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Bonding in phosphaferrocenes and reactivity of the phospholyl ligand studied by molecular orbital calculations

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Organometallics, **1983**, 2 (8), 1008-1013• DOI: 10.1021/om50002a012 • Publication Date (Web): 01 May 2002

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spectrum of liquid tetramethyldiarsine, which showed bands at 272 and 254 cm^{-1} for the trans and gauche conformers, respectively.[26]

While the Raman spectra of **3** show no evidence for the presence of the trans conformer, it can be argued that there is unlikely to be any large energy difference between the gauche and trans forms. The molecular structure of **3** shows two nonequivalent methyl groups (C(3),C(14) and C(8),C(9)). Rotation about the As–As bond through the transoid (or less likely the cisoid) conformation will interconvert different methyl (C(3) → C(8), C(9) → C(14). The ^1H NMR spectrum of **3** in tetrahydrofuran-d_8 shows only a single methyl and methine signal even at −100 °C. The implied fast rotation about the As–As bond on the NMR time scale suggests only a small energy of difference between the gauche and trans forms.

Since biarsolyl **3** is not isostructural with bistibolyl **1**, it is difficult to compare solid-phase effects for the two compounds. However, it is interesting to note the four series of dipictongen compounds **1** and **3**, **9a–c**, **11a–c** and **12a–c**. In each case the diarsines are not thermochromic while the distibines and for **9c**, **11c**, and **12c** the dibismuthines are thermochromic. Structural data have now been reported for **1**,[1] **3**, **9a**,[9] and **9b**.[10] Clearly, comparable data for other members of these series are needed.

Experimental Section

General Data. All operations were performed under an atmosphere of nitrogen or argon. NMR spectra were taken on a Brüker WM 360 MHz spectrometer. The IR spectrum was obtained on a Beckmann IR 4240 spectrometer calibrated with polystyrene 1601.4-cm^{-1} absorption band. The mass spectrum was determined by using a Finnigan 4023 GC/MS using methane chemical ionization. The Raman spectra were taken with a Spex 1401 double spectrometer using the 6328-Å excitation line of a Spectra Physical Model 125 He–Ne laser. The combustion analysis was determined by the Spang Microanalytical Laboratory, Eagle Harbor, MI.

1-Phenyl-2,5-dimethylarsole. A solution of 4.0 g (18 mmol) of phenylarsenic dichloride in 10 mL of tetrahdyrofuran was added dropwise with stirring to 3.0 g (10 mmol) of 1,1-dibutyl-2,5-dimethylstannole[14] in 15 mL of tetrahydrofuran. After being stirred at 25 °C for 2 h, the reaction mixture was added to 100 mL of dilute NaOH. A large precipitate formed which was extracted with 3 × 50 mL of pentane. The extracts were washed with excess water and then dried over anhydrous magnesium sulfate. Distillation gave 1.3 g (59%) of 1-phenyl-2,5-dimethylarsole, bp 60–65 °C (0.15 torr). The ^1H NMR spectrum was identical with that reported in the literature.[29]

2,2′,5,5′-Tetramethyl-1,1′-biarsolyl. Lithium wire (0.25 g, 36 mmol) was cut into pieces approximately 2 mm in diameter and then placed in 20 mL of tetrahydrofuran. 1-Phenyl-2,5-dimethylarsole (1.5 g, 6.5 mmol) in 10 mL of tetrahydrofuran was added in one batch. The initially light yellow solution became brick-red and the solution spontaneously warmed to 50 °C over 15 min. After 3 h, the solution was decanted from the excess lithium, and a solution of iodine in tetrahydrofuran was added dropwise until the brown iodine color persisted. Removal of solvent left an oil which sublimed at 40 °C (0.05 torr) over a period of 2 days. Blocklike yellow crystals of product, mp 74–75 °C, were obtained. This product is oxygen sensitive: ^1H NMR (C_4D_4O) δ 1.99 (12 H, s), 6.49 (4 H, s), MS ($CI-CH_4$), *m/e* (relative intensity) 311 (36) ($M^+ + 1$ for $C_{12}H_{16}As_2$), 251 (17), 233 (12), 193 (19), 191 (13), 190 (16), 171 (26), 161 (30), 157 (25), 155 (13), 151 (20), 115 (57), 113 (100); IR (CCl_4) 3010, 2960, 2920, 2860, 1450, 1250, 1130, 900, 825 cm^{-1}; Raman (He–Ne laser, 6328-Å exciting line) solid (cm^{-1}) 50 (14), 105 (10), 124 (51) 218 (24), 241 (100), 285 (1), 315 (vw), 334 (w), 391 (2), 432 (1), 502 (3), 529 (3), 695 (w), *liquid* (cm^{-1}) 94 (74), 125 (10), 215 (51), 239 (100), 280 (4), 322 (w), 391 (1), 428 (3), 502 (vw), 530 (23), 696 (w). Anal. Calcd for $C_{12}H_{16}As_2$: C, 46.48; H, 5.20. Found: C, 46.29; H, 5.10.

Acknowledgment. Support of our work by A.F.O.S.R. (Grant No. 81-099) is gratefully acknowledged.

Registry No. 3, 85650-31-3; 4, 77214-60-9; 5, 20527-10-0; $C_6H_5AsCl_2$, 696-28-6.

Supplementary Material Available: A table of observed and calculated structure factors for **3** (8 pages). Ordering information is given on any current masthead page.

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Bonding in Phosphaferrocenes and Reactivity of the Phospholyl Ligand Studied by Molecular Orbital Calculations

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Received July 26, 1982

We carried out nonparametrized molecular orbital calculations on PpFeCp and on three conformations of Pp_2Fe; Pp represents η^5-$C_4H_4P^-$ and Cp represents η^5-$C_5H_5^-$. The Pp and Cp ligands have similar bonding abilities and form π bonds with the metal d orbitals. The P lone pair is not affected appreciably by the coordination of Ph to the Fe atom. The calculated and observed distributions of electron density in PpFeCp fully agree with each other. Compound Pp_2Fe adopts the conformation in which those molecular orbitals that are important for bonding are stabilized most. Electrophilic substitutions into these "sandwich" molecules are highly regioselective, apparently because these reactions are charge controlled. Although the phosphorus lone pair in Pp remains localized on this atom, the P atoms in the "sandwich" molecules are not nucleophilic because the lone pair is not in a frontier molecular orbital. The P atoms are even weakly electrophilic; the nucleophilic substitutions into the "sandwich" molecules apparently are controlled by orbital and charge effects in concert.

Introduction

Since the discovery of ferrocene, transition-metal "sandwich" complexes have attracted attention of many chemists. Several cyclic molecules or ions containing heteroatoms are isoelectronic with η^5-$C_5H_5^-$ anion (designated Cp) and also from π complexes with transition metals. One such ligand is the phospholyl anion, $C_4R_4P^-$ drawn schematically in **1**. Regardless of the groups R, which in our study are H atoms, we will designate it Pp.

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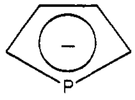

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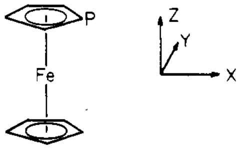
(The symbol Ph, used in the previous papers about phospholyl complexes, is commonly used for phenyl group.) This ligand, like aromatic hydrocarbons and their derivatives, forms "sandwich",[1-11] and ether[16b] complexes with several transition metals. Most of the research on these complexes has been done by F. Mathey and his coworkers. Particularly interesting to us are phosphaferrocenes (PpFeCp), shown in **2**, and 1,1′-diphosphaferrocenes (Pp_2Fe), shown in **3**. The latter compound



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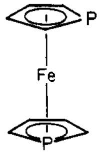

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adopts an interesting conformation.[5] Unlike the phospholes, C_4H_4PR, or any other P–C heterocycles, the η^5–Pp ligand in the complexes shows chemical signs of aromaticity. Most interesting, the Pp ligand appears to contain a localized pair of electrons on the *phosphorus* atom,[8] and yet the electrophilic substitutions in **2** and **3** occur exclusively at the *carbon* atoms in that ligand.[1,2,5,7] The P atom retains only a little of the nucleophilicity it has in phospholes;[10] it even acquires some electrophilicity and reacts with strong nucleophiles.[5,9,10]

We are interested in the nature of bonding in transition-metal π complexes,[17,18] in the conformations of transition-metal compounds,[19,20] and in the regioselectivity of nucleophilic and electrophilic attacks at organometallic complexes.[21-23] Led by these interests, we examined bonding, conformations, and reactivity of PpFeCp, **2**, and Pp_2Fe, **3**.

Details of the Calculations

An approximation to the Hartree–Fock–Roothaan technique, the Fenske–Hall method, has been described elsewhere.[24] The method is devoid of adjustable or empirical parameters, so that results of a calculation (eigenvalues and eigenvectors) are determined completely by molecular geometry and the basis functions.

We divided each "sandwich" molecule into the closed-shell fragments. A molecule of **2** consists of three fragments, viz., Fe^{2+}, Pp, and Cp; a molecule of **3** consists of two fragments, viz., Fe^{2+} and Pp_2. Such "cleavage" allows inspection of important orbital interactions that affect structure and reactivity. We first carried out calculations on separate fragments (the ligands) and then on the "sandwich" molecules made from them. After the iterative calculation on the complete "sandwich" molecule would converge with the atomic basis set, the molecular orbitals would be transformed into the basis set of the fragment orbitals. The redistribution of electrons between the fragments to make them closed shells and the transformation of basis set do not affect the numerical results of the calculations but make them easier to interpret. The energies of the fragment orbitals in the molecular orbital diagrams are diagonal elements of the Fock matrices for the complete molecules, so they reflect the influence of the molecular environment upon the fragments "ready for bonding". We estimated relative stabilities of different conformations by comparing summed eigenvalues of those occupied molecular orbitals in them that are affected by the changes in conformations (i.e., by the rotations of the ligands).

The basis functions were the same as in our previous studies.[21-23] The interatomic distances and angles for **2**[1,8] and **3**[5] were taken from the crystallographic data for these molecules. The Fe atom lay at the origin of the right-hand coordinate system; the centroids of the Pp and Cp rings lay at the z axis.

Cp and Pp Ligands. The electronic structure of the Cp ring, whose symmetry is D_{5h}, is well-known and need not be detailed here. The five carbon p orbitals of π-type interact to produce five π molecular orbitals. The most important for bonding to transition metals are the two degenerate molecular orbitals of e_1'' symmetry, which constitute the HOMO level of the Cp anion. When the two orbitals need to be identified separately, we will attach superscripts x and y to them. The e_1'' orbitals are drawn schematically, and their percent compositions (localizations) indicated in **4**. Less important for bonding with transition metals is the doubly degenerate LUMO level of e_2'' symmetry.

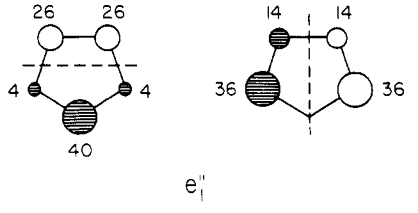

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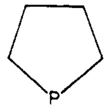
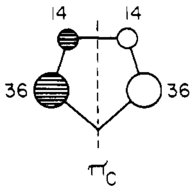
Table I. Energies and Percent Compositions of the Important MO's in $(\eta^5\text{-}C_4H_4P)Fe(\eta^5\text{-}C_5H_5)$

	Fe							$\eta^5\text{-}C_4H_4P$				$\eta^5\text{-}C_5H_5$	
ϵ, eV	d_{z^2}	$d_{x^2-y^2}$	d_{xy}	d_{xz}	d_{yz}	p_x	p_y	π_C	σ_P	π_P	π^*_P	$e_1''^x$	$e_1''^y$
2.43											91		
−1.63				3	59			14				9	8
−1.70 (LUMO)				55	4					15		8	9
−8.82 (HOMO)	91								2				
−10.10			89										
−10.43		84							2		8		
−12.03	3								78	12			
−13.23				7		10			9	62		7	3
−13.97							13	39				14	33
−14.49				22		3			5			45	18
−14.70					26			37				8	21

The Pp ring in **2** or **3** contains its P atom slightly out of the C_4 plane, which makes its symmetry C_s; the only nontrivial element of symmetry is the mirror plane through the P atom. This low symmetry prevents orbital degeneracy. The four most important orbitals of Ph are designated π_C, σ_P, π_P (the HOMO), and π^*_P (the LUMO). They are shown, with their localizations and nodal planes, in drawings **5** through **8**. Orbitals σ_P, π_P, and π^*_P are symmetric to the mirror plane (and belong to representation a′), whereas π_C is asymmetric to that plane (and thus belongs to representation a″). The main difference between the two rings is that Cp does not have a counterpart of the phosphorus lone-pair orbital σ_P. The e_1'' orbitals of the Cp ring and the π_C and π_P orbitals of the Pp ring obviously have similar shapes (localizations). But the two e_1'' orbitals are degenerate, whereas the π_C and π_P orbitals are separated by about 1.0 eV in the free Ph anion. The cause of that separation is evident in **5** and **7**. Since phosphorus is less electronegative than carbon, orbital π_P has higher energy than orbital π_C.





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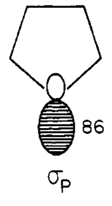

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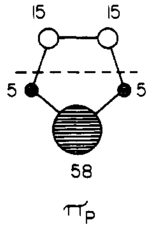

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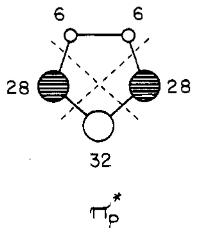

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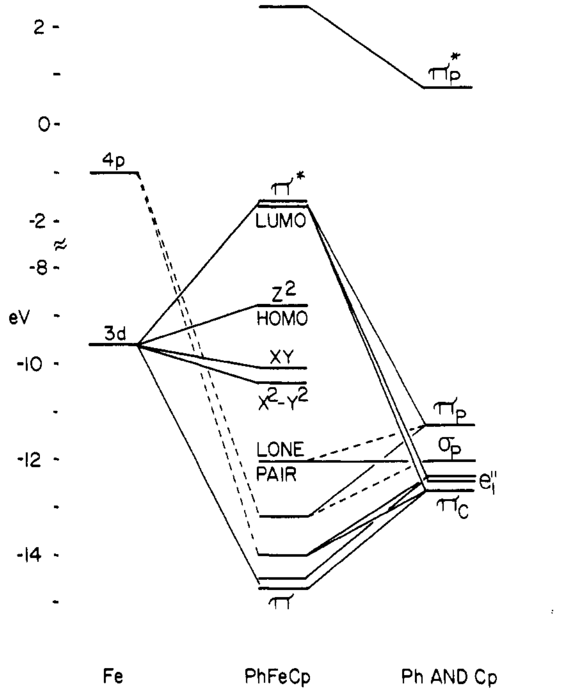


Figure 1. Molecular orbital diagram for $(\eta^5\text{-}C_4H_4P)Fe(\eta^5\text{-}C_5H_5)$. Dashed lines represent minor contributions. Orbitals π_C, σ_P, π_P, and π^*_P belong to the C_4H_4P ligand; orbitals e_1'' belong to the C_5H_5 ligand. Since the two lowest unoccupied molecular orbitals are very close to each other in energy, their compositions can better be seen in Table I.

The orbitals in the Pp_2 fragment are simply sums and differences of the corresponding orbitals in the Pp rings. We combine two Pp ligands into a single fragment because this permits us to examine a molecule of Pp_2Fe in terms of just two fragments; this simplifies the analysis of orbital interactions in the molecule.

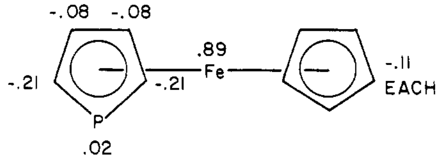
Bonding in PpFeCp and Atomic Charges. The electronic structure of this "mixed sandwich" molecule is summarized in Figure 1 and Table I. Not only do the high-lying, filled orbitals of the Cp and Pp rings have analogous shapes, but also they are close to each other in energy. Because of these similarities, the orbitals of both rings interact strongly with the π-type orbitals (d_{xz} and d_{yz}) of the Fe atom. The covalent bonding of the metal with the ligands is represented mainly by the two molecular orbitals at −14.49 and −14.70 eV, designated π in Figure 1. Their antibonding counterparts are the LUMO and the next vacant orbital, which are designated π^* in Figure 1. The p_x and p_y orbitals of Fe also have π symmetry with respect to the two rings, but they interact weakly with the ring orbitals because their energy is high. Table I shows that the corresponding mixing in the molecular orbitals at −13.23 and −13.97 eV is relatively small, so that these two molecular orbitals are essentially localized in the ligands. An important feature of the electronic structure of PpFeCp is the molecular orbital at −12.03 eV, corresponding to orbital σ_P of the free Ph ring. Evidently, the phosporus lone pair remains practically unperturbed by coordination of the Ph ring to the Fe atom, except for small mixing with π_P because both σ_P and π_P have a′ symmetry. Orbital π^*_P is destablized by its weak δ interaction with the $d_{x^2-y^2}$ orbital of iron. The three highest occupied molecular orbitals of the complex are practically pure d orbitals of the Fe atom. The d_{z^2} orbital is destablized by slight repulsive σ interactions with the low-lying, filled

Table II. Populations (in Electrons) of the Important Fragment Orbitals in $(\eta^5\text{-}C_4H_4P)Fe(\eta^5\text{-}C_5H_5)$

Fe		$\eta^5\text{-}C_4H_4P$		$\eta^5\text{-}C_5H_5$	
d_{z^2}	1.93	π_C	1.57	$e_1''^x$	1.52
$d_{x^2-y^2}$	1.75	σ_P	1.97	$e_1''^y$	1.52
d_{xy}	1.82	π_P	1.53	$e_2''^x$	0.09
d_{xz}	0.78	π^*_P	0.17	$e_2''^y$	0.09
d_{yz}	0.72				
p_x	0.17				
p_y	0.15				

orbitals of the ligands. The d_{xy} and $d_{x^2-y^2}$ orbitals are stabilized by weak attractive δ interactions with the high-lying, vacant orbitals of the ligands (e_2'' in Cp and π^*_P in Pp). These σ and δ interactions are relatively unimportant for covalent bonding in PhFeCp. The ordering of the d-like molecular orbitals in this "sandwich" molecule is $x^2 - y^2 < xy < z^2 < xz \approx yz$, similar to the ordering in metallocenes, arene "sandwiches", and mixed "sandwich" complexes of 3d transition metals.[25,26]

The results of our calculations fully agree with the results of a crystallographic determination of electron density in PpFeCp.[8] The experiment showed high electron density near the P atom, in the plane of the Pp ring. our calculation shows essentially a lone pair of phosphorus electrons, which do not participiate significantly in the delocalization within the Pp ring. The experiment showed high electron density at the Fe atom toward the centroids of the rings and in the plane parallel to the rings and low electron density toward the ring atoms. Our calculation shows that iron orbitals d_{z^2}, d_{xy}, and $d_{x^2-y^2}$ are essentially filled and that orbitals d_{xz} and d_{yz} are only partly filled. (Orbital d_{z^2} points toward the centroids of the rings; d_{xy} and $d_{x^2-y^2}$ are parallel to the rings; and d_{xz} and d_{yz} point toward the ring atoms.) The calculated populations of the principal orbitals of the fragments in the complete PpFeCp molecule are given in Table II. The electron charge is transferred from the filled π-type orbitals of the rings mainly into two empty π-type d orbitals of the Fe^{2+} ion, whose configuration is d^6. The electron-donating abilities of the Pp and Cp rings are nearly equal: about 0.9 e are lost from the filled π orbitals in each ring. The π_P orbital is somewhat closer in energy to the 3d orbitals than are the e_1'' orbitals, but the π_P–3d overlap is somewhat smaller than the e_1''–3d overlap because π_P is largely localized on the P atom, whereas e_1'' is localized over the rings. Their electron-accepting abilities are also nearly equal: about 0.2 e are acquired into the empty π orbitals in each ring. The net electron transfer reduces the formal negative charges of the ligands (1− each) and the formal positive charge of the metal atom (2+). The gross charges of all atoms other than hydrogens are shown in 9. The two carbon atoms (C-2) adjacent to the P atom are the most negative ones in the molecule; the P atom is the only (barely) positive atom in the ligands. Most theorists agree that Mulliken atomic charges often are not true in the absolute sense but that their qualitative pattern is realistic.[27] The calculation on the free ligand (Pp anion) shows that the P atom is somewhat more negative (−0.28) than the four C atoms (−0.15 to −0.20), chiefly because the HOMO (π_P) of the Pp ring is 58% localized on the P atom, as 7 shows. Coordination to the metal atom changes this charge distribution. The π donation from π_P to the Fe atom in the complex reduces the electron density on the P atom more than π donation from the π_C and π_P reduces the electron densities on the C atoms because π_P is more localized on the P atom than π_C and π_P are localized on the C atoms. The consequence of the Pp → Fe donation is that the P atom has less electron density than any C atom. We will use atomic charges when we discuss reactivity of the phospholyl complexes.



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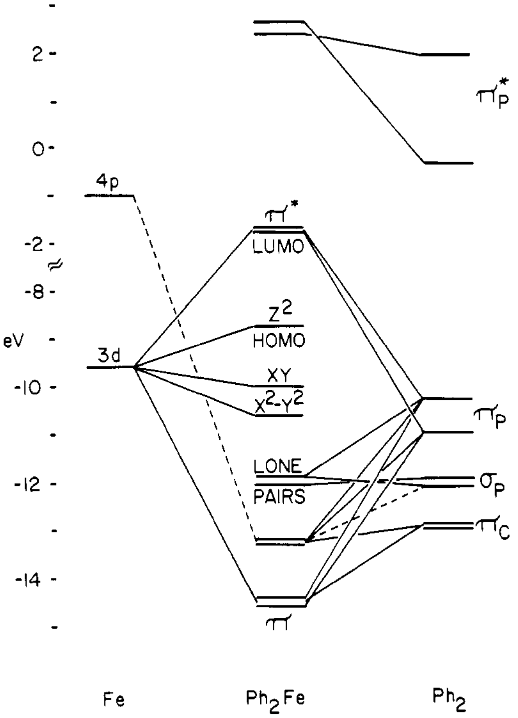
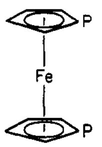


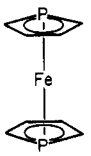
Figure 2. Molecular orbital diagram for $(\eta^5\text{-}C_4H_4P)_2Fe$ with C_1 symmetry (isomer **12**). Dashed lines represent minor contributions.

Bonding in Pp$_2$Fe and Its Conformations. Three conceivable conformations for the "sandwich" molecule Pp$_2$Fe are shown in **10**–**12** and designated according to their symmetry. The molecule adopts conformation **12** (C_1) in the solid state.[5] Its electronic structure, summarized in Figure 2 and Table III, obviously is similar to the electronic structure PpFeCp. This analogy confirms that the isoelectronic ligands Cp and Pp have similar bonding abilities with respect to transition metals. The only qualitative difference between the molecular orbital diagrams in Figures 1 and 2 is that the former contains one orbital corresponding to the phosphorus lone pair, whereas the latter contains two such orbitals. The main covalent



C_{2v}

10



C_{2h}

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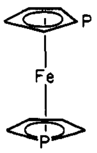

C_1

12

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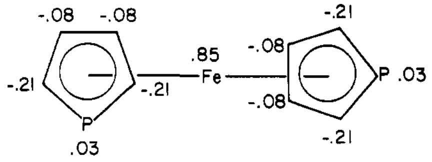
Table III. Energies and Percent Compositions of the Important MO's in $(\eta^5\text{-}C_4H_4P)_2Fe$ with C_1 Symmetry

	Fe							$(\eta^5\text{-}C_4H_4P)_2$			
ϵ, eV	d_{z^2}	$d_{x^2-y^2}$	d_{xy}	d_{xz}	d_{yz}	p_x	p_y	π_C	σ_P	π_P	π^*_P
2.56		13									83
2.36											92
−1.72				41	19			2		31	
−1.74 (LUMO)				18	40			2	2	31	
−8.76 (HOMO)	89								4		
−10.01		5	82								3
−10.57		75	5						4		14
−11.88		3		2					66	27	
−12.06	5							3	84	7	
−13.26				2	4	6	4	41	10	29	
−13.29				6	3	3	5	35	22	22	
−14.45				11	7			49	6	18	
−14.57				8	12			40		30	

bonding of iron with the Pp ligands corresponds to the molecular orbitals at −14.45 and −14.57 eV. The Pp_2 orbitals derived from σ_P (the lone pairs of the P atoms) are partly mixed with the Pp_2 orbitals derived from π_P, which are also largely localized on the P atoms, but remain essentially unperturbed by coordination to the metal atom. The atomic charges in Pp_2Fe are practically the same as those in PpFeCp, as can be seen from **9** and **13**. The orbital populations in Pp_2Fe are also similar to those in PpFeCp, shown in Table II.



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We compared the electronic structures of three conformations of Pp_2Fe (**10**–**12**) in an attempt to understand its apparent preference for **12**. The direct overlaps of orbitals in the two Pp rings separated by 3.3 Å are small, and the steric interactions must be negligible. The only intramolecular interactions that can affect the conformations are the covalent bonds the Fe atom forms with the ligands. Our analysis indicates that π-bonding molecular orbitals, lying about −14 eV in each conformation, are most affected by rotation of the rings. The structure **12** has no symmetry element other than the trivial identity (E), so all orbital interactions in it are allowed by symmetry. As Table III shows, both d_{xz} and d_{yz} and both π_C-derived and π_P-derived orbitals contribute to each of the two π-bonding molecular orbitals in **12**. This mixing of the metal orbitals and also of the ligand orbitals causes the two π-bonding molecular orbitals in **12** to be nearly degenerate: the energy gap between them is about 0.1 eV. The structures **10** and **11** each possess a mirror plane through the P atoms, and this additional symmetry (in comparison with **12**) prevents mixing between the d_{xz} and d_{yz} orbitals[28] and also among the ligand orbitals. The two π-bonding molecular orbitals in **10** and also in **11** are separated by about 0.8 eV. The filled molecular orbitals above and below those π-bonding ones are little perturbed by the conformational changes because they are chiefly localized on the metal atom or on the ligands. According to our calculations, the conformations **10** and **11** have almost equal energies of the nine uppermost filled molecular orbitals; this total energy for the observed conformation **12** is about 6 kcal mol^{-1} lower than the values for **10** and **11**. The preference is weak because iron orbitals d_{xz} and d_{yz} have similar energies and ligand π orbitals have similar energies, so that "hybridization" of d_{xz} with d_{yz} and of the various π orbitals with one another is not accompanied by large changes in energy. This relatively weak preference for one conformation over the other two cannot be attributed to any particular orbital interaction because the molecules have low symmetry and because most molecular orbitals in them (including the π-bonding ones) are very delocalized. The conformational preference of ferrocene is even weaker (the rings in it rotate freely) because Cp_2Fe has high symmetry; the molecular potential for a system consisting of two fivefold rotors is unlikely to vary enough to cause any sizeable barrier to rotation. As we noted before,[19,20] the *criterion of minimum orbital energy is particularly well suited to conformational analysis of molecules with low symmetry*, in which no single interaction (overlap) of orbitals influences the structure decisively. Since the intramolecular bonding forces do not appear to favor greatly any conformation over any other, the actual structures of 1,1′-diphosphaferrocenes in the solid state may well be affected by intermolecular interactions and packing forces.

Reactivity. Having examined the electronic structures of PpFeCp and Pp_2Fe, we turn to the discussion of their notable chemical properties; we are interested chiefly in regioselectivity of their substitution reactions. The electrophilic substitutions (acylation, formylation, and indirect carboxylation) into both "sandwich" complexes occur almost exclusively at the carbon atom (C-2) next to the phosphorus atom in the phospholyl ring.[1,2,5,7] As **9** and **13** show, this atom seems to be the most negative one in each complex. Thus the electrophilic substitutions seem to be charge controlled. However, the calculations do not exclude an orbitally controlled attack of the electrophile onto the Fe atom, followed by a shift to the C-2 atom.

The behavior of the P atom in the Pp ligand is intriguing. The experiment showed,[8] and the calculation confirmed, *that this atom has a lone pair of electrons, yet the electrophiles do not attack it.* In other words, the electrophilic substitutions into the Pp ring apparently are not orbitally controlled. We believe that the "inactivity" of the phosphorus lone pair is due to its relatively low energy in the "sandwich" molecules. As we discussed in our previous theoretical studies of reactivity,[21-23] if a molecular orbital is to determine the site of the attack by some reagent, it needs to be (1) a frontier orbital, (2) energetically isolated from other molecular orbitals, and (3) appreciably localized on the reactive site. The lone pair on the P atom in the Pp ligand satisfies the last two requirements but not the first one. Figures 1 and 2 show

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[28] We use the coordinate system shown with **2** and **3** for all conformations and define the orbitals in it. Orbital d_{xz} is symmetric, and orbital d_{yz} is antisymmetric with respect to the mirror plane (*xz*) through the P atoms in **9** and **10**. If we were to align the *z* axis with the C_2 axis in **9** and **10** (a convention adopted in most character tables), the corresponding orbitals would have different designations in different conformations.

that the lone pair in each "sandwich" molecule lies beneath several other filled molecular orbitals. This seems to be so in $PpMn(CO)_3$ as well.[9,15]

Although the lone pair apparently is not the frontier orbital, the P atoms in PpFeCp and in Pp_2Fe can coordinate to $Fe(CO)_4$,[3,6,7] as classical phosphines do. Our calculations on **2** and **3** give some credence to the proposition that the P atom in the coordinated Pp ligand acts as a π acceptor when **2** and **3** form adducts with $Fe(CO)_4$.[6] Orbital π^*_P presumably can accept electrons from the filled iron orbitals in $Fe(CO)_4$. The observed lengthening of the Fe–Cp and Fe–Pp distances upon formation[6] of the adducts might be caused by the donation of electrons from the $Fe(CO)_4$ group into the two lowest unoccupied molecular orbitals of **2** and **3**; as Figures 1 and 2 show, these molecular orbitals are antibonding between the Fe atom and the rings.

The P atom in the Pp ligand exhibits some electrophilicity and reacts with strong nucleophiles, such as RLi.[5,9] The calculated electronic structures of the complexes 2 and 3 indicate that this weak electrophilicity of the P atom may be caused by orbital and charge effects in concert. Tables I and III show that the LUMO of **2** and the lowest unoccupied molecular orbitals of **3** have appreciable contributions from the phospholyl orbital π_P. This partial localization of the vacant frontier orbitals on the P atom may guide the incoming nucleophile to this atom. Since the phospholyl orbitals π_P and σ_P are essentially orthogonal to each other, the nucleophile directed toward the vacant π_P will largely miss the lone pair in σ_P. Drawings **9** and **13** indicate that the P atom seems to be the most positive one in the ligands. Although its positive charge probably is small, it might contribute to the observed weak electrophilicity of phosphorus.

Acknowledgment. We are grateful the the National Science Foundation for financial support (Grant No. 7950005). N.M.K. has been a Fulbright Fellow since 1978 and is a Procter and Gamble Fellow for 1981–1982.

Registry No. 2, 63287-55-8; **3**, 73153-27-2.

Stereochemistry of Palladium Migration on Coordinated Cyclooctenyl. Molecular Structure and Dechloropalladation of Tetrakis(μ-chloro)bis[1–3-η-6-(α-chloroethyl)cyclooctenyl]-tripalladium(II)

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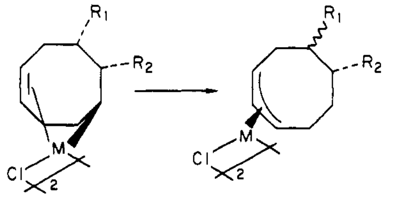
Received December 28, 1982

Bis(μ-chloro)bis[1,4,5-η-8-(α-chloroethyl)cyclooctenyl]dipalladium(II), **1c**, is found to undergo palladium migration [via hydrogen shifts(s)] in solution to form π-allylic bis(μ-chloro)bis[1–3-η-6-(α-chloroethyl)-cyclooctenyl]dipalladium(II), **2c**. Attempted growth of **2c** crystals leads to isolation of a tripalladium complex which results from insertion of $PdCl_2$ into the bridge in **2c**, namely, tetrakis(μ-chloro)bis[1–3-η-6-(α-chloroethyl)cyclooctenyl]tripalladium(II)–chloroform (or $\mathbf{2c}\cdot PdCl_2\cdot CHCl_3$). Crystal structure analysis of this latter material shows that palladium migrates such that it stays on the original face of the cyclooctenyl. Thus Pd and α-chloroethyl are mutually trans in both **1c** and $\mathbf{2c}\cdot PdCl_2\cdot CHCl_3$. Reaction of **2c** (or $\mathbf{2c}\cdot PdCl_2\cdot CHCl_3$) with aqueous cyanide leads to the new hydrocarbons *anti*-9-methylbicyclo[4.2.1]non-2-ene, **3a**, and *syn*-9-methylbicyclo[4.2.1]non-2-ene, **3b**, in 78% and 15% yields, respectively. Hydrocarbons **3a** and **3b** result from cyanide-induced dechloropalladation via intramolecular electrophilic attack on what was a terminal π-allyl carbon. The **1c** → **2c** rearrangement is the first reported for a Pd σ,π-cyclooctenyl which bears a substituent trans to palladium on carbon 8.

Introduction

In a previous report from this laboratory,[1] we demonstrated the **1a** → **2a** rearrangement shown in eq 1. This



(1)

1a-d **2a-d**

a, M = Pd, R_1 = Cl, R_2 = H
b, M = Ni, R_1 = R_2 = H
c, M = Pd, R_1 = H, R_2 = α-chloroethyl
d, M = Pd, R_1 = H, R_2 = H

type of cyclooctenyl isomerization has also been observed by Wilke in a related organonickel system: **1b** → **2b**.[2]

Complexes of type 1 (R_1 = H, R_2 = RO, R_2N, R_3C, etc.) are readily accessible through nucleophilic attack on coordinated cycloocta-1,5-diene. Although such complexes are potentially valuable precursors to π-allylic rearrangement products, we noted earlier[1] that $\sigma,\pi \rightarrow \pi$-allyl rearrangements had not been reported for any of the large number of complexes of type 1 prepared by the nucleophilic attack route. We now report the first example of $\sigma,\pi \rightarrow \pi$-allyl isomerization in a cyclooctenyl having $R_2 \neq$ H, namely, **1c** → **2c**. The rearrangement proceeds with "face retention" (i.e., Pd and α-chloroethyl remain trans). The π-allylic product **2c** reacts readily with cyanide ion to liberate in high yield hydrocarbons **3a** and **3b**. This

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