

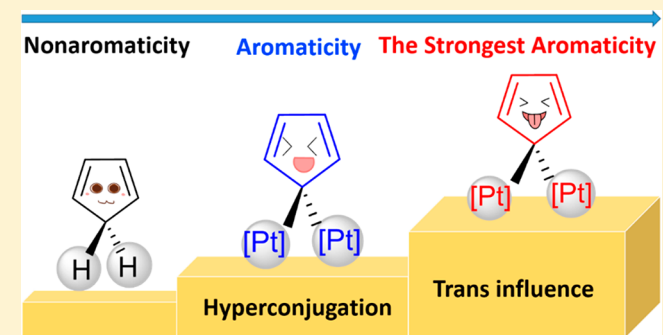
Probing the Strongest Aromatic Cyclopentadiene Ring by Hyperconjugation

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Supporting Information

ABSTRACT: Hyperconjugation, an interaction of electrons in a σ orbital or lone pair with an adjacent π or even σ antibonding orbital, can have a strong effect on aromaticity. However, most work on hyperconjugative aromaticity has been limited to main-group substituents. Here, we report a thorough density functional theory study to evaluate the aromaticity in various cyclopentadienes that contain both main-group and transition-metal substituents. Our calculations reveal that the strongest aromatic cyclopentadiene ring can be achieved by the synergy of trans influence and hyperconjugation caused by transition-metal substituents. Our findings highlight the great power of transition metals and trans influence in achieving hyperconjugative aromaticity, opening an avenue to the design of other novel aromatic organometallics.



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INTRODUCTION

Aromaticity, one of the most important concepts in chemistry, has attracted considerable experimentalists and theoreticians for decades.^{1–7} Hyperconjugation,^{8–18} an interaction of electrons in a σ orbital or lone pair with an adjacent π or even σ antibonding orbital, was first reported by Mulliken in 1939, in which the CH_2 saturated group can provide “pseudo 2π electrons” to the olefinic skeleton, resulting in an aromatic cyclopentadiene ring to have formal 6π electrons. Later, Schleyer and co-workers examined various cyclopentadienes with different substituents¹⁹ by computing their nucleus-independent chemical shifts (NICS)^{20,21} and aromatic stabilization energies (ASE)^{22–25} in 1999, confirming the concept of hyperconjugative aromaticity. Their calculations demonstrated that electropositive substituents (e.g., SiH_3 , GeH_3 , SnH_3) can contribute “pseudo 2π electrons” by hyperconjugation and lead to aromaticity, whereas electronegative substituents (e.g., F, Cl) result in antiaromaticity. It should be noted that a different opinion on hyperconjugative aromaticity in substituted cyclopentadiene appeared in 2006. Specifically, Stanger claimed that there is no special stabilization or destabilization for any of the derivatives and that the energetic effects previously attributed to aromatic stabilization or antiaromatic destabilization are the result of interaction in the reference systems.²⁶ However, subsequent studies by various computational and experimental groups have been reported to support the concept of hyperconjugative aromaticity. For instance, Schleyer and co-workers extended this concept to cyclopropene, cycloheptatriene, and cyclo-

nonatetraene derivatives.²⁷ Ottosson and co-workers reported that the variation in polarities and excitation energies of different substituted cyclopentadienes could be understood by the effect of hyperconjugative aromaticity.^{28–30} In addition, O’Ferrall and co-workers showed computationally and experimentally that the concept of hyperconjugative aromaticity can be justified by the higher stability of the benzenium ion and 1,2-dihydroxycyclohexadienide anion.^{31,32} Recently, the difference in the Diels–Alder reactivities of substituted cyclopentadienes and cyclopropenes explored by Houk further validated the concept of hyperconjugation.^{33,34} In 2016, we extended this concept to triplet-state aromaticity.³⁵

However, all these studies mentioned above have focused on main-group substituents only. In 2016, we reported that a transition-metal substituent (AuPPh_3) could perform better than a main-group substituent (SnH_3) in achieving hyperconjugative aromaticity via density functional theory calculations.³⁶ Along with quite a few studies on substituted cyclopentadienes^{37–40} and the hyperconjugative effects on metal–carbon bonds,^{41–44} we extended the concept of hyperconjugative aromaticity to the silver-containing system, revealing the greater performance of silver over gold.⁴⁵ Furthermore, when the push–pull effect is considered, the most aromatic and antiaromatic pyrrolium can be achieved. However, the influence of other transition metals on hyperconjugative aromaticity remains unclear. On the other

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hand, the strong trans influence^{46–53} of the ligand can significantly influence the ground state thermodynamic properties of a transition metal, such as stabilizing both the ground state and transition state in transition-metal catalysis.^{54,55} Could the trans influence affect hyperconjugative aromaticity? In this work, we evaluate the aromaticity in Pt-containing substituted cyclopentadienes and report the strongest neutral cyclopentadiene ring by the synergy of trans influence and hyperconjugation (Figure 1).

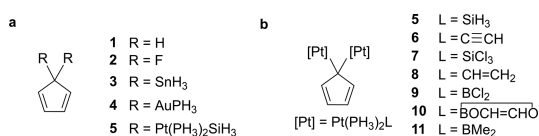


Figure 1. Proposed substituted cyclopentadienes: (a) cyclopentadienes containing different substituents; (b) Pt-containing substituted cyclopentadienes with different ligands.

COMPUTATIONAL DETAILS

All of the species were optimized at the TPSS level^{56–59} of density functional theory (DFT). The dispersion corrections were described by “EmpiricalDispersion = GD3”.⁵⁹ The frequency calculations were performed to verify the minima of all stationary points. The effective core potentials (ECPs) with the ECP46MDF basis set served as the pseudo basis set for the Sn atom⁶⁰ and the ECP60MDF basis set was used to describe Au and Pt atoms,^{61,62} whereas the B, C, N, O, F, P, Si, Cl, and H atoms were calculated by the description of the standard 6-31G(d) basis set.⁶³ All of the optimizations were performed with the Gaussian 09 software package.⁶⁴ The reliability of our calculations was supported in a previous study which showed that the experimental geometry was reasonably reproduced at the same level.³⁶ The interaction of the fragment analysis and the energy decomposition analysis (EDA) analysis was determined with the Amsterdam Density Functional (ADF) program by the meta-GGA:TPSS-D3 functional, in which we used the uncontracted Slater-type orbitals (STOs) as basis functions.⁶⁵ A triple- ζ STO basis with two sets of polarization functions was employed for the elements H, F, Sn, Au, and Pt. This level of calculations is denoted metaGGA:TPSS-D3/TZ2P. An auxiliary set of s, p, d, f, and g STO functions was used to fit the molecular densities and to represent the accurate Coulomb and exchange potentials in each SCF cycle. Scalar relativistic effects were considered by means of the zero-order regular approximation (ZORA).⁶⁶

RESULTS AND DISCUSSION

We first optimized all the species shown in Figure 1a and provide their corresponding Δ BL values (the difference between the longest and the shortest C–C bond length in the cyclopentadiene ring) in Figure 2a. A small Δ BL value

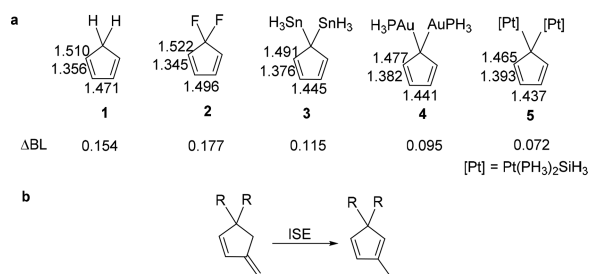


Figure 2. (a) C–C bond lengths (Å) and Δ BL values (Å) of cyclopentadienes 1–5. (b) The equation for ISE values of substituted cyclopentadienes.

indicates high delocalization. The Δ BL values (0.115, 0.095, and 0.072 Å) in cyclopentadienes 3–5 with electropositive substituents are in sharp contrast with that of the unsubstituted cyclopentadiene (0.154 Å in 1), indicating a better delocalization. On the other hand, an electronegative substituent (F) leads to the localized cyclopentadiene 2 with the largest Δ BL (0.177 Å). Note that 5 has the smallest Δ BL (0.072 Å) among all the species in Figure 2a, indicating the strongest delocalization in its five-membered ring.

The strain-balanced methyl–methylene “isomerization stabilization energy” (ISE) method is particularly effective for probing the magnitude of aromatic π conjugation for highly strained systems in both the singlet and triplet states.^{23–25}

Therefore, we use ISE values including the zero-point energy corrections to calculate the aromatic stabilization energies of the cyclopentadiene rings with different substituents (Figure 2b). In general, negative ISE values denote aromaticity, whereas positive values indicate antiaromaticity. As shown in Table 1, the ISE values of cyclopentadienes with different

Table 1. Δ BL Values (Å), ISE Values (kcal mol^{−1}), NICS Values (ppm), and FCI Values of Compounds 1–5

	1	2	3	4	5
ISE	−2.4	7.2	−14.6	−14.9	−19.4
NICS(0)	−3.4	2.9	−6.8	−8.2	−10.7
NICS(1) _{zz}	−10.6	8.1	−23.3	−21.5	−25.9
FCI	0.028	0.016	0.048	0.056	0.066

substituents are in good agreement with the Δ BL values. The positive ISE value of 2 (7.2 kcal mol^{−1}) indicates antiaromaticity, whereas the close to zero value (−2.4 kcal mol^{−1}) of 1 suggests nonaromaticity. In sharp contrast, the ISE values of 3 (−14.6 kcal mol^{−1}), 4 (−14.9 kcal mol^{−1}), and 5 (−19.4 kcal mol^{−1}) are significantly more negative, indicating aromaticity. Note that species 5 has the most negative ISE value (−19.4 kcal mol^{−1}) and the smallest Δ BL value (0.072 Å), whereas species 2 has the most positive ISE value (7.2 kcal mol^{−1}) and the largest Δ BL value (0.177 Å) among the counterparts of these cyclopentadiene rings.

As a manifestation of the ring current arising from the cyclic electron delocalization, aromaticity can be also described by the NICS.^{20,21} In general, negative values indicate aromaticity and positive values antiaromaticity. As shown in Table 1, the NICS values of the cyclopentadiene rings are in line with the ISE values. The NICS(1)_{zz} values of 3 (−23.3 ppm), 4 (−21.5 ppm), and 5 (−25.9 ppm) are significantly more negative than that of 1 (−10.6 ppm), demonstrating the switch from nonaromaticity to aromaticity in these cyclopentadiene rings. In contrast, the NICS(1)_{zz} value of 2 (8.1 ppm) is positive, supporting its antiaromaticity. In addition, anisotropy of the induced current density (ACID), first introduced by Herges and co-workers, can be employed to visualize aromaticity in cyclic species.^{67,68} Thus, we computed it to confirm the (anti)aromaticity of 1–5. In general, a diatropic ring current indicates aromaticity whereas a paratropic ring current denotes antiaromaticity. As shown in Figures S1–S5, the clockwise ring current density vectors plotted on the ACID isosurfaces of complexes 3–5 demonstrate their aromatic character, whereas antiaromaticity in complex 2 is indicated by the paratropic ring current. Note that the most negative NICS(0) (−10.7 ppm) and NICS(1)_{zz} (−25.9 ppm) values of 5 further suggest the

strongest aromaticity in the five-membered ring among all the substituted cyclopentadienes.

The multicenter index of aromaticity (MCI), first proposed by Ponec in 1997, has been proven to be a critical and commonly accepted criteria to evaluate the aromaticity of organic and inorganic species.^{69–73} The five-center index (FCI) values computed by the Multiwfn package⁷⁴ for the substituted cyclopentadienes ranging from 0.016 to 0.066 are smaller than that (0.086) of benzene, indicating weaker aromaticity in these cyclopentadienes. Note that complex **5** has the largest FCI value (0.066) among these five substituted cyclopentadienes, supporting its strongest aromaticity.

Our calculations reveal that electropositive substituents can significantly enhance the hyperconjugative aromaticity in the five-membered ring of the cyclopentadienes in comparison with the parent species. In particular, the Pt-containing substituent can perform better than the Au-containing substituent in maintaining the hyperconjugative aromaticity of cyclopentadiene.

We hypothesize that the orbital interaction between the CR₂ orbitals and the C₄H₄ orbitals might be important to hyperconjugative aromaticity of the substituted cyclopentadienes. Our assumption is supported by the single-point calculation of the HOMO of the CR₂ fragment and the LUMO of the C₄H₄ fragment taken from the substituted cyclopentadiene, which was computed by the Amsterdam density functional (ADF) program.^{44,64,65,75,76} As shown in Figure 3,

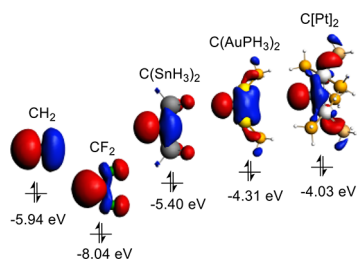


Figure 3. HOMO plots of CH₂, CF₂, C(SnH₃)₂, C(AuPH₃)₂, and C[Pt]₂ ([Pt] = Pt(PH₃)₂SiH₃) fragments.

the HOMO energy (−4.03 eV) of the C[Pt]₂ fragment ([Pt] = Pt(PH₃)₂SiH₃) is the highest among all of the species, indicating the strongest electron-donating ability and the best performance of hyperconjugative aromaticity. In contrast, the CF₂ fragment has the lowest HOMO (−8.04 eV), which makes it particularly difficult to donate its electrons to the C₄H₄ fragment, resulting in (pseudo 4π e) antiaromaticity in the cyclopentadiene ring. Moreover, we also carried out EDA calculations by using the neutral fragments C₄H₄ and CR₂ in the respective open-shell singlet state, in which two unpaired electrons in each fragment are in σ orbitals for the formation of the C–C bond. As shown in Table S1, the total orbital interaction (ΔE_{orb}) of cyclopentadiene rings with electropositive substituents becomes more and more negative (from −489.2 to −786.6 kcal mol^{−1}), indicating an enhanced orbital interaction in these species.

We next evaluate the trans influence of ligand L on hyperconjugative aromaticity in cyclopentadienes with Pt-containing substituents. The increasing order of trans influence (−C≡CH < −SiCl₃ < −CH=CH₂ < −SiH₃ < −BCl₂ < −BOCH=CHO < −BMe₂) was reported by us previously.⁵¹ In general, the trans effect is known as a kinetic phenomenon; i.e., certain ligands facilitate the departure of trans groups

during ligand substitution reactions by an external ligand in square-planar complexes.^{45–50} Trans influence, known as the static trans effect, is associated with the ground state thermodynamic properties and can be defined as the bonds trans to strong σ donors being significantly elongated.^{51,52} For instance, a long M–L bond length corresponds to a short M–C bond distance in a linear C–M–L system. Therefore, the trans influence can be straightforwardly measured by the Pt–C bond lengths in cyclopentadienes with Pt-containing substituents. As shown in Figure 4, the Pt–C bond lengths of the

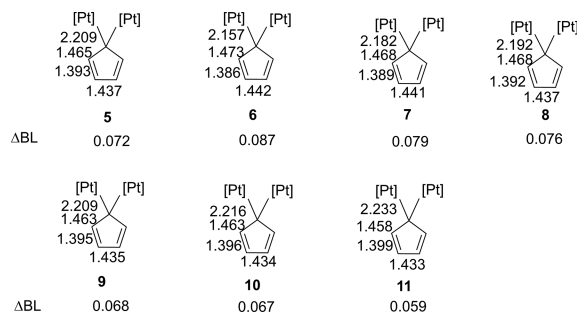


Figure 4. C–C bond lengths (Å), Pt–C bond lengths (Å), and ΔBL values (Å) of Pt-containing cyclopentadienes **5–11**.

cyclopentadiene rings are in line with the order reported previously.⁵⁰ The Pt–C bond length of complex **11** (2.233 Å) is the longest among all the Pt-containing species, indicating the strongest trans influence, whereas the shortest Pt–C bond length in complex **6** suggests the weakest trans influence among all the Pt-containing species.

To gain a deep insight into the effect of trans influence on hyperconjugative aromaticity, we performed geometric, magnetic, energetic, and electronic evaluations of the aromaticity of complexes **5–11**. As shown in Figure 4, the ΔBL values decrease gradually in accord with the increasing order of trans influence. Specifically, the largest ΔBL value is found in complex **6** (0.087 Å), whereas complex **11** shows the smallest ΔBL value (0.059 Å), indicating the strongest delocalization among all the Pt-containing cyclopentadienes. In line with the geometric differences, the energetic evaluations (ISE values) also show an excellent agreement with the order of trans influence. The most negative ISE of complex **11** (−22.0 kcal mol^{−1}) further demonstrates the strongest aromaticity among all the Pt-containing substituted cyclopentadienes. In accord with the most negative NICS(1)_{zz} value (−28.1 ppm) and the largest MCI value (0.072) of complex **11**, we can safely draw a conclusion that the strongest trans influence can be found in complex **11** containing the BMe₂ ligand, leading to the most aromatic cyclopentadiene ring reported so far. Furthermore, the aromaticities of complexes **5–11** are also confirmed by ACID plots in Figures S6–S11 of the Supporting Information.

To further explore the correlation between trans influence and hyperconjugative aromaticity, we calculated the EDA calculations with the ADF program.⁶⁴ The negative values of the total orbital interaction (ΔE_{orb}) reveal a strong orbital interaction between the two fragments (C[Pt]₂ and C₄H₄) in the substituted cyclopentadienes. As shown in Table 2, the total orbital interaction (ΔE_{orb}) increases gradually in accord with the increasing order of trans influence, ranging from −766.5 kcal mol^{−1} (complex **6**) to −803.0 kcal mol^{−1} (complex **11**). In general, an increasing total orbital interaction indicates a higher stabilization caused by hyperconjugation,

Table 2. Pt–C Bond Lengths (Å), Δ BL Values (Å), ISE Values (kcal mol^{-1}), FCI Values, NICS Values (ppm), and Total Orbital Interactions (kcal mol^{-1}) of Pt cyclopentadienes 5–11

	Pt–C	Δ BL	ISE	FCI	NICS(1) _{zz}	ΔE_{orb}
6	2.157	0.087	−16.1	0.059	−23.8	−766.5
7	2.182	0.079	−17.3	0.061	−23.6	−777.4
8	2.192	0.076	−18.4	0.065	−25.7	−778.7
5	2.209	0.072	−19.4	0.066	−25.9	−786.6
9	2.209	0.068	−20.0	0.067	−27.8	−790.1
10	2.216	0.067	−21.0	0.069	−27.4	−786.6
11	2.233	0.059	−22.0	0.072	−28.1	−803.0

which could account for the strongest aromaticity in the five-membered ring of complex **11** among all Pt-containing cyclopentadienes. The details of the EDA results are given in Table S2.

In addition, the excellent correlations (Figure 5) of the ISE values against Δ BL (0.951) and NICS values (0.963) of all

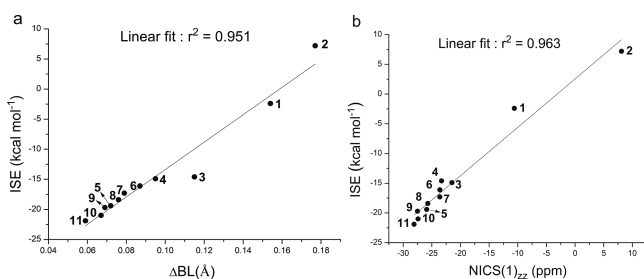


Figure 5. Correlation between the ISE values against Δ BL (a) or NICS values (b) for all of the substituted cyclopentadienes.

species demonstrate the high reliability of our calculations. In order to examine the correlations of the aromatic cyclopentadiene rings, the correlations without **1** (nonaromaticity) and **2** (antiaromaticity) have been provided in the Supporting Information and moderate correlations were found, as shown by Figure S12. Note that even the weakest trans influence ligand among all the Pt-containing substituents can perform better than an Au-containing substituent in achieving hyperconjugative aromaticity. For instance, complex **6** has a Δ BL value (0.087 Å) smaller than that of **4** (0.095 Å). Similarly, the ISE value of complex **6** ($-16.1 \text{ kcal mol}^{-1}$) is more negative than that of **4** ($-14.9 \text{ kcal mol}^{-1}$), indicating slightly enhanced aromaticity in the cyclopentadiene ring. In addition, complex **6** has a relatively more negative NICS(1)_{zz} value (-23.8 ppm) in comparison with **4** (-21.5 ppm), supporting the greater performance of Pt-containing substituents over Au-containing substituents in achieving hyperconjugative aromaticity.

On the other hand, we also examined ligand effects on the aromaticity of **4'** and **11'** with PMe_3 ligands, more realistic models in experiments. Our calculations showed that the ligand dependence is small, as the Pt-containing substituents can also perform better than Au-containing substituents in maintaining the hyperconjugative aromaticity of cyclopentadiene, which is supported by the Δ BL, ISE, and NICS values of complexes **4'** and **11'** (Figure S13). Our findings highlight the importance of the transition metal and trans influence on hyperconjugative aromaticity. Note that optimizing a dipotassium derivative leads to a distorted η^5 complex (Figure S14), in which the cyclopentadiene ring carries a formal negative

charge. Its aromaticity is not discussed here, as we focus only on the neutral cyclopentadiene ring in this study.

CONCLUSION

In summary, our calculations reveal that Pt-containing substituents can perform better than Au-containing substituents in achieving the hyperconjugative aromaticity of cyclopentadiene. In addition, when the trans influence is considered, the BMe_2 ligand performs best among all of the ligands, leading to the strongest aromatic cyclopentadiene ring reported so far, which is supported by the smallest Δ BL values, the most negative ISE values, the largest FCI values, and the most negative NICS values. Our findings highlight the importance of the transition metal and trans influence on hyperconjugative aromaticity, opening an avenue to design other novel aromatic organometallics.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.8b00571.

ACID plots of substituted cyclopentadienes and details of EDA calculations (PDF)

Cartesian coordinates for all the complexes. (XYZ)

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Notes

The authors declare no competing financial interest.

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