Electronegativity Versus Lone Pair Shape: A Comparative Study of Phosphaferrocenes and Azaferrocenes

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The electron localization function (ELF), calculated at the DFT/B3LYP level of theory, has been used to analyze various phosphaferrocenes and azaferrocenes. The analysis of the bonding situation and electronic structure in the complexes reveals the importance of the shape of the heteroelement lone pair. Thus, the electron-withdrawing capability of the heteroatom-substituted ring is not only a consequence of electronegativity but also a result of the extension of the lone pair. Our data allow a model of the electrophilic reactivity of these complexes to be proposed.

Introduction

Since first synthesized by one of us in 1977,[1,2] phosphaferrocenes, labeled PFe hereafter, have been the subject of increasing interest, especially in the fields of catalysis and coordination chemistry.[3−18] PFes might be considered to belong to the wider phosphametallocene family[19] and are the heavier analogues of azaferrocenes, which have also been studied intensively.[20] The PFes result from η^5 coordination of a phospholyl ring to an organometallic fragment. From an orbital point of view, the η^5 coordination of either $C_5H_5^-$ or $C_4H_4P^-$ to transition metals has been shown to be comparable,[21] the main interaction involving electron donation from the ring to the metal. In the phospholyl case, the η^5 coordination mode competes with η^1 coordination through the lone pair at phosphorus. η^5 coordination can also be achieved with polyphospholyl rings $(CH)_{5−n}P_n^-$ ($2 \leq n \leq 5$),[19] which have similar aromaticity to that of cyclopentadienyl $C_5H_5^{-}$ [22] and where the same kind of interaction is still present.[23,24] This situation contrasts with the case of five-membered rings containing several nitrogen atoms, where η^5 coordination is very rare when dealing with rings incorporating two nitrogen atoms[25] and, as far as we know, is still unknown with more than two nitrogen atoms. Furthermore, it should be noted that the dearth of η^5-coordinated nitrogen-containing five-membered heterocycles does not seem to come from weak interaction energy: a recent calculation comparing $FeCp_2$ with $Fe(\eta^5\text{-}N_5)_2$ shows N_5^- to have a bonding energy to iron comparable to that of cyclopentadienyl.[26]

The reactivity of phosphametallocenes exhibits subtle differences that depend on the nature of the complex. On one hand, in their $[Mn(CO)_3)]$ complexes, the reactivity of the phospholyl ring toward electrophiles is much lower than that of the Cp ring,[27] as expected from intuitive arguments based on a lower value of the electronegativity for phosphorus (2.1) than for carbon (2.5). On the other hand, Friedel−Crafts acetylation of phosphaferrocene occurs solely on the phospholyl ring,[2] which is consistent with IR and Raman spectroscopic studies showing that the monophospholyl ligand is a better electrophile and poorer π-electron donor than cyclopentadienyl.[28] Electrochemical investigations, which indicate that PFes are harder to oxidize than ferrocene,[29,30] also confirm this view. From these studies, it has been concluded that the P atom in the ring exerts a greater electron-withdrawing effect on the metal than on the C atoms.[31] A similar conclusion has been recently reached from a combined photoelectron spectroscopy and density functional theory analysis of polyphospholyl sandwich compounds, which showed that the replacement of RC fragments by P atoms in η^5-ligated cyclopentadienyl rings increases their acceptor properties.[24]

A better understanding of the electron distribution in these systems makes a more detailed study worthwhile. Recently, we have shown that ELF analysis[32,33] gives interesting insights into the η^5 and η^6 bonding modes in ferrocene and dibenzenechromium, respectively.[34] In this context, we have decided to investigate phosphaferrocenes and azaferrocenes using the same methodology.

Methodology

We performed DFT/B3LYP calculations on all of the metallocenes given in Chart 1. All calculations were carried out with the Gaussian 98[35] suite of programs using the 6-31G* basis set[36,37] containing 6 Cartesian d and 10 Cartesian f functions. Geometry optimizations were performed by utilizing Becke's hybrid three-parameter exchange functional and the nonlocal correlation functional of Lee, Yang, and Parr (B3LYP)[38,39] for all compounds. All of the heterometallocenes that were studied were optimized in both the eclipsed and staggered conformations (C_s symmetry). A vibrational analysis was performed at each stationary point. In each case, one almost-zero frequency corresponding to the free rotation of the rings was found. ELF calculations were then effected using the wfn output from B3LYP runs with the TopMod series of programs.[40] Inspections of charge and hybridization were performed using the natural bond orbital (NBO) partitioning scheme.[41]

The difference between the eclipsed and staggered structures is negligible for all of the compounds examined in this study. So, for the sake of conciseness, only data obtained for staggered

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CHART 1: Molecules Studied in This Investigation

X = CH, N, P,
N→BH$_3$, P→BH$_3$

X$_5$ = (CH)$_{5-n}$P$_n$, (CH)$_{5-n}$N$_n$
(2 ≤ n ≤ 5)
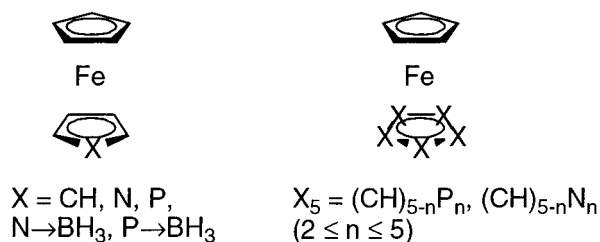
structures are presented here. Cartesian coordinates and absolute energies of all of the optimized structures are given in the Supporting Information.

Results and Discussion

Table 1 shows selected results for compounds **1**−**17**. We first describe data obtained for a single substitution of a CH group by N or P (compounds **1**−**3**). Subsequently, we give the results obtained upon N and P complexation by BH$_3$ (compounds **4** and **5**), and finally give results pertaining to the polysubstitution of CH by N or P atoms (compounds **6**−**17**).

Prior to the detailed analysis of the calculated results, we briefly review the vocabulary of ELF, which is now widely used. An ELF calculation partitions molecular space in terms of attractors and basins. We thus define monosynaptic basins, labeled V(X), for which the electronic domain of the attractor bears a single boundary with an atomic core of atom X, labeled C(X). These basins are associated with classical lone pairs. Disynaptic basins, labeled V(X, Y), correspond to bonds between X and Y, and trisynaptic basins, labeled V(X, Y, Z,) are typical of three-centered bonds between atoms X, Y, and Z.

Monosubstitution of CH by N or P. In reference compound **1**, the C atoms are linked to the metal by two kinds of bonds, which are described by the η^1 (disynaptic type, entries V(Fe, 1), V(Fe, 2), V(Fe, 3)) and η^2 modes (trisynaptic type, entries V(Fe, 1, 2), V(Fe, 2, 3), V(Fe, 3, 3′)). The Fe core bears a total electron population of 24.14, showing that slightly fewer than two electrons are provided to the rings. This result is in good agreement with the classical formalism that invokes a central Fe^{II} atom. The ELF partition of the molecular space into basins is roughly the same for **2** and **3** (Figure 1), but both of these compounds differ strikingly from **1**. Whereas the trisynaptic basins V(Fe, 1, 2), V(Fe, 2, 3), and V(Fe, 3, 3′) have electronic populations ranging from 2.10 to 2.65 e, which are similar to those in **1**, the populations of the disynaptic V(Fe, 1) basins sharply increase to 3.08 e (V(Fe, N)) and 3.33 e (V(Fe, P)) (Table 1).

These η^1 bonds implicate the heteroelement lone pair whose contact with the Fe core gives rise to V(Fe, N) and V(Fe, P) basins. A surprising result is found with these two basins: unlike the V(Fe, C) basins in **1**, the attractor is not located between the Fe and the ring atom but remains in the ring plane, as would be expected for a true monosynaptic lone pair.

Whereas this result seems to indicate a discontinuity between the C−Fe bonds and their N− or P−Fe counterparts in heteroferrocenes, it is deceptive and does not reflect the chemical situation. For carbon atoms that have a hydrogen atom, the ELF function shows two attractors corresponding to the V(C, H) and V(Fe, C) basins. For the V(Fe, C) basins, the difference between the ELF value at its maximum (ELF = 0.732 for **1**) and at its border with the V(C, H) basin (ELF = 0.664 for **1**) is small. Therefore, minor variations of electronic density can make this

saddle point disappear and generate a single basin, which is what happens when N or P atoms replace CH.

The shapes of V(Fe, N) and V(Fe, P) are not the same for each heteroelement (Figure 1). In **2**, V(Fe, N) is compact and directional. This result is in accordance with the high p character of the N atom in the localized orbital corresponding to the lone pair because sp$^{1.84}$ hybridization is found in the NBO analysis. In **3**, V(Fe, P) is diffuse and spherical as a result of the high s character (hybridization sp$^{0.48}$) implicit in the closeness of the CPC angle (88.3°) to 90°, where there is no sp hybridization. This difference in shape clearly indicates that the iron will overlap less with the nitrogen atom than with the phosphorus. Experimentally, both the pyrrolyl[42] and phospholyl[43] ligands have been shown to undergo ring-slippage from η^5 to η^1 coordination modes through their lone pairs. However, unlike phospholyl, where the equilibrium is largely displaced in favor of an η^5 coordination mode, the pyrrolyl shows predominantly η^1 coordination. Our results could then explain this greater preference for the η^1 coordination mode in N heterocycles than in their P-containing counterparts. In **3**, the spherical nature of the basin still affords the possibility of bonding the lone pair of phosphorus to other transition metals or to Lewis acids lying below or above the ring plane.[3,15]

The electron populations in V(Fe, N) (3.08 e) and V(Fe, P) (3.33 e) are higher than that in the CH bond in **1**, whose calculated value is 2.16 e, and are also larger than the sum of the populations of V(C, H) and V(Fe, C) (2.55 e in **1**). Two different types of effects could explain why V(Fe, N) and V(Fe, P) show such high electronic populations. For nitrogen, high electronegativity concentrates the electrons close to N. For phosphorus, the greater radii of the 3s and 3p atomic orbitals provide more space for the electrons, so even though phosphorus is less electronegative than carbon, it can withdraw π electrons into the space formally associated with its polarizable lone pair. This effect reflects the soft character of the P atom that becomes a "π acceptor" and constitutes a general characteristic in unsaturated phosphorus compounds where the V(P) basin often possesses many more than two electrons (2.7 e in H$_2$C=PH and 3.5 e in HC≡P, which could be compared to the value of 2.2 e in H$_3$C−PH$_2$).[44]

The large electron populations of the V(Fe, N) and V(Fe, P) basins induce population decreases in the adjoining basins V(Fe, N, C) and V(Fe, P, C) (2.10 and 2.30 e in **2** and **3**, respectively, instead of 2.54 e in V(Fe, C, C) in **1**). However, although significant electronic relocalization is observed upon CH substitution by N or P, no major change is found in the total population of either the Cp or the substituted ring, as shown by the $\Delta[\Sigma(Cp)]$ and $\Delta[\Sigma(Xp)]$ values in Table 1. Both the pyrrolyl and phospholyl rings "gain" fewer than 0.06 electrons. The large population increase around the heteroelement shows that the C$_4$ fragment in the heterocycle becomes less populated by electrons, and this lower population could explain why the reactivity of the phospholyl ring toward electrophiles is lower than that of Cp.[27] This change is amplified by polysubstitution, as will be discussed latter.

BH$_3$ Complexes 4 and 5. The above results defining the η^5 coordination of the pyrrolyl and phospholyl complexes in **2** and **3**, respectively, were extended to a study of their complexes with the Lewis acid BH$_3$ to give **4** and **5**, respectively.

First, the vibrational analysis shows differences in the curvature of the potential energy surface in the neighborhood of the optimized structures (Table 2). Both the out-of-plane and in-plane BH$_3$ bending modes are noticeably smaller for **5** (70 and 138 cm^{-1}) than for **4** (113 and 275 cm^{-1}). These values

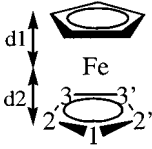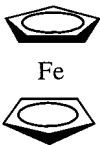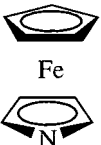**TABLE 1: Bond Lengths, Natural Charges, and ELF Analysis of Compounds 1−17 at the B3LYP/6-31G* Level**
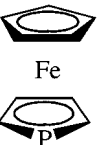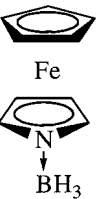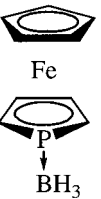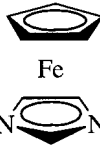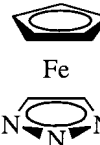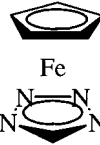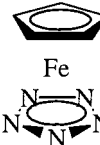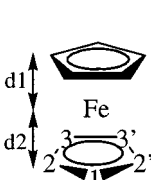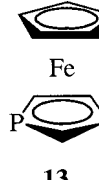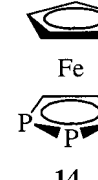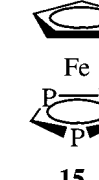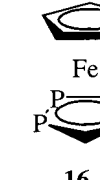
	1[a]	2	3	4	5
Bond Lengths, Å					
1−2	1.427	1.382	1.789	1.387	1.764
2−3	1.427	1.423	1.417	1.416	1.419
3−3′	1.427	1.424	1.425	1.425	1.426
Fe-1	2.053	2.039	2.321	2.013	2.271
Fe-2	2.053	2.025	2.078	2.024	2.085
Fe-3	2.053	2.068	2.056	2.073	2.056
$d1$	1.655	1.653	1.662	1.658	1.663
$d2$	1.655	1.659	1.651	1.654	1.646
Natural Charges					
$q(Fe)$	+1.02	+1.03	+0.99	+1.03	+0.98
$q(Cp)$	−0.51	−0.47	−0.45	−0.38	−0.40
$q(Xp)^b$	−0.51	−0.56	−0.54	−0.65	−0.58
Population in Electrons					
$V(Fe, 1, 2)^c$	2.54	2.10	2.30	2.12	2.44
$V(Fe, 2, 3)^c$	2.54	2.65	2.54	2.70	2.52
$V(Fe, 3, 3′)$	2.54	2.50	2.59	2.52	2.62
$V(Fe, 1)$	0.39	3.08	3.33	2.97^h	0.85^i
$V(Fe, 2)^c$	0.39	0.45	0.39	0.45	0.43
$V(Fe, 3)^c$	0.39	0.38	0.29	0.33	0.30
$C(Fe)$	24.14	24.16	24.11	24.18	24.09
$\Delta[\Sigma(Cp)]^d$	−0.07	−0.10	−0.10	−0.17	−0.15
$\Delta[\Sigma(Xp)]^{b,e}$	−0.07	−0.06	−0.01	−0.01	+0.06
$\Sigma V(Fe, C)^f$	1.95	1.78	1.82	1.75	1.78
$\Sigma V(Fe, C, C)^g$	12.65	12.69	12.73	12.70	12.69

	6	7	8	9	10	11
Bond Lengths, Å						
1−2	1.416	1.375	1.381	1.368	1.364	1.361
2−3	1.380	1.380	1.372	1.375	1.369	1.361
3−3′	1.386	1.419	1.409	1.385	1.379	1.361
Fe-1	2.087	1.997	1.969	2.075	2.032	2.006
Fe-2	2.037	2.051	2.015	2.013	2.036	2.006
Fe-3	2.000	2.037	2.057	2.015	1.983	2.006
$d1$	1.651	1.650	1.650	1.648	1.649	1.647
$d2$	1.650	1.658	1.645	1.656	1.644	1.638
Natural Charges						
$q(Fe)$	+1.05	+1.04	+1.06	+1.06	+1.08	+1.09
$q(Cp)$	−0.42	−0.43	−0.37	−0.37	−0.32	−0.26
$q(Xp)^b$	−0.63	−0.62	−0.69	−0.69	−0.76	−0.83
Population in Electrons						
$V(Fe, 1, 2)^c$	2.62	2.16	1.67	2.15	2.27	1.78
$V(Fe, 2, 3)^c$	2.19	2.06	2.19	2.31	1.67	1.78
$V(Fe, 3, 3′)$	1.59	2.77	2.75	1.58	1.75	1.78
$V(Fe, 1)$	0.34	0.56	3.45	3.05	0.47	3.34
$V(Fe, 2)^c$	0.42	3.08	3.20	0.50	3.20	3.34
$V(Fe, 3)^c$	3.24	0.44	0.39	3.23	3.41	3.34
$C(Fe)$	24.18	24.18	24.18	24.18	24.19	24.20
$\Delta[\Sigma(Cp)]^d$	−0.16	−0.15	−0.20	−0.19	−0.28	−0.33
$\Delta[\Sigma(Xp)]^{b,e}$	−0.02	−0.03	+0.02	+0.01	+0.09	+0.13
$\Sigma V(Fe, C)^f$	1.80	1.80	1.70	1.72	1.62	1.62
$\Sigma V(Fe, C, C)^g$	12.68	12.71	12.74	12.72	12.74	12.69

TABLE 1: (Continued)

	12	13	14	15	16	17
Bond Lengths, Å						
1−2	1.415	1.774	2.156	1.769	1.766	2.137
2−3	1.782	1.783	1.778	1.771	2.148	2.137
3−3′	2.171	1.410	1.407	2.161	2.143	2.137
Fe-1	2.061	2.102	2.408	2.330	2.082	2.407
Fe-2	2.072	2.325	2.362	2.094	2.371	2.407
Fe-3	2.361	2.085	2.078	2.368	2.408	2.407
$d1$	1.667	1.668	1.674	1.676	1.684	1.695
$d2$	1.639	1.642	1.627	1.622	1.605	1.578
Natural Charges						
q(Fe)	+0.96	+0.97	+0.93	+0.95	+0.91	+0.87
q(Cp)	−0.39	−0.39	−0.33	−0.34	−0.29	−0.25
q(Xp)[b]	−0.57	−0.58	−0.60	−0.61	−0.62	−0.62
Population in Electrons						
V(Fe, 1, 2)[c]	2.57	2.25	1.82	2.29	2.25	1.80
V(Fe, 2, 3)[c]	2.68	2.66	2.63	2.23	1.85	1.80
V(Fe, 3, 3′)	1.85	2.54	2.56	1.92	1.82	1.80
V(Fe, 1)	0.20	0.52	3.46	3.17	0.47	3.39
V(Fe, 2)[c]		3.24	3.32	0.48	3.26	3.39
V(Fe, 3)[c]	3.37			3.28	3.40	3.39
C(Fe)	24.10	24.07	24.08	24.04	24.06	24.08
Δ[Σ(Cp)][d]	−0.15	−0.13	−0.19	−0.20	−0.24	−0.27
Δ[Σ(Xp)][b,e]	+0.05	+0.06	+0.11	+0.16	+0.18	+0.19
ΣV(Fe, C)[f]	1.71	1.68	1.63	1.58	1.50	1.42
ΣV(Fe, C, C)[g]	12.76	12.78	12.77	12.82	12.83	12.88

[a] Ref 34. [b] Xp designates the 1233′2′ ring. [c] Basin that appears twice in each compound. [d] Difference between the populations of the free and the complexed Cp⁻ ring. A negative value indicates a loss of electrons due to complexation. [e] Difference between the populations of the free and complexed Xp⁻ ring. [f] Sum of the population of the V(Fe, C) basin of the Cp ring. [g] Sum of the population of the V(Fe, C, C) basin of the Cp ring. [h] Population of V(Fe, N, B). [i] V(P, B) is populated by 2.25 electrons.
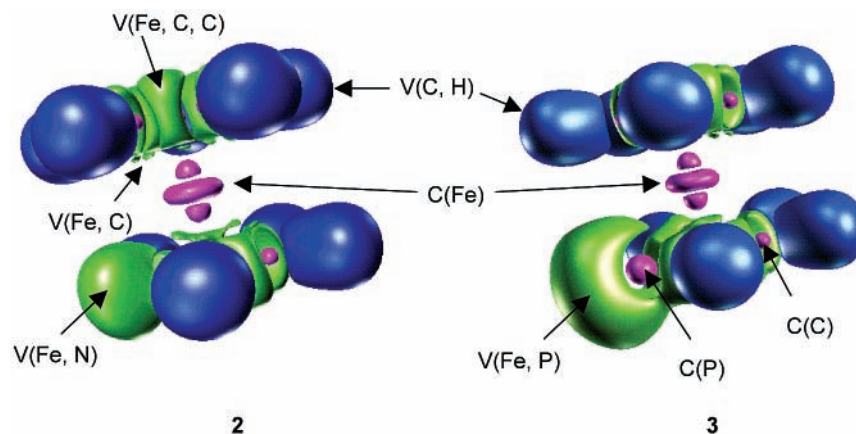
Figure 1. ELF Isosurfaces of **2** and **3**.

reflect the difference in shape of the heteroelement lone pairs that was noted previously.

The strength of the bonding between heteroferrocenes **2** and **3** and the Lewis acid BH_3 has been evaluated by calculating the bond dissociation energy (Table 2). These values provide a measure of the σ-donating capacity of both compounds and clearly show that the azaferrocene (33 kcal mol⁻¹) binds much more strongly to the Lewis acid than the phosphaferrocene (17 kcal mol⁻¹) does. These results also reveal a much greater difference in binding ability upon passing from sp²- to sp³-hybridized N than is found for the corresponding change from sp²- to sp³-hybridized P (complexation energies of 26 and 21

kcal mol⁻¹ for NH_3-BH_3 and PH_3-BH_3, respectively, at the G2(MP2) level[45]). These calculated differences between complexation energies for phosphaferrocene and azaferrocene agree well with experimental results. It is well-known that the phosphorus atom in phosphaferrocene shows little Brönsted[46] or Lewis[47] base character, unlike the azaferrocene nitrogen atom that, for example, is N-protonated in quite weakly acidic media.[48]

The difference in the strength of the donor−acceptor bond described above is reflected in the topological description of the bond. Complexation to BH_3 modifies the valence basins V(Fe, N) and V(Fe, P) in **2** and **3**, respectively. The disynaptic

TABLE 2: Frequencies[a] of the Bending of BH_3 and Bond Dissociation Energies $D_e{}^b$ of the X−B Bond[c] Calculated at the B3LYP/6-31G* Level

	4	**5**
out-of-plane bending	70	113
in-plane bending	138	275
D_e	33.0	17.4

[a] cm^{-1}. [b] kcal mol^{-1}. [c] X = N, P.

V(Fe, N) basin in **2** is transformed, by the contact of Fe, N, and B cores in **4**, into a trisynaptic V(Fe, N, B) basin that retains almost all its electron population (2.97 e in **4** as opposed to 3.08 e in **2**). However, the V(Fe, P) basin in **3** splits into two basins in **5**. The majority of the electron density (2.25 e) is found in a disynaptic bonding basin V(P, B) that is localized between the phosphorus and boron atoms. The remainder (0.85 e) is located between the ring and the metal where it forms the new disynaptic V(Fe, P) basin (Table 1). Because the P lone pair is involved in a σ-donor bond to B, it becomes less spherical, with the P showing $sp^{1.12}$ hybridization in the P−B bond. The electrons previously found in the P lone pair cannot all be accommodated within this more contracted area, and a second basin is formed. The low P−B bond strength relative to that of N−B might thus be regarded as a consequence of the nonparticipation of all of the electron lone pairs in the P−B bond.

The attractor of the disynaptic basin V(Fe, P) in **5** is located between the P and Fe atoms. This is not the case for the V(Fe, N, B) basin in **4** where the attractor is found in the ring plane between N and B. This situation indicates that, for η^5 coordination, the Fe atom is more strongly bound to P than to N. Again, this result is consistent with the greater ability of phospholyl, when compared to pyrrolyl, to bind as an η^5 ligand.

Polysubstitution. The ring-bearing phosphorus or nitrogen atoms will be labeled Xp (X = N or P). The substitution of several CH groups by P/N atoms in one ring leads to noticeable trends in geometry and electronic distribution.

With respect to the model compounds **1** and **3**, the compounds in the polyphospholyl series **12**−**17** show an increase in the Cp−Fe distance (1.655 Å in **1**, 1.695 Å in **17**) and a decrease in the Pp−Fe distance (1.655 Å in **1**, 1.578 Å in **17**). This result is in agreement with experimental X-ray structures of the iron sandwich complex [Fe(η^5-C$_5$Me$_4$Et)(η^5-P$_5$)], which indicate an Fe−P$_5$ distance (1.526 Å) that is smaller than the Fe−C$_5$Me$_4$Et distance (1.707 Å).[49] These data can obviously be explained by the increased area of the Pp ring that result from the differences among CC (1.41 Å), CP (1.78 Å), and PP (2.15 Å) bond lengths. The Pp ring has to remain closer to the metal to allow for reasonable C−Fe and P−Fe bond lengths. It should indeed be noticed that we find increases of the Fe−C and Fe−P bond lengths of the Pp ring in **12**−**17** with respect to those of **1** and **3**, even if the Fe−Pp distance becomes shorter. For the nitrogen compounds **2** and **6**−**11**, smaller variations of the bond lengths are observed. **11** shows Cp−Fe and Np−Fe bond lengths of 1.647 and 1.638 Å, respectively, which are only 0.02 Å smaller than the Fe−Cp bond length in **1** (1.655 Å). This finding is in accordance with the very small differences among the mean CC (1.41 Å), CN (1.37 Å), and NN (1.37 Å) bond lengths in **1**, **2**, and **6**−**11**. No experimental structures exist for compounds resembling **6**−**11**. However, Fe(η^5-N$_5$)$_2$ has recently been studied theoretically,[26] and the same trends are observed for **11** and Fe(η^5-N$_5$)$_2$ with respect to **1**.

The structural changes also modify the natural charges. For both the nitrogen and phosphorus compounds, we find a decrease in the negative charge of the Cp ring (−0.51 in **1**, −0.26 in **11**, −0.25 in **17**). The electrons given up by the Cp

are localized differently in the azaferrocene and phosphaferrocene series. For the azaferrocenes **6**−**11**, we observe a small increase of the positive charge on the metal (+1.02 in **1**, +1.09 in **11**) and a rather large negative charge located on Np (−0.51 in **1**, −0.83 in **11**), as expected in view of the higher electronegativity of nitrogen compared to that of carbon. For the phosphaferrocenes **12**−**17**, the electrons lost by Cp are gained by both the metal (+1.02 in **1**, +0.87 in **17**) and the Pp ring (−0.51 in **1**, −0.62 in **17**). These variations from **1** to **3** and **12** to **17**, which are also observed in the ELF results, contradict electronegativity arguments.

Upon moving from **1** to **3** and **12** to **17**, Cp ring basins become globally less populated whereas Pp rings have more electrons. When referred to the free Cp⁻ anion, the Cp ring is more electron-poor in **17** ($\Delta[\Sigma(Cp)]$ = −0.27 e) than in **1** ($\Delta[\Sigma(Cp)]$ = −0.07 e). The opposite trend is observed for the Pp ring, which has more electrons in polysubstituted systems than in the free Pp⁻ anion (+0.19 e in **17**). The back-bonding from the CpFe⁺ fragment outweighs donation from the Pp⁻ ring in cases where the Pp ring possesses two or more phosphorus atoms ($\Delta[\Sigma(Xp)]$ > 0 for **11**−**17**). As already observed for the atomic charges, the same trend as that for phosphaferrocenes is observed for the basin populations of azaferrocenes **2** and **6**−**11**. The Cp ring basins are depopulated compared to those of the free Cp⁻ ($\Delta[\Sigma(Cp)]$ = −0.07 e in **1** and −0.33 e in **11**), and the Np rings are more populated than the free Np⁻ rings in cases where three or more nitrogens atoms are located in the ring ($\Delta[\Sigma(Xp)]$ > 0 for **8**−**11**).

An examination of the various basin populations sheds light on the reasons behind this trend. Substitution of CH by N or P leads to a modification of the electronic populations in η^1 and η^2 bonds. The η^2 bond basins are depopulated upon heteroatom substitution (about 2.55 e in V(Fe, C, C) compared to about 1.70 e in V(Fe, N, N) and 1.85 e in V(Fe, P, P)), resulting in η^2 bonds that should be less electron-donating in substituted systems. Conversely, V(Fe, P) (between 3.24 and 3.46 e) and V(Fe, N) (between 3.05 and 3.45 e) basins are much more populated than V(Fe, C) basins, where values range from 0.0 to 0.52 e. Because the Xp ring is globally less donating in cases of polysubstitution, we can conclude that even if V(Fe, N) and V(Fe, P) basins are much more populated than V(Fe, C) they do not compensate for the donation lost though the trisynaptic basins. The substitution of CH by N or P entails a decrease of donor capacity on the Xp ring, which may reflect the localization of the V(Fe, N) and V(Fe, P) attractor basins in the ring plane rather than between the ring and the metal.

These electronic effects could account for the increase of the distance between Fe and the Cp ring upon moving from ferrocene to phosphaferrocenes. As the FePp⁺ metallic fragment becomes more electron-withdrawing, the Cp ring receives less back-bonding. The V(Fe, C) basins between Fe and C of the Cp ring are consistently depopulated ($\Sigma V(Fe, C)$ = 1.95 e in **1**, 1.42 e in **17**), and this loss of electron density could not be explained exclusively by the increase of the adjacent V(Fe, C, C) basins ($\Sigma V(Fe, C, C)$ = 12.65 e in **1**, 12.88 e in **17**). However, a similar electron-withdrawing effect due to the Np rings in **6**−**11** does not induce an increase in the Fe−Cp bond length. This inconsistency probably reflects different Cp−Fe electrostatic interactions that result from variations in the atomic charge on iron (an increase of the positive charge from **6** to **11** and a decrease of the positive charge from **12** to **17**).

The reactivity of phosphaferrocenes toward electrophiles may be explained qualitatively by the changes in donation and back-donation upon replacing CH by P . As back-bonding into the

Cp ring decreases, the ring becomes less reactive toward electrophiles. Conversely, the Pp ring is more negatively charged, but we have seen previously than in its [Mn(CO)₃] complexes its reactivity is lower than that of the Cp ring. The electrophilic reactivity of the carbon atoms of a phospholyl ring in a phosphametallocene complex does not seem to exceed that of a carbon atom of a cyclopentadienyl ring in the analogous metallocene. This result follows from the observation that the charge density is localized principally on the phosphorus lone pair, so it seems probable that the preferential electrophile attack at the Pp ring instead of at the Cp ring in phosphaferrocene is governed mainly by the decrease of the charge density of the Cp ring.

Conclusions

The results of this study provide a qualitative picture of the electronic structure and the bonding in aza- and phosphaferrocenes. η^5 coordination is characterized by both η^1 and η^2 interactions for cyclopentadienyl as well as for heterocyclopentadienyl ligands. Both heteroelements N and P have η^1 bonds to the metal through their lone pair, which entails a difference in the interaction as a function of the shape of the lone pair. The lone pairs are able to hold more electrons than are CC and CH bonds. For the nitrogen lone pair, this effect is due to the high electronegativity of the atom, whereas the greater spatial extension of the atomic orbital for phosphorus is responsible for this effect, despite its lower electronegativity.

Both N- and P-substituted cyclopentadienyls have an η^5 coordination mode that corresponds to a minimum. However, the difference in the lone pair shape means that the N-substituted cyclopentadienyl, unlike P-substituted systems, prefers to slip to an η^1 coordination mode where the lone pair of one nitrogen is directed toward the metal center. Any synthesis of a complex containing an η^5-N₅ ligand, as recently proposed,[26] seems difficult without protecting the nitrogen lone pairs.

CH substitution by N or P atoms leads to a decrease of the donating ability of heterocyclopentadienyl rings with respect to that of Cp rings. The resulting change in the electron density of such substituted complexes provides some explanation of their observed reactivity toward electrophiles.

Supporting Information Available: Tables of Cartesians coordinates and absolute energies of all optimized structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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