

Testing the Effectiveness of the Isoelectronic Substitution Principle through the Transformation of Aromatic Osmathiophene Derivatives into their Inorganic Analogues

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Abstract.

The objective of the current work is to evaluate the effectiveness of isoelectronic substitution (IS) principle on a series of complexes with general formula $\text{OsCl}_2(\text{SX}_3\text{H}_3)(\text{PH}_3)_2$, where X_3 represents the moieties CCC, CCB, CCN, CBN, CNB or NCB, formed by substitution of the carbon atoms in CCC by either the isoelectronic B^- or N^+ separately, or by both. The SX_3H_3 moiety forms, together with Os, an aromatic five-membered ring (5-MR) called osmathiophene. The preservation of stability and aromaticity in the resulting systems is used to indicate the effectiveness of the IS principle. The aromaticity of the proposed molecules is analyzed according to magnetic (induced magnetic field (\mathbf{B}^{ind})) and electronic (through the multicenter index (MCI)) criteria. Besides, a chemical bonding analysis on selected species is performed by the adaptive natural density partitioning (AdNDP) method.

Keywords.

Metallacycles, aromaticity, induced magnetic field, AdNDP, electronic delocalization

Introduction

The isoelectronic substitution (IS) principle, an important concept in chemistry, could be useful as a guide to design new molecules. It consists in replacing atoms in known chemical species by their isoelectronic counterparts (atoms of a different nature).¹⁻² For instance, Olson and Boldyrev proposed boron-hydrogen analogues of saturated hydrocarbons; showing that one CH unit can be changed by one BH⁻ anion (both with five valence electrons) to form stable compounds. They called it “electronic transmutation” (ET).³⁻⁴ On the other hand, CH can also be replaced by other isoelectronic species, such as N. If one replaces all CH units of benzene by N, the N₆(D_{6h}) structure is obtained. Based on a theoretical research, Roberts suggested in 1961 that this all-nitrogen benzene analogue, called hexazine, would present the same π -delocalization pattern, provided the unshared electron pairs are regarded as strictly localized.⁵ However, in 1974, it was confirmed that hexazine is not the most stable structure of N₆, the (N₂)₃ trimer being the most stable form.⁶⁻⁷ Additionally, Gimarc proposed that the instability is generated by the lone pairs repulsion.⁸

Moreover, if the valence isoelectronic fragment has an approximate shape and energy (in their respective frontier orbitals) to the fragment being replaced, the IS coincides with the isolobal principle, proposed by Hoffmann in 1982.⁹

Recently, using the IS principle, the theoretical prediction of boron analogues of aromatic hydrocarbon rings has been highly effective, while it has failed for the non-aromatic ones.¹⁰⁻¹² Furthermore, the link between hydrocarbons and borohydrides has also been analyzed, finding that these compounds share a common root regulated by the number of valence electrons in a confined space.¹³⁻¹⁴ Interestingly, these authors demonstrated the existence of a relation between planar aromatic annulenes and tridimensional aromatic closo boron hydride clusters.¹⁵ These results seem to indicate that the IS principle applies effectively when designing boron analogues of aromatic organic compounds. However, in some cases the IS could drastically change the chemical bonding patterns in the designed compounds. In this way, after applying IS of CC units by BN moieties on

organic aromatic rings, the geometrical properties persist, but the electronic ones change.¹⁶⁻¹⁷ For instance, borazine¹⁸ ($B_3N_3H_6$), also known as “inorganic benzol”,¹⁹ has structural parameters such as planarity and bond equalization and number of π electrons similar to benzene. However, its chemical bonding is different: whereas benzene is aromatic, borazine has been classified as non-aromatic or marginally aromatic.²⁰⁻²⁶

The aim of the present work is to evaluate, in an extreme situation, the validity of the concepts mentioned in the preceding paragraphs, in order to design new stable molecules. The chosen system to achieve this goal is $[OsCl_2(SC_3H_3)(PH_3)_2]^+$, which presents some characteristics that make it suitable for this purpose: **1**) it is a simplified model of the osmabicycles (aromatic compounds where one Os atom is present in five-membered metallacycles), studied both experimentally and theoretically by Esteruelas et al.,²⁷ **2**) this system was classified as clearly aromatic,²⁸ with participation of Os-d-orbital (especially d_{xz} and d_{yz} orbitals) closing the circuit of π -orbitals and allowing electronic delocalization on the planar OsC_3S fragment.²⁹ Additionally, the presence of an Os-S bond is another interesting aspect, even though S has almost the same electronegativity that C, it is nearly double the size of its covalent radius and it has an extra lone pair of electrons (this is expected to play an important role in electronic delocalization after performing the IS procedure). Moreover, the Os atom has two axial ligands, which are expected to directly affect the π delocalization. The question is how all these particular characteristics will evolve as the system is transformed to preserve, or not, the aromaticity as a key stabilizing factor. The aromaticity in metallacyclopentadienes, like those analyzed in the present work, has been less studied than metallabenzenes. For the latter, in 2015, Fernández et. al, published a review discussing the role of the d orbitals of the metallic atoms in the electronic delocalization and aromaticity of these species.³⁰

The current study involves the sequential transformation of $[OsCl_2(SC_3H_3)(PH_3)_2]^+$ into its completely inorganic analogues $OsCl_2(SB_2NH_3)(PH_3)_2$ and $[OsCl_2(SBN_2H_3)(PH_3)_2]^{2+}$. This has been

performed starting from the $[\text{OsCl}_2(\text{SC}_3\text{H}_3)(\text{PH}_3)_2]^+$ complex by all possible single substitutions of C atoms by N^+ or B^- , double substitutions of CC by BN units, and triple substitutions of CCC by B_2N^- or BN_2^+ moieties. To evaluate the consequence of these substitutions, structural parameters and electronic delocalization have been thoroughly analyzed.

Methodology

All geometry optimizations, vibrational frequency, wave function stabilities, and relative energy calculations were performed with Gaussian 09 program³¹ using the B3PW91 functional³²⁻³³ and the def2-TZVP basis set,³⁴ including pseudo-potentials for Os atom.³⁵

Chemical bonding analysis was performed with the adaptive natural density partitioning (AdNDP) method³⁶ at the B3PW91/def2-TZVP level. The AdNDP method analyzes the first-order reduced density matrix and it represents the electronic structure in terms of n-center–two-electron (nc–2e) bonds. This is done in order to recover both Lewis bonding elements (1c–2e or 2c–2e, i.e., lone pairs or two-center two-electron bonds) and delocalized bonding elements, which are associated with the concepts of aromaticity. The AdNDP method has been previously applied to analyze the chemical bonding and aromaticity in both organic³⁷⁻³⁸ and inorganic systems.³⁹⁻⁴² AdNDP analyses were performed with the Multiwfn program.⁴³

The magnetic shielding tensors were computed with PBE0⁴⁴⁻⁴⁵ functional and def2-TZVP basis set. The induced magnetic field was calculated following the formula

$$\mathbf{B}^{\text{ind}} = -\sigma_{\alpha\beta}\mathbf{B}^{\text{ext}}, \quad (1)$$

where $\sigma_{\alpha\beta}$ represents the magnetic shielding tensor and \mathbf{B}^{ext} is associated with the magnetic external field vector.⁴⁶⁻⁴⁷ In all cases, five-membered rings (5-MRs) were placed in the xy plane with the geometrical center coinciding at the origin of the Cartesian coordinates. The units of the \mathbf{B}^{ind} are ppm considering $|\mathbf{B}^{\text{ext}}| = 1$ T. The negative of the zz (or **33**) magnetic shielding tensor component,

equivalent to B_z^{ind} (and NICS_{zz}), is a good descriptor for the magnetic response of (anti)aromatic compounds⁴⁸ that has been employed successfully in previous 5-MR's heterometallacycles work.²⁸ This methodology has been fruitfully employed in other different kind of systems such as silicon star-shaped molecules,^{10, 49-50} boron clusters,⁵¹⁻⁵⁵ metallic clusters,⁵⁶⁻⁵⁷ compounds with planar *tetra*-,⁵⁸⁻⁶⁰ *penta*-,⁶¹⁻⁶² or even *hexacoordinated* carbon atoms.⁶³ Besides, in classic chemical entities such as benzene and other organic compounds including carbomer-typesystems,⁶⁴⁻⁶⁷ or where NICS_{iso} interpretation is not clear.⁶⁸⁻⁶⁹

The electron delocalization multicenter index (MCI) was used as an electronic index of aromaticity. MCI stemmed from the I_{ring} index which was defined by Giambiagi in 2000⁷⁰ as:

$$I_{\text{ring}}(\mathbf{A}) = 2^n \sum_{i_1, i_2, i_3, \dots, i_n}^{\text{OCC}} S_{i_1 i_2}(A_1) S_{i_2 i_3}(A_2) \dots S_{i_n i_1}(A_n) \quad , \quad (2)$$

where $S_{ij}(A_k)$ is the overlap between molecular orbitals i and j within the domain of atom k . In this formula, it is considered that the ring is formed by atoms in the string $\{\mathbf{A}\} = \{A_1, A_2, \dots, A_n\}$. An extension of this I_{ring} index, by Bultinck and coworkers,⁷¹ resulted in the so-called MCI index:

$$\begin{aligned} \text{MCI}(\mathbf{A}) &= \frac{1}{2^n} \sum_{P(\mathbf{A})} I_{\text{ring}}(\mathbf{A}) = \\ &= \frac{2^{n-1}}{n} \sum_{P(\mathbf{A})} \sum_{i_1, i_2, i_3, \dots, i_n}^{\text{OCC}} S_{i_1 i_2}(A_1) S_{i_2 i_3}(A_2) \dots S_{i_n i_1}(A_n), \end{aligned} \quad (3)$$

where $P(\mathbf{A})$ stands for the $n!$ permutations of the elements in the string $\{\mathbf{A}\}$. The MCI index has been successfully applied to a broad number of situations, from simple organic compounds to complex all-metal clusters with multiple aromaticity.⁷² The numerical integrations over the atomic domains were carried out within the “fuzzy atom” framework,⁷³ using the Becke- ρ partitioning scheme⁷⁴ with the APOST-3D program.⁷⁵ The I_{ring} and MCI indexes were obtained with the ESI-3D program⁷⁶⁻⁷⁸ at the B3PW91/def2-TZVP level.

Results and discussion

Application of the isoelectronic substitution principle

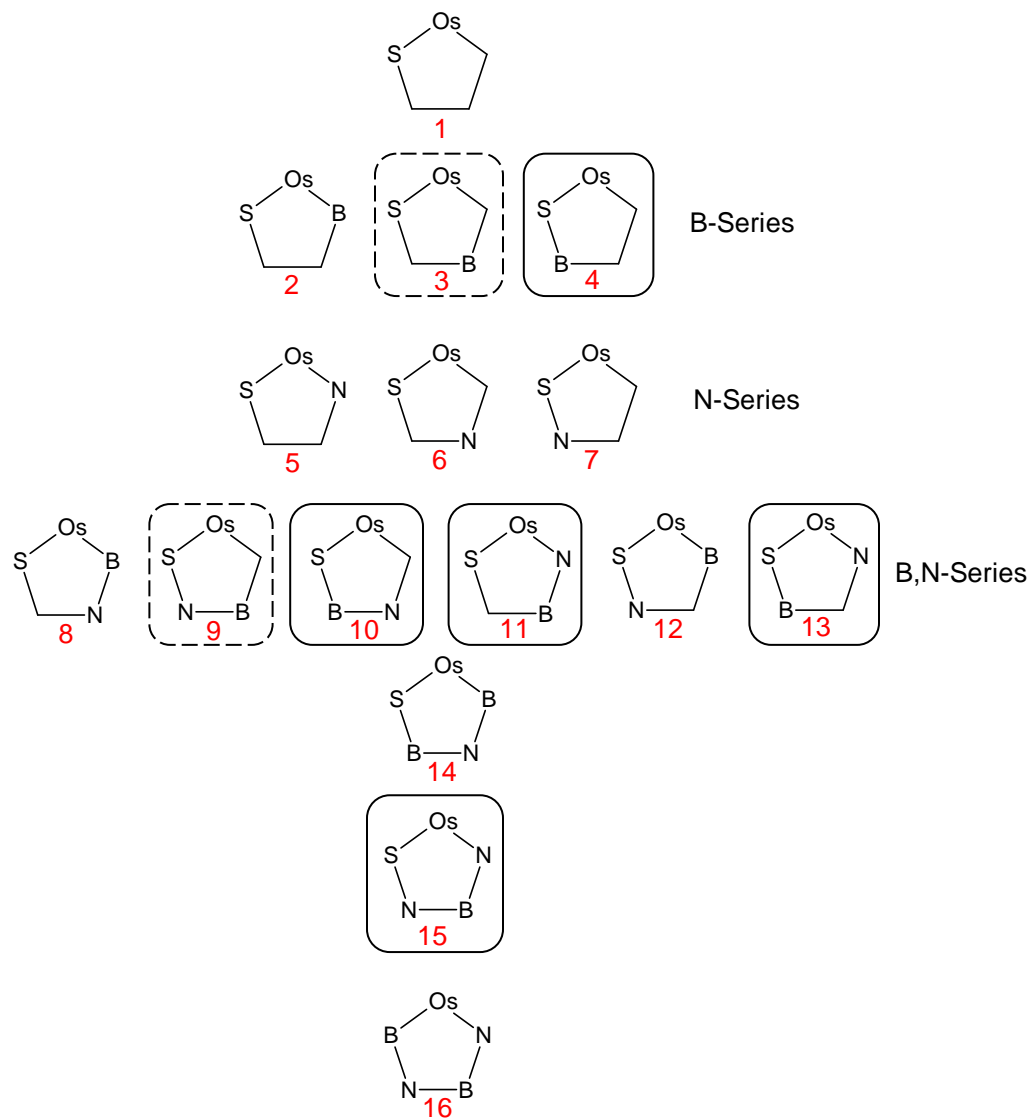
Complex $[\text{OsCl}_2(\text{SC}_3\text{H}_3)(\text{PH}_3)_2]^+$ (labeled as **1** in this work) was chosen to test the effectiveness of the IS principle. In a previous work, it was proven that **1** has the most diatropic response among the systems with the general formula: $\text{M}(\text{XC}_3\text{H}_3)(\text{PH}_3)_2$, where $\text{M} = \text{OsH}_3, \text{OsCl}_3, \text{OsCl}_2, \text{RuCl}_2, \text{RhCl}_2$ or IrCl_2 , and $\text{X} = \text{NH}, \text{O}, \text{S}, \text{CH}^-,$ or $\text{CH}^+.$ ²⁸ Therefore, any change in the structure and in the electronic delocalization after the IS should be noticeable. The IS procedure consisted in replacing carbon atoms in **1** by other 4-valence electron species: the anion B^- and the cation N^+ . In the first step, only one carbon atom was replaced by one B^- anion, yielding the B-series, conformed by three neutral isomers (**2-4** in Scheme 1). In system **2**, the boron atom is bonded to the transition metal; in system **3**, to two carbon atoms, and in system **4**, to the sulfur atom. In the second step, the same procedure was performed, but this time with the nitrogen cation, obtaining the series N-series with three isomers (**5-7** in Scheme 1). In system **5**, the nitrogen atom is bonded to the transition metal, in system **6**, to two carbon atoms, and in system **7**, to the sulfur atom. In the third step, starting again from **1**, a double substitution was carried out. This systematic substitution consisted of one C replaced by one N^+ , and another C by one B^- . With these substitutions, a series (N,B-series) with six isomers (**8-13** in Scheme 1) was obtained. These included those where a C-C unit is replaced by a B-N one (systems **8-11**); whereas in systems **12** and **13**, the boron and the nitrogen atoms are bonded through a carbon atom. In the last step, all carbon atoms were replaced, in order to obtain two “inorganic” analogues of **1** (see systems **14** and **15** in Scheme 1). Finally, with the aim of studying the role of sulfur in the stability and aromaticity in these series, the S^{2+} unit in system **15** was replaced by a B^- one, to retrieve system **16**.

All the obtained systems after IS procedure were optimized and the stability of the wave functions was analyzed. The B-series is conformed by **2, 3** and **4** systems (see Scheme 1). Among them, **2** is the only stable system with similar geometry (planarity) and electronic structure to the

original system **1**, since system **3** is not planar and **4** presents singlet instability for restricted wave function. System **4** in its triplet ground state is 59.8 kcal mol⁻¹ more stable than in its lowest-lying singlet closed-shell state and system **3** is 26.5 kcal mol⁻¹ less stable than system **2**. Meanwhile, the N-series is conformed by three stable isomers (**5**, **6**, and **7**) without instabilities in their respective wave functions, and besides they present comparable structural parameters as planar 5-MR rings.

The wave function of the six B,N-series isomers were also analyzed, and it was found UHF instabilities in the systems **10**, **11**, and **13**. Additionally, system **9** is not a planar 5-MR ring. Only systems **8** and **12** are stable in the closed-shell, and structurally comparable to **1**, being system **8** more stable than **12** by 32 kcal mol⁻¹. Next, systems **14**, **15**, and **16** (not isomers, see Scheme 1) contain planar rings, but **15** presents UHF wave function instability.

However, the spin-restricted closed-shell results of **4**, **10**, **11**, **13**, and **15** are reported in the structural analysis and in the induced magnetic sections in order to make comparison of all systems at the same level of calculation and in the same electronic state. All the systems are depicted in Scheme 1, where the UHF unstable systems are marked by a solid-line square, and the non-planar ones with a dashed-line square.



Scheme 1. Complexes proposed in this work. In this scheme Os represents $\text{Os}(\text{PH}_3)_2\text{Cl}_2$. N and B represent N-H and B-H units, respectively. The systems with UHF wave function instability are encircled in a solid-line square, and non planar 5-MR in a dashed-line square.

Structural parameters

The geometries reported in Table 1 show the bond lengths (only for cycles) and internal angles of the fifteen compounds proposed in this work (see Scheme 1). When compared with system **1**, deviations in Os-S bond length are not longer than 0.172 Å. The shortest bond length deviation is at system **12** (0.003 Å) and the longest one is at system **9** (0.172 Å). For Os-X bonds (where X = C, B⁻ or N⁺ in the **1-15** systems), the longest deviation is at system **3** (0.129 Å) and the shortest one is at system **10** (0.008 Å). The internal angles are also affected; the most dramatic change is at system **3**, where the α and ϵ angles change by more than 10° each. Internal angles ϵ and γ in system **14** are also affected by the IS, with 12° and 15°, respectively.

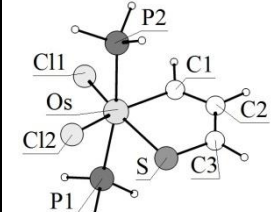
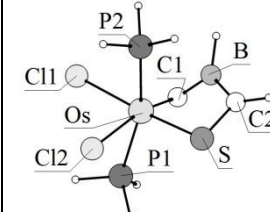
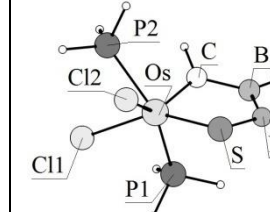
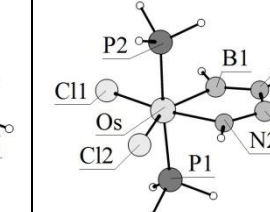
Table 1. Charge (electrons), bond lengths (Å), and internal angles (deg) of the 5-MRs computed at the B3PW91/def2-TZVP.

Complex	Charge	d1	d2	d3	d4	d5	α	β	γ	δ	ϵ
1	1	2.383	1.655	1.391	1.369	2.014	103.26	117.29	115.74	126.57	77.14
2	0	2.451	1.714	1.374	1.470	1.919	104.51	120.13	100.74	145.77	68.83
3	0	2.339	1.649	1.537	1.522	1.885	93.25	109.24	119.67	91.77	89.69
4	0	2.435	1.729	1.526	1.344	2.064	104.51	112.06	116.35	129.77	77.22
5	2	2.305	1.644	1.405	1.306	2.027	104.66	115.59	116.11	126.53	77.09
6	2	2.351	1.639	1.344	1.342	1.962	101.93	116.46	118.91	124.35	78.29
7	2	2.258	1.643	1.328	1.382	1.988	102.81	118.58	116.37	122.28	79.94
8	1	2.456	1.645	1.335	1.436	2.050	104.31	118.47	115.82	126.84	74.57
9	1	2.211	1.689	1.405	1.560	1.924	103.23	117.60	110.77	119.82	82.73
10	1	2.427	1.749	1.461	1.314	2.006	102.60	111.81	119.73	127.90	77.84
11	1	2.365	1.627	1.548	1.394	2.023	106.49	115.80	110.81	129.26	77.43
12	1	2.380	1.682	1.319	1.500	1.907	104.39	120.78	105.10	136.98	72.75
13	1	2.361	1.751	1.556	1.286	2.106	107.09	109.93	117.02	128.96	76.83
14	0	2.501	1.790	1.455	1.378	1.903	105.56	113.03	100.16	156.35	64.89
15	2	2.216	1.621	1.437	1.415	1.986	106.20	118.00	110.49	125.69	79.61
16*	0	2.141	1.379	1.462	1.386	2.105	123.13	111.04	110.98	124.25	70.60

*For **16**, d1 and d5 are the Os-N and Os-B bonds, respectively

As shown in Table 2 (where the dihedral angles of some selected systems are depicted), the IS not only affects the bond lengths and the internal angles, but the planarity of the rings is also affected; this is more evident in systems **3** and **9** (the most distorted rings). The equality of bond lengths and planarity are the most characteristic structural parameters of aromatic compounds; therefore, the results presented above suggest dramatic changes in aromaticity after the IS. This aspect will be further discussed in the next section, using different theoretical approximations.

Table 2. Selected dihedral angles of some representative molecules (**1**, **3**, **9**, and **16**). The angles are in degrees.

							
1		3		9		16	
Os-C1-C2-C3	0.8	Os-C1-B-C2	64.2	Os-C-B-N	-18.8	Os-B1-N1-B2	0.0
Os-S-C3-C2	0.5	Os-S-C2-B	-5.5	Os-S-N-B	15.6	Os-N2-B2-N1	0.0
C1-C2-C3-S	-0.8	C1-B-C2-S	-38.4	C-B-N-S	-0.8	B1-N1-B2-N2	0.0

Aromaticity

In Figure 1, the B_z^{ind} profiles along the z-axis are plotted for all the analyzed systems. When B_z^{ind} is calculated at $R=0$ (geometrical center of the ring placed in the xy plane) it is called $B_z^{\text{ind}}(0)$. The larger the $B_z^{\text{ind}}(0)$ values, the more paratropic (antiaromatic) the system is, meanwhile the smaller the $B_z^{\text{ind}}(0)$, the more diatropic (aromatic) the system is. Please note that the non-planar structures **3** and **9** were discarded here and in further analyses. Systems with UHF instabilities (4, 10, 11, 13 and 15) are studied in their lowest lying closed shell singlet excited state. The profiles of four of the studied compounds are highlighted by broader lines in the plot: the reference molecule **1**, the systems with the largest and the smallest $B_z^{\text{ind}}(0)$ values (**14** and **7**, respectively) and finally, the

boroazometalloycycle **16**. For comparison purposes, benzene (the aromatic compound *par excellence*) and thiophene are included in the plot. It is highly striking to notice that some of the proposed systems are more aromatic than the starting point (system **1**). The aromatic character increases (according to $B_z^{\text{ind}}(0)$) as follows: **1**<**6**<**15**<**5**<**12**<thiophene \approx **7**<benzene. It is also important to remark that nitrogen mono-substituted cycles are more diatropic than the boron mono-substituted ones, reaching $B_z^{\text{ind}}(0)$ values similar to the one of benzene in system **7**. Moreover, systems **7**, **12**, and **15** (where there is an S-N bond) present a higher diatropic response compared to other compounds. This is particularly interesting because of the relatively large difference in electronegativity of S and N atoms, and thus a ring current disturbance could be expected. The counterpart is found in the systems with the S-B bond, which present a significant increase of the B_z^{ind} values. Even some of them are predicted to be anti-aromatic compounds. The close relation between the presence of an S-B bond and the anti-aromatic character is evidenced when B replaces S in system **14** to produce system **15**. Both systems are fully inorganic rings, but the first one has a $B_z^{\text{ind}}(0)$ close to 8 ppm, compared with -5 ppm in the second one. Finally, the *boroazometalloycycle* **16** is a non-aromatic system in spite of its structural parameters, such as its perfect planarity. From Table 1, it is clear that this system resembles the non-aromatic cyclopentadiene with two localized B=N double bonds (d2 and d4) and one B-N single bond (d3).

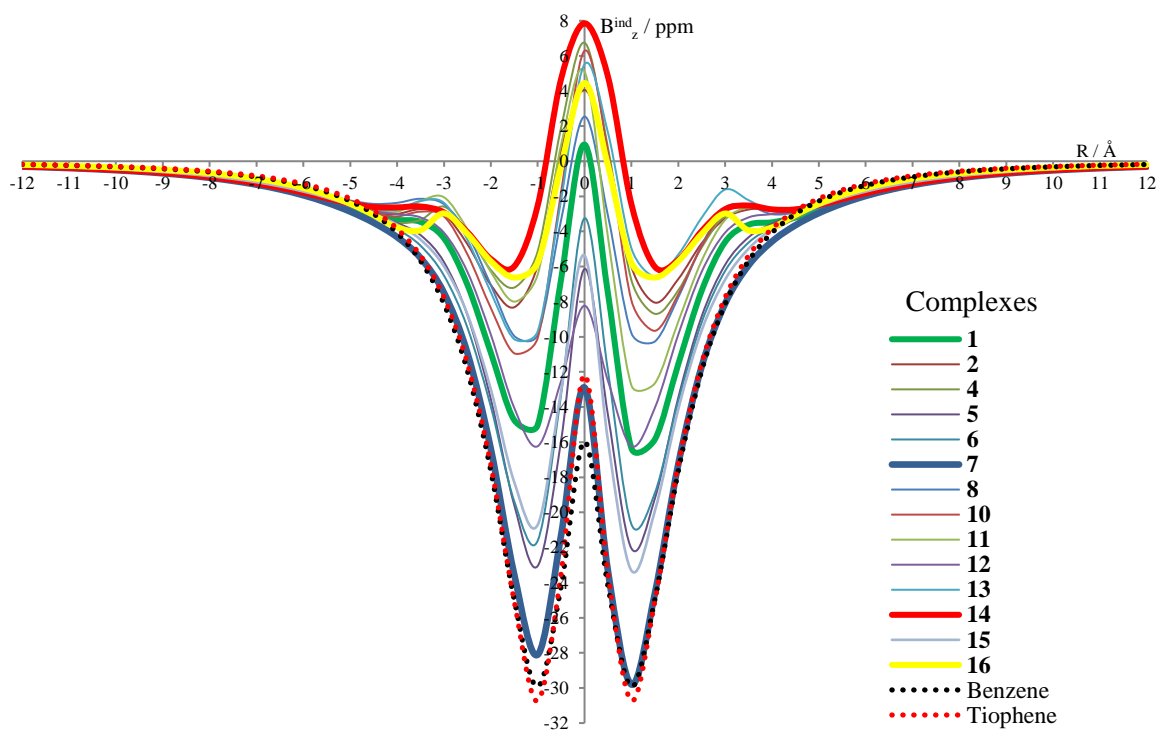


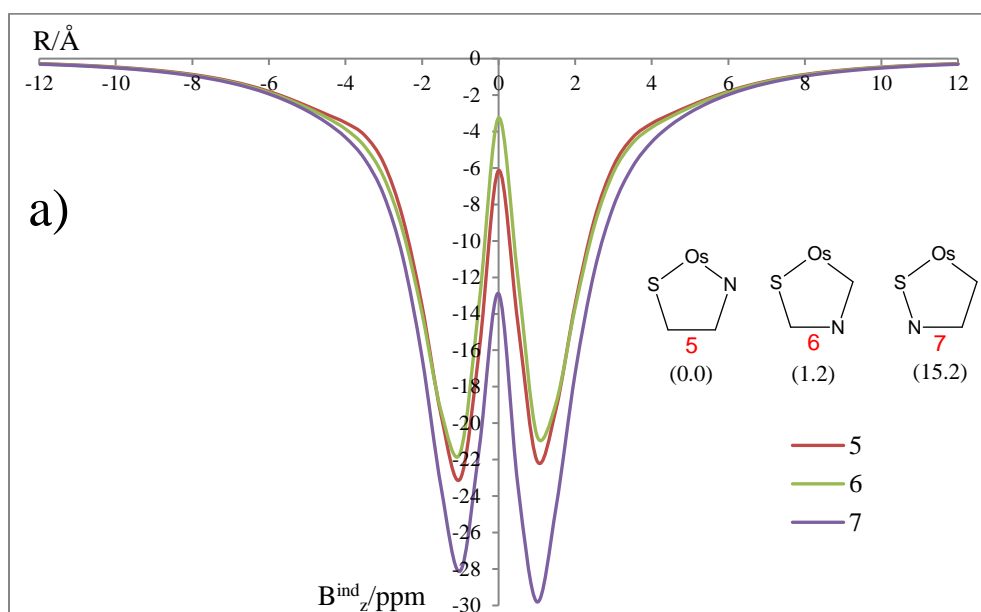
Figure 1. Profile plots of the B_z^{ind} computed in all the heterometallobenzene complexes proposed. Benzene is included for a better comparison. $R = 0$ corresponds to the center of the ring placed in the xy plane. The shielding tensors were computed at PBE0/def2-TZVP.

At this point of the discussion, the question of the role of aromaticity on the stabilization of the proposed systems arises. In an attempt to answer this question, the aromaticity (according to the B_z^{ind} profiles) is compared with the relative stabilities among the isomers forming each proposed series (see Figure 2).

The B-series systems are not depicted in Figure 2 because only **2** is planar and described by a stable wave function. For the N-series, isomer **6** is only 1 kcal mol⁻¹ less stable than **5** and both systems present a very similar magnetic response. On the other hand, the most diatropic compound **7** is 15 kcal mol⁻¹ higher in energy than **5** (the most stable and least aromatic compound in this series). This behavior could be attributed to the presence of a weak S-N bond in complex **7**. While this bond favors the electronic delocalization, its weakness leads to species that are relatively unstable. In

fact, the bonding energies (computed at B3PW91//def2-TZVP level) for the hemolytic dissociation in species HS-NH₂, HS-BH₂, H₃C-NH₂, H₃C-BH₂, and H₂B-NH₂, are -69.4, -115.5, -88.3, -106.9, and -145.2 kcal/mol, respectively. This situation resembles the one of imidazole and pyrazole isomers, where the first one is the most stable despite the second one being somewhat more aromatic; which has been attributed to the presence of a weak N-N bond in the pyrazole ring.⁷⁹⁻⁸⁰

For the B,N-series (**8**, **9**, and **12** systems), the B^{ind}_z profiles indicate that **12** is the most diatropic isomer even though it is 32 kcal mol⁻¹ less stable than the most stable **8**. Whereas the non-planar system, **9**, is 35 kcal mol⁻¹ less stable than **8**. Again, the presence of S-N bonds in **9** and **12** justifies their lower stabilities as compared to **8**. These results show, once again, that in this double substituted series thermodynamic stability is associated to the strength of their formed chemical bonds rather than to their electronic delocalization in the ring.



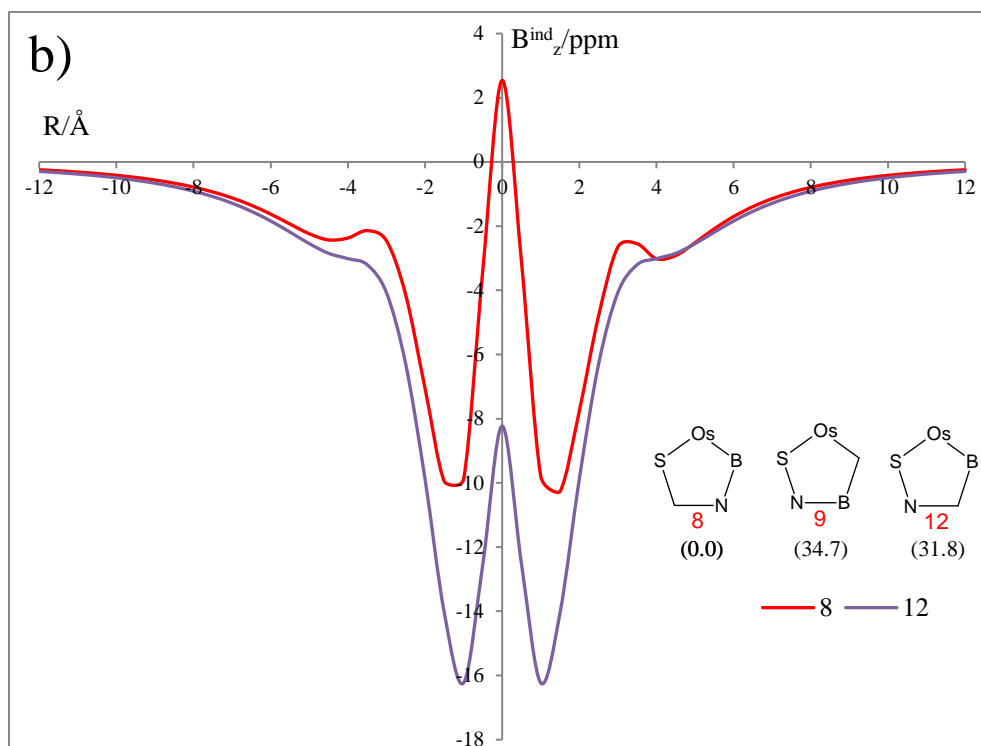


Figure 2. B_z^{ind} profiles of the a) nitrogen-, and b) double substituted rings. The relative energies of the isomers are in parentheses and their units are kcal mol^{-1} computed at B3PW91/def2-TZVP including zero point corrections.

The main objective of this work is to assess whether IS is a reliable tool for molecular design. One of the most sensitive changes is the electronic delocalization. As mentioned in the introduction of the current work, one of the differences between benzene and borazine is their aromatic character. It has been extensively documented that superficial analysis of magnetic properties could lead to erroneous interpretations about aromaticity.⁶⁸⁻⁶⁹ To complement the analysis of the magnetic properties performed in this work, maps of isolines of B_z^{ind} computed for **1**, **7**, and **14** are plotted in Figure 3. These complexes were selected because **1** is the reference point, whereas **7** and **14** are the most diatropic and paratropic compounds, respectively. The xz plane was chosen in such a way that it contains the Os atom and bisects the ring; whereas the yz plane contains the sulfur atom. The maps show that a paratropic region surrounds the osmium atom in the three systems. However, **1** and **7** can be considered as diatropic rings. The nitrogen atom in **7** is

surrounded by diatropic regions, which could be contributing to negative values of the B_z^{ind} at the center of the ring. On the other hand, the isolines of B_z^{ind} , plotted in the xy plane, of the double boron substituted system **14** show two paratropic regions: one in the center of the ring and another one around the boron bonded to the Os atom. As a consequence, **14** is the best candidate to prove that IS can affect, in an unpredictable way, the electronic delocalization in rings with a transition metal; and thus, it is not an infallible methodology, at least when trying to tune the magnetic response.

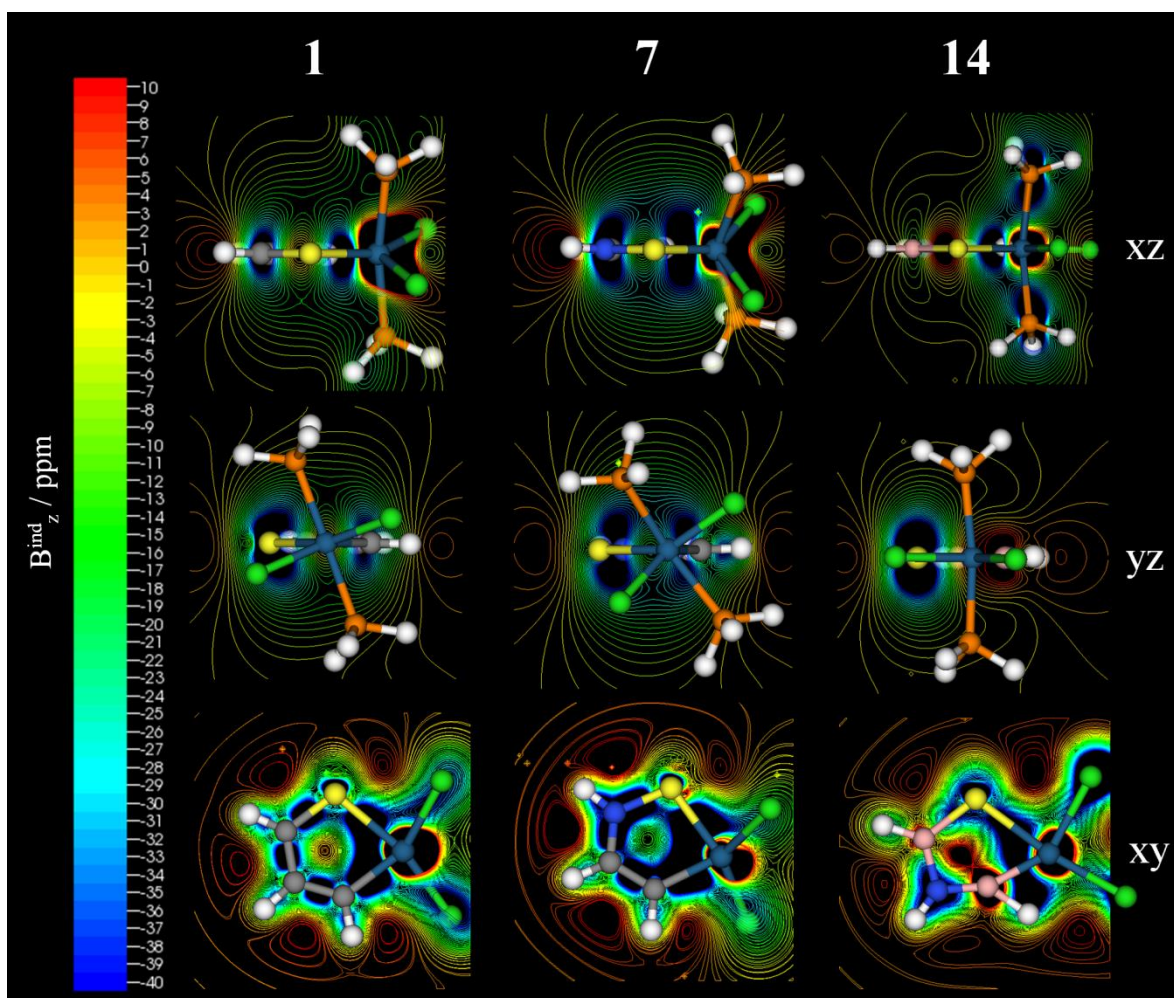


Figure 3. Isolines of B_z^{ind} computed in **1**, **7**, and **14**. The isolines are plotted in the xy , xz , and yz planes. For xy plane the PH_3 units were removed from the picture for a better appreciation of the in-plane B_z^{ind} isolines. Grey, yellow, white, blue, dark blue, green, pink and orange, represent carbon, sulfur, hydrogen, nitrogen, osmium, chlorine, boron and phosphorus atoms, respectively. Units are ppm.

The MCI index was also computed to analyze from an electronic point of view the electronic delocalization in the complexes studied. The values of this index are enclosed in Table 3. For a better comparison, benzene, borazine, and thiophene are also included as reference systems (benzene is the most aromatic, followed by thiophene, and finally borazine that can be considered non-aromatic). There is a good consensus between the general aromatic trends obtained by this electronic MCI and the magnetic response (B^{ind}); although the scaling of the aromaticity, achieved by these two indexes, is different (for instance, B_z^{ind} yields **7**, **12** and **15** more aromatic than **1**, whereas the reverse is indicated by MCI). Therefore, N-substituted systems **5-7** are more aromatic than B-substituted **2-4**, and even more than the doubly substituted **8-13**. Besides, MCI somewhat confirms the magnetic criteria predictions: system **7** (the most diatropic) as aromatic, whereas **14** (the most paratropic) as antiaromatic. Interestingly, the most aromatic system is **6** according to MCI. This result agrees with the fact that the two different C-N bond lengths (d_2 and d_3) are almost equal, which is an indication of effective delocalization. The current results show that the change of one or two atoms of complex **1** by either B^- or N^+ can have a large effect on either the corresponding magnetic response or the electronic delocalization of the compounds. Depending on the location of the IS, delocalization can be reduced or increased. Single substitution of a C by an N^+ results in an increase in the diatropic response; while the electronic delocalization measured with MCI indexes remains more or less the same. On the other hand, in all cases a single substitution of a C by a B^- results in a reduction of the diatropic response and the electronic delocalization. The result of multiple substitutions is more difficult to predict. In general, this leads to a reduction in both the diatropic response and the electronic delocalization (for instance, consider complex **15**).

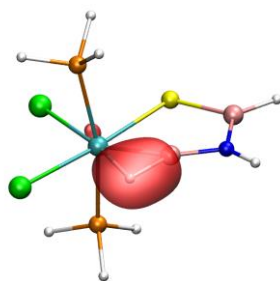
Table 3. Calculated MCI of complexes **1-16** under study.^a Units are electrons.

1				
0.020				
2	4			
0.009	-0.004			
5	6	7		
0.020	0.027	0.014		
8	10	11	12	13
0.011	0.003	-0.004	0.005	-0.004
14				
-0.002				
15				
0.012				
16				
0.000				
Benzene	Borazine	Thiophene		
0.059	0.003	0.035		

^a Non-planar **3** and **9** complexes not included

Chemical Bonding Analysis.

For a deeper understanding of the chemical bonding of these complexes, we performed an AdNDP analysis in the following systems: the reference (**1**), the most diatropic (**7**) and the most paratropic (**14**) systems. The figures corresponding to the σ bonding pattern of molecules **1,7**, and **14**, revealed by AdNDP, are available in the Supporting Information. As it can be seen, AdNDP showed eight lone pairs: three on each chlorine atom, one on the osmium atom, and another one on the sulfur atom. The σ bonding pattern of these three systems is similar: almost all bonds are classic 2c-2e, with the exception of the Os-S and the Os-C (only in system **1**) σ bonds. All bonds involving the hydrogen atoms are found as classic 2c-2e σ bonds, except for **14** in which boron, hydrogen, and osmium atoms form up a small σ delocalized triangle, where AdNDP reveals that two electrons are delocalized in the three centers (3c-2e) (see Figure 4).



3c-2e σ bond
ON = 1.88|e|

Figure 4. Delocalized B-H-Os bond in molecule **14**. ON stands for occupation number in |e|.

The π -bonding pattern of molecules **1**, **7**, and **14** is shown in Figure 5. In all three systems, two 3c-2e π bonds, involving the sulfur atom, were found with a relatively high occupation number (1.87-2.00|e|), which suggest delocalization of these electrons. The third π -bonding element, which is centered on the osmium atom, was also found as a 3c-2e element with ON of 1.71, 1.57 and 1.70 |e|, for systems **1**, **7** and **14**, respectively. However, it is worth mentioning that only in systems **1** and **7** the last bond could be considered as π (having a nodal plane coinciding with the plane of the molecule). Then, according to AdNDP, systems **1** and **7** should be aromatic (six π -electrons) and system **14** should be antiaromatic (four π -electrons). Moreover, the π -bond that is centered on the Os, is distributed on the molecular ring of system **7** (which is the most aromatic, according to the magnetic criteria), whereas in system **1** it is delocalized to the phosphine axial ligands. Therefore, this result agrees with the analysis of the magnetic properties, discussed above.

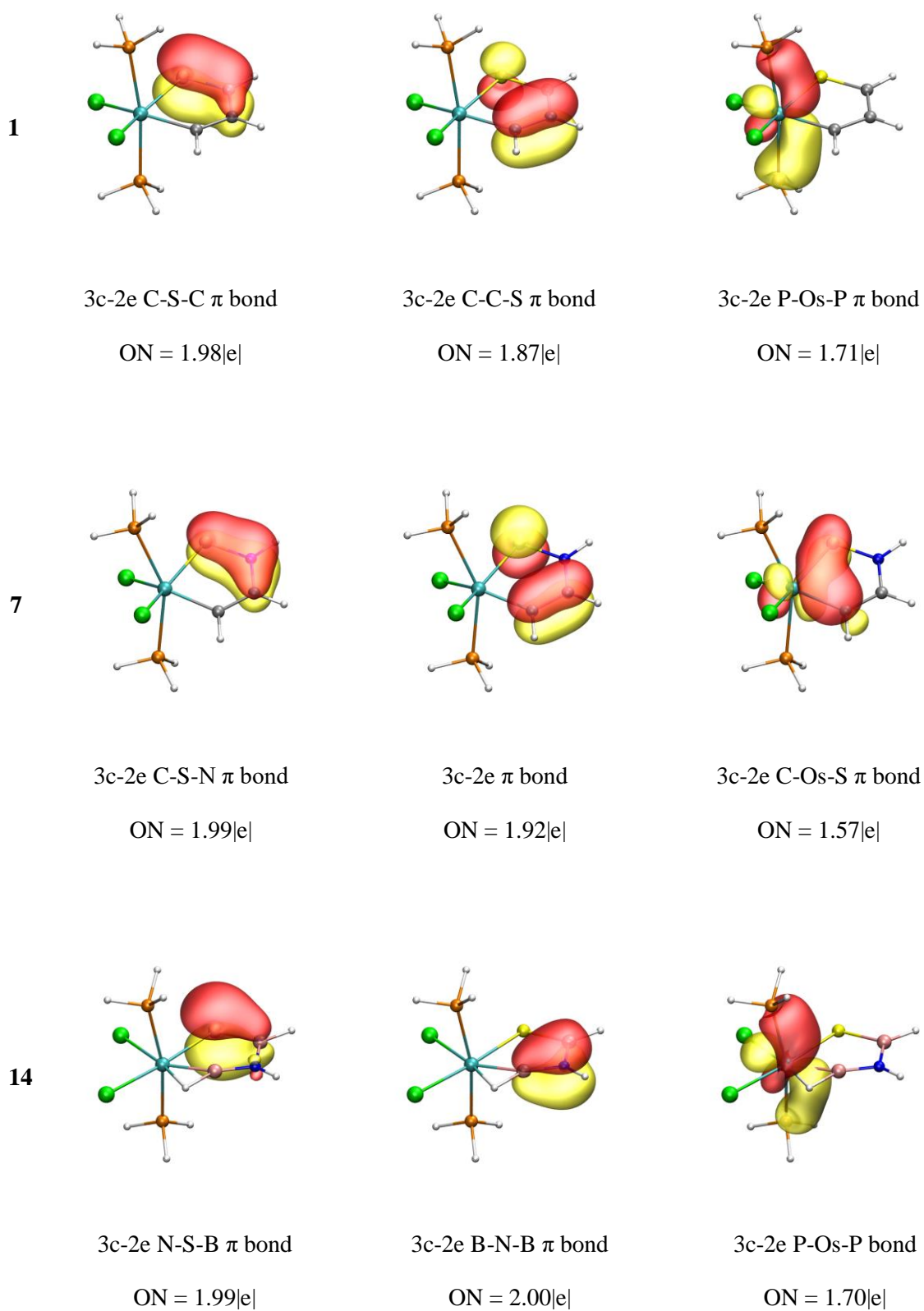


Figure 5. π bonding pattern of molecules **1**, **7**, and **14**. ON stands for occupation number in |e|.

Conclusions

In this work, the effectiveness of the IS principle has been tested *in silico* in a series of osmathiophene derivatives. Structural parameters, electronic delocalization, and bonding patterns were analyzed with the objective of quantifying the impact of the C \rightarrow B $^-$, the C \rightarrow N $^+$ and the C,C \rightarrow B $^-$,N $^+$ substitutions. As a general conclusion, we have found that when a transition metal atom is part of a 5-MR, the IS procedure could result in similar or quite different compounds depending on the type of electronic transmutation performed. Other conclusions of our analysis are the following:

- The replacement of one C by one B has an important impact on the geometry: the bond lengths, internal and dihedral angles present important changes. Besides, electronic delocalization decreases. Then it is possible to conclude that the IS procedure does not adequately work in this case. Additionally, system **4** wave function presents an UHF instability suggesting that the electronic structure of this system is of different nature when compared to system **1**.
- On the other hand, the N $^+$ cation seems to be a better isoelectronic substituent for carbon; the geometries are not drastically altered and the electronic delocalization is increased when they are compared with system **1**. It is particularly interesting that among all 16 proposed systems, **7** is the complex with the highest diatropic response (similar to that of benzene) and **6** is the most aromatic compound according to MCI calculations. Then, according to geometric and electronic similitude between the transformed systems and **1**, it is possible to conclude that the IS procedure adequately works in this case.

For the selected systems, based on the bonding analysis performed by AdNDP, systems **1** and **7** show similar delocalized π -orbitals. System **14** has two π -orbitals localized on the 5-MR,

supporting the paratropic response computed with B_z^{ind} . The electronic delocalization of these compounds is not the key for their stability, other factors, such as the bond strength of the different bonds involved plays a more important role in determining the stability of these systems.

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