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Donor–acceptor interactions with electrophilic terminal phosphinidene complexes

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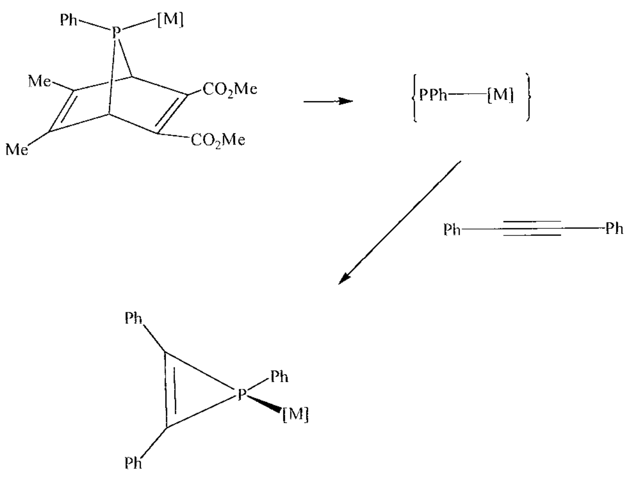
Abstract

Donor–acceptor interactions of Lewis bases, such as amine, phosphine, cyanic acid and phosphaalkine with various phosphinidene complexes carrying a $W(CO)_5$ fragment are studied by means of density functional calculations. Accordingly, the donor interactions can be divided into two categories. In terms of energy an amine binds stronger than a phosphine to a phosphinidene, the resulting Do–P bond is longer (N–P) or equal (P–P) with respect to a corresponding single bond. This tendency is also revealed in the corresponding transition metal complexes. In all cases the singlet-triplet energy separation values of the resulting donor-adducts are fairly small. A donor with a π-system, such as HCN yields a shorter N–P bond, but the resulting donor-adduct is even less stable with respect to decomposition into a singlet PH complex and cyanic acid. Similar considerations with HCP reveal only a weak donor addition of this fragment to the parent PH complex but a facile rearrangement of the adduct to the diphosphirene transition metal complex. The diaminophosphino–PH possesses a singlet ground state, its corresponding transition metal complex reveals a fairly small singlet–triplet energy separation. It can be considered as a nucleophilic PH complex in contrast to the other homologues which reveal an electrophilic behaviour. © 2002 Published by Elsevier Science B.V.

Keywords: Donor–acceptor interactions; Lewis bases; Phosphinidene complexes; Density functional calculations

1. Introduction

Mathey et al. in their prolific work developed several synthetic methods for the generation and trapping of terminal phosphinidene (PH) complexes [1–3]. In these cases the PH unit is complexed with a d^6-ML_5 fragment (M = Cr, Mo, W; L = CO) and reveals an electrophilic behaviour. It can be trapped, e.g. by π-bonded systems, as it is shown in a pertinent example as follows (Scheme 1) [4]. Apart from such electrophilic PH complexes of the Fischer-type, transition metal complexes of the Schrock-type are also well known, as described for example in the work of Lappert et al. [5] and of Stephan et al. [6] (Fig. 1). The stable or transient η^1-transition metal complexes are summarized in recent reviews [7]. Experimental investigations scaled the elec-



Scheme 1.

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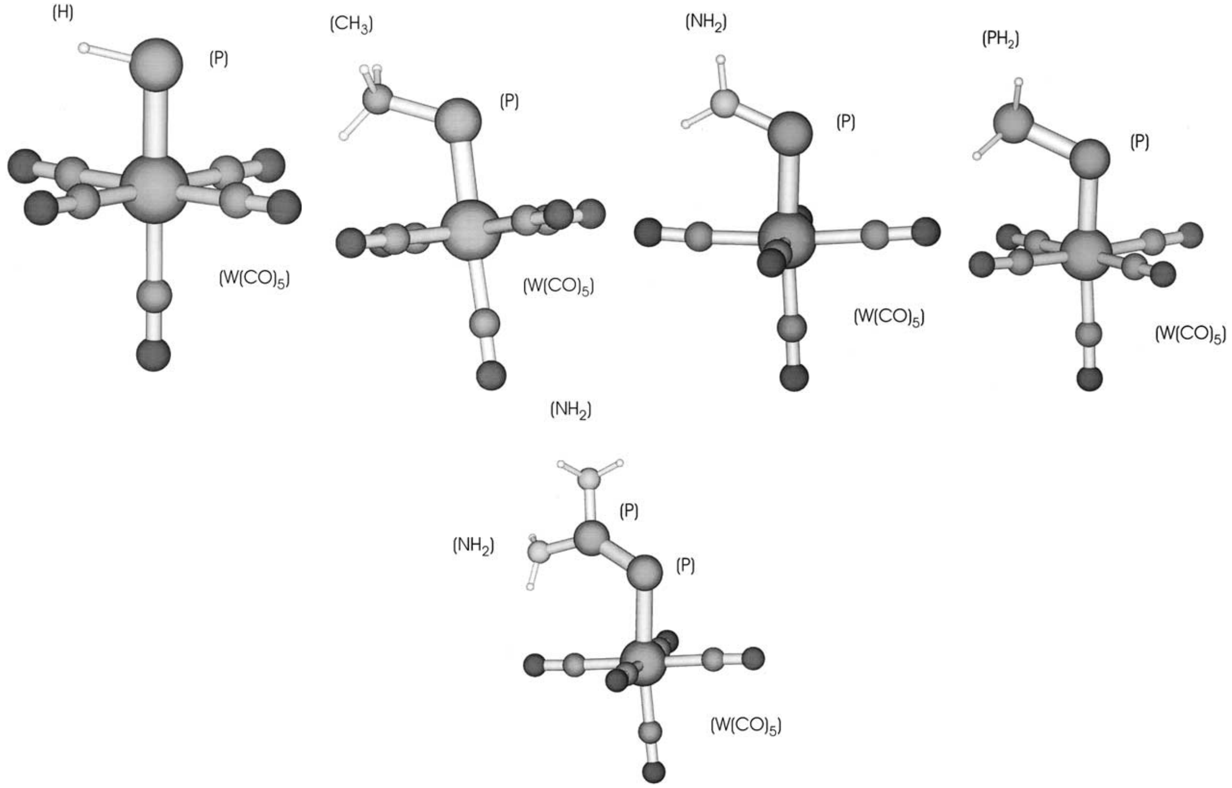


Fig. 1. Plots of the donor-free transition metal complexes.

trophilic nature of these species, on the basis of skillfully deviced trapping experiments [8].

Furthermore, phosphinidene complexes were also studied by means of photoelectron spectroscopy [9], as well as quantum chemical investigations [10–13].

In the present study, we deal with a quantum chemical investigation of phosphinidenes and their complexes stabilized by donor interactions of different nature, by (a) Lewis donors with a lone pair, such as amine or phosphine and (b) Lewis donors with a lone pair and a π-system, such as HC≡N and HC≡P. It will be shown that the latter donors form only weak adducts with the free phosphinidenes as well as with their transition metal complexes.

2. Theoretical section

Qualitative considerations were deduced from EH calculations [14], these results were further supported by density functional calculations [15]. For the latter we used relativistically corrected effective core potentials, as reported in the work of Stevens, Basch and Krauss [16]. For the heavy main group elements the valence electron basis sets were augmented by one set of polarization functions. The type of basis set is herein denoted as SBK-31g(d). The density functional calculations [17] were performed with Becke's three-parameter function [18], with local and non-local electron correlation contributions estimated by the Lee–Yang–Parr correlation functional [19] (B3LYP). All structures were fully optimized and characterized as energy minima on the corresponding hypersurfaces by means of vibrational analyses. The energy optimization of geometrical parameters and the calculations of the force constants were derived analytically. The population analysis of the wavefunction was made according to the Weinhold–Reed partitioning scheme [20].

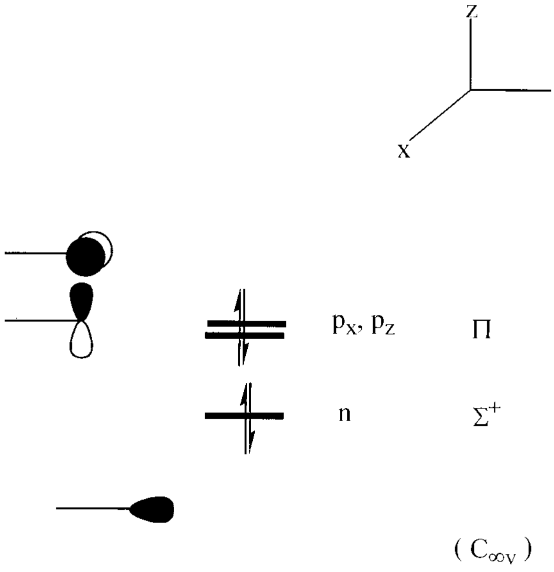
3. Results and discussion

3.1. Free phosphinidenes

We begin the discussion with a parent phosphinidene. It possesses two degenerate nonbonding frontier p-orbitals (p_x, p_y) which are occupied by two electrons [21]. Thus it has a triplet ground state [21] (Scheme 2). Within $C_{\infty v}$ symmetry these orbitals refer to Π (p_x, p_y) and Σ^+ (n) irreducible representations, a proper quantum chemical treatment of the various states for the parent compound is given by a MCSCF procedure [22].

In case a phosphinidene is substituted by a π-conjugating substituent, the orbital degeneracy is removed and the singlet stability increases [23–25]. These cases can be effectively calculated at a density functional level (including one Slater determinant). Singlet–triplet (ΔE_{S-T}) energy separation values for various substituted phosphinidenes are given in Table 1.

While the energy difference for the unsubstituted phosphinidene is too large in comparison with the experiment [12] (at the single determinant level), a theory of substituent effects (at density–functional level) is successfully provided for other cases with non-degenerate frontier orbital systems (see Table 1). Accordingly, for the amino- and hydroxy-substituted species a triplet is still slightly more stable than a singlet [12]. A considerable singlet stability is only found for the diaminophosphino–phosphinidene, in accord with our previous considerations on nitrenes [26] and carbenes [27].



Scheme 2.

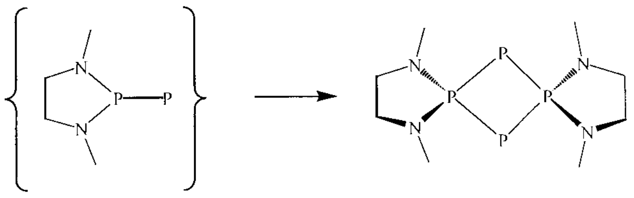
Table 1
Singlet–triplet energy differences (ΔE_{S-T} in kcal mol^{-1}) of free phosphinidenes RP, as a function of the substituent at phosphorus

Substituent R	ΔE_{S-T}
H	28.0 [a]
	[22.0] [b]
CH_3	26.0 [a]
OH	18.3 [a]
NH_2	1.2 [a]
	(2.2) [c]
PH_2	2.5 [a]
	(2.1) [c]
$P(NH_2)_2$	(−10.0) [c]

[a] Ref. [12], Table 1.

[b] Experimental value (P.E. Cade, Can. J. Phys., 46 (1968) 1989).

[c] Own work (B3LYP/6-311++g(d,p), plus zero-point vibrational energy corrections).



Scheme 3.

We note that an intermediately generated monomeric diaminophosphino–phosphinidene derivative dimerizes forming a four-membered ring system [28] (Scheme 3). Hence, its reaction behaviour is similar to the related diaminophosphino-nitrenes [29].

3.2. Transition metal complexes

A variety of chromium complexes were carefully studied by Creve et al. [12] and also by Ehlers et al. [13]. The latter study also includes investigations on the tungsten complexes of the aminophosphinidene. Here we present only pentacarbonyltungsten complexes; relevant bonding parameters obtained for the singlet and triplet state structures are summarized in Table 2.

All of the investigated structures are energy minima on the corresponding hypersurfaces, as proven by corresponding vibrational analyses. The singlet and triplet species throughout adopt bent geometries with one stereochemically active lone pair at phosphorus. The position of the substituent R with respect to the transition metal fragment is determined by steric interactions and as the rotational barriers around the P–W bonds are negligible small, a staggered position of R is preferred with respect to the tungsten fragment. In the singlet geometries the trigonal phosphorus centers become almost (e.g. $R = PH_2$) or even completely planar ($R = P(NH_2)_2$). The bonding situation is different for the triplet states. The P(N)–P distances are albeit longer and the trigonal phosphorus atoms are sizeably pyramidalized (π-conjugation would raise the energy of the LUMO and destabilize the triplet state). The found S–T energy differences and equilibrium geometries are in accord with the results of Ehlers et al. [13] reported for R = H and NH_2. Thus the phosphinidene complexes prefer singlet ground states, in contrast to the free phosphinidenes with a triplet ground state (R = H, CH_3, NH_2, PH_2).

Surprising results emerge for the diaminophosphino–phosphinidene complex. This case was hitherto not investigated. We predict a S–T energy separation which is smaller than that of the corresponding amino-phosphinidene complex (see Table 2), although the free phosphinidene exhibits pronounced singlet stability. What is the reason? A priori complexation can be of advantage to the singlet and/or the corresponding triplet structure. The transition metal complexation stabilizes stronger the singlet as compared with the triplet

Table 2
Relevant bonding parameters (bond lengths (Å), bond angles (°)) of RP-W(CO)$_5$ and relative energies (E_{rel}, in kcal mol^{-1}) of singlets and triplets, at SBK-31g(d) level

Substituent R	State	W–P	P–R	<W–P–R	W–C_{trans}	E_{rel} [a]
H	S	2.423	1.455	103.2	2.093	0.0
	T	2.496	1.440	121.2	2.039	7.9 (7.4) [a]
CH_3	S	2.430	1.869	111.9	2.088	0.0
	T	2.508	1.860	125.5	2.034	7.2
NH_2	S	2.466	1.671	112.9	2.067	0.0
	T	2.536	1.710	121.1	2.027	25.2 (29.9) [a]
PH_2	S	2.455	2.159	112.5	2.072	0.0
	T	2.491	2.213	126.5	2.040	9.5
$P(NH_2)_2$	S	2.609	2.000	113.5	2.019	0.0
	T	2.500	2.243	118.4	2.043	9.3

[a] Values in parentheses are taken from ref. [12].

state. Concomitantly in the singlet states the W–P distances are shorter than in the corresponding triplet states. For R = $P(NH_2)_2$ the situation is different, the W–P distance is larger in the singlet as compared with the triplet geometry and the calculated S–T energy separation in the free phosphinidene is unchanged by complexation.

The bond energies for complex formation from singlet species are defined in equation (1).

$$RP + W(CO)_5 \rightarrow RP - W(CO)_5 + \Delta E_1 \qquad (1)$$

The energy balances were calculated for R = PH_2 (i), NH_2 (ii) and $P(NH_2)_2$ (iii) and result exothermic as follows, (i) −42.9, (ii) −39.4, (iii) −34.2 kcal mol^{-1}.

It is of further interest to analyze the electron densities. The relevant quantities are the charge densities and the Wiberg bond indices (in italics) within the NBO partitioning scheme (Scheme 4).

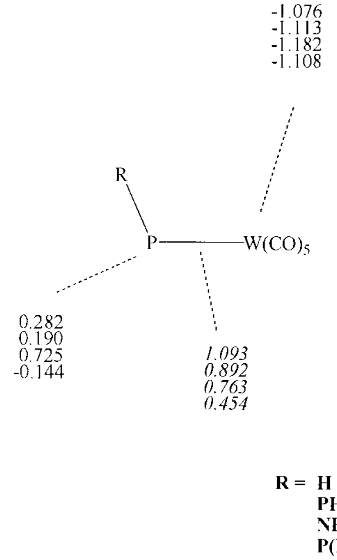
The positive charge at phosphorus diminishes in the order R = NH_2 > H > PH_2, hence this parallels its electrophilic character [11]. In contrast for R = $P(NH_2)_2$ a negative charge at phosphorus is obtained. This indicates a prevailing phosphid character of the free phosphinidene [26].

3.3. Donor adducts with amine and phosphine

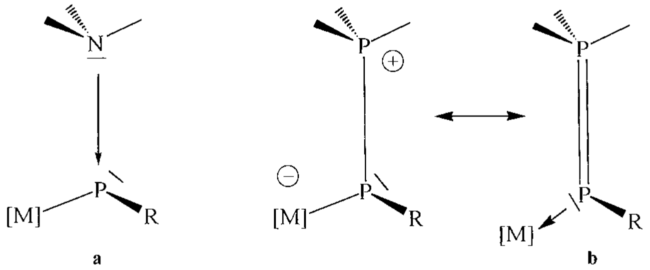
The addition of Lewis donors to Lewis acids can be divided into two classes [30]. In case the donor atom is strongly electronegative such as in NH_3, the resulting donor–acceptor bond is largely dative. If, however, the donor atom is constituted from a second row element, such as in PH_3 (or even higher element homologous of the periodic table), the resulting donor–acceptor bond is predominantly covalent. On the other hand the resulting bond energy by donor–acceptor adduct formation is stronger for coordination of an amine than a phosphine [30a]. This implies the canonical structure **a** for amine and the structures **b** for phosphine addition (Scheme 5).

The structure **b** can be alternatively understood as a complexed PH–phosphorane [1,2].

We have calculated the equilibrium structures of (a) the donor-adducts (with NH_3, PH_3) of the tungsten complexes, and (b) the corresponding donor adducts of the free phosphinidenes, it allows a further analysis of the effect of metal coordination on the donor–acceptor structures. The results of our investigations are summarized in Table 3.



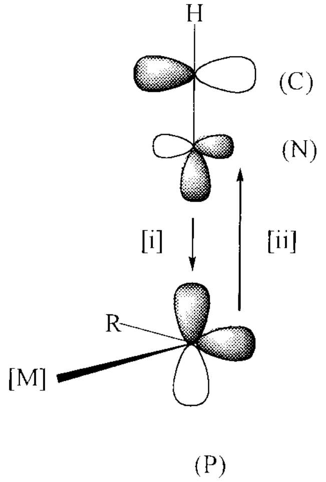
Scheme 4.



Scheme 5.

Table 3
Bond lengths (in Å) for donor–acceptor complexes of PHs, energy differences ΔE_{S-T} and ΔE_2 (in kcal mol^{-1}), at SBK-31g(d) level

Donor	Acceptor	Do–P [W–P]	ΔE_{S-T} [ΔE_2]
NH_3	PH	1.980	−4.8
	PH–W(CO)$_5$	1.984 [2.591]	[−20.7]
PH_3	PH	2.123	−16.9
	PH–W(CO)$_5$	2.194 [2.637]	[−17.9]
	P(CH$_3$)–W(CO)$_5$	2.196 [2.636]	[−14.5]
NH_3	P(NH$_2$)	2.183	−7.6
	P(NH$_2$)–W(CO)$_5$	2.136 [2.591]	[−8.1]
PH_3	P(PH$_2$)	2.136	−14.5
	P(PH$_2$)–W(CO)$_5$	2.272 [2.635]	[−11.5]
NH_3	P(PF$_2$)	1.958	−18.5
PH_3	P(PF$_2$)	2.141	−21.5
PH_3	P(P(NH$_2$)$_2$)	2.132	−12.6



Scheme 6.

The ΔE_{S-T} energy values were calculated for all phosphinidenes and their donor adducts. The results can be summarized as follows. (1) The donor addition brings a singlet state to the fore. The resulting Do–P bonds for amine coordination are longer than a single bond (N–P = 1.76 Å). The strongest N–P bond is obtained for R = PF$_2$ and parallels the increasing S–T energy separation of the donor–acceptor complexes. (2) Phosphine coordination results Do–P bonds comparable in lengths to a single bond (P–P = 2.2 Å) and the S–T energy separations of the adducts are throughout larger than for amine coordination. It can be understood by the tendency for the latter donor (PH_3) to form more covalent and for the former donor (NH_3) more dative Do–P bonds.

The results of the investigations are collected in Table 3. Amine coordination causes a slight extension of the W–P bond, e.g. for R = H (2.591 vs. 2.423 Å in the uncoordinated species, see Table 2). The W–P bond elongation is stronger pronounced for the phosphine coordination (e.g. for R = H to 2.637 Å). Due to the enormous computational effort to evaluate these structures, calculations were only performed for the case R = H, CH_3, NH_2 and PH_2.

A supplementary information on the donor–acceptor complexes is given by the equation (2).

$$[M]\text{-PR} + \text{Do} \rightarrow \{[M]\text{-PR}\}\text{Do} + \Delta E_2 \qquad (2)$$

It provides the energy balances for the donor addition to the coordinated phosphinidene complexes. We have evaluated these only for the phosphinidene complexes, at times considering singlet ground state species. The donor–acceptor interactions result only fairly small energy profits. They are slightly smaller than for amine or phosphine coordination to silylene (ca. −20 to −25 kcal mol^{-1}, at the same computational level [30a]).

3.4. Donor adducts with HCN and HCP

The hitherto discussed donor–acceptor structures can be grasped by the canonical structures **a** and **b** (Scheme 5). In the parent phosphinidene complex, however, one more lone pair is present. This could provide back-donation, if the adding donor possesses energetically low-lying acceptor orbitals. The donors in question are here HC≡N and HC≡P. The situation is schematically illustrated as follows (Scheme 6).

A mutual flow of electron density occurs, from the n-orbital of the donor into the acceptor orbital (LUMO) of the phosphinidene (i) and from the lone pair orbital at phosphorus into the acceptor orbital of the donor (π*) (ii) (as described in Scheme 5 an alternative formulation implies for the adducts a partial multiple bond character between PP- and PN-bonds). We may note, that the resulting structures refer to end-on transition metal coordinated complexes of HPNCH or HPPCH. The more detailed discussion of end-on and side-on coordination of these compounds will be given in the following chapter.

We have first probed the case of HCN coordination with phosphinidene complexes, for the whole triad of pentacarbonylmetal complexes ([M], M = Cr, Mo, W). A corresponding plot of one representative (M = W) is given in Fig. 2 (left). The phosphorus of the phosphinidene unit is strongly pyramidalized and the donor HCN is almost perpendicular to the plane spanned by the atoms H–P–M.

The most relevant bonding parameters of the structures are collected in Table 4.

As one would expect on the basis of the previous considerations, additional back donation strengthens the P–N bond and it becomes shorter than in the amine coordinated compounds (see previous section). The P–N distances are almost independent on the chosen transition metal M.

These complexes bear relation to the parent PH complexes in either of two ways, as defined by equations (2) and (3).

$$[\mathrm{M}] + (\mathrm{HP})\mathrm{Do} \rightarrow \{[\mathrm{M}]\text{-}\mathrm{HP}\}\mathrm{Do} + \Delta E_3 \qquad (3)$$

While equation (2) refers to the reaction of the corresponding phosphinidene metal complex with the donor, equation (3) yields the energies for P-complexation of the already formed HPNCH closed shell fragment. The energy balances of both processes were again investigated for the whole triad of transition metal complexes. The corresponding energy quantities are collected in Table 4. The donor addition towards the PH metal complex (equation (2)) is much less exothermic than the complexation of the donor adduct itself (equation (3)).

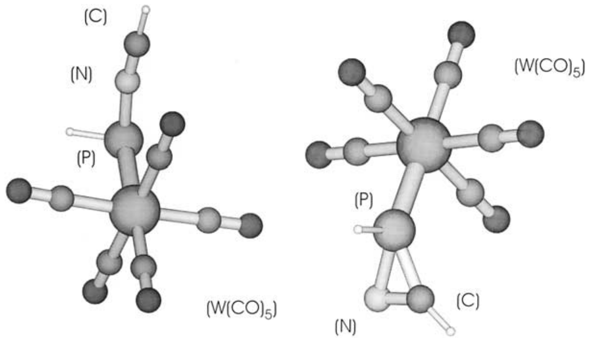
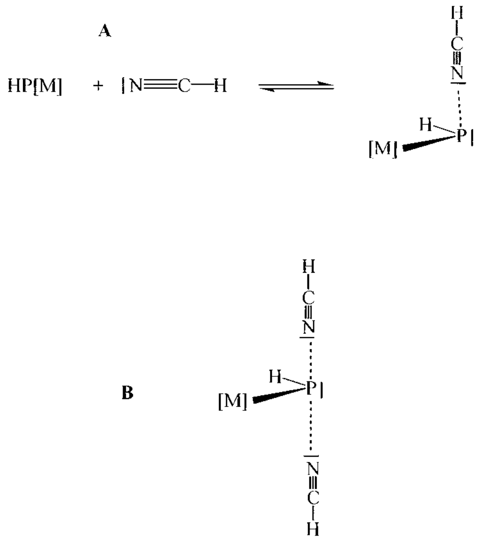


Fig. 2. Plots of the valence isomers of the HCN adduct to the parent phosphinidene tungsten complex; nitrilium phosphanylid complex (left) and 2*H*-azaphosphiridene complex (right).

Table 4
Bond lengths (in Å) and energies (in kcal mol^{-1}) for the complexation of nitrilium phosphanylides (ΔE_3) and for donor (HCN) addition (ΔE_2)

M	D–P	M–P	ΔE_3 (ΔE_2)
Cr	1.789	2.477	−20.2 (−13.1)
Mo	1.785	2.627	−26.8 (−13.6)
W	1.795	2.611	−31.2 (−11.7)



Scheme 7.

Our findings suggest the following scheme for the addition of Do=HCN to PH complexes (Scheme 7).

The donor adds weakly to the phosphinidene complex, as shown in **A**, thus giving a nitrilium phosphanylid complex. The interaction energies turned out to be fairly small and one can consider this situation as an equilibrium. This was previously found experimentally in the transylidation reactions [31]. Our findings make it unlikely that the replacement of one donor by a second donor will occur over a trigonal bipyramide, as schematically indicated in **B**. The Lewis acidity of the phosphinidene complex is already so weakened by the addition of the first donor that a second donor cannot coordinate. The matter is reminescent to the two-donor addition to silylene [30a]. Although the Lewis acidity of a silylene is larger, the bis-donor adducts are there not stable and tend to separate easily into a free donor plus a one-donor adduct.

We have also investigated addition of HCP to the parent phosphinidene tungsten complex. According to the calculations the overall bonding between both fragments is negligible, no sizeable advantage by P–P bond formation is detected. Furthermore, the weak encounter complexes undergo facile rearrangement to corresponding diphosphirene complexes.

3.5. 2*H*-azaphosphirene complexes

Finally, we will complete the discussion by reporting the results for the 2*H*-azaphosphirene complexes, which are valence isomers of the above discussed nitrilium phosphanylid structures. A representative drawing of the 2*H*-azaphosphirene tungsten complex is included in Fig. 2 (right). Here the complexation of the ring system can be evaluated in equation (4).

$$(\mathrm{ring})[2H-\mathrm{azaphosphirene}] + [\mathrm{M}] \rightarrow \mathrm{ring}\text{-}[\mathrm{M}] + \Delta E_4 \qquad (4)$$

The relevant bonding parameters and energy quantities are collected in Table 5.

The coordination at the phosphorus shortens the adjacent P–N and P–C bonds. According to our findings, the energy profit due to addition of the transition metal to phosphorus is, however, almost similar to that for P-complexation of the nitrilium phosphanylides. So far, only structures with M = Cr and Mo are known [32], the experimentally found bond lengths and angles are in accord with the results of our calculations. Structures of non-coordinated 2*H*-azaphosphirenes are hitherto unknown.

Table 5
Bond lengths (in Å) and energies (in kcal mol^{-1}) for complexation of 2*H*-azaphosphirenes

Metal	P–M	P–N	P–C	N–C	ΔE_4
Cr	2.358	1.848 (1.905)	1.787 (1.820)	1.279 (1.267)	−25.1
Mo	2.509	1.853	1.789	1.278	−26.1
W	2.496	1.849	1.787	1.279	−30.1

In parentheses the values for the uncoordinated ring.

The information on these valence isomeric species would not be complete without considering the energy differences between the 2*H*-azaphosphirene complex (ring-[M]) and the nitrilium phosphanylid complexes (open-[M]) which are defined by equation (5).

$$\text{ring-[M]} \rightarrow \text{open-[M]} + \Delta E_5 \quad (5)$$

The 2*H*-azaphosphirene complexes are slightly more stable than their valence isomeric complexes. The resulting energies (ΔE_5) for the chromium triad are, −4.9 (Cr), −5.1 (Mo) and −4.8 (W) kcal mol^{-1}. It may be compared with the energy balances for the uncoordinated structures. At the given effective core potential level the energetic advantage of the ring is −8.5 kcal mol^{-1}. It indicates that transition metal coordination stabilizes both valence isomers almost equally.

4. Summary

Our investigations is the first contribution to the large area of different donor interactions with terminal phosphinidene complexes. The results of our investigations can be summarized as follows:

1. While free phosphinidenes in general possess triplet ground states, transition metal coordination brings a singlet to the fore. However, the resulting S–T energy separations are small. An exception is the diaminophosphino–phosphinidene. It is the only phosphinidene which possesses a singlet ground state and reveals clearly pronounced phosphid character at the monovalent phosphorus. Coordination by $W(CO)_5$ does not enhance the S–T energy separation of this species.
2. The addition of a donor with only a n-orbital as the donor function results in a weak adduct for amine and an even weaker adduct for phosphine.
3. The phosphinidene complexes possess a second lone-pair at the phosphorus which is capable to back donation. Thus, if the adding donor bears an acceptor orbitals, back donation can further stabilize the donor adduct. It is the case for the addition of Do=HCN. The resulting P–N bond length is shorter than in the amine adduct.

We have presented also two valence isomeric systems, the nitrilium phosphanylid complexes and the 2*H*-azaphosphirene complexes, which contain differently bonded π-systems as donor.

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