogonal with respect to the ring plane and points upward (clockwise currents are diatropic).

In addition, σ-aromaticity in the completely unsaturated three-membered ring of **C$_4$H$_4$-Os** is further supported by the anisotropy of the induced current density (ACID) analysis. As shown in Figure 5, the current density vectors plotted on the ACID isosurface indicate a strong diatropic ring current is displayed in the 3MRs in the σ system of methylenecyclopropene and complex **C$_4$H$_4$-Os** whereas the diatropic ring current in the π system is along the periphery of fused 5MRs in **C$_4$H$_4$-Os**, confirming the σ-aromaticity in the 3MR and π-aromaticity in fused 5MR of **C$_4$H$_4$-Os** (see also Figures S3 and S4).

Conclusions

σ-aromaticity, proposed by Dewar in 1979, has been mainly confined within a saturated system. Now by utilizing VB and MO

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theory calculations, we demonstrate that difference from the saturated cyclopropane, the unsaturated cyclopropene has enhanced σ-aromaticity. The gain of σ-aromaticity in cyclopropene is attributed to the shortened C=C bond length, evidenced by the more negative NICS(0) values and larger ECREs when the C-C bond length in cyclopropane becomes shorter. More importantly, switching the sp^3-hybridised carbon in the 3MR to the sp^2-hybridised one does not affect σ-electron delocalization significantly, leading to the first σ-aromatic ring dominating in a fully unsaturated organic species. Metalation of the 3MR in methylenecyclopropene results in complex **C_4H_4-Os**, which is also σ-aromatic in the completely unsaturated 3MR, supported by the isodesmic reactions, CMO-NICS and ACID calculations. All these findings could revolutionize the fundamental scope of the concept of σ-aromaticity, thus opening an avenue to design of σ-aromaticity in other fully unsaturated systems, which are traditionally reserved for the domain of π-aromaticity.

Experimental Section

Computational Details. All structures were optimized at the B3LYP level of density functional theory.[23] In addition, the frequency calculations were performed at 298K to confirm the characteristics of the calculated structures as minima. In the B3LYP calculations, the effective core potentials (ECPs) of Hay and Wadt with a double-ζ valence basis set (LanL2DZ) were used to describe the Os, P, Cl and Si atoms, whereas the standard 6-311++G(d,p) basis set was used for the C, F and H atoms[24] for all the compounds. Polarization functions were added for Os ($\zeta(f)$ = 0.886), Cl ($\zeta(d)$ = 0.514), P ($\zeta(d)$ = 0.340) and Si ($\zeta(d)$ = 0.262).[25] NICS calculations were performed at the same level. All the optimizations were performed with the Gaussian 03 software package,[26] whereas the CMO-NICS calculations were carried out with the NBO 6.0 program.[27] The ACID calculations were carried out with the ACID program.[28]

In addition, all the "Resonance Energy" (RE) and "Extra Cyclic Resonance Energy" (ECRE)[29] calculations were performed using XMVB software[30] at VBSCF/6-31G* level of theory. The ECRE$^\pi$ and ECRE$^\sigma$ were calculated separately with the same scheme as the previous study of cyclopropane,[7] in which the RE was evaluated as the energy difference between the electron localized state and delocalized state. The definitions of the σ and π orbitals for cyclopropane follow the previous VB study.[7] In the VB calculations of cyclopropene, the orbitals of two C-H bonds in the CH_2 group are recombined as one σ and one π orbitals according to the C_s symmetry. Then there are six double occupied σ orbitals, including three orbitals for the C-C bonds, two orbitals for the C-H bonds and one orbitals for the CH_2 group. As shown in Figure S2, these σ orbitals are placed on the x-y plane. Two π orbitals, one located at the C-C double bond whereas the others coming from the CH_2 group are placed on the z-axis. In the electron localized state, each orbital is localized in the circle shown in Figure S2 whereas in the delocalized state, all the orbitals are delocalized.

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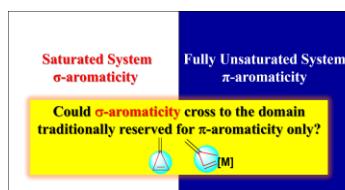
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σ-**Aromaticity** dominating in a fully unsaturated ring is first reported, revolutionizing the fundamental scope of the concept of σ-aromaticity, thus opening an avenue to design of σ-aromaticity in other fully unsaturated systems, which are traditionally reserved for the domain of π-aromaticity.

Saturated System
σ-aromaticity

Fully Unsaturated System
π-aromaticity

Could σ-aromaticity cross to the domain traditionally reserved for π-aromaticity only?

[M]

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σ-**Aromaticity in a Fully Unsaturated Ring**

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