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Aromaticity in Metallabenzenes and Related Compounds

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This work is dedicated to the memory of Prof. Paul von Ragué Schleyer

Abstract

The concept of aromaticity was initially introduced in chemistry to account for the stability, reactivity, molecular structures, and other properties of many unsaturated organic compounds. Despite that, it has been extended to other species with mobile electrons including saturated systems, transition structures, and even inorganic molecules. In this review, we focus on the aromaticity of a particular family of organometallic compounds known as metallabenzenes, which are characterized by the formal replacement of a CH group in benzene by an isolobal transition metal fragment. In addition, aromaticity in related compounds such as heterometallabenzenes is considered as well. To this end, we shall describe herein the insight gained by the available experimental data as well as by the application of the state-of-the-art computational methods developed as descriptors for aromaticity together with a critical evaluation of their performance to quantitatively estimate the strength of aromaticity in these systems.

1. Introduction.

The seminal prediction by Thorn and Hoffmann in 1979[1] that metallabenzenes might be synthesized as stable molecules was the starting point of a new family of organometallic compounds characterized by the formal replacement of a CH unit in benzene by an isolobal transition-metal fragment. Only three years later, Roper and co-workers isolated and fully characterized the first osmabenzene complex.[2] Since then, the chemistry of these compounds has experienced a tremendous development [3] and as a result, a great number of metallabenzenes including related compounds such as heteroatom-containing analogues (metallapyridines,[4] metallapyryliums,[5] metallathiobenzenes[6]), fused-ring metallabenzenes (as metallabenzofurans,[7] metallabenzothiophenes,[8] and metallanaphtalenes[9]), metallabenzynes[10] or even dimetallabenzenes,[11] which incorporate two transition-metals into the six-membered ring (6MR), have been successfully prepared.

Aromaticity has been described as a "*typical example of an unicorn of chemical bonding models*" because everybody seems to know what it means although it is just a virtual quantity rather than experimentally observable.[12] The aromaticity of metallabenzenes is not an exception. From the very beginning, the aromatic character of these organometallic species has attracted considerable attention by both experimental and theoretical chemists. In the pioneering work by Thorn and Hoffmann, electronic delocalization within the 6MR was considered as a crucial mechanism to stabilize metallabenzenes.[1] Despite that, the aromatic nature of these compounds, which involves the participation of the d-atomic orbitals of the transition metal, remains a controversial issue. This is mainly due to two reasons: (i) the difficulties associated with measuring or quantifying the degree of aromaticity in metallabenzenes or, in general, metalloaromaticity,[13] and (ii) the fuzzy nature of the concept of aromaticity, which itself is not universal or free of ambiguities.

In this paper, we shall shed more light onto the different manifestations of aromaticity in metallabenzenes and related compounds by reviewing the different approaches, mainly derived from the interpretative tools provided by computational chemistry, to this fundamental topic.

2. Experimental Insights into the Aromaticity of Metallabenzenes

Before going into details on the computational descriptors to analyse and quantify the aromaticity of metallabenzenes and related metallacycles, we first describe in this section the insight gained by the available experimental data.

The structural criterion, i.e. the tendency of aromatic molecules to exhibit planar rings with bond length equalization, is arguably the most direct method to evaluate the aromatic character of a compound.[14] Benzene presents a delocalized D_{6h} planar structure, whose C–C bond distances are intermediate between double and single bonds. By contrast, cyclobutadiene, the archetypal antiaromatic compound,[15] exhibits a localized D_{2h} structure with bond length alternation. Metallabenzenes have invariably C–C and M–C bond lengths intermediate between double and single bonds based on the available experimental (X-ray diffraction) data.[2,3] Furthermore, the average of the four C–C distances is very close to the C–C distances of ca. 1.4 Å in benzene.[16] In this sense, metallabenzenes satisfy the so-called structural criterion for aromaticity. Regarding planarity, the five carbon atoms of the metallabenzene ring are essentially coplanar, but the transition metal can either be placed within this plane or be significantly displaced.

Aromatic compounds are also characterized by exhibiting peculiar ^{1}H- and ^{13}C-NMR chemical shifts (typically ranging between 6.0-8.0 ppm and 100-140 ppm, respectively). The anomalous behaviour of arene ^{1}H-NMR (and ^{13}C-NMR) chemical shifts are due to the ability of aromatic compounds to sustain an induced diatropic ring current as suggested by Pople's ring current model.[17] With the exception of the CH groups directly attached to the transition metal, which exhibit distinctive very low field chemical shifts, the rest of the CH groups in the metallabenzene ring usually present chemical shifts in the "aromatic" range (5.5-8.0 ppm and 120-150 ppm in the ^{1}H and ^{13}C-NMR spectra, respectively). For instance, the $Ir[C_5H_4(SMe\text{-}1)]Cl(PPh_3)_2$ complex shows in the ^{1}H-NMR spectrum a low-field resonance at 12.31 ppm attributable to the Ir-CH, whereas the other ring protons appear in the typical aromatic region (6.25, 6.38 and 6.99 ppm).[18]

Reactivity can be also considered as an indicator of aromaticity. Typically, aromatic compounds like benzene undergo electrophilic aromatic substitution reactions, SEAr, rather than addition reactions. Indeed, some metallabenzenes undergo bromination or nitration reactions where the substitution is directed in the same way as for benzenes by the ring substituents.[3,7a,c,19] However, in some cases metallabenzenes may also engage in reactions which are unusual for classical aromatic systems. For instance, the treatment of iridabenzene $Ir[C_5H_3(Me\text{-}2,4)](PEt_3)_3$ with halogens results only in the oxidative addition of the halogen to the transition metal.[20] Furthermore, this particular metallabenzene easily undergoes cycloaddition reactions with acetone, CO_2, CS_2, O_2, SO_2, $PhNO_2$, and maleic anhydride,[21,22] a behaviour which is not restricted to low oxidation state iridabenzenes. For instance, platinabenzene $Pt[C_5H_3(Ph\text{-}1,2)](Cp^*)$ also affords a 1,4-cycloaddition product when reacts with maleic anhydride.[23] In addition, metallabenzenes can also undergo nucleophilic aromatic substitution (SNAr)[24] of hydrogen via the corresponding Meisenheimer intermediates.[25] Interestingly, metallabenzenes exhibit a strong tendency to rearrange to cyclopentadienyl complexes.[26] This rearrangement reaction, where the two metal-bound carbon atoms in the metallabenzene couple to form a cyclopentadienyl ligand, has been identified as the main decomposition route for metallabenzenes. According to computational studies, this transformation finds its origin in the higher thermodynamic stability of the cyclopentadienyl complex over the metallabenzene.[27] Therefore, although metallabenzenes are able to undergo reactions typical for aromatic compounds, they also present a rich and markedly different reactivity.

Taking into account all these experimentally derived descriptors for aromaticity, it can be concluded that metallabenzenes are not as aromatic as their all-carbon analogues.

3. Computational Descriptors for Aromaticity in Metallabenzenes

3.1. Molecular Orbitals

The electronic structure of metallabenzenes agrees with an aromatic nature. The molecular orbitals (MO's) of metallabenzenes resemble, in general, those of benzene. This becomes evident when comparing the MO's for benzene with those for the model platinabenzene $Pt[C_5H_5](Cp)$ depicted in Figure 1. Thus, the well-known "doughnut shaped" HOMO-2 of benzene is clearly the same that the HOMO-9 of platinabenzene. Similarly, the HOMO-1 and HOMO of the complex match the doubly degenerate HOMO of benzene. Although rather similar MO's have been calculated for different metallabenzenes, their relative energies and the participating metal d-atomic orbital may vary.[27a] In fact, it was generally found that in those complexes involving the participation of the d_{z^2} orbital, a slight deviation from planarity occurs to allow for a better molecular overlap.

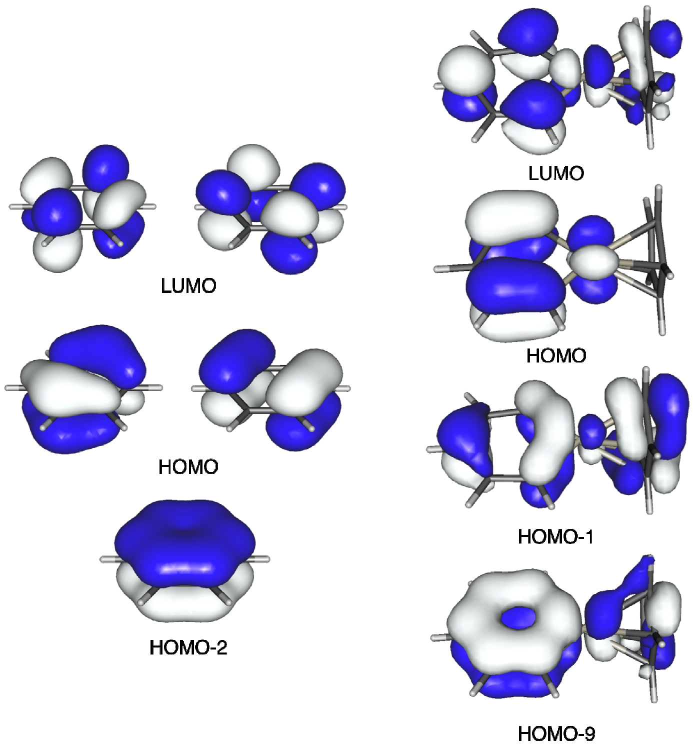


Figure 1. Representative molecular orbitals computed for benzene (left) and model platinabenzene Pt[C_5H_5](Cp) (right). Figure adapted from reference 27a.

Despite this resemblance in the calculated MO's, the total number of π-electrons, which are associated with the aromatic character of metallabenzenes, remains under debate. In their original report, Thorn and Hoffmann partitioned the metallabenzene into contributions coming from the $[M]^+$ moiety and the four π-electron fragment $[C_5H_5]^-$ (Figure 2).[1] Within this fragmentation scheme, the most important π-bonding contribution comes from the $d_{xz}(M)\rightarrow 3\pi^*(C_5H_5^-)$ π-backdonation, due to the strong π-acceptor character of the vacant 3π* MO. Thus, metallabenzenes are suggested to possess 6π-electrons, therefore satisfying the [4*n*+2]-rule[28] for Hückel aromatic compounds. Alternatively, Schleyer has suggested that the doubly-occupied d_{yz} metal orbital (Figure 2) significantly contributes to the π-orbital interactions in metallabenzenes as well.[29] Thus, the interaction with the occupied 2π orbital of $C_5H_5^-$ yields a pair of bonding and antibonding π-orbitals, whereby the latter becomes stabilized by mixing with the vacant 4π* MO of $C_5H_5^-$. This alternative interpretation, which has been more recently supported by Jia and co-workers considering a different fragmentation scheme,[30] suggests that metallabenzenes are actually 8π-electron systems, therefore formally violating the [4*n*+2]-rule. However, the additional orbital which involves the d_{yz} metal AO and the π orbitals of the $C_5H_5^-$ anion has *δ* instead of π symmetry. As a result, metallabenzenes could be considered as Möbius aromatic[31] species.

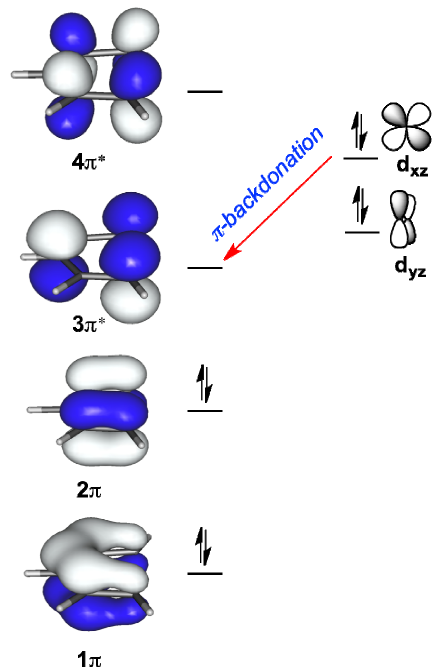


Figure 2. Schematic representation of the π-orbital interactions in metallabenzenes, adapted from reference 3a.

Fernández and Frenking studied in detail the π-bonding in the C_{2v} symmetric model rhodabenzene $Rh[C_5H_5](Cl)_2(PH_3)_2$.[32] In their analysis, it was found that this particular metallabenzene possesses seven occupied π-molecular orbitals, where five of them (in the energetic order $4b_1 < 2a_2 < 6b_1 < 3a_2 < 4a_2$, see Figure 3) have coefficients in the 6MR. Hence, it was suggested that this rhodabenzene is actually a 10 π-electron species, i.e. a Hückel-aromatic compound. Closer examination of the π-molecular orbitals indicates that the $4b_1$ MO is the result of the interaction of 1π fragment orbital of $C_5H_5^-$ (Figure 2) with the appropriate vacant orbital of the transition metal fragment. The $6b_1$ orbital clearly shows the

$d_{xz}(M) \rightarrow 3\pi^*(C_5H_5^-)$ π-backdonation suggested by Thorn and Hoffmann.[1] Interestingly, the $2a_2$ MO is the result of the bonding contribution between the d_{yz} metal orbital and the 2π-orbital of the $C_5H_5^-$ fragment. Finally, the two antibonding orbitals $3a_2$ and $4a_2$ arise from the bonding and antibonding combinations between the metal d_{yz} atomic orbital and the chlorine p(π) orbitals. The antibonding nature of these MO's is somewhat diminished by mixing with the vacant 4π* of $C_5H_5^-$. This view of metallabenzenes as 10π-electron systems is found also in different heterometallabenzenes and related metallacycles, as it will be shown later on (see section 4).

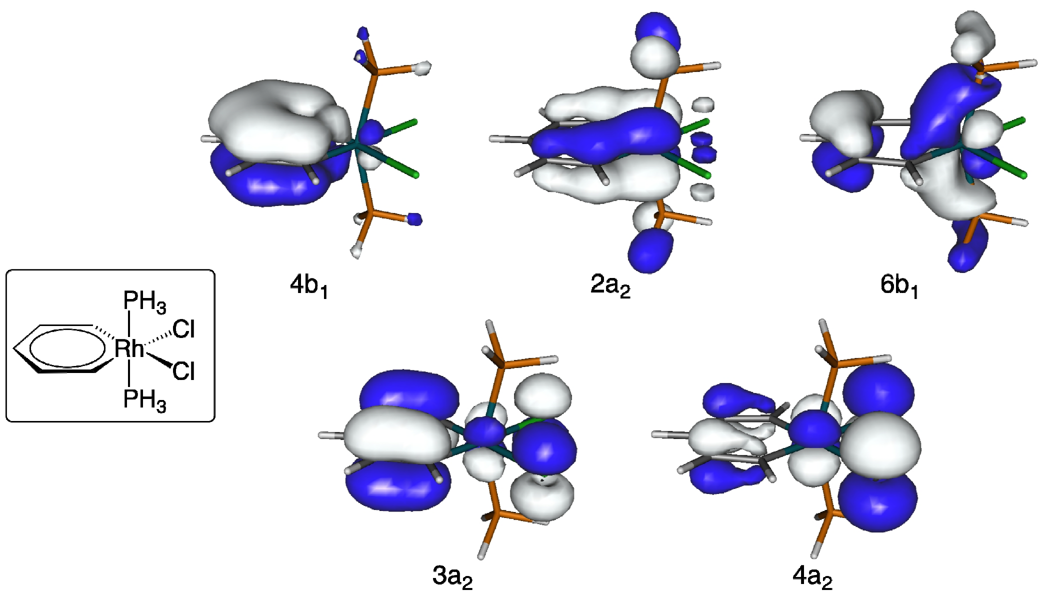


Figure 3. π-Molecular orbitals computed for model rhodabenzene $Rh[C_5H_5](Cl)_2(PH_3)_2$ (figure adapted from reference 32).

Absolute Hardness: an Aromaticity Descriptor based on Molecular Orbitals

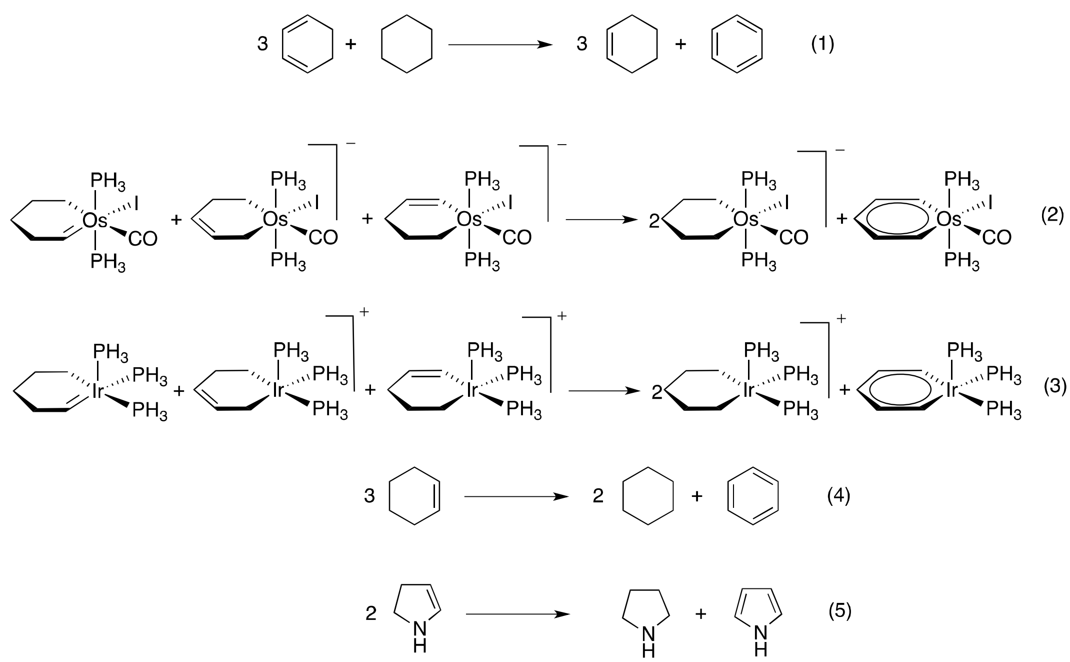
Absolute hardness (η) is a well-established indicator to estimate the stabilization and reactivity of a molecule.[33] Following Koopman's theorem, it has been defined as half the HOMO–LUMO gap for Hartree–Fock (HF), i.e. $\eta = (\varepsilon_{LUMO} - \varepsilon_{HOMO})/2$.[34] This parameter has been developed as a quantitative aromaticity measure as well. According to Zhou and Parr, the frontier between aromatic and antiaromatic species in typical organic compounds is defined as $0.2\eta_B$, where η_B is the absolute hardness of benzene.[35] In general, a higher aromatic strength is expected for compounds having a larger absolute hardness.

Using the extended Hückel method, Chamizo and co-workers concluded that the iridabenzene $Ir[C_5H_3(Me\text{-}2,4)](PEt_3)_3$ should not be considered as an aromatic molecule in view of its rather low calculated absolute hardness (0.60 eV) as compared to benzene (2.27 eV) or thiophene (2.17 eV).[36] These earlier calculations were revisited by Yang and co-workers, who optimized the model osma- and iridabenzenes $Os[C_5H_5](PH_3)_2(CO)(I)$ and $Ir[C_5H_5](PH_3)_3$ at the DFT level.[37] The authors computed an absolute hardness of 4.43 and 4.22 eV, respectively, which corresponds ca. 65% of the value calculated for benzene at the same level of theory (6.47 eV), therefore confirming the aromatic nature of these species. It should however be noted that, although the Zhou and Parr hardness values perform relatively well for polycyclic benzenoid hydrocarbons, serious deficiencies have been found when heterocyclic compounds are considered.[38] Therefore, the absolute hardness as a quantitative measure of aromaticity must be used with caution. Nevertheless, this MO-based descriptor also suggests that the degree of stabilization or aromaticity in metallabenzenes is significantly lower than in benzene.

3.2. Energetic Descriptors

Properties such as NMR chemical shifts and bond length equalization are secondary manifestations of aromaticity, which in many cases can be misleading. For instance, it is well established that the equalized bond lengths in D_{6h}-benzene arise from σ- rather than π-electron delocalization.[39] The fundamental property of aromatic compounds is their enhanced thermochemical stability with regard to the acyclic conjugated references. Therefore, the energetic criterion is considered to be the principal descriptor for aromaticity as it governs the reactivity and much of the chemical behaviour of a molecule.

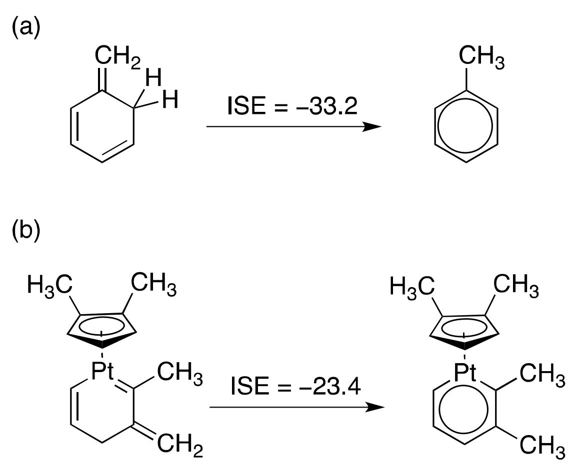
One of the simplest ways to evaluate the stabilization due to aromaticity is the Aromatic Stabilization Energy (ASE). The ASE is based on the reaction energies of isodesmic equations, where the number and type of bonds is exactly the same in both sides of the equation. As a reference, an ASE value of 28.8 kcal/mol has been computed for benzene (Scheme 1, eq. 1).[40] However, in many cases these equations are contaminated by different flaws such as strain, hyperconjugation, "proto"-branching, or *syn-anti* effects which make the calculated ASE values not always reliable. [41] Yang and co-workers proposed the homodesmotic equations 2 and 3 to estimate the ASE values of two model osma- and iridabenzenes.[37] In view of the calculated data (–18.0 and –14.7 kcal/mol, respectively), a significant aromatic stabilization exists in both metallabenzenes, although they are clearly less aromatic than benzene (–32.2 kcal/mol, eq. 4) or heteroaromatic pyrrole (–21.5 kcal/mol, eq. 5, Scheme 1).



Scheme 1. Isodesmic equations to estimate ASE values.

In order to avoid the problems associated with these types of equations, Schleyer and Pühlhofer introduced the so-called "isomerization method" (ISE) to evaluate ASE values.[41]

This approach is based on the differences between the total energies computed for only two species: a methyl derivative of the aromatic system and its nonaromatic exocyclic methylene isomer. Using this approach, an ASE value of 33.2 kcal/mol was calculated for benzene (Scheme 2a)[41] which is close to the value obtained using the strain-balanced equation 1 (see above). De Proft and Geerlings applied the ISE method to the metallabenzene $Pt[C_5H_3Me_2](Me_2Cp)$ and computed an ASE value of 23.4 kcal/mol (Scheme 2b), which is ca. two-thirds of the value for benzene (33.8 kcal/mol) at the same level (B3LYP/6-311+G*&LANL2DZ for Pt).[42] Using this method, the authors also calculated the relative hardness ($\Delta\eta$, defined as the difference between the absolute hardness of both isomers) for this particular metallabenzene. The calculated value ($\Delta\eta$ = 0.022 au) confirms that the aromaticity strength of this species is lower than in benzene ($\Delta\eta$ = 0.081 au).



Scheme 2. Isomerization (ISE) method applied to benzene (a) and platinabenzene $Pt[C_5H_3Me_2](Me_2Cp)$ (b). The ISE values are in kcal/mol.

More recently, Lin et al. reported the synthesis and characterization of a series of rhenabenzenes.[43] To support the aromatic character of the compounds, the ASE values were also estimated using the ISE method. While the model aromatic rhenium complex has an ISE value of 21.5 kcal/mol, the corresponding value for the partially unsaturated, nonaromatic Re complex is only 2.0 kcal/mol (Figure 4), which confirms the aromatic nature of the former species. For comparison, the authors also computed the ISE values for some related metallabenzenes with Pt, Ir, and Os, which are also depicted in Figure 4. The calculated values suggest that the strength of aromaticity of the model rhenabenzene is lower than that of platinabenzene and iridabenzene, and comparable to osmabenzene.

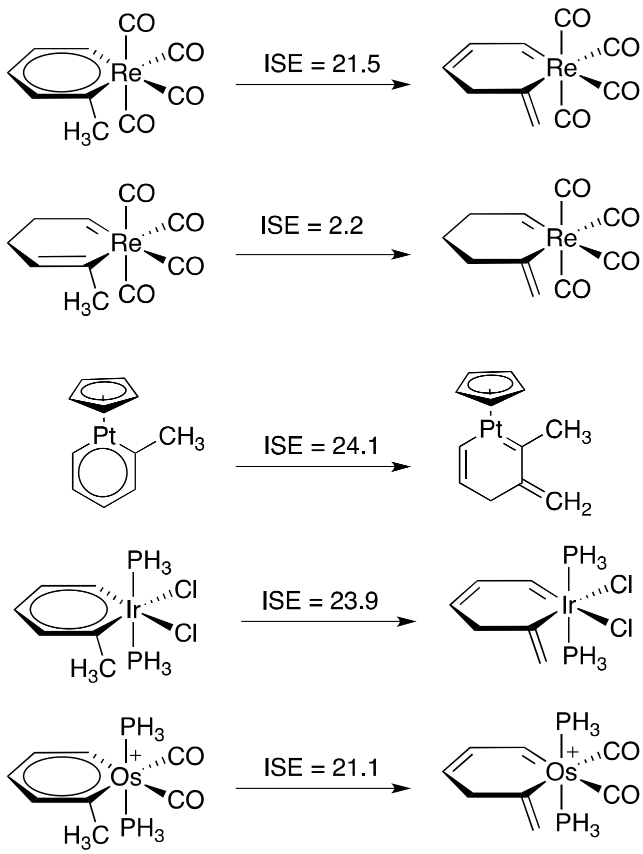


Figure 4. Isomerization (ISE) method applied to different metallacycles. The ISE values are in kcal/mol.

Frenking and Fernández developed a different approach[39c, 44] to estimate ASE values which is based on the Energy Decomposition Analysis (EDA)[45] method. Considering that the stability of a cyclic π-conjugated compound with respect to an acyclic compound is the primary quantity defining aromaticity, the ASE values can be easily calculated by comparing the π-cyclic conjugation strength with the π-conjugation of an appropriate acyclic reference system. However, two problems are traditionally associated with this approach: (i) a robust method to directly estimate the strength of π-conjugation is required, and (ii) the choice of the acyclic reference, which is not trivial. As suggested by Mo and Schleyer,[46] a reference molecule with the same number of diene conjugations is a better choice than a molecule with the same number of π-electrons, because the ASE values (computed with the block-localized wavefunction, BLW,[47] method) exhibit a better correlation with the nuclear-independent chemical shift (NICS)[48] values.

The direct estimation of the π-conjugative strength has challenged chemists for decades. Typically, π-conjugation has been estimated by using either isodesmic reactions or following the suggestion by Kistiakowsky,[49] which is based on comparing heats of hydrogenation. However, both approaches suffer from the problem that the difference between the conjugated molecule and the reference system comprises not only alterations of the π-bonding but also changes in other parts of the systems. In contrast, the EDA method[45] is able to consider only the π-orbitals of the interacting fragments in the geometry of the molecule to exclusively estimate π-interactions without recourse to reference molecules. Indeed, it is showed that the ΔE_π values given by the EDA method can be safely used as a direct estimation of the π-conjugation and hyperconjugation of a molecule, even in complex π-extended systems.[50]

The ASE values can therefore be estimated simply by the difference between the ΔE_π value of the cyclic molecule and the ΔE_π of the acyclic reference, which has the same number of diene conjugations (eq. 6).[39c,44] Within this procedure, aromatic molecules exhibit ASE > 0, whereas antiaromatic species possess ASE < 0. This methodology has been successfully applied to different organic aromatic/antiaromatic and heteroaromatic molecules,[39c,51] and recently to study the substituent effects on hyperconjugative aromaticity.[52]

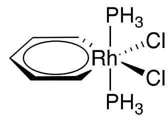
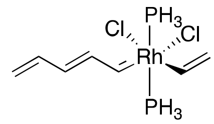
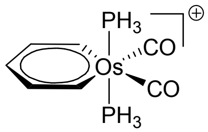
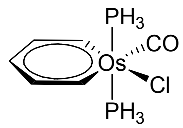
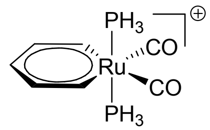
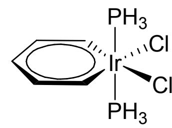
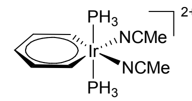
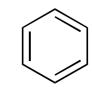
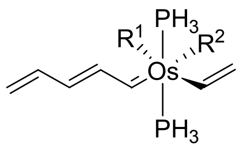
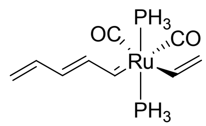
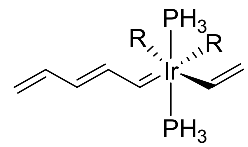
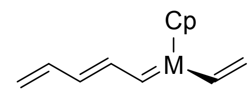
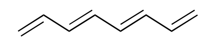
ASE = ΔE_{π}  − ΔE_{π}  (6)

Table 1 gathers a representative selection of the different metallabenzene models considered by Fernández and Frenking.[32] In all cases, the complexes present positive ASE values ranging from 8.7 kcal/mol for cationic iribenzene $Ir[C_5H_5](PH_3)_2(MeCN)_2^+$ to 37.6 kcal/mol for platinabenzene $Pt[C_5H_5](Cp)$ and, therefore, they should be considered as aromatic compounds. Considering the ASE value calculated for benzene at the same level (ASE = 42.5 kcal/mol, BP86/TZVP), it becomes clear that the extra-stabilization due aromatic conjugation in metallabenzenes is weaker than in benzene. Finally, no clear correlation between the computed ASE values and the nature of the transition metal fragment (charge, metal, ligands, or oxidation state of the metal) was found.

3.3. Magnetic Descriptors: Ring Currents, Magnetic Susceptibility Exaltations, Nucleus Independent Chemical Shifts

The ability to sustain an induced diatropic ring current, either in two or three dimensions, is a common feature shared by aromatic compounds. This magnetic response can be evaluated via the induced magnetic field[53] or by probing the ring current directly.[54] The challenge of quantifying a magnetic descriptor is the difficulty in identifying the magnetic response associated exclusively with aromaticity, since lone pairs, atom cores, or irrelevant σ-electrons (i.e., those not related to the principal induced "π" or aromatic ring current), also respond to external applied magnetic fields. The magnetic responses of aromatic molecules can be probed both *globally* (e.g., exalted diamagnetic susceptibilities[55] and anisotropies for the entire molecule) and more *locally* by means of Nucleus Independent Chemical Shifts (NICS)[48] and induced magnetic field, $\boldsymbol{B}^{ind}$,[53] values, Aromatic Ring Current Shieldings (ARCS),[56] Gauge Including Magnetically Induced Current (GIMIC) method,[57] Anisotropy of the Induced Current Density (ACID),[58] ring currents,[54] etc. Only few of them have been applied to understand the electron delocalization in metallabenzenes.

Table 1. Results of EDA calculations for representative model metallabenzenes.[a]

								
ΔE_{π}	–97.5	–78.1	–97.5	–97.2	–103.3	–100.1	–97.3	–107.7
Reference Compound								
	$R^1 = R^2$ = CO	R^1 = CO, R^2 = Cl		R = Cl	R = NCMe	M = Pt	M = Pd	
ΔE_{π}	–79.9	–59.4	–76.9	–63.7	–94.6	–62.5	–64.5	–65.2
ASE	**17.6**	**18.7**	**17.7**	**33.5**	**8.7**	**37.6**	**32.8**	**42.5**

[a] Energy values are given in kcal/mol. All data have calculated at the BP86/TZVP level (data taken from reference 32).

Table 2. Computed NICS(0) and NICS(1) (in ppm) and magnetic susceptibility anisotropy ($\Delta\chi$□□in cgs ppm) values for the systems studied by Martin et al. (see reference 27a).

Compound		NICS(0)	NICS(1)	$\Delta\chi$
$(C_5H_5Ir)(PH_3)_3$		-3.7	-8.8	93.9
trans,*cis*-$(C_5H_5Os)(PH_3)_2(CO)Cl$		2.5	-3.5	-10.0
$(C_5H_5Pt)Cp$				43.2
	Metallabenzene ring	-2.6	-6.4	
	Cp ring	-16.1	-7.9	
$[(C_5H_5Pt)(PH_3)_2]^+$		9.1	3.9	72.0
$[(C_5H_5Pt)(PH_3)_3]^+$		-1.2	-5.5	60.0
$(C_5H_5Pt)(PH_3)_2(CH_3)$				45.4
	syn to CO	-6.5	-7.9	
	anti to CO		-10.0	
$(C_5H_5Ir)(PH_3)_2Cl_2$		2.8	-3.2	-22.7
trans,*cis*-$(C_5H_5Ru)(PH_3)_2(CO)Cl$		3.2	-3.2	-43.4
$(C_5H_5Ru)Cp(CO)$	*syn* to CO	1.0	-6.0	-46.6
	anti to CO		-1.0	
	Cp ring	-19.8	-10.5	

The magnetic susceptibility anisotropy ($\Delta\chi$), defined as $\Delta\chi = \chi$□□$-(1/2)(\chi_{xx}+\chi_{yy})$, is the degree of magnetization that arises from a compound in response to an applied magnetic field. In general, aromatic compounds display enhanced diamagnetic susceptibilities, because their induced magnetic fields oppose the externally applied magnetic field. Martin and co-workers[27a] computed the $\Delta\chi$ values for a series of metallabenzenes and compared them with a number of criteria that are commonly used to diagnose aromaticity, including NICS. As commented above, the selected metallabenzenes have planar geometries with bond length equalization and have MOs that are akin to those of benzene. So, in principle they should be classified as aromatic and large negative $\Delta\chi$ values are expected for them. However, the computed $\Delta\chi$ values, summarized in Table 2, do not support the presence of the putative aromaticity in these metallabenzene complexes. In contrast, the negative NICS values obtained for most systems indicate that these complexes are indeed aromatic (Table 2). The authors noted that the applicability of NICS and $\Delta\chi$ computations with metallabenzenes has severe limitations because both shielding and magnetic susceptibility tensors are disturbed by the close proximity to ligands on the metal centre. Martin and co-workers concluded that "…*based on the above-mentioned methods, it is difficult to state with any certainty whether the metallabenzene complexes are truly aromatic or not*".

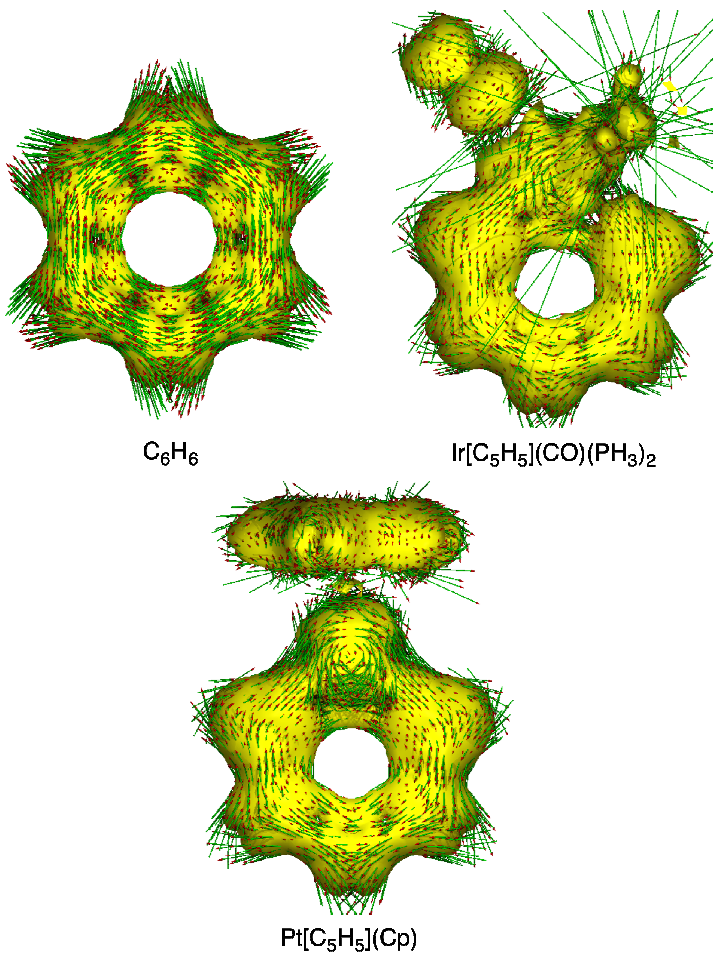


Figure 5. ACID plots (isosurface of 0.03 au) computed for benzene, $Ir[C_5H_5](CO)(PH_3)_2$ and $Pt[C_5H_5](Cp)$. Adapted from reference 58b.

Herges and co-workers applied the ACID method to visualize the delocalization of electrons in the model iridabenzene $Ir[C_5H_5](CO)(PH_3)_2$.[58b] The aromatic character of this complex is confirmed by the presence of a clear diatropic (clockwise vectors) circulation within the six-membered metallacycle (Figure 5). The aromatic nature of this species becomes evident when comparing the corresponding ACID diagram with that calculated for benzene, where an even much clearer diatropic current is observed. The ACID method was also applied to platinabenzene $Pt[C_5H_5](Cp)$ for comparison. As seen in Figure 5, the latter species also exhibits a diatropic ring current, which is delocalized within the metallabenzene moiety, therefore confirming its aromatic nature.

In 2008, Periyasamy et al. studied the aromaticity of a series of metallabenzenes containing Ir, Rh, Os, Ru, Pt, and Pd via the ring current circulations.[59] They divided this series into three groups, namely 18-electron Ir and Rh systems, 16-electron Ru and Os complexes and finally, some platinum and palladium complexes. Despite this electron counting seems questionable,[60] it was found that the induced current corresponding to the out-of-plane MOs in the metallabenzene 6MR of the first set is diatropic (aromatic) in each case. In contrast, the ring current is paratropic (antiaromatic) for each of the 16-electron complexes, despite having the same occupancy of π-MOs as the 18-electron Ir and Rh systems. The platinum and palladium metallabenzenes are highly aromatic compounds but only when they are coordinated to the cyclopentadienyl ligand. More recently, Havenith et al.[61] calculated the ring currents including relativistic effects for four systems studied by Periyasamy et al.[59] Only small differences were found in the ring current obtained at the different levels of relativistic theories, the overall maps being very similar.

Mauksch and Tsogoeva[62] reported *in silico* a series of metallacycloheptatrienes and metallacyclooctatetraenes with different oxidation states and types of the metal. The former systems contain eight π-electrons, three conjugated C=C double bonds, and a metal lone pair capable of interacting with the hydrocarbon fragment in a δ-type fashion. In contrast, metallacyclooctatetraenes have four conjugated double bonds (one M=C bond and three C=C bonds), but they still have eight π-electrons. Despite the different number of conjugated double bonds, both series of complexes fulfil the requirement of Möbius aromaticity.[31] Aromaticity was supported by ASE, NICS, and Harmonic Oscillator Model of Aromaticity (HOMA, which is based on the geometry of the molecule)[63] calculations. Particularly, the dissected $NICS(1)_{zz}$ values, which account for the contributions arising from the zz vector component of the shielding tensor and were reported to perform better than isotropic NICS(0) values,[64] range from –1.2 to –65.3 ppm, therefore confirming the aromatic nature of these species.

Among the different magnetic descriptors, NICS is arguably the most popular magnetic tool to diagnose aromaticity in metallabenzenes. This is because its evaluation does not rely on reference compounds and is easy to compute. Despite that, and as commented above, the application of this method to estimate the metallabenzene's aromaticity has severe limitations due to the anisotropy of the metal centre and to the effect of the corresponding ligands. For instance, Han et al.[65] reported the synthesis of the first example of *m*-osmaphenols and they carried out NICS(1) computations in order to establish the aromatic character in such metallaphenols. Although the computed NICS(1) values are negative (around -3.0 ppm), the absolute values are not very large, which does not give a definite support for aromaticity. Zhang et al.[66] studied the interconversion of ruthenabenzene $[(C_9H_6NO)Ru\{CC\text{-}(PPh_3)CHC(PPh_3)CH\}(C_9H_6NO)(PPh_3)]Cl_2$ into ruthenacyclohexa-1,4-diene $[(C_9H_6NO)Ru\{CC\text{-}(PPh_3)CH_2C(PPh_3)CH\}(C_9H_6NO)(PPh_3)]Cl$ promoted by $NaBH_4$. Particularly, they found that ruthanacyclohexa-1,4-diene can readily convert to ruthenabenzene under an oxygen atmosphere, which is consistent with the calculated small energy of conversion (< 6 kcal/mol). In this case, the NICS(1) and $NICS(1)_{zz}$ values computed for the ruthenabenzene are –3.2 and –11.3 ppm, respectively. This supports some aromatic character for the species which agrees with the lack of reactivity observed experimentally when the ruthenabenzene is treated with common electrophiles and nucleophiles such as H_2O, MeOH, $[PyH]Br_3$, and $NOBF_4$.

4. Aromaticity in Heterometallabenzenes and Related Metallacycles

Heterometallabenzenes are a particular class of metallabenzenes where a CH group of the metallacycle has been formally replaced by a heteroatom (typically, nitrogen and oxygen atoms). The number of heterometallabenzenes (featuring a 6MR) experimentally prepared and fully characterized is remarkable,[4-10] which correlates with the strong coordination ability of the heteroatom towards the transition metal. However, despite the enormous amount of experimental work dedicated to the chemistry of this family of organometallic compounds, the estimate of their aromatic character has received comparatively little attention. In this section, reports on the aromaticity of genuine 6MR-heterometallabenzenes are discussed together with those involving five-membered ring metallacycles for comparison (the latter species cannot be considered formally as heterometallabenzenes).

Esteruelas and co-workers prepared the 3-ruthenaindolizine complex depicted in Figure 6 directly from the corresponding dihydro-3-ruthenaindolizine by loss of a hydrogen molecule and in the absence of any hydrogen acceptor.[67] The geometry of this species, as revealed by X-ray diffraction, indicates that the metallabicycle is almost planar having Ru–C, Ru–N, and C–C bond lengths intermediate between single and double bonds. Furthermore, the ^{13}C chemical shift for the carbon atom directly attached to the transition metal is similar to those reported for related metallapyrroles.[68] Both experimental features suggest that this complex can be considered as an aromatic species. Indeed, the calculated π-orbitals of the model complex, where the bulky P^iPr_3 ligand was replaced by PMe_3, indicate that the molecule possesses 10 π-electrons and, therefore, it obeys the Hückel rule (see Figure 6). Similar experimental and computational findings were observed in the π-extended binuclear 1,7-diosma-2,4,6-triaza-s-indacene and 1,7-diosma-pyrrolo[3,4,f]isoindole derivatives prepared in the Esteruelas' laboratory.[69]

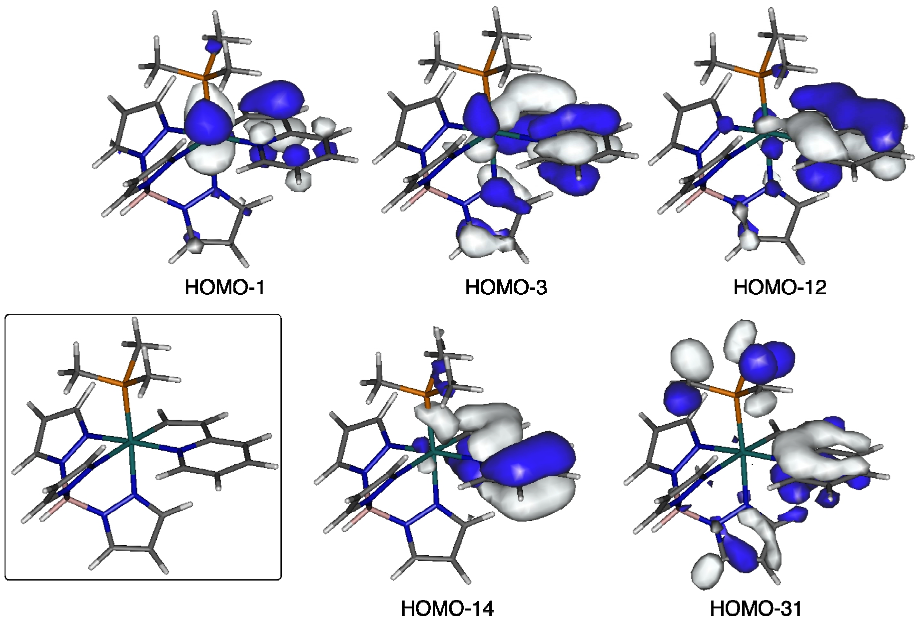


Figure 6. π-Molecular orbitals computed for model 3-ruthenaindolizine complex (figure adapted from reference 63).

Isotropic NICS(0) and NICS(1) values, calculated at the [3,+1] ring critical point of the electron density,[70] were used to diagnose the aromatic character of the first d^4-heterometallahelicene described in the literature, namely the [6]-azaosmahelicene complex depicted in Figure 7.[71] The computed NICS values (–1.2 and –4.5 ppm, respectively) support some degree of electronic delocalization within the five-membered osmacycle. In agreement with this, the X-ray derived structure indicates again planarity and Os–C and C–C bond length equalization (i.e. intermediate between single and double bonds). Hence, this compound can be view as an aromatic species despite the calculated low negative NICS values. Similarly, the observed planarity and bond length equalization, and particularly, the negative NICS values (NICS(0) = –12.6 ppm, NICS(1) = –11.9 ppm) calculated for the osmabicycle $OsH_2(\kappa\text{-N,N-}o\text{-HNC}_6H_4NH)(PiPr_3)_2$ resemble the values computed for the aromatic benzimidazolium cation (NICS(0) = –12.9 ppm, NICS(1) = –9.3 ppm).[72] This finding suggests that the π-delocalization is similar in both systems.

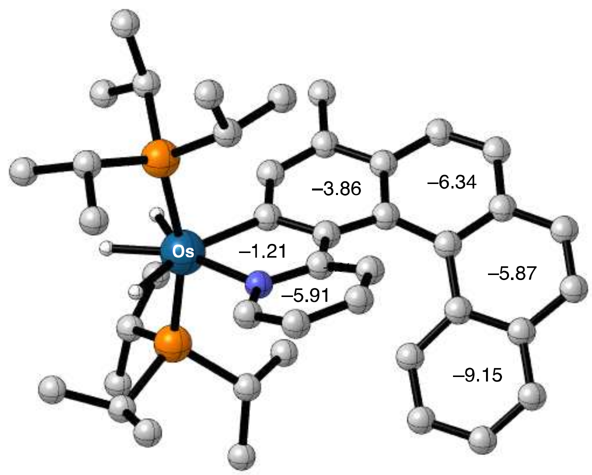
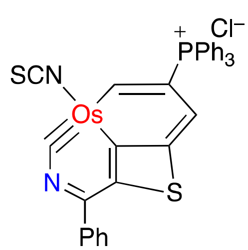


Figure 7. Representation of the first d^4-heterometallahelicene (C–H hydrogen atoms were removed for clarity) and associated calculated NICS values (in ppm) for each aromatic ring. Figure adapted from reference 71.

Recently, Winter and co-workers described the preparation of novel metallapyrimidines and metallapyrimidiniums by means of oxidative addition of pyrazolate N−N bonds to niobium(III), niobium(IV), and tantalum(IV).[73] It was suggested that the niobacycles are weakly aromatic in comparison to the highly aromatic 3,5-di-*tert* -butylpyrazolate ligands and pyrimidine because the former species exhibit low negative NICS values (NICS(1) ranging from –1.9 to –4.4 ppm, and $NICS(1)_{zz}$ from –5.5 to –9.9 ppm), while more negative values were computed for the latter non-organometallic species (NICS(1) ca. –10 ppm and $NICS(1)_{zz}$ ca. –24.0 ppm). In a subsequent report,[74] the authors thoroughly examined the aromaticity of these and related species by a combination of NICS calculations (used to gauge the amount of aromaticity) and Natural Chemical Shielding (NCS)[75] analyses where the chemical shifts are decomposed in terms of diamagnetic and paramagnetic contributions from individual molecular orbitals. It was found that, whereas $NICS(1)_{zz}$ values for niobapyrimidine, $[(pz)_2(Nb\text{-}pyr)]^0$ (pz = pyrazolate) suggest slightly aromatic character, the NCS analysis shows that this is due to the diamagnetic contribution. In contrast, the calculated positive paramagnetic contribution indicates that niobapyrimidine may be slightly antiaromatic. Following a similar approach, a series of d^0 metallapyrimidines, $[(pz)_2(M\text{-}pyr)]$ with M = Y(III), Zr(IV), Nb(V), Mo(VI) and Tc(VII), was considered and found to behave similarly. At variance, M(V) metallapyrimidines, $[(pz)_2(M\text{-}pyr)]$ where M = Mo, Tc, Ru, and Rh, are strongly aromatic in view of their highly negative NICS values ($NICS(1)_{zz}$ values of −15.4, −36.0, −31.6, and −22.4 ppm, respectively). According to NCS analysis, the aromaticity in the latter species is favoured by an unoccupied d−π orbital that serves as an acceptor to facilitate conjugation in the metallapyrimidine ring.

Closely related to the above azametallabenzenes, the metallapyridyne complex depicted in Figure 8 was synthesised and fully characterised by Lin, Xia and co-workers.[4e] The aromaticity of a model species, where the bulky PPh_3 ligands were replaced by PH_3 groups, was evaluated by means of NICS and ISE methods. The calculated NICS values (NICS(0) = –4.5 ppm and NICS(1) = –4.2 ppm) are again comparable to other metallabenzenes and suggest that this azametallabenzyne can be considered as a weakly aromatic molecule. Indeed, the computed ISE value of only 11.3 kcal/mol (for a model complex where the phenyl group is further replaced by a methyl group) is at the lower end of the values obtained for other metallaaromatic compounds.



metallapyridyne

NICS(1) = –4.5 ppm
ISE = 11.3 kcal/mol

Figure 8. Aromatic character of the metallapyridyne ring prepared by Lin, Xia and co-workers (see reference 4e).

In 2013, the group of Solà analysed the relative stabilities of the *ortho*, *meta*, and *para* isomers of a series of heterometallabenzenes with formula $MClY(XC_4H_4)(PH_3)_2$ (M = Ir, Rh; X = N, P; Y = Cl and M = Os, Ru; X = N, P; Y = CO).[76] They found that the *meta* isomer is the most stable species for IrN and RhN complexes, while the *ortho* form is favoured for all selected metallaphosphinines. In contrast, the *ortho* and *meta* isomers are energetically nearly degenerated for the RuN and OsN species. Considering the corresponding molecular orbitals, it was concluded that these heterometallabenzenes are best described as 10π-electron (i.e. Hückel aromatic) species. Interestingly, according to the NICS values as well as the so-called multicentre index (MCI),[77] an electronic descriptor for aromaticity, these complexes can be classified as aromatic or slightly aromatic species. Despite that, no clear correlation between aromaticity and stability was found.

More recently, Solà group has studied the structure and aromaticity of a set of experimental and in silico designed five-membered (5MRs) heterometallacycles with the general formula $M(XC_3H_3)(PH_3)_2$, where M = OsH_3, $OsCl_3$, $OsCl_2$, $RuCl_2$, $RhCl_2$, or $IrCl_2$ and X=NH, O, S, CH^-, or CH^+.[78] Particularly, the electronic delocalization was analysed using the induced magnetic field, $\mathbf{B}^{ind}$, NICS, and MCIs in order to diagnose aromaticity in these heterometallacycles. The (quasi)planar systems exhibit a nonintense diatropic response and low MCIs values thus indicating a nonaromatic or low aromatic character, with the notable exception of the five-membered ring complexes with X = CH^+, which are clearly paratropic in nature and antiaromatic.

5. Concluding Remarks and Outlook

In this review, we have described the efforts, mainly derived from computational tools, which were made to assess and understand the aromatic nature of metallabenzenes. These species span from nonaromatic or low aromatic compounds through to highly aromatic species (see for instance, the series of compounds gathered in Table 1 whose ASE-EDA values range from 8.7 kcal/mol, weakly aromatic, to 37.6 kcal/mol, i.e. highly aromatic). In general, it can be stated that the aromaticity for this family of organometallic compounds is lower than that for their all-carbon analogues. This is confirmed by the observed reactivity of the complexes, which undergo typical reactions for aromatic species but also other type of transformations such as nucleophilic substitutions or rearrangement reactions.

Taking into account that aromaticity is a complex phenomenon, the diagnosis of the aromaticity in metallabenzenes is an even more complicated and challenging issue. We have shown that the most popular computational methods to analyse and quantify aromaticity have severe limitations when applied to metallabenzenes. This is mainly due to the anisotropy of the metal centre and to the effect of the corresponding ligands which contaminate the computed values making them misleading in many cases. The rapid development of novel computational methods and descriptors for aromaticity such as MCI's, dissected NICS and ASE values derived from the EDA method, make it possible to gain more insight into the controversial aromatic nature of these species. However, other issues such as the relationship between the nature of the transition metal and the type and number of ligands surrounding it and the aromaticity magnitute are still far away to be fully understood. We expect that the future development of novel computational approaches will solve the shortcomings associated with these traditional aromaticity descriptors and provide a better understanding of the aromatic nature of these species.

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