Can the *cyclo*-P$_5$ Ligand Introduce Basicity at the Transition Metal Center in Metallocenes? A Hybrid Density Functional Study on the *cyclo*-P$_5$ Analogues of Metallocenes of Fe, Ru and Os

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Density functional theory (DFT) calculations and natural population analysis (NPA) performed on metallocenes of Fe, Ru and Os triad reveal that the *cyclo*-P$_5$ ligand introduces basicity at the metal center. All-electron calculations at the B3LYP/6-311+G$^{\bullet}$ level yield NPA charges of 0.28, −0.28 and −0.91 at the iron center in [FeCp$_2$], [FeCp(η^5-P$_5$)] and [Fe(η^5-P$_5$)$_2$], respectively. The same trend in the charges is observed even when the core electrons of the metal are replaced by effective core potentials (ECPs). The accumulation of negative charge at the metal center is found to be similar in the *cyclo*-P$_5$ analogues of ruthenocene and osmocene. Thus, for example, the net NPA charges on Ru and Os in the decaphosphametallocenes are predicted to be −0.6 to −0.9, respectively, at different levels of calculations involving ECPs. The natural orbital populations show a small transfer of electron density from each phosphorus atom to the metal center, leading to a significant build-up of negative charge on the metal in [M(η^5-P$_5$)$_2$]; this is a new feature observed in the transition metals bound to *cyclo*-P$_5$ ring. This finding is indeed supported by the indirect evidence observed by Scherer and co-workers from the diamagnetic behavior in an iridium derivative of Fe(P$_5$), that the Fe atom is negatively charged while one of the P atoms is positively charged. Natural bond orbital analysis reveals that the extent of covalent bond formation between the metal and the ligand is more pronounced for the *cyclo*-P$_5$ than the cyclopentadienyl ligand. While Cp retains 56–68% of aromaticity, the P$_5$ ring exhibits 26–51% aromaticity as compared to the free anionic rings.

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Introduction

Cyclopentadienyl, C$_5$H$_5$ (Cp), is a very common and versatile ligand in the field of organometallic chemistry.[1−4] The inorganic ring *cyclo*-P$_5$, also known as pentaphospholyl or pentaphosphacyclopentadienyl, is π isoelectronic with Cp and is known to form complexes with several transition metals.[5−7] The first carbon-free entirely inorganic sandwich complex [Ti(η^5-P$_5$)$_2$]$^{2-}$ was synthesized and characterized in 2002 by Urnezius et al.[8] The crystal-structure analyses of mixed metallocenes [M(η^5-C$_5$Me$_4$R)(η^5-P$_5$)] (M = Fe, Ru; R = Me, Et) and [Ti(η^5-P$_5$)$_2$]$^{2-}$ show a sandwich structure with two parallel η^5- or π-bonded rings.[6a,6b,8] Besides the pentaphospolyl ligand, inorganic rings of the type E$_n$ (E = As, P; n = 3−6) are also known to form complexes with transition metals.[7] Numerous transition metal complexes have been studied with heterocyclic ligands of the type P$_n$(CH)$_{5-n}$ (n = 1−4).[9−11] Phosphorus heterocycles are also known to form sandwich complexes with some lanthanides.[10] The similarity between *cyclo*-P$_5$ and the Cp ligands towards complex formation is a manifestation of the "diagonal relationship" of the elements carbon and phosphorus in the Periodic Table; they have similar electronegativity values.[7,11] In recent years the role of planar aromatic heterocycles possessing novel structural and bonding features in catalysis has been recognised.[12]

Although experimental studies illustrate the potential of the P$_5$ ring as a ligand and can lead to a wealth of interesting complexes, there is still not much known about the structure and bonding in complexes containing a P$_5$ ring. Semiempirical and ab initio molecular orbital studies show that *cyclo*-P$_5^-$ is aromatic in nature.[13−15] Early investigations[16] on bonding and stabilities in the pentaphospholyl complexes of iron were based on the extended Hückel theory. A number of studies document the importance of electron-correlation methods in obtaining reliable predictions in transition metal compounds.[17−19] Recent studies show that density functional theory (DFT)[20] calculations are remarkably successful in predicting a variety of properties to an accuracy which rivals that of more expensive correlated ab initio methods. Several recent works reveal that the DFT method provides reliable results in the case of transition metal and lanthanide complexes.[21] DFT analysis

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of the electronic structure and bonding in some azaferrocenes and phosphaferrocenes by Frison et al.[22] has revealed the role of the heteroatom electronegativity as well as the shape of the lone pair in bonding. Frunzke et al.[23] have shown that in the ferrocene analogues [Fe(η^5-E$_5$)$_2$] (E = N, P, As, Sb), bis(pentaphospholyl)ferrocene [Fe(η^5-P$_5$)$_2$] exhibits the strongest bonding. A DFT study of Lein et al.[24] has shown that the metal−ligand bonding in [Ti(η^5-E$_5$)$_2$]$^{2-}$ (E = N, P, As, Sb) is more covalent than electrostatic. In addition to the complexes containing phosphorus rings, those of the analogous aza-rings have also received attention in recent years.[25] The recent DFT study of Malar[26] reveals novel structural and bonding features in the metallocenes of lithium and beryllium containing the *cyclo*-P$_5$ ligand. In the lowest energy structure, *cyclo*-P$_5$ exhibits η^1-coordination with the metal center and is perpendicular to the second ligand, which is η^5-coordinated. The absence of a metal−dπ interaction with the ligand results in a tilting of the *cyclo*-P$_5$ ring such that it becomes perpendicular to the second ligand. The above study shows that the *cyclo*-P$_5$ ligand behaves as a better donor than Cp and results in a lowering of the net charges on the lithium and beryllium centers.[26] It is of interest to know the influence of *cyclo*-P$_5$ on the electronic population of the metal centers in the title compounds.

The present study is aimed at getting detailed information on the molecular and electronic structures and the nature of the bonding in metallocenes of Fe, Ru and Os containing the *cyclo*-P$_5$ ligand. Both the mono- and bis-(*cyclo*-P$_5$) analogues of ferrocene, ruthenocene and osmocene are examined by hybrid DFT calculations. The electronic structures, properties and stabilities of these compounds are compared with those of the carbocyclic metallocenes Cp$_2$M, which are well characterized experimentally and theoretically.

Results and Discussion

Energetics

The relative stabilities of the complexes with reference to their ionic components are shown in Table 1. The binding energies ΔE are calculated with reference to the metal dication and the two anionic Cp/P$_5$ rings using the equation $\Delta E = E(\text{LML}') - E(\text{L}^-) - E(\text{L}'^-) - E(\text{M}^{2+})$. The heterolytic dissociation energy in the metallocene is given by $-\Delta E$.

The heterolytic dissociation energy of 615 kcal/mol predicted for the eclipsed geometry of ferrocene, based on the present B3LYP/6-311+G* analysis, agrees very closely with the observed value of 635 ± 15 kcal/mol.[27] Table 1 shows that the binding energies of ferrocene and its *cyclo*-P$_5$ analogues predicted by Type-II and -III basis sets are close to those of the all-electron 6-311+G* results. Type-I calculations deviate significantly from the B3LYP/6-311+G* values, though the trends in the stabilities are similar. Examination of the present results show that the predictions based on B3LYP/Type-III calculations, which use triple-split valence basis on the metal, agree better with those of the all-electron calculations at the B3LYP/6-311+G* level for ferrocene and its analogues. Although the all-electron calculations are more accurate, in systems with Ru or Os centers that require the use of ECPs, B3LYP/Type-III results are expected to be reliable. The dissociation energies predicted in this work by B3LYP/Type-I, B3LYP/Type-II, B3LYP/Type-III, and B3LYP/6-311+G* for ferrocene (608−638 kcal/mol) show better agreement with the experimental results than the value of 663 kcal/mol reported using the B_PW91 method of density functional theory.[21d] Our study shows that in a series of analogous metallocenes, the heterolytic dissociation energy increases in the order ferrocene < ruthenocene < osmocene; thus osmocenes are pre-

Table 1. Binding energies (kcal/mol) of the metallocenes at the eclipsed and staggered geometries; relative energies are given in parentheses

System	Point group	B3LYP/Type-I	B3LYP/Type-II	B3LYP/Type-III	B3LYP/6-311+G*
FeCp$_2$	D_{5h}	−638.11 (0.0)	−608.23 (0.0)	−606.93 (0.0)	−615.04 (0.0)
	D_{5d}	−637.56 (0.55)	−607.81 (0.42)	−606.47 (0.46)	−614.58 (0.46)
FeCpP$_5$	C_{5v}(e)	−581.55 (0.0)	−574.23 (0.0)	−574.95 (0.0)	−583.60 (0.0)
	C_{5v}(s)	−580.84 (0.71)	−573.48 (0.75)	−574.35 (0.60)	−582.80 (0.80)
Fe(P$_5$)$_2$	D_{5h}	−507.12 (0.0)	−519.94 (0.0)	−521.99 (0.0)	−530.71 (0.0)
	D_{5d}	−506.14 (0.98)	−519.18 (0.76)	−521.34 (0.73)	−529.79 (0.92)
RuCp$_2$	D_{5h}	−681.25 (0.0)	−650.88 (0.0)	−655.29 (0.0)	
	D_{5d}	−680.91 (0.34)	−650.62 (0.26)	−654.89 (0.40)	
RuCpP$_5$	C_{5v}(e)	−639.29 (0.0)	−629.60 (0.0)	−636.94 (0.0)	
	C_{5v}(s)	−638.65 (0.64)	−629.00 (0.60)	−636.32 (0.62)	
Ru(P$_5$)$_2$	D_{5h}	−578.34 (0.0)	−591.22 (0.0)	−600.32 (0.0)	
	D_{5d}	−577.28 (1.06)	−590.24 (0.98)	−599.47 (0.85)	
OsCp$_2$	D_{5h}	−728.61 (0.0)	−699.27 (0.0)	−701.30 (0.0)	
	D_{5d}	−727.94 (0.67)	−698.72 (0.55)	−700.75 (0.55)	
OsCpP$_5$	C_{5v}(e)	−692.59 (0.0)	−683.61 (0.0)	−690.64 (0.0)	
	C_{5v}(s)	−691.65 (0.94)	−682.71 (0.90)	−689.80 (0.84)	
Os(P$_5$)$_2$	D_{5h}	−635.55 (0.0)	−648.07 (0.0)	−659.74 (0.0)	
	D_{5d}	−633.95 (1.60)	−646.56 (0.51)	−658.07 (1.67)	

dicted to be more stable than the corresponding ferrocenes and ruthenocenes. This is in agreement with the earlier observation of Mayor-López et al[21d] that ruthenocene has a higher heterolytic dissociation energy than ferrocene. The present work shows that the stability of the *cyclo*-P$_5$ analogues of the metallocenes follows the order: MCp$_2$ > MCpP$_5$ > M(P$_5$)$_2$. In the pentaphosphaferrocene [FeCp(η^5-P$_5$)], the magnitude of the binding energy is 31−35 kcal/mol lower than in ferrocene when Type-II, Type-III, and 6-311+G* basis sets are used. However there is a more pronounced lowering of stability in the carbon-free metallocene [Fe(η^5-P$_5$)$_2$], by about 53 kcal/mol relative to the pentaphospha analogue. A similar but less marked lowering in the stabilities of the *cyclo*-P$_5$ analogues of ruthenocene and osmocene is evident from Table 1. The heterolytic dissociation energies of [M(η^5-P$_5$)$_2$] (M = Fe, Ru and Os) are lower than the corresponding values for MCp$_2$ by 85, 55, and 41 kcal/mol, respectively, according to Type-III calculations. A similar trend in the relative stabilities is also observed in penta- and decaphospha analogues of beryllocene using B3LYP/6-31G*, B3LYP/6-31+G*//B3LYP/6-31G*, B3LYP/6-311+G**//B3LYP/6-31G* and B3LYP/LANL2DZ calculations.[26] The prediction based on the present B3LYP/6-311+G* analysis, that [Fe(η^5-P$_5$)$_2$] is about 84 kcal/mol less stable than ferrocene towards heterolytic cleavage, contradicts the conclusion of Frunzke et al.[23] that the former is as stable as ferrocene.

The bonding in metallocenes is generally explained on the basis of interaction between the occupied π-orbitals of the ligands and the vacant d_{xz} and d_{yz} orbitals of the metal, which leads to stabilization of the bonding e_1'' orbitals and destabilization of the antibonding $(e_1'')^*$ orbitals. The earlier study of Mayor-López et al.[21d] on the electronic structures of ferrocene and ruthenocene showed that the HOMO−LUMO gap is about 0.8 eV larger for the latter than for the former. This led the authors to conclude that metal-ligand covalency, and hence the binding energy, is

greater in ruthenocene than in ferrocene. Figure 1 depicts the energetics of the highest occupied and lowest vacant MOs generated by the B3LYP/6-311+G* method in the eclipsed structure of ferrocene analogues. The HOMO−LUMO energy gap follows the order FeCp$_2$ (5.09) > FeCp(P$_5$) (4.35) > Fe(P$_5$)$_2$ (3.12). The lower HOMO−LUMO gap in the phospha analogues indicates that the interaction between the ligand π-orbitals and the vacant metal orbitals is smaller and it may account for their lower binding energies. The trends in the MO energies in ferrocene and its *cyclo*-P$_5$ analogues appear to be very similar to those of the beryllocenes with eclipsed structures.[26] The HOMO−LUMO energy gap in the beryllocenes is BeCp$_2$ (6.53) > BeCp(P$_5$) (3.83) > Be(P$_5$)$_2$ (2.99) by the B3LYP/6-31G* method.[26] The resemblance in the MO energetics in the two different classes of metallocenes with sandwich structures reveals that the nature of the orbital interactions is quite similar irrespective of the type of the metal center. It is apparent that the ligand donor π-orbitals play a major role in the stabilization of the bonding and the destabilization of the antibonding MOs in these metallocenes.

The relative energies shown in parentheses in Table 1 reveal that the eclipsed sandwich arrangement is more stable than the staggered geometry by 0.3−1.7 kcal/mol. The small energy difference between the eclipsed and staggered arrangements is in agreement with the ^{13}C NMR study of ferrocene at cryogenic temperatures, which shows that ferrocene is freely rotating about its fivefold symmetry axis above 45−50 K.[21b] An eclipsed structure for ferrocene and ruthenocene was confirmed by an electron-diffraction study[28] and a crystal-structure analysis.[29] Negligibly small energy difference between the staggered and eclipsed geometries have been reported in different DFT studies of carbocyclic metallocenes MCp$_2$ [21b−21g] and in aza- and phosphaferrocenes.[22,23] Analysis of the vibrational frequencies in the present work reveals that all values are real
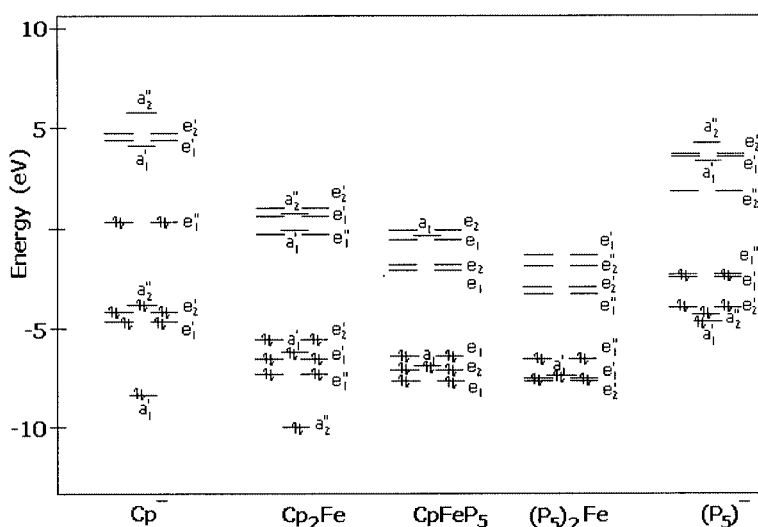

Figure 1. B3LYP/6-311+G* energy level diagram showing the highest occupied and lowest vacant molecular orbitals of the anionic ligands (D_{5h} point group) and their ferrocene analogues in their eclipsed sandwich geometries

in the eclipsed structure and it is thus a minimum in the potential energy surface. However, the staggered sandwich structure exhibits one imaginary vibrational frequency in the range $20-50\ i\ cm^{-1}$, which indicates that the staggered arrangement is not a potential minimum and is likely to be the rotational transition state. In a recent study using different DFT methods, Schaefer and co-workers[21g] found that the eclipsed sandwich structure is the global minimum in the metallocenes of the first transition metal series. These authors have reported that the staggered structure of ferrocene is $0.75-1.13$ kcal/mol higher in energy than the eclipsed geometry and is in agreement with the present results.

Geometries of Ferrocene, Ruthenocene and Osmocene and their cyclo-P_5 Analogues

Table $2-4$ display selected geometrical parameters in the optimized eclipsed sandwich structures. It is found that the structural parameters of the ligands and the metal–ligand separations are nearly identical in both the eclipsed sandwich and the staggered sandwich arrangements. In a given system, the calculations at the different levels yield structures that vary only marginally. The predicted values are found to be closer to experimental results in Type-III calculations when ECPs are used. The computed ring bond lengths for the C–C and P–P bonds in the metallocenes are in the ranges $1.43-1.44$ and $2.14-2.16$ Å, respectively, and agree satisfactorily with the available experimental and the reported DFT studies.[21b−21d,21g,22−24] Although the C–C and P–P bonds in these complexes are characteristic of aromatic bonds, the present results show that the ligand

rings expand along the series Fe, Ru, and Os. Thus the C–C and P–P lengths are the longest in osmium metallocenes. The present P–P bond lengths are very similar to the observed mean value of 2.154(9) Å[8] in the decaphosphatitanium complex $[Ti(\eta^5\text{-}P_5)_2]^{2-}$.
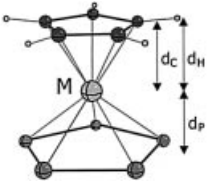
The distance between the metal and the center of the Cp ring (d_C; Table 2) in ferrocene is predicted to be $1.686-1.687$ Å and it is 0.026 Å longer than the experimental value of 1.66 Å reported by Haaland.[28] In ruthenocene, there is an elongation of about 0.18 Å in the metal−ring distance as compared to that in ferrocene; this value is similar to the experimental increase of about 0.16 Å. However, the calculations predict that the d_C values are quite similar in $RuCp_2$ and $OsCp_2$. Similar trends in d_C are also maintained in the pentaphosphametallocenes. The longer separation between the metal and Cp ligands in ruthenium and osmium metallocenes leads to an increase of about 0.15 Å in Ru−C and Os−C bond lengths as compared to those of the Fe−C bonds.

The distance between the metal and the center of the P_5 ring, d_P, is shorter than the M−Cp(centre) in pentaphosphametallocenes. The experimental d_P values in the alkyl derivatives of pentaphosphametallocenes are 1.55, 1.65 and 1.66 Å for M = Fe, Ru and Os, respectively.[6a,6b] These values are about 0.20 Å shorter than the corresponding d_C values. The d_P values predicted by B3LYP are 1.597, 1.716 and 1.711 Å in $MCpP_5$ (M = Fe, Ru, Os) by Type-III calculations. The metal−Cp separations are longer than d_P and the values are 1.712, 1.888, and 1.897 Å, respectively. The distances between the metal and P_5 center in decaphosphametallocenes are 1.693, 1.788 and 1.788 Å for Fe, Ru

Table 2. B3LYP optimized geometries and bond orders (in parentheses) in metallocenes MCp_2 with eclipsed sandwich geometries
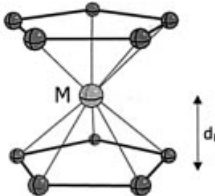

System	Parameter	Type I	Type II	Type III	6-311+G*	Expt.
FeCp$_2$	C−C	1.428 (1.289)	1.427 (1.289)	1.426 (1.285)	1.426 (1.286)	1.440[a]
	Fe−C	2.079(0.285)	2.078 (0.286)	2.078 (0.292)	2.077 (0.295)	2.064[a]
	d_C	1.687	1.687	1.687	1.686	1.660[a]
	d_H	1.660	1.661	1.662	1.664	
	θ	1.8	1.7	1.6	1.4	3.7±0.9[a]
RuCp$_2$	C−C	1.431 (1.278)	1.429 (1.278)	1.430 (1.275)		1.430[b]
	Ru−C	2.233 (0.300)	2.231 (0.302)	2.226 (0.314)		2.186[b]
	d_C	1.872	1.871	1.864		1.816[b]
	d_H	1.882	1.883	1.875		
	θ	−0.7	−0.8	−0.7		
OsCp$_2$	C−C	1.436 (1.255)	1.434 (1.255)	1.434 (1.249)		
	Os−C	2.224 (0.340)	2.220 (0.343)	2.221 (0.352)		
	d_C	1.858	1.855	1.856		
	d_H	1.870	1.872	1.870		
	θ	−0.8	−1.1	−0.8		

[a] Refs.[28a,28b] [b] Ref.[30]

Table 3. B3LYP optimized geometries and bond orders (in parentheses) in the eclipsed sandwich metallocenes MCpP$_5$

System	Parameter	Type I	Type II	Type III	6-311+G*	Expt.
FeCpP$_5$	C−C	1.427 (1.282)	1.424 (1.284)	1.423 (1.280)	1.423 (1.282)	1.42[a]
	P−P	2.148 (1.227)	2.144 (1.213)	2.143 (1.202)	2.142 (1.207)	2.10,[a] 2.12[b]
	Fe−C	2.093 (0.290)	2.095 (0.288)	2.097 (0.286)	2.097 (0.290)	2.09[a]
	Fe−P	2.444 (0.365)	2.429 (0.381)	2.423 (0.386)	2.419 (0.387)	2.35[a]
	d_C	1.705	1.709	1.712	1.713	1.71,[a] 1.75[b]
	d_P	1.624	1.604	1.597	1.592	1.53,[a] 1.55[b]
	d_H	1.666	1.686	1.679	1.685	
	θ	2.6	1.5	2.2	1.8	
RuCpP$_5$	C−C	1.431 (1.283)	1.428 (1.284)	1.428 (1.280)		1.42[c]
	P−P	2.160 (1.203)	2.160 (1.193)	2.159 (1.180)		2.10[c]
	Ru−C	2.247 (0.263)	2.248 (0.264)	2.245 (0.279)		2.21[c]
	Ru−P	2.528 (0.397)	2.520 (0.408)	2.513 (0.426)		2.43[c]
	d_C	1.888	1.892	1.888		1.85[c]
	d_P	1.737	1.725	1.716		1.65[c]
	d_H	1.881	1.897	1.886		
	θ	0.5	−0.3	−0.1		
OsCpP$_5$	C−C	1.434 (1.272)	1.431 (1.272)	1.431 (1.270)		1.42[d]
	P−P	2.167 (1.161)	2.167 (1.152)	2.162 (1.143)		2.11[d]
	Os−C	2.251 (0.279)	2.248 (0.283)	2.254 (0.291)		2.22[d]
	Os−P	2.522 (0.467)	2.518 (0.474)	2.512 (0.499)		2.44[d]
	d_C	1.890	1.890	1.897		1.86[d]
	d_P	1.722	1.715	1.711		1.66[d]
	d_H	1.892	1.902	1.899		
	θ	−0.1	−0.7	−0.1		

[a] Experimental values for [Fe(η^5-C$_5$Me$_4$Et)(η^5-P$_5$)]. [b] Experimental values for [Fe(η^5-C$_5$Me$_5$)(η^5-P$_5$)].[6a,7b] [c] Experimental values for [Ru(η^5-C$_5$Me$_4$Et)(η^5-P$_5$)].[6a,7b] [d] Experimental values for [Os(η^5-C$_5$Me$_4$Et)(η^5-P$_5$)].[6l]

Table 4. B3LYP optimized geometries and bond orders (in parentheses) in eclipsed metallocenes M(P$_5$)$_2$

System	Parameter	Type I	Type II	Type III	6-311+G*
Fe(P$_5$)$_2$	P−P	2.141 (1.229)	2.139 (1.218)	2.137 (1.210)	2.136 (1.211)
	Fe−P	2.488 (0.352)	2.487 (0.369)	2.484 (0.341)	2.481 (0.342)
	d_P	1.694	1.695	1.693	1.689
Ru(P$_5$)$_2$	P−P	2.157 (1.215)	2.156 (1.207)	2.154 (1.194)	
	Ru−P	2.571 (0.332)	2.566 (0.341)	2.561 (0.346)	
	d_P	1.800	1.795	1.788	
Os(P$_5$)$_2$	P−P	2.162 (1.181)	2.161 (1.175)	2.158 (1.170)	
	Os−P	2.570 (0.377)	2.569 (0.382)	2.562 (0.408)	
	d_P	1.796	1.795	1.788	

and Os, respectively, according to B3LYP/Type-III calculations. These values are longer than those in the pentaphosphametallocenes by 0.07−0.10 Å. The d_P values in the decaphospa analogues of Ru and Os closely resemble the value of 1.797 Å observed in [Ti(η^5-P$_5$)$_2$]$^{2-}$.[8]

The theoretical lengths for d_C, d_P, metal−carbon, and metal−phosphorus deviate from the experimental values by about 0.05 Å. The Ru−P distance in RuCpP$_5$ exhibits a maximum deviation of about 0.08 Å. The experimental data shown in Table 3 are from the crystal structure of the alkyl

derivatives of MCpP$_5$ that exhibit staggered geometries, and thus a comparison with these values may not be appropriate.

Even though the B3LYP geometries deviate from the experimental results, they nevertheless reveal the right trend regarding the changes in lengths among the homologues. The results obtained are helpful to understand the nature of bonding in these metallocenes.

The complete structural analysis shows that the hydrogen atoms in the Cp ring move away from the plane of the carbon atoms, in agreement with different experimental and theoretical observations in metallocenes of main group elements and transition metals.[31] The bend angle, θ, given in Table 2 and 3 reveals that the hydrogens of the Cp ring are bent away from the metal (θ negative) except in ferrocene and pentaphosphaferrocene. In these two systems, the hydrogens are bent towards Fe by about 1.5°, which results in a lowering of the d_H distance by about 0.02−0.03 Å (Table 2 and 3). Experimental studies show that the hydrogen atoms are bent out of the Cp plane towards the metal center in metallocenes such as FeCp$_2$, CrCp$_2$ and NiCp$_2$ by 3.0−6.5°.[28,31b−31h] The present study predicts the right direction of bending of the hydrogens in ferrocene and the magnitude of the bend angle is also close to the value of 1.6(0.4)° reported in a neutron diffraction study.[32] The hydrogens in ruthenocene and osmocene and their pentaphospha analogues bend away from the metal center and the bend angle is smaller in magnitude (<1°).

Nature of the Bonding in the Complexes

The force constant of the Cp−M stretching vibration is considered to be one of the most important parameters to assign the character of the Cp−M bonding.[18h] NMR and Mossbauer spectroscopic studies of ferrocene and related complexes have shown the covalent nature of the Fe-ligand bonding, originating essentially from the π-contribution of the ligands.[33−35]

The covalent bond orders for the C−C bonds in the different MCp$_2$ and MCpP$_5$ complexes under study are in the range 1.25 −1.29 (Table 2 and 3). Comparison of these values with the B3LYP/6-31G* and B3LYP/6-311+G* C−C bond orders of 1.406 and 1.405 in the free cyclopentadienyl anion shows that the covalent bonding is reduced in the Cp unit of the complexes studied. The calculations reveal that the build-up of covalent bonding between the metal and the ligand carbons, with M−C bond orders in the range 0.25−0.35, is at the expense of bonding within the ligand. The highest M−C bond order of 0.34−0.35 is observed in osmocene, which has the lowest C−C bond order of 1.25−1.26. The B3LYP/Type-III predicted M−C bond orders of 0.29, 0.31, and 0.35 in ferrocene, ruthenocene and osmocene, respectively, reflect that the metal−ligand covalency increases in the Fe triad, as predicted by Mayor-López et al.[21d]

The M−P bond indices in the metallocenes of *cyclo*-P$_5$ are in the range 0.37−0.50 (Table 3 and 4). The ligated P$_5$ rings have P−P bond orders of 1.14−1.23, which are significantly lower than the value in the *cyclo*-P$_5$ anion (1.409

and 1.406 at B3LYP/6-31G* and B3LYP/6-311+G* levels, respectively). The bond orders for the M−P bonds in MCpP$_5$ are more pronounced than those of the M−C bonds. This is reflected in the shorter separation between the metal and P$_5$ ring as compared to that of M−Cp(centre), in agreement with the observed distances. The present analysis also reveals that the metal−P$_5$ covalent bonding increases along the iron triad.

Natural Population and Net Atomic Charges

The natural population of the valence orbitals of the metal and the ligand atoms and their net NPA charges obtained from the NBO analysis are shown in Table 5. It can be seen that the total population on the transition metal on the metallocene (Cp)$_2$M is less than the free-atom value of eight electrons and that the metal center exhibits a small positive charge of 0.16−0.28 at the different levels of calculations, in agreement with earlier observations.[23] However, the metal d-population increases in the order MCp$_2$ < MCpP$_5$ < M(P$_5$)$_2$. The ns and np valence orbital populations of the metal also increase in the above order, although the contribution of the np orbital is very small. According to B3LYP/Type-III calculations on the decaphosphametallocenes, 0.42, 0.41 and 0.50 electrons populate the ns orbitals in Fe, Ru and Os, respectively. The population of the metal d-orbitals exceeds eight electrons on the Fe and Ru centers and the total valence populations are 8.92, 8.88 and 8.56 for Fe, Ru, and Os, respectively. Thus, the population analysis reveals a significant accumulation of negative charges of −0.92, −0.88 and −0.56 on Fe, Ru and Os, respectively, in the decaphosphametallocenes. In these complexes, the 3s populations of phosphorus are 1.67, 1.68 and 1.69, while the corresponding 3p populations are 3.23, 3.23 and 3.25, respectively. Thus it is seen that the total valence orbital populations of the phosphorus atoms in the above complexes are lower than the free-atom value of five electrons, which indicates a small transfer of electron density from each phosphorus to the metal center. This leads to positive charges of 0.09, 0.09, and 0.06 on the phosphorus atoms of bis(*cyclo*-P$_5$) metallocenes of Fe, Ru and Os, respectively. Consequently the novel situation arises in which the metal attains significant negative charge (Fe: −0.92; Ru: −0.88; Os: −0.56). The present work establishes the fact that the *cyclo*-P$_5$ ligand is responsible for accumulation of excess electron density on the transition metal center by a small transfer of electron density from each P atom. This is also observed at B3LYP/Type-I and B3LYP/Type-II levels and even when ECPs are used for phosphorus atoms at the B3LYP/LANL2DZ level. The more reliable B3LYP/6-311+G* study on ferrocenes corroborates this finding. A small negative charge of −0.05 on Fe in both mono- and bis(*cyclo*-P$_5$) ferrocenes has been reported by Frunzke et al.[23] Our recent work on the phosphorus analogues of lithocene anion and beryllocene also supports the fact that the P$_5$ ring transfers significant electron density to the metal center.[26] In these cases the metal center becomes less positive when the Cp ligand in the carbocyclic metallocene is replaced by *cyclo*-P$_5$ ligand. The present calculations

Table 5. Natural population of valence orbitals of the ligand and metal atoms and their natural charges for the eclipsed sandwich metallocenes by the B3LYP method

System[a]	Element	Natural population			Net NPA charge
		Ns	np	$(n-1)d$	
FeCp$_2$	C	0.96	3.29		−0.25
		0.96	*3.29*		*−0.24*
		0.97	**3.27**		**−0.25**
	Fe	0.17	0.02	7.53	0.28
		0.19	*0.02*	*7.61*	*0.18*
		0.17	**0.01**	**7.61**	**0.21**
FeCpP$_5$	C	0.97	3.24		−0.22
		0.97	*3.23*		*−0.21*
		0.97	**3.24**		**−0.22**
	P	1.66	3.30		0.03
		1.67	*3.27*		*0.05*
		1.69	**3.31**		**−0.00**
	Fe	0.31	0.06	7.92	−0.28
		0.34	*0.06*	*8.00*	*−0.40*
		0.30	**0.04**	**7.78**	**−0.11**
Fe(P$_5$)$_2$	P	1.66	3.25		0.09
		1.67	*3.23*		*0.09*
		1.69	**3.26**		**0.04**
	Fe	0.41	0.13	8.39	−0.91
		0.42	*0.12*	*8.39*	*−0.92*
		0.37	**0.11**	**7.87**	**−0.36**
RuCp$_2$	C	*0.97*	*3.28*		*−0.25*
		0.97	**3.27**		**−0.25**
	Ru	*0.21*	*0.01*	*7.54*	*0.25*
		0.18	**0.01**	**7.65**	**0.16**
RuCpP$_5$	C	*0.98*	*3.25*		*−0.24*
		0.98	**3.23**		**−0.22**
	P	*1.69*	*3.29*		*0.01*
		1.68	**3.29**		**0.03**
	Ru	*0.42*	*0.06*	*7.58*	*−0.08*
		0.26	**0.04**	**7.96**	**−0.27**
Ru(P$_5$)$_2$	P	*1.68*	*3.23*		*0.09*
		1.69	**3.23**		**0.08**
	Ru	*0.41*	*0.10*	*8.37*	*−0.88*
		0.38	**0.08**	**8.32**	**−0.77**
OsCp$_2$	C	*0.97*	*3.29*		*−0.26*
		0.97	**3.29**		**−0.26**
	Os	*0.33*	*0.02*	*7.36*	*0.27*
		0.30	**0.01**	**7.43**	**0.26**
OsCpP$_5$	C	*0.98*	*3.25*		*−0.24*
		0.98	**3.25**		**−0.24**
	P	*1.69*	*3.29*		*0.01*
		1.68	**3.28**		**0.03**
	Os	*0.42*	*0.06*	*7.58*	*−0.08*
		0.38	**0.05**	**7.76**	**−0.19**
Os(P$_5$)$_2$	P	*1.69*	*3.25*		*0.06*
		1.69	**3.22**		**0.08**
	Os	*0.50*	*0.13*	*7.92*	*−0.56*
		0.51	**0.11**	**8.15**	**−0.76**

[a] Numbers in normal typeface correspond to the 6-311+G* basis set; bold values and those in italics correspond to Type-II and Type-III calculations, respectively.

on the mono(*cyclo*-P$_5$) metallocenes of Fe, Ru and Os also show that the phosphorus atoms exhibit a small positive charge and the metal center attains a negative charge, although it is less pronounced. Thus the B3LYP/Type-III calculations on CpMP$_5$ yield net charges of −0.40, −0.08 and −0.08 on Fe, Ru and Os, respectively. This finding corrob-

orates the experimental observation of diamagnetic behavior in an iridium derivative of Fe(P$_5$), which led Scherer and co-workers to conclude that the Fe atom is negatively charged while one of the P atoms is positively charged.[7g] The observation that the metal center is electron rich and the P$_5$ ring is electron deficient in M(P$_5$)$_2$ may have an impact in catalysis, since the heterocyclic complexes are increasingly used as catalysts.[12]

Aromaticity in the Ligand Species

There has been a recent surge of interest in the aromaticity of heterocycles containing phosphorus with different coordination numbers.[36] The *cyclo*-P$_5$ anion contains six π-electrons in the ring and is classified as aromatic, similar to the Cp anion, based on its UV spectrum[5b] and according to geometric, energetic and magnetic criteria of aromaticity.[13−15] However, the change in the degree of aromaticity in the Cp and P$_5$ ligands in metal complexes has not been explored so far. Knowledge of the degree of aromaticity in the ligand moieties in the complexes will aid in the understanding of the bonding in the metallocenes. The ring expansion and the consequent weakening of ring bonds in the Cp and *cyclo*-P$_5$ ligands in the different complexes under study shows that the aromaticity of the ligand moieties is lower than in the free anions of Cp and P$_5$, respectively. We have estimated the relative aromaticity RI_x of the Cp and P$_5$ rings in the complexes with reference to the free Cp and P$_5$ anions, respectively, using the relationship

$$RI_x = \frac{I_x \text{ (complex)} - I_\text{ethane}}{I_x \text{ (anion)} - I_\text{ethane}}$$

where x denotes the Cp or P$_5$ ring and I_x denotes the aromaticity index. Although different geometric, energetic and magnetic criteria are widely used to quantify aromaticity in cyclic systems,[37−41] in the present analysis the aromaticity index is taken as the lowest ring bond-order, in accordance with the ring-current definition of Jug.[37a] I_ethane is the C−C bond order in the archetypal nonaromatic compound ethane. The bond orders obtained from the NBO analysis were used in the comparison. Since bond orders are less sensitive to the basis sets than the bond lengths (Table 2−4), meaningful estimates of relative aromaticity can be obtained from this analysis. Table 6 lists the relative aromaticity in the ligands obtained using bond orders at the same level of the theory. These results indicate that the Cp ring retains 56−68% of aromaticity in the complexes MCp$_2$ and MCpP$_5$ (M = Fe, Ru, Os), and that the aromaticity of the Cp ligand is highest when the central metal is Fe and lowest when it is Os. A similar trend exists in the relative aromaticity of the P$_5$ ring in the complexes MCpP$_5$ and M(P$_5$)$_2$ (M = Fe, Ru, Os) but the magnitude is considerably lower (26−51%).

In the metallocenes under study, the decrease of aromaticity is more pronounced in the P$_5$ ring than in the Cp

Table 6. Relative aromaticitiy (in %) of Cp and P₅ ligands in the metallocenes of Fe, Ru and Os in an eclipsed sandwich (D_{5h}/C_{5v}) arrangement

[a]	Cp ligand				P₅ ligand			
	Type I	Type II	Type III	6-311+G*	Type I	Type II	Type III	6-311+G*
FeCp₂	67.9	67.2	66.1	66.4				
FeCpP₅	66.0	65.8	64.7	65.3	50.5	45.6	42.5	43.9
Fe(P₅)₂					51.1	47.0	44.8	45.1
RuCp₂	64.9	64.1	63.3					
RuCpP₅	66.3	65.8	64.7		44.0	40.0	36.3	
Ru(P₅)₂					47.3	43.9	40.3	
OsCp₂	58.6	57.6	55.9					
OsCpP₅	63.3	62.4	61.9		32.6	28.5	25.9	
Os(P₅)₂					38.0	34.9	33.5	

[a] C−C bond orders: B3LYP/6-31G*: Cp^- = 1.406; ethane = 1.041; B3LYP/6-311+G*: Cp^- = 1.405; ethane = 1.051. P−P bond orders in P₅ anion: B3LYP/6-31G*: 1.409; B3LYP/6-311+G*: 1.406.

ring. This situation is compensated by stronger metal−P₅ bond formation, as observed earlier. It is evident from the significant bond indexes for M−C and M−P bonds that considerable π-electron density of the ligand moiety is directed towards bonding with the central metal. Even though the ligands are weakened, the complex gains stability due to covalent bonding of the ligand atoms with the central atom.

Conclusions

The present study reveals that the metal attains a negative charge of about one unit in the decaphosphametallocenes $[M(\eta^5\text{-}P_5)_2]$ (M = Fe, Ru and Os). The natural population analysis establishes the fact that the *cyclo*-P₅ ligand is responsible for an accumulation of excess electron density on the transition metal center by a small transfer of electron density from each P atom. The observation that the metal center is electron rich and the P₅ ring is electron deficient in M(P₅)₂ may have an impact in catalysis, since the heterocyclic complexes are increasingly being used as catalysts.

The B3LYP/6-311+G* bond-dissociation energy of 615 kcal/mol in ferrocene agrees very well with the experimental value of 635 ± 15 kcal/mol. The calculations reveal that the build-up of covalent bonding between the metal and the ligand is at the expense of bonding within the ligand. The present analysis also shows that both the M−Cp and M−P₅ covalent bonding increases along the iron triad.

Computational Aspects

All computations reported in this study were carried out using the Gaussian 03 suite of programs.[42] Hybrid Hartree−Fock−DFT calculations were performed with Becke's three parameter hybrid-exchange functional and the gradient-corrected nonlocal correlation functional of Lee, Yang and Parr (B3LYP).[43] We performed all-electron calculations on ferrocene and its *cyclo*-P₅ analogues $[FeCp(\eta^5\text{-}P_5)]$ and $[Fe(\eta^5\text{-}P_5)]$ with a triple-split valence basis set, which includes polarization and diffuse functions on the heavy atoms, at the B3LYP/6-311+G* level.[44] The calculations make use of the McLean−Chandler[44b,44c] (12s,9p) → (621111, 52111) basis set ("negative-ion" basis set) for phosphorus atoms. The Watchers−Hay all-electron basis set,[44d,44e] including the scaling factor of Raghavachary and Trucks,[44f] was used for the iron center. In the metallocenes of Ru and Os, the calculations invoked an electron core potential (ECP) approximation for the chemically inactive core electrons of the metal. Three different types of calculations were performed using the ECPs: in Type-I, the ligand atoms (H, C, and P) were treated with the split valence basis set including polarization at the 6-31G* level; in Type-II and Type-III, the 6-311+G* basis set was used for the ligand atoms. The core electrons of the metal were treated, in these three types of calculations, by the Los Alamos small-core potentials (LanL2)[45a] which incorporate some relativistic effects for post third-row atoms and are found to be the "best known" ECPs.[44a] In Type-I and Type-II, the metal valence electrons are treated by the double-zeta basis set of Hay and Wadt (LanL2DZ).[45a] The Type-III calculations invoke the Stevens−Basch−Krauss triple-split valence basis[45b−45d] for the valence electrons of the metal. Complete structural optimization was carried out for the eclipsed sandwich (D_{5h}/C_{5v}) and the staggered sandwich (D_{5d}/C_{5v}) geometries of the metallocenes.

Vibrational frequencies were calculated at the optimized geometries and the total energies were corrected for zero-point vibrational energy (ZPE). A scaling factor of 0.98 for ZPE, which is reported to be suitable for B3LYP/6-31G* calculations,[46] was used in the present work. The dications of the metals were calculated at their ⁵D ground state. The total energies of the complexes E(LML′) and their ionic components E(L⁻), E(L′⁻) and E(M²⁺) are included in the Supporting Information (Table S1).

The bonding in the metallocenes was examined by natural atomic orbital (NAO) and natural bond orbital (NBO) analyses using the NBO program incorporated in the Gaussian package.[47] Natural Population Analysis (NPA) performed in the NAO basis is well known to yield reliable estimates of atomic charges, in contrast to the Mulliken Population Analysis (MPA) charges, which are highly sensitive to the basis sets employed.[48] The extent of covalent bond formation between the metal and the ligand atoms was analyzed using bond orders[49] calculated in terms of natural atomic orbitals.

Acknowledgments

[1] C. Elschenbroich, A. Salzer, *Organometallics − A Concise Introduction*, VCH Verlagsgesellschaft, Weinheim, Germany, **1989**.

[2] [2a] P. Jutzi, N. Burford, *Chem. Rev.* **1999**, *99*, 969. [2b] J. C. Green, *Chem. Soc. Rev.* **1998**, *27*, 263.

[3] A. Togni, L. Halterman, *Metallocenes: Synthesis, Reactivity, Applications*, Wiley-VCH, Weinheim, **1998**.

[4] N. J. Long, *Metallocenes*, Blackwell Science, Oxford, **1998**.

[5] [5a] M. Baudler, D. Düster, D. Ouzounis, *Z. Anorg. Allg. Chem.* **1987**, *544*, 87. [5b] M. Baudler, S. Akpapoglou, D. Ouzounis, F. Wasgestian, B. Meinigke, H. Budzikiewicz, H. Munster, *Angew. Chem.* **1988**, *100*, 288; *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 280. [5c] M. Baudler, D. Ouzounis, *Z. Naturforsch., Teil B* **1989**, *44*, 831. [5d] B. M. Gimarc, *Pure Appl. Chem.* **1990**, *62*, 423.

[6] [6a] O. J. Scherer, T. Brück, G. Wolmershäuser, *Chem. Ber.* **1988**, *121*, 935. [6b] B. Rink, O. J. Scherer, G. Wolmershäuser, *Chem. Ber.* **1995**, *128*, 71. [6c] M. Baudler, T. Etzbach, *Angew. Chem.* **1991**, *103*, 590; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 580. [6d] B. Rink, O. J. Scherer, G. Heckmann, G. Wolmershäuser, *Chem. Ber.* **1992**, *125*, 1011. [6e] A. K. Hughes, V. J. Murphy, D. O'Hare, *J. Chem. Soc., Chem. Commun.* **1994**, 163. [6f] O. J. Scherer, G. Berg, G. Wolmershäuser, *Chem. Ber.* **1995**, *128*, 635. [6g] O. J. Scherer, T. Hilt, G. Wolmershäuser, *Organometallics* **1998**, *17*, 4110. [6h] O. J. Scherer, S. Wiegel, G. Wolmershäuser, *Chem. Eur. J.* **1998**, *4*, 1910. [6i] A. R. Kudinov, P. V. Petrovskii, M. I. Rybinskaya, *Russ. Chem. Bull.* **1999**, *48*, 1362. [6j] A. R. Kudinov, M. I. Rybinskaya, *Russ. Chem. Bull.* **1999**, *48*, 1615. [6k] A. R. Kudinov, D. A. Loginov, Z. A. Starikova, P. V. Petrovskii, M. Corsini, P. Zanello, *Eur. J. Inorg. Chem.* **2002**, 3018.

[7] [7a] O. J. Scherer, *Comments Inorg. Chem.* **1987**, *6*, 1. [7b] O. J. Scherer, *Angew. Chem.* **1990**, *102*, 1137; *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 1104. [7c] M. Baudler, K. Glinka, *Chem. Rev.* **1993**, *93*, 1623. [7d] O. J. Scherer, *Acc. Chem. Res.* **1999**, *32*, 751 and references therein. [7e] K. H. Whitemire, *Adv. Organomet. Chem.* **1998**, *42*, 1. [7f] M. Herberhold, G. Frohmader, W. Milius, *J. Organomet. Chem.* **1996**, *522*, 185. [7g] M. Detzel, T. Mohr, O. J. Scherer, G. Wolmershäuser, *Angew. Chem.* **1994**, *106*, 1142; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1110. [7h] L. Weber, *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 2618.

[8] E. Urnezius, W. W. Brennessel, C. J. Cramer, J. E. Ellis, P. v. R. Schleyer, *Science* **2002**, *295*, 832.

[9] J. F. Nixon, *Chem. Rev.* **1988**, *88*, 1327; A. G. Avent, F. G. N. Cloke, K. R. Flower, P. B. Hitchcock, J. F. Nixon, *Angew. Chem. Int. Ed.* **1994**, *33*, 2330; P. B. Hitchcock, C. Jones, J. F. Nixon, *Angew. Chem. Int. Ed.* **1994**, *33*, 463.

[10] F. T. Edelmann, D. M. M. Freckmann, H. Schumann, *Chem. Rev.* **2002**, *102*, 1851.

[11] K. B. Dillon, F. Mathey, J. F. Nixon, *Phosphorus: The Carbon Copy*, Wiley, Chichester, **1998**.

[12] [12a] L. Weber, *Angew. Chem. Int. Ed.* **2002**, *41*, 563. [12b] Deschamps, L. Ricard, F. Mathey, *J. Organomet. Chem.* **1997**, *548*, 17. [12c] K. Tanaka, G. C. Fu, *J. Org. Chem.* **2001**, *66*, 8177. [12d] K. Tanaka, S. Qiao, M. Tobisu, M. M.-C. Lo, G. C. Fu, *J. Am. Chem. Soc.* **2000**, *122*, 9870. [12e] S. Qiao, G. C. Fu, *J. Org. Chem.* **1998**, *63*, 4168.

[13] E. J. P. Malar, *J. Org. Chem.* **1992**, *57*, 3694.

[14] T. P. Hamilton, H. F. Schaefer III, *Angew. Chem.* **1989**, *101*, 500; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 485.

[15] A. Dransfeld, L. Nyulaszi, P. v. R. Schleyer, *Inorg. Chem.* **1998**, *37*, 4413.

[16] [16a] M. C. Kerins, N. J. Fitzpatrick, M. T. Nguyen, *Polyhedron* **1989**, *8*, 1135. [16b] J. A. Chamizo, M. Ruiz-Mazon, R. Salcedo, R. A. Toscano, *Inorg. Chem.* **1990**, *29*, 879.

[17] [17a] C. W. Bauschlicher Jr., S. R. Langhoff, H. Partridge, in *Modern Electronic Structure Theory, Part II* (Ed.: D. R. Yarkony), World Scientific, Singapore **1995**, p. 1280. [17b] M. A. Pietsch, M. Couty, M. B. Hall, *J. Phys. Chem.* **1995**, *99*, 16315. [17c] L. W. Mire, S. D. Wheeler, E. Wagenseller, D. S. Marynick, *Inorg. Chem.* **1998**, *37*, 3099. [17d] M. Couty, C. A. Bayse, R. Jimenez-Catano, M. B. Hall, *J. Phys. Chem.* **1996**, *100*, 13976. [17e] K. Pierloot, B. Persson, B. O. Roos, *J. Phys. Chem.* **1995**, *99*, 3465.

[18] [18a] R. L. Williamson, M. B. Hall, *Int. J. Quantum Chem., Quantum Chem. Symp.* **1987**, *21*, 503. [18b] T. E. Tailor, M. B. Hall, *Chem. Phys. Lett.* **1985**, *114*, 338. [18c] H. P. Lüthi, J. H. Ammeter, J. Almlöf, K. Faegri Jr., *J. Chem. Phys.* **1982**, *77*, 2002. [18d] J. Almlöf, K. Faegri, B. R. Schilling, H. Lüthi, *Chem. Phys. Lett.* **1984**, *106*, 266. [18e] H. Lüthi, P. E. M. Siegbahn, J. Almlöf, K. Faegri Jr., A. Heiberg, *Chem. Phys. Lett.* **1984**, *106*, 1. [18f] M. L. McKee, *J. Phys. Chem.* **1992**, *96*, 1683. [18h] E. Diana, R. Rossetti, P. L. Stanghellini, S. F. A. Kettle, *Inorg. Chem.* **1997**, *36*, 382.

[19] C. Park, J. Almlöf, *J. Chem. Phys.* **1991**, *95*, 1829.

[20] [20a] P. Hohenberg, W. Kohn, *Phys. Rev. B* **1964**, *136*, 864. [20b] R. G. Parr, W. Yang, *Density Functional Theory of Atoms and Molecules*, Oxford University Press, New York, **1989**.

[21] [21a] T. Yasuike, S. Yabushita, *J. Phys. Chem. A* **1999**, *103*, 4533. [21b] A. M. Orendt, J. C. Facelli, Y. J. Jiang, D. M. Grant, *J. Phys. Chem. A* **1998**, *102*, 7692. [21c] N. Matsuzawa, J. Seto, D. A. Dixon, *J. Phys. Chem. A* **1997**, *101*, 9391. [21d] M. J. Mayor-López, J. Weber, *Chem. Phys. Lett.* **1997**, *281*, 226. [21e] L. Maron, O. Eisenstein, *J. Phys. Chem. A* **2000**, *104*, 7140. [21f] M. Kaupp, P. v. R. Schleyer, M. Dolg, H. Stoll, *J. Am. Chem. Soc.* **1992**, *114*, 8202. [21g] Z.-F. Xu, Y. Xie, W.-L. Feng, H. F. Schaefer III, *J. Phys. Chem. A.* **2003**, *107*, 2716.

[22] G. Frison, F. Mathey, A. Sevin, *J. Phys. Chem. A.* **2002**, *106*, 5653.

[23] J. Frunzke, M. Lein, G. Frenking, *Organometallics* **2002**, *21*, 3351.

[24] M. Lein, J. Frunzke, G. Frenking, *Inorg. Chem.* **2003**, *42*, 2504.

[25] [25a] M. Lein, J. Frunzke, A. Timoshkin, G. Frenking, *Chem. Eur. J.* **2001**, *7*, 4155. [25b] L. Gagliardi, P. Pyykkö, *J. Phys. Chem. A* **2002**, *106*, 4690.

[26] E. J. P. Malar, *Inorg. Chem.* **2003**, *42*, 3873.

[27] M. F. Ryan, J. R. Eyler, D. E. Richardson, *J. Am. Chem. Soc.* **1992**, *114*, 8611 and references therein.

[28] [28a] A. Haaland, J. E. Nilsson, *Acta Chem. Scand.* **1968**, *22*, 2653. [28b] A. Haaland, *Acc. Chem. Res.* **1979**, *12*, 415.

[29] A. Hess, J. Sehnert, T. Weyhermüller, N. Metzler-Nolte, *Inorg. Chem.* **2000**, *39*, 5437.

[30] P. Seiler, J. D. Dunitz, *Acta Crystallogr., Sect. B* **1980**, *36*, 2946.

[31] [31a] K. C. Waterman, A. Streitwieser, R. Blom, K. Faegri Jr., T. Midtgaard, *J. Am. Chem. Soc.* **1991**, *113*, 3230. [31b] R. K. Bohn, A. Haaland, *J. Organomet. Chem.* **1966**, *5*, 470. [31c] B. J. Drouin, P. A. Cassak, S. G. Kukolich, *Inorg. Chem.* **1997**, *36*, 2868. [31d] S. Shibata, L. S. Bartell, R. M. Gavin, *J. Chem. Phys.* **1964**, *41*, 717. [31e] A. Haaland, J. Lusztyk, D. P. Norak, J. Brunvoll, *Chem. Commun.* **1974**, 54. [31f] I. A. Ronova, D. A. Bochvar, A. L. Chistjakov, Y. T. Struc, J. Alekseev, *J. Organomet. Chem.* **1966**, *5*, 470. [31g] P. Jutzi, F. Khol, P. Hofmann, C. Kruger, Y. H. Tsay, *Chem. Ber.* **1980**, *113*, 757. [31h] S. Alexandratos, A. Streitwieser Jr., H. F. Schaefer III, *J. Am. Chem. Soc.* **1976**, *98*, 7959. [31i] K. K. Jespersen, J. Chandrashekhar, P. v. R. Schleyer, *J. Org. Chem.* **1980**, *45*, 1608. [31j] K. C. Waterman, A. Streitwieser Jr., *J. Am. Chem. Soc.* **1984**, *106*, 3138.

[32] F. Takusagawa, T. F. Koetzle, *Acta Crystallogr., Sect. B* **1979**, *35*, 1074.

[33] R. H. Herber, I. Gattinger, F. H. Köhler, *Inorg. Chem.* **2000**, *39*, 851.

[34] A. A. Koridze, P. V. Petrovskii, S. P. Gubin, E. I. Fedin, *J. Organomet. Chem.* **1975**, *93*, C26.

[35] P. S. Nielsen, R. S. Hansen, H. J. Jacobsen, *J. Organomet. Chem.* **1976**, *114*, 145.

[36] [36a] L. Nyulaszi, *Chem. Rev.* **2001**, *101*, 1229 and references therein. [36b] G. Frison, A. Sevin, N. Avarvari, F. Mathey, P. Le Floch, *J. Org. Chem.* **1999**, *64*, 5524. [36c] E. Mattmann, F. Mathey, A. Sevin, G. Frison, *J. Org. Chem.* **2002**, *67*, 1208.

[37] [37a] K. Jug, *J. Org. Chem.* **1983**, *48*, 1344. [37b] K. Jug, A. Köster, *J. Phys. Org. Chem.* **1991**, *4*, 163. [37c] E. J. P. Malar, K. Jug, *J. Phys. Chem.* **1984**, *88*, 3508. [37d] E. J. P. Malar, K. Jug, *J. Phys. Chem.* **1985**, *89*, 5235. [37e] E. J. P. Malar, K. Jug, *Tetrahedron* **1986**, *42*, 417. [37f] K. Jug, E. J. P. Malar, *J. Mol. Struct.* **1987**, *153*, 221. [37g] E. J. P. Malar, F. Neumann, K. Jug, *J. Mol. Struct.* **1995**, *336*, 81. [37h] J. Jeevanandam, E. J. P. Malar, R. Gopalan, *Organometallics* **2003**, *22*, 5454.

[38] [38a] T. M. Krygowski, M. K. Cyranski, *Chem. Rev.* **2001**, *101*, 1385. [38b] J. A. N. F. Gomes, R. B. Mallion, *Chem. Rev.* **2001**, *101*, 1349. [38c] R. H. Mitchel, *Chem. Rev.* **2001**, *101*, 1301. [38d] A. R. Katritzky, K. Jug, D. C. Oniciu, *Chem. Rev.* **2001**, *101*, 1421. [38e] M. Randić, *Chem. Rev.* **2003**, *103*, 3449.

[39] [39a] A. R. Katritzky, P. Barczynski, G. Musamarra, D. Pisano, M. Szafran, *J. Am. Chem. Soc.* **1989**, *111*, 7. [39b] A. R. Katritzky, M. Karelson, S. Sild, T. M. Krygowski, K. Jug, *J. Org. Chem.* **1998**, *63*, 5228.

[40] [40a] P. v. R. Schleyer, P. K. Freeman, H. Jiao, B. Goldfuss, *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 337. [40b] P. v. R. Schleyer, H. Jiao, *Pure Appl. Chem.* **1996**, *68*, 209. [40c] L. Nyulaszi, P. v. R. Schleyer, *J. Am. Chem. Soc.* **1999**, *121*, 6872.

[41] M. K. Cyranski, T. M. Krygowski, A. R. Katritzky, P. v. R. Schleyer, *J. Org. Chem.* **2002**, *67*, 1333.

[42] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, *Gaussian 03, Revision B.04*, Gaussian, Inc., Pittsburgh PA, **2003**.

[43] [43a] A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648. [43b] C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785.

[44] [44a] J. B. Foresman, A. Frisch, *Exploring Chemistry with Electronic Structure Methods*, Gaussian, Inc., Pittsburgh, PA, **1996**. [44b] A. D. McLean, G. S. Chandler, *J. Chem. Phys.* **1980**, *72*, 5639. [44c] R. Krishnan, J. S. Binkley, R. Seeger, J. A. Pople, *J. Chem. Phys.* **1980**, *72*, 650. [44d] A. J. H. Wachters, *J. Chem. Phys.* **1970**, *52*, 1033. [44e] P. J. Hay, *J. Chem. Phys.* **1977**, *66*, 4377. [44f] K. Raghavachari, G. W. Trucks, *J. Chem. Phys.* **1989**, *91*, 1062.

[45] [45a] P. J. Hay, W. R. Wadt, *J. Chem. Phys.* **1985**, *82*, 270, 284, 299. [45b] W. Stevens, H. Basch, J. Krauss, *J. Chem. Phys.* **1984**, *81*, 6026. [45c] W. J. Stevens, M. Krauss, H. Basch, P. G. Jasien, *Can. J. Chem.* **1992**, *70*, 612. [45d] T. R. Cundari, W. J. Stevens, *J. Chem. Phys.* **1993**, *98*, 5555.

[46] C. W. Bauschlicher, H. Patridge, *J. Chem. Phys.* **1995**, *103*, 1788.

[47] [47a] J. P. Foster, F. Weinhold, *J. Am. Chem. Soc.* **1980**, *102*, 7211. [47b] E. D. Glendening, A. E. Reed, J. E. Carpenter, F. Weinhold, *NBO Version 3.1*.

[48] [48a] A. E. Reed, R. B. Weinstock, F. Weinhold, *J. Chem. Phys.* **1985**, *83*, 735. [48b] A. E. Reed, L. A. Curtiss, F. Weinhold, *Chem. Rev.* **1988**, *88*, 899. [48c] C. Lambert, P. v. R. Schleyer, *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1129.

[49] [49a] K. B. Wiberg, *Tetrahedron* **1968**, *24*, 1083. [49b] M. S. Gopinathan, K. Jug, *Theor. Chim. Acta* **1983**, *63*, 511.