

Phosphinidene Complexes $M(\text{CO})_5\text{-PR}$: A Density Functional Study on Structures and Electronic States

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Received January 28, 1998

Density functional studies have been carried out for the equilibrium structures of the phosphinidene transition-metal complexes $M(\text{CO})_5\text{-PR}$, with $M = \text{Cr}, \text{Mo},$ and W and $\text{R} = \text{H}, \text{Ph}, \text{OH},$ and NH_2 . The free phosphinidenes P-R have triplet ground states, but their $M(\text{CO})_5$ complexes prefer singlet states because of the substantial stabilization of the unoccupied phosphorus p_π acceptor orbital. This follows from calculations based on the local density approximation, including nonlocal corrections for correlation and exchange self-consistently. The $M(\text{CO})_5\text{-PR}$ 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, which gives an interpretation of the donor–acceptor complexes within the Dewar–Chatt–Duncanson model. It is shown that the investigated ligands are strong π -acceptors and even stronger σ -donors. In the case of unsubstituted PH complexes, the ground state is a singlet due to strong preferential stabilization by π -back-donation into the empty phosphorus p_π orbital. When substituents are present, the singlet state is already relatively stabilized in the free phosphinidene due to π -donation from the substituent. The π -back-donation from the metal fragment decreases accordingly due to competition with this substituent π -donation but remains effective in further preferentially stabilizing the singlet.

1. Introduction

Transition-metal phosphinidene complexes $\text{W}(\text{CO})_5\text{-PR}$ are important intermediates in phosphorus chemistry.¹ Mathey and co-workers developed an elegant route to in situ generation of terminal phosphinidene complexes, making them convenient precursors in organic synthesis.² The chemical behavior of these transition-metal complexes is indicative of a singlet state for the phosphinidenes. This assumption is supported by recent mechanistical studies.³

The high reactivity and short lifetime of these species make their direct observation difficult. Compared to similar carbene complexes, little is known about the electronic structure of the phosphinidene complexes. Theoretical methods can, in principle, provide such information. Only two, rather dated, studies have been reported on the electronic structure of phosphinidenes

stabilized through complexation with transition-metal fragments. Lee, Boggs, and Cowley used the restricted Hartree–Fock (HF) method for their study on $\text{Cr}(\text{CO})_5\text{-PH}$.⁴ Mathey and co-workers performed extended Hückel (EHT) as well as HF calculations on $\text{Cr}(\text{CO})_5\text{-PH}$ and $\text{Fe}(\text{CO})_4\text{-PH}$.⁵ Due to the limited computational resources at the time, these studies have to be considered as qualitative. It is striking that the former group finds a triplet state while the latter predicts a singlet state as the electronic ground state for the chromium complex using the same level of theory.

Modern density functional theory (DFT) is known to give accurate structures and energetics for transition-metal complexes.⁶ Thus, DFT seems to be the method of choice for investigating the electronic structure of phosphinidene complexes. In connection with the generalized transition method, the metal phosphinidene bond can be analyzed within the Dewar–Chatt–Duncanson model, while inclusion of relativistic effects enables an investigation of the experimentally interesting second- and third-row transition-metal complexes. The present work deals with the influence of the π -donor substituents NH_2 , OH , and C_6H_5 on the electronic properties of the $\text{RP-M}(\text{CO})_5$ complexes containing the transition metals $\text{Cr}, \text{Mo},$ and W .

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2. Method

A. General Procedure. The calculations were carried out using the parallelized Amsterdam density functional (ADF) program.⁷ The MOs were expanded in a large, uncontracted set of Slater-type orbitals (STOs) containing diffuse functions: TZP. The TZP basis set is of triple- ζ quality for all atoms and has been augmented with one set of 4p functions on each transition-metal atom and one set of d-polarization functions on each main-group atom.⁸ The 1s core shell of carbon, nitrogen, and oxygen and the 1s2s2p core shells of phosphorus were treated by the frozen-core (FC) approximation.^{7b} The metal centers were described by an uncontracted triple- ζ STO basis set for the outer ns , np , nd , $(n + 1)s$, and $(n + 1)p$ 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 accurately represent the Coulomb and exchange potentials accurately in each self-consistent field (SCF) cycle.⁹ The numerical integration was done using the scheme developed by te Velde et al.¹⁰

All calculations were performed at the NL-SCF level, using the local density approximation (LDA) in the Vosko–Wilk–Nusair parametrization¹¹ with nonlocal corrections for exchange (Becke88)¹² and correlation (Perdew86).¹³ All geometries were optimized using the analytical gradient method implemented by Versluis and Ziegler.¹⁴

B. Bonding Energy Analysis. The transition-metal–phosphorus bond in the complexes is analyzed using the well-known decomposition¹⁵ of the interaction energy in an exchange (or Pauli) repulsion plus electrostatic interaction energy part (ΔE°) and an orbital interaction energy (charge transfer, polarization). It is sometimes necessary to prepare the fragments 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, eq 1

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

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., $\Delta E = E(\text{molecule}) - \sum E(\text{fragments})$, thereby giving negative values for stable bonds. ΔE_{elst} represents the electrostatic interaction between the prepared fragments when they are put—with unchanged electron densities—at the positions they occupy in the complex. This interaction is usually attractive. The Pauli repulsion ΔE_{Pauli} is comprised of the four electron-destabilizing interactions between the occupied orbitals and is responsible for the steric repulsion. For neutral

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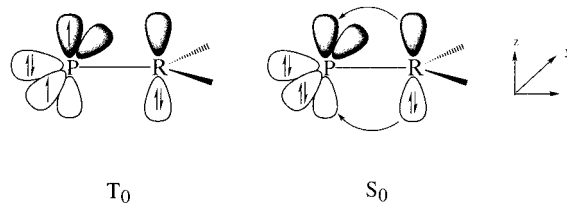
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Scheme 1



fragments, it can be useful to combine ΔE_{elst} and ΔE_{Pauli} in the “steric interaction” term ΔE° (eq 1). The orbital interaction ΔE_{oi} accounts for the charge transfer (interaction between occupied orbitals on one moiety with unoccupied orbitals of the other, including the HOMO–LUMO interactions) and polarization (empty/occupied orbital mixing on one fragment). We will not try to separate the charge transfer and polarization components but will use the extended transition state (ETS) method developed by Ziegler and Rauk^{15b,c} to decompose the ΔE_{oi} term into contributions from each irreducible representation Γ of the interacting system, eq 2. In systems with a clear

$$\Delta E_{\text{oi}} = \sum_{\Gamma} \Delta E_{\Gamma} \quad (2)$$

σ, π separation, this symmetry partitioning proves to be most informative.

3. Results and Discussion

The increasing importance of phosphinidenes in organic chemistry together with the experimental difficulties to examine these short-lived species has led to a number of recent theoretical studies.¹⁶ Most informative is the high-level ab initio study of Nguyen et al.¹⁷ on the singlet–triplet splitting of free phosphinidenes with substituents covering almost all elements of the first three periods. Therefore, we first give a brief overview of the electronic structure of the free phosphinidenes PR with focus on the influence of its substituent R together with a comparison of our DFT results to high-level ab initio studies. Next, we present our analysis of the bonding of PR to the transition-metal fragment $M(\text{CO})_5$.

A. Free Phosphinidenes PR. The electronic configurations expected for the low-energy triplet (denoted as T) and closed shell singlet electronic states (denoted as S) of the phosphinidenes are shown in Scheme 1. Considering the molecules arranged in the xy -plane, the sp-hybridized nonbonding orbital n_x on phosphorus is doubly occupied in both states. The two configurations differ in the occupation of the phosphorus p_y and p_z orbitals. Note that for the investigated phosphinidenes the triplet state is reported to be the ground state. Another low-lying state, the open-shell singlet state (not displayed), is reportedly more stable than the closed-shell singlet state for P–H, P–Ph, and P–OH, while this is not the case for P–NH₂.¹⁶ We consider here only the closed-shell singlet state, which is characterized by an empty phosphorus p_z acceptor orbital.

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Table 1. Relative Energies (kcal/mol) and Bond Distances (Å) of Free Phosphinidenes

		P-H	P-Ph	P-OH	P-NH ₂
<i>T</i>	<i>E_{rel}</i>	0.0	0.0	0.0	0.0
	<i>r</i> (P-R)	1.474	1.818	1.700	1.748
<i>S</i>	<i>E_{rel}</i>	34.8 (33.8 ^a)	24.3 (22.8 ^b)	19.7 (20.5 ^a)	3.4 (3.1 ^a)
	<i>r</i> (P-R)	1.470	1.802	1.677	1.668

^a CISD(Q)/6311G(d,p), ref 17. ^b CISD/6311G(d,p), ref 16b.

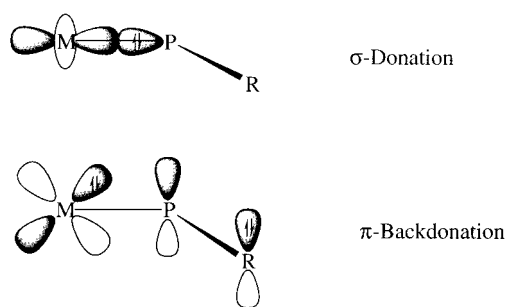
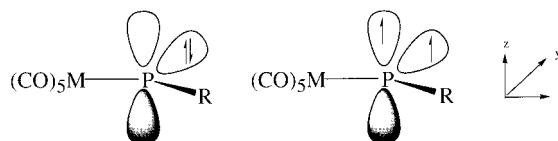
All four free phosphinidenes investigated were calculated to have triplet ground states. The singlet–triplet energy differences (*S*–*T*) are given in Table 1. The (closed-shell) singlet state is particularly stabilized in the case of P–NH₂ due to classical π -donation of the amine lone pair into the empty phosphorus 3p orbital. This also leads to a rather short P–N bond distance. Nguyen et al. showed that the *S* state even becomes the ground state on introducing additional π -donating groups, e.g., P–NCl₂. While the OH group also acts as π -donor, the stabilization of the *S* state of P–OH is significantly smaller than that of P–NH₂ due to the higher electronegativity of oxygen. The singlet–triplet splitting for P–Ph is also calculated to be smaller than that for the parent P–H. Nguyen et al.¹⁷ argued that the ca. 10 kcal/mol reduction for P–Ph is caused by destabilization of the triplet state rather than by stabilization of the singlet state. They based their argument on the presumed small π -donor character of the phenyl group. The extent of this interaction can, however, be quantified with the fragment-based approach of the ADF program. Using this method, we calculate a stabilization energy of 25.5 kcal/mol for the highest lying π orbital of the phenyl group, which results from mixing with the empty phosphorus *p_z* orbital. The magnitude of this stabilization is sizable and compares with those of 32.0 and 43.8 kcal/mol obtained for the respective similar interactions of the π lone pairs of OH and NH₂.

It is evident from the data provided in Table 1 that the DFT results are in excellent agreement with the reported high-level ab initio calculations using comparable basis sets. The differences in relative *S*–*T* energies of only 1.0–1.5 kcal/mol may be fortuitously small.

B. Transition Metal Complexes M(CO)₅–PR. Mathey and co-workers⁵ described the M–P bond of the complexed phosphinidenes in a similar manner as the M–C bond of the well-known Fischer carbene complexes. In this description charge is donated from the phosphorus lone pair of the PR group into an empty metal d orbital of the M(CO)₅ group (σ -donation) but charge also flows back from an occupied metal d orbital into the empty phosphorus *p_z* orbital (π -back-donation). This is illustrated in Scheme 2.

Besides metal π -back-donation, the closed-shell singlet state of the phosphinidene complex can also be stabilized by the above-discussed classical π -donation resulting from the phosphinidene substituent R. Scheme 2 illustrates that both effects compete with each other, especially when the phosphorus carries the π -donating OH and NH₂ substituents. It is then expected that π -back-bonding from the M(CO)₅ group in these substituted derivatives is weaker than in the M(CO)₅–PH complexes. This, in fact, is confirmed by our calculations.

To examine the transition-metal phosphinidene complexes, we fully optimized the structures in their triplet

Scheme 2**Scheme 3****Table 2. Selected Bond Lengths (Å), Bond Angles (deg), and Relative Energies (kcal/mol) of M(CO)₅–PR**

		<i>r</i> (M–P)	<i>r</i> (P–R)	α (M–P–R)	<i>r</i> (M–C _{tr})	<i>E_{rel}</i>
Cr(CO) ₅ P–H	<i>S</i>	2.271	1.458	102.5	1.918	–9.5
	<i>T</i>	2.347	1.433	113.9	1.889	0.0
Mo(CO) ₅ P–H	<i>S</i>	2.416	1.458	102.8	2.048	–7.4
	<i>T</i>	2.472	1.434	120.5	2.031	0.0
W(CO) ₅ P–H	<i>S</i>	2.417	1.458	102.7	2.080	–9.3
	<i>T</i>	2.459	1.436	123.5	2.037	0.0
W(CO) ₅ P–Ph	<i>S</i>	2.423	1.837	121.7	2.061	–10.3
	<i>T</i>	2.448	1.783	131.2	2.039	0.0
W(CO) ₅ P–OH	<i>S</i>	2.393	1.699	111.4	2.083	–22.7
	<i>T</i>	2.468	1.692	123.7	2.033	0.0
W(CO) ₅ P–NH ₂	<i>S</i>	2.448	1.693	113.1	2.059	–29.9
	<i>T</i>	2.480	1.711	120.0	2.062	0.0

(*T*) and closed-shell singlet (*S*) electronic states. All structures possess *C_s* symmetry in their lowest energy geometries. The configurations differ in the occupation of the phosphorus lone pair and *p_z* orbitals as illustrated in Scheme 3.

The results of the geometry optimizations are collected in Table 2 for selected structural parameters. Mathey and co-workers⁵ reported that Cr(CO)₅–PH prefers a conformation in which the Cr–P–H plane bisects an equatorial CO–Cr–CO angle (staggered conformation). They found a rotational barrier for the Cr–P bond of less than 1 kcal/mol. Our calculations show that this conformation is also preferred for the heavier congeners of the group VI transition-metal complexes (Figure 1). The rotational barriers around the M–P axis are estimated at 0.5–1.0 kcal/mol. For the substituents R = Ph and NH₂, rotation around the P–R bond can also be considered. The minimum energy structure of M(CO)₅–PNH₂ has a planar NH₂ group in the M–P–N plane due to conjugation. Rotation of the NH₂ group by 90° breaks the conjugation and leads to another *C_s* symmetry structure. Optimization within the symmetry constrains then results in a structure that is a significant 24.6 kcal/mol higher in energy. The nitrogen is now pyramidal with its lone pair lying in the M–P–N plane. Rotating the phenyl group by 90° around the P–R axis leads to another *C_s* symmetry structure that is a modest 5.6 kcal/mol less stable.

The data in Table 2 show that the metal–phosphorus (M–P) distances of the singlet-state complexes are 0.05–0.07 Å shorter than those of the triplet states. The

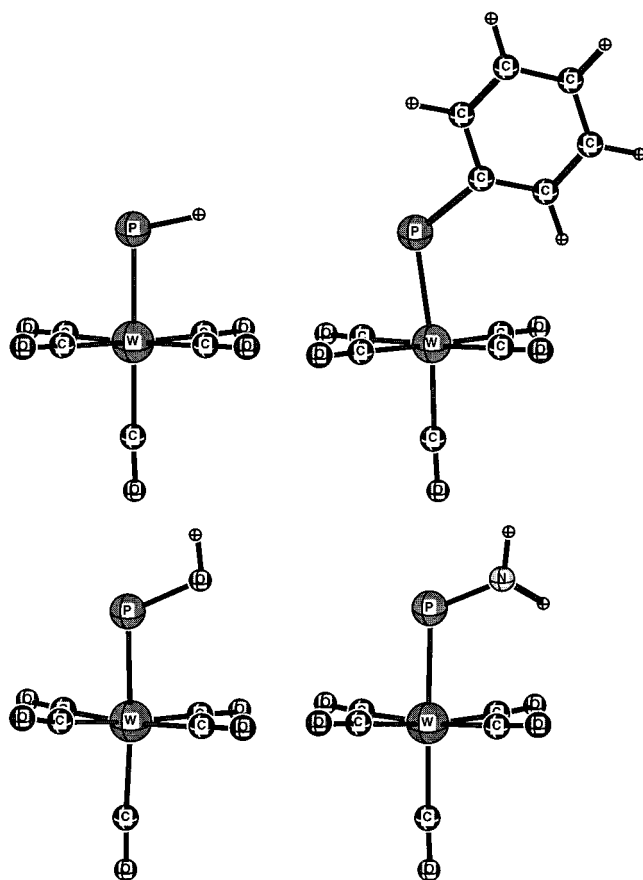


Figure 1. Optimized structures of $\text{W}(\text{CO})_5\text{-PR}$, $\text{R} = \text{H}$, Ph , OH , NH_2 .

shorter M-P bond length is accompanied by a longer distance between the metal and its trans carbonyl group. This trans effect is structural evidence for the stronger π -back-bonding into the empty phosphorus p_z orbital of the singlet phosphinidenes.¹⁸ Consequently, all P-R distances (except for $\text{R} = \text{H}$) are longer in the complexes than in the free phosphinidenes. They are also longer in the S state than in the T state, with the exception of $\text{W}(\text{CO})_5\text{-PNH}_2$. The predicted 2.27 Å Cr-P bond length in $\text{Cr}(\text{CO})_5\text{-PH}$ is substantially longer than the reported value of 1.9 Å estimated with the EHT method.⁵

The M-P-R bond angles of the singlet phosphinidenes range from 103° ($\text{R} = \text{H}$) to 124° ($\text{R} = \text{Ph}$) and increase with the size of the substituent. They are about 10° smaller than the bond angles of the corresponding complexes in their triplet states. This seems reasonable since the expansive phosphorus lone pair of the singlet lies in the same plane as the metal atom and the P substituent.

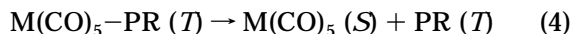
The most important result of the calculations is that the singlet state is the electronic ground state for the transition-metal phosphinidenes whereas it is the triplet state for the free phosphinidenes. The singlet-triplet splitting for the phosphinidene complexes with P-H and P-Ph substituents is ca. 10 kcal/mol in favor of the singlet state and as much as 30 kcal/mol for $\text{W}(\text{CO})_5\text{-PNH}_2$. Thus, the ca. 20 kcal/mol relative stabilization

Table 3. Bond Energy Decomposition (kcal/mol) of the Complexes $\text{M}(\text{CO})_5\text{-PR}$

		ΔE_σ	ΔE_π	ΔE°	ΔE_{prep}	BDE
PH Complexes						
$\text{Cr}(\text{CO})_5\text{-PH}$	S	-62.4	-40.9	25.8	2.2	75.3
	T	-55.8	-12.6	34.4	1.4	32.6
$\text{Mo}(\text{CO})_5\text{-PH}$	S	-52.6	-41.2	19.2	4.2	70.4
	T	-48.3	-12.2	28.9	1.8	29.8
$\text{W}(\text{CO})_5\text{-PH}$	S	-58.5	-43.0	19.2	4.5	77.8
	T	-55.5	-13.7	31.5	2.1	35.6
Substituted Phosphinidenes						
$\text{W}(\text{CO})_5\text{-PPh}$	S	-59.6	-27.0	14.2	5.0	67.4
	T	-57.3	-14.2	33.5	2.6	35.4
$\text{W}(\text{CO})_5\text{-POH}$	S	-64.7	-31.0	19.1	4.8	71.8
	T	-51.6	-11.9	30.2	1.9	31.4
$\text{W}(\text{CO})_5\text{-PNH}_2$	S	-59.5	-21.3	14.4	4.0	62.4
	T	-47.3	-12.8	23.1	1.5	35.5

of the S state on replacing the P-Ph group for a P-NH_2 group that was found for the free phosphinidenes is also found in their transition-metal complexes.

To investigate both the origin of the extra stabilization of the singlet states and the influence of the transition-metal fragments, we calculated bond enthalpies for the dissociative processes shown in eqs 3 and 4. The triplet



phosphinidene complexes are dissociated into the singlet metal carbonyl and triplet phosphinidene fragments (eq 4), while the singlet complexes are dissociated into products in their singlet states (reaction 3). Note that the electronic relaxation energy $S \rightarrow T$ of the free phosphinidenes (Table 1) is not included in the bond enthalpies of eq 3. The calculated bond enthalpies are given in Table 3 together with the partitioning into ΔE_σ (σ -donation), ΔE_π (π -back-donation), and ΔE° (steric repulsion). The term ΔE° summarizes, as noted, the attractive electrostatic interaction ΔE_{elst} and the Pauli repulsion ΔE_{Pauli} . The preparation energy ΔE_{prep} is the energy difference between the valence states of the fragments at their equilibrium structure and at the geometries they possess in the complex.

It is evident from the data in Table 3 that the singlet phosphinidenes form very strong bonds with the transition-metal fragments. The bond dissociation energies show the well-known trend $\text{Mo} < \text{Cr} < \text{W}$ for the group VI transition metals,¹⁹ with $\text{W}(\text{CO})_5\text{-PH}$ having the highest predicted value of 77.8 kcal/mol. Comparison with the experimental value of 46 kcal/mol for the first W-CO bond dissociation energy of $\text{W}(\text{CO})_6$ ²⁰ demonstrates that the metal-phosphinidene bond is, indeed, particularly strong. We want to stress, however, that the thermodynamic stability of a metal-ligand bond gives no information about the observed reactivity of the short-lived phosphinidene complexes.

The energy components listed in Table 3 show the high bonding energy of the singlet phosphinidenes to result from strong σ -bonding (ΔE_σ) and albeit less (particularly for substituted systems) also from significant π -back-bonding (ΔE_π). We consider first the unsubstituted $\text{M}(\text{CO})_5\text{-PH}$. The π -back-donation component of the M-P bond energies amounts to 41–43 kcal/

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mol and that resulting from σ -donation to ca. 60 kcal/mol for both the chromium and tungsten complexes and 53 kcal/mol for the molybdenum complex. These energy components relate directly to the significant differences in BDEs for the singlet and triplet phosphinidenes (Table 3) and, thereby, illustrate the energetic preference for the singlet states (Table 2). While all major BDE components (ΔE_σ , ΔE_π , and ΔE°) favor the singlet over the triplet state, the ca. 30 kcal/mol difference in π -back-bonding is clearly the main factor. The singlet states also benefit from a modest 3–6 kcal/mol stronger σ -donation, possibly due to the synergetic effect, and 10 kcal/mol less steric repulsion. Thus, the strong π -back-bonding of the transition metals Cr, Mo, and W into the empty phosphorus p_z orbital of PH is responsible for the energetic preference of the closed-shell singlet ground state of complexed phosphinidenes. However, because this preference over the triplet state amounts to less than 10 kcal/mol, it is evident that for the singlet state favorable ΔE_σ and ΔE° contributions are also needed.

We now turn to the substituted $W(CO)_5$ -PR complexes. As noted, the energy of the closed-shell singlet state of free phosphinidenes P-R is considerably lowered with respect to the preferred triplet ground state due to π bonding of the substituent's lone pair with the empty phosphorus $3p_z$ orbital (Table 1). Consequently, this phosphorus p_z orbital becomes partially occupied and is also destabilized due to the complementary antibonding interaction with the π donor orbital on R. This reduces the metal π -back-bonding contribution to the coordinative bond. As a result, the ΔE_π term is much smaller for the substituted singlet phosphinidenes complexes even though π -back-donation remains substantial, with values of 31 kcal/mol for R = OH, 27 kcal/mol for R = Ph, and 21 kcal/mol for R = NH_2 . The preferential ΔE_π stabilization of the singlet state is likewise reduced, ranging from 8.5 for $W(CO)_5$ - PNH_2 to 19.1 kcal/mol for $W(CO)_5$ -POH. Thus, while the BDE values of these substituted singlet phosphinidenes complexes remain much larger than those of the triplets, π -back-donation is no longer the main reason for the singlet stabilization. Instead, the σ -donation and steric repulsion become more pronounced. For example, the main contributor for the phenyl derivative is the ΔE° term, which favors the singlet state by as much as 19.3 kcal/mol, while it is the ΔE_σ term (12.2 kcal/mol) for the amine derivative. In conclusion, the enhanced stabilization of the singlet over the triplet state on substitution of the complexed phosphinidene is a culmination of (a) the preferred stabilization of the singlet state of the free phosphinidene P-R and (b) the significant preference of the coordinative bond for the singlet. In the free phosphinidenes, the S - T energy splitting is reduced by ca. 30 kcal/mol on going from PH to the substituted PNH_2 . Complexation of the phosphinidenes to the transition-metal fragment gives an extra contribution to this stabilization, which, however, decreases upon substitution. As a result, the energy gap for the singlet $W(CO)_5$ -PR complexes increases by only 20 kcal/mol (from 9.3 to 29.9 kcal/mol) in the order P-H < P-Ph < P-OH < P- NH_2 with a trend-setting decrease in the ΔE_π contribution (from 29.3 to 8.5 kcal/mol).

Table 4. Mulliken Gross Populations and Overlap of the Fragment Orbitals of Singlet $W(CO)_5$ -PR

		H	Ph	OH	NH_2
σ -donation	HOMO (PR)	1.53	1.57	1.57	1.58
	LUMO ($M(CO)_5$)	0.48	0.45	0.42	0.44
	S(HOMO,LUMO)	0.30	0.28	0.27	0.28
π -back-donation	HOMO ($M(CO)_5$)	1.37	1.54	1.55	1.65
	LUMO (PR)	0.62	0.44	0.46	0.34
	S(HOMO,LUMO)	0.18	0.14	0.16	0.15

For a more detailed evaluation of the transition-metal-phosphinidene bond, we summarize in Table 4 the overlap S and the occupations for the fragment orbitals that contribute to the σ - and π -bonds. There are only small differences in σ -bonding between the differently substituted phosphinidenes. The overlap between the lone pair on phosphorus and the empty metal d-orbital lies in the range of 0.27–0.30 and the charge transfer is about 0.4–0.5 electrons. Expectantly, the variation in π -back-bonding is larger. The overlap integral is smaller (0.15–0.18), while the amount of charge transfer reflects the noted trends of the energy terms and decreases for P-H > P-OH > P-Ph > PNH_2 from 0.6 to 0.3 electrons. Still, for the entire set there is a close balance between σ - and π -transfer. This is in contrast to the earlier findings of Mathey and co-workers.⁵ On the basis of HF calculations, they predicted much more σ -transfer (0.95 e^-) than π -transfer (0.49 e^-) for $Cr(CO)_5$ -PH. We assume that their rather large value for σ -donation originates from the too short Cr-P bond distance that was used. Our DFT-based results give no indication for an accumulation of positive charge on phosphorus.

Conclusions

The present DFT investigation of the electronic structure of transition-metal-complexed phosphinidenes shows, without doubt, that their electronic ground states are singlets. The singlet-triplet energy difference for the experimentally much used $W(CO)_5$ -PPh amounts to 10 kcal/mol and increases to 30 kcal/mol for the amine derivative. The excellent agreement with high-level ab initio data for the singlet-triplet splittings of the free phosphinidenes underscores the reliability of the DFT method used.

The symmetry decomposition scheme for the bond energy analysis of the $M(CO)_5$ -PR bond affords a quantitative estimate of its σ and π bond strengths. It is shown that the ligands investigated are strong σ -donors as well as π -acceptors. The π -acceptor capability decreases with increasing π -donation of the substituent R into the vacant phosphorus p_z orbital in the order P-H > P-OH > P-Ph > P- NH_2 . It is this joint metal π -back-donation and substituent π -donation that makes the stabilization of the singlet states so effective.

Acknowledgment. A.W.E. would like to thank the European Union for the Marie Curie postdoctoral fellowship. We thank The Netherlands Organization for Scientific Research (NCF/NWO) for providing a grant for supercomputer time. K.L. acknowledges support by the National Science Foundation.