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Nucleophilic or Electrophilic Phosphinidene Complexes ML_n=PH; What Makes the Difference?

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Abstract: Density functional studies, based on the local density approximation including nonlocal corrections for correlation and exchange self-consistently, have been carried out for the equilibrium structures of the phosphinidene transition metal complexes ML_n=PH, with M = Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W, Fe, Ru, Os, Co, Rh, Ir and L = CO, PH_3, Cp. The chemical reactivity of the transition metal-stabilized phosphinidene P−R is influenced by its spectator ligands L. Ligands with strong σ-donor capabilities on the metal increase the electron density on the phosphorus atom, raise the π*-orbital energy, and enhance its nucleophilicity. Spectator ligands with strong π-acceptor capabilities lower the charge concentration on P and stabilize the π*-orbital, which results in a higher affinity for electron-rich species. The ML_n=PH bond is investigated using a bond energy analysis in terms of electrostatic interaction, Pauli repulsion, and orbital interaction. A symmetry decomposition scheme affords a quantitative estimate of the σ- and π-bond strengths. It is shown that the investigated phosphinidenes are strong π-acceptors and even stronger σ-donors. The metal−phosphinidene interaction increases on going from the first to the second- and third-row transition metals.

Phosphinidenes, stabilized by transition metal complexes (L_n-MPR), are a rapidly growing class of viable reagents in phosphaorganic chemistry. Their properties and behavior relate to those of carbenes and support the notion that low-coordinate phosphorus compounds mimic the chemistry of their related hydrocarbons remarkably well.[1] In analogy with the transition metal-complexed carbenes, it is attractive to classify the phosphinidene complexes as electrophilic and nucleophilic. Such a generalized distinction for the carbene complexes L_nMCR_2 is made in terms of Fischer- and Schrock-type complexes and depends on the carbene substituent R, the choice of the transition metal M, its oxidation state, and the nature of its ligands L.[2] Is a similar distinction also appropriate for the complexed phosphinidenes? The literature of the past two decades does suggest the existence of phosphinidenes with rather different properties.

In the early 1980s, Mathey and co-workers developed a convenient cheletropic route for the in situ generation of phosphinidenes stabilized by a terminal $M(CO)_5$ (M = Cr, Mo, W) group.[3] The latest representative in this group is $(OC)_4Fe$=PNR_2, which is formed in situ by a condensation reaction.[4,5] Complexes of the general type $(OC)_nM$=PR are characterized by their high reactivity and short lifetime. So far, these reactive intermediates have eluded direct observation. However, their chemical reactivity toward, for example, alkenes and alkynes, is indicative of electrophilic behavior of singlet-state species. The analogy of the $M(CO)_n$-complexed phosphinidenes with Fischer carbenes is appealing despite their difference in stability.[6] The stability increases with a Cp* ligand. This is illustrated by the recently reported crystal structures of the cationic complexes $[Cp^*(OC)_nM$=$PNR_2][AlCl_4]$ (M = W, Ru; n = 3, 2), which display electrophilic behavior.[7]

Remarkably stable neutral transition metal-complexed phosphinidenes are also known. For example, crystal structures were reported for the bis(cyclopentadienyl)molybdenum,[8] -tungsten,[9] and -zirconium[10] complexes (Cp_2M)=PR as well as for the polydentate−tantalum complex $(N_3N)Ta$=PR [N_3N = $(Me_3SiNCH_2CH_2)_3N$, R = Ph, Cy, *t*-Bu)].[11] The reactivity of these phosphinidenes differs substantially from those that are complexed by the $M(CO)_n$ group. Illustrative is the reaction with aldehydes, which results in phosphaalkenes, while no addition

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to olefins has been observed. This nucleophilic behavior suggests a similarity with the Schrock carbenes.[12]

What drives this distinction in properties of the phosphinidenes? Can a classification be applied analogous to the Fischer- and Schrock-type carbene complexes? For example, the transition metal of the electrophilic $(OC)_5W{=}PR$ is in a low oxidation state, while the nucleophilic $(N_3N)Ta{=}PR$ contains an early transition metal in a high oxidation state. However, the spectator ligand can be of equal or of even more importance. For example, replacing the CO ligands in $(OC)_5Mo{=}PR$ for cyclopentadienyl groups while maintaining the same transition metal, as in $Cp_2Mo{=}PR$, changes the behavior from electrophilic to nucleophilic.

The pivotal issue we address in this investigation is how the chemical behavior of phosphinidene complexes may be tuned by modifying the transition metal and its ligands. Our primary aim is to determine what distinguishes electrophilic from nucleophilic phosphinidene complexes. Answering this question requires insight into the influence of the transition metal group on the phosphorus atom, which can be obtained with density functional theoretical (DFT) methods. DFT studies have been applied successfully to highlight the influence of both the $M(CO)_5$ (M = Cr, Mo, W) group and the π-donating P−R substituent on the singlet−triplet splitting of phosphinidenes.[13] The applicability of the DFT method for these systems has been supported by an ab initio study using high-level correlation schemes.[14] In the present study, we will use the DFT method first to rationalize the electrophilic versus nucleophilic behavior using the electronic structures of the $(OC)_4Fe{=}PR$ and $(Cp_2Cr){=}PR$ complexes, respectively. Next we will investigate a broad spectrum of phosphinidene complexes containing the CO, phosphine (PH_3), and cyclopentadienyl (Cp) ligands to establish whether they fall into one of the extreme categories or exhibit a gradual transition from nucleophilicity to electrophilicity. Finally, we will examine the changes on going from the first- to the second- to the third-row transition metals.

Method

General Procedure. The calculations were carried out using the parallelized Amsterdam density functional (ADF) program.[15] The MOs were expanded in a large, uncontracted set of Slater-type orbitals (STOs) containing polarization functions. The used TZP basis set is of triple-ζ quality for all atoms and has been augmented with one set of 4p functions for each transition metal atom and one set of d-polarization functions for each main group atom.[16] The 1s core shell of carbon and oxygen and the 1s2s2p core shells of phosphorus were treated by the frozen-core (FC) approximation. The metal centers were described by an uncontracted triple-ζ STO basis set for the outer *n*s, *n*p, *n*d, $(n+1)$s, $(n+1)$p orbitals and in the case of the third-row transition metals also for the 4f orbitals, whereas the shells of lower energy were treated by the frozen core approximation. An auxiliary set of s, p, d, f, and g STOs, centered on all nuclei, was used to fit the molecular density and to represent the Coulomb and exchange potentials accurately in each self-consistent field (SCF) cycle.[17] The numerical integration and the calculation of the VDD charges was done with the scheme developed by te Velde and Baerends.[18]

All calculations were performed at the nonlocal exchange self-consistently (NL-SCF) level, using the local density approximation (LDA) in the Vosko−Wilk−Nusair parametrization[19] with nonlocal corrections for exchange[20] and correlation (BP).[21] All geometries were optimized using the analytical gradient method implemented by Versluis and Ziegler[22] including relativistic effects by the ZORA approximation.[23]

Bonding Energy Analysis. The transition metal−phosphorus bond is analyzed by decomposing the interaction energy in an exchange (or Pauli) repulsion plus electrostatic interaction energy part (ΔE^{elst}) and an orbital interaction energy (charge transfer, polarization).[24] Usually fragments need to be prepared for interaction, either by deforming them from their equilibrium structure to the geometry they acquire in the overall molecule or by electronic excitation to a "valence state" electronic configuration. The overall bond energy ΔE is thus made up of three major components:

$$\Delta E = \Delta E^{\text{prep}} + \Delta E^{\circ} + \Delta E^{\text{oi}} \quad (1)$$

where

$$\Delta E^{\circ} = \Delta E^{\text{elst}} + \Delta E^{\text{Pauli}}$$

Note that ΔE is defined as the negative of the bond dissociation energy (BDE), i.e., $\Delta E = \text{E(molecule)} - E\text{(fragments)}$, thereby giving negative values for stable bonds. ΔE^{elst} represents the usually attractive electrostatic interaction between the prepared fragments when they are put (with unchanged electron densities) at the positions they occupy in the complex. The Pauli repulsion term ΔE^{Pauli} consists of the four-electron destabilizing interactions between occupied orbitals and is responsible for the steric repulsion. For neutral fragments, ΔE^{elst} and ΔE^{Pauli} are usually combined in the term ΔE° (eq 1). The orbital interaction ΔE^{oi} accounts for charge transfer (interaction between occupied and unoccupied orbitals on the two fragments) and polarization (empty/occupied orbital mixing on one fragment). We will not try to separate charge-transfer and polarization components, but will use the extended transition state (ETS) method developed by Ziegler and Rauk to decompose the ΔE^{oi} term into contributions from each irreducible representation of the interacting system. In systems with a clear σ, π-separation, this symmetry partitioning proves to be most informative.

Results and Discussion

The presentation of the data is as follows. First we discuss two typical cases, an electrophilic phosphinidene complex, $(OC)_4Fe{=}PH$, and a nucleophilic one, $Cp_2Cr{=}PH$. Next we compare the computed structures and reactivities for a selected group of phosphinidene complexes including a comparison with reported X-ray crystal structures and observed reaction behavior. Finally, we evaluate the ligand (CO, PH_3, Cp) substitution for all the first-, second-, and third-row transition metal complexes.

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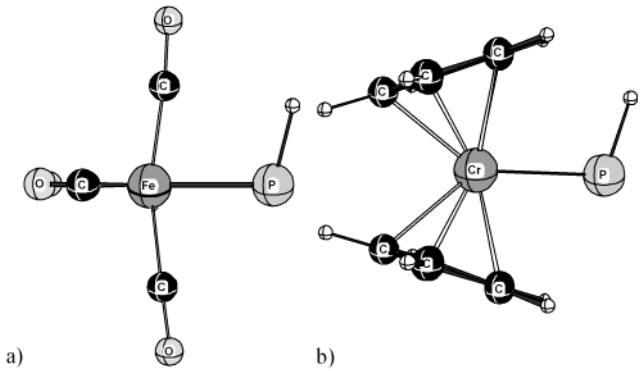


Figure 1. Optimized structures of (a) $Fe(CO)_4$=PH and (b) $CrCp_2$=PH.

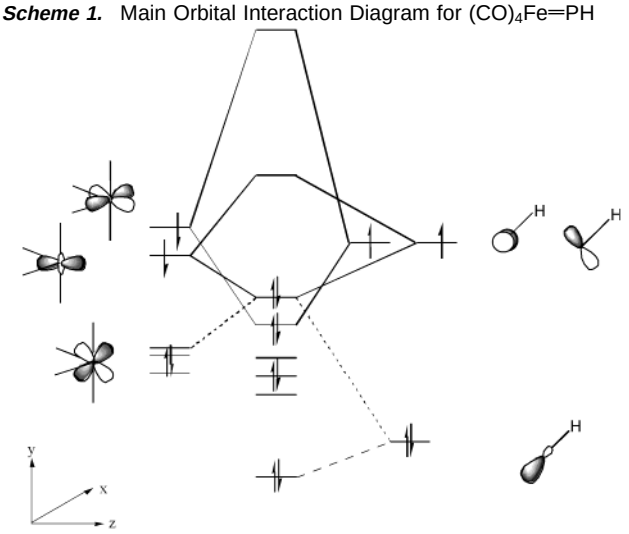
I. Electrophilic versus Nucleophic Reactivity. (A) Electrophilic Phosphinidene Complex $(OC)_4Fe$=PH. The transient P−N^{i}Pr$_2$ derivative of this complex, which is synthesized in situ from ^{i}Pr$_2$NPCl$_2$ and Collman's reagent ($Na_2Fe(CO)_4$), adds to alkynes and olefins below 0 °C. Evidently, it possesses electrophilic character despite its electron-donating amine substituent. So far, it is the only reported derivative with a complexing $Fe(CO)_4$ group. A broader spectrum of derivatives is known for the electrophilic $(OC)_5MPR$ (M = W, Mo, Cr) phosphinidenes. These reagents typically require higher temperatures for their generation (about 100° without and 60 °C with CuCl as catalyst). Theoretical studies showed a stabilizing influence of the NH_2 group versus the H, CH_3, and Ph groups, for both $M(CO)_5$ complexed and "free" phosphinidenes. We focus on the parent iron complex because of its simpler orbital analysis as will become evident.

Geometry. The optimized geometry of $(OC)_4Fe$=PH, shown in Figure 1a, has a distorted trigonal bipyramidal form with the phosphinidene group in the equatorial plane of the transition metal. The P−H bond is in an eclipsed conformation with one of the axial COs. The two axial CO ligands are slightly bent (∠C−Fe−C = 164.1°) toward the phosphorus. Rather small values are calculated for the Fe−P−H angle of 104.9° and the Fe=P bond distance of 2.192 Å. This distance is even shorter than the earlier reported calculated Cr=P distance of 2.271 Å for $(OC)_5Cr$=PH, which was interpreted to possess significant double bond character.[13] Unfortunately, there are no experimental data available for comparison.

MO Interaction Diagram. To establish the orbital interactions for the iron complex, we construct a qualitative MO diagram from the $Fe(CO)_4$ and PH fragments, both of which have triplet ground states.[13,25] The diagram is given in Scheme 1. It shows the preformed $Fe(CO)_4$ fragment (C_{2v} symmetry) in its typical d^8 configuration with two unpaired electrons in the d_{z^2} and d_{xy} hybrid orbitals of iron. The $^3Fe(CO)_4$ is calculated to be 17.9 kcal/mol more stable than the corresponding closed-shell singlet state.

The ^{3}PH fragment is depicted with one electron in each of the degenerate p_x and p_z orbitals; the ^{1}PH − ^{3}PH energy difference amounts to 34.8 kcal/mol in favor of the triplet state. The main feature of the orbital interaction diagram is that the singly occupied orbitals of both the fragments are of similar energy. One-electron energies of 5.47 eV are calculated for those of PH and 5.20 (d_{z^2}) and 5.60 (d_{xy}) eV for those of $Fe(CO)_4$. This similarity in fragment orbital energies suggests that little, if any, net charge transfer takes place between the P and Fe atoms in the phosphinidene complex.

Scheme 1. Main Orbital Interaction Diagram for $(CO)_4Fe$=PH



Atomic Charges. Indeed, the calculated VDD charge[18] of only −0.060e on the phosphorus atom supports the depicted view; all atomic charges are given in Table 1. Whereas the magnitude and mathematical sign of calculated partial charges are not directly related to observable quantities, a comparison within a series of similar structures, however, shows trends that can be related to physical and chemical properties. We shall pursue this comparative analysis in the following sections.

(B) Nucleophilic Phosphinidene Complex Cp_2Cr=PH. The P-supermesityl (2,4,6-^{t}Bu$_3$−C$_6$H$_2$)-substituted derivatives of the heavier Mo and W congeners of this complex are both reported to be stable compounds, much in contrast to the transient electrophilic metal−carbonyl complexes. The crystallographically determined short Mo=P bond distance of 2.370(2) Å with a rather bent phosphorus (∠MoPC = 115.8(2)°) suggests double bond character despite the bulkiness of the supermesityl group. The ^{31}P NMR resonance of the WCp_2 complex at 661.1 ppm has a surprisingly small ^1J(P,W) coupling constant of 153 Hz,[8] suggesting a rather negatively charged phosphorus. We chose the parent nucleophilic system of the lighter, "first-row" Cp_2Cr complex for our analysis.

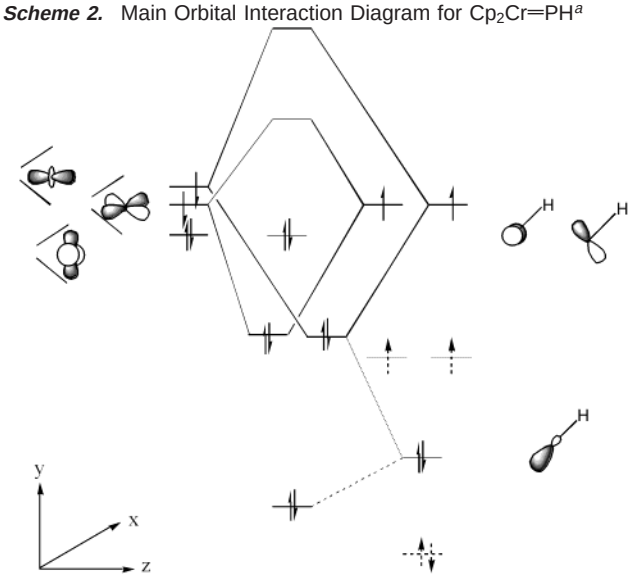
Geometry. The optimized typical sandwich-like geometry of Cp_2Cr=PH (C_s symmetry), shown in Figure 1b, has a rather short Cr=P bond length of 2.289 Å with a Cr−P−H angle of 106.8°, both of which are indicative of double bond behavior. The CrP bond length is only modestly longer than the 2.271 Å for the electrophilic $(OC)_5Cr$=PH.[13] Analogous to the crystallographic structure of Cp_2Mo=PMes*, the PH bond in the parent $CrCp_2$ structure is in an eclipsed conformation with one of the Cp ligands. The Cp−Cr−Cp angle of 147.4° is also similar to the experimental value of 144.6 ° for the Mo structure.[8]

MO Interaction Diagram. Again we construct a molecular interaction diagram from the Cp_2Cr and PH fragments to inspect the electronic properties of the complex (Scheme 2). Like $Fe(CO)_4$, the Cp_2Cr fragment also has a preferred triplet ground state as well, making a comparison straightforward. Since the chromium atom in Cp_2Cr is formally doubly charged (+2), a typical d^4 configuration results. Two electrons are in the doubly occupied $d_{x^2-y^2}$ orbital, which lies in the plane separating the two cyclopentadienyl rings. The other two d electrons are

Table 1. Calculated VDD Charges on the Phosphorus Atom of Phosphinidene Complexes ML_n=PH

Cp_2Ti=PH	Cp_2Cr=PH	$Cp(PH_3)_3V$=PH	$Cp(PH_3)Co$=PH	Cp(CO)Co=PH	$Cp(CO)_3V$=PH	$(CO)_4Fe$=PH
−0.270	−0.220	−0.210	−0.170	−0.118	−0.081	−0.060
Cp_2Zr=PH	Cp_2Mo=PH	$Cp(PH_3)_3Nb$=PH	$Cp(PH_3)Rh$=PH	Cp(CO)Rh=PH	$Cp(CO)_3Nb$=PH	$(CO)_4Ru$=PH
−0.295	−0.239	−0.243	−0.153	−0.145	−0.137	−0.109
Cp_2Hf=PH	Cp_2W=PH	$Cp(PH_3)_3Ta$=PH	$Cp(PH_3)Ir$=PH	Cp(CO)Ir=PH	$Cp(CO)_3Ta$=PH	$(CO)_4Os$=PH
−0.323	−0.236	−0.234	−0.151	−0.146	−0.144	−0.124

Scheme 2. Main Orbital Interaction Diagram for Cp_2Cr=PH[a]



[a] The dashed lines for PH indicate its orbital energies at infinite separation from Cp_2Cr.

divided over the d_{z^2} and d_{xz} orbitals, which are in the direction of the triplet PH fragment. Cr=P double bond character results from the combined σ ($P(p_z)-Cr(d_{z^2})$) and π ($P(p_x)-Cr(d_{xz})$) interactions. The π-interaction forces the P-substituent into the sterically most hindered position, i.e., pointing toward one of the cyclopentadienyl rings.

The important feature distinguishing the interaction diagram of Cp_2Cr=PH from that of $(OC)_4Fe$=PH is the much larger difference in energies between the singly occupied orbitals of the fragments. For the equilibrium geometries of the two fragments (at infinite distance), these energies are −3.10 eV for Cp_2Cr and −5.47 eV for PH; the energy diagram is depicted in Scheme 2. It is then not surprising that upon bond formation the PH fragment acts as an electron acceptor, causing significant charge to transfer from the metal to the phosphorus atom. Consequently, the PH fragment orbitals increase in energy and this is illustrated in Scheme 2. The transfer of charge seems to have less influence on the Cr orbitals, since the energy of the $d_{x^2-y^2}$ orbital, which shows no mixing with other orbitals, remains almost unchanged.

Atomic Charges. That indeed significant transfer of charge takes place is evident from the calculated charge of −0.220e on the phosphorus atom. This charge is substantially more than the −0.060e calculated for the $Fe(CO)_4$ complex. Hence, the relatively negatively charged phosphorus of Cp_2Cr=PH agrees with its nucleophilic character.

(C) M=P Bond Strengths. In preparation of an evaluation of the bond strength between phosphorus and all of the first-, second-, and third-row transition metals of the phosphinidene complexes, we determine in this section first those for the discussed $(OC)_4Fe$=PH and Cp_2Cr=PH. Computation of their BDEs is readily performed as the fragments are already available from the MO interaction analysis. The choice of the electronic ground state of all species involved is crucial. We emphasize again that the BDE analysis of the two (singlet) phosphinidene complexes is straightforward because their fragments have strongly favored triplet ground states. In this context, it is worth noting that an analysis of the BDE of $(OC)_5Cr$=PH is less straightforward as the $Cr(CO)_5$ fragment has a preferred singlet ground state. Consequently, dissociating such a complex in either singlets (S) or triplets (T) would require incorporating T→S or S→T relaxation energies for $Cr(CO)_5$ or PH, respectively. As noted, this S→T relaxation energy is a significant 34.8 kcal/mol for the free phosphinidene.

$(OC)_4Fe$=PH. The singly occupied PH orbitals contribute equally, ∼45% each, to the $\sigma-$ and π-bonding orbitals of the complex, which are its highest occupied orbitals and separated by only 0.42 eV (Scheme 1). A reasonable participation of π-character to the Fe=P bonding seems plausible. Indeed, the orbital interaction energy ΔE^{oi} has a significant ΔE_π component of −32.2 kcal/mol besides a strong ΔE_σ contribution of −90.7 kcal/mol. Together with the interaction energy $\Delta E°$ of +55.3 kcal/mol and the small preparation energy ΔE^{prep} of +6.0 kcal/mol for the fragments, this results in a final BDE of −61.6 kcal/mol.

Cp_2Cr=PH. This complex has a slightly different bonding arrangement (Scheme 2). The PH fragment's contribution of ∼60% to the highest occupied MO with σ-bond character, the HOMO-1 (A′ symmetry), comes largely from its singly occupied p_z orbital with some participation of the phosphorus lone pair orbital. This mixing-in of the lone pair represents a slight shift from sp toward sp^2 hybridization on complexation of the phosphinidene. The π-bonding orbital (A″ symmetry) is more balanced as the singly occupied p_x (P) and d_{xz} (Cr) orbitals contribute equally. Compared to the $(OC)_4Fe$=PH complex, this bonding arrangement translates into a smaller ΔE_σ component (−79.5 kcal/mol), but with nearly equal contributions from ΔE_π (−30.0 kcal/mol), $\Delta E°$ (+53.3 kcal/mol), and ΔE^{prep} (+17.1 kcal/mol). Consequently, a smaller BDE of −39.1 kcal/mol results. However, it is evident that both the electrophilic $(OC)_4Fe$=PH and the nucleophilic Cp_2Cr=PH have double bonds between the transition metal and the phosphorus.

(D) Charge Control and Orbital Control. We showed that the charges on the phosphorus atoms of $(OC)_4Fe$=PH and Cp_2Cr=PH are rather different from each other due to the different frontier orbital energies of their transition metal fragments. This transfer of charge (*charge control*) is significant for the nucleophilic Cp_2Cr=PH. However, the reactivity of a phosphinidene complex also depends on its orbital energies (*orbital control*). Nucleophilic phosphinidenes are expected to have a filled donor orbital of high energy (HOMO) and electrophilic ones a low-lying empty acceptor orbital (LUMO). This is indeed the case.

Thus, the theoretically predicted energy of −4.4 eV for the LUMO of $(OC)_4Fe$=PH, which is the π*-orbital formed from an antibonding combination of the phosphorus p_x orbital and the metal d_{xz} orbital, is much lower in energy than that for Cp_2Cr=PH (−2.2 eV). Likewise, the orbital energy of −4.4 eV for the phosphorus lone pair in Cp_2Cr=PH is much higher in energy than that for the corresponding orbital in $(OC)_4Fe$=PH (−6.4 eV). How can this harmony between charge control and orbital control be rationalized?

On P=M bond formation, PH acts as an electron acceptor when the metal moiety has high-lying frontier orbitals (i.e., Cp_2Cr); charge will transfer from the metal to phosphorus. As a result, the orbitals of the phosphinidene fragment rise in energy, which explains the relatively high energy of the phosphorus lone pair and hence its enhanced nucleophilicity. Simultaneously, the singly occupied orbitals of PH destabilize in the effective field of its enhanced negative charge, thereby reducing the energy gap with the d orbitals of the metal fragment, which consequently increases the interaction with these obitals. In fact, the interaction between the phosphorus p_x orbital and the d_{xz} orbital of the metal fragment is of comparable strength for the two metal fragments $Fe(CO)_4$ and $CrCp_2$. The interaction destabilizes the high-lying d_{xz} orbital of Cp_2Cr, which is ∼2.5 eV higher in energy than that of $Fe(CO)_4$, resulting in an antibonding π* (p_x-d_{xz}) LUMO of Cp_2Cr=PH that is 2.2 eV higher in energy than the π* LUMO of $(OC)_4Fe$=PH. Evidently, also orbital control suggests Cp_2Cr=PH to have nucleophilic character and identifies $(OC)_4Fe$=PH as electrophilic.

II. Ligand Variation for the First-Row Transition Metal Groups. So far, we have seen that electrophilic and nucleophilic phosphinidene complexes can be distinguished from each other by the relative energies of the highest (singly) occupied orbitals of the transition metal fragment. We have also seen that as a result the charge on the phosphorus atom differs for these complexes. What influences the orbital energies most? Is it the choice of the transition metal, its ligands, or both? And how adequate does the calculated charge on phosphorus reflect this influence?

To answer these questions, we apply Hoffmann's isolobal approach[26] to the transition metals of the first row. We consider three ligands with different properties, namely, the 6e η^5-donor Cp^-, the 2e σ-donor/2e π-acceptor CO, and PH_3, which is a moderate σ-donor and weak π-acceptor 2e ligand.[27] Moreover, we will consider only neutral systems. Consequently, replacing the negatively (−1) charged Cp ring for three CO ligands requires also a change of transition metal, to a column to the left in the periodic table.

Thus, Cp(OC)Co=PH and $(OC)_4Fe$=PH are isolobal as are Cp_2Cr=PH and $Cp(OC)_3V$=PH. Furthermore, this row of investigated transition metal phosphinidene complexes has been extended with the group IV bis(cyclopentadienyl) complexes. These compounds are $16e^-$ complexes and differ from the group VI analogues by their unoccupied $d_{x^2-y^2}$ orbital. However, the Zr congener is known for its nucleophilic reactivity and the $16e^-$ complex Cp_2Zr=PR can be isolated if it is stabilized by an extra trimethylphosphine ligand.[10] The X-ray structure shows a rather long distance of 2.74 Å for this additional ligand. We did not include the apparent weak interaction with additional ligands in our survey.

Table 2. Selected Bond Lengths (Å) and Angles (deg) of Phosphinidene Complexes ML_n=PH

	Cp_2Ti=PH	Cp_2Zr=PH	Cp_2Hf=PH
M−P	2.352	2.473	2.456
P−H	1.448	1.444	1.445
M−Cp_{anti}	2.055	2.229	2.188
M−Cp(2)	2.042	2.230	2.192
H−P−M	104.2	100.4	100.2
P−M−Cp(1)	104.9	103.8	104.6
P−M−Cp(2)	111.3	111.9	113.1
	Cp_2Cr=PH	Cp_2Mo=PH	Cp_2W=PH
M−P	2.286	2.377	2.379
P−H	1.453	1.447	1.446
M−Cp_{anti}	1.845	1.998	1.981
M−Cp(2)	1.834	1.992	1.980
H−P−M	106.8	103.6	103.1
P−M−Cp(1)	103.6	102.7	103.1
P−M−Cp(2)	108.9	110.0	110.7
	Cp(CO)Co=PH	Cp(CO)Rh=PH	Cp(CO)Ir=PH
M−P	2.090	2.203	2.216
P−H	1.451	1.450	1.451
M−Cp(1)	1.728	1.961	1.973
M−L	1.725	1.862	1.850
M−P−H	106.6	105.9	105.1
P−M−Cp(1)	133.5	133.6	132.5
P−M−L	90.1	88.9	90.8
	$Cp(PH_3)Co$=PH	$Cp(PH_3)Rh$=PH	$Cp(PH_3)Ir$=PH
M−P	2.085	2.195	2.210
P−H	1.463	1.462	1.465
M−Cp(1)	1.705	1.949	1.950
M−L	2.113	2.234	2.226
M−P−H	107.1	106.7	105.9
P−M−Cp(1)	133.9	4.7	135.1
P−M−L	91.4	88.8	90.0
	$Cp(CO)_3V$=PH	$Cp(CO)_3Nb$=PH	$Cp(CO)_3Ta$=PH
M−P	2.307	2.440	2.436
P−H	1.446	1.441	1.441
M−Cp(1)	1.980	2.172	2.150
M−L	1.938	2.114	2.091
M−L′	1.933	2.093	2.073
M−P−H	106.5	106.2	105.6
P−M−Cp(1)	114.4	112.0	111.9
P−M−L	126.6	126.7	127.3
Cp(1)−M−L′	127.2	129.4	128.9
	$Cp(PH_3)_3V$=PH	$Cp(PH_3)_3Nb$=PH	$Cp(PH_3)_3Ta$=PH
M−P	2.326	2.441	2.434
P−H	1.451	1.449	1.447
M−Cp(1)	1.993	2.165	2.140
M−L	2.414	2.563	2.538
M−L′	2.362	2.506	2.486
M−P−H	105.9	105.0	104.2
P−Mn−Cp(1)	108.9	106.9	107.5
P−M−L	139.8	140.2	140.4
Cp(1)−M−L′	126.2	129.6	129.4
	$(CO)_4Fe$=PH	$(CO)_4Ru$=PH	$(CO)_4Os$=PH
M−P	2.192	2.317	2.337
P−H	1.447	1.445	1.445
M−COax(1)	1.817	1.973	1.972
M−COax(2)	1.797	1.953	1.960
M−COeq	1.793	1.944	1.940
M−P−H	104.9	102.6	101.9
P−Mn−COeq	130.2	131.3	131.4

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Table 3. Calculated Energy Levels (in eV) for the Singly Occupied Orbitals of the Transition Metal Fragments ML_n

	Cp_2Ti	Cp_2Cr	$Cp(PH_3)_3V$	$Cp(PH_3)Co$	$Cp(CO)Co$	$Cp(CO)_3V$	$(CO)_4Fe$
a′	−2.95	−3.10	−2.86	−3.27	−4.01	−4.36	−5.20
a″	−3.21	−3.10	−3.47	−3.47	−4.39	−5.34	−5.60
	Cp_2Zr	Cp_2Mo	$Cp(PH_3)_3Nb$	$Cp(PH_3)Rh$	$Cp(CO)Rh$	$Cp(CO)_3Nb$	$(CO)_4Ru$
a′	−2.88	−2.96	−2.81	−3.31	−3.90	−4.26	−4.93
a″	−2.63	−3.28	−3.48	−3.57	−4.45	−5.24	−5.23
	Cp_2Hf	Cp_2W	$Cp(PH_3)_3Ta$	$Cp(PH_3)Ir$	$Cp(CO)Ir$	$Cp(CO)_3Ta$	$(CO)_4Os$
a′	−2.84	−2.95	−2.78	−3.39	−4.11	−4.22	−4.93
a″	−2.40	−3.19	−3.47	−3.38	−4.34	−5.16	−5.22

Geometries. The complexes $Cp_2Ti{=}PH$, $Cp(H_3P)_3V{=}PH$, $Cp(OC)_3V{=}PH$, $Cp(H_3P)Co{=}PH$, and $Cp(OC)Co{=}PH$ were investigated in addition to the already discussed $Cp_2Cr{=}PH$ and $(OC)_4Fe{=}PH$. Geometrical parameters of the optimized structures are given in Table 2. The geometry of $Cp_2Ti{=}PH$ is in good agreement with data derived at the B3LYP/LANL2DZ level of theory.[6] The most relevant geometrical parameter for the present discussion is the M═P bond length. Using a shorthand representation, this is 2.352 (2.348)[6] Å for Ti═P, 2.286 Å for Cr═P, 2,326 and 2.307 Å for V═P, 2.192 Å for Fe═P, and 2.090 and 2.113 Å for Co═P. It appears that the M═P bond lengths decrease in the order Ti > V > Cr > Fe > Co, which corresponds exactly with the relative position of these transition metals in the periodic table. This suggests that *the M═P bond length depends solely on the size of the transition metal*. We note that the same metal size dependency appears to apply to the Cp−M distances, which are 2.042 and 2.055 Å for Cp−Ti, 1.993 and 1.980 Å for Cp−V, 1.834 and 1.845 Å for Cp−Cr, and 1.728 and 1.705 Å for Cp−Co.

MO Interaction Diagrams. Following the discussions on $Cp_2Cr{=}PH$ and $(OC)_4Fe{=}PH$, it suffices here to focus on the energy levels of the singly occupied orbitals of the ML_n fragments in the geometry they possess in the complex. These are listed in Table 3 and make abundantly clear that *the frontier orbital energies are directly related to the type and number of metal ligands* (Cp > PH_3 > CO) rather than to the nature of the transition metal. The energy levels decrease gradually by replacing the Cp rings via PH_3 for CO ligands, and therefore, a smooth transition from nucleophilic $Cp_2M{=}PH$ (M = Ti, Cr) to electrophilic $(OC)_4Fe{=}PH$ can be expected. Illustrative are $Cp(H_3P)_3V$ and $Cp(OC)_3V$, which have the same transition metal but will differ in their philicity due to their different ligands.

Atomic Charges. The calculated charges on the phosphorus atom in the complexes are listed in Table 1 and are graphically displayed in Figure 2. They *give the same decreasing order* as the ML_n fragment orbital energies do, namely, $Cp_2Ti{=}PH$ > $Cp_2Cr{=}CH$ > $Cp(H_3P)_3V{=}PH$ > $Cp(H_3P)V{=}PH$ > $Cp(OC)$-$Co{=}PH$ > $Cp(OC)_3V{=}PH$ > $(OC)_4Fe{=}PH$. Thus, in accordance with the fragment MO energy analysis, the charges also emphasize the importance of the type of metal ligand on the philicity of the phosphinidene complex. Their values range from −0.270e for $Cp_2Ti{=}PH$ to −0.060e for the discussed $(OC)_4Fe{=}PH$. We note that Frison et al.[6] also reported a concentration of charge on the phosphorus atom of $Cp_2Ti{=}PH$ in comparison to $(OC)_5Cr{=}PH$.

Bond Strengths. The BDEs of the first-row transition metal phosphinidene complexes, listed in Table 4, show modest variations. They range from 39.1 kcal/mol for $Cp_2Cr{=}PH$ to 66.1 kcal/mol for $Cp(H_3P)Co{=}PH$. Their ΔE_π interaction energies are fairly constant (between −28.6 and −34.2 kcal/mol), while the differences are somewhat larger in the sizable ΔE_σ (up to 18.5 kcal/mol) and still larger in the $\Delta E°$ components (up to 21.1 kcal/mol). The π-bond strength is in all cases about one-third (32−39%) of the σ−bond strength. It seems that the phosphinidene bond strength is relatively independent of the spectator ligands of the metal.

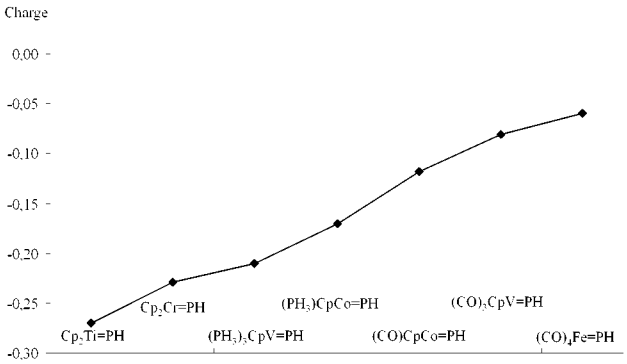

Figure 2. Calculated charges on the phosphorus atom of the first-row transition metal phosphinidene complexes $ML_n{=}PH$.

Charge and Orbital Control. The energy level of the LUMO of the phosphinidene complexes, which is the π^*-orbital[28] formed from an antibonding combination of the $P(p_x)$ orbital and the metal d_{xz} orbital, depends on the amount of charge transferred from ML_n to the phosphorus and on the strength of the orbital interaction. Because the π-interaction is of the same order of magnitude for the entire series, this means that the position of the LUMO in the final complex is also predetermined by the relative energy of the fragment orbitals.

In fact, the orbital energy of the lowest unoccupied orbitals of the complexes increases with decreasing π-acceptor capability of the spectator ligands (Table 5) making an electrophilic attack on the phosphorus less likely. This trend is evident from the linear relationship ($r^2 = 0.992$) of the LUMO orbital energies of the first-row phosphinidenes complexes with the corresponding P charges, as shown in Figure 3. Because charge control and orbital control work in the same direction, we are able to predict their philicity and thus the reactivity for these phosphinidene complexes.

III. Ligand Variation for the Second- and Third-Row Transition Metal Groups. In this section, we evaluate in a similar, but more condensed manner, the properties of those phosphinidene complexes that contain transition metals of the

(28) In the case of the group IV complexes, the π^*-orbital is the LUMO + 1 due to the unfilled d shell of the transition metal.

Table 4. Bond Energy Analysis (in kcal/mol) for the Phosphinidene Complexes ML_n=PH

	Cp_2Ti=PH	Cp_2Cr=PH	$Cp(PH_3)_3V$=PH	$Cp(PH_3)Co$=PH	Cp(CO)Co=PH	$Cp(CO)_3V$=PH	$(CO)_4Fe$=PH
ΔE_σ	−91.0	−79.5	−98.0	−88.0	−85.4	−94.3	−90.7
ΔE_π	−33.9	−30.0	−34.2	−27.9	−28.6	−37.2	−32.2
$\Delta E°$	−10	−14	−10	6.0	8	2	11
ΔE^{tot}	−74.4	−56.2	−67.0	−70.9	−70.5	−65.4	−67.6
BDE	60.0	39.1	49.5	66.1	65.8	52.8	61.7
	Cp_2Zr=PH	Cp_2Mo=PH	$Cp(PH_3)_3Nb$=PH	$Cp(PH_3)Rh$=PH	Cp(CO)Rh=PH	$Cp(CO)_3Nb$=PH	$(CO)_4Ru$=PH
ΔE_σ	−100.7	−92.5	−101.6	−96.6	−93.9	−92.0	−91.2
ΔE_π	−39.4	−35.7	−35.5	−32.7	−32.7	−34.1	−36.2
$\Delta E°$	−6	5	−5	2	12	6	14
ΔE^{tot}	−88.4	−76.8	−77.4	−81.0	−79.9	−70.9	−74.8
BDE	75.3	64.9	63.2	78.5	77.5	60.4	69.7
	Cp_2Hf=PH	Cp_2W=PH	$Cp(PH_3)_3Ta$=PH	$Cp(PH_3)Ir$=PH	Cp(CO)Ir=PH	$Cp(CO)_3Ta$=PH	$(CO)_4Os$=PH
ΔE_σ	−105.2	−103.3	−110.9	−112.3	−108.0	−97.8	−98.5
ΔE_π	−43.0	−39.5	−38.1	−39.1	−38.7	−35.5	−40.0
$\Delta E°$	−8	0	−11	8	10	0	−1
ΔE^{tot}	−98.3	−87.6	−83.3	−95.7	−93.6	−75.6	−83.4
BDE	80.7	75.6	68.1	92.4	90.7	68.1	77.1

Table 5. Calculated Energy Levels (eV) of the Lowest Lying Unoccupied Orbitals (LUMOs) of the Transition Metal Phosphinidene Complexes ML_n=PH

Cp_2Ti=PH	Cp_2Cr=PH	$Cp(PH_3)_3V$=PH	$Cp(PH_3)Co$=PH	Cp(CO)Co=PH	$Cp(CO)_3V$=PH	$(CO)_4Fe$=PH
−2.16	−2.57	−2.93	−3.12	−3.72	−4.09	−4.41
Cp_2Zr=PH	Cp_2Mo=PH	$Cp(PH_3)_3Nb$=PH	$Cp(PH_3)Rh$=PH	Cp(CO)Rh=PH	$Cp(CO)_3Nb$=PH	$(CO)_4Ru$=PH
−1.86	−2.44	−2.83	−3.11	−3.70	−4.03	−4.00
Cp_2Hf=PH	Cp_2W=PH	$Cp(PH_3)_3Ta$=PH	$Cp(PH_3)Ir$=PH	Cp(CO)Ir=PH	$Cp(CO)_3Ta$=PH	$(CO)_4Os$=PH
−1.65	−2.25	−2.66	−2.78	−3.45	−3.96	−3.97

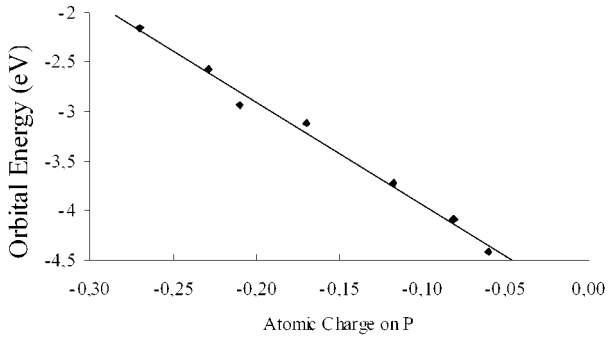

Figure 3. Dependency of the π*-orbital energy of the first-row transition metal phosphinidene complexes on the atomic charge on phosphorus.

second and third rows. Relevant geometrical parameters, orbital energies, and atomic charges are summarized in Tables, 2, 3, and 1, respectively, in addition to the data of the discussed systems with first-row transition metals.

Again, we see that, irrespective of the nature of the organometallic ligand (Cp or PH_3 or CO), the M=P bond lengths follow the position of the transition metals in the periodic table. For the second row, this is Zr (2.473) > Nb (2.440, 2.441) > Mo (2.377) > Ru (2.317) > Rh (2.195, 2.203), with bond lengths (in Å) given in parentheses.

For the third row, the sequence is Hf (2.456) > Ta (2.436, 2.434) > W (2.379) > Os (2.337) > Ir (2.216, 2.210). The second-row M=P bonds are about the same length as those of the third row, and both are distinctly longer than the ones containing first-row transition metals.

In the case of the Cp_2M=PH (M = Mo, W), the calculated structures compare very well with existing experimental data determined by X-ray crystallography for Cp_2M=PR (M = Mo, W) with R = (2,4,6-*t*-Bu)$_3C_6H_2$.[8,9] The experimental Mo=P and W=P distances are 2.370(2) and 2.349(5) Å, respectively. The two Mo−Cp distances of 1.998 and 1.992 Å are also similar to those of the experimental Mo structure, i.e., 1.966 and 1.962 Å, as are the W−Cp distances (calculated, 1.981 and 1.980 Å; experimental, 1.98 and 1.93 Å). The theoretically predicted M−P−H angles of 103.6° (M = Mo) and 103.1° (M = W) are slightly smaller than the experimental ones (115.8(5)° and 125.8(2)°, respectively), reflecting the high steric hindrance of the (2,4,6-*t*-Bu)$_3C_6H_2$ group.

The main distinguishing feature is again the charge on the phosphorus atom, which follows the same order as seen for the complexes containing first-row transition metals. Thus, Cp_2M=PH > $Cp(H_3P)_3M$=PH (Zr, Mo, Hf, W) > $Cp(H_3P)M$=PH (Nb, Ta) > Cp(OC)M=PH (Rh, Ir) > $Cp(OC)_3M$=PH (Nb, Ta) > $(OC)_4M$=PH (Ru, Os), where the metals M are given in parentheses. This differentiation comes about because of the different energy levels of the highest singly occupied a′ and a″ orbitals of the triplet ML_n fragment. The data of all first-, second-, and third row phosphinidene complexes in Tables 1 and 3 illustrate nicely the decrease in the ML_n orbital energy and in the charge on phosphorus on going from charge-donating to charge-accepting ligand systems.

The P=M bond dissociation energies (given in kcal/mol) do vary between the various types of phosphinidene complexes (Table 4), but they are remarkably similar for the most electrophilic and nucleophilic ones within each row, i.e., Cp_2-Ti=PH (60.0) and $(OC)_4$Fe=PH (61.7) for the first row, Cp_2-Zr=PH (75.3) and $(OC)_4$Ru=PH (69.7) for the second row, and Cp_2Hf=PH (80.7) and $(OC)_4$Os=PH (77.1) for the third row. The most apparent systematic deviations are as follows: (1) the BDEs of the Cp_2M=PH complexes of group VI (Cr, Mo, W) are smaller than those of group IV (Ti, Zr, Hf), and (2) within each row, the complexes of group V (V, Nb, Ta) have

the smallest BDEs (except for $Cp_2Cr{=}PH$), which appears to result from their larger $\Delta E°$ contribution. Throughout all phosphinidene complexes, the π-bond strength is slightly more than one-third of the σ-bond strength, i.e., 34−41% for both the second row and third row, and ranges from 32.7 to 43 kcal/mol. Even more striking is that, like the total BDEs, the ΔE_π are also virtually identical for the most nucleophilic and electrophilic complexes within each row. Within each column of the periodic table, the BDEs of the third row phosphinidene complexes are larger than those of the second row, which are again larger than those of the first row.

The entries in Table 5 show that the orbital energy of the LUMO increases on going from the first- to the second- and third-row transition metals too, which is in line with the strength of the orbital interactions discussed above.

Conclusions

The reactivity of phosphinidene complexes, stabilized by a transition metal group ($L_nM{=}P{-}R$), has been rationalized by theoretical methods in terms of their philicity. The calculated partial charge on the phosphorus atom together with the energy level of the π*-orbital determines a phosphinidene complex to be electrophilic or nucleophilic. This distinction depends on the metal moiety and can be influenced by its spectator ligands L.

The calculated geometries, which agree well with those known for Schrock-type complexes, show the length of the metal−phosphorus bond for all studied complexes to depend solely on the atomic size of the transition metal and not on the nature of its ligands. This M=P bond, which can be described in terms of an interaction between triplet ML_n and triplet PH, has a strong π-component and an even stronger σ-component. This metal−phosphinidene interaction increases on going from the first- to the second- and third-row transition metals.

The chemical reactivity of experimentally yet unknown phosphinidene complexes can be predicted. Those that have a transition metal with strong σ-donor ligands, such as Cp^-, concentrate negative charge on the phosphorus atom and raise the energy of the π*-orbital, thereby enhancing their nucleophilicity. Conversely, ligands with strong π-acceptor capabilities, such as CO, reduce the charge concentration on P and stabilize the π*-orbital, both of which enhance the electrophilicity of the phosphinidene complex.

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Supporting Information Available: Cartesian coordinates of the optimized structures (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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