


Article

Are Metallacyclopentadienes Always Non-Aromatic?

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Abstract: Even though metallacyclopentadienes (MCPs) are among the most common metallacycles, their electron delocalization (aromaticity) has received far less attention than other metallacycles, such as metallabenzenes. We systematically studied the aromaticity of MCPs with energetic (isomerization stabilization energy), density (delocalization index) and magnetic (current density) aromaticity indices. The indices agree that metallacyclopentadienes are, in general, weakly aromatic at most. The $18e^-$ complexes showed the expected weak aromaticity, and only the d^8 molecules are somewhat anti-aromatic. However, the theoretical account of the aromaticity of the $16e^-$ MCPs is more convoluted. We find that the aromatic criteria for a $16e^- d^4$ ruthenacyclopentadiene disagree. The lack of agreement shows that significant electron delocalization is not always related to great stability or to strong diatropic currents.

Keywords: aromaticity; metallacycles; ring currents



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1. Introduction

One of the first families of metallocycles discussed in the literature were the metallacyclopentadienes (MCPs). In fact, in the famous paper of Thorn and Hoffmann [1] in which the metallabenzenes (MBs) were predicted, the principal topic of the manuscript was the metallacyclopentadienes. At that time, several crystal structures of MCPs were already known [2–9], many years before the first metallabenzene was synthesized [10]. Furthermore, a simple search in the Cambridge Structural Database (CSD) shows far more MCP than MB structures. However, the electronic structure of the former has received much less attention than the latter. The aromaticity of metallabenzenes has been thoroughly discussed in the literature [11–22] and some general conclusions have been drawn. Their C–C bonds have a significant degree of equalization, and most of them are planar [12,13,22], although some of them strongly deviate from planarity [23,24]. In general, the MBs' aromatic stabilization energy (ASE) are around 10 kcal/mol below the value for benzene [14,15,25,26]. Moreover, their nuclear independent chemical shifts (NICS) are negative [27–32], a common characteristic of aromatic compounds. Therefore, all these results indicate that metallabenzenes are at least slightly aromatic. However, some contradictory results have also been published. For example: Iron et al. and Periyasamy et al. found that the NICS and magnetic susceptibility anisotropy values of some complexes are positive, indicating a certain degree of anti-aromaticity [16,27]. These contradictions could be because these two magnetic indices depend not only on the magnetically induced electron current around the ring, but also on all the currents circulating around each atom. In aromatic organic molecules the contribution of these atomic currents to NICS is negligible compare to the ring current, but in metallacycles, the current around the metal is not negligible. The magnetically induced current density ($j(r)$) avoids this problem and has also been calculated for some metallabenzenes. The calculations have shown that the $18e^-$ rings have diatropic currents, indicating aromaticity, while the $16e^-$ rings have paratropic currents, which suggest the opposite [16,18].

In the case of metallacyclopentadienes, there are not so many papers that discuss their aromaticity, maybe because, since the beginning, they were classified as non-aromatic [1],

although there is a large number of published MCP structures [33], which suggest that they are quite stable. From the published studies, we draw some tendencies about the aromaticity of the MCPs. Their equalization of C–C bonds is significantly lower than for MBs. It has been shown that the maximum difference between C–C distances is around 0.09 Å [1,34–36] for metallacyclopentadienes, while for metallabenzenes this difference is approximately 0.03 Å [12,13,36]. There is an exception for this low C–C equalization: in bimetallic complexes all C–C bond distances are very similar [37–42], as Thorn and Hoffman described in their seminal work [1]. The vast majority of reported crystal structures are almost planar (see CSD or Supplementary Materials), although there are a few examples that are not [43–48]. This bending is less common than in metallabenzenes (we found 18 significantly bent structures for MBs and only 6 for MCPs). The ASE reported until now for metallacyclopentadienes are very low, around 4 kcal/mol, compared to metallabenzenes (~15 kcal/mol) [36]. Moreover, it has also been shown that half sandwich nickel-, pallada- and platinacyclopentadiene complexes are less stable than their corresponding metallabenzene isomers [49]. The NICS has been the most widely used index to evaluate the aromaticity of the metallacyclopentadienes. Jemmis et al. found very small negative NICS values for Ti and Zr complexes [34]. Islas et al. also found small negative values for a series of Os, Ru, Rh and Ir compounds [35]. On the other hand, Zeng et al. found small positive values for a Pd and a Pt metallacyclopentadiene (large positive values are normally associated with anti-aromatic rings) [49]. The discussed results seem to indicate a non-aromatic or a small aromatic character of these metallacycles. However, metallacyclopentadienes are very stable and more common than metallabenzenes, but their aromaticity and its electronic structure has only been studied in a handful of complexes. In addition, the NICS were used as the primary tool to evaluate its aromaticity, although, as mentioned, their values can be affected by the strong metal currents [50,51]. This effect can be more significant for weak ring currents, such as the currents that these compounds presumably have. Therefore, it is necessary to study systematically the aromaticity of these types of important metallacycles and with different aromaticity indexes that do not suffer the same drawbacks as NICS. In this contribution, we studied the aromaticity of a series of d^0 , d^2 , d^4 , d^6 and d^8 metallacyclopentadienes using $j(\mathbf{r})$, isomerization stabilization energy (ISE) and the delocalization indices (DI).

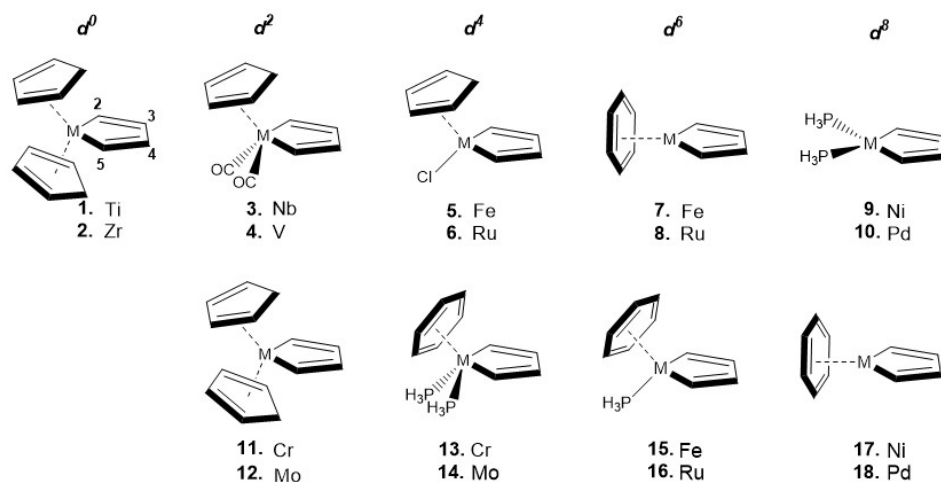
2. Computational Methods

All the geometries were fully optimized, unless otherwise stated in the main text, at the M062x/Def2TZVP level of theory. The M062x functional has broad applicability and has shown good results for π conjugated systems [52], which is a common characteristic of the studied molecules. A frequency calculation was performed to ensure that the stationary points were true minima. Because of the use of core potentials in the Def2TZVP basis set for the second row transition metals, we prefer to use a full electron basis set for all the calculations of the magnetic properties (Sapporo-TZP-2012 [53]). The magnetic perturbed wave functions were calculated with gauge-including atomic orbitals, GIAO, at the M062x/Sapporo-TZP-2012 level of theory (For the analysis of the contribution of independent MO to $j(\mathbf{r})$ the CSGT method was used, see below). All these calculations were performed with Gaussian 16 [54].

The DI and $j(\mathbf{r})$ were calculated with AIMALL [55]. The triple product of $j(\mathbf{r})$ ($\text{tp}j(\mathbf{r}) = \mathbf{B} \cdot \nabla \times j(\mathbf{r})$) was calculated numerically using python scripts and the ppython module included in Paraview 5.2 as has been previously described [56–58]. The calculations of the single orbital contributions to $j(\mathbf{r})$ were performed with the CTOCD-DZ (continuous transformations of the origin of the current density-diamagnetic zero) or ipsocentric method [59,60], because only this method can guarantee that the orbital contributions do not include magnetic transitions between occupied molecular orbitals (MOs) [61]. The calculations of the MO contributions were performed with AIMALL and SYSMOIC [62].

3. Results

The 18 metallacyclopentadienes of the first and second transition series that we studied are shown in Scheme 1. The studied metallacycles can be divided into two main groups: $16e^-$ (1–10) and $18e^-$ (11–18). Moreover, the two groups can be subdivided into d^0 (1,2), d^2 (3,4,11,12), d^4 (5,6,13,14), d^6 (7,8,15,16) and d^8 (9,10,17,18) complexes.



Scheme 1. Structures of the studied metallacyclopentadienes.

The optimized structures of the studied compounds are similar to what has been previously reported (for some examples see [4,5,8,63–71]). The C–C bonds are poorly equalized: the C2–C3 and C4–C5 bonds are around 1.35 Å and the C3–C4 distances are approximately 1.46 Å, and the bond distance differences between C2–C3 or C4–C5 with C3–C4 are ~0.11 Å (Table 1). All these differences are larger than 0.09 Å except for the d^4 complex 6 with a bond distance differences between C2–C3 and C3–C4 of only 0.06 Å. Another $16e^-$ complex than stands apart from the C–C distance trend is 8, in which the C–C distances are inverted. The C3–C4 bond is the shortest (1.34 Å) and C2–C3 and C4–C5 are longer (1.48 Å). Moreover, the M–C bonds are particularly short, only 1.84 Å. This is indicative that 8 resembles the structure of a metallacyclopentatriene. In the literature, there are some Ru complexes with this type of structure, although with a different d electron count [65,72–76]. Another geometrical feature related to aromaticity is the planarity. We estimated it with the M–C2–C3–C4 dihedral. Only d^0 and d^8 rings have a perfectly planar structure. The others present a slight deviation from the plane, except for the d^2 complexes 3 and 4. The fully optimized structure of 3 is significantly bent, with a M–C2–C3–C4 dihedral of 36° and 4 does not even converge with 5-membered ring structure. For these two molecules, we force the planarity to be able to compare them with the all the other MCPs. In the literature, we could not find any stable d^2 $16e^-$ metallacyclopentadiene. The lack of stable d^2 $16e^-$ metallacyclopentadienes is compatible with our results.

Table 1. Selected geometrical parameters.

Molecule	d_{M-C2} (Å)	d_{C2-C3} (Å)	d_{C3-C4} (Å)	$\phi_{MC2C3C4}$ (°)
1	2.12	1.34	1.47	0.1
2	2.24	1.35	1.48	0.1
3	2.25	1.33	1.47	1.0
4	2.13	1.33	1.47	0.2
5	1.92	1.34	1.45	3.4
6	1.94	1.36	1.42	5.0
7	2.00	1.34	1.49	5.7
8	1.84	1.48	1.34	0.0
9	1.97	1.34	1.47	0.0
10	2.05	1.34	1.46	0.0
11	2.06	1.33	1.46	2.2
12	2.16	1.34	1.46	0.0
13	2.14	1.34	1.45	1.4
14	2.16	1.35	1.44	2.3
15	2.01	1.35	1.46	3.3
16	2.03	1.35	1.45	2.5
17	1.92	1.34	1.47	0.0
18	1.98	1.33	1.46	0.0

Energetically, the aromaticity is normally evaluated with the ASE. To estimate this energy, we use the ISE proposed by Schleyer and Pühlhofer et al. [77]. De Proft and Geerlings have used these energies to evaluate the aromaticity of 5-membered heterocycles [25]. The ISE values depicted in Table 2 are predominantly small compared to well-known aromatic molecules like thiophene or the cyclopentadienyl anion, which have an ISE at the same level of theory of 18.68 and 27.59 kcal/mol, respectively. This confirms the low aromatic or anti-aromatic character of these metallacycles. Most of $16e^-$ metallacyclopentadienes have slightly negative energies (i.e., the non-aromatic isomer is favoured, see Supplementary Materials) and again, an exception appears with the Ru complex **8**, a large negative ISE, which indicates that its aromatic isomer is strongly disfavoured. The d^0 and d^4 $16e^-$ complexes are the ones with the energy values slightly positive or very close to zero. In contrast, the most negative ISE values are for the d^6 complexes, although we should not forget that the planar d^2 complexes are not even a minimum in the potential energy surface. A CSD search shows that the most common $16e^-$ complexes are d^0 and d^8 (see Supplementary Materials). Therefore, we were surprised that the ISEs were clearly negative for both d^8 molecules. A closer look at the CSD search shows that all the reported d^8 structures have strong electron withdrawing groups around the ring or/and secondary ligands that are not π acceptors, which could help in the stability of the aromatic structure. Indeed, the metallacyclopentadiene complexes with the best C–C bond equalization have strong electron withdrawing groups, as COOH or CF₃ [2,78–80]. Moreover, there are some reports on metallabenzenes that indicate that the aromaticity of the ring is enhanced when there are electron withdrawing groups attached to the ring [28,30,31]. On the other hand, the $18e^-$ complexes are slightly positive except for the d^8 compounds. This result shows that, apart from the d^8 complexes, all the others are slightly aromatic.

Table 2. ISE, DI and ring's $j(r)$.

Molecule	ISE (kcal/mol)	DI _{M-C2} (a.u.)	DI _{C2-C3} (a.u.)	DI _{C3-C4} (a.u.)	ΔDI (a.u.)	$j(r)$ (nA/T)
1	0.94	0.643	1.739	1.091	0.647	-0.14
2	-0.24	0.615	1.769	1.082	0.687	0.28
3	-3.70	0.654	1.758	1.060	0.698	-20.58
4	-5.15	0.513	1.753	1.062	0.691	-7.86
5	-1.20	0.894	1.683	1.118	0.564	13.93
6	0.57	1.147	1.539	1.214	0.324	-13.58
7	-7.82	0.793	1.801	1.047	0.753	0.70
8	-26.60	1.690	1.075	1.670	-0.594	-55.99
9	-5.71	0.774	1.784	1.066	0.718	-2.91
10	-5.94	0.865	1.764	1.076	0.688	-5.43
11	4.94	0.739	1.690	1.106	0.585	7.43
12	3.40	0.775	1.702	1.104	0.598	3.86
13	2.04	0.610	1.684	1.120	0.564	3.94
14	4.77	0.732	1.631	1.153	0.478	5.41
15	0.91	0.768	1.700	1.106	0.594	7.02
16	3.38	0.945	1.665	1.117	0.548	5.12
17	-5.71	0.884	1.783	1.069	0.715	-2.50
18	-4.99	0.993	1.748	1.082	0.666	-4.89

The DIs measure the number of electron pairs that are shared between two atoms, and they have been used as a bond order index [81–84]. Then, the DIs of a single and double C–C bond are slightly below 1.0 and 2.0 a.u., respectively, and an aromatic bond has a value between these two [83,84]. Poater et al. have studied the aromaticity of five-member heterocycles by subtracting the DI of the formal C–C double bond from the DI of the single bond (Δ DI) [85], because in a totally aromatic pentacyclic ring, these two should be equal (we define the Δ DI as $DI_{C2-C3} - DI_{C3-C4}$). They found that for classical aromatic heterocycles such as pyrrol or thiophene, Δ DI < 0.4 a.u., and for non-aromatic rings such as cyclopentadiene, Δ DI > 0.6 a.u. The Δ DI values (Table 2) show that all the studied $18e^-$ complexes, except the d^8 molecules again, can be classified as only slightly aromatic. Most of the $16e^-$ metallacyclopentadienes are non-aromatic according to this criteria. However, there are two exceptions, again, complexes **6** and **8**. In the latter, the C–C DI are inverted, DI_{C2-C3} indicates a single bond character while DI_{C3-C4} a double bond nature. Moreover, the DI_{M-C2} also suggests that the Ru–C is a double bond. These results coincide with the geometrical parameters discussed above. We can confirm that **8** is a metallacyclopentatriene. On the other hand, the Δ DI of **6** is significantly smaller than the values of all the other complexes. Indeed, its value is similar to the Δ DI of thiophene, calculated at the same level of theory (0.304 a.u.). This results contradicts the ISE, which suggests that **6** is non-aromatic. Therefore, the significant electron delocalization found in this complex does not imply an important stabilization.

Instead of calculating the NICS that have contributions of all the present currents, it is possible to calculate directly $j(r)$ and integrate it to calculate the current flux of the ring of interest. If gauge independent atomic orbitals are used, this method is known as gauge-including magnetically induced currents (GIMIC) [86]. The current density has been used to study multiple aromatic compounds [87,88] including metallacyclobenzenes [16,18]. We used $j(r)$ and its triple product ($tpj(r) = \mathbf{B} \cdot \nabla \times j(r)$) [56,57], which reveals the local direction of the rotation of $j(r)$ (negative/diatropic, positive/paratropic), to evaluate the aromaticity of the metallacyclopentadienes. As in case of the other aromaticity indices, the ring current values are predominately smaller (Table 2) than in case of well-known aromatic rings, as benzene, which support a induced current density of around 12.0 nA/T [86,89–91]. The $18e^-$ complexes have low diatropic currents (positive), except for the d^8 rings, which have negative values (paratropic currents). As mentioned in the introduction, strong diatropic currents

are related to aromatic rings while strong paratropic currents to anti-aromatic compounds. Then, the small positive $j(r)$ values of $18e^-$ metallacyclopentadienes also indicates a low aromaticity, excepting d^8 complexes that are slightly anti-aromatic (small negative $j(r)$ values). The $16e^-$ molecules do not show a clear trend. The d^0 rings show a very low current, which confirms their non-aromatic character. The d^8 complexes have a low paratropic current, which coincides with the low anti-aromatic character predicted by the ISE and the Δ DI values. The d^2 molecules have strong paratropic currents, which is compatible with their lack of stability. The d^6 compound **8** have an extremely strong paratropic current, which agrees with the strong anti-aromatic nature indicated by its very negative ISE. Finally, the two $16e^-$ d^4 metallacyclopentadienes present a very odd behaviour. Both have currents comparable with the benzene but one has a diatropic current (**5**) and the other a paratropic current (**6**), even though both have very similar structures. Even more intriguing is that several crystal structures of Ru complexes similar to **6** have been reported in the literature [65,72–76], which suggests that this type of molecule is seemingly stable. Moreover, the $j(r)$ value of **6** does not coincide with the non-aromatic nature predicted by its near-zero ISEs or the aromatic character predicted by its low Δ DI value. This lack of coincidence between aromatization energy a ring currents has been previously reported in the literature. The currents for 9b-boraphenylene and 9b-azaphenylene are strongly paratropic but their ASE values are positive [92]. To explain the mismatch, the authors analyse the currents with the ipsocentric method to show that the strong paratropic currents were a consequence of symmetry of magnetic virtual excitation and not due to a lack of stability. The ipsocentric method has shown that the symmetry of the virtual excitations determine the strength and direction of the current density and not the electron delocalization [60,93,94].

To further investigate the opposed behaviour of $j(r)$ in very similar complexes, we studied the contributions of the frontier molecular orbitals to the total current density. As mentioned above the direction of the rotation (tropicity) of the currents depends on the symmetry of the magnetic virtual excitation, as has been described by the Steiner–Fowler selection rules [61]. The diamagnetic contribution to $j(r)$ is determined by the accessibility of transitionally allowed transitions, while the paramagnetic contribution by the accessibility of rotationally allowed transitions. Figure 1 shows the current and $tpj(r)$ of **5** and **6** at 1.0 Å from the molecular plane. In this region, the current is mainly diatropic for **5** (Figure 1a) and mainly paratropic for **6** (Figure 1b), as the currents strength suggest (Table 2). Figure 1 also shows the contributions of some frontier MOs to the current. The HOMO contribution for both complexes is very small (Figure 1c,d), even though the transition HOMO (a'') \rightarrow LUMO (a'') is transitionally allowed (**5** and **6** have a C_s symmetry). However, the HOMO and LUMO are spatially different (Figure 2), the HOMO is mainly located in C_4H_4 ligand, while the LUMO is at the metal centre. These spatial differences reduce the probability of the transition [61]. The $j(r)$ maps show that the transitions from the HOMO-1 are significantly different between the Fe and Ru complexes (Figure 1e,f, respectively). The HOMO-1 current for **5** is very weak around the ring, while for **6** it has a strong paratropic nature. In case of the Ru complex, the energy of the HOMO-1 is very close to the HOMO, and it has a spatial distribution similar to the LUMO (Figure 2). Both are mainly at the metal and have a π nature at the C_4H_4 moiety. Then, HOMO-1 (a') \rightarrow LUMO (a''), which is rotationally and transitionally allowed, should be very relevant. Contrary, the HOMO-1 of the Fe complex is significantly lower in energy and the C_4H_4 ligand has a σ character. These two factors reduce the relevance of the HOMO-1 (a') \rightarrow LUMO (a'') transition in complex **5**. Above the molecular plane, it is the HOMO-2 which contributes the most to the current for **5** (Figure 1g). This MO has a π nature as the LUMO, which is favourable for a HOMO-2 \rightarrow LUMO transition. Then, the opposite $j(r)$ tropicity between the Fe and the Ru complexes are mainly the result of the much higher energy of the HOMO-1 in **6** and due to the differences in the spatial distribution of the two HOMO-1s.

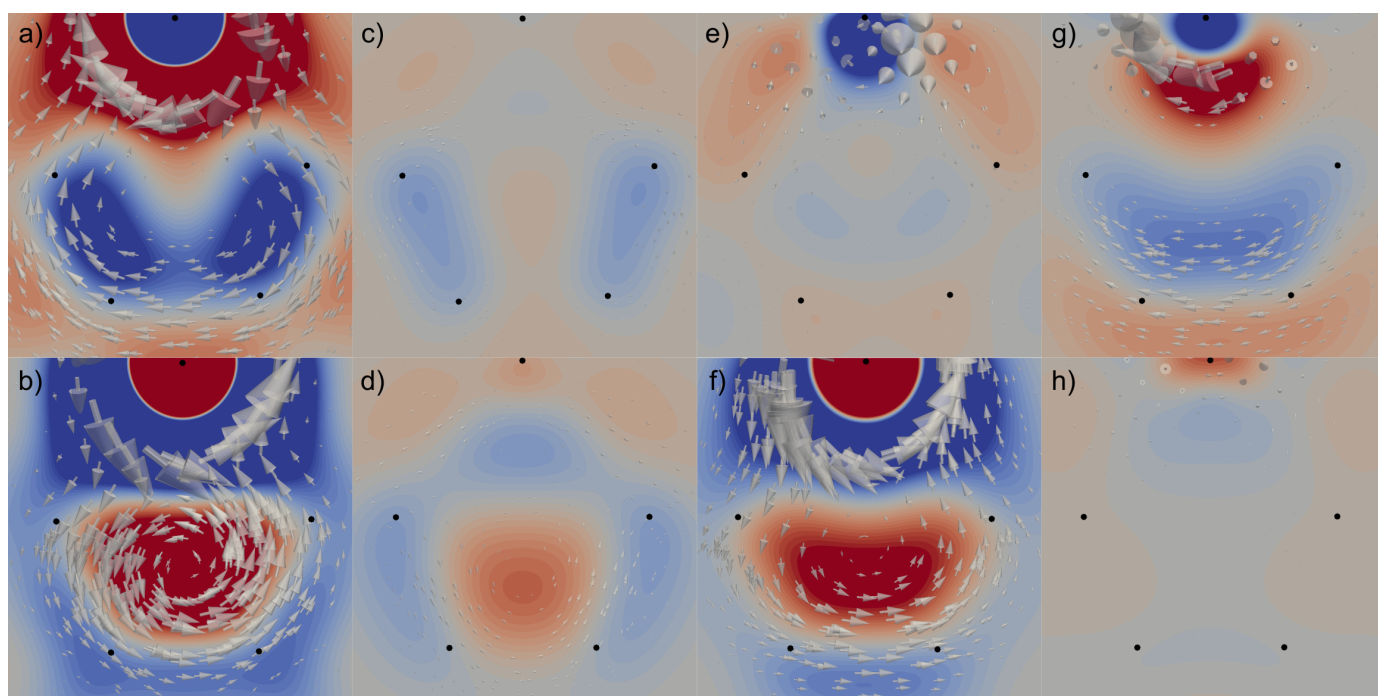


Figure 1. $j(r)$ and $tpj(r)$ maps of complexes 5 (a) and 6 (b). The contributions to $j(r)$ of HOMO (c,d), HOMO-1 (e,f) and HOMO-2 (g,h) are also shown. Colour code: $\leq -3.0 \times 10^{-4}$ a.u. (dark blue), 0.0 a.u. (white) and $\geq 3.0 \times 10^{-4}$ a.u. (red). The plane is parallel to the ring at 1.0 Å from it. The magnetic field, \mathbf{B} , is pointing toward the observer, then clockwise/anticlockwise currents are diatropic/paratropic.

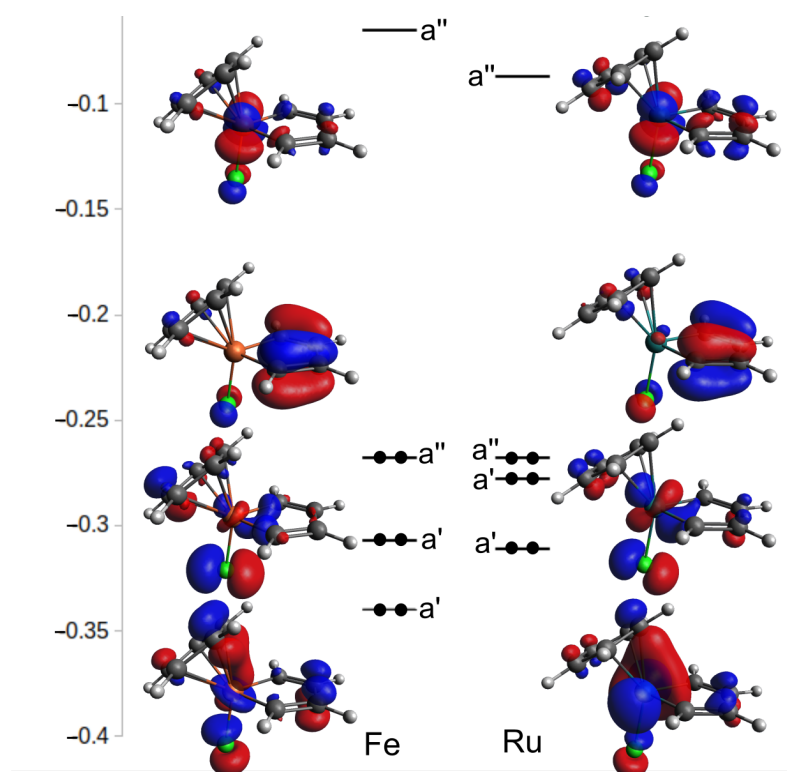


Figure 2. Frontier MO and their energies of complexes 5 and 6. Energy in a.u.

4. Conclusions

We found that the electron delocalization in metallacyclopentadienes is more interesting than was previously thought. All the types of aromaticity indices (energetic, electron density, magnetic) coincide in predicting that all the $18e^-$ metallacyclopentadienes are slightly aromatic, except for the d^8 complexes that are slightly anti-aromatic. However, the picture of the $16e^-$ complexes is more complicated. We found that the d^0 compounds are non-aromatic, as previous studies have reported. From the lack of stability of the rings and their strong paratropic electron currents, we conclude that d^2 complexes are anti-aromatic, these results also explain the lack of $16e^- d^2$ metallacyclopentadienes crystal structures. The d^8 are, according to all the aromaticity indices, slightly anti-aromatic. At first, this result was a surprise because many structures have been reported for this type of complex, although all these structures have electron withdrawing groups. We anticipate that these groups help to stabilize the ring, but more research is needed in that direction. The two d^6 $16e^-$ metallacyclopentadienes that we studied are anti-aromatic. Indeed, complex **8** shows the most anti-aromatic behaviour of all the studied complexes. To gain some stability, it forms localized double bonds with the carbons of the C_4H_4 moiety to become a formally $18e^-$ metallacyclopentatriene. However, as mentioned above, there are some examples of d^6 $16e^-$ metallacyclopentadienes in the literature. The structure of these complexes involve again electron withdrawing groups or non π acceptor ligands. This could help in the stabilization of the complexes. This observation suggests that the low aromaticity or anti-aromaticity character of MCPs could be reversed by the nature of the groups attached to the ring or by the ligands bonded to the metal centre. We leave $16e^- d^4$ complexes at the end, because they present the largest discrepancies between the aromaticity indices. The extreme is the compound **6**: the energetic criterion (ISE) predicts that it is non-aromatic, the density index (ΔDI) indicates that it is aromatic, while the magnetic fields ($j(r)$ and $tpj(r)$) suggests that it is anti-aromatic. Moreover, there are reports of some structures similar to **6**, which suggest that the $16e^- d^4$ complexes are stable. Thus, the magnetic anti-aromaticity (paratropicity) of **6** seems not to be related to its stability. The paratropic currents of this complex are not a consequence of highly localized electrons, but rather due to the symmetry, the energy and the spatial distribution of the frontier MOs, as the ipso-centric description of the current postulates. The $16e^- d^4$ metallacyclopentadienes deserves more attention because their large electron delocalization does not turn into large stabilization and diatropic currents, as in case of most aromatic compounds.

Supplementary Materials: The following are available online at <https://www.mdpi.com/article/10.3390/chemistry3040094/s1>, Figure S1: Isomeration reaction for the calculation of ISE, Figure S2: Maps of contributions to $j(r)$ of HOMO-1 of complex **6** and its rotational and translational part, Table S1: XYZ coordinates of the studied metallacyclopentadienes.

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Abbreviations

The following abbreviations are used in this manuscript:

MCP	Metallacyclopentadiene
MB	Metallabenzene
CSD	Cambridge Structural Database
ASE	Aromatic stabilization energy
NICS	Nuclear independent chemical shifts
ISE	Isomerization stabilization energy
DI	Delocalization index
MO	Molecular orbital
CTOCD-DZ	Continuous transformations of the origin of the current density-diamagnetic zero
GIAO	Gauge-including atomic orbital

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