Structures and Properties of Carboimidophosphene (HP=C=NH) and Carbodiphosphene (HP=C=PH). An *ab initio* Study

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Ab initio calculations are reported for carboimidophosphene (iminomethylenephosphine), carbodiphosphene (1,3-diphospha-allene) and their conjugate acids. Isomerization is favoured by inversion about the C=N bond and by rotation about C=P bonds and is negligibly small (4.2 kcal mol^{-1} at DZP//4-31G) for HP=C=NH, and large (42 kcal mol^{-1}) for HP=C=PH. The electronic structures, harmonic vibrational frequencies, and proton affinities are reported and compared with those of other phospha-cumulenes such as HP=C=O and H_2C=C=PH. The protonation occurs preferentially at the P atom in HP=C=NH (**1**) and the C atom in HP=C=PH (**4**). At the MP4SDQ/6-31G** level, the proton affinities are predicted to be 210 ± 5 for (**1**) and 193 ± 5 kcal mol^{-1} for (**4**) (with zero-point energy corrections). The regiospecificity of the dimerization, (2 + 2) cycloadditions, additions to HX reagents, and reactions with metals are rationalized or predicted.

Recently we have completed *ab initio* calculations of the molecular structures and chemical properties of the simplest phosphaketene HP=C=O [1] and 1-phospha-allene H_2C=C=PH.[2] We now extend the study to two remaining members of the phospha-allene family: the carboimidophosphene (or iminomethylenephosphine) and the carbodiphosphene HP=C=PH (or 1,3-diphospha-allene).

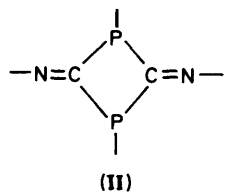
The first carboimidophosphene (**I**; $R^1 = R^2$ = t-butyl) was synthesized by Kolodyazhnyi in 1982.[3] This molecule is stable at room temperature and undergoes addition and cycloaddition reactions. In 1982—1983, a more general method for the preparation of cumulenes (**I**) which are unstable and dimerize to diphosphetanes (**II**) at low temperature, as well as more stable analogues of (**I**), by steric protection with bulky substituents was described.[4,5] More recently, employing the steric protection technique, different groups[6—8] have also reported the synthesis of the first (stable) carbodiphosphene (**III**; $R^1 = R^2$ = 2,4,6-tri-t-butylphenyl) for which an *X*-ray crystallographic structure[7] has also been available. The present work aims to assess, by means of *ab initio* calculations, the similarities and the differences between structures and properties of different phospha-allene members.

$R^1{-}P{=}C{=}N{-}R^2$

(**I**)

$R^1{-}P{=}C{=}P{-}R^2$

(**III**)



(**II**)

Calculations.—*Ab initio* calculations were performed by using the Monsterguass[9] and Gaussian-80[10] programs in their IBM/VM-CMS versions. Geometries of stationary points were optimized making use of the analytical gradient procedure and the 4-31G basis set. The full harmonic force fields were computed by the gradient differences employing the VA05AD subroutines.[11] The harmonic frequencies and normal coordinates were calculated by the standard GF-matrix method. Improved relative energies were determined from single-point calculations with 4-31G geometries at the Hartree–Fock level employing both 6-31G** and DZP (11*s*7*p*2*d*/6*s*4*p*2*d* for P atom) basis sets[12] as well as at the Møller–Plesset perturbation theory[13] (second—fourth order).

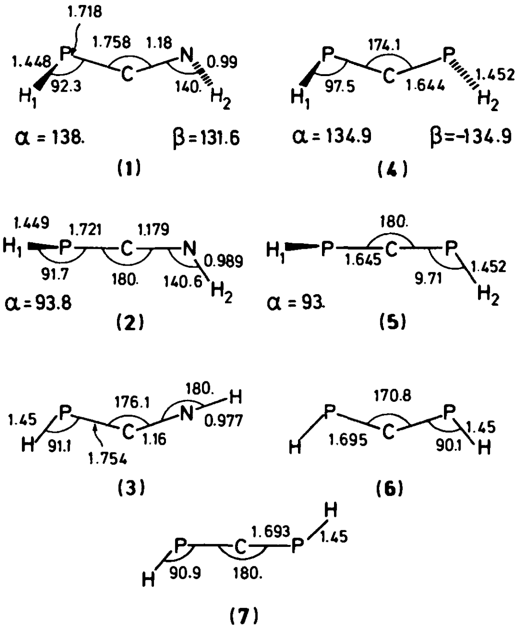


Figure 1. 4-31G-Optimized geometries of carboimidophosphenes (**1**)—(**3**) and carbodiphosphenes (**4**)—(**7**). Distances in Å and bond angles in degrees; α is the dihedral angle H_1PCN, β the angle PCNH_2

Results and Discussion

(1) *Geometries and Configurational Stabilities*.—The fully optimized geometries determined by 4-31G basis set of three configurations of carboimidophosphene (**1**)—(**3**) and four configurations of carbodiphosphene (**4**)—(**7**) are shown in Figure 1. The calculated total and relative energies with respect to the most stable structures at both 4-31G//4-31G and DZP//4-31G levels of (**1**)—(**7**) are listed in Table 1.

First, we have compared the structural data obtained by different methods for the phosphaethene (**8**) (H_2C=PH) for which microwave values are available. Table 2 shows the excellent agreement obtained between the 4-31G and micro-

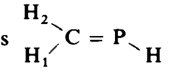
Table 1. Calculated total and relative energies of different configurations of HP=C=NH and HP=C=PH using two basis sets (4-31G and DZP)

Molecule[a]		E(4-31G//4.31G) (a.u.)	E(DZP//4-31G) (a.u.)	ΔE(4-31G)/ kcal mol^{-1}	ΔE(DZP)/ kcal mol^{-1}
HP=C=NH	(1)	−433.588 31	−434.155 45	0.0	0.0
	(2)	−433.587 93	−434.154 72	0.3	0.5
	(3)	−433.587 02	−434.148 71	0.8	4.2
HP=C=PH	(4)	−719.500 61	−720.391 37	0.0	0.0
	(5)	−719.499 96	−720.390 70	0.4	0.4
	(6)	−719.435 43	−720.325 35	40.9	41.4
	(7)	−719.435 23	−720.324 86	41.0	41.7

[a] The corresponding 4-31G geometries are given in Figure 1.

Table 2. Calculated and experimental geometries of $H_2C=PH$ (**8**). Bond lengths in Å and bond angles in degrees

Method	r(C–P)	r(P–H)	r(C–H$_1$)[a]	r(C–H$_2$)[a]	CPH	H$_1$CP	H$_2$CP	Ref.
MINDO/3	1.632	1.421			108.2	129.1		14
STO-3G	1.615	1.390	1.080	1.081	97.0	126.3	120.7	15,16
3-21G	1.683	1.433	1.073	1.073	98.8	124.7	119.5	16
4-31G	1.672	1.449	1.071	1.072	98.4	125.2	119.7	15, 16
6-21G	1.686	1.434	1.073	1.073	98.7	124.7	119.6	16
3-21G*	1.645	1.408	1.075	1.074	99.0	125.1	119.9	17
4-31G*	1.643	1.419	1.082	1.079	98.3	125.4	119.5	
Microwave	1.671	1.425	1.082	1.082	95.5	124.5	119.1	18
Microwave	1.673	1.420	1.09	1.09	97.4	124.4	118.4	19

[a] The atom numbering is 
$$\overset{H_2}{\underset{H_1}{}}\!\!>C=P\!\!\underset{H}{\searrow}$$

wave geometries, especially for the carbon–phosphorus bond and the CPH bond angle. These results confirm that the basis sets of split valence and double-zeta reproduce the best geometric parameters for multiple bonds featuring P atoms[12] (in neutral molecules). Both calculation levels yield a similar order of the relative energies for each cumulene. In the following discussion, we refer to our DZP//4-31G results, unless otherwise mentioned.

$HP=CH_2$	$H_2C=NH$	$HN=C=NH$
(**8**)	(**9**)	(**10**)

From Figure 1 and Table 1, the following points can be noted.

(*a*) The most stable form of each cumulene exhibits a non-linear P=C=X frame with an PCX angle of 176° in (**1**) and of 174° in (**4**). The latter compares well with the *X*-ray value of 172.6° in Ar–P=C=P–Ar.[7]

(*b*) The C=P bond lengths in the symmetrical cumulene (**4**) are calculated to be compressed (0.03 Å) compared with that in (**8**). The value of 1.644 Å is in the same order of magnitude as the *X*-ray one of 1.630—1.635 Å.[7] By contrast, the C=P bond in the unsymmetrical species (**1**) is significantly stretched (0.05 Å) while the C=N bond is markedly compressed (0.08 Å) compared with the C=N group in the methyleneimine (**9**) ($H_2C=NH$). As a consequence, the sum of C=P and C=N bond lengths in (**1**) is still slightly less than that in (**8**) and (**9**) (2.898 Å compared with 2.927 Å). The C=P bond length of 1.718 Å in (**1**) is similar to that of 1.728 Å calculated for the phosphaketene HP=C=O[1] (4-31G).

(*c*) The HPC bond angles of 92.3° in (**1**) and 97.5° in (**4**) are comparable to those of 90.6° in HP=C=O[1] and of 98.5° in $H_2C=PH$ (**8**). The rather large HNC bond angle in (**1**) (140.6°) may be due to an artefact of the 4-31G basis set, like that found in the HN=C=O molecule (HNC = 157° with 4-31G instead of 124° by microwave).[20]

(*d*) Both cumulenes adopt *trans*-configurations relative to the PCX planes. The angles α and β in (**4**) are almost the same as those calculated for the carbodi-imide HN=C=NH (**10**) (±134.2° at 4-31G).[21]

(*e*) The energy difference between non-linear and linear P=C=X minima configurations is not significant: 0.5 for (**1**) and 0.4 kcal mol^{-1} for (**4**) (0.9 kcal mol^{-1} at 6-31G**//4-31G for the carbodi-imide).[21]

(*f*) The isomerization process occurs by an inversion at the C=N bond and by rotation around the C=P bonds. Structures (**3**), (**6**), and (**7**) can be regarded as the transition structures for the racemization of (**1**) and (**2**), (**4**), and (**5**), respectively. The calculated energy barrier for such a transformation is negligible for HP=C=NH (4.2 kcal mol^{-1}) but is substantial for HP=C=PH (42 kcal mol^{-1}). For HN=C=NH, the inversion barrier was calculated as 8 kcal mol^{-1} (6-31G**//4-31G).[21] In other words, we can expect that carboimidophosphene, like carbodi-imide, will be unstable towards configurational change, while carbodiphosphene will be relatively stable. For the latter, it appears that both configurations (**4**) and (**5**) might exist. However, when the H atoms are replaced by bulkier substituents, the balance of stability might be tipped in favour of a compromise structure, *i.e.* one containing two substituents orthogonal with respect to the P–P axis; a non-linear P=C=P skeleton as has, in fact, been observed experimentally (*X*-ray).[7] In summary, the geometry of HP=C=NH is similar to that of HP=C=O for which the electronic factors governing the geometry have been discussed.[1]

(2) *Electronic Structures and Charge Distributions.*—The four HOMO and the LUMO energies computed with the DZP basis set are summarized as a correlation diagram for five species (**1**), (**4**), and (**8**)—(**10**) in their ground states in Figure 2. First, we note the π^*-character of the LUMOs in all of the molecules. The HOMOs in both symmetrical cumulenes, HP=C=PH (**4**) and HN=C=NH (**10**), are more or less similar to two sets of quasi-degenerate n and π orbitals of the XCX parts, except for the identity of the highest orbital of each molecule. As a matter of fact, the HOMO in carbodiphosphene (**4**) is a π-orbital (with an important localization on the carbon atom) while in carbodi-imide (**10**), this corresponds to a nitrogen lone pair n-orbital. The splitting of the first n,π-orbital sets takes place in both $CH_2=PH$ (**8**) and $CH_2=NH$ (**9**), respectively, giving rise to the

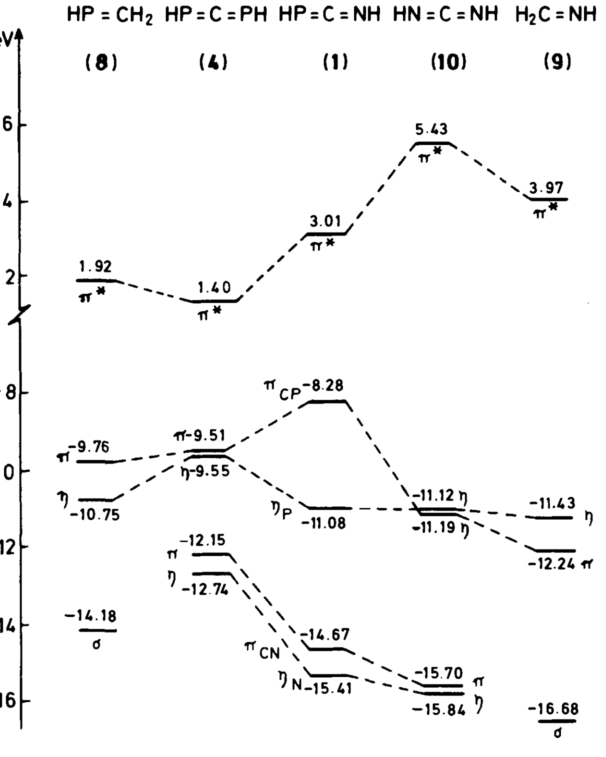


Figure 2. Orbital correlation diagram for the LUMO and some HOMOs in five molecules at the DZP//4-31G level

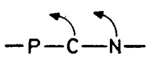
difference between the MO ordering.[12] A similar ordering has been predicted for the second n,π-orbital sets in all cumulenes. More interesting, perhaps, is the situation in the unsymmetrical HP=C=NH (**1**). This molecule shows a large separation of the first set of n,π-orbitals (both belonging to the CP part). So, one can say that the CN group, when cumulated with a C=P bond, creates two opposite effects, first by stabilizing the lone pair P electrons and secondly by destabilizing the π-electrons of the C–P bond. In contrast, the CP group tends to destabilize both n and π-electrons of the CN group, with a larger effect on π-orbitals. This suggests, on one hand, the existence of two quite distinct n and π bands in the photoelectron spectrum of carboimidophosphenes, and on the other hand, a clear preference for these compounds to form π-complexes with transition metals. Note that the calculated n–π separation of 0.81 eV in H_2C=NH (**9**) is somewhat larger than that of 0.51 eV observed from the photoelectron spectrum of the formaldoxime H_2C=N–OH.[17] Comparing the MO levels of CN groups, we can observe in Figure 2 an overall shift to lower ionization potentials and electron affinities. That means that the CP group is less electronegative than the CN group, as has already been emphasized in the case of C≡P and C≡N triple bonds.

Thus, the structure of HP=C=NH can be understood as clearly showing the electron-withdrawing effect of the CN group. This is well correlated with the calculated overlap populations listed in Table 3. Indeed, a decrease in the C=N bond populations in the sequence HPC=NH > HNC=NH > H_2C=NH and an increase in the C=P bond populations in the sequence HNC=PH < HPC=PH < H_2C=PH have been calculated. That confers a partial double bond character onto the carbon–phosphorus bond and a partial triple bond character onto the carbon–nitrogen bond in (**1**). Such a situation obviously favours the inversion at $C\overset{..}{=}N$ *via* a linear configuration and rotation around the $C\overset{..}{-}P$ bond. It follows that the motion of the nuclear skeleton of (**1**) is, as mentioned above, quasi-free.

Table 3. Net charges and overlap populations (DZP)

	HP=CH$_2$ (**8**)	HP=C=PH (**4**)	HP=C=NH (**1**)	NH=C=NH (**10**)	H$_2$C=NH (**9**)
Net charges					
C	−0.494	−0.142	−0.062	0.276	−0.195
P	0.173	0.023	−0.009		
N			−0.253	−0.404	−0.253
H(P)	0.006	0.048	0.037		
H(N)			0.286	0.266	0.199
Overlap populations					
C=P	1.084	0.856	0.850		
C=N			1.506	1.494	1.378
P–H	0.698	0.629	0.696		
N–H			0.712	0.732	0.694

Although strongly dependent on the basis sets, the net charges calculated from the Mulliken population analysis (Table 3) indicate some qualitative characteristics: (*a*) the charges on P atoms are always positive or nearly zero while N atoms are always negatively charged; (*b*) the charge on the C atom is positive in the carbodi-imide (**10**) and negative in the carbodiphosphene (**4**); (*c*) for carboimidophosphene (**1**), the charge distribution is somewhat ambiguous. However, in comparing compounds (**1**), (**4**), and (**8**), we note a charge transfer towards the P atom, particularly in (**1**):


—P—C—N—

This is in fact reflected by the ^{31}P n.m.r. signal observed at high-field region (δ_P = 65 p.p.m.) for carboimidophosphene.[3–5] The chemical shift of the ^{31}P atoms in carbodiphosphene, at *ca.* 140 p.p.m., is high in comparison with those at 200—400 p.p.m. in phospha-alkenes.[22]

The difference in the dipole moments between HP=C=PH (**4**) and HN=C=NH (**10**) on the one hand, and H_2C=PH (**8**) and H_2C=NH (**9**) on the other, obviously arises from the difference in polarity of C=P and C=N bonds.

The q_{zz} components of the electric field gradients indicate the relative ionic character of the chemical bonds. From Table 4, it follows that the N atoms become more negative in cumulative systems (with smaller q_{zz} values) and thus the polarity of C=N bonds decreases in the sequence: $H\overset{-}{N}-\overset{+}{C}NH > H\overset{-}{N}-\overset{+}{C}PH \gg H\overset{-}{N}-\overset{+}{C}H_2$. P atoms become less positive and thereby the ionic character of C=P bonds increases as follows: $H\overset{+}{P}-\overset{-}{C}PH < H\overset{+}{P}-\overset{-}{C}NH < H\overset{+}{P}-\overset{-}{C}H_2$. This is consistent with the analysis based on the net charge distribution alone (see Table 3).

(3) *Vibrational Frequencies*.—The harmonic frequencies of both molecules (**1**) and (**4**) are collected in Table 5 together with their assignments. Of interest are the frequencies relevant to the stretching of the P=C=X frames. The normal co-ordinates of these modes of vibration are displayed in Figure 3.

In (**1**), the mode (**11**) can be assigned to the stretching of the C=N bond and the mode (**12**) to the stretching of the C=P bond. Such a situation is close to that found in 1-phospha-allene H_2C=C=PH[2] and phosphaketene HP=C=O,[1] where there are no stretching modes involving the entire P=C=X skeleton. By contrast, the whole P=C=P group participates in both the

Table 4. Calculated molecular properties (DZP)

	$HP{=}CH_2$ (8)	$HP{=}C{=}PH$ (4)	$HP{=}C{=}NH$ (1)	$HN{=}C{=}NH$ (10)	$H_2C{=}NH$ (9)
Dipole moment (D)					
	1.02 (0.87)[a]	0.78	2.76	2.12	2.18
Electric field gradient (a.u.)					
q_{xx} (P)	−0.470	−0.438	0.379		
q_{yy} (P)	−0.978	−0.684	0.932		
q_{zz} (P)	1.384	1.123	−1.311		
η (P)[b]	0.411	0.219	0.422		
q_{xx} (N)			−0.298	0.500	−0.280
q_{yy} (N)			−0.364	0.122	−0.837
q_{zz} (N)			0.662	0.622	1.117
η (N)[b]			0.100	0.606	0.498

[a] Experimental value from refs. 18 and 19. [b] Asymmetric parameter = $|q_{xx} - q_{yy}|/|q_{zz}|$.

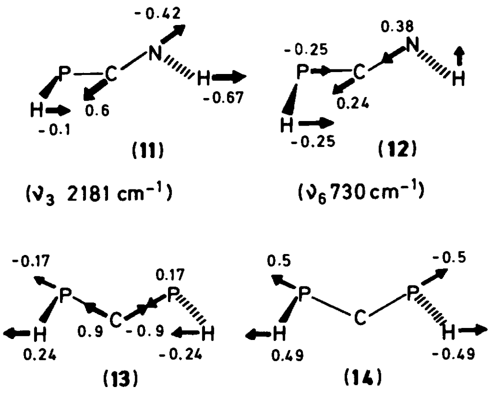


Figure 3. Normal co-ordinates of vibrational modes involving the P=C=X frame in (**1**) [modes (**11**) and (**12**)] and in (**4**) [modes (**13**) and (**14**)]

asymmetric (**13**) and symmetric (**14**) stretching modes of (**4**), as would be expected from symmetry considerations. The rather long C=P bond distance in (**1**) may be reponsible for this difference. In a complex-like structure such as (**1**) (between PH and HNC fragments) the C=N and C=P bonds can vibrate independently. If we consider now a scale factor ν(predicted)/ν(4-31G) = 0.9 for the vibrational frequencies of the HNC groups (see ref. 2), we can predict a frequency ν_3 = 1 965 cm^{-1} (Table 5). This value can be compared with the i.r. frequencies of 1 845—1 915 cm^{-1} observed for a number of carboimidophosphenes[3–5] and usually believed to be the asymmetric stretching mode of the P=C=N group. The asymmetric stretching frequency of (**4**) [mode (**13**), ν_7 = 1 493 cm^{-1}] is found to be slightly larger than the C=P stretching frequency of 1 146 cm^{-1} in the phosphaethene (**8**).[23] There are as yet no available experimental data for the carbodiphosphene compounds.

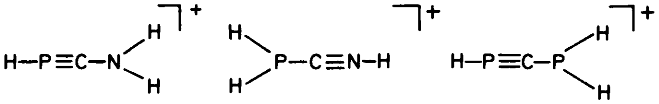
(4) *Proton Affinities.*—(*a*) *Sites of protonation in* (**1**) *and* (**4**). The 4-31G-optimized geometries of the possible minima structures of protonated HP=C=NH [(**15**)—(**20**)] and protonated HP=C=PH [(**23**)—(**26**)] are given in Figures 4 and 5, respectively. The total and relative energies of neutral and protonated species calculated at different levels of theory are recorded in Tables 6 and 7.

Table 5. Vibrational frequencies of HP=C=NH (**1**) and HP=C=PH (**4**) (4-31G)[a]

			Wavenumber (cm^{-1})[b]	Assignment
(1)		ν_1	3 925 (3 532)	NH stretching
		ν_2	2 226	PH stretching
		ν_3	2 183 (1 965)	CN stretching (P=C=N)
		ν_4	1 001	HPC bending
		ν_5	815	HN(+)HP(−) torsion
		ν_6	732	CP stretching (P=C=N)
		ν_7	514	PCN bending
		ν_8	436	HN(+)HP(+) torsion
		ν_9	403 (363)	HNC bending
(4)	A	ν_1	2 184	PH symmetric stretching
		ν_2	972	HPC symmetric bending
		ν_3	712	Symmetric torsion
		ν_4	590	P=C=P symmetric stretching
		ν_5	338	PCP symmetric bending
	B	ν_6	2 186	PH asymmetric stretching
		ν_7	1 493	P=C=P asymmetric stretching
		ν_8	984	HPC asymmetric bending
		ν_9	342	Asymmetric torsion

[a] Details of the calculation of vibrational frequencies making use of the force-constant matrix which are computed by a modified version of the VA05AD subroutines will be published elsewhere. Although the number of molecules so far considered is limited it appears that the difference between frequencies obtained by this procedure and those computed by a more direct numerical or analytical determination of force constants is *ca.* 2%. [b] In parentheses are the reduced values by a scale factor of 0.9. See text.

The C–P bond lengths in the HP=C=NH protonated species become much longer than the corresponding ones in the protonated HP=C=PH. However, the former are still shorter than those found in the protonated phosphaketene (H_2PCO^+, 1.97—2.05 Å).[1] This finding confirms that the C–P distances in the P=C=X molecules are governed by the electronegativity of the X atoms. Note that all linear and planar structures, (**21**) and (**22**) for H_3PCN^+ and (**27**) for H_3PCP^+, are found to be transition structures in the relative energy surfaces.



(**21**) (**22**) (**27**)

As shown in Tables 6 and 7, the protonation occurs preferentially at the P atom in (**1**) and the C atom in (**4**). The *C*-protonation of (**1**) [structures (**17**)—(**20**)] can be excluded because of the large energy difference with respect to the most stable compound, (**15**) (*ca.* 46 kcal mol^{-1} at MP4SDQ/6-31G**). The *N*-protonation (**16**) turned out, however, to be quite competitive with the *P*-one. The energy difference between the two proton affinities is indeed only 5 kcal mol^{-1} (MP4SDQ/6-31G**). This is in line with the fact that there is in carboimidophosphene a considerable charge transfer towards the P atom. Usually, the proton affinities of amines are larger than those of phosphines (*ca.* 15 kcal mol^{-1} between NH_3 and PH_3).[24]

Possessing a C=P distance of 1.899 Å and a perpendicular configuration, the *P*-protonated species (**15**) appears likely to be the complex between PH_2^+ and HNC fragments. Nevertheless,

$$\begin{array}{lll} H_2P\text{–}C{\equiv}N\text{–}H^+ \longrightarrow & PH_2^+\ (\text{singlet}) + & HNC \\ -434.911\,35 & -341.627\,60 & -93.146\,20 \end{array} \qquad (1)$$

(MP4SDQ/6-31G**)

Table 6. Calculated total (a.u.) and relative (in parentheses, kcal mol^{-1}) energies of the neutral and protonated HP=C=NH at different levels

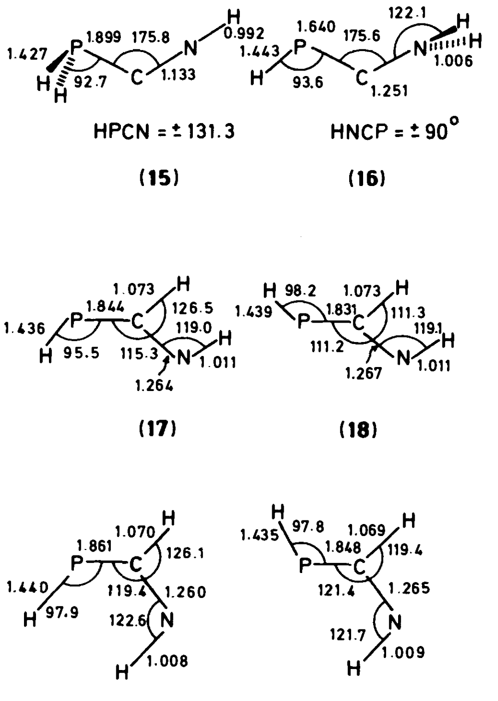
Species[a]	HF/4-31G	HF/6-31G**	MP2/6-31G**	MP3/6-31G**	MP4SDQ/6-31G**
(**1**) (neutral)	−433.587 82 (0.0)	−434.142 61 (0.0)	−434.542 32 (0.0)	−434.557 74 (0.0)	−434.566 14 (0.0)
(**15**) (*P*-protonated)	−433.933 86 (−217.1)	−434.493 81 (−220.3)	−434.881 75 (−212.9)	−434.901 92 (−215.9)	−434.911 35 (−216.6)
(**16**) (*N*-protonated)	−433.922 17 (−209.7)	−434.474 78 (−208.4)	−434.871 17 (−206.3)	−434.895 68 (−212.0)	−434.903 56 (−211.7)
(**17**) (*C*-protonated)	−433.856 89 (−168.8)	−434.415 89 (−171.4)	−434.798 06 (−160.4)	−434.825 48 (−168.0)	−434.833 41 (−167.7)
(**18**) (*C*-protonated)	−433.854 97 (−167.6)	−434.417 39 (−172.4)	−434.799 58 (−161.4)	−434.827 16 (−169.0)	−434.835 04 (−168.7)
(**19**) (*C*-protonated)	−433.840 52 (−158.6)	−434.401 81 (−162.6)	−434.786 52 (−153.2)	−434.813 12 (−160.2)	−434.821 75 (−160.4)
(**20**) (*C*-protonated)	−433.842 29 (−159.7)	−434.404 87 (−164.5)	−434.789 18 (−154.9)	−434.815 85 (−161.9)	−434.824 30 (−162.0)

[a] Energies calculated using the 4-31G geometries given in Figure 3.

Table 7. Calculated total (a.u.) and relative (in parentheses, kcal mol^{-1}) energies of the neutral and protonated HP=C=PH at different levels

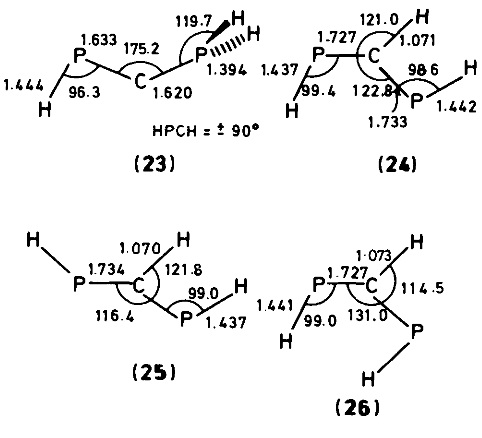
Species[a]	HF/4-31G	HF/6-31G**	MP2/6-31G**	MP3/6-31G**	MP4SDQ/6-31G**
(**4**) (neutral)	−719.500 61 (0.0)	−720.384 76 (0.0)	−720.738 08 (0.0)	−720.763 42 (0.0)	−720.773 05 (0.0)
(**23**) (*P*-protonated)	−719.791 50 (−182.5)	−720.678 74 (−184.4)	−721.025 61 (−180.4)	−721.055 07 (−183.0)	−721.064 52 (−182.9)
(**24**) (*C*-protonated)	−719.830 93 (−207.2)	−720.715 10 (−207.2)	−721.050 39 (−195.9)	−721.083 26 (−200.7)	−721.090 35 (−199.1)
(**25**) (*C*-protonated)	−719.832 27 (−208.6)	−720.716 06 (−207.8)	−721.050 53 (−196.0)	−721.083 61 (−200.9)	−721.090 63 (−199.3)
(**26**) (*C*-protonated)	−719.827 90 (−205.3)	−720.712 14 (−205.4)	−721.048 16 (−194.5)	−721.080 97 (−199.3)	−721.088 12 (−197.7)

[a] Energies calculated using the 4-31G geometries given in Figure 4.



(**15**) (**16**) (**17**) (**18**) (**19**) (**20**)

Figure 4. 4-31G-Optimized geometries of protonated HP=C=NH species. Bond lengths in Å and bond angles in degrees



(**23**) (**24**) (**25**) (**26**)

Figure 5. 4-31G-Optimized geometries of protonated HP=C=PH species. Bond lengths in Å and bond angles in degrees

at MP4SDQ/6-31G** level [equation (1)], (**15**) lies *ca.* 86 kcal mol^{-1} below the dissociation limit. This structure is thus very stable with respect to the fragmentation in comparison with the dissociation energy of 46 kcal mol^{-1} in the *P*-protonated phosphaketene $H_2P–CO^+$ (at the same level).[1]

The energy difference between the *P*- (**23**) and *C*-protonated (**25**) amounts to 15 kcal mol^{-1} (MP4SDQ/6-31G**). This energy is too small to exclude unambiguously *P*-protonation in the carbodiphosphene. The 6-31G**//4-31G proton affinity of 208.3 kcal mol^{-1} at the N atom of (**1**) is somewhat smaller than that of 214 kcal mol^{-1} calculated for the carbodi-imide (**10**) at the same level.[21] On the other hand, the *P*-proton affinity of (**1**) is much larger than that of (**4**) (217 against 183 kcal mol^{-1}, MP4SDQ/6-31G**). Such a result is consistent with the ionization picture (Figure 2). So, replacing P by N in the carbodiphosphene (**4**) stabilizes the lone-pair electrons of the remaining P atom and hence increases its basicity. Conversely, replacing N by P in the carbodi-imide destabilizes the lone pair of the remaining N atom and consequently decreases its basicity.

Combined with a negative contribution of the zero-point energies (ZPE) of *ca.* 7—8 kcal mol^{-1} to the proton affinities, our best values (MP4SDQ/6-31G**) predict the proton affinities of 210 ± 5 kcal mol^{-1} for HP=C=NH (**1**) and 193 ± 5 kcal mol^{-1} for HP=C=PH (**4**).

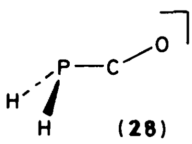
(*b*) *Comparison with protonation in other phospha-allenes.* The protonation of four phospha-allenes, namely, phosphaketene HP=C=O, 1-phospha-allene $H_2C=C=PH$, carboimidophosphene HP=C=NH, and carbodiphosphene HP=C=PH, studied in the present and previous work (see refs. 1 and 2) are best discussed together. The preferred processes can be summarized as follows (the proton affinities PA are given in kcal mol^{-1} and estimated from MP4SDQ/6-31G**//HF/4-31G with ZPE corrections):

HP=C=O: *P*-protonation giving $H_2P–CO^+$ (**28**); PA 184 (ref. 1);

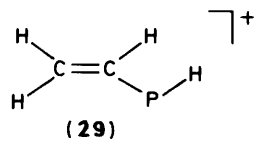
HP=C=NH: *P*-protonation giving the phosphinonitrilium cation $H_2P–CNH^+$ (**15**); PA 210 (see above);

$HP=C=CH_2$: α-*C*-protonation giving the vinylphosphenium cation (**29**); PA 193 (see ref. 2);

HP=C=PH: α-*C*-protonation giving the phosphaimidoylphosphenium cation (**24**); PA 193 (see above).



(**28**)



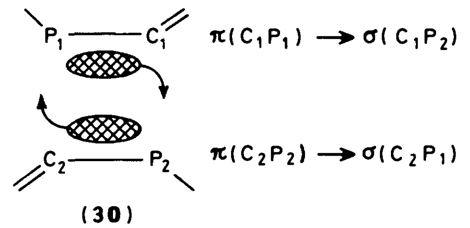
(**29**)

Thus, there are two *P*- and two α-*C*-protonations among the four phosphacumulenes considered. Within each couple, the PAs are very close for the α-*C* site but there is a large difference for the P site. The origin of this variation can be found in the different electronic interaction of the third X atom with the C=P bond. The α-C atom in $H_2C=C=PH$ and the second P atom in HP=C=PH both exhibit no significant inductive effect in the C=P moieties[2] and hence do not compete in attracting the positive charge (both compounds have almost the same proton affinities). Between α-C and P, α-C is preferred because either vinyl $H_2C=CH–$ or phosphaimidoyl HP=CH– can appreciably stabilize the phosphenium cation by conjugation. By contrast, both the N atom in HP=C=NH and the O atom in HP=C=O radically affect the C=P bonds by the inductive effect, giving a dative character to the C=P bonds, thus creating a complex-like structure for neutral cumulenes. The stability of such structures appears to outweigh other factors in the protonation of these molecules. This result suggests different routes for preparing the phosphenium cation, $R–P–R'^+$ or $R–P–H^+$, with phospha-allenes as starting materials.

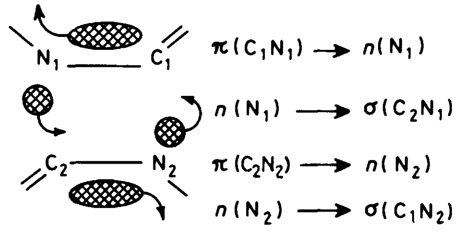
(5) *Chemical Reactivities.*—These data enable us now to interpret tentatively or predict the reactivity of the phospha-allenes (**1**) and (**4**) in chemical reactions. We now consider cycloaddition, addition, and reactions with metals.

(*a*) *Cycloaddition.* Cycloadditions leading to heterocycles are one of the typical reactions of heterocumulenes. The 1:1 self-condensation of carboimidophosphene (I) was found to generate the diphosphetane (**II**) (see above). The preference for reactions at the C=P bond to occur as head-to-tail additions is consistent with the polar character of the bond. The electrophilic centre is situated at the P atom.

By comparison with the carbodi-imide (**10**), the motion of the electron-pairs in cycloaddition should be different, as schematically given by (**30**) and (**31**), respectively.



(**30**)



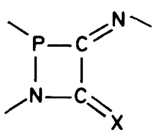
(**31**)

The (2 + 2) cycloaddition is often represented as occurring from a HOMO–LUMO interaction. Because of the large differences in HOMO–LUMO energy separation between the C=P bonds in (**1**), (**4**), and (**8**) and the C=N bonds in (**1**), (**9**), and (**10**) (Figure 2), a stronger stabilizing interaction could be expected when two C=P bonds approach each other. That implies a greater reactivity of phosphacumulenes towards dimerization compared with the nitrogen analogues.

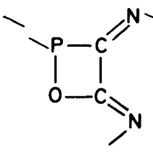
The condensations of carboimidophosphene (**1**) with carbodi-imide (**10**) and isocyanates R–N=C=O (**32**) have also been reported.[3] For these reactions, a regioselectivity problem is involved: in both (**10**) and (**32**), the question arises as to whether a head-to-tail or a head-to-head reaction has occurred; for (**32**), a C=N or a C=O addition may take place.

According to the polarities of the double bonds involved, head-to-head additions of (**1**) to (**10**) and (**32**) yield adducts (**33**) and (**34**), respectively, whereas head-to-tail additions generate (**35**) and (**36**).

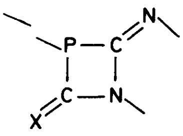
The first adducts isolated of di-t-butylcarboimidophosphine ($Bu^t–P=C=N–Bu^t$) and diphenylcarbodi-imide (Ph–N=C=N–Ph) and phenyl isocyanate (Ph–N=C=O) have both been assigned the head-to-tail structure (**35**).



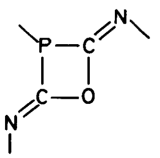
(**33**)



(**34**)



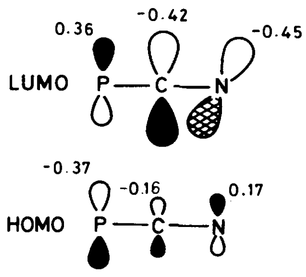
(**35**)



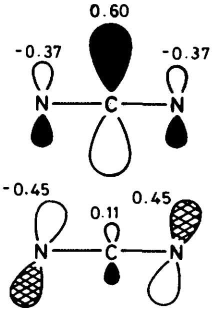
(**36**)

(X = NH or O) (X = NH or O)

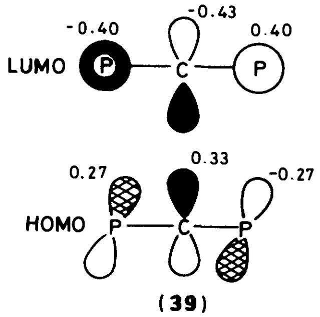
The absence of (**36**) is not surprising since more favourable C=N additions for isocyanates have been generally demonstrated.[25] A few examples of dimerization of phospha-alkenes (**8**) *via* head-to-head addition have also been observed.[22]



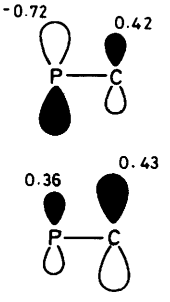
(37)



(38)



(39)



(40)

If these results are confirmed by further investigations, then first, the ylide Wittig-type reactions do not participate in additions of carboimidophosphene and secondly, such additions are not controlled by charge alone.

Within the framework of the frontier orbital theory (2 + 2) addition between carboimidophosphene (**1**) and carbodi-imide (**10**) is shown to be controlled by a HOMO (**1**)–LUMO (**10**) interaction (see Figure 2). It is symmetry-forbidden, and occurs stepwise. The first step is consequently the formation of the bond between two atoms (one of each partner) having the largest MO coefficients.

As seen in (**37**) and (**38**) [HOMO and LUMO coefficients of (**1**) and (**10**) from DZP//4-31G calculations], it is confirmed that bond formation between the P atom of (**1**) and the C atom of (**10**) in the first step leads to the head-to-tail adduct (**35**). As seen in (**39**) and (**40**) the same orbital-based arguments also favour the head-to-head additions of HP=C=PH (**4**) and $H_2C=PH$ (**8**) [with a smaller HOMO–LUMO separation between the LUMO of (**4**) or (**8**) and the HOMO of HN=C=NH (**10**); (for an example see Figure 2)]. However, such correlations must be considered tentative when H is replaced by bulkier substituents, since both π-withdrawing and π-donating substituents appreciably alter the π-formation orbitals and hence could modify the stereoselectivity.[26]

(*b*) *Addition.* Without catalysis, reaction of Bu^t–P=C=N–Bu^t with butylamine is relatively slow, giving an adduct across the C=P bond with the structure Bu^tPH–C(NHBu)=N–Bu^t.[3] Accordingly, the nucleophile part of HX adds to the C atom; this is followed by a proton transfer to the P atom. A reversed reactivity of phospha-alkene (**8**) towards proton-acidic reagents has been established.[22] This difference in direction of addition can be interpreted by both charge and orbital considerations.

For phospha-alkene (**8**), it is quite clear that the strongly positive charge (Table 3) and the large LUMO-coefficient [see (**40**)] of the P atom both attract exclusive fixation of anionic X^- to phosphorous.

By contrast, for unsymmetrical cumulenes (**1**), the shift of the electronic density to the *P* atom, as demonstrated by charge distribution and electric-field gradient calculations, gives it a certain nucleophilic character, enabling it to capture the proton. Furthermore, the largest HOMO coefficient on P and a rather large LUMO coefficient on C [see (**37**)] favour protonation of the P atom and a nucleophilic attack on the C atom, respectively.

For the symmetrical cumulenes (**4**), the situation seems to be similar to that of the phospha-alkene (**8**) rather than to the unsymmetrical cumulene (**1**).

(*c*) *Reaction with metals.* This remains the potentially most promising type of reaction for P-containing cumulenes. Carboimidophosphene (**1**) could be predicted preferentially to form π-complexes with metals, while the behaviour of carbodiphosphene (**4**) is more confusing (see above). Figure 2 shows that both (**4**) and (**10**) have quasi-degenerate *n* and π-HOMOs. Carbodi-imide (**10**) is known to be ambivalent towards metals: it forms π-type complexes at the C atom with electron-rich metals (electrophilic centre), and σ-type complexes with one or both N atoms (nucleophilic centre) acting as ligands.[25–27] However, because the P atoms of (**4**) are electrophilic centres, any similarity between (**4**) and (**10**) cannot be established. It might be expected that carbodiphosphene (**4**) would have some difficulty in forming σ-complexes.

It is also important to note that phospha-alkene (**8**) is able to co-ordinate with carbonyl metal compounds by replacing carbon monoxide.[22] The experimental structures of the products have not, however, yet been elucidated. From Figure 2, π-complex formation at the C=P regions seems to be plausible. Results on metal complexes of phospha-alkynes R–C≡P[28] support this suggestion. These interact with metals like alkynes (forming π-complexes) rather than nitriles (forming σ-complexes).

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