

Syntheses, Structures, Bonding and Photoelectron Spectra of “Push-Pull”-Substituted *P*-[2,6-Bis(trifluoromethyl)phenyl]- $\sigma^2\lambda^3$ -iminophosphanes^[‡]

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$\sigma^2\lambda^3$ -“Push-pull” iminophosphanes $\text{Ar}_f\text{-P=N-R}$, bearing an electron-acceptor substituent at phosphorus [Ar_f = 2,6-bis(trifluoromethyl)phenyl] and a donor group at nitrogen ($\text{R} = t\text{Bu}$, NMe_2), have been synthesized and characterized by NMR spectroscopy and X-ray analysis. Density functional calculations [B3LYP/6-311G(d,p)] have been carried out on different iminophosphanes: HP=NH (**1**), $\text{Ar}_f\text{P=NH}$ (**2**), $\text{Ar}_f\text{P=NSiMe}_3$ (**3**), $\text{Ar}_f\text{P=N}t\text{Bu}$ (**4**), HP=NNMe_2 (**5**) and $\text{Ar}_f\text{P=NNMe}_2$ (**6**) in order to determine the electronic effect of the Ar_f substituent and the influence of the donor group R on the stability of the monomeric species. A comparison of the theoretical results

and UV photoelectron spectroscopy data for the iminophosphanes **4** and **6** is presented. Theoretical and experimental data suggest that for all iminophosphanes under investigation the π -system of the Ar_f group is almost orthogonal to the $\pi_{\text{P=N}}$ system, preventing any stabilizing interaction between the $\pi_{\text{P=N}}$ and the $\pi^*_{\text{b1(aryl)}}$ orbitals previously observed for the Ar_fPH^- anion. Here, the Ar_f substituent effect is mainly steric.

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Introduction

$\sigma^2\lambda^3$ -Iminophosphanes, XP=NR , have been the subject of enthusiastic study for the last two decades because they constitute a bridge between the classical chemistry of C-C unsaturated systems and unconventional $p\pi$ -bonded compounds of heavy main group elements.^[1] Consequently, a plethora of structures have been reported and characterized, including several short-lived species.^[2,3] In general,

because of the inherent “electronegativity” of the P-N double bond, most of the known iminophosphanes feature π -donors (R_2N , RO , R_2P) or electron-rich alkyl/aryl substituents ($t\text{Bu}$, Mes , Mes^*) at the dicoordinated phosphorus atom.^[3–5] Compared with the rich chemistry of iminophosphanes having electron-donating substituents, little is known about iminophosphanes containing electron-accepting groups. Notable exceptions are the heteroatom-substituted iminophosphanes Cl-P=NMe^* and TfO-P=NMe^* . In these examples the X–P bond tends to become ionic due to the large difference in electronegativity between phosphorus, chlorine and oxygen. This large difference in electronegativity promotes the formation of a close ion-pair $[\text{X}]^-\text{[PNMe}^*\text{]}^+$.^[6–9] Theoretical studies of iminophosphanes, using simple models, have demonstrated that replacement of the hydrogen atom at phosphorus in HP=NH by more electronegative substituents (π -acceptors) results in an appreciable strengthening of the double bond. At the same time the *Z*-configuration becomes more stable with respect to the *E*-configuration. Exactly opposite effects have been predicted for the influence of the corresponding substituents at nitrogen.^[10,11] This concept is strongly operative in *P*-halo- and *P*-oxy-iminophosphanes, but its application to highly sterically crowded *P*-carbosubstituted species has evident limitations. We expected iminophosphanes bearing electron-acceptor carbon substituents at the phosphorus

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atom would be interesting, since the presence of an electron-acceptor substituent at the phosphorus atom should considerably increase the polarity of the P=N double bond. Moreover, the combination of substituents with acceptor and donor properties at the P=N bond ("push-pull" substitution) should lead to unusually stable XP=NR species.

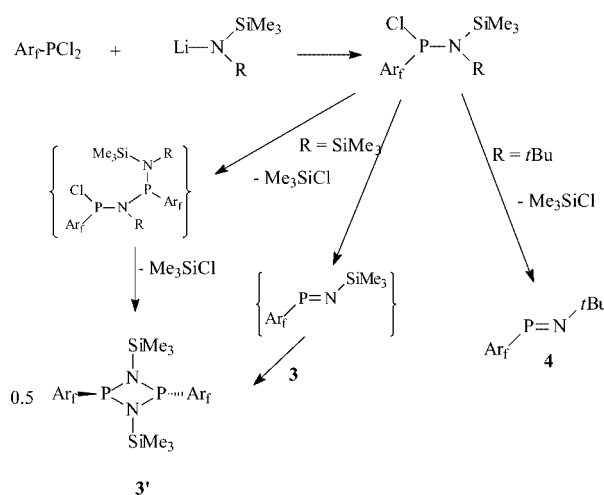
Recently, molecular design utilizing the highly electro-negative 2,6-bis(trifluoromethyl)phenyl group^[12] allowed us to prepare the first phosphanide salt, $[K([15]\text{-crown-}5)_2]^+[\text{Ar}_f\text{PH}]^-$, featuring a "naked" dicoordinated phosphorus anion.^[13] Our observations indicate that the planar structure is a privileged form of the anion, due to a strong interaction between the p^π phosphorus lone-pair and the $\pi^*_{b1(\text{aryl})}$ orbital (localized on the C1 and C4 atoms of the aryl ring). Thus, the Ar_f group behaves like a π -electron acceptor and contributes considerably to the observed structure of the Ar_fPH^- anion. Along these lines, desiring to study the *P*-carbosubstituted iminophosphanes bearing electron-withdrawing substituents, we turned our attention to *P*-[2,6-bis(trifluoromethyl)phenyl]- $\sigma^2\lambda^3$ -iminophosphanes. Two different stabilizing interactions may be envisioned in these compounds because of energetically closely spaced π (P=N) and σ (combination of lone-pair at P and N) frontier orbitals: (i) n^+ (*trans*) or n^- (*cis*) $\rightarrow \pi^*_{b1(\text{aryl})}$ [π system of Ar_f orthogonal to the $\pi_{\text{P=N}}$ system, as observed for the carbene $(i\text{Pr}_2\text{N})_2\text{PCAr}_f$ ^[14] or (ii) $\pi_{\text{P=N}} \rightarrow \pi^*_{b1(\text{aryl})}$ (π system of Ar_f coplanar to $\pi_{\text{P=N}}$ system, as previously observed for Ar_fPH^-).^[13] The latter type of stabilizing interaction is related to electronic effects previously observed for the Ar_fPH^- anion and would be especially pronounced in the case of "push-pull" substitution.

This paper deals with the preparation and characterization of a series of iminophosphanes $\text{Ar}_f\text{-P=NR}$. Along with our exploration into the synthesis of new and highly reactive PN multiple-bond systems, we performed a theoretical analysis of their structures to study the effect of the Ar_f group and the variation of the donor group R. The following iminophosphanes were studied theoretically: HP=NH (**1**), $\text{Ar}_f\text{P=NH}$ (**2**), $\text{Ar}_f\text{P=NSiMe}_3$ (**3**), $\text{Ar}_f\text{P=N}t\text{Bu}$ (**4**), HP=NNMe_2 (**5**) and $\text{Ar}_f\text{P=NNMe}_2$ (**6**). Full characterization of the iminophosphanes **4** and **6** included an investigation by NMR spectroscopy and X-ray analysis. A comparison of the results of our theoretical calculations [B3LYP/6-311G(d,p)] and UV/PE studies is also reported.

Results and Discussion

Iminophosphanes containing a CP=N skeleton are rare. These compounds are usually unstable due to their dimerization or oligomerization and can only be isolated in the presence of bulky substituents. Very effective in this sense is the 2,4,6-tri-*tert*-butylphenyl group (Mes*), which provides access to a series of stable R-P=NMe_s^* compounds upon condensation of phosphorus chlorides RPCl_2 with the silylamide $[\text{LiN}(\text{SiMe}_3)\text{Mes}^*]$ followed by a 1,2-elimination reaction.^[15] Iminophosphanes $\text{Mes}^*\text{P=NR}$ are not accessible by this route since the reaction of the sterically crowded

dichlorophosphate Mes^*PCl_2 with silylamides $[\text{LiN}(\text{SiMe}_3)\text{R}]$ leads exclusively to the diphosphene $\text{Mes}^*\text{P=PMe}_s^*$.^[3] We found that the interaction of Ar_fPCl_2 with silylamides $[\text{LiN}(\text{SiMe}_3)\text{R}]$ proceeds by the "normal" way, allowing the isolation of amino(chloro)phosphanes $\text{Ar}_f\text{P}(\text{Cl})\text{N}(\text{SiMe}_3)\text{R}$. Thus, treatment of Ar_fPCl_2 with an equimolar quantity of $[\text{LiN}(\text{SiMe}_3)_2]$ in THF solution at -78°C afforded the corresponding amino(chloro)phosphane in virtually quantitative yield (Scheme 1). However, elimination of Me_3SiCl from $\text{Ar}_f\text{P}(\text{Cl})\text{N}(\text{SiMe}_3)_2$ occurs only at high temperatures ($>180^\circ\text{C}$) and leads to 1,3,2,4-diazadiphosphetidine **3'** instead of the expected monomeric iminophosphane **3**. The ^{19}F NMR spectrum of **3'** exhibits doublets at $\delta = 23.0$ ppm ($^4J_{\text{F,P}} = 72.3$ Hz) and $\delta = 27.4$ ppm ($^4J_{\text{F,P}} = 134.7$ Hz), corresponding to the resonances of two magnetically non-equivalent *ortho*- CF_3 groups on the Ar_f substituent. The ^{31}P resonance is observed as a multiplet at $\delta = 277.3$ ppm.



Scheme 1

The molecular structure of **3'** is presented in Figure 1. The four-membered P_2N_2 cycle is planar, as observed in most other *trans*-1,3,2,4-diazadiphosphetidines.^[16] The Ar_f rings form a twist angle of 39.3° . The geometry around the nitrogen atoms is trigonal planar. The average P–N bond length is about 1.722 Å and the PNP and NPN bond angles are 95.73° and 84.27° , respectively.

In contrast to *N,N*-disilyl analogues, thermolysis of $\text{Ar}_f\text{P}(\text{Cl})\text{N}(\text{SiMe}_3)t\text{Bu}$ (120°C , 80 h) afforded the monomeric iminophosphane **4**. The latter was characterized by mass spectrometry and NMR spectroscopy. The ^{31}P NMR spectrum shows a septet at $\delta = 412.4$ ppm ($^4J_{\text{F,P}} = 28$ Hz), in a region characteristic of the CP=N backbone.^[2] The X-ray crystal structure of **4** is shown in Figure 2. Molecules of **4** adopt a *trans* geometry and the P=N bond length of 1.537 Å is consistent with a bond order of two; it is 0.019 Å shorter than that in *trans* $\text{Mes}^*\text{-P=N-}t\text{Bu}$.^[17] The P–C bond length (1.866 Å) falls in the normal range for a single bond. The aromatic ring is in an orthogonal orientation to the CPN plane (the corresponding dihedral angle is 99.8°).

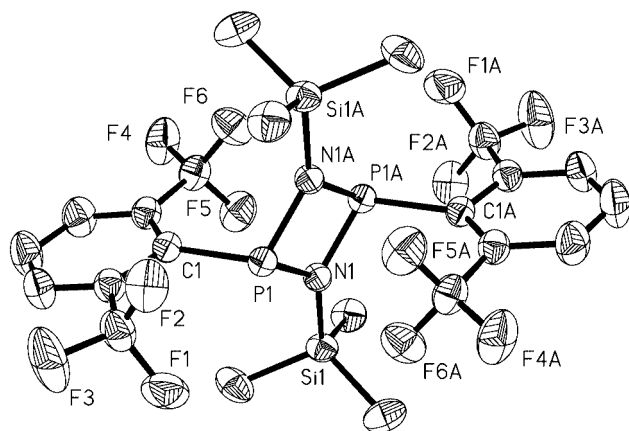


Figure 1. Crystal structure of $(\text{Ar}_f\text{PNSiMe}_3)_2$ (**3'**); hydrogen atoms are omitted for clarity; selected bond lengths (Å) and bond angles (deg): P1–N1(A) 1.713(2), P1(A)–N1(A) 1.714(2), P1–C1 1.935(2); P1–N1–P1(A) 95.73(1), N1–P1–N1(A) 84.27(1)

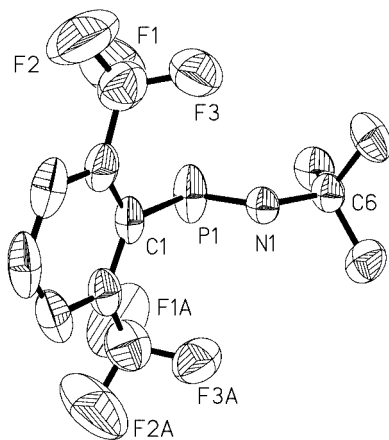
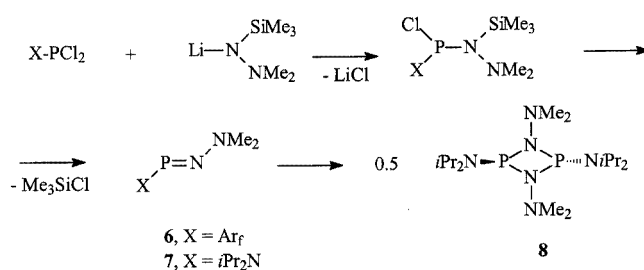


Figure 2. Crystal structure of $\text{Ar}_f\text{P}=\text{N}t\text{Bu}$ (**4**); hydrogen atoms are omitted for clarity; selected bond lengths (Å) and bond angles (deg): P1–N1 1.537(3), P1–C1 1.866(4), N1–C6 1.489(4); C1–P1–N1 99.73(1), C6–N1–P1 123.82(0)

The C1P1N1 and C6N1P1 angles are 99.73° and 123.82° , respectively. In the related iminophosphane $R_f\text{P}=\text{NR}_f$ [$R_f = 2,4,6\text{-(CF}_3)_3\text{C}_6\text{H}_2$] the angle around the phosphorus is 99.81° , while the angle at nitrogen is more opened (130.22°).^[18]

The strategy for the preparation of **4** was successfully extended to the synthesis of iminophosphanes **6** containing the π -donor NMe_2 group at the nitrogen atom (Scheme 2). Compared to $\text{Ar}_f\text{P}(\text{Cl})\text{--N}(\text{SiMe}_3)\text{R}$ ($\text{R} = \text{Me}_3\text{Si}$, $t\text{Bu}$), the corresponding dimethylhydrazino derivative splits off Me_3SiCl under considerably milder conditions (0.05 Torr, $< 100^\circ\text{C}$). However, attempts to isolate **6** in pure form by vacuum distillation failed. In contrast to the quite thermally stable compound **4**, compound **6**, which is stable for extended periods of time in pure form and in solution, easily disproportionates on heating to form the diphosphene $\text{Ar}_f\text{P}=\text{PAR}_f$

($\delta_{\text{P}} = 478 \text{ ppm}$).^[19] This property is without precedent in iminophosphane chemistry and suggests that the $\text{P}=\text{N}$ bond strength is dramatically reduced by "push-pull" substitution. Interestingly, the iminophosphane **7** ($\delta_{\text{P}} = 173.1 \text{ ppm}$), which can be obtained by a similar route starting from $i\text{Pr}_2\text{NPCl}_2$ and $\text{Me}_2\text{NN}(\text{SiMe}_3)\text{Li}$, undergoes dimerization to form *trans*- $[\text{Pr}_2\text{NPN}(\text{NMe}_2)_2]$ ($\delta_{\text{P}} = 74.2 \text{ ppm}$) instead of disproportionation. We found, however, that chloroform as solvent promotes Me_3SiCl elimination reaction from $\text{P}(\text{Cl})\text{--N}(\text{SiMe}_3)\text{R}$ moiety. Thus, when $\text{Ar}_f\text{P}(\text{Cl})\text{--N}(\text{SiMe}_3)_2\text{NMe}_2$ was treated with anhydrous CHCl_3 (25°C , 14 h), Me_3SiCl elimination with formation of **6** takes place quantitatively. In **6** the signal for the two-coordinate phosphorus atom is shifted drastically up field ($\delta_{\text{P}} = 224.3 \text{ ppm}$) in comparison to that of **4** ($\delta_{\text{P}} = 412.4 \text{ ppm}$).



Scheme 2

Bright-yellow crystals of **6** were grown from a saturated toluene solution. The molecular structure of the compound is shown in Figure 3. Essentially, the molecule adopts a *trans*-configuration and the aromatic ring system is almost orthogonal to the CPN system (the corresponding dihedral angle is 110°). The planar-coordinated N atoms of the hy-

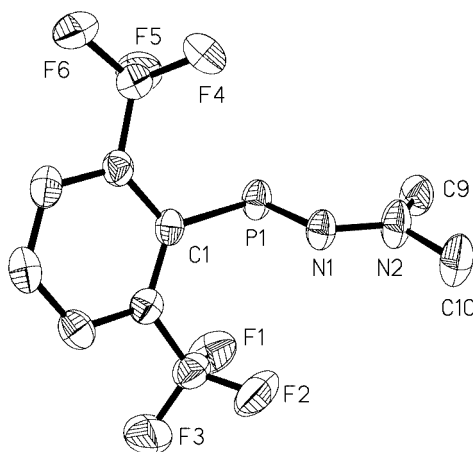


Figure 3. Crystal structure of $\text{Ar}_f\text{P}=\text{NNMe}_2$ (**6**); hydrogen atoms are omitted for clarity; selected bond lengths (Å) and bond angles (deg): P1–N1 1.629(1), P1–C1 1.863(5), N1–N2 1.319(2); C1–P1–N1 95.31(7), P1–N1–N2 121.13 (1)

drazine moiety and the P atom of the double-bond system are located in one plane (three-center, four π -electron system). The P–N bond in **6** is the longest (1.629 Å) ever found for iminophosphanes.^[20,21] The opposite effect is observed for the N–N single bond (1.319 Å). Thus, the tendency of the iminophosphane **6** to disproportionate at high temperatures can be inferred from the remarkably long P–N bond, which is evident in the X-ray structure analysis of the molecule.

Theoretical and PE Spectroscopic Studies

HP=NH (**1**), Ar_fP=NH (**2**) and Ar_fP=NSiMe₃ (**3**)

In order to estimate the effect of the Ar_f substituent on the CP=N part we compared the HP=NH (**1**) and Ar_fP=NH (**2**) model molecules. The geometrical parameters of these species are summarized in Table 1. Two minima were found on the potential-energy surface corresponding to the *cis* and *trans* isomers. For **2**, the π -system of the aryl substituent in both isomers is almost orthogonal to the $\pi_{\text{P=N}}$ system (the dihedral angles for *cis* and *trans* structures are 116.6° and 115.6° respectively). The P–N bond lengths in *cis*- and *trans*-**2** are slightly shorter than those in **1**. The *cis*-**2** isomer is more stable than *trans*-**2** by 1.42 kcal/mol. This is in agreement with an opening of the P and N bond angles on passing from *trans*-**2** to *cis*-**2**. Unlike **1** and **2** only the *cis*-**3** isomer was found on the potential energy surface, as was previously observed for CIP=NSiMe₃ and ClAs=NSiMe₃.^[22] The aromatic ring in **3** is almost orthogonal to the plane of the CPN skeleton (dihedral angle is 89.6°). Such a conformation excludes any interaction between the π -system of the P=N bond and the $\pi^*_{\text{b1(aryl)}}$ orbital of the aromatic ring. As a consequence, the P–C (1.957 Å) and P–N (1.539 Å) bond lengths correspond to a single and double bond, respectively. The latter is longer than the experimental value for the P–N bond of *cis*-CIP=NMe₃* (1.495 Å).^[6] The silyl group at the nitrogen atom leads to a shortening of the P=N bond [1.574 Å (*cis*-**1**), 1.562 Å (*cis*-**2**), 1.539 Å (*cis*-**3**)] and an opening of the bond angle at nitrogen, as was previously observed for FP=NSiH₃.^[23] Moreover, we observed a lengthening of the P–C bond.

For the *cis* isomers of **1**, **2** and **3** the energetic positions of the n^+ , π and n^- orbitals as well as the plot^[24] of the MO are displayed in Figure 4. For *cis*-**2**, the antibonding combination of lone pairs (n^-) is mixed with the σ_{PC} orbital while the bonding combination of lone pairs (n^+) is mixed with the $\pi_{\text{b1(aryl)}}$ orbital of the Ar_f ring. For *trans*-**2**, the bonding combination of lone pairs (n^+) is mixed with the σ_{PC} orbital while the antibonding combination of lone pairs (n^-) is mixed with the σ_{PC} and the $\pi_{\text{b1(aryl)}}$ orbitals (Figure 5).

Thus, in this case, the stabilizing effect of the CF₃ groups is attenuated or counterbalanced by destabilizing interactions with the σ_{PC} orbital and the $\pi_{\text{b1(aryl)}}$ orbital, respectively (see Figure 4 and Figure 5). For **2**, the energetic position of the n^- orbital is weakly modified when going from **1** to **2**. At the same time the n^+ orbital is destabilized.

Table 1. Bond angles (°) and bond lengths (Å) for the minima (mini: Ar_f almost orthogonal to the PNR moiety) and transition states (ts: Ar_f coplanar to the PNR moiety) of HP=NH (**1**), Ar_fP=NH (**2**), Ar_fP=NSiMe₃ (**3**), Ar_fP=N*t*Bu (**4**), HP=NNMe₂ (**5**), Ar_fP=NNMe₂ (**6**); corresponding energies in ua (E_{elec} for electronic energy and E_{rep} for repulsive energy)

Parameter	<i>cis</i>	<i>trans</i> (mini)	<i>trans</i> (ts)
HP=NH (1)			
P=N	1.574 (1.539) ^[10] (1.611) ^{[b][38]}	1.588 (1.578) ^{[a][10]} (1.618) ^{[b][38]}	/
PNH	118.52 (120.0) ^[10] (113.7) ^{[b][37]}	109.79 (112.3) ^[10] (107.6) ^{[b][37]}	/
HPN	105.95 (104.8) ^[10]	98.77 (99.9) ^[10]	/
E_{elec}	-446.929393	-446.859285	
E_{rep}	49.626276	49.555519	
Ar _f P=NH (2)			
P=N	1.562	1.576	1.571
P–C _{Arf}	1.920	1.890	1.893
PNH	120.91	110.66	105.59
C _{Arf} PN	108.23	100.14	110.53
E_{elec}	-2624.280808	-2624.457073	-2618.133251
E_{rep}	1321.595174	1321.774013	1315.457185
Ar _f P=NSiMe ₃ (3)			
P=N	1.539	–	–
P–C _{Arf}	1.957	–	–
PNSi	154.63	–	–
C _{Arf} PN	107.29	–	–
E_{elec}	-3764.610290		
E_{rep}	2053.155544		
Ar _f P=N <i>t</i> Bu (4)			
P=N	1.546	1.576	1.567
P–C _{Arf}	1.962	1.895	1.902
PNC _t Bu	146.14	99.34	126.17
C _{Arf} PN	111.86	124.68	104.85
E_{elec}	-3378.517746	-3347.618957	-3338.250879
E_{rep}	1918.535908	1887.636238	1878.275201
HP=NNMe ₂ (5)			
P=N	1.629	1.655	–
N–N	1.301	1.303	–
PNN	131.82	122.58	–
HPN	102.98	93.38	–
E_{elec}	-758.689409	-759.664804	
E_{rep}	227.388860	228.363706	
Ar _f P=NNMe ₂ (6)			
P=N	1.600	1.637	1.629
P–C _{Arf}	1.937	1.878	1.875
N–N	1.300	1.304	1.296
PNN	142.12	123.93	124.54
C _{Arf} PN	110.28	96.70	102.24
E_{elec}	-3202.638297	-3173.831281	-3168.455747
E_{rep}	1765.966288	1737.156040	1731.785927

^[a] SCF double zeta basis set. ^[b] QCISD/LanL2DZdp.

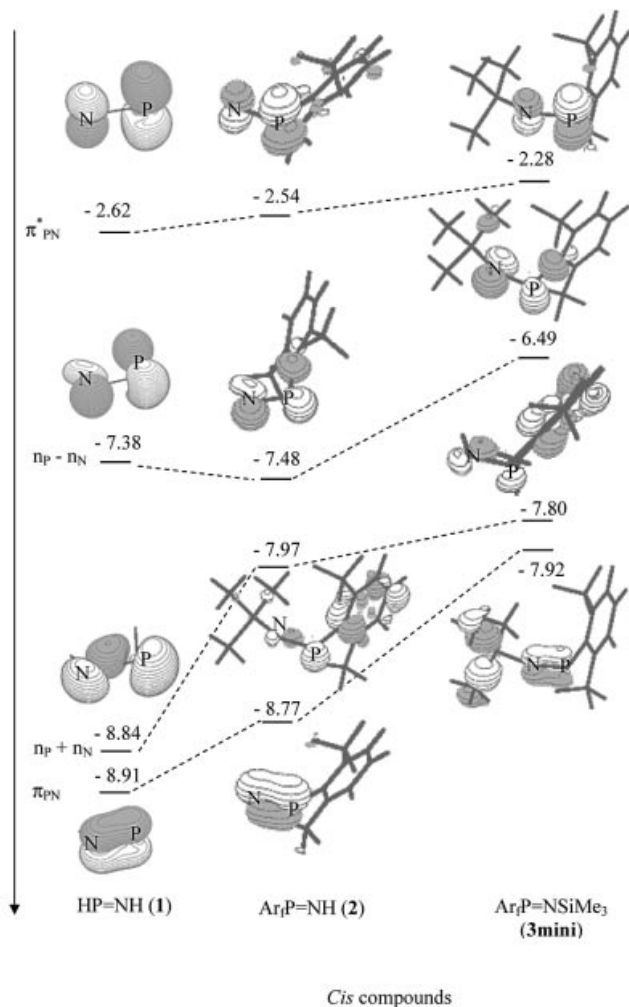


Figure 4. Kohn–Sham energies in eV and Kohn–Sham orbitals calculated with the B3LYP functional hybrid and the 6-311G(d,p) basis set for the *cis* isomers of HP=NH (1) and Ar_fP=NR [R = H (2), SiMe₃ (3); π_{CC}(Ar_f) almost perpendicular to π_{P=N}]

The H/SiMe₃ substitution promotes destabilization of the n⁺, n⁻ and π orbitals. The destabilization of the n⁻ orbital is more important than that of the n⁺ orbital because of the strong p character of the nitrogen lone pair in the n⁻ orbital. In fact, for the previous system only the push effect is observed.

Ar_fP=NtBu (4)

In addition to X-ray analysis, compound **4** was studied by coupling the Ultraviolet Photoelectron Spectroscopy in the gas phase (UV-PES) and calculations. The UV-PE spectrum of **4** presents a first ionization at 8.5 eV, a second band at 10.0 eV with a broad shoulder at 9.8 eV and then a broad signal with different shoulders at 11.0 and 11.8 eV (Figure 6, a).

In contrast to **3**, the *trans* isomer of **4** is slightly more stable than the *cis* isomer (0.72 kcal/mol). The energetically privileged form *trans*-**4mini** features an aromatic ring almost perpendicular to the CPN plane (dihedral angle is 116.1°), in agreement with the X-ray structure.

We studied the rotation process of the aryl group theoretically. One transition state has been found on the potential energy surface. It corresponds to a structure where the π-system of the aromatic ring is coplanar with the π_{P=N} system (**4ts**). The latter is energetically very close to the minimum (4.38 kcal/mol). Thus, taking into account this weak energetic difference, a free rotation of the Ar_f group can occur in the gas phase. The geometric parameters of **4mini** and **4ts** are summarized in Table 1. It is noteworthy to mention that the geometric parameters for both rotamers are similar in spite of the different positions of the aromatic ring. Moreover, the P=N (1.576 Å for **4mini**; 1.567 Å for **4ts**) and P–C (1.895 Å for **4mini**; 1.902 Å for **4ts**) bonds are slightly longer than the experimental ones (1.537 Å and 1.866 Å, correspondingly). In the same way, the calculated Kohn–Sham energies (Figure 5) are energetically close (n_P + n_N, σ_{PC}: -6.44 eV for **4mini** and -6.33 eV for **4ts**; π_{P=N}: -7.64 eV for **4mini** and -7.49 eV for **4ts**). All these observations show that the orientation of the aromatic ring seems to have a negligible effect on the geometric and electronic structures of Ar_fP=NtBu. In contrast to the coplanar structure of the [Ar_fPH]⁻ anion where only the interaction between n_P → π*_{b1(aryl)} occurs (9.4 kcal/mol),^[13] for **4ts** the stabilizing π_{P=N} → π*_{b1(aryl)} interaction [4.8 kcal/mol (NBO calculation)] is added to the destabilizing interaction π_{P=N} → π_{b1(aryl)} (the plot of the molecular orbital in Figure 7 visualizes these interactions). On the contrary, for **4mini** the stabilizing (n_P → π*_{b1(aryl)}) interaction is not observed.

Considering the free P–C rotation in the gas phase, the UV-PE spectrum (Figure 6, a) corresponds to the superposition of all the rotamers' spectra close to **4mini** and **4ts**. Thus, taking into account this observation as well as the nature of the molecular orbital, the ΔSCF values for the first ionic state (**4mini**: n_P + n_N + σ_{PC}: 8.25 eV; **4ts**: n_P + n_N + σ_{PC}: 8.10 eV) and the energetic position of the Kohn–Sham orbitals for **4mini** and **4ts** (Table 2), we assigned the first band in the PE spectrum (8.5 eV) to the removal of an electron from the n_P + n_N orbitals mixed with the σ_{PC} orbital. The second band (centered at 10 eV), which is more intense and broader than the first band, is associated with the ionization of the π_{P=N} - π_{b1(aryl)} and π_{P=N} + π_{b1(aryl)} orbitals as well as the π_{a2} ionizations of the aromatic ring. Finally, the ionization at 11.0 eV was assigned to the removal of an electron from the n_P - n_N orbitals (in interaction with the σ_{PC} orbital).

Surprisingly, the energetic positions of the n⁺ and π ionizations of **4** were found to be close to the spectroscopic findings for tBuP=NtBu. Indeed, the HeI PE spectrum of the latter presents two first ionizations at 8.11 and 9.70 eV, which have been assigned to the n⁺ and π_{PN} orbitals, respectively.^[25] The close energetic position of the π_{PN} orbital for **4** and tBuP=NtBu (9.8 eV and 9.7 eV, respectively) means that the Ar_f group has a destabilizing effect on the π-system close to the tBu group.

As for the σ-bond system, one could expect an important gap between the n⁺ orbitals of **4** (σ-attraction effect of Ar_f) and tBuP=NtBu (σ-donor effect of tBu), whereas the gap

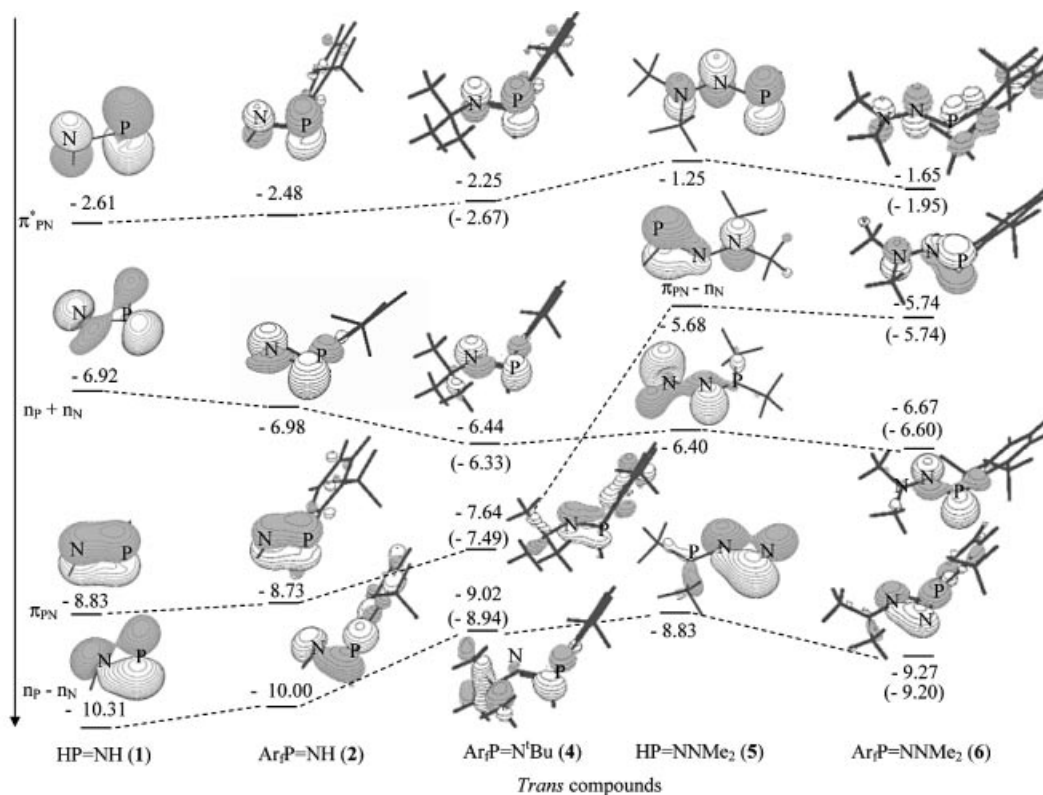


Figure 5. Kohn-Sham energies in eV and Kohn-Sham orbitals calculated with the B3LYP functional hybrid and the 6-311G(d,p) basis set for the *trans* isomers of HP=NH (1), HP=NNMe₂ (5) and Ar_fP=NR [R = H **2mini**; R = *t*Bu **4mini**; R = NMe₂ **6mini**; Ar_f almost orthogonal to the PNR moiety]; Kohn-Sham energies in brackets for the transition state (Ar_f planar to the PNR moiety)

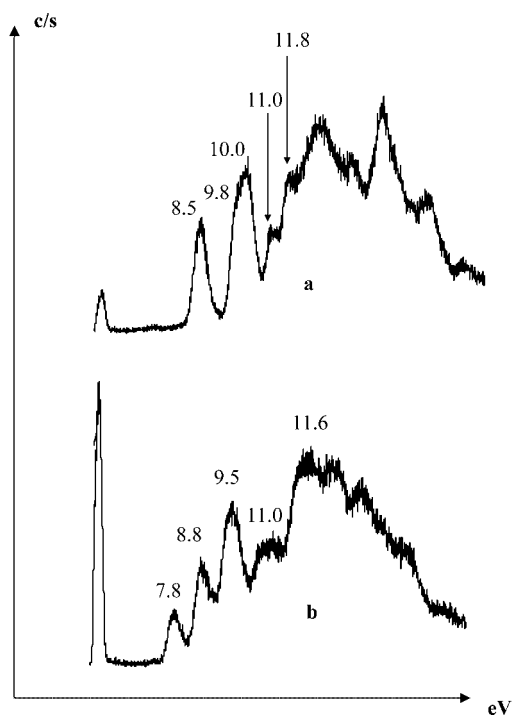


Figure 6. HeI photoelectron spectra of a) Ar_fP=N^{*t*}Bu (4) and b) Ar_fP=NNMe₂ (6)

was actually found to be relatively weak (0.4 eV). This is consistent with the previous theoretical conclusion: the strong stabilizing effect of the fluorinated aryl group is bal-

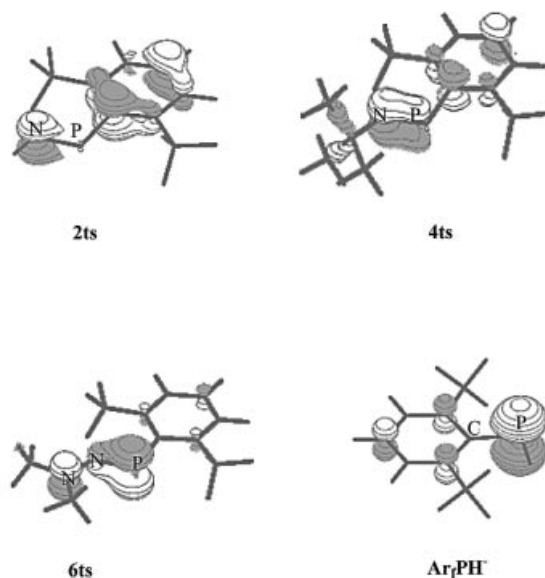


Figure 7. Plot of the $\pi_{P=N} - \pi_{b1(aryl)} (+ \pi^*_{b1(aryl)})$ orbital for the transition state (Ar_f coplanar to the PNR moiety) of Ar_fP=NH (2ts), Ar_fP=N^{*t*}Bu (4ts) and Ar_fP=NNMe₂ (6ts); plot of the $n_P - \pi^*_{b1(aryl)}$ for the minimum of Ar_fPH⁺

anced by the destabilizing interaction between the bonding or antibonding combination of lone pairs and the σ_{PC} orbital. The expected stabilizing effect of the Ar_f group is not really observed either on the σ - or the π -systems. Indeed, *t*BuP=N^{*t*}Bu and Ar_fP=N^{*t*}Bu present close electronic

Table 2. Kohn–Sham energies in eV and Kohn–Shan orbitals for the minimum (mini) and transition state (ts) of $\text{Ar}_f\text{P}=\text{NSiMe}_3$ (**3**), $\text{Ar}_f\text{P}=\text{N}t\text{Bu}$ (**4**) and $\text{Ar}_f\text{P}=\text{NNMe}_2$ (**6**); ΔSCF values (in eV) in brackets

3		4		6		
Theor.	Theor.		Exp.	Theor.		Exp.
3mini	4mini ^[a]	4ts	4	6mini ^[a]	6ts	6
−6.49 $n_{\text{P}} - n_{\text{N}}$	−6.44 (8.25) $n_{\text{P}} + n_{\text{N}} + \sigma_{\text{PC}}$	−6.33 (8.10) $n_{\text{P}} + n_{\text{N}} + \sigma_{\text{PC}}$	band at 8.5 eV	−5.74 (7.51) $\pi_{\text{P}=\text{N}} - n_{\text{Namino}}$	−5.74 (7.44) $\pi_{\text{P}=\text{N}} - n_{\text{Namino}}$	band at 7.8 eV
−7.80 $\pi_{\text{b1(aryl)}} (-n^+)$	−7.64 $\pi_{\text{P}=\text{N}} (-\pi_{\text{b1(aryl)}})$	−7.49 $\pi_{\text{P}=\text{N}} - \pi_{\text{b1(aryl)}}$		−6.67 $n_{\text{P}} + n_{\text{N}} + \sigma_{\text{PC}}$	−6.60 $n_{\text{P}} + n_{\text{N}} + \sigma_{\text{PC}}$	band at 8.8 eV
−7.92 $\pi_{\text{P}=\text{N}} - \pi_{\text{SiC}}$	−8.05 π_{a2}	−8.09 π_{a2}	band centred at 10.0 eV	−7.73 $\pi_{\text{b1(aryl)}}^{\text{[b]}}$	−7.74 $\pi_{\text{a2(aryl)}}^{\text{[c]}}$	band at 9.5 eV
−8.19 π_{a2}	−8.11 $\pi_{\text{P}=\text{N}} (+\pi_{\text{b1(aryl)}})$	−8.58 $\pi_{\text{P}=\text{N}} + \pi_{\text{b1(aryl)}}$		−7.78 $\pi_{\text{a2(aryl)}}$	−7.91 $\pi_{\text{b1(aryl)}}$	
−8.24 σ_{SiC}	−9.02 $n_{\text{P}} - n_{\text{N}} + \sigma_{\text{PC}}$	−8.94 $n_{\text{P}} - n_{\text{N}} + \sigma_{\text{PC}}, \sigma_{\text{CC}}$	band at 11.0 eV	−9.27 $n_{\text{P}} - n_{\text{N}} + \sigma_{\text{PC}}$	−9.20 $n_{\text{P}} - n_{\text{N}} + \sigma_{\text{PC}}$	band at 11.0 eV
−9.13 $\pi_{\text{P}=\text{N}} + \pi_{\text{SiC}}$	−9.50 σ_{CC}	−9.49 $n_{\text{P}} - n_{\text{N}} + \sigma_{\text{NC}}, \sigma_{\text{CC}}$	band at 11.8 eV	−9.71 “ $\pi_{\text{N}=\text{N}}$ ”	−9.92 “ $\pi_{\text{N}=\text{N}}$ ”	band at 11.6 eV

^[a] $\pi_{\text{CC(Arf)}}$ almost orthogonal to the $\pi_{\text{P}=\text{N}}$ system. ^[b] Symmetrical orbital against the C_1C_4 axis of the aryl group. ^[c] Anti-symmetrical orbital against the C_1C_4 axis of the aryl group.

properties [π : 9.7 eV (**4**) and 9.8 eV ($t\text{BuP}=\text{N}t\text{Bu}$); n : 8.5 eV (**4**) and 8.11 eV ($t\text{BuP}=\text{N}t\text{Bu}$)]. Thus, Ar_f seems to exert a kinetic rather than a stabilizing electronic effect on the $-\text{P}=\text{N}t\text{Bu}$ system bonds. In passing, we note that the **3** $\rightarrow$ **3'** dimerization process cannot be explained either by the nature of the energetic position of the π and π^* orbitals or the polarity of the $\text{P}=\text{N}$ bond. In fact, for **3** and **4**, the gap between the $\pi_{\text{P}=\text{N}}$ and the $\pi_{\text{P}=\text{N}}$ orbitals is relatively large and more pronounced in the case of the silyl derivative (5.64 eV vs. 5.39 eV: see Figure 4 and 5). Moreover, the polarity of the $\text{P}=\text{N}$ double bonds are also close, although slightly higher for **3** (Figure 8). On this basis, it seems that the reason for the higher stability of **4** in comparison with **3** is that SiMe_3 is a less-bulky protecting group than $t\text{Bu}$. Indeed, the $\text{Si}-\text{C}$ bond is longer than the $\text{C}-\text{C}$ bond and the bond angle at Si is more open than the bond angle at C. Consequently the dimerization is easier with SiMe_3 .

$\text{Ar}_f\text{P}=\text{NNMe}_2$ (**6**)

In order to determine the role of the Ar_f group on the $-\text{P}=\text{N}-\text{NMe}_2$ moiety, a theoretical study of the model molecule $\text{HP}=\text{NNMe}_2$ (**5**) was undertaken. The isomer *trans*-**5** was found to be slightly more stable than the *cis* isomer (0.22 kcal/mol). This corresponds to the form where the electronic energy is more important (see Table 1). The geometrical parameters of the *cis* and *trans* forms are described in Table 1. In contrast to the previously studied iminophosphanes $\text{Tmp}-\text{P}=\text{N}-\text{N}(\text{SiMe}_3)_2$,^[26] ($\text{Tmp} = 2,2,6,6$ -tetramethylpiperidino) and $t\text{Bu}_2\text{P}-\text{P}=\text{N}-\text{N}(\text{SiMe}_3)_2$,^[20] the NMe_2 group in **6** is coplanar with the $\text{C}_{\text{Arf}}\text{PN}$ moiety. This orientation involves the presence of an important stab-

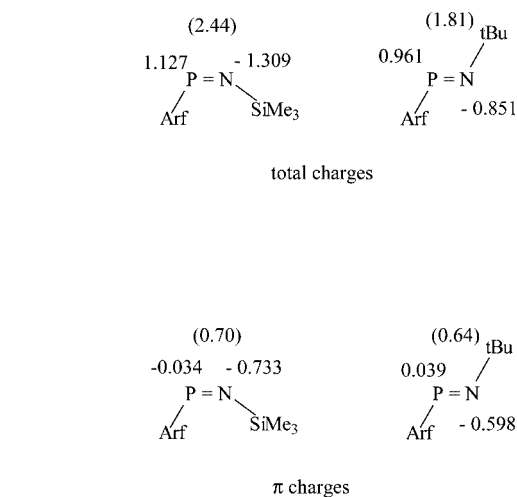


Figure 8. NBO charges (total and π) for $\text{Ar}_f\text{P}=\text{NSiMe}_3$ (**3**) and $\text{Ar}_f\text{P}=\text{N}t\text{Bu}$ (**4**); polarity of the PN bond in brackets

ilizing interaction between the amino nitrogen lone-pair and the $\pi^*_{\text{P}=\text{N}}$ orbital [$n_{\text{N}} \rightarrow \pi^*_{\text{P}=\text{N}} = 77$ kcal/mol (*cis*); $n_{\text{N}} \rightarrow \pi^*_{\text{P}=\text{N}} = 76.5$ kcal/mol (*trans*)]. The *trans* form features a $\text{P}-\text{N}$ bond (1.653 Å) that is significantly longer than the corresponding distance in **1** (1.588 Å). The $\text{N}-\text{N}$ bond (1.302 Å) is intermediate between a single (1.450 Å) and a double bond (1.250 Å). As can be seen in Figure 5, the replacement of H by an NMe_2 group at the nitrogen atom destabilizes the $\pi_{\text{P}=\text{N}}$ orbital by 3.15 eV (Figure 5). The NMe_2 group also has an important influence on the energetic position of the antibonding combination of lone pairs mainly localized on nitrogen. On the other hand, the bonding combination of lone pairs is less affected by this sub-

stituent (the difference in the energies is 1.48 eV and 0.52 eV, respectively).

Next we carried out calculations on compound **6**. Two minima corresponding to the *trans* and *cis* isomers were found on the potential energy surface. In both isomers, the amino nitrogen atom is sp^2 hybridized and the NMe_2 group is coplanar with the CPN moiety, thus establishing a three-center, four-electron system. The *trans* form **6mini** (energetic minimum) is more stable than the *cis* form by 2.07 kcal/mol because of less steric hindrance (see Table 1, E_{rep}). For **6mini** the dihedral angle between the Ar_f group and the CPN system is 126.4° . The substitution of H by Ar_f in **5** has only a weak influence on the geometrical parameters of the CPN system (Table 1). The P–C bond length (1.878 Å) remains characteristic of a single bond. These theoretical results are in agreement with the RX structure (Figure 3). As previously observed, the structure with the Ar_f group coplanar with the PNN moiety (**6ts**) corresponds to a transition state. It is energetically very close to the minimum (3.3 kcal/mol) and should involve a free rotation of the aromatic group in the gas phase. For **6ts**, the P–N, P–C and N–N bond lengths are slightly shorter than in **6mini**.

The calculated NBO charges of the $Ar_fP=N-R$ (R: *t*Bu **4**, NMe_2 **6**) system show that the phosphorus charge is about 0.961 au for **4** and 0.638 au for **6**. This modification affects the ^{31}P NMR chemical shift (**4**: $\delta = 412.4$ ppm; **6**: $\delta = 224.2$ ppm). The peak due to the NMe_2 -substituted phosphorus atom appears at higher field than the *t*Bu-substituted phosphorus atom. This result is in agreement with those previously reported by Yoshifuji et al.^[1b] on the $-P=$ part.

The weak geometrical changes between the forms **5**, **6mini** and **6ts** lead to negligible modifications of their electronic structure. Figure 9 summarizes the energetic positions of the n^+ , n^- and $\pi_{P=N}$ orbitals for these compounds. The inductive σ -attractor effect of Ar_f exerts a weak stabilizing influence on the n^+ and n^- orbitals (0.2–0.3 eV for n^+ and 0.37–0.44 eV for n^-); this stabilization is more pronounced for the n^- orbital since it is mainly localized on phosphorus. The plots of the combination of lone pairs show a destabilizing interaction with the σ_{PC} orbital (as previously observed for **3** and **4**), which reduces the stabilizing inductive effect of the CF_3 groups. This is the reason why the energetic positions of the n^+ and n^- orbitals in **5** and **6** are not strongly modified. In the same way, whatever the orientation of the fluorinated aromatic group, the substitution on phosphorus by Ar_f group seems to have no effect on the energetic position of the $\pi_{P=N}$ orbital. Indeed, the Kohn–Sham energies are similar for these three compounds [–5.68 (**5**), –5.74 (**6mini**), –5.74 eV (**6ts**)]. For **6ts**, taking into account the orientation of the aryl group, we might expect an interaction between the $\pi_{b1(aryl)}$ orbital of Ar_f and the $\pi_{P=N}$ system. In fact, the presence of a planar amino group coplanar with the PNN moiety involves a destabilization of the $\pi_{P=N}$ orbital (interaction $n_N \rightarrow \pi_{P=N}$). Consequently, the energy gaps $\pi_{P=N}/\pi_{b1(aryl)}$ and $\pi_{P=N}/\pi_{b1(aryl)}$ are decreased and increased, respectively. In the particular case of **6ts**, the strong destabilizing $\pi_{P=N} \rightarrow \pi_{b1(aryl)}$

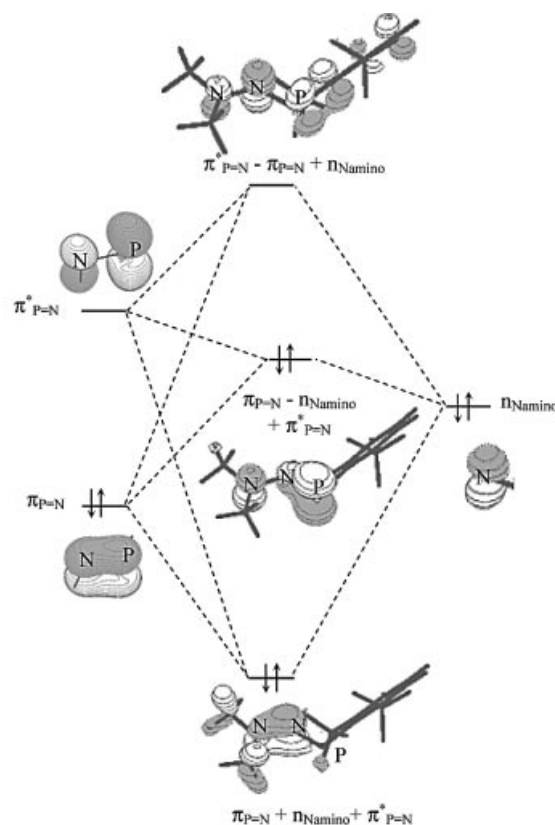


Figure 9. Plot of the molecular orbitals for the minimum of $Ar_fP=NNMe_2$ (**6mini**)

interaction is counterbalanced by the stabilizing $\pi_{P=N} \rightarrow \pi_{b1(aryl)}$ interaction (see MO plots Figure 7). However, it should be noted that even when the aromatic group is coplanar with the PNN system the $\pi_{P=N} \rightarrow \pi_{b1(aryl)}$ interaction is not important enough to allow a strong delocalization of the $\pi_{P=N}$ system. Perhaps, the presence of strong σ -donor groups on the amino nitrogen would allow the stabilizing $\pi_{P=N} \rightarrow \pi_{b1(aryl)}$ interaction to be more important than the destabilizing $\pi_{P=N} \rightarrow \pi_{b1(aryl)}$ interaction. In this case a structure close to the Ar_fPH^- anion structure would be observed.

We have recorded the He^I PE spectrum of **6** in order to confirm the modifications of the electronic structure of the $CP=N$ part on going from **4** to **7** (Figure 6b). It presents three first-ionization bands at 7.8, 8.8 and 9.5 eV which are lower in energy than the first ionizations of $Ar_fP=NtBu$ (8.5, 10.0 and 11.0 eV). The ΔSCF values (**6mini**: $\pi_{P=N} - n_{Namino} = 7.51$ eV; **6ts**: $\pi_{P=N} - n_{Namino} = 7.44$ eV) as well as the Kohn–Sham energy orbitals allowed us to assign the first band at 7.8 eV to the removal of an electron from the $(\pi_{P=N} - n_{Namino} - \pi_{P=N}^*)$ orbital of all rotamers around **6mini** and **6ts** (see Figure 9); the second band at 8.8 eV was assigned to the phosphorus and nitrogen bonding combination of lone pairs ($n_P + n_N$) for the different rotamers. The experimental gap (1 eV) between the first two orbitals is theoretically well represented (0.86–0.93 eV). The third ionization at 9.5 eV corresponds to the removal of an elec-

tron from the π_{a2} orbitals of the aromatic ring. We can note an inversion of the first two orbitals. Compared to **4** (n^+ , $\pi_{P=N}$ for **4** and $\pi_{P=N}$, n^+ for **6**), the $\pi_{P=N}$ orbital is being destabilized because of the interaction with the nitrogen lone pair of the amino group. The following bands at 11.0 and 11.6 eV are assigned to the ionization from the ($n_P - n_N$) orbital and the ($\pi_{P=N} + n_{\text{N amino}} + \pi^*_{P=N}$) orbitals, respectively. In fact, the plot of this latter looks like the plot of a $\pi_{N=N}$ orbital, since the interaction between the $\pi_{P=N}$ and $\pi^*_{P=N}$ orbitals cancels the weight on the phosphorus atom (Figure 9).

In summary, previous works on the effect of the Ar_f group on the stabilization of the reactive part of the molecule have shown that this latter could act as a spectator group or a π -acceptor group. For instance, for the two following compounds: the carbene $\text{Ar}_f\text{CP}(\text{NiPr}_2)_2$ [¹⁴] and the anion Ar_fPH^- , [¹³] a delocalization of the carbene lone pair (carbene) or the π phosphorus lone pair (anion) in the Ar_f group was observed, respectively. The $\text{C}_{\text{carb}}-\text{C}_{\text{aryl}}$ (1.390 Å) or $\text{P}-\text{C}_{\text{aryl}}$ (1.794 Å) bonds are short and the $\text{C}_{\text{A(aryl)}}-\text{C}_{\text{B(aryl)}}$ or $\text{C}_{\text{A(aryl)}}-\text{C}_{\text{B'(aryl)}}$ bonds [$\text{C}_{\text{A(aryl)}}$: carbon linked to the carbon center or phosphorus, $\text{C}_{\text{B(aryl)}}$ and $\text{C}_{\text{B'(aryl)}}$: carbon in α position to $\text{C}_{\text{A(aryl)}}$] of the Ar_f groups are longer than the other bonds of the ring (1.43–1.44 Å compared to 1.37–1.39 Å), indicating a delocalization of the carbene lone pair or the negative charge (phosphanide anion) over the ring. In this case, the Ar_f group behaves like a π -electron acceptor by the $\pi^*_{b1(\text{aryl})}$ orbitals of the aryl group.

A recent publication [²⁷] has shown that the potentially π -acceptor Ar_f group can also act as a spectator group. Indeed, for the amino(aryl)carbene $\text{Ar}_f\text{CN}(\text{Me})t\text{Bu}$, it has been shown that the $\text{C}_{\text{carb}}-\text{C}_{\text{aryl}}$ bond is long (1.453 Å), the carbene bond angle acute and the C–C bonds of the aryl group quite similar (1.37–1.42 Å), which indicates that the Ar_f group does not interact with the carbene lone pair and is therefore a spectator.

In our case [iminophosphanes $\text{Ar}_f\text{P}=\text{N}t\text{Bu}$ (**4**) and $\text{Ar}_f\text{P}=\text{NNMe}_2$ (**6**)], all the C–C bonds of the aryl group are almost similar (1.38–1.41 Å) and the $\text{P}-\text{C}_{\text{aryl}}$ bond quite long (single bonds: 1.866 Å for **4** and 1.863 Å for **6**). We did not observe a shortening of the $\text{P}-\text{C}_{\text{aryl}}$ bond or a lengthening of the $\text{C}_{\text{A(aryl)}}-\text{C}_{\text{B(aryl)}}$ or $\text{C}_{\text{A(aryl)}}-\text{C}_{\text{B'(aryl)}}$ bonds. These geometrical data can be compared to the previous ones and allow us to conclude that the Ar_f substituent effect is mainly steric.

Conclusion

The experimental (NMR, X-rays and UV Photoelectron Spectroscopy data) and theoretical studies on the iminophosphanes $\text{Ar}_f-\text{P}=\text{NR}$ (R : $t\text{Bu}$, NMe_2) show that the Ar_f group is orthogonal to the PNR moiety. This orientation could have allowed an interaction between the phosphorus lone pair and the $\pi^*_{b1(\text{aryl})}$ orbital of the Ar_f group, as previously observed for $(i\text{Pr}_2\text{N})_2\text{PCAr}_f$ (p character of the carbon σ lone pair, short $\text{C}_{\text{carb}}-\text{C}_{\text{aryl}}$ bond). However, taking

into account the strong s character of the phosphorus lone pair (phosphorus angle shrunk), this interaction is not efficient. In fact, in these compounds the Ar_f group acts mainly as a sterically protective ligand. The stabilizing effect of Ar_f is not efficient in the σ system because it is attenuated by a destabilizing interaction between the phosphorus and nitrogen combination of lone pairs and the σ_{PC} orbital. Moreover, in spite of a different electronic effect between SiMe_3 and $t\text{Bu}$, the isolation of the monomer in the latter case can only be explained by a smaller protecting effect of the SiMe_3 substituent compared to $t\text{Bu}$.

In addition, all these results show that the Ar_f group only stabilizes a system which presents a weakly nucleophilic lone pair with a strong p character. In this case, it can behave like an acceptor group with the $\pi^*_{b1(\text{aryl})}$ orbital. Thus, it seems interesting to use Ar_f in order to stabilize anionic species with a heteroatom. This substituent could allow us to stabilize the singlet state of phosphinidenes and homologues.

Experimental Section

General Remarks: All reactions and manipulations were carried out under argon using standard Schlenk techniques. Solvents were dried according to the appropriate method: dichloromethane and chloroform with P_4O_{10} , pentane and hexane with calcium hydride, toluene, xylene, tetrahydrofuran and diethyl ether with sodium/benzophenone.

NMR spectra were recorded on Bruker AC200, and WM250 spectrometers. ^1H and ^{13}C chemical shifts are reported in ppm relative to tetramethylsilane as an external reference. ^{19}F and ^{31}P NMR downfield chemical shifts are expressed with a positive sign relative to external CF_3COOH and 85% H_3PO_4 , respectively. Mass spectra were obtained on a Nermag R 10–10 instrument. The photoelectron spectra were recorded on a Helectros 0078 instrument equipped with a 127° cylindrical analyser and monitored by a micro-computer supplemented with a digital analogic converter. The spectra were calibrated with the known auto-ionization of helium at 4.98 eV [$\text{HeII}(\text{He})$] and nitrogen ionization at 15.59 eV.

$\text{Ar}_f\text{P}(\text{Cl})-\text{N}(\text{SiMe}_3)_2$: A 1.6 M solution of $n\text{BuLi}$ in hexane (6.92 mmol) was added to a solution of $\text{HN}(\text{SiMe}_3)_2$ (1.12 g, 6.92 mmol) in THF (8 mL) at -50°C . The mixture was then warmed to ambient temperature and stirred for 1 h. This solution of $\text{LiN}(\text{SiMe}_3)_2$ was added dropwise to a solution of Ar_fPCl_2 (2.18 g, 6.92 mmol) in THF (5 mL) at -80°C . The reaction mixture was slowly warmed to ambient temperature, stirred for 1 h and the solvents evaporated. Pentane was added to the residue and the precipitated LiCl was filtered off. Removal of solvent and volatiles in vacuo yielded $\text{Ar}_f\text{P}(\text{Cl})\text{N}(\text{SiMe}_3)_2$ as a yellow oil. Yield 86% (95% pure by NMR). ^1H NMR (CDCl_3): δ = 0.02 (s, 9 H, SiMe_3), 6.59 (t, $^3J_{\text{H,H}} = 7$ Hz, 1 H, $p\text{-H}_{\text{arom}}$), 7.82 (d, $^3J_{\text{H,H}} = 7$ Hz, 2 H, $m\text{-H}_{\text{arom}}$) ppm. ^{13}C NMR (CDCl_3): δ = 4.1 (d, $^3J_{\text{PC}} = 7.4$ Hz, SiMe_3), 124.1 (dq, $^3J_{\text{PC}} = 5.6$, $^1J_{\text{PC}} = 275.6$ Hz, CF_3), 129.3 (d, $^4J_{\text{PC}} = 2.8$ Hz, $p\text{-C}_{\text{arom}}$), 130.7 (m, $m\text{-C}_{\text{arom}}$), 134.7 (dq, $^2J_{\text{PC}} = 11.1$, $^2J_{\text{C,F}} = 32.4$ Hz, $o\text{-C}_{\text{arom}}$), 149.0 (d, $^1J_{\text{PC}} = 110.9$ Hz, $ipso\text{-C}_{\text{arom}}$) ppm. ^{19}F NMR (CDCl_3): δ = 24.45 (d, $^4J_{\text{F,P}} = 39$ Hz) ppm. $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): δ = 143.9 (sept, $^4J_{\text{F,P}} = 39$ Hz) ppm.

$[\text{Ar}_f\text{PNSiMe}_3]_2$ (3'**):** A solution of $\text{Ar}_f\text{P}(\text{Cl})\text{N}(\text{SiMe}_3)_2$ (1.20 g, 2.73 mmol) in 1,2,4-trichlorobenzene (5 mL) was heated at 150°C

for 40 h. The solvent was evaporated in vacuo (60 °C, 0.1 Torr) and the crude **3'** was purified by washing with hexane (5 mL). This procedure gave 0.81 g (90% yield) of pure product. ^1H NMR (CD_2Cl_2): δ = -0.28 (s, 18 H, SiMe_3), 7.73 (t, $^3J_{\text{H,H}} = 8$ Hz, 2 H, $p\text{-H}_{\text{arom}}$), 8.11 (two d, $^3J_{\text{H,H}} = 8$ Hz, 4 H, $m\text{-H}_{\text{arom}}$) ppm. ^{13}C NMR (CD_2Cl_2): δ = -1.1 (s, SiMe_3), 124.1 (q, $^1J_{\text{F,C}} = 275.3$ Hz, CF_3), 124.6 (q, $^1J_{\text{F,C}} = 276.7$ Hz, CF_3), 130.7 (s, $p\text{-C}_{\text{arom}}$), 131.3 (q, $^3J_{\text{F,C}} = 32.1$ Hz, $m\text{-C}_{\text{arom}}$), 139.6 (dq, $^2J_{\text{C,P}} = 36.1$, $^2J_{\text{F,C}} = 29.4$ Hz, $o\text{-C}_{\text{arom}}$), 151.4 (d, $^1J_{\text{C,P}} = 132.3$ Hz, $ipso\text{-C}_{\text{arom}}$) ppm. ^{19}F NMR (CD_2Cl_2): δ = 23.04 (d, $^4J_{\text{F,P}} = 72.3$ Hz) and 27.39 (d, $^4J_{\text{F,P}} = 134.7$ Hz) ppm. $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ = 277.3 (m) ppm. $\text{C}_{22}\text{H}_{24}\text{F}_{12}\text{N}_2\text{P}_2\text{Si}_2$ (662.54): calcd. C 39.88, H 3.65; found C 39.65, H 3.89.

$\text{Ar}_f\text{P}(\text{Cl})\text{-N}(\text{SiMe}_3)t\text{Bu}$: A solution of $[\text{LiN}(\text{SiMe}_3)t\text{Bu}]$ in THF (12 mL), prepared from $\text{HN}t\text{Bu}(\text{SiMe}_3)$ (1.44 g, 9.89 mmol) and an equimolar amount of a 1.6 M solution of $n\text{BuLi}$ in hexane at -30 °C, was added dropwise to a solution of Ar_fPCl_2 (3.12 g, 9.89 mmol) in THF (7 mL) at -80 °C. The reaction mixture was slowly warmed to ambient temperature, stirred for 1 h and the solvents evaporated. Pentane was added to the residue and the precipitated LiCl was filtered off. Removal of the solvent and volatiles in vacuo yielded 3.4 g (81%) of product. ^1H NMR (CDCl_3): δ = 0.03 (s, 9 H, SiMe_3), 1.54 (s, 9 H, $t\text{Bu}$), 7.56 (t, $^3J_{\text{H,H}} = 7.4$ Hz, 1 H, $p\text{-H}_{\text{arom}}$), 7.79 (d, $^3J_{\text{H,H}} = 7.4$ Hz, 2 H, $m\text{-H}_{\text{arom}}$) ppm. ^{13}C NMR (CDCl_3): δ = 6.4 (s, Me_3Si), 32.7 (d, $^3J_{\text{P,C}} = 13.9$ Hz, CMe_3), 61.5 (d, $^2J_{\text{C,P}} = 29.6$ Hz, CMe_3), 123.9 (dq, $^1J_{\text{F,C}} = 242.3$, $^4J_{\text{C,P}} = 5.5$ Hz, CF_3), 129.0 (d, $^4J_{\text{C,P}} = 3.7$ Hz, $p\text{-C}_{\text{arom}}$), 129.9 and 131.6 (m, $m\text{-C}_{\text{arom}}$), 134.9 (m, $o\text{-C}_{\text{arom}}$), 148.4 (d, $^1J_{\text{P,C}} = 98.0$ Hz, $ipso\text{-C}_{\text{arom}}$) ppm. ^{19}F NMR (CDCl_3): δ = 24.89 (*pseudo* t, $^4J_{\text{F,P}} = 37$ Hz) ppm. $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): δ = 145.0 (sept, $^4J_{\text{F,P}} = 36$ Hz) ppm.

$\text{Ar}_f\text{P}=\text{N}t\text{Bu}$ (4**):** A solution of $\text{Ar}_f\text{P}(\text{Cl})\text{N}(\text{SiMe}_3)t\text{Bu}$ (1.95 g, 4.61 mmol) in xylene (4 mL) was heated at 120 °C for 80 h, then the solvent was evaporated. Distillation in vacuo afforded 0.80 g (55%) of **4**; b.p. 56–60 °C at 0.05 Torr. ^1H NMR (CDCl_3): δ = 1.49 (d, $^4J_{\text{H,P}} = 1.8$ Hz, 9 H, $t\text{Bu}$), 7.63 (t, $^3J_{\text{H,H}} = 7.8$ Hz, 1 H, $p\text{-H}_{\text{arom}}$), 7.89 (d, $^3J_{\text{H,H}} = 7.8$ Hz, 2 H, $m\text{-H}_{\text{arom}}$) ppm. ^{13}C NMR (CDCl_3): δ = 32.5 (d, $^3J_{\text{C,P}} = 15.7$ Hz, CMe_3), 64.6 (d, $^2J_{\text{C,P}} = 10.2$ Hz, CMe_3), 124.1 (dq, $^1J_{\text{F,C}} = 275.6$, $^3J_{\text{C,P}} = 1.9$ Hz, CF_3), 129.8 (s, $p\text{-C}_{\text{arom}}$), 129.9 (q, $^3J_{\text{F,C}} = 5.6$ Hz, $m\text{-C}_{\text{arom}}$), 133.2 (dq, $^2J_{\text{C,P}} = 4.6$, $^2J_{\text{F,C}} = 31.5$ Hz, $o\text{-C}_{\text{arom}}$), 147.0 (d, $^1J_{\text{C,P}} = 84.2$ Hz, $ipso\text{-C}_{\text{arom}}$) ppm. ^{19}F NMR (CDCl_3): δ = 21.65 (d, $^4J_{\text{F,P}} = 28$ Hz) ppm. $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): δ = 412.4 (sept, $^4J_{\text{F,P}} = 28$ Hz) ppm. $\text{C}_{12}\text{H}_{12}\text{F}_6\text{NP}$ (315.19): calcd. C 45.73, H 3.84; found C 45.40, H 3.55.

$\text{Ar}_f\text{P}(\text{Cl})\text{-N}(\text{SiMe}_3)\text{NMe}_2$: A 1.6 M solution of $n\text{BuLi}$ in hexane (10.38 mmol) was added to a solution of $\text{HN}(\text{SiMe}_3)(\text{NMe}_2)$ (1.37 g, 10.38 mmol) in THF (15 mL) at -30 °C. The mixture was then warmed to ambient temperature and stirred for 1 h. This solution of lithium hydrazide was added dropwise to a solution of Ar_fPCl_2 (3.27 g, 10.38 mmol) in THF (7 mL) at -80 °C. The reaction mixture was slowly warmed to ambient temperature, stirred for 1 h and the solvents evaporated. Pentane was added to the residue and the precipitated LiCl was filtered off. Solvent and volatile compounds were removed in vacuo. The resulting solid contained the chlorophosphane $\text{Ar}_f\text{P}(\text{Cl})\text{N}(\text{SiMe}_3)\text{NMe}_2$ and about 20% of the diphosphane $\text{Ar}_f\text{P}=\text{PAr}_f$. Recrystallization from diethyl ether afforded the pure product as dark yellow crystals. Yield 2.1 g (49%). ^1H NMR (C_6D_6): δ = 0.02 (s, 9 H, SiMe_3), 2.51 (br. s, 6 H, Me_2N), 6.71 (t, $^3J_{\text{H,H}} = 7.8$ Hz, 1 H, $p\text{-H}_{\text{arom}}$), 7.38 (d, $^3J_{\text{H,H}} = 7.8$ Hz, 2 H, $m\text{-H}_{\text{arom}}$) ppm. ^{13}C NMR (C_6D_6): δ = 1.9 (d, $^3J_{\text{P,C}} = 2.8$ Hz, Me_3Si), 47.1 (d, $^3J_{\text{P,C}} = 103.6$ Hz, Me_2N), 124.6 (q, $^1J_{\text{F,C}} =$

275.6 Hz, F_3C), 130.8 (s, $p\text{-C}_{\text{arom}}$), 130.9 (br. m, $m\text{-C}_{\text{arom}}$), 135.6 (dq, $^2J_{\text{P,C}} = 19.4$, $^2J_{\text{C,F}} = 31.4$ Hz, $o\text{-C}_{\text{arom}}$), 138.2 (d, $^1J_{\text{P,C}} = 83.23$ Hz, $ipso\text{-C}_{\text{arom}}$) ppm. ^{19}F NMR (C_6D_6): δ = 22.50 (d, $^4J_{\text{F,P}} = 46$ Hz) ppm. $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6): δ = 122.5 (sept, $^4J_{\text{F,P}} = 46$ Hz) ppm. MS (70 eV): m/z (%) = 375 (100) [$\text{M} - \text{Cl}$] $^+$. $\text{C}_{13}\text{H}_{18}\text{ClF}_6\text{N}_2\text{PSi}$ (410.80): calcd. C 38.01, H 4.42; found C 38.19, H 4.22.

$\text{Ar}_f\text{P}=\text{N}-\text{NMe}_2$ (6**):** A solution of $\text{Ar}_f\text{P}(\text{Cl})\text{N}(\text{SiMe}_3)\text{NMe}_2$ (1.96 g, 4.78 mmol) in xylene (4 mL) was heated at 120 °C for 2 h, then the solvent was evaporated. Distillation in vacuo (60–70 °C, 0.05 Torr) afforded **6** in ca. 50% yield and, according to the NMR spectra, $\text{Ar}_f\text{P}=\text{PAr}_f$ ($\delta_{\text{P}} = 478$ ppm) as a side product (ca. 10%). Pure **6** was isolated after stirring a solution of the amido(chloro)-phosphane (1.52 g, 3.70 mmol) in CHCl_3 (2 mL) at 25 °C for 14 h. Yield 95%; b.p. 65–70 °C at 0.5 Torr. ^1H NMR (CDCl_3): δ = 3.34 (d, $^4J_{\text{H,P}} = 7.4$ Hz, 6 H, Me_2N), 7.55 (t, $^3J_{\text{H,H}} = 8$ Hz, 1 H, $p\text{-H}_{\text{arom}}$), 7.89 (d, $^3J_{\text{H,H}} = 8$ Hz, 2 H, $m\text{-H}_{\text{arom}}$) ppm. ^{13}C NMR (CDCl_3): δ = 47.9 (d, $^3J_{\text{C,P}} = 12.95$ Hz, Me_2N), 124.1 (q, $^1J_{\text{F,C}} = 275.6$ Hz, CF_3), 128.6 (s, $p\text{-C}_{\text{arom}}$), 129.6 (q, $^3J_{\text{F,C}} = 5.5$ Hz, $m\text{-C}_{\text{arom}}$), 135.3 (dq, $^2J_{\text{C,P}} = 4.6$, $^2J_{\text{F,C}} = 29.6$ Hz, $o\text{-C}_{\text{arom}}$), 144.0 (d, $^1J_{\text{C,P}} = 71.2$ Hz, $ipso\text{-C}_{\text{arom}}$) ppm. ^{19}F NMR (CDCl_3): δ = 20.92 (d, $^4J_{\text{F,P}} = 23.5$ Hz) ppm. ^{31}P NMR (CDCl_3): δ = 224.3 (br.s) ppm. $\text{C}_{10}\text{H}_9\text{F}_6\text{N}_2\text{P}$ (302.16): calcd. C 39.75, H 3.00; found C 40.10, H 3.38.

$i\text{Pr}_2\text{NP}(\text{Cl})\text{-N}(\text{SiMe}_3)\text{NMe}_2$: A 1.6 M solution of $n\text{BuLi}$ in hexane (6.36 mmol) was added to a solution of $\text{HN}(\text{SiMe}_3)(\text{NMe}_2)$ (0.84 g, 6.36 mmol) in THF (10 mL) at -30 °C. This solution of lithium hydrazide was added dropwise to a solution of $i\text{Pr}_2\text{NPCl}_2$ (1.27 g, 6.36 mmol) in THF (5 mL) at -80 °C. The reaction mixture was slowly warmed to ambient temperature, stirred for 1 h and the solvents evaporated. Pentane (20 mL) was added to the residue and the precipitated LiCl was filtered off. The solution was evaporated to yield colorless crystals of the product (89%). M.p. 32–34 °C. ^1H NMR (C_6D_6): δ = 0.39 (s, 9 H, SiMe_3), 1.08 and 1.28 (d, $^3J_{\text{H,H}} = 6.8$ Hz, 12 H, $\text{CH}(\text{CH}_3)_2$), 2.52 and 2.61 (s, 6 H, NMe_2), 3.71 [m, 2 H, $\text{CH}(\text{CH}_3)_2$] ppm. ^{13}C NMR: δ = 3.2 (d, $^3J_{\text{P,C}} = 3.7$ Hz, Me_3Si), 23.2 [d, $^3J_{\text{P,C}} = 12.95$ Hz, $\text{CH}(\text{CH}_3)_2$], 23.9 [d, $^3J_{\text{P,C}} = 4.62$ Hz, $\text{CH}(\text{CH}_3)_2$], 46.7 [d, $^3J_{\text{P,C}} = 10.2$ Hz, $\text{N}(\text{CH}_3)_2$], 47.4 [d, $^2J_{\text{P,C}} = 44.4$ Hz, $\text{CH}(\text{CH}_3)_2$], 47, 6 [d, $^2J_{\text{P,C}} = 39.8$ Hz, $\text{CH}(\text{CH}_3)_2$] ppm. ^{31}P NMR (CDCl_3): δ = 129.3 (s) ppm. $\text{C}_{13}\text{H}_{18}\text{ClF}_6\text{N}_2\text{PSi}$ (410.80): calcd. C 38.01, H 4.42; found C 38.19, H 4.22.

$i\text{Pr}_2\text{NP}=\text{NNMe}_2$ (7**):** A solution of $i\text{Pr}_2\text{NP}(\text{Cl})\text{N}(\text{SiMe}_3)\text{NMe}_2$ (1.43 g, 4.80 mmol) in toluene (10 mL) was heated at 100 °C for 10 h. Solvent was removed in vacuo to afford iminophosphane **7** contaminated by a small amount (<10%) of the dimer $[\text{iPr}_2\text{NPNNMe}_2]_2$.

7: ^1H NMR (C_6D_6): δ = 1.19 and 1.44 [br. s, 12 H, $\text{CH}(\text{CH}_3)_2$], 2.58 (s, 6 H, NMe_2), 3.32 and 4.10 [br. s, 2 H, $\text{CH}(\text{CH}_3)_2$] ppm. ^{13}C NMR (C_6D_6): δ = 22.2 and 27.6 [br. s, $\text{CH}(\text{CH}_3)_2$], 44.8 [s, $\text{N}(\text{CH}_3)_2$], 49.3 [*pseudo* t, $^2J_{\text{P,C}} = 5.55$ Hz, $\text{CH}(\text{CH}_3)_2$] ppm. ^{31}P NMR (C_6D_6): δ = 173.13 (s) ppm. MS (70 eV): m/z (%) = 189 (15) [M^+]. $\text{C}_8\text{H}_{20}\text{N}_3\text{P}$ (189.24).

Iminophosphane **7** slowly dimerizes at room temperature to give 1,3,2,4-diazadiphosphetidine $[\text{iPr}_2\text{NPNNMe}_2]_2$ according to X-ray analysis. ^1H NMR (CDCl_3): δ = 1.24 [d, $^3J_{\text{H,H}} = 6.8$ Hz, 12 H, $\text{CH}(\text{CH}_3)_2$], 2.69 (s, 6 H, NMe_2), 3.84 [br. s, 2 H, $\text{CH}(\text{CH}_3)_2$] ppm. ^{13}C NMR (CDCl_3): δ = 24.6 [br. s, $\text{NCH}(\text{CH}_3)_2$], 43.6 (t, $^3J_{\text{P,C}} = 4.6$ Hz, NMe_2), 49.1 (t, $^2J_{\text{P,C}} = 5.6$ Hz, $\text{CH}(\text{CH}_3)_2$) ppm. ^{31}P NMR (CDCl_3): δ = 74.2 (s) ppm. MS (70 eV): m/z (%) = 378 (17) [M^+]. $\text{C}_8\text{H}_{20}\text{N}_3\text{P}$ (189.24): calcd. C 50.77, H 10.65, N 22.20; found C 50.86, H 10.84, N 22.08. $\text{C}_{16}\text{H}_{40}\text{N}_6\text{P}_2$ (378.48): calcd. C 50.77, H 10.65, N 22.20; found C 50.55, H 10.49, N 22.13.

Table 3. Crystallographic data for **3'**, **4** and **6**

	3'	4	6
Empirical formula	C ₁₁ H ₁₂ F ₆ NPSi	C ₁₂ H ₁₂ F ₆ NP	C ₁₀ H ₉ F ₆ N ₂ P
Molecular mass	331.28	315.20	302.16
Temp. (K)	223(2)	193(2)	193(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	monoclinic	orthorhombic	triclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> nma	<i>P</i> $\bar{1}$
<i>a</i> (Å)	10.378(2)	7.031(1)	7.160(1)
<i>b</i> (Å)	17.730(3)	13.348(1)	9.245(1)
<i>c</i> (Å)	15.790(4)	15.263(2)	10.565(1)
α (°)	—	—	67.164(2)
β (°)	93.75(2)	—	78.394(2)
γ (°)	—	—	85.958(2)
<i>V</i> (Å ³)	2899.3(9)	1432.4(3)	631.4(1)
<i>Z</i>	8	4	2
θ range for data collection (°)	1.73 to 28.28	2.03 to 24.71	2.13 to 29.46
No. of rflns collected	21424	6955	4296
No. of indep rflns.	7171 [<i>R</i> (int) = 0.0246]	1278 [<i>R</i> (int) = 0.0452]	3074 [<i>R</i> (int) = 0.0231]
No. of parameters	385	102	174
Goodness of fit on <i>F</i> ²	1.021	1.043	1.026
<i>R</i> 1 [<i>I</i> > 2 σ (<i>I</i>)]	0.0504	0.0537	0.0476
<i>wR</i> 2 (all data)	0.1572	0.1471	0.1387
Largest diff peak, hole (e [−] Å ^{−3})	1.158 and −0.283	0.357 and −0.311	0.342 and −0.297

Computational Details: Calculations were performed with the Gaussian 98 program^[28,29] using the Density Functional theory method.^[30] The various structures were fully optimized at the B3LYP level.^[31] This functional is built with Becke's three-parameter exchange functional^[31a] and the Lee–Yang–Parr correlation functional.^[31c] The 6-311G(d,p) basis set was used. All atoms were augmented with a single set of polarization functions. The second derivatives were calculated in order to determine if a minimum or a transition state (one negative eigenvalue) existed for the resulting geometry.

All total energies have been zero-point energy (ZPE) and temperature corrected using unscaled density functional frequencies.

NBO analysis population^[32] was performed in order to determine the presence of stabilizing interactions between a filled orbital and an empty orbital. Ionization energies were determined as the difference between the cation and the neutral molecule energies ($IE = E_{\text{cation}} - E_{\text{molecule}}$; Δ SCF method). For the large molecules, an association between the ionization potential and Kohn–Sham (KS) energies calculated with common functionals (Koopmans' theorem-like) has been discussed in depth. Arduengo and co-workers^[33] first used DFT calculations at the nonlocal level to assign their photoelectron spectra. They applied a uniform shift to the orbital energies considering the difference between the calculated and experimental molecular ionization potentials. The aim was to directly compare the KS energies to the experimental energies. Moreover, Werstiuk and Rademacher^[34] have developed and successfully applied a routine for the interpretation of PE spectra based on B3LYP theory. This routine requires the calculation of the molecule's first vertical ionization potential IP_v . Calculated orbital energies $-\epsilon$ are then shifted uniformly so that the HOMO energy equals that of the IP_v , giving the higher IPs. More recently, Hoffmann^[35] has underlined that the KS orbitals are a good basis for qualitative interpretation of molecular orbital. He concluded that if one wants to go a step beyond a qualitative interpretation and look at orbital energies as rough ionization potentials, and if the DFT calculations are done with commonly used potentials,

then one must take the absolute constant and linear orbital energy shift into account by applying a suitable ($ax + b$) scaling. In the case of large molecules, the ordering of levels found by using the DFT calculations seems to be qualitatively as well translated as by using HF methods. This fact, despite the evident limits of correlation, gives a good basis for discussion about the ionizations assignments which cannot be reached by a direct calculation.

X-ray Crystallographic Study: Crystal data for **3'**, **4** and **6** are presented in Table 3. All data were collected at low temperature (−50 °C for **3'** and −80 °C for **4** and **6**) on a Bruker-AXS CCD 1000 diffractometer with Mo-*K*_α radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods by means of SHELXS-97^[36] and refined with all data on *F*² by means of SHELXL-97.^[37] All non-hydrogen atoms were refined anisotropically. CCDC 223052–223054 (for **3'**, **4** and **6** respectively) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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