

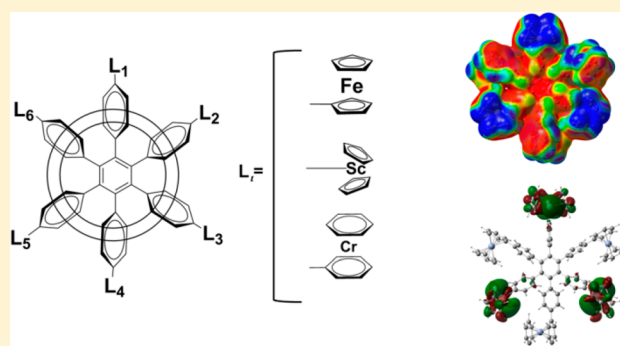
Which Is The Best Sandwich Compound? Hexaphenylbenzene Substituted By Sandwich Compounds Bearing Sc, Cr, and Fe

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Supporting Information

ABSTRACT: The electronic properties of nine different hexaarylbenzene molecules substituted by sandwich compounds have been studied by applying density functional theory. Different structures and the particular electron donor power of these systems have been considered in order to analyze their oxidant capacity, using bis(ciclopentadienyl) scandium, ferrocene, and bis(benzene)chromium as sandwich compounds. Both monometallic and bimetallic combinations are investigated. According to the ionization energies and electron affinities, compounds with Cr are nucleophiles and represent the best electron donors, whereas compounds with Sc are electrophiles and represent the best electron acceptors. The worse electron donor or acceptor is hexakis(4-ferrocenyl phenyl) benzene. This is very significant, as it implies that the very well-known electronic properties of hexakis(4-ferrocenyl phenyl) benzene can be improved by substituting with other metals, such as Sc and Cr. This suggests several possible applications for these compounds.



INTRODUCTION

The study and design of 3D molecules containing chromophores is a topic of great interest due to the properties related to charge transport and luminescence materials.^{1–5} In particular, hexaarylbenzene (HAB) molecules have gained popularity as scaffold in complex chromophore systems because they can be used to collect light.^{6–8} HAB have a propeller-shaped conformation and may have many applications.^{9–17} They can be used as supramolecular electronic materials,¹⁰ redox materials,¹⁴ molecular wires,¹⁶ and metal sensors.¹⁷ There are also a variety of HAB derivatives, where the vertices of the hexaphenylbenzene core are decorated with electroactive chromophores. The propeller-shaped conformation enables π - π interactions between all the aromatic rings at the periphery of the molecule. This phenomenon has been called “toroidal delocalization”,^{16,18} and several articles exist in which this delocalization has been extensively studied.^{19–21} The general shape of these molecules, as well as the toroidal delocalization phenomenon, is illustrated in Figure 1.

Results related to the toroidal delocalization from a thermodynamic point of view²¹ have been reported previously. It has been established that the nature of the substituents on the lateral aromatic rings as well as the nature and the position of the frontier molecular orbitals are important factors for enabling electronic dissipation, which subsequently gives place to toroidal delocalization. Indeed, the particular π electron clouds in all the aromatic rings create an electronic communication that forms a totally novel electronic system.²⁰

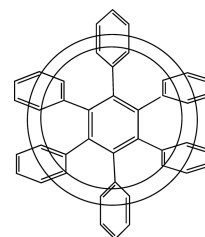


Figure 1. Schematic representation of the toroidal delocalization phenomenon.

HAB analogue molecules, in particular those with six ferrocene moieties connected to the vertices of the propeller of each peripheral aromatic ring (HAB-Fe of Figure 2), have been investigated previously.²² Ferrocene is a very well-known active redox species.²³ It can undergo one-electron oxidation at a low potential of 0.5 V (with respect to a saturated calomel electrode). The oxidation of ferrocene produces a very stable cation named ferricinium. HAB-Fe presents the characteristics of both ferrocene and hexaphenylbenzene derivatives. This explains that this compound may eject six electrons in only one excitation event, a phenomenon caused by the combination of very redox-active ferrocene and the toroidal delocalization of the hexaphenylbenzene derivative.

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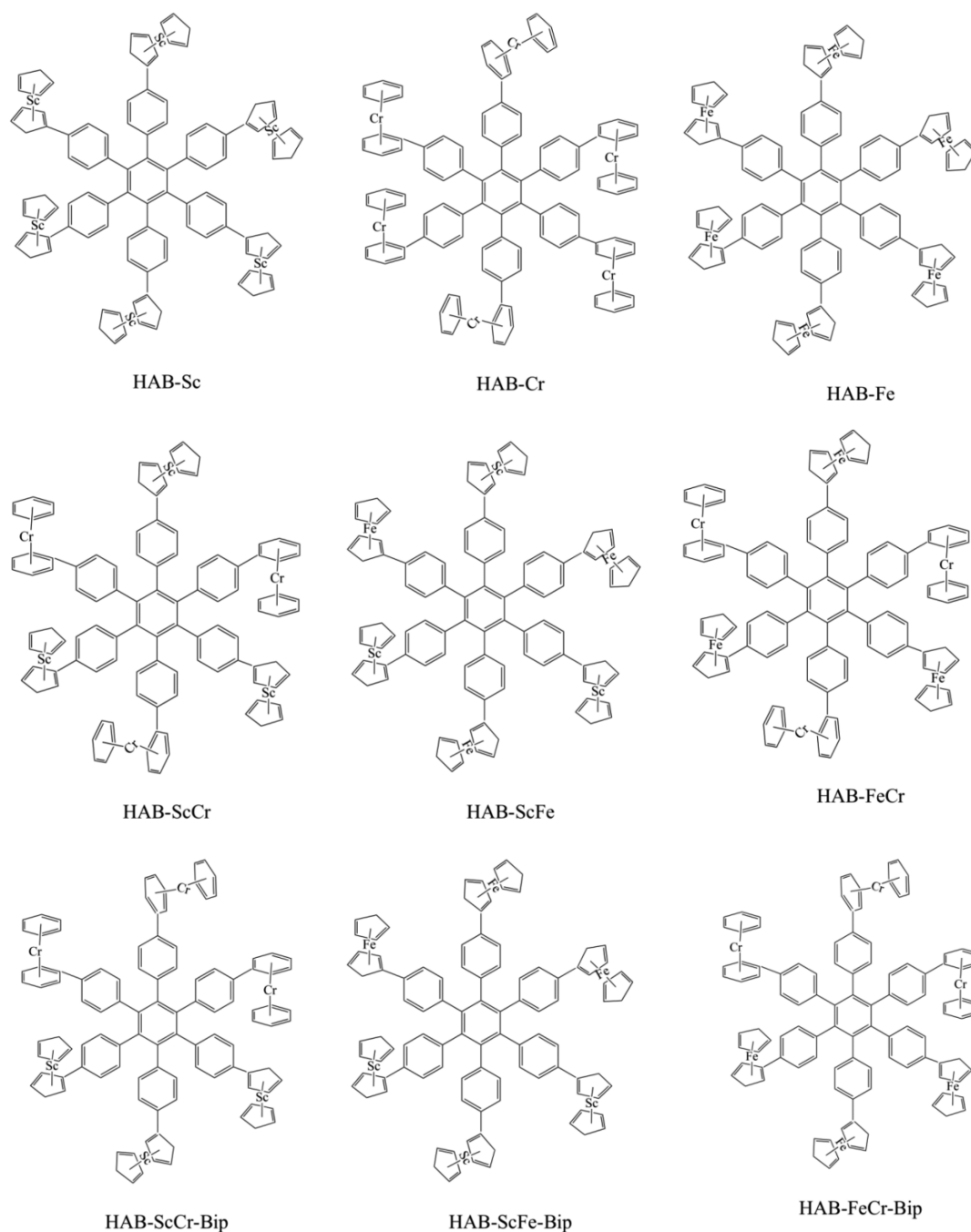


Figure 2. Schematic representation of hexakis(4-ferrocenylphenyl) benzene [HAB-Fe] and the molecules being studied.

There is another molecule that has caught the attention of many researchers. This is bis(benzene)chromium. The stability of this molecule is explained by the fact that each benzene molecule will donate its 6π electrons into the six vacant chromium atomic orbitals. Bis(benzene)chromium and ferrocene are two molecules that provoked interest and inspired the imagination of organometallic, inorganic, and organic chemists.²⁴ Due to its particular characteristics, it may be interesting to use bis(benzene)chromium as a moiety in HAB instead of ferrocene. Similar to ferrocene, bis(benzene)chromium can be connected to the vertices of the propeller of the hexaphenylbenzene molecule. In fact, other metal-bis(cyclopentadienyl) or metal-bis(benzene) molecules may reveal different properties when they are bonded to the HAB core. It is thus

interesting to study the electronic structure of HABs using this type of sandwich compound instead of ferrocene.

In spite of all results reported for different hexakis(4-ferrocenylphenyl) benzene, there are no studies which consider other sandwich compounds bonded to the propellers. For this reason, in this paper we report the electronic configuration and different reactivity properties for HABs substituted with bis(cyclopentadienyl)scandium (HAB-Sc), bis(benzene)-chromium (HAB-Cr), and ferrocene (HAB-Fe). The studied molecules are illustrated in Figure 2. We select these metal atoms due to their electronic configuration: scandium presents four empty d orbitals, and chromium has six orbitals with only one electron. Iron provides us with the opportunity to propose a model to explain the simultaneous ejection of six electrons.

The lack of synthetic methods is reflected by the fact that the functional HABs reported to date are symmetrical. For this reason, we used sandwich compounds that have the same metal atom. However, a programmed synthesis that allows the isolation and characterization of HABs with different aryl substituents at all positions was reported recently.²¹ Authors report the first synthesis of a HAB with five or six different aryl groups and indicate that the properties of these nonsymmetrical compounds are apparently very promising. In order to increase knowledge of the properties of nonsymmetrical compounds, we also study HABs with different sandwich compounds located at different positions [see Figure 2; three scandium atoms and three chromium atoms (HAB-ScCr and HAB-ScCr-Bip); three scandium atoms and three iron atoms (HAB-ScFe and HAB-ScFe-Bip); and three chromium atoms and three iron atoms (HAB-CrFe and HAB-CrFe-Bip)]. Two different bimetallic systems are analyzed: those with different metals in alternate positions (see Figure 2: HAB-ScCr, HAB-ScFe, HAB-FeCr) and systems with the same sandwich compounds on one side of the molecule (see HAB-ScCr-Bip, HAB-ScFe-Bip and HAB-FeCr-Bip in Figure 2). As shown in this paper, the latter present very interesting properties. For all the systems being studied, we analyzed the structure and effect of the electronic configuration of the metal atoms in terms of the electronic properties of these compounds. Optimized geometries, electronic structure, and electron donor–acceptor capacity are all considered in this paper. The best electron acceptors are those containing Sc, whereas those containing Cr are better electron donors. HAB-ScCr and HAB-ScCr-Bip are the best electron donors and acceptors, whereas HAB-Fe is the worst electron donor and also the worst electron acceptor. These new functional materials could be very useful for further applications and represent a challenge for those carrying out experiments.

■ COMPUTATIONAL DETAILS

Calculations related to geometry optimization and electronic properties of HAB substituted by sandwich compounds are undertaken using Gaussian 09 implementation.²⁵ The initial geometries are fully optimized without symmetry constraints at B3PW91/6-31G(d,p) level of theory.^{26–29} All neutral molecules are singlets. Triplets and quintets are less stable than singlets by more than 15 kcal/mol. In order to verify optimized minima, harmonic analyses are performed, and local minima are identified (zero imaginary frequencies). To investigate the single electron transfer mechanism, vertical ionization energy (I) and vertical electron affinity (A) are obtained from single point calculations of cationic and anionic molecules, using the optimized structure of the neutrals and the doublet spin state. To analyze the relaxation effect, some of the ionized states were fully optimized. The energy difference between adiabatic and vertical states is less than 5 kcal/mol, and the order of the molecular orbitals is the same. With these results we can conclude that the relaxation has no effect on the ionized states. When an electron is removed (cation) or is added (anion) from/to one of these orbitals, it could be a Jahn–Teller effect. To analyze the potential Jahn–Teller effect, the eigenvalues and geometries of two optimized ionic examples were analyzed. The geometries of ions and neutrals are very similar. Anion and cation are doublets, and both present a single electron in a nondegenerated orbital, but the degeneracy of the orbitals (other than the HOMO) remains. It was not possible to break the degeneracy and optimize a distorted structure, probably because the geometry optimization starting from a distorted

structure can progress on an excited state. Although we recognize that this is a challenge, it is out of the scope of this report. Since there are many degenerated orbitals, the stabilization due to the Jahn–Teller effect is small and does not modify the conclusions of this investigation. In order to see the results starting from excited states, we performed some geometry optimizations at the TDDFT level of theory. The results that we obtained are almost the same. Apparently, calculations considering excited states converge to similar ground states.

The reactivity indexes used in this work are the electrodonating and electroaccepting powers.^{30,31} The propensity to donate charge or electrodonating power is defined as

$$\omega^- = \frac{(3I + A)^2}{16(I - A)} \quad (1)$$

Lower values of the electrodonating power imply a greater capacity for donating charge. The propensity to accept charge or electroaccepting power is equal to

$$\omega^+ = \frac{(I + 3A)^2}{16(I - A)} \quad (3)$$

For the electroaccepting power, higher values imply a greater capacity for accepting charge. With these two parameters it is possible to analyze the partial charge transfer capacity. For one electron transfer, I and A are the helpful parameters. It is important to note that these approximations consider the external potential fixed. For this reason, I and A must be vertical.

A useful tool to analyze the electron donor–acceptor properties was defined previously and is named full electron donor–acceptor map (FEDAM).^{32,33} In this map (see Figure 3) I and A are plotted and allow us to classify substances as

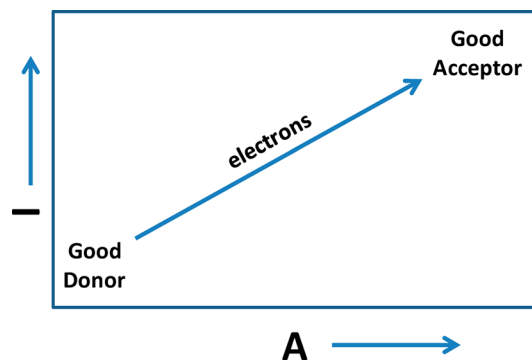


Figure 3. Full electron donor–acceptor map.

donors or acceptors of electrons. Electrons will be transferred from molecules located down to the left of the map (good electron donors) to those molecules that are up to the right (good electron acceptors).

■ RESULTS AND DISCUSSION

Geometry Optimization. The optimized geometries for all compounds being studied are presented in Figure 4. As is evident, the geometrical structures depend on the metal atom. The most important difference is the σ bond between Sc and one of the carbon atoms of the six-member ring of the hexaphenylbenzene core. The systems containing Fe and Cr present a C–C σ bond with the six-member ring of the

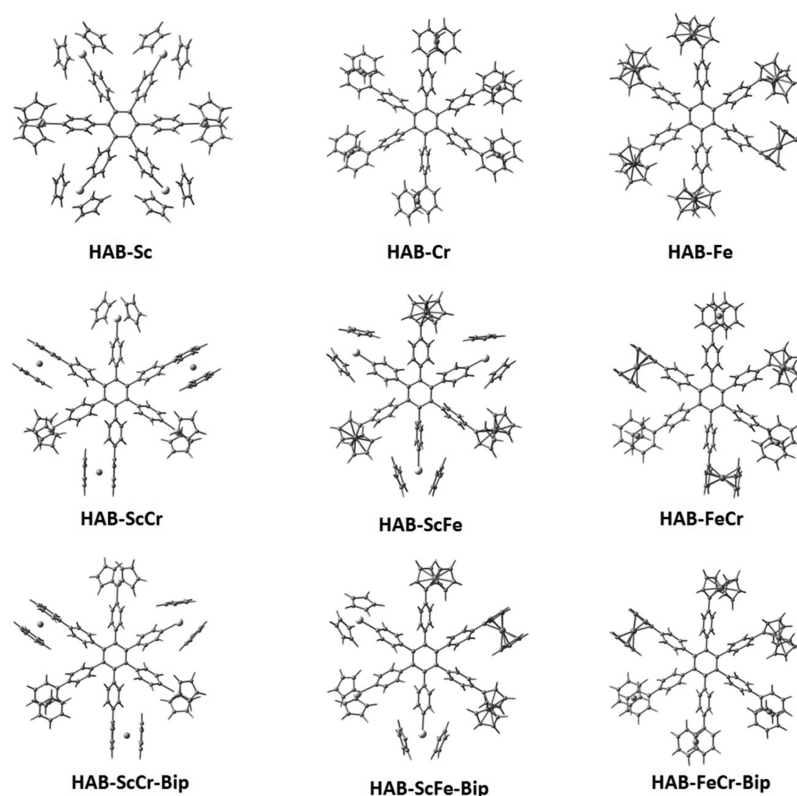


Figure 4. Optimized structures of the systems being studied.

hexaphenylbenzene. The cyclopentadienyl structures bonded to Sc are not parallel, whereas compounds containing Cr show two benzene molecules parallel to each other (similar to the cyclopentadienyls in ferrocene). The propellers are located in different positions, depending on the metal atom: with Sc and Cr, they are parallel to each other, whereas this is not the case for Fe since ferrocene molecules are not parallel to each other. HAB-ScCr and HAB-ScFe present bis(cyclopentadienyl) scandium perpendicular to ferrocene molecules or to bis(benzene)chromium. For all the systems being studied, the six peripheral phenyls that form the propeller of the hexaphenylbenzene core are parallel to each other and twisted 120° with respect to the central benzene in all cases. Apparently with this configuration the steric impediment is less.

A systematic investigation (considering similar methodology) of electronic and molecular structures for the first transition metal series metallocenes $[M(C_5H_5)_2]$ ($M = V, Cr, Mn, Fe, Co,$ and Ni) was reported before.³⁴ Authors report that the D_{5h} structures (eclipsed) are slightly more stable than D_{5d} structures (staggered) in all cases, but the energy difference between both is very small. In our results, the metallocenes show eclipsed structures for Fe and Cr. For the structures with $Sc(C_5H_5)_2$, the cyclopentadienyl rings are not parallel to each other, and therefore the structures are not fully eclipsed. The molecules under study are C_1 structures. Considering this point group, it is possible to analyze the electronic configuration as can be seen later in this report.

The optimized HAB molecules with bimetallic sandwich compounds located at different positions are also reported in Figure 4. For each combination of metal atoms, there are two isomers: those with different metals in alternate positions (HAB-ScCr, HAB-ScFe, and HAB-FeCr) and systems with the same sandwich compounds at one side of the molecule (see

HAB-ScCr-Bip, HAB-ScFe-Bip, and HAB-FeCr-Bip). The energy difference between the isomers is very small (Table 1), meaning that they are degenerate, and both manifest the

Table 1. Results for the Systems under Study^a

identification of compds	<i>I</i>	<i>A</i>	ω^-	ω^+	ΔE (kcal/mol)
HAB-Sc	5.94	0.69	4.08	0.76	
HAB-Cr	4.65	0.37	3.00	0.49	
HAB-Fe	5.80	0.25	3.51	0.48	
HAB-ScCr	4.60	0.63	3.28	0.67	
HAB-ScFe	5.97	0.68	4.09	0.76	
HAB-FeCr	4.58	0.29	2.86	0.43	
HAB-ScCr-Bip	4.37	0.61	3.25	0.65	0.71
HAB-ScFe-Bip	5.74	0.62	3.89	0.71	0.29
HAB-FeCr-Bip	4.67	0.25	2.88	0.42	-0.02

^aValues in eV. ΔE is the energy difference between isomers with the same bimetallic compounds.

same stability. This is interesting because both isomers can coexist in an experiment. Bond distances and angles are very similar, but as we show in the following, the electronic properties are quite different.

In Figure 5, we present bond distances and angles, with the schematic representations of the bond distances and angles that we selected to analyze the structural differences. σ bond distances with Sc are larger (2.2 Å) than σ C–C bond lengths (1.5 Å). The M–C–M bond angles (see Figure 5) indicate whether the metals are aligned. This bond angle is almost 180° for HAB-Sc but smaller for HAB-Cr and HAB-Fe (164 – 171°). When there are two different metal atoms, the bond angles are also smaller (163 – 173°) than in the case of monometallic compounds with Sc. We can explain these differences in terms

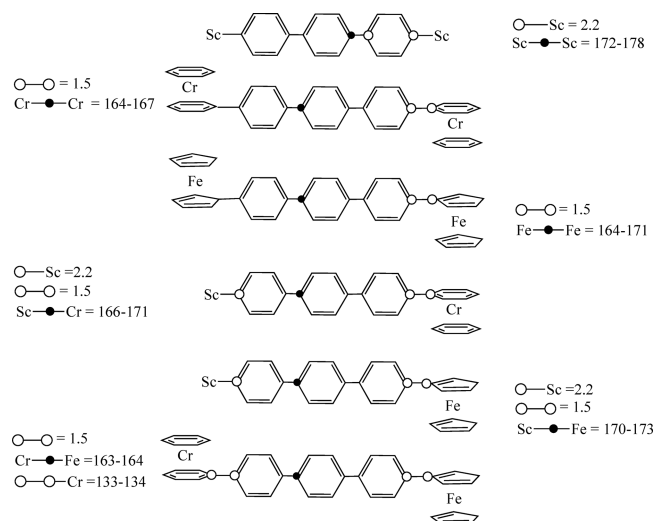


Figure 5. Selected bond distances (in Å) and angles (in deg). Schematic representation of the bond angles and distances used to characterized the structural differences.

of steric hindrance. Sc presents a σ bond with one carbon atom of the benzene molecule of the core, and therefore, the metal atoms are aligned with the carbon atoms of the benzene molecules and also with the scandium atoms that are at the opposite site of the molecule. However, when the σ bond is between two carbon atoms, the structures are not centered or aligned, and there is more steric hindrance. For this reason, the orientations of the bis(benzene)chromium or ferrocene groups with respect to the peripheral phenyls are much more varied than in the case of bis(cyclopentadienyl)scandium. Due to the σ bond between Sc and C of the benzene ring, there is no resonance effect between cyclopentadienyl and benzene. In contrast, the σ bonds between two carbon atoms of HAB-Fe and HAB-Cr connect two benzene rings, thus causing a resonance effect. This accounts for the resonance stabilization of the molecule due to the delocalization of the charge. The same effect is found among other systems that have two different metal atoms. Bimetallic compounds present resonance and nonresonance effects depending on the position of Sc. HAB-CrFe and HAB-CrFe-Bip manifest a resonance effect in all propellers.

Electron Donor–Acceptor Properties. Table 1 reports I , A , and the electron donor–acceptor powers (ω^- , ω^+) for the systems being studied. The FEDAM is reported in Figure 6. It is easy to see that compounds with Sc represent better electron

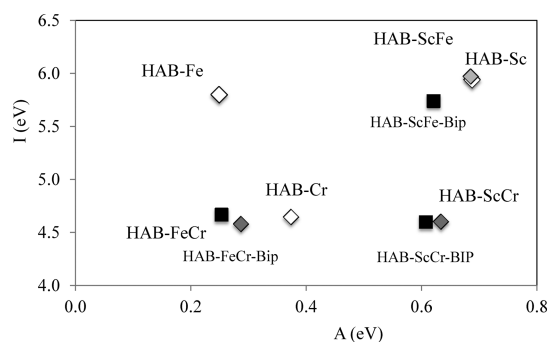


Figure 6. Full electron donor–acceptor map of the substances being studied.

acceptors than the others (which are in the right part of the map). Compounds with Cr represent the best electron donors (lower I values). Electrons can be transferred from HAB-FeCr, HAB-FeCr-Bip, and HAB-Cr (down to the left), and to HAB-ScFe, HAB-ScFe-Bip, and HAB-Sc (up to the right). The worst electron donor/acceptor compound is HAB-Fe, and the best are HAB-ScCr and HAB-ScCr-Bip. In what follows, we will explain these results, providing electronic configurations and molecular orbitals.

Monometallic Compounds (HAB-Sc, HAB-Cr, HAB-Fe). In an analysis of the monometallic systems, the best electron acceptor (A larger) is HAB-Sc. This is a logical result due to the electronic configuration of Sc that presents empty d orbitals. Figure 7 shows the frontier molecular orbitals and the molecular electrostatic potential of the optimized monometallic compounds (HAB-Sc, HAB-Cr, HAB-Fe). It is important to note that HOMOs are degenerated in all cases. If we look at the LUMO, evidently this is a bonding orbital of the bis-(cyclopentadienyl)scandium. This molecular orbital is located at the periphery of the molecule, and therefore, it is more available for electron acceptance. This could be an explanation of its high electron acceptor capacity compared with other systems. HAB-Sc is also the worst electron donor (I larger). The electronic configuration did not indicate this, as it appears that the electron situated on the d orbital of Sc could easily be donated. The explanation arises from the molecular orbitals (Figure 7). For HAB-Sc, HOMO mainly acts as a bonding orbital to the hexaphenylbenzene core. The valence electrons are not situated on the d orbitals of the scandium atoms but in a bonding orbital of HAB. Moreover, these electrons are less available as they are located inside the molecule. This contributes to the poor electron donor capacity of HAB-Sc.

Table 1 presents HAB-Cr as the best electron donor (I smaller) of any monometallic sandwich compounds. With analysis of the molecular orbitals for HAB-Cr, evidently HOMO represents a bonding orbital of bis(benzene)-chromium. It represents a π bonding orbital for the benzene rings and also bonding orbitals for the d orbitals of the metal atoms. It is located at the periphery of the molecule, and therefore, the valence electrons are more available. This may explain why HAB-Cr is the best electron donor. The HOMO of HAB-Fe is also a π bonding orbital of ferrocene and is also located at the periphery of the molecule. Notwithstanding, the HOMO of HAB-Fe is similar to the HOMO of HAB-Cr; the first represents a worse electron donor than the second because Fe is more electronegative than Cr. A comparison with HAB-Sc indicates that HAB-Fe is a slightly better electron donor than HAB-Sc (although Fe is more electronegative than Sc). The model that could explain this result arises from the valence electrons of HAB-Fe, that are more accessible than the valence electrons of HAB-Sc. A similar analysis can be made with the molecular electrostatic potentials that are also reported in Figure 7. For HAB-Sc, negative surface (in red) is located inside the molecule, while the positive surface (in blue) is outside. For HAB-Cr and HAB-Fe, the negative electrostatic potential is located outside the molecule.

HAB-Fe is the worst electron acceptor, but is not the best electron donor considering A and I values. It is a better electron donor than HAB-Sc but worse than HAB-Cr. It was reported previously²³ that this compound undergoes the loss of six electrons in a single stage. This compound has six degenerated double occupied molecular orbitals localized at the periphery of the molecule. This means that there are 12 valence electrons

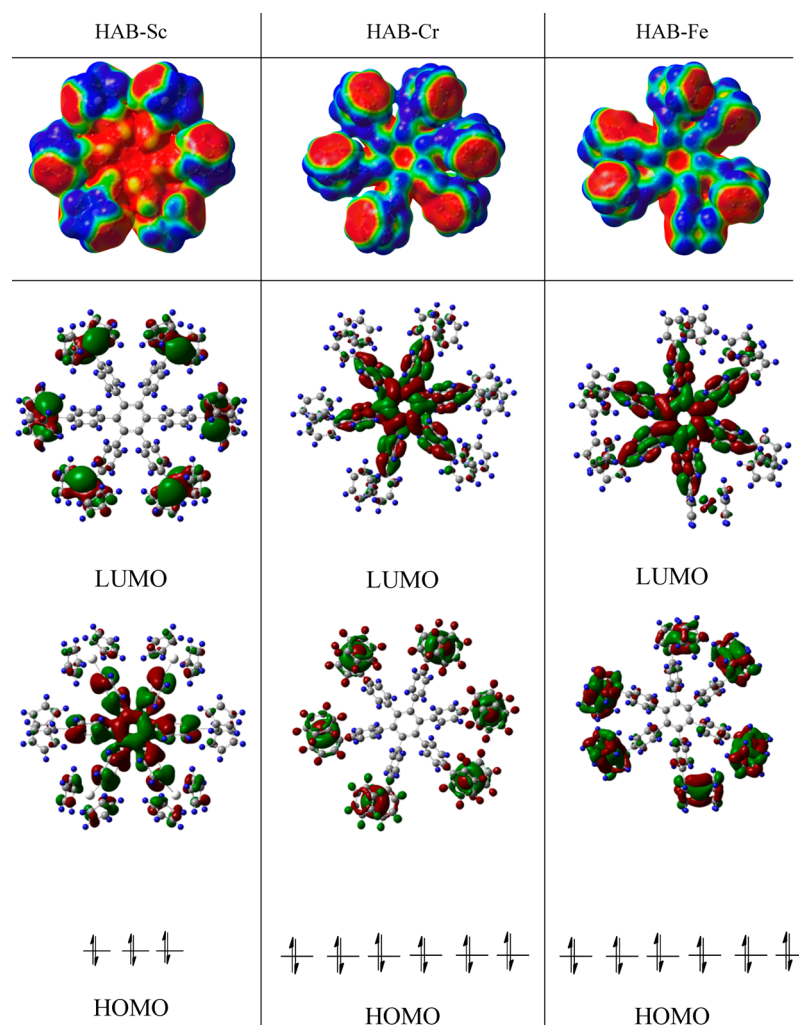


Figure 7. Molecular electrostatic potential and frontier molecular orbitals of the optimized monometallic compounds.

that have the same energy. When a constant potential is applied, six electrons are ejected, and a highly charged hexacationic compound is formed, with six unpaired electrons at the HOMO. HAB-Cr also has six degenerated double occupied molecular orbitals. Apparently, this molecule is also able to lose six electrons. Likewise, I is lower than the value for HAB-Fe, and therefore, HAB-Cr may be a better donor of six electrons than HAB-Fe. HAB-Sc is different because there are only three degenerated double occupied molecular orbitals, and valence electrons are less available as we explained previously.

Bimetallic Compounds. Figure 6 reveals the similarity between electron donor and acceptor properties of the isomers of bimetallic compounds. Those with different metals in alternate positions (HAB-ScCr, HAB-ScFe, HAB-FeCr) and systems with the same metals on one side of the molecule (HAB-ScCr-Bip, HAB-ScFe-Bip, and HAB-FeCr-Bip) are very closely located and in the same region of the map, depending on the metal atoms. It is easy to see that systems with Sc are the best electron acceptors, and those with Cr are the best electron donors (see Table 1 and Figure 6). Figures 8–10 report the molecular electrostatic potential and the frontier orbitals of the bimetallic compounds. Notably, the localization of the molecular orbitals depends on the metal atom. For example, HOMOs of HAB-ScCr and HAB-ScFe indicate no participation on the part of the scandium atoms, and LUMOs are mainly

located at the Sc atoms. For molecules with Sc and Cr, HOMO is a bonding molecular orbital of bis(benzene)chromium, whereas LUMO is a bonding molecular orbital of bis(cyclopentadienyl) scandium. In Figure 9, a similar situation is apparent for systems with Sc and Fe: HOMOs are bonding orbitals of ferrocene groups, and LUMOs are bonding orbitals of the bis(cyclopentadienyl)scandium. Figure 10 shows that, for molecules with Fe and Cr, HOMOs are located at the bis(benzene)chromium, and LUMOs are bonding orbitals of the hexaphenyl benzene core.

LUMOs of HAB-ScCr and HAB-ScFe are bonding orbitals of the bis(cyclopentadienyl) scandium, similar to the LUMO of HAB-Sc. When molecules act as acceptors the accepted electrons will occupy these orbitals. This may explain the similarity of A values for all systems with Sc. In summary, Sc dominates the electron acceptor capacity. Similarly, we can explain electron donor capacity. Systems with Cr are the best electron donors. HOMOs of HAB-ScCr and HAB-FeCr are bonding orbitals of bis(benzene)chromium, comparable to the HOMO of HAB-Cr, and therefore, I values are similar and lower than for the systems without Cr that manifest more than 1 eV. Clearly Cr dominates electron donor capacity. For all the molecules being studied, evidently the influence of Fe on electron donor/acceptor capacity is less.

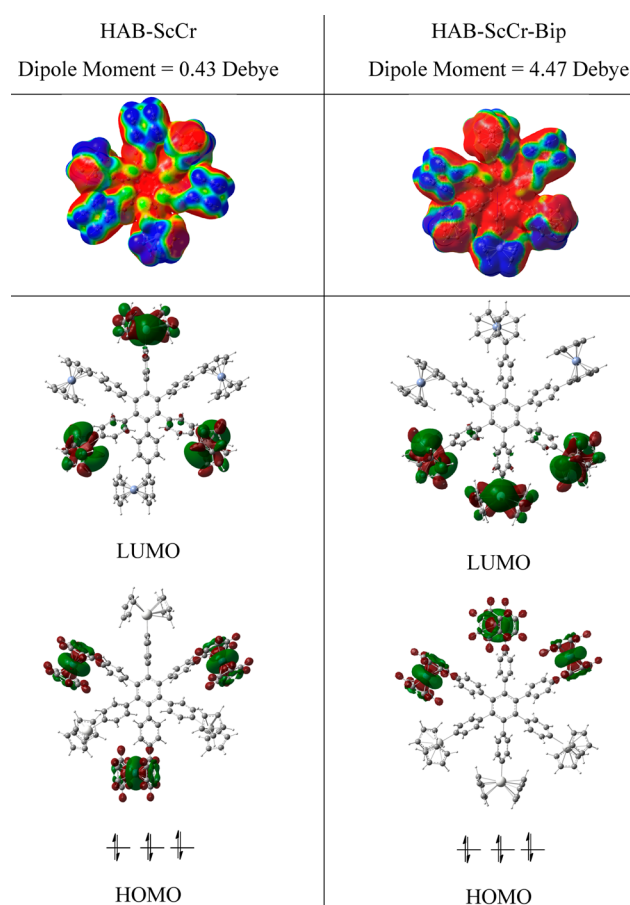


Figure 8. Molecular electrostatic potential and frontier molecular orbitals of compounds with Sc and Cr. Red color indicates negative values of molecular electrostatic potential. Blue color corresponds to positive values of molecular electrostatic potential. Dipole moments are also reported.

Molecular electrostatic potentials reported in Figures 8–10 show important differences. The surfaces of bimetallic compounds with metals located in alternated positions are homogeneous [positive regions (in blue) are outside the molecule, and negative regions (in red) are inside], but this is not the case for systems with the metal atoms situated in one side of the molecules. For HAB-ScCr-Bip and HAB-ScFe-Bip, the positive regions are located on the Sc atoms, and the negative regions (in red) close to Cr and Fe, respectively. This is reflected in the values of the dipole moment that are also reported in Figures 8 and 9. As expected, molecules with the metal atoms located in one side present large dipole moments, compared to their isomers. Large dipole moments are important for solubility and also for reactivity. These molecules have atoms to accept electrons, but they can donate electrons from other atoms. At a local level, they may simultaneously be electron donors and acceptors. Bimetallic compounds with the same metal atom located on one side of the molecule may have two “faces”: one that accepts electrons and another that is able to donate electrons. Therefore, bimetallic compounds may be more effective than monometallic compounds. For example, the combination of Cr and Sc produces a better material, as HAB-ScCr simultaneously represents a good electron donor and good electron acceptor, compared to the other compounds presented in Table 1.

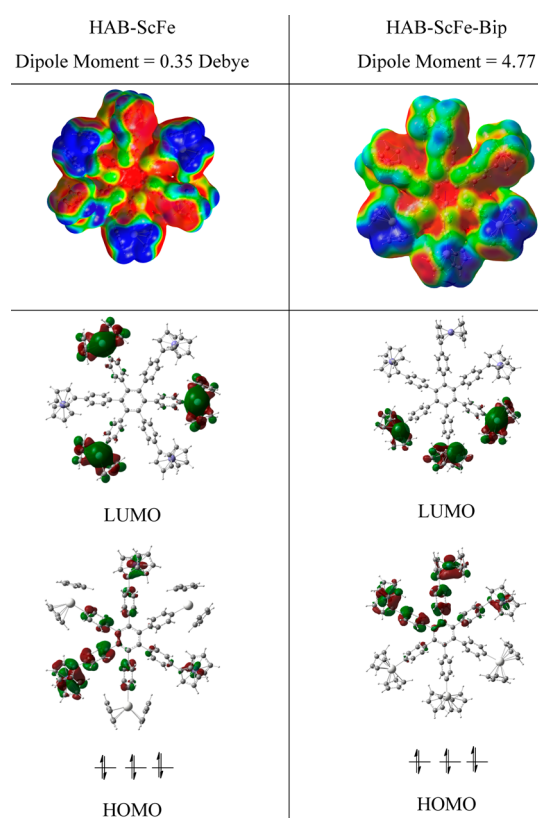


Figure 9. Molecular electrostatic potential and frontier molecular orbitals of compounds with Sc and Fe. Red color indicates negative values of molecular electrostatic potential. Blue color corresponds to positive values of molecular electrostatic potential. Dipole moments are also reported.

Compounds with Cr and Fe show different charge distribution. The differences between HAB-FeCr and HAB-FeCr-Bip are not as great as those for the other systems being studied. The small dipole moment for HAB-FeCr (0.37 D) is similar to the dipole moment of HAB-FeCr-Bip (0.26 D), probably resulting from certain cancellation effects. Both systems show similar molecular electrostatic potential, emphasizing the relevance of the charge distribution onto the donor–acceptor electronic properties of the molecules (very similar for both isomers, see Figure 6). HOMOs are located at bis(benzene)chromium, and LUMOs are bonding orbitals of the benzene rings. As a global result (stability, electron density distribution, and reactivity), it will thus be difficult to distinguish between these isomers.

It is important to note that the toroidal delocalization effect previously reported for HAB disappears due to the presence of the metal atoms. Metals attract electrons, and therefore, electrons cannot be delocalized on the rings that are bonded to the metals. Different properties may be expected for these potential functional materials.

Electrodonating and Electroaccepting Powers. I and A measure the propensity of a system to donate or accept one electron. The electrodonating and electroaccepting powers (ω^- , ω^+) measure the propensity to donate or accept fractional amounts of charge. In this context, these parameters represent reactivity indexes, as one possibility for a reaction is to share electrons that could be measured as the transfer of fractional amounts of charge. In summary, it is possible to classify the systems according to their capacity to share electrons. We

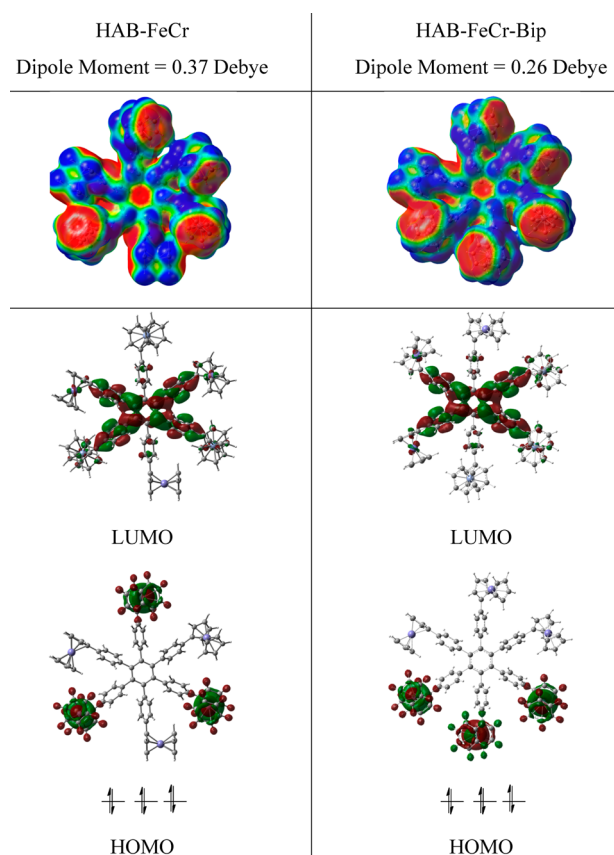


Figure 10. Molecular electrostatic potential and frontier molecular orbitals of compounds with Fe and Cr. Red color indicates negative values of molecular electrostatic potential. Blue color corresponds to positive values of molecular electrostatic potential. Dipole moments are also reported.

classify as electrophiles those compounds with higher ω^+ values and as nucleophiles those with lower ω^- values. Table 1 indicates that HAB-Sc, HAB-ScFe, and HAB-ScFe-Bip are electrophiles and HAB-CrFe and HAB-CrFe-Bip are the best nucleophiles. These results, together with the fact that bimetallic compounds with the same metal atom located at one side of the molecule could have two “faces”, one able to accept electrons and another one able to donate electrons, indicate the possibility that these compounds could have several potential applications.

CONCLUSIONS

The most important geometrical difference between the systems being studied is the σ bond between Sc and one of the carbon atoms of the six member ring of the hexaphenylbenzene core. The systems with Fe and Cr have a C–C σ bond with the six-member ring of the hexaphenylbenzene and present resonance stabilization of the molecule due to the delocalization of the charge. Bimetallic compounds present resonance and nonresonance effects, depending on the position of Sc.

The presence of Sc dominates the electron acceptor capacity and the presence of Cr the electron donor capacity. The sandwich compounds with Cr and Sc produce the best material, as HAB-ScCr is simultaneously the best electron donor and the best electron acceptor. The worst electron donor or acceptor is hexakis(4-ferrocenyl phenyl) benzene. The molecular orbital

picture provides an explanation of the simultaneous ejection of six electrons of HAB-Fe, while also suggesting that HAB-Cr may represent a better electron donor and could also eject six electrons at the same time, similar to hexakis(4-ferrocenyl phenyl) benzene. This is very significant as it means that the very well-known electronic properties of hexakis(4-ferrocenyl phenyl) benzene can be improved by substitution with other metals, such as Sc and Cr. Bimetallic compounds with the same metal atom located on one side of the molecule may have two “faces”, one able to accept electrons and another able to donate electrons. Moreover, compounds with Sc are electrophiles, and compounds with Cr are nucleophiles. This suggests that these compounds could have several potential applications, making it worth the effort to experimentally synthesize this type of functional material.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpca.5b06352.

MO diagrams, cartesian coordinates and total energies of the optimized structures, eigenvalues of some frontier orbitals, and complete references with more than 10 authors (PDF)

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Notes

The authors declare no competing financial interest.

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