

## Metallacycles

 $\sigma$  Aromaticity Dominates in the Unsaturated Three-Membered Ring of Cyclopropametallapentalenes from Groups 7–9: A DFT StudyYulei Hao, Jingjing Wu, and Jun Zhu\*<sup>[a]</sup>*In memory of Professor Paul von Ragué Schleyer*

**Abstract:** Aromaticity, an old but still fantastic topic, has long attracted considerable interest of chemists. Generally,  $\pi$  aromaticity is described by  $\pi$ -electron delocalization in closed circuits of unsaturated compounds whereas  $\sigma$ -electron delocalization in saturated rings leads to  $\sigma$  aromaticity. Interestingly, our recent study shows that  $\sigma$  aromaticity can be dominating in an unsaturated three-membered ring (3MR) of cyclopropametallapentalene. An interesting question is raised: Can the  $\sigma$  aromaticity, which is dominant in the unsaturated 3MR, be extended to other cyclopropametallapen-

talenes? If so, how could the metal centers, ligands, and substituents affect the  $\sigma$  aromaticity? Here, we report a thorough theoretical study on these issues. The nucleus-independent chemical shift calculations and the anisotropy of the current-induced density plots reveal the dominant  $\sigma$  aromaticity in these unsaturated 3MRs. In addition, our calculations show that substituents on the 3MRs have significant effects on the  $\sigma$  aromaticity, whereas the ligand effect is particularly small.

## Introduction

Aromaticity, one of the most fundamental and fascinating concepts in chemistry, has attracted both experimentalists and theoreticians for decades.<sup>[1]</sup> Generally speaking,  $\pi$  aromaticity results from the  $\pi$ -electron delocalization in closed circuits of unsaturated compounds. For  $\pi$  aromaticity, both classical Hückel aromaticity (i.e.,  $4n+2$   $\pi$  electrons)<sup>[2]</sup> and the novel Möbius aromaticity (i.e.,  $4n$   $\pi$  electrons)<sup>[3]</sup> are possible. Compared with classical organic aromatics, metallaaromatics<sup>[4]</sup> are less developed. In 1979, three hypothetical classes of metallabenzene were proposed<sup>[5]</sup> by Thorn and Hoffmann. Three years later, Roper and co-workers synthesized the first isolated metallabenzene.<sup>[6]</sup> Since then, a series of metallaaromatics such as metallabenzene,<sup>[7]</sup> metallabenzynes,<sup>[8]</sup> metallapentalynes,<sup>[9]</sup> and metallapentalene,<sup>[10]</sup> have been studied both theoretically and experimentally.<sup>[11]</sup>

On the other hand,  $\sigma$ -electron delocalization in saturated rings results in  $\sigma$  aromaticity. Dewar firstly proposed the concept of  $\sigma$  aromaticity in 1979 to explain the abnormal energet-

ic and magnetic behavior of cyclopropane,<sup>[12]</sup> which was further supported by subsequent studies.<sup>[13]</sup> Although this aromatic paradigm was questioned,<sup>[14]</sup> real systems with  $\sigma$ -electron delocalization,<sup>[15]</sup> such as small saturated inorganic rings,<sup>[15a,b]</sup> hydrogen clusters,<sup>[15c,d]</sup> metal hybrid clusters,<sup>[15e-g]</sup> and all-metal elements<sup>[15h,i]</sup> are suggested to have  $\sigma$ -aromatic character both from theoretical and experimental viewpoints. Recently, Xia and co-workers<sup>[10c]</sup> reported  $\sigma$  aromaticity in an unsaturated osmacyclopropene unit of osmapentalene derivatives. Dissected nucleus-independent chemical shift (NICS)<sup>[16]</sup> calculations reveal dominant  $\sigma$  aromaticity in the unsaturated three-membered ring (3MR) because the NICS(0) values from all the  $\sigma$  orbitals are  $-34.8$  ppm whereas key  $\pi$  MOs contribute  $-5.8$  ppm only. This is the first example with  $\sigma$  aromaticity dominating in an unsaturated system. Could the unsaturated 3MR unit in other cyclopropametallapentalenes also be  $\sigma$ -aromatic (Figure 1)? If so, how could the metal centers, ligands, and substituents affect the  $\sigma$  aromaticity? Our ongoing interest in aromaticity<sup>[17]</sup> has led us to address these issues. Here, we carry out density functional theory (DFT) calculations on this interesting system.

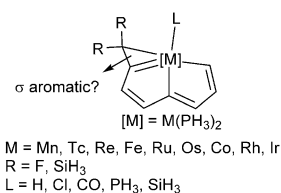


Figure 1. Proposed structure of the cyclopropametallapentalenes.

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## Computational Methods

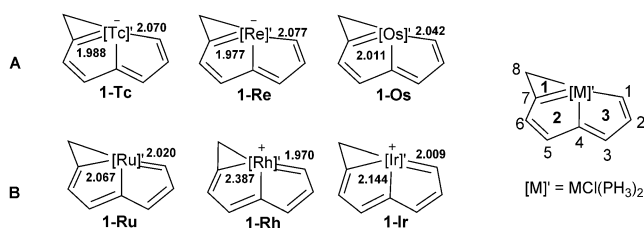
All structures were optimized at the **B3LYP** level of the density functional theory without any constraints on the geometries.<sup>[18]</sup> Frequency calculations were performed at the same level to confirm that all stationary points were minima (no imaginary frequency). The effective core potentials (ECPs) of Hay and Wadt with a double- $\zeta$  valence basis set (LanL2DZ) were used to describe Mn, Tc, Re, Fe, Ru, Os, Co, Rh, Ir, Cl, P, and Si atoms, whereas the standard **6-311++G(d,p) basis set was used for the carbon, hydrogen, and fluorine atoms.**<sup>[19]</sup> Polarization functions were added for Mn ( $\zeta(f)=2.195$ ), Tc ( $\zeta(f)=1.134$ ), Re ( $\zeta(f)=0.869$ ), Fe ( $\zeta(f)=2.462$ ), Ru ( $\zeta(f)=1.235$ ), Os ( $\zeta(f)=0.886$ ), Co ( $\zeta(f)=2.780$ ), Rh ( $\zeta(f)=1.350$ ), Ir ( $\zeta(f)=0.938$ ), Cl ( $\zeta(d)=0.514$ ), P ( $\zeta(d)=0.34$ ), and Si ( $\zeta(d)=0.262$ ).<sup>[20]</sup> All the optimizations were performed with the Gaussian 03 software package at 298 K.<sup>[21]</sup> To examine the effect of the functional for the isomerization stabilization energy (ISE) of **1-Os** shown in Figure 3, the M05,<sup>[22]</sup> TPSS,<sup>[23]</sup> and PBE<sup>[24]</sup> functionals have been used with the basis sets being unchanged. The computed ISE values are +26.5, +27.2, and 27.1 kcal mol<sup>-1</sup>, respectively, which is comparable to that (+25.2 kcal mol<sup>-1</sup>) at the B3LYP/6-311++G(d,p) level, indicating that the functional dependence is very small. The CMO-NICS calculations and Wiberg bond indices were carried out with the NBO 6.0 program<sup>[25]</sup> interfaced with the Gaussian 09 program.<sup>[26]</sup> The anisotropy of the induced current density (AICD) calculations were carried out with the AICD program.<sup>[27]</sup> **The energies (in [kcal mol<sup>-1</sup>]) are given including the zero-point energy corrections.**

## Results and Discussion

### Geometry of the cyclopropametallapentalenes

We first examined nine cyclopropametallapentalenes including Group 7, 8, and 9 elements, from the first- to the third-row transition metals. However, we found that the first-row transition-metal Co was unable to form a stable cyclopropametallapentalene. For example, the Co–C7 (see Figure S1 in the Supporting Information) bond length is 2.627 Å (the Wiberg bond index is 0.065), indicating negligible bonding interaction. Therefore, only the second- and third-row transition metals were chosen for the following discussion.

As shown in Figure 2, the six cyclopropametallapentalenes could be classified into “A” and “B” depending on their structural feature. Such a classification could be due to the empirical diagonal rule between diagonally adjacent elements of the second and third rows of the transition metals in the periodic



**Figure 2.** Optimized structures of six cyclopropametallapentalenes with M–C1 and M–C7 bond lengths given in [Å]. Labels on atoms and rings are also included.

table. For class A compounds, the metal carbon double bonds lie in the 3MRs, whereas for class B compounds, these double bonds are on the opposite side. **This is understandable because experimental data have proven the existence of two dominating resonance structures for cyclopropaospentalene in a previous study.**<sup>[10c]</sup> The fused five-membered rings (5MRs) and the 3MR in Figure 2 are **almost coplanar**, which is reflected by particularly small dihedral angles (ranging from 0.012–0.2°). The metal–carbon bond lengths (i.e., M–C1, M–C4, and M–C7) are all in the range of other metallaaromatics<sup>[7]</sup> except **1-Rh**, in which the **Rh–C7 bond length is 2.387 Å, which is much longer than that in the first-reported aromatic rhodacyclopentadiene (1.983 Å).**<sup>[28]</sup> The C–C bond lengths in **1-Tc** (1.389–1.408 Å), **1-Re** (1.395–1.414 Å), and **1-Os** (1.378–1.401 Å) of the fused 5MRs are between single and double carbon–carbon bond lengths, close to those in benzene (1.396 Å). Thus, the fused 5MRs in class A compounds are delocalized. In sharp contrast, the delocalization of the C–C bonds in fused 5MRs for class B compounds (1.365–1.412 Å for **1-Ru**, 1.340–1.430 Å for **1-Rh**, and 1.354–1.419 Å for **1-Ir**) is reduced, suggesting weaker  $\pi$  aromaticity.

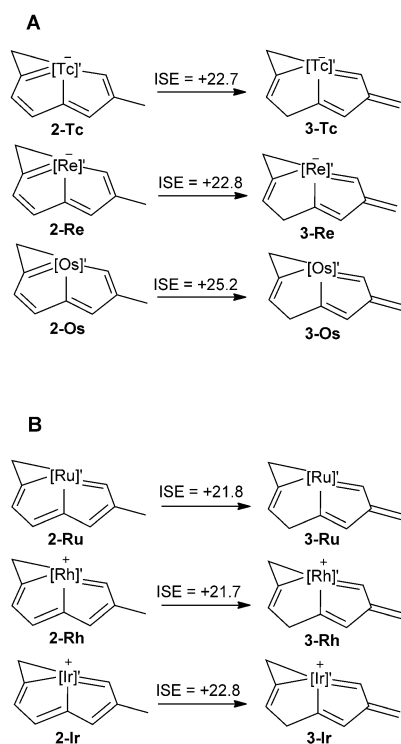
Indeed, as shown in Table 1, the harmonic oscillator model of aromaticity (HOMA) indices<sup>[29]</sup> in class A compounds are generally larger than those in class B compounds. In addition, the Wiberg bond indices of the metal–carbon bonds (i.e., M–C1, M–C4, and M–C7, M–C8) in class B compounds are smaller than those in class A compounds. Especially for the Rh–C7 and Rh–C8 bonds, the Wiberg bond indices are 0.16 and 0.13, respectively, indicating weak interaction between Rh and those two carbon atoms. What is more, the components of the s and p orbitals for its C7 atom are 46 and 53%, respectively, indicating sp hybridization. For the C8 atom, the s and p components are 38 and 62%, respectively, suggesting sp<sup>2</sup> hybridization. Thus, the resonance structure with an allene unit could be dominant in **1-Rh** (see Figure S2 in the Supporting Information).

**Table 1.** Bond indices of the metal carbon bonds and HOMA indices of the 5MRs.

Class	Metal	M–C8	M–C7	M–C4	M–C1	HOMA
A	Tc	0.44	0.82	0.67	0.83	0.955
	Re	0.45	0.91	0.71	0.86	0.937
	Os	0.42	0.68	0.63	0.78	0.959
B	Ru	0.34	0.51	0.60	0.77	0.937
	Rh	0.13	0.16	0.54	0.74	0.791
	Ir	0.28	0.38	0.55	0.71	0.889

### Aromaticity of the cyclopropametallapentalenes

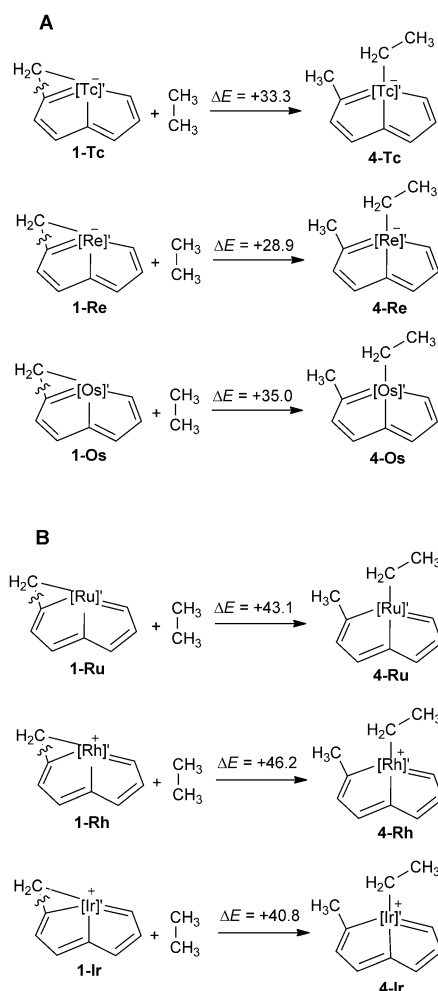
The strain-balanced “isomerization stabilization energy” (ISE)<sup>[30a,b]</sup> method proposed by Schleyer and Pühlhofer, is an effective method to evaluate the aromatic stabilization energy of a  $\pi$  system in both the ground state and the lowest triplet state.<sup>[30c]</sup> So, we used the ISE method to examine the aromaticity of the fused 5MRs. As shown in Figure 3, the ISE values of the fused 5MRs including zero-point energy corrections in



**Figure 3.** Aromaticity of the fused 5MRs computed by strain-balanced ISE methods. The values are given in [kcal mol<sup>-1</sup>].

class A compounds are slightly larger than those in class B compounds. These positive values are in sharp contrast to the negative value (−8.8 kcal mol<sup>-1</sup>) of antiaromatic pentalene,<sup>[9]</sup> indicating the switch of antiaromaticity in pentalene to aromaticity due to the introduction of a metal fragment.<sup>[10a]</sup> Similar stabilization caused by a metal fragment was also found in other cases.<sup>[31]</sup> However, the ISE values are all smaller than that of the osmapentalene (+30.7 kcal mol<sup>-1</sup>),<sup>[10a]</sup> revealing that appending strained 3MRs could perturb  $\pi$ -electron delocalization in fused 5MRs.<sup>[10c]</sup> The stability of 3MRs can be studied by calculating the energies of isodesmic reactions.<sup>[32]</sup> In contrast to the similar reactions designed for cyclopropene (−55.1 kcal mol<sup>-1</sup>) and cyclopropane (−26.6 kcal mol<sup>-1</sup>),<sup>[10c]</sup> the computed energies for the six equations given in Figure 4 are highly positive, indicating that **the aromaticity in the metallacyclopropene ring is large enough to overcome the ring strain**. In addition, the endothermicity for the 3MRs in class A compounds is smaller than that in class B compounds. What causes their difference? The more negative isodesmic reaction energy of cyclopropene (−55.1 kcal mol<sup>-1</sup>) than that of cyclopropane (−26.6 kcal mol<sup>-1</sup>) indicates the larger strain energy of cyclopropene. So for metallacyclopropene-like class A compounds, the strain of the 3MRs is expected to be larger than that for metallacyclopropane-like class B compounds.

The NICS is a key magnetic aromaticity index introduced by Schleyer and co-workers.<sup>[16]</sup> The NICS(0) is defined as the negative magnetic shielding computed at the ring center. The NICS(1)<sub>zz</sub>, which describes the zz component at 1.0 Å above the center, was proven to be a nice indicator for  $\pi$  aromaticity.<sup>[16c]</sup>

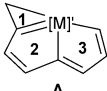
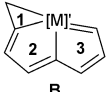


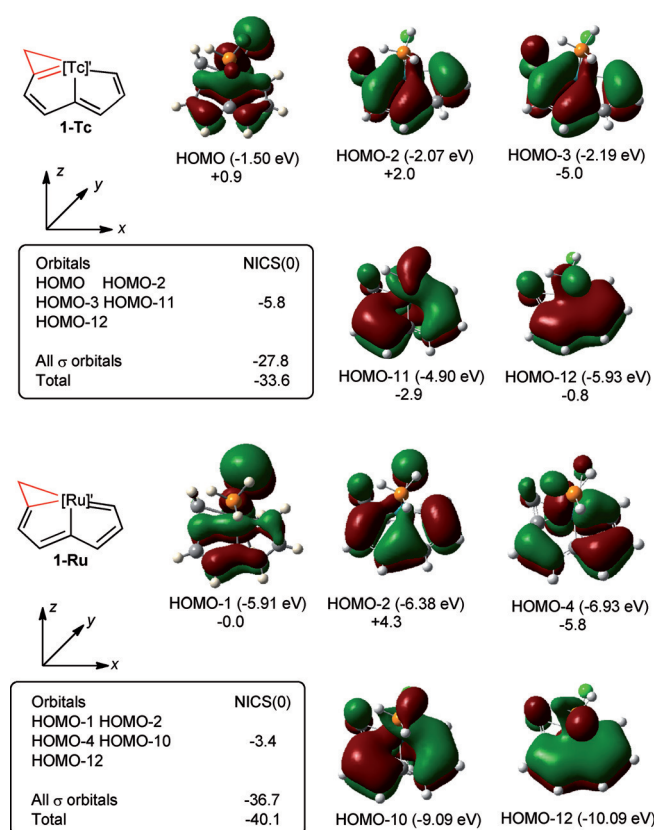
**Figure 4.** Isodesmic reactions of the 5MRs by breaking the C–C bonds suggest the aromaticity in the 3MRs. The values are given in [kcal mol<sup>-1</sup>].

We therefore performed NICS calculations to examine the aromaticity in the 3MRs and the 5MRs. As shown in Table 2, the NICS(0) values of these 3MRs are largely negative, further indicating the aromaticity of the 3MRs. However, the NICS(1)<sub>zz</sub> values of rings 2 and 3 in class B compounds are less negative than that of class A compounds. For 1-Rh, the NICS(1)<sub>zz</sub> values of rings 2 and 3 are −2.9 and −4.8 ppm, respectively. These two values are close to zero, implying very weak  $\pi$  aromaticity, which is consistent with the low HOMA index (0.791) mentioned above.

To further confirm the aromatic nature in these 3MRs, we performed canonical molecular orbital (CMO) NICS calculations, which were also used in our previous work.<sup>[9,10]</sup> The total contributions of the NICS(0) value for the 3MRs from five key occupied  $\pi$  molecular orbitals are listed in parentheses in Table 2. These computed NICS(0) <sub>$\pi$</sub>  values for the 3MRs of the six compounds are all very small, indicating significantly weak  $\pi$  aromaticity. As shown in Figure 5, five occupied  $\pi$  molecular orbitals (MOs) for 1-Tc (HOMO, HOMO−2, HOMO−3, HOMO−11, and HOMO−12) in class A compounds and for 1-Ru (HOMO−1, HOMO−2, HOMO−4, HOMO−10, and HOMO−12)

**Table 2.** NICS(0) values of the 3MRs with the NICS(0)<sub>π</sub> values in parentheses and NICS(1)<sub>zz</sub> values of the 5MRs in the cyclopropametallapentalenes.

Structure	Metal	NICS(0) <sup>[a]</sup> ring 1	NICS(1) <sub>zz</sub> <sup>[a]</sup> ring 2	ring 3
 A	Tc	-33.6 (-5.8)	-18.9	-17.3
	Re	-33.1 (-4.9)	-18.9	-18.0
	Os	-39.6 (-6.4)	-19.1	-17.1
 B	Ru	-40.1 (-3.4)	-15.9	-14.0
	Rh	-33.5 (+0.6)	-2.9	-4.8
	Ir	-41.7 (-2.1)	-11.7	-11.0

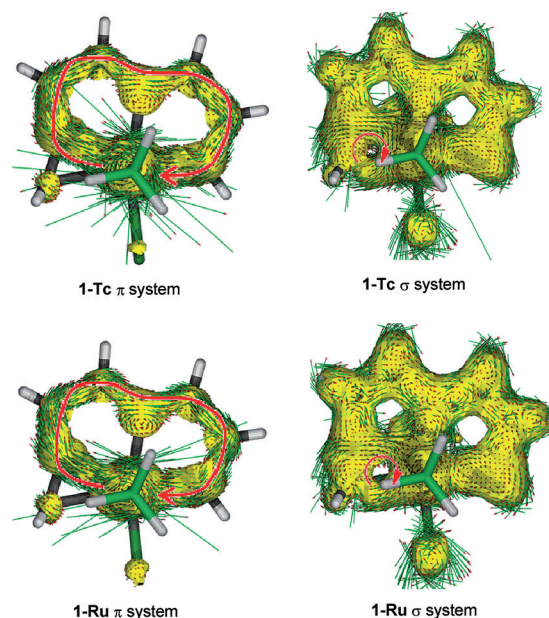


**Figure 5.** Five key occupied  $\pi$  MOs and their eigenvalues (in [eV]) together with their contributions to the NICS(0) values (in [ppm]) of the 3MR in **1-Tc** and **1-Ru**.

in class B compounds are derived from the orbital interactions between the  $p_{z\pi}$  atomic orbitals of the  $C_7H_5$  unit in the fused 5MRs (perpendicular to the bicycle plane) and the metal  $5d_{yz}$  and  $5d_{xz}$  orbitals. The NICS(0) values from all the  $\sigma$  orbitals are much more negative than those from the  $\pi$  MOs contribution, indicating the dominant  $\sigma$  aromaticity (see Figure S3 in the Supporting Information for CMO-NICS calculations for key occupied  $\pi$  MOs of other cyclopropametallapentalenes).

The  $\sigma$  aromaticity in the unsaturated 3MRs is further supported by AICD<sup>[27]</sup> analysis. In general, aromatic species exhibit clockwise diatropic circulation, whereas antiaromatic com-

pounds have anticlockwise paratropic circulations. As shown in Figure 6, the diatropic ring currents in the 3MRs of **1-Tc** and **1-Ru** only appear in the  $\sigma$  system, whereas the clockwise circulation in the  $\pi$  system is only displayed along the fused 5MRs, confirming  $\sigma$  aromaticity in the 3MRs and  $\pi$  aromaticity in the fused 5MRs, respectively (See Figure S4 in the Supporting Information for the AICD plots of other cyclopropametallapentalenes).

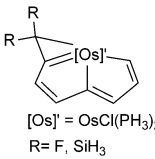


**Figure 6.** Computed AICD plots of **1-Tc** and **1-Ru** separated by the  $\sigma$  and  $\pi$  contribution with an isosurface value of 0.035. Aromatic species exhibit clockwise diatropic circulations.

### Effect of F and SiH<sub>3</sub> substituents on the aromaticity of the 3MRs

The aromaticity of planar cyclopolyenes can be tuned by the electropositive substituent SiH<sub>3</sub> and the electronegative substituents F as previously reported.<sup>[33]</sup> Can the aromaticity of 3MR containing a metal fragment in our system be affected by the substituents, too? We choose the most studied compound **1-Os**<sup>[9,10]</sup> to probe the substituent effect of F and SiH<sub>3</sub> on the aromaticity in the osmacyclopropene unit by CMO-NICS calculations. As shown in Table 3, the  $\sigma$ -orbital contributions to the NICS(0) values for **1-Os**, **1-Os-F**, and **1-Os-SiH<sub>3</sub>** are -33.2, -26.7 and -44.5 ppm, respectively, indicating that  $\sigma$  aromaticity of the 3MR is reduced by the F substituent and strengthened by the SiH<sub>3</sub> group. Interestingly, the opposite effect was found for the  $\pi$  aromaticity, as the NICS(1)<sub>zz</sub> and NICS(0)<sub>π</sub> values of the 3MR in **1-Os-F** are the most negative ones compared with **1-Os-SiH<sub>3</sub>** and **1-Os**. The significant aromaticity difference caused by the F and SiH<sub>3</sub> substituents could be ascribed to their hyperconjugative effects and electronic effects on  $\pi$  and  $\sigma$  aromaticity. Fluorine is an electron-withdrawing group and reduces the  $\sigma$ -electron density, leading to weaker  $\sigma$  aromaticity. On the other hand, the CF<sub>2</sub> group acts like a partially vacant p orbital and results in a  $4n+2$  electron system

**Table 3.** NICS(1)<sub>zz</sub>, NICS(0), NICS(0)<sub>ov</sub>, and NICS(0)<sub>π</sub> values of the 3MRs of complexes **1-Os**, **1-Os-F**, and **1-Os-SiH<sub>3</sub>**.

Complex	NICS <sup>[a]</sup>	<b>1-Os</b>	<b>1-Os-F</b>	<b>1-Os-SiH<sub>3</sub></b>
	NICS(1) <sub>zz</sub>	-26.4	-30.0	-18.8
	NICS(0)	-39.6	-39.3	-34.4
	NICS(0) <sub>ov</sub>	-33.2	-26.7	-44.5
	NICS(0) <sub>π</sub>	-6.4	-12.6	+10.1

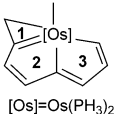
[a] Values are given in [ppm].

for the 3MR, indicating  $\pi$  aromaticity.<sup>[33b]</sup> In sharp contrast, the C(SiH<sub>3</sub>)<sub>2</sub> group supplies two "pseudo"  $\pi$  electrons, resulting in  $4n$   $\pi$  antiaromaticity in **1-Os-SiH<sub>3</sub>**. But as an electron-donating group, SiH<sub>3</sub> makes the 3MR  $\sigma$ -electron rich, leading to stronger  $\sigma$  aromaticity (see Figure S5 in the Supporting Information for the detailed influence of selected  $\pi$  MOs).

### Effect of ligands on the aromaticity of the 3MRs and the 5MRs

We also examined the effect of ligands by changing Cl to H, CO, SiH<sub>3</sub> and PH<sub>3</sub> for **1-Os**. As shown in Table 4, the influence on the aromaticity of the fused 5MRs and the 3MRs by different ligands is particularly small according to the NICS values.

**Table 4.** Computed NICS(0) and NICS(0)<sub>ov</sub> values of the 3MRs as well as NICS(1)<sub>zz</sub> values of the 5MRs in the cyclopropametallapentalenes with different ligands.

Complex	NICS <sup>[a]</sup>	Ring	Cl	H	CO	SiH <sub>3</sub>	PH <sub>3</sub>
	NICS(0)	1	-39.6	-42.0	-44.4	-42.9	-43.5
	NICS(0) <sub>ov</sub>	1	-33.2	-35.1	-41.7	-39.7	-40.2
	NICS(1) <sub>zz</sub>	2	-19.1	-18.3	-18.1	-17.9	-20.8
		3	-17.1	-17.7	-17.6	-18.6	-20.0

[a] Values are given in [ppm].

### Conclusion

DFT calculations have been performed to examine the aromaticity in the fused 5MRs and the  $\sigma$  aromaticity in the unsaturated 3MRs of cyclopropametallapentalenes of Group 7–9 transition metals. Specifically, positive ISE values, negative NICS(1)<sub>zz</sub> values, and diatropic ring currents in the 5MRs of the  $\pi$  system indicate  $\pi$  aromaticity of the fused 5MRs, whereas the dominant  $\sigma$  aromaticity in these metallacyclopropene units is revealed through isodesmic reactions, dissected NICS(0) values, and AICD plot of the  $\sigma$  systems. Moreover, SiH<sub>3</sub> and F groups can be used to tune the  $\sigma$  and  $\pi$  aromaticity of the osmacyclopropene unit. The electropositive SiH<sub>3</sub> substituent strengthens the  $\sigma$  aromaticity and weakens the  $\pi$  aromaticity. Conversely, the electronegative F substituent weakens the  $\sigma$  aromaticity

and strengthens the  $\pi$  aromaticity of the 3MRs. Our findings of  $\sigma$  aromaticity in the unsaturated 3MRs could allow further exploration of the possibility of  $\sigma$  aromaticity in other unsaturated systems.

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**Keywords:** aromaticity · density functional calculations · metallaaromatics · unsaturated compounds

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