Structure and Nature of the Metal−Ligand Interactions in Mixed Iron(II) Phosphametallocenes

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Quantum mechanical calculations at the density functional level (DFT) were carried out in order to analyze the structure and nature of the metal−ligand interactions in mixed iron(II) metallocenes of the type Fe(Cp)(**L**), where **L** stands for the ligands $[C_5H_5]^-$, $[C_4H_4P]^-$, $[1,3\text{-}P_2C_3H_3]^-$, and $[1,2,4\text{-}P_3C_2H_2]^-$. The nature of the metal−ligand interactions is analyzed by means of the charge decomposition analysis (CDA), in which the extent of donation, back-donation, and repulsive polarization of the electron density, in the region of the bond, is discussed in light of the varying number of heteroatoms at the rings. The aromaticity of the free ligands and the energies involved in the ligand displacement reactions for the process $[Fe(Cp)_2] + \mathbf{L}^- \rightarrow [Fe(Cp)(\mathbf{L})] + Cp^-$ were also computed and are discussed. Our results reveal that changing a CH group of the cyclopentadienyl ligand to phosphorus has the effect of changing drastically the electronic structure of the resulting metallocene and, thus, the reactivity of these compounds.

Introduction

Since the first synthesis of phosphaferrocene (a ferrocene analogue having the η^5-cyclopentadienil ligand, Cp, replaced by the phospholyl, $[\eta^5\text{-}C_4H_4P]^-$, ligand) by Mathey and co-workers,[1,2] phosphametallocene complexes have attracted much attention from the chemical community.[3] This is in part motivated by the fact that many metallocenes are well-established active catalysts in many homogeneous catalytic cycles, such as polymerization and hydrogenation of olefins,[4] and thus, the activity and stereo- and regioselectivity of metallocene-based catalysts can, in principle, be changed by replacing one or both Cp's by phospholyl ligands. In fact, in the last 10 years many applications of phosphametallocenes in catalytic reactions have appeared in the literature.[3] As an example, Fu and Garrett[5] and Ganter and co-workers[6] investigated the use of chiral phosphaferrocenes in asymmetric catalysis. Applications of phosphazirconocenes and phosphatitanocenes as catalysts in the polymerization of olefins have also been reported.[7−9] Very recently, Wang and Hollis[10] showed for the first time the application of phosphazirconocene and phosphaferrocene as catalysts for the asymmetric ring opening of epoxides. The authors showed that the reaction does not take place if conventional (Cp-based) zirconocene and ferrocene was used, and so, it was shown that the phospholyl ligand plays a crucial role in the reaction mechanism, which is not fully understood. All these studies have shown the potential of the phospholyl-based metallocenes as alternatives to conventational metallocene-based catalysts, as well as the importance of extensive ligand variation in tuning the catalytic properties. Another important class of five-membered rings containing phosphorus is the polyphospholyl anions[11] $[1,3\text{-}P_2C_3]^-$ and $[1,2,4\text{-}P_3C_2]^-$, which have the ability to coordinate to the transition metal center in several different ways.[11] In fact, ferrocene-like complexes of the type $[Fe(\eta^5\text{-}C_2R_2P_3)_2]$ and $[Fe(\eta^5\text{-}C_2R_2P_3)(\eta^5\text{-}C_3R_3P_2)]$ have been fully structurally characterized by X-ray diffraction,[12] and also, mixed sandwich compounds with iron containing both $\eta^5\text{-}C_5H_5$ and $\eta^5\text{-}C_2R_2P_3$ and $\eta^5\text{-}C_3R_3P_2$ five-membered rings have also been reported.[13] Mössbauer studies on these compounds indicate that the presence of phosphorus atoms in the rings exerts an overall electron-withdrawing effect on the transition metal atom.[11]

The understanding of the electronic structure of these compounds as well as the nature of the metal−ligand interactions involved is an important step for rational ligand design and for the understanding of the reactivity of the phosphametallocenes and polyphosphametallocenes in catalytic reactions. Despite the growing field

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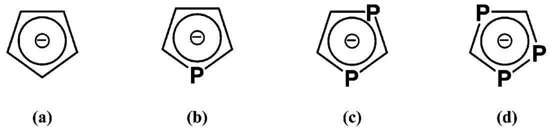
Scheme 1



of applications of phosphametallocenes in catalysis and organic synthesis, there are only a few theoretical studies related to the electronic structure and reactivity of these compounds. Fenske and Kosti,[14] who investigated the bonding in phosphaferrocenes and the reactivity of the phospholyl ligand by means of the Fenske–Hall method,[15] carried out the first theoretical study on phosphametallocenes. In this study it was shown that Cp and phospholyl ligands have similar bonding abilities and form π bonds with the metal d orbitals. It was shown that the electron-donating and electron-accepting properties are nearly equal for both ligands, and the phosphorus lone pair is not affected appreciably upon coordination of the phospholyl ligand to Fe, in accordance with the experimental charge density distribution obtained at low temperature.[16] The influence of electronic and steric effects on the polymerization conditions of ethylene, employing a series of $Cp'(C_5H_5)ZrCl_2$ and Cp'_2ZrCl_2 precatalysts ($Cp' = C_5Me_4H$, C_4Me_4P, C_5Me_5) together with $(C_5H_5)_2ZrCl_2$, was investigated by Janiak and co-workers, in a combined theoretical (ZINDO/1 and DFT) and experimental study.[7] It was concluded that the lower activities of the phospholyl versus the tetra- and pentamethylcyclopentadienyl compounds might imply an electronic effect such that the electron-withdrawing phosphorus substituent decreases the activity, although the authors were unable to measure this effect.

In this work theoretical calculations at the density functional level (DFT) were carried out in order to analyze the structure and the nature of the metal–ligand interactions in mixed iron(II) metallocenes of the type Fe(Cp)(**L**), where **L** stands for the ligands $[C_5H_5]^-$, $[C_4H_4P]^-$, $[1,3\text{-}P_2C_3H_3]^-$, and $[1,2,4\text{-}P_3C_2H_2]^-$, shown in Scheme 1. The ligands **a** and **b** are cyclopentadienyl and phospholyl, respectively. Ligands **c** and **d** are the anionic prototypes of the di- and triphosphols ligands, respectively, synthesized by Nixon and co-workers.[17,18]

Our purpose is to investigate how these ligands change the electronic structure and the reactivity of the resulting iron(II) phosphametallocene complexes. The nature of the metal–ligand interactions will be analyzed by means of the charge decomposition analysis (CDA), in which the extent of donation, back-donation, and repulsive polarization of the electron density, in the region of the bond, will be discussed in light of the varying number of heteroatoms in the rings. The aromaticity of the free ligands and the energies involved in the ligand displacement reactions for the process $[Fe(Cp)_2] + \mathbf{L}^- \rightarrow [Fe(Cp)(\mathbf{L})] + Cp^-$ were also computed and will be discussed.

Theoretical Details

Full geometry optimization and frequency calculations were performed at the gradient-corrected density functional theory (DFT) level using the three-parameter fit of the exchange–correlation potential suggested by Becke[19] in conjunction with the LYP [20] correlation potential (B3LYP). The inner shell electrons (1s, 2s, and 2p) of Fe were treated by the effective core potential of Hay and Wadt (LANL2DZ),[21] and the valence electrons (3s, 3p, 3d, and 4s) were included explicitly in the calculations, using the associated double-ζ basis set in which the original [55/5/5] contraction scheme was changed to a more flexible [441/2111/41] contraction. The use of this contraction scheme for the valence basis set of first-row transition metals has been shown to give good structural results for transition metal complexes.[22] The 6-31G(d) all-electron basis set[23,24] was employed for the ligands, and the atomic charges were computed within the natural bond orbital approach.[25] To obtain better energetic results, we carried out single-point calculations at the fourth-order Møller–Plesset perturbation level of theory (MP4), on the B3LYP optimized geometries, using the same basis set (MP4(SDQ)//B3LYP).

To understand the nature of the metal–ligand interactions in these complexes, we analyzed the B3LYP wave function, using the charge decomposition analysis (CDA) of Dapprich and Frenking.[26] The CDA method consists of using a linear combination of fragment orbitals (LCFO) of properly chosen fragments A and B for the interpretation of the interactions in a molecule AB. The interaction is divided into three main contributions: (i) the mixing between the occupied orbitals of A and empty orbitals of B, which indicates the magnitude of electron donation from A to B (A → B), (ii) the mixing between the occupied orbitals of B with the empty orbitals of A, which gives the extent of back-donation, i.e., the electron donation from B to A (A ← B), and (iii) the mixing between the occupied orbitals of A and the occupied orbitals of B, which indicates the extent of charge polarization in the region of the bonding. Equations 1–3 show the linear combination of fragment orbitals, used in the CDA procedure to obtain the charge donation, qd_i, charge back-donation, qb_i, and charge polarizarion, qr_i, between two fragments of the molecule.

$$qd_i = \sum_{k}^{occ.,A} \sum_{n}^{vac.,B} m_i c_{ki} c_{ni} \langle \Phi_k | \Phi_n \rangle \tag{1}$$

$$qb_i = \sum_{l}^{occ.,B} \sum_{m}^{vac.,A} m_i c_{li} c_{mi} \langle \Phi_l | \Phi_m \rangle \tag{2}$$

$$qr_i = \sum_{k}^{occ.,A} \sum_{m}^{occ.,B} m_i c_{ki} c_{mi} \langle \Phi_k | \Phi_m \rangle \tag{3}$$

This method has been shown to be very useful to explain the nature of the metal–ligand interaction in transition metal compounds.[27] All calculations have been carried out using the program package Gaussian 98.[28]

Results and Discussion

Structure and Aromaticity of the Free Ligands. The optimized B3LYP/6-31G(d) structural parameters

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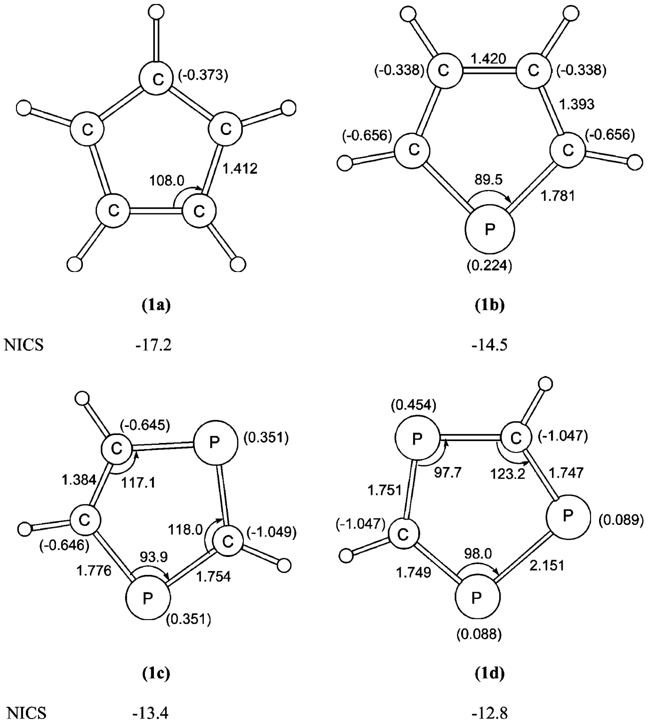

Figure 1. Atomic charges (in parentheses), nucleus-independent chemical shifts at the ring center (in ppm), and optimized structural parameters for the free ligands, computed at the B3LYP/6-31G(d) level of theory. Distances are in Å and angles in deg.

and charge distribution for the free ligands are shown in Figure 1. All six ligands exhibit a planar structure. As seen in Figure 1, the replacement of a C−H group in the cyclopentadienyl (**1a**), by phosphorus, generating structures **1b**−**1d**, decreases the internal bond angle. As a result, structures **1b**−**1d** are more tensioned than Cp (**1a**). The bond angle around phosphorus is increased on going from the monophospholyl (**1b**) to the triphospholyl ligand (**1d**). The P−C bond distance follows an opposite tendency, diminishing on going from **1b** to **1d**, varying from 1.781 to 1.748 Å, respectively. It is important to mention that the phosphorus lone pair in the monophospholyl ligand (**1b**) does not contribute to the highest occupied molecular orbital, HOMO, and the natural atomic charges (see Figure 1) revealed that the carbon atoms adjacent to phosphorus have a high negative charge of −0.656*e*. However, the phosphorus lone pair has a great contribution to the HOMO of the diphospholyl (**1c**) and triphospholyl (**1d**). The carbon atoms of **1d** are negatively charged, with a value of −1.047*e* for each. The carbon atom between the phosphorus in **1c** has a negative charge of −1.049*e*, and the other carbon atoms have negative charges of −0.645*e*. These results indicate that the phosphorus lone pair of ligands **1c** and **1d** may be involved in the bonding to transition metal atoms, which will be discussed later. The fact that the phosphorus lone pair does not contribute to the HOMO of the monophospholyl ligand (**1b**) and the fact that the adjacent carbon atoms are negatively charged may explain the intriguing fact that despite having a lone pair on the P atom, electrophilic substitution into the **1b** ring occurs at the adjacent carbon atoms of the phospholyl nucleus.[16]

Since the synthesis of the first five-membered rings containing phosphorus, phosphole (C_4H_4PR), the key issue concerning these heterocyclic ring systems was their potential aromaticity. Mathey and co-workers[29] and Mislow and co-workers[30] were the first to consider the aromaticity of phosphole and how this aromaticity is connected with the inversion barrier around the phosphorus atom of alkyl-substituted phospholes, by means of photoelecton and NMR spectroscopy. There are several quantitative criteria to measure the aromaticity of a given compound.[31] The most widely used are energetic (aromatic stabilization energies, ASE),[32] structural (nearly equal bond lengths in the ring),[33] and magnetic properties such as magnetic susceptibilities.[34] Schleyer and co-workers[35] proposed the use of absolute magnetic shielding, computed at ring centers, as a criterion to measure the aromatic character of cyclic structures, referred to as NICS (nucleus-independent chemical shifts). Negative NICS values denote aromaticity, whereas small and positive NICS values indicate nonaromaticity. The NICS is indeed a consistent aromaticity probe[35] and has been applied recently to study the aromaticity of poplyphosphaphospholes[36] and arsadiphospholes.[37] We have applied the NICS index to investigate the aromatic character of the free ligands **1a**−**1d**, which is also shown in Figure 1. With the cyclopentadienyl ligand (**1a**), which is a well-known aromatic five-membered ring, the NICS value of −14.5 ppm computed for the phospholyl ligand **1b** is 84% of the NICS value of −17.2 computed for **1a**. The percentage of aromaticity, compared with **1a**, decreases with the increasing number of phosphorus atoms at the ring, being 78% for **1c** and 74% for **1d**. If we compare the absolute NICS values computed for structures **1b**−**1d** with the values computed[35] for pyrrole (−17.3), thiophene (−14.7), and furan (−13.9), which are also well-known aromatic five-membered rings, we can see that the ligands (**1b**−**1d**) are indeed aromatic. In conclusion, we

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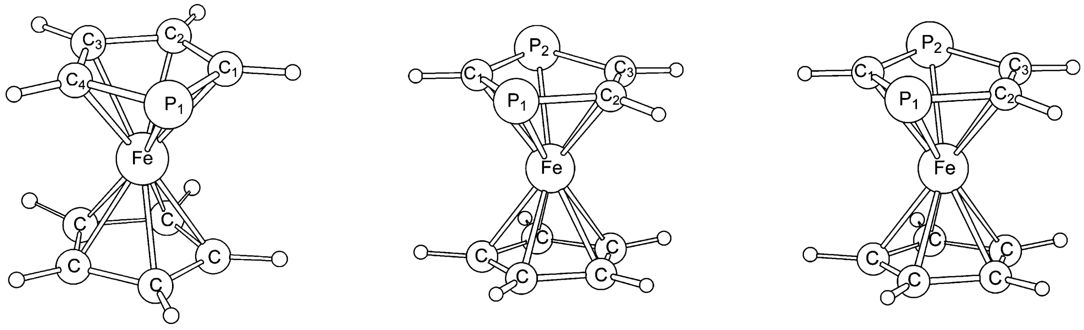

(2a) **(2b)** **(2c)**

(2a)

Fe-P$_1$ = 2.353 (2.283)
Fe-C$_1$ = 2.103 (2.071)
Fe-C$_2$ = 2.073 (2.057)
Fe-C$_3$ = 2.073 (2.053)
Fe-C$_4$ = 2.103 (2.059)
Fe-Cp = 1.679 (1.655)
Fe-L = 1.682 (1.634)
P-C$_1$ = 1.791 (1.774)
P-C$_4$ = 1.791 (1.774)
C$_1$-C$_2$ = 1.418 (1.424)
C$_2$-C$_3$ = 1.426 (1.436)
C$_3$-C$_4$ = 1.436 (1.422)
∠ L-Fe-Cp = 178.6

(2b)

Fe-P$_1$ = 2.354 (2.294)
Fe-P$_2$ = 2.353 (2.292)
Fe-C$_1$ = 2.131 (2.191)
Fe-C$_2$ = 2.107 (2.158)
Fe-C$_3$ = 2.107 (2.153)
Fe-Cp = 1.685 (1.710)
Fe-L = 1.675 (1.680)
P$_1$-C$_1$ = 1.776 (1.747)
P$_1$-C$_2$ = 1.786 (1.790)
C$_2$-C$_3$ = 1.410 (1.439)
P$_2$-C$_3$ = 1.796 (1.796)
P$_2$-C$_1$ = 1.776 (1.741)
∠ L-Fe-Cp = 179.3

(2c)

Fe-P$_3$ = 2.356 (2.302)
Fe-P$_2$ = 2.399 (2.312)
Fe-P$_1$ = 2.399 (2.319)
Fe-C$_1$ = 2.125 (2.130)
Fe-C$_2$ = 2.124 (2.131)
Fe-Cp = 1.688 (1.683)
Fe-L = 1.660 (1.620)
P$_3$-C$_1$ = 1.771 (1.764)
C$_1$-P$_2$ = 1.772 (1.755)
P$_2$-P$_1$ = 2.172 (2.061)
P$_1$-C$_2$ = 1.772 (1.770)
C$_2$-P$_3$ = 1.771 (1.765)
∠ L-Fe-Cp = 179.7

Figure 2. Selected structural parameters computed at the B3LYP level of theory. Experimental values are in parentheses and were taken from refs 16, 38, and 39. Fe−**L** and Fe−Cp are the distances of the iron atom to the center of the phospha- and cyclopentadienyl ligands, respectively. Distances are in Å and angles in deg.

can say that the mono-, di-, and triphospholyl ligands have a planar structure with a high degree of aromaticity.

Structure of the Mixed Sandwich Complexes and Nature of the Metal−Ligand Interactions. The optimized B3LYP structural parameters for the mixed coordination compounds Fe(Cp)(**L**) (**L** = **1b**−**1d**) are shown in Figure 2. As seen in Figure 2, the optimized structures are in reasonable agreement with the experimentally determined structures. The largest deviations are found for the bond distances between the metal and the phosphorus atoms. For instance, the Fe−P bond length of 2.353 Å in **2a** deviates 0.07 Å from the experimental value of 2.283 Å obtained for the [Fe(η^5-Cp)(η^5-(3,4-dimethyl-1-phosphacyclopentadienyl))] complex.[16] The Fe−P$_1$ and Fe−P$_2$ bond lengths of 2.354 and 2.353 Å, respectively, in **2b** are 0.06 Å overestimated as compared with the experimental values of 2.294 and 2.292 Å, respectively, in the compound [Fe(η^5-Cp*)-(η^5-(tri-*tert*-butyl-1,3-diphosphacyclopentadienyl)].[38] In compound **2c** the Fe−P$_1$ bond length is 0.08 Å greater than the experimental value of 2.130 Å found for the complex [Fe(η^5-Cp)(η^5-(3,5-di-*tert*-butyl-1,2,4-triphosphacyclopentadienyl))].[39] The Fe−C$_1$ (2.125 Å) and Fe−C$_2$ (2.124 Å) bond distances in **2c** are well reproduced when compared with the experimental values of 2.130 and 2.131 Å, respectively. In compound **2a** the computed Fe−C distances are within 0.04 Å of error. For compound **2b**, there is an underestimation of all Fe−C bonds, compared with the experimental value, the deviation being within 0.06 Å. It is interesting to see that if we compare the bond lengths computed for the free ligands, shown in Figure 1, with those computed for the coordinated ligands in Figure 2, we can see that upon coordination there is an increase of all bond lengths at the ring. For instance, the C−C distance of 1.420 Å in **1b** changes to 1.426 Å (C$_2$−C$_3$) in **2a**. This fact may be connected with the nature of the metal−ligand interaction, which will be discussed later. The computed distance of the iron atom to the center of the rings of the ligands (Fe−**L**) shows an interesting trend. If we compare the Fe−**L** distances in **2a**−**2c**, in which the number of phosphorus atoms at the ring increases from one to three, the Fe−**L** distance diminishes from 1.682 Å in **2a** to 1.660 Å in **2c**. The distance between the Fe atom and the center of the Cp ring in complexes **2a**−**2c**, on the other hand, increases with the increasing number of phosphorus atoms at the opposite side, assuming the value of 1.679 Å in **2a**, 1.685 Å in **2b**, and 1.688 in **2c**. These facts suggest that, upon coordination, the ligands **1b**, **1c**, and **1d** have a more effective interaction with the iron atom, which reduces the Fe−**L** distance and weakens the Fe−Cp interaction. It should be clear that the experimentally determined structures contain bulky substituents at the ring that, in our model, were all replaced by hydrogen. These bulky substituents (for example, *tert*-butyl in **2b** and **2c**) will exerts some kind of steric pressure at the ring, which may be the source of disagreement between the computed and experimental structural parameters. Regardless, we may say that the computed B3LYP structural values are in overall reasonable agreement with the experiment.

The energetics involved in the ligand displacement reactions is quoted in Table 1. Substitution of Cp in [Fe(Cp)$_2$] by the ligands **1b**−**1d** is not an spontaneous process. The variation of the Gibbs free energy, ΔG, computed at the B3LYP level, for the replacement of Cp by the monophospholyl (**1b**) was 16.4 kcal/mol, and this value increases with an increasing number of phosphorus at the ring, being 28.8 and 37.6 kcal/mol for the di- and triphospholyl **1c** and **1d**, respectively. The inclusion of higher correlation levels decreases drastically both ΔE and ΔG values, compared with those

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Table 1. Energies (kcal/mol) Involved in the Ligand Displacement Reactions $Fe(Cp)_2 + L^- \rightarrow Fe(Cp)(L) + Cp^-$ (L = 1b−1d)

	B3LYP		MP4(SDQ)//B3LYP	
displacement reaction	ΔE	ΔG	ΔE	ΔG
$Fe(Cp)_2$ + (**1b**) → Fe(Cp)(**1b**) + Cp^-	17.8	16.4	14.6	13.2
$Fe(Cp)_2$ + (**1c**) → Fe(Cp)(**1c**) + Cp^-	30.2	28.8	22.1	20.7
$Fe(Cp)_2$ + (**1d**) → Fe(Cp)(**1d**) + Cp^-	39.3	37.6	24.5	23.9

Table 2. Summary of the Charge Decomposition Analysis (CDA) for the Mixed Complexes [Fe(Cp)(L)] (L = 1a−1d)[a]

	Fe(Cp)(**1a**)	Fe(Cp)(**1b**)	Fe(Cp)(**1c**)	Fe(Cp)(**1d**)
Σ donation	1.115	1.056	0.901	0.461
Σ back donation	0.248	0.310	0.355	0.385
Σ rep.	−0.303	−0.252	−0.221	−0.197
Σ res.	−0.056	−0.113	−0.165	−0.251
$\sum b/\sum d$ (%)	22.2	29.4	39.4	83.5
q_{Fe}	0.232	0.176	0.115	0.057

[a] The CDA analyses were performed assuming $[Fe(Cp)]^+$ as the acceptor fragment.

obtained at the B3LYP level of theory. For instance, the ΔE and ΔG values, computed for the displacement reaction of Cp by **1d**, decreases by 14.8 and 13.7 kcal/mol, respectively, by inclusion of fourth-order perturbation at the B3LYP geometries (MP4//B3LYP). The MP4 results presented in Table 1 should be treated with caution, since it is not a full MP4 calculation with inclusion of triple substitution, which may be important. However both results presented in Table 1 show that the ligand displacement reactions are an endothermic process.

To obtain a better insight into the nature of the metal−ligand interactions, we have analyzed the B3LYP wave function using the charge decomposition analysis (CDA) method,[26] and the results for the metallocene complexes Fe(Cp)(**L**) (**L** = **1a**−**1d**) are shown in Table 2. As can be seen from the first entry of Table 2, the mono- (**1b**), di- (**1c**), and triphospholyl (**1d**) ligands are weaker donor than the cyclopentadienyl ligand **1a**. The extent of donated charges from the ligand to the metallic fragment reduces from 1.115*e* for Cp to 0.461*e* in the triphospholyl ligand (**1d**), which corresponds to a reduction of 59% of the donated charges. All ligands are stronger π-acceptors than Cp, as can be seen in the second entry of Table 2. The magnitude of the back-donated charges from the metallic fragment to the ligand increases progressively on going from (Cp), 0.248*e*, to the triphospholyl (**1d**), 0.385*e*, which corresponds to an increase of 55% of the back-donated charges. These trends in the donated and back-donated charges can also be seen in Figure 3, in which the increasing of back-donated charges and the diminishing of the donated charges can easily be seen. The ratio between the back-donated charges from the metallic fragment and the donated charges from the ligand, $\sum b/\sum d$ (entry 6 in Table 2), reveals that the triphospholyl ligand (**1d**) is the stronger π-acceptor ligand, within the ligands studied, showing a ratio of 83.5%.

Since the ligands **1b**−**1d** are stronger π-acceptors than Cp, we should expect a decrease of the charges at the iron atom, compared with the computed charge for ferrocene. In fact the last entry of Table 2 shows that these ligands remove electron density away from the metal, with the computed NBO charges for the iron atom changing from 0.232*e* in $[Fe(Cp)_2]$ to 0.057*e* in [Fe(Cp)(**1d**)]. The ligands **1b**−**1d**, due to their more effective interaction with the metallic fragment, exert an overall *trans* effect, which weakens the Fe−Cp bond, and as a result, the Fe−Cp distance will progressively increase on going from **2a** to **2c** (see Figure 2).

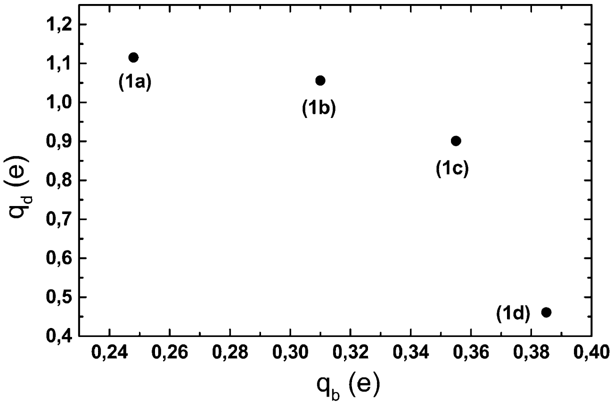

Figure 3. Variation of the donated charges from the ligand and back-donated charges from the metallic fragment for the mixed complexes [Fe(Cp)(**L**)], in which **L** is specified in the figure.

The analysis of the molecular orbitals reveals that the phosphorus lone pair of the mono- and diphospholyl ligands does not participate in the frontier orbitals of the complexes. Figure 4 shows the highest occupied molecular orbital (HOMO) for the complexes **2a**−**2c**. The HOMOs of complexes **2a** and **2b** are centered on the metal (exclusively $3d_{xy}$). The phosphorus lone pair contributes only to the HOMO−2 orbital, which is 5 kcal lower in energy than the HOMO orbital in **2b** and 16 kcal lower in energy than the HOMO orbital of **2a**. However, the HOMO orbital of complex **2c** has a great contribution of the phosphorus lone pair, with the HOMO−1 orbital, which is centered at the metal, lying 3.6 kcal below the HOMO orbital. These results indicate that in the mixed complex [Fe(Cp)(**1d**)] the lone pair of the phosphorus atoms may coordinate to another transition metal atom through a σ donation of electron density from the lone pairs. In fact, complexes of the type $[Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_2R_2P_3)W(CO)_5]$, in which the tungsten is attached to one of the last sterically hindered phosphorus atoms, have been fully characterized by X-ray diffraction.[13] In complexes **2a** and **2b**, the phosphorus lone pairs are lower in energy, which makes it difficult to participate in this kind of interaction.

All these results reveal that changing a CH group of the cyclopentadienyl ligand to phosphorus changes drastically the electronic structure of the resulting metallocene and, thus, the reactivity of these compounds. For instance, the results suggest that if the compound [Fe(Cp)(**1d**)] is employed in some reactions in which the substrate is electron deficient, the reaction will take place, preferentially, at the ring containing the phosphorus atoms. This is consistent with the experimental findings, which show that electrophilic substitution reactions (acylation, formylation, and carboxylation) into the monophosphaferrocene complexes takes place most exclusively at the phospholyl ring.[1−3] Mixed iron(II) complexes with the triphospholyl ligand, in which one of the phosphorus atoms is also coordinated

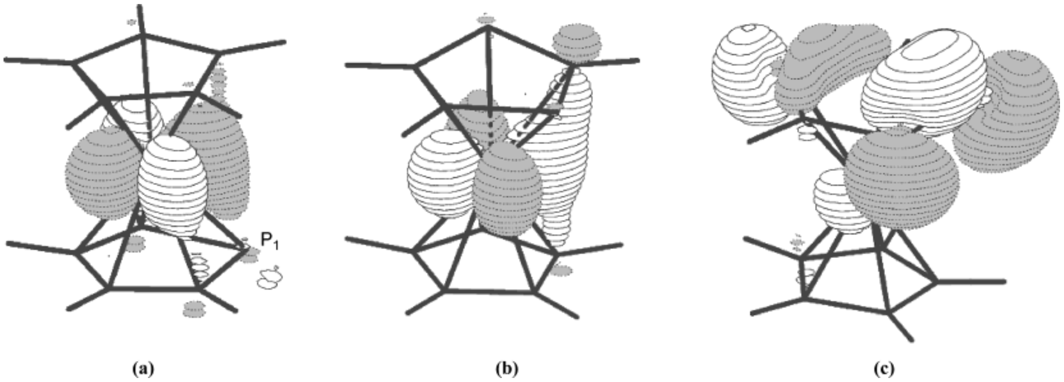

Figure 4. Highest occupied molecular orbital (HOMO) for the mixed complexes Fe(Cp)(**1b**) (a), Fe(Cp)(**1c**) (b), and Fe(Cp)(**1d**) (c).

to an organometallic unit, have also been observed experimentally,[11] which gives support to our assumptions.

Summary and Conclusions

In this work quantum mechanical calculations at the density functional level (DFT) were carried out in order to understand the structure and the nature of the metal−ligand interactions in mixed iron(II) compounds of the type Fe(Cp)(**L**), where **L** stands for the ligands $[C_5H_5]^-$, $[C_4H_4P]^-$, $[1,3\text{-}P_2C_3H_3]^-$, and $[1,2,4\text{-}P_3C_2H_2]^-$. Geometry optimization and frequency calculations were performed using the hybrid B3LYP functional, which gave good geometrical results for the free ligands and for the mixed phosphametallocenes as compared with the experimental data available. The nucleus-independent chemical shifts (NICS) analysis showed that the replacement of CH groups of Cp by phosphorus reduces the aromaticity of the resulting anionic rings, but the structures remain with a high degree of aromaticity. All bond lengths of the free ligands increase upon coordination to the metallic fragment. The ligand displacement reaction $\mathrm{Fe(Cp)_2} + \mathbf{L}^- \rightarrow \mathrm{Fe(Cp)}(\mathbf{L}) + \mathrm{Cp}^-$ (**L** = **1b**−**1d**) is an endothermic process, and the inclusion of a higher electronic correlation, up to the fourth-order level of perturbation theory, at the B3LYP optimized geometries, MP4(SDQ)//B3LYP, decreases the endothermicity of the reaction. The analysis of the metal−ligand interactions, using the charge decomposition analysis (CDA), revealed that replacing a CH group of the cyclopentadienyl ligand with phosphorus changes drastically the electronic structure of the resulting phosphametallocene and, thus, the reactivity of these compounds. The extent of donated charges from the ligands to the metallic fragment decreases with the increasing number of phosphorus atoms at the ring, and the magnitude of the back-donated charges from the metallic fragment to the ligands increases. That is, the phosphacyclopentadienyl ligands are stronger π-acceptors and weaker σ-donors than Cp. The phosphorus lone pairs do not contribute to the frontier molecular orbital HOMO of the mixed phosphametallocene when the mono- and diphospholyl ligands are used. However, the major contribution for the HOMO in the mixed complex comes from the phosphorus lone pair when the triphospholyl ligand is used. The analysis of the nature of the metal−ligand interactions presented here is consistent with the experimental evidence of the reactivity of these iron(II) phosphametalocenes. There are many (not understood) aspects of the reactivity of phosphametallocenes in homogeneous catalysis, which are under investigation in our group, mainly in asymmetric catalysis, and we do believe that the results presented here are an important step for these studies, which will be available in future publications.

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Supporting Information Available: Tables containing total energies, zero-point vibrational energies, and thermal corrections to the Gibbs free energy computed for the free ligands **1a**−**1d** and the complexes **2a**−**2c** and the optimized structures of the free ligands and complexes, in Cartesian coordinates. This material is available free of charge via the Internet at http://pubs.acs.org.

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