Unsubstituted 1- and 2-Phosphabutadienes: Preparation and Spectroscopic Characterization

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The present work is devoted to the preparation of unsubstituted 1- and 2-phosphabutadienes. 2-Phosphadiene **3a** is formed by HCl-elimination of the (chloromethyl)vinylphosphine **8** and 1-phosphadienes **1** by 1,4-dehydrochlorination of the corresponding (chloroallyl)phosphine **13a** (**1a**) and by FVT of diallylphosphines **15a,b** via a retro-ene reaction (**1a,b**). All the dehydrohalogenations occurred either in solution at low temperature with a Lewis base or in the gas phase (VGSR). Whichever the method used, only the opened structures **1a,b** and **3a** have been observed both in solution as well as in the gas-phase. 2-Phosphabutadiene **3a** has been unambiguously characterized in solution by ^{1}H and ^{31}P NMR. Adducts of **1a** and **3a** were isolated when 2-propanethiol was introduced either with the Lewis base and chlorophosphine precursors **8** and **13a** or with the condensed products from the VGSR and FVT apparatus (vacuum gas-phase dehydrochlorination of **8** and **13a** and thermolysis of the diallylphosphine **15a**). Other structural evidence for **1a,b** and **3a** has been given by coupling the VGSR or FVT apparatus with the IR, MS, and PE spectrometers. In particular, the PE spectra of the opened chains **1a** and **3a** have been qualitatively estimated (Koopman's approximation and direct calculation (CIPSI)). These results are consistent with the experimental IP values [9.28 eV ($\pi_{CP} - \pi_{CC}$), 9.96 eV (n_P), 11.14 eV ($\pi_{CP} + \pi_{CC}$) for **3a**, 9.00 eV ($\pi_{CP} - \pi_{CC}$), 10.13 eV (n_P), 11.47 eV ($\pi_{CP} + \pi_{CC}$) for **1a**]. The possibility of ring closure of **1a** and **3a** to dihydrophosphetes **2a** and **4a** is discussed.

Introduction

Recent interest in 1-monophosphadienes has been stimulated by their ability to isomerize to dihydrophosphetes[1] or under certain conditions to be formed by ring opening of these heterocycles.[2,3] X-ray crystal structure of a η^4-1-phosphadiene–tungsten complex has been reported.[4] The reversibility of the heterocyclization has been attributed more to the variation in substituents than to effects of metal coordination on phosphorus.[5] To our knowledge, only a few 1-phosphadienes have been isolated in stable conditions.[2,6] The *1H*-phosphole/*2H*-phosphole equilibrium was used as a model to study the reactivity of the 1-phosphadiene structure.[1] The reactivity of phosphabutadienes in cycloaddition and electrocyclic reactions and their similarity to their butadiene counterparts has been recently reviewed by Mathey.[1] Recent theoretical studies[7,8] predict that the ring closure of the 1-phosphabutadiene **1a** and 2-phosphabutadiene **3a** parent compounds to their corresponding dihydrophosphete counterparts **2a** and **4a** are nearly thermoneutral[8] and that activation barriers for these transformations are less than 130 kJ·mol^{-1}. We present in the first part of this work the synthesis and characterization of the highly unstable parent compounds **1a** and **3a** and of the corresponding *P*-methyl derivative **1b**. A more extensive discussion on the PE spectra, supported by an ab initio calculation of the ionization potentials (IP), will be then developed. The possibility of the ring closure of **1a** and **3a** to their corresponding dihydrophosphetes **2a** and **4a** is discussed.

Synthesis and Characterization of 1- and 2-Phosphabutadienes 1a and 3a

Preparation of the Chlorophosphines 8 and 13. We have already shown that β-dehydrochlorination of primary α-chloroalkylphosphines led to transient P-unsubstituted phosphaalkenes.[9,10] This reaction, which has been recently extended to the synthesis of phosphaalkenes bearing various substituents at phosphorus and carbon atoms appears to be quite general.[11] We have prepared in this work the 2-phosphabutadiene **3a** by β-dehydrochlorination of the (α-chlorovinyl)phosphine **8**. Since the (α-chlorovinyl)-

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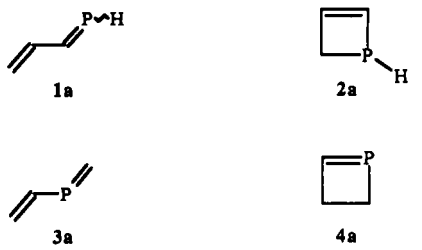
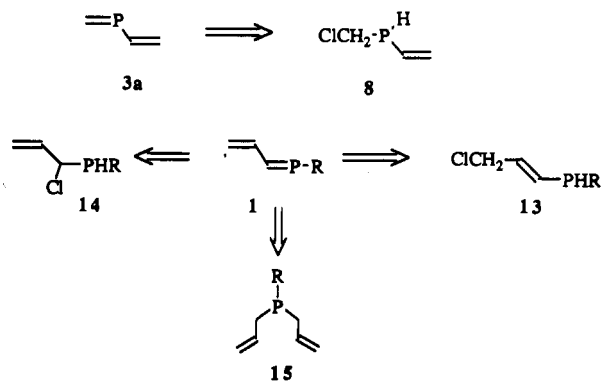
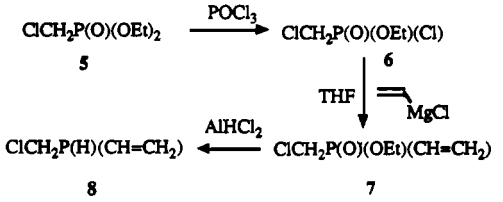
Chart I



Scheme I



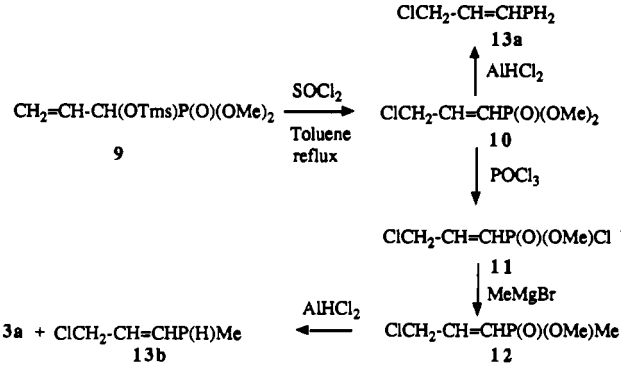
Scheme II



phosphine isomers **14** are not easily available, we succeeded in the synthesis of 1-phosphabutadienes **1a,b** by two different routes: 1,4-HCl elimination of (chloropropenyl)phosphines **13** and gas-phase thermolysis (retro-ene reaction) of diallylphosphines **15a,b** (R = H, Me) (Scheme I). The sequence consisting of selective P-chlorination of (chloromethyl)phosphonate **5** using $POCl_3$[12] followed by addition of the vinylic Grignard reagent[13] afforded (chloromethyl)vinylphosphinate **7** in 56% overall yield. The reduction of vinylphosphonic and phosphinic esters with $AlHCl_2$ has been recently described to be an efficient method for the preparation of vinylphosphines.[14] Following the same procedure, the reduction of chlorovinylphosphinate **7** appeared to be critical. After various experiments, we found that the cleavage of the P–vinyl bond and oligomerization of the required chlorophosphine **8** can be minimized by evacuation of the product under vacuum (10^{-2} hPa) as soon as it was formed from a tetraglyme solution cooled to −10 °C. Phosphine **8** is then purified by trap to trap distillation. The yield ranges between 65 and 75% (Scheme II).

The (chloromethyl)phosphine isomer **13a** was prepared by a sequence involving chlorination of silylether **9**[15] with $SOCl_2$ followed by reduction of vinylphosphonic ester **10** with $AlHCl_2$ (Scheme III). In spite of various experiments, vinylphosphine **13b** was only obtained as a minor product (<20%) by reduction

Scheme III



of the corresponding vinylphosphinate **12**. Since separation from the main product **13a**, which was formed by cleavage of the P–methyl bond, was unsuccessful, the formation of 1-phosphadiene **1b** by HCl-elimination of **13b** appeared to be tedious.

To circumvent this difficulty, we searched for another approach. The flash vacuum thermolysis (FVT) of a heterodiallyl system through a retroene reaction is known to be an efficient route for the preparation of reactive heterodienes such as 1-azabutadiene[16] and 1-silabutadiene.[17] This reaction has been recently extended to the preparation of *tert*-butylphosphadiene.[18] We found that FVT (1023 K) of diallylphosphine **15a**[20] is an alternative route for the preparation of **1a** and FVT of **15b** is the best method for the preparation of **1b** (Scheme V).

Methods Used To Characterize Transient Phosphadienes 1a and 3a. The transient phosphadienes **1a** and **3a** are formed by HCl-elimination of chlorophosphine precursors **8** and **13a** respectively; dehydrochlorination occurs either in solution with a Lewis base or in the gas-phase in a vacuum gas solid reaction (VGSR) (Scheme IV).[19] As an alternative, the phosphadiene **1a** is also produced by heating diallylphosphine **15a**[20] under FVT conditions. Compounds **1a** and **3a** are characterized by IR spectroscopy, mass spectrometry, and chemical trapping. 2-Phosphabutadiene **3a** is also analyzed by ^1H and ^{31}P NMR spectroscopy.

Formation of 1-Phosphabutadiene 1a and 2-Phosphabutadiene 3a in Solution. In order to detect the transient phosphadienes **1a** and **3a** by ^{31}P NMR, dehydrochlorination of phosphines **13a** and **8** was carried out into the NMR probe by slowly warming up the cooled solution in the presence of a Lewis base while acquiring the ^{31}P FT-NMR; such experiments have proven to be fruitful for the NMR observation of various unstabilized phosphaalkenes.[9,11] Dehydrochlorination of the chlorophosphine **8** with triethylamine is observed at 263 K: we observe only one peak at low field (δ_P = 268 ppm), which increases slowly, while the signal of the phosphine precursor **8** (δ_P = −46.2 ppm) grows gradually smaller. The chemical shift of the five hydrogens and the corresponding coupling constants have been observed by ^1H NMR. It may be mentioned that, as for the parent compound CH_2=PH,[9] the magnitude of the $^2J_{PH}$ coupling constants of the two protons Ha and Hb are identical ($^2J_{PHa} \approx {}^2J_{PHb} \approx 29$ Hz), within precision

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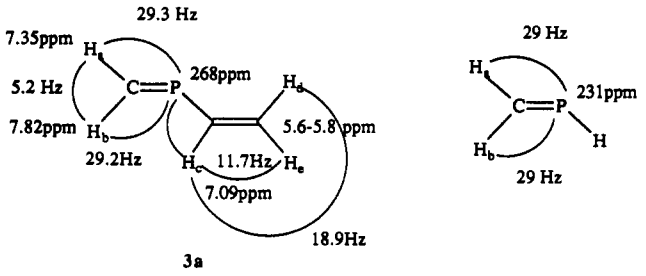
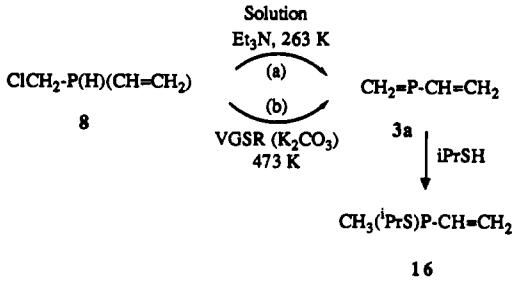
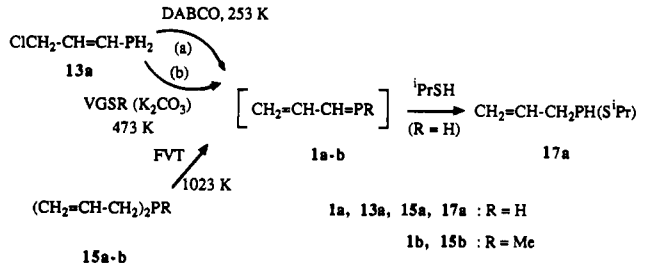
Chart II



Scheme IV



Scheme V



of the measurements. All the NMR data are in good agreement with the 2-phosphadiene structure **3a**.

Surprisingly compound **3a** was found to be more stable than the other simple phosphaalkenes, the decomposition occurring only at *ca.* 263 K. Conclusive proof for the formation of **3a** was obtained by chemical trapping: after addition of an excess of 2-propanethiol at 263 K followed by warming up the solution to room temperature, we observed the formation of adduct **16** characterized after purification via trap to trap distillation by ^{31}P, ^{1}H, and ^{13}C NMR spectroscopy and mass spectrometry (Scheme IV, method a).

On the contrary, all attempts to characterize the phosphadiene **1a** by ^{31}P NMR were unsuccessful: dehydrochlorination of phosphine **13a** occurred at low temperature (253 K) in the presence of DABCO, but the expected low field signal corresponding to the phosphorus of phosphabutadiene **1a** was never observed. The only evidence for the formation of the open chain structure by this approach was given by chemical trapping with iPrSH and formation of the corresponding adduct **17a** (Scheme V, method a).

From these experiments, transient 1-phosphabutadiene **1a** appears to be very unstable, probably even more than the parent compound CH_2=PH. On the other hand, 2-phosphabutadiene **3a** is relatively stable. This higher stability of the 2-phosphabutadiene derivatives with respect to 1-phosphabutadienes has already been mentioned in the literature.[21]

Formation of 1-Phosphabutadienes 1a,b and 2-Phosphabutadiene 3a in the Gas Phase. Using the VGSR technique,[19] dehydrochlorination of chlorophosphines **8** and **13a** occurred under vacuum on K_2CO_3; this solid base covered half the area of a fixed-bed flow reactor heated to 473 K. The FVT apparatus was also used to produce 1-phosphabutadienes **1a,b** by a retro-ene reaction starting from diallylphosphines **15a,b**. In both techniques, the gaseous flow was condensed onto a KBr window cooled at 77 K for IR spectroscopy. The VGSR and FVT apparatus were also fitted to a spectrometer (MS or PES) for direct analysis of the gaseous flow.[10,22]

The 2-phosphadiene **3a** produced by VGSR of **8** has been characterized by low temperature IR spectroscopy (77 K) and chemical trapping (Scheme IV, method b). In the IR spectrum, $\nu_{C=C}$ was observed at 1578 cm^{-1}; the band at 978 cm^{-1} was tentatively assigned to the $\nu_{C=P}$ stretching.[23] These two bands broaden upon warming up the KBr window. The mass spectrum confirms the loss of HCl and the presence of molecular ion m/z 72 (calculated, 72.0129; found, 72.0131) corresponding to $[C_3H_5P]^{+}$. The corresponding adduct **16** was isolated when 2-propanethiol was introduced as a cosolvent and condensed with transient **3a** on the cold trap. However, all attempts to characterize this species by NMR after condensation on a cold trap were unsuccessful. That seems to be a surprising result since we have mentioned above that the characterization by NMR was possible when this species was slowly formed by HCl-elimination of **8** in a dilute solution. The polymerization of **3a** on the condensed phase at a temperature lower than the melting point of the solvent (≈173 K) can explain this result.

As expected, 1-phosphabutadiene **1a**, which was prepared by dehydrochlorination of **13a** (VGSR) or by thermolysis of **15a** (FVT), was too unstable to be characterized by low temperature NMR (173 K). However identical IR and mass spectra were obtained from these two approaches. The IR spectrum (77 K) supplied strong arguments in favor of the 1-phosphabutadiene structure **1a**: the intensity of the two bands at 1610 and 968 cm^{-1}, which were assigned respectively to the $\nu_{C=C}$ and $\nu_{C=P}$ stretch, decreases slowly at 77 K (half-life *ca.* 30 min). The mass spectrum confirmed the presence of the molecular ion m/z 72 corresponding to the C_3H_5P structure. Elsewhere, traces of the adduct **17a** were observed when 2-propanethiol was introduced as a cosolvent and condensed with transient **1a** on the cold trap. The 1-phosphabutadiene **1b** synthesized by FVT of **15b** has been also characterized by IR and MS spectrometry.

Discussion of the Results. Analysis of the gaseous flow by low temperature IR spectroscopy (77 K) is in favor of the opened structures **1a** and **3a** (vide supra). The structure of **3a** was confirmed by NMR spectroscopy when the HCl-elimination of **8** occurs in dilute solution. 1-Phosphadiene **1a** is too unstable to be characterized by NMR whatever the procedure used for the synthesis (in solution or the gas-phase). However, the presence of transient species **1a** and **3a** was unambiguously confirmed by chemical trapping which was performed by addition of 2-propanethiol in solution or on the cold trap.

In all the experiments, the presence of the dihydrophosphete isomers **2a** and **4a** cannot be excluded, but all attempts to detect them by NMR or chemical trapping failed. It should be remembered that, owing to the activation barrier, (*ca.* 140–160 $kJ \cdot mol^{-1}$ for both **1a** and **3a**) calculated by Bachrach and Liu[7,8] and calculated independently in this work (see below), the primary products of the reaction, namely phosphabutadienes **1a** and **3a**, are probably the only ones to be expected when the HCl-elimination of the chlorophosphine precursors **13a** or **8** occurred in solution at low temperature with a Lewis base. The very low temperature oligomerization of phosphadienes **1a** or **3a** was the only observed process. On the other hand, when the formation of the products is performed at higher temperature in the gas-

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phase (VGSR or FVT), the 4π-electrocyclization can be promoted. The molecular ion corresponding to $[C_3H_5P]^{\cdot+}$ was observed by real time analysis of the gaseous flow by HRMS, but the CAD-MIKE experiments did not permit to precise the structure of each isomer. The last part of this paper will be devoted to PE spectroscopy, which has proved to be a powerful method for structural determination of reactive species in the gas-phase.[24]

Theoretical Studies and Photoelectron Spectroscopy

Theoretical Results. The calculations were performed using the Monstergauss[25-27] program with a modified 4-31G basis set in which one set of d polarization functions was added on phosphorus ($\xi_P^d = 0.57$).[28] This basis set allows us to compare our results with those obtained for other molecular systems containing P=C and P—C bonds. This theoretical study has been independently developed of that one recently published by Bachrach and Liu[7,8] (6-31G* + MP_2). Since our results concerning the ground-state properties are close to their results, we report here only the essential conclusions. The values for the P=C unit in the acyclic compounds(1.66 Å for the P=C length of **1a** and 1.64 Å for the P=C length of **3a**)[29] are close to the P=C length previously obtained for $HP{=}CH_2$:1.64Å.[30] For **1a**, we observe a slightly lengthened C=C double bond (1.34 Å) and a slightly shortened C—C central bond (1.45 Å). In contrast, the C=C bond of **3a** has a true double bond character (1.32 Å) whereas the PC central bond corresponds to a true single bond (1.83 Å). The calculated structural data for **1a** and **3a** are in good agreement with the experimentally measured data for metal carbonyl complexes of 1-phosphabutadiene by Boyd et al.[2] and 2-phosphabutadiene by Marinetti et al.[1b]

The 1,2-dihydrophosphete ring **2a** and 3,4-dihydrophosphete **4a** are nearly planar. For **2a**, the data are in good agreement with the reported X-ray structure of a η_1-tungsten complex of a substituted 1,2-dihydrophosphete:[3] localized C=C double bond (calculated, 1.328 Å; experimental, = 1.331 Å), weak P—C single bond (calculated, 1.904 Å, experimental = 1.902 Å), identical strain at phosphorus (CPC calculated, 73.2°, CPC experimental, 74°). The 3,4-dihydrophosphete **4a** is slightly less strained at phosphorus than isomeric **2a** but the P–C and C–C bonds are rather long (1.892 and 1.560 Å, respectively) and are probably weak.

The phosphadienic compounds **1a** and **3a** are nearly isoenergetic with their four membered ring isomers **2a** and **4a** ($\Delta E_{1-2} = -18.9$ kJ·mol^{-1}, $\Delta E_{3-4} = -14.6$ kJ·mol^{-1}, the cyclic compound being the least stable in both cases). The barrier heights to isomerization into dihydrophosphetes **3a** or **4a** are, at CI level, respectively, 139.2 and 157.7 kJ·mol^{-1}. This means that isomer **1a** and **3a** should be observable at low temperature and the conversions 1 → 2 and 3 → 4 could be promoted by thermal energy.

We report in addition our results concerning the Mulliken populations which have not been previously reported. They show

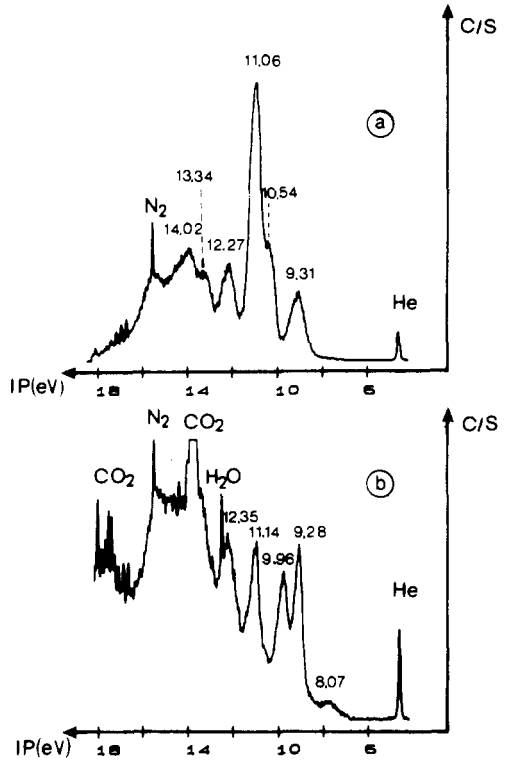

Figure 1. Photoelectron spectra: (a) chlorophosphine **8**; (b) VGSR products of **8**.

an overall polarity P^+—C^- for **1a** ($Q_P = +0.11$, $Q_C = -0.34$) and **3a** ($Q_P = +0.28$, $Q_C = -0.51$) as for the P=C unit of $HP{=}CH_2$ ($Q_P = +0.23$, $Q_C = -0.60$); on the other hand, the π electron distribution is always characterized by a quasi-symmetry. It should be pointed out a much stronger polarity for the 2-phosphabutadiene **3a** than for the isomeric phosphadiene **1a**. Since the phosphorus atom of **3a** is more positive and the P=C bond more polarized, a reactivity different from that of the isomeric **1a** should be observed.

Experimental Results. The VGSR dehydrochlorination of phosphines **8** and **13a,b**, as well as the FVT of diallylphosphines **15a,b**, is followed by real-time PE spectroscopy analysis. By slowly vaporizing the chlorophosphine **8** over K_2CO_3 at 448 K a spectrum, different from that of the starting material (Figure 1a), is obtained. Three bands are observed at 9.28, 9.96, and 11.14 eV (Figure 1b). A fourth band, partially hidden by water ionization at 12.62 eV, is deduced to lie at 12.35 eV. High-intensity signals, attributed to CO_2, are detected at 13.78, 17.59, and 18.05 eV. A low-intensity signal at 8.07 eV is probably related to unknown decomposition products.

On the other hand, dehydrohalogenation of **13a** never gave reproducible spectra. This result may be accounted for by the high instability of **1a** (vide supra) and by the too long distance between the VGSR reactor outlet and the ionization head of the PE spectrometer (60 cm). However FVT of diallylphosphines **15a,b** (Scheme V) (performed inside the ionization chamber of the spectrometer, with a few centimeters distance between the oven outlet and the ionization head) yielded the reliable thermolysis spectra depicted in Figures 2b and 3b, respectively. The diallylphosphines **15a,b** (Figures 2a–3a) are totally cleaved at 873 K (Figures 2b–3b). The difference spectra (Figures 2c–3c) are obtained after digital substraction of propene. Three bands are thus observed at 9.0, 10.13, and 11.47 eV in the thermolysis spectrum of the parent diallylphosphine **15a** (Figure 2c). These three bands are shifted to 8.7, 9.64, and 11.17 eV for the thermolysis spectrum of the methylated compound **15b** (Figure 3c).

Discussion of the Results. We first analyzed the results obtained by dehydrochlorination of phosphine **8**. The PE spectrum of the

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(28) (a) Ditchfield, R.; Hehre, W. J.; Pople, J. A. *J. Chem. Phys.* **1971**, *54*, 724–728. (b) Kutzelnigg, A.; Wallmeir, H. *Theor. Chim. Acta* **1979**, *51*, 261–273.
(29) We have examined in each case the $S_{cis}D_{trans}$ and $S_{trans}D_{trans}$: the bond lengths obtained are very similar, so we only report one value.
(30) (a) Gonbeau, D.; Pfister-Guillouzo, G.; Barrans, *J. Can. J. Chem.* **1983**, *61*, 1371–1378. (b) Watts, J. D.; Rittby, M.; Bartlett, R. J. *J. Am. Chem. Soc.* **1989**, *111*, 4155–4160. (c) Bruna, P. J.; Krumbach, V.; Peyerimhoff, S. D. *Can. J. Chem.* **1985**, *63*, 1594–1608.

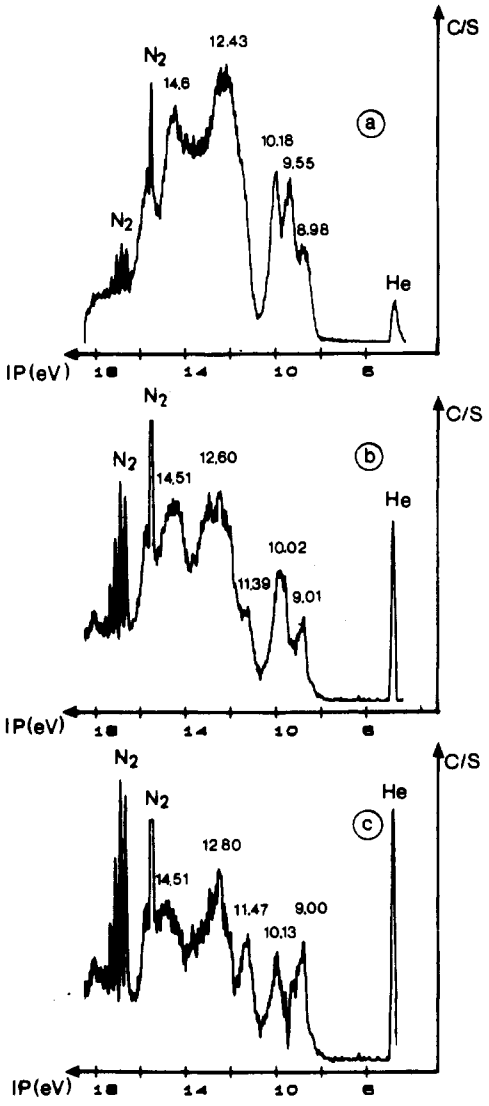


Figure 2. Photoelectron spectra: (a) spectrum of diallylphosphine **15a**; (b) spectrum of products of thermolysis of **15a** at 873 K; (c) difference spectrum with propene.

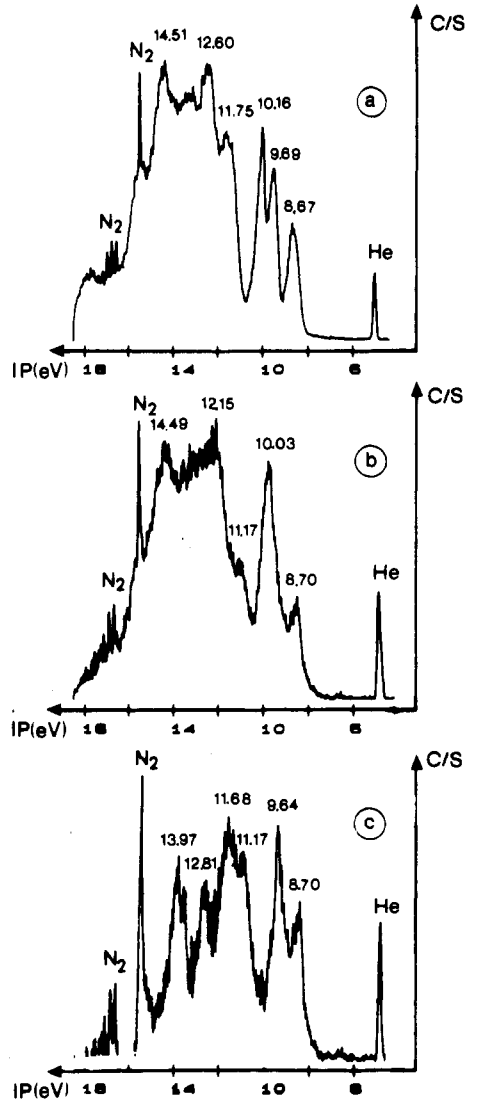


Figure 3. Photoelectron spectra: (a) spectrum of diallylphosphine **15b**; (b) spectrum of products of thermolysis of **15b** at 873 K; (c) difference spectrum with propene.

open-chain product **3a** has been qualitatively estimated. We expect for this compound three bands at low ionization potentials. Two of them will be associated with π symmetry orbitals resulting from the interaction between the π_{CP} (10.30 eV)[10] and the π_{CC} (10.54 eV) orbitals. The former (antisymmetric combination) is estimated to lie around 9 eV and the latter (symmetric combination) around 11 eV. The last band corresponding to the phosphorus lone pair ionization should occur at a lower potential than in methylidenephosphine (10.70 eV)[10] due to the substitution at phosphorus. These estimates are consistent with the experimental IP's observed (Figure 3b) at 9.28 eV ($\pi_{CP} - \pi_{CC}$), 9.96 eV (n_p) and 11.14 eV ($\pi_{CP} + \pi_{CC}$) (Scheme VI). If the cyclic isomer **4a** was obtained, it may be assumed, from the examination of the IP's of the related 2-phosphapropene (Table I)[31] that the energy gap between the first two bands should be much smaller and that the third σ_{PC} ionization should occur at a much higher energy.

These qualitative estimates are supported by the evaluation of the IP's with Koopmans' approximation (IP = $-\epsilon_i$) and by direct calculation (CIPSI). It is known from the previous report on $CH_2{=}PH$[10] that IP's for the π ionic state calculated by CIPSI are found to be within 0.3 eV of the experimental values, while the calculated energy for the phosphorus lone pair ionization is underestimated by about 0.7 eV in this formalism (Table I). Taking these corrections into account for the 2-phosphadiene **3a** and its cyclic isomer **4a**, the experimental IP's are in better agreement with the open-chain structure than with the heterocycle for which, as previously estimated, the first two bands are calculated to lie closer to each other.

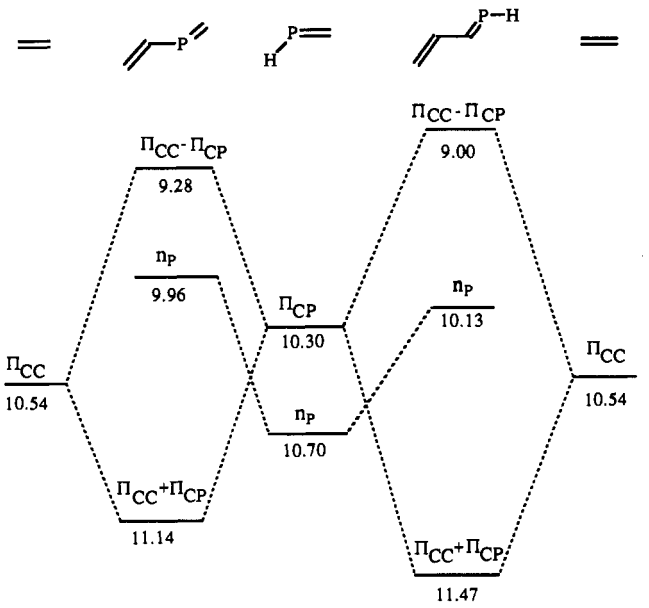
In the case of 1-phosphadiene **1a**, three first bands, with the same assignment as already described for the 2-phosphadiene unit, are expected. Their energetic positions, though different from those observed for **3a**, should not differ markedly. On the other hand, the first three bands of 1,2-dihydrophosphete **2a** should be attributed, as in the related vinylphosphines (Table II), to the ionization of three orbitals strongly localized on the phosphorus lone pair for the first, on the π_{CP} double bond for the second, and on the σ_{PC} bond for the third. From examination of the experimental IP's of either 2-phosphadiene **3a** (9.28, 9.96, and 11.14 eV—Table I) or of the methylated vinylphosphine (9.50, 10.30, and 12.05 eV—Table II), no definite conclusion may be drawn for the structure of the thermolysis product of diallylphosphine **15a** with 9.00, 10.13, and 11.47 eV as experimental IP's.

The evaluation of the IP's of vinylphosphine[32] within CIPSI formalism is better than that for $CH_2{=}PH$.[10] Taking into account the adequate corrections to the CIPSI calculated IP's of either

(31) Bock, H.; Bankmann, M. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 265–266.

(32) Gonbeau, D.; Lacombe, S.; Lasne, M. C.; Ripoll, J. L.; Pfister-Guillouzo, G. *J. Am. Chem. Soc.* **1988**, *110*, 2730–2735.

Scheme VI



the 1,2-dihydrophosphete **2a** or the 1-phosphabutadiene **1a** (Table II) still does not allow us to decide on the structure of the observed product.

Assignment of the structure is finally supported by the examination of the methyl substituent effect at phosphorus on the experimental IP's (parent compound **1a** 9.00, 10.13, 11.47 eV (Figure 2c); P-methylated compound **1b** 8.70, 9.64, 11.17 eV (Figure 3c)). The greatest shift on substitution (≈0.50 eV) is observed for the second band: this argues strongly in favor of the attribution of this band to a phosphorus lone pair ionization. Hence, the observed structure is that of the open chain compound **1a**. Consequently the first and third bands at 9.00 and 11.47 eV for the parent structure are related to the ionizations of the ($\pi_{CP} - \pi_{CC}$) and ($\pi_{CP} + \pi_{CC}$) orbitals. The greater interaction between the π_{CC} and π_{CP} orbitals (2.47 eV) than for the 2-phosphadiene isomer **3a** (1.86 eV) is in agreement with a shorter single C–C than C–P bond (Scheme VI). The greater destabilization of the phosphorus lone pair orbital in 2-phosphadiene **3a** relative to CH_2=PH (0.74 eV) than in 1-phosphadiene **1a** (0.57 eV) is consistent with the substitution at phosphorus.

Conclusion

Transient 1-phosphabutadiene **1a** and 2-phosphabutadiene **3a** are formed by HCl-elimination of the unsaturated chlorophosphine precursors in solution at low temperature by addition of a Lewis base or in the gas-phase under VGSR conditions using K_2CO_3 as solid base. Additionaly, 1-phosphabutadiene **1a** can also be formed by FVT of diallylphosphine (retro-ene reaction). These phosphaalkenes have been unambiguously characterized by chemical trapping, ^1H and ^{31}P NMR (for **3a**), and IR spectroscopy. The high resolution mass spectrometry confirms the presence of the molecular ion $[C_3H_5P]^{\cdot+}$. The IP values obtained by photoelectron spectroscopy are also in favor of the open chain structures. Although the corresponding dihydrophosphete isomers **2a** and **4a**, which can be formed by electrocyclization, have never been detected, their presence in small amounts cannot be excluded. In all the different experimental conditions used in this work, we have no evidence for the existence of an equilibrium between the opened chain structures and the corresponding heterocycles.

Experimental Section

The calculations were performed using the Monstergauss[25-27] program with a modified 4-31G basis set in which one set of d polarization functions was added on phosphorus ($\xi_P^d = 0.57$).[28] This basis set allows us to compare our results with those obtained for other molecular systems containing P=C and P—C bonds.

The effects of electronic correlation on these optimized geometries were estimated by configuration interaction using a variation-perturbation method (CIPSI algorithm).[33] In this formalism a variational zeroth order wave function is built up from an iterative selection of the most important determinants according to a threshold on the coefficients. The perturbative step is a multireference second order Möller-Plesset treatment and includes all single and double excitations from the main determinants.

In light of the size of the systems, we used a method of pseudopotentials[34] (PS HONDO program[35]) for the rigorous calculation of ionization potentials. The pseudo potentials and the double-ζ quality basis set previously determined[36] were adopted including d polarization and s diffuse type functions for phosphorus ($\xi^d = 0.57$,[28] $\xi^s = 0.0348$[37]). The ionization potentials were evaluated by the configuration interaction method previously used (CIPSI algorithm), which includes the effect of electron correlation and reorganization and thus leads to more accurate IP values than Koopmans' values. However it should be noted in the case of π-bonded second row molecules that some discrepancies occur and corrections are necessary in order to compare CIPSI results with experimental values.[10]

All reactions were carried out under an atmosphere of dried nitrogen. Tetraglyme was purified by refluxing over and distillation from sodium/benzophenone under reduced pressure (0.01 hPa). Chlorotrimethylsilane and thionyl chloride were distilled from magnesium, and pyridine was distilled from potassium hydroxide pellets. IR spectra of the phosphadienes were obtained on a Perkin-Elmer Model 157G using a KBr window cooled with liquid nitrogen. ^1H, ^{31}P, ^{13}C NMR spectra were recorded on a Bruker AC 300 P. Chemical shifts are given in ppm relative to internal $SiMe_4$ for ^1H and ^{13}C spectra and external H_3PO_4 for ^{31}P NMR spectra. Chemical shifts upfield from the standard are defined as negative. High resolution mass spectra were recorded on a Varian MAT 311 spectrometer. Photoelectron spectra were recorded on a Helectros 0078 photoelectron spectrometer equipped with a 127° cylindrical analyzer and monitored by a microcomputer supplemented with a digital analog converter. The spectra are calibrated with the known ionizations of xenon (12.13 and 13.43 eV) and argon (15.76 and 15.93 eV). The IP's are accurate within 0.02 eV.

Diethyl (chloromethyl)phosphonate is commercially available. Dimethyl (1-((trimethylsilyl)oxy)prop-2-enyl)phosphonate **9**,[15] chloromethyl phosphonochloridic acid, ethyl ester (**6**),[12] diprop-2-enylphosphine (**15a**),[20a] and methyldiprop-2-enylphosphine (**15b**)[20b] were prepared as previously reported.

Dimethyl (3-Chloroprop-1-enyl)phosphonate (10). In a 500-mL round-bottom flask were placed phosphonate **9**[15] (23.8 g, 0,1 mol) and toluene (300 mL). Thionyl chloride (13.1 g, 0.11 mol) was added at room temperature over 5 min. and the mixture was heated at toluene reflux for 4 h and then allowed to cool to room temperature. The toluene was evaporated under reduced pressure (20 hPa, 60 °C). Distillation in vacuo afforded 14.4 g, (78%) of phosphonate **14** ($bp_{0.1}$: 52 °C). ^1H NMR (300 MHz, $CDCl_3$): 3.51 (d, 6H, $^3J_{PH}$ = 10.9 Hz), 3.99 (ddd, 2H, $^3J_{HH}$ = 5.2 Hz, $^4J_{PH}$ = $^4J_{HH}$ = 1.7 Hz), 5.79 (ddt, 1H, $^2J_{PH}$ = $^3J_{HHtrans}$ = 16.9 Hz, $^4J_{HH}$ = 1.6 Hz), 6.62 (ddt, 1H, $^3J_{HH}$ = 16.9 Hz, $^3J_{PH}$ = 21.3 Hz, $^3J_{HH}$ = 5.2 Hz). ^{31}P NMR (121 MHz, $CDCl_3$): 20.2. ^{13}C NMR (75.5 MHz, $CDCl_3$): 43.7 ($^1J_{CH}$ = 151.5 Hz (q), $^2J_{CP}$ = 26.0 Hz (d)), 52.5 ($^1J_{CH}$ = 148.3 Hz (t), $^3J_{CP}$ = 6.0 Hz (d)), 118.3 ($^1J_{CH}$ = 188.9 Hz (d), $^1J_{CP}$ = 158.7 Hz (d)), 147.1 ($^1J_{CH}$ = 162.9 Hz (d), $^2J_{CP}$ = 6.9 Hz (d)). Anal. Calcd for $C_5H_{10}ClO_3P$: C, 32.52; H, 5.42. Found: C, 32.33; H, 5.60.

(3-Chloro-1-propenyl)phosphonochloridic Acid, Methyl Ester (11). **11** was prepared in 73% yield from phosphonate **10** according to the procedure described for the preparation of **6**[12] ($bp_{0.1}$: 56 °C). ^1H NMR (300 MHz, $CDCl_3$): 3.80 (d, 3H, $^3J_{PH}$ = 13.6 Hz), 4.16 (ddd, 2H, $^3J_{HH}$ = 5.0 Hz, $^4J_{HH}$ = 1.8 Hz, $^4J_{PH}$ = 1.8 Hz), 6.22 (ddt, 1H, $^3J_{HH}$ = 15.4 Hz, $^3J_{HH}$

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(35) Pshondo algorithm: a modified version of the HONDO package (program 338, Quantum Chemistry Program Exchange, University of Indiana, Bloomington, IN)—pseudo potentials adapted by Daudey J. P. .
(36) Laboratoire de Physique Quantique, Toulouse, Ateliers, October 1981.
(37) Frisch, M. J.; Pople, J. A.; Binkley, J. S. *J. Chem. Phys.* **1984**, *80*, 3265–3269 and references cited.
(38) (a) Gonbeau, D.; Lacombe, S.; Lasne, M. C.; Ripoll, J. L.; Pfister-Guillouzo, G. *J. Am. Chem. Soc.* **1988**, *110*, 2730–2735. (b) Unpublished results.

Table I. Calculated (Method of Pseudopotentials—Koopmans, CIPSI) and Observed Ionization Potentials (eV)

		CH_2 = PH				3a				4a	
		calcd				calcd				calcd	
	CH_2 = PMe exptl[31]	Koopmans	CIPSI	epxtl[9]		Koopmans	CIPSI	exptl		Koopmans	CIPSI
π_{CP}	9.69	9.63	10.03	10.30	$\pi_{CP} - \pi_{CC}$	9.08	8.92	9.28	π_{CP}	9.26	9.19
n_P	9.97	10.43	9.91	10.70	n_P	10.44	9.25	9.96	n_P	9.90	8.82
σ_{PC}	12.42	14.02		13.20	$\pi_{CP} + \pi_{CC}$	11.66	10.84	11.14	σ_{PC}	12.82	11.17

Table II. Calculated (Method of Pseudopotentials—Koopmans, CIPSI) and Observed Ionization Potentials (eV)

	Me, PH_2	PH_2		2a			1a		
		calcd[38] (gauche form)		calcd			calcd ($S_{trans}D_{trans}$)		
	extpl[38b]	Koopmans	CIPSI	exptl[38a]	Koopmans	CIPSI		Koopmans	CIPSI	exptl
$n_P - \pi_{CP}$	9.50	9.35	9.10	9.60	9.26	9.07	$\pi_{CP} - \pi_{CC}$	8.65	8.62	9.00
$\pi_{CP} + n_P$	10.30	11.41	10.80	10.85	10.51	10.19	n_P	10.74	9.58	10.13
σ_{PC}	12.05	13.04		12.60	12.38	11.49	$\pi_{CP} + \pi_{CC}$	12.24	11.08	11.47

= 1.8 Hz, $^2J_{PH}$ = 26.0 Hz), 6.90 (ddt, 1H, $^3J_{HH}$ = 15.4 Hz, $^3J_{PH}$ = 16.6 Hz, $^4J_{HH}$ = 1.8 Hz). ^{31}P NMR (121 MHz, $CDCl_3$): 28.8. ^{13}C NMR (75.5 MHz, $CDCl_3$): 43.2 ($^1J_{CH}$ = 150.5 Hz (q), $^3J_{CP}$ = 19.3 Hz (d)), 53.2 ($^1J_{CH}$ = 149.9 Hz (q), $^2J_{CP}$ = 8.0 Hz (d)), 122.7 ($^1J_{CH}$ = 145.0 Hz (d), $^1J_{CP}$ = 178.2 Hz (d)), 147.6 ($^1J_{CH}$ = 163.5 Hz (d), $^2J_{CP}$ = 7.4 Hz (d)). This compound is very hygroscopic. All attempts to characterize it by HRMS were unsuccessful.

General Procedure: Addition of Grignard Reagent to an Alkenylphosphonic Acid Chloride. The method described by Minowa and co-workers[13] was used. To a solution of phosphonochloridate (0.05 mol) dissolved in dry THF (100 mL) and cooled to −70 °C was added dropwise the Grignard reagent (0.05 mol) in dry THF. Stirring was continued for 1 h. The reaction was allowed to warm to room temperature and then quenched with 20 mL of a cooled saturated NH_4Cl solution. The aqueous layer was extracted with CH_2Cl_2, and the combined organic extracts were washed with water (2 × 5 mL) and then dried over $MgSO_4$. After concentration *in vacuo*, a small amount (≈0.05%) of hydroquinone was added to the crude oil to minimize polymerization. Vacuum distillation afforded vinylphosphinate.

(Chloromethyl)ethenylphosphonic Acid, Ethyl Ester (7) ($bp_{0.2}$ = 60 °C, yield 77%). ^{1}H NMR (300 MHz, $CDCl_3$): 1.37 (t, 3H, $^3J_{HH}$ = 7.0 Hz), 3.58 (d, 2H, $^2J_{PH}$ = 7.1 Hz), 4.14 (dq, 2H, $^3J_{HH}$ = $^3J_{PH}$ = 7.1 Hz), 6.23–6.53 (m, 3H). ^{31}P NMR (121 MHz, $CDCl_3$): 33.5. ^{13}C NMR (75.5 MHz, $CDCl_3$): 16.5 ($^1J_{CH}$ = 127.5 Hz (q), $^3J_{CP}$ = 6.0 Hz (d)), 35.6 ($^1J_{CH}$ = 147.2 Hz (t), $^1J_{CP}$ = 105.2 Hz (d)), 61.6 ($^1J_{CH}$ = 147.6 Hz (t), $^2J_{CP}$ = 6.3 Hz (d)), 125.7 ($^1J_{CH}$ = 167.4 Hz (d), $^1J_{CP}$ = 131.7 Hz (d)), 138.3 ($^1J_{CH}$ = 163.5 Hz (t)). IR (cm^{-1}): 2995 and 2940 (s), $\nu_{C=C}$ 1612 (w), 1400 (s), $\nu_{P=O}$ 1205 (s), 1035 (vs). MS, *m/z* (%): 133 (4.1), 123 (6.2), 119 (44.9), 101 (10.0), 93 (5.4), 91 (100), 83 (6.8), 75 (7.2). HRMS: calcd for $C_5H_9ClO_2P$ $[M - H]^{+\cdot}$, 167.0029; found, 167.003.

(3-Chloro-1-propenyl)methylphosphonic Acid, Methyl Ester (12) ($bp_{0.2}$ = 51 °C, yield 72%). ^{1}H NMR (300 MHz, $CDCl_3$): 1.41 (d, 3H, $^2J_{PH}$ = 14.7 Hz); 3.48 (d, 3H, $^3J_{PH}$ = 11.5 Hz), 4.08 (m, 2H), 5.93 (dd, 1H, $^2J_{PH}$ = 23.0 Hz, $^3J_{HHtrans}$ = 15.7 Hz), 6.70 (ddt, 1H, $^2J_{PH}$ = 18.0 Hz, $^3J_{HHtrans}$ = 15.7 Hz, $^3J_{HH}$ = 5.0 Hz). ^{31}P NMR (121 MHz, $CDCl_3$): 43.5. ^{13}C NMR (75.5 MHz, $CDCl_3$): 14.4 ($^1J_{CH}$ = 128.3 Hz (q), $^1J_{CP}$ = 103.9 Hz (d)), 44.0 ($^1J_{CH}$ = 151.5 Hz (t), $^3J_{CP}$ = 20.9 Hz (d)), 51.3 ($^1J_{CH}$ = 147.6 Hz (q), $^2J_{CP}$ = 6.6 Hz (d)), 122.8 ($^1J_{CH}$ = 156.8 Hz (d), $^1J_{CP}$ = 124.7 Hz (d)), 147.0 ($^1J_{CH}$ = 162.2 Hz (d), $^2J_{CP}$ = 5.5 Hz (d)). HRMS: calcd for $C_5H_9ClO_2P$, 168.0107; found, 168.009.

General Procedure for the Synthesis of the Phosphines 8 and 13a. The apparatus already described for the reduction of α-chlorophosphonates was used.[14] Tetraglyme was purified by refluxing it over and distilling it from sodium/benzophenone under reduced pressure (10^{-2} mbar). The solution of $AlHCl_2$ was prepared according to the procedure recently reported.[14a] The flask containing the reducing mixture (10^{-2} mol of $AlHCl_2$ in 20 mL of tetraglyme) was fitted on the vacuum line and degassed. Then, the unsaturated phosphinate (10^{-2} mol in 5 mL of tetraglyme) was slowly added (10 min) at room temperature with a flexible needle through the septum. During and after the addition, phosphine **8** or **13a** and the carried away tetraglyme were condensed into a liquid nitrogen trap. After the reaction was completed (1 h), the cold trap was allowed to warm to room temperature and the volatile species were condensed with a cosolvent onto the cold finger (77 K). After disconnection from the vacuum line by stopcocks, the apparatus was filled with dry nitrogen; liquid nitrogen was subsequently removed. The product was collected in a Schlenk flask and characterized by spectroscopy.

(Chloromethyl)ethenylphosphine (8) (yield 72%). ^{1}H NMR (300 MHz, $CDCl_3$): 3.55 (m, 1H), 3.69 (m, 2H), 5.87 (ddd, 1H, $^3J_{PHcis}$ = 20.5 Hz, $^2J_{HH}$ = 1.9 Hz, $^3J_{HH}$ = 14.9 Hz), 5.92 (ddd, 1H, $^3J_{PH}$ = 32.6 Hz, $^2J_{HH}$ = 1.9 Hz, $^3J_{HH}$ = 11.7 Hz), 6.49 (ddd, 1H, $^2J_{PH}$ = 18 Hz, $^3J_{HH}$ = 14.9 Hz, $^3J_{HHcis}$ = 11.7 Hz). ^{31}P NMR (121 MHz, $CDCl_3$): −46.2 ($^1J_{PH}$ = 217.3 Hz). ^{13}C NMR (75.5 MHz, $CDCl_3$): 36.6 ($^1J_{CH}$ = 151.6 Hz (t), $^1J_{CP}$ = 24.6 Hz (d)), 129.2 ($^1J_{CP}$ = 11.8 Hz (d), $^1J_{CH}$ = 156.1 Hz (d)), 132.0 ($^1J_{CH}$ = 158.2 Hz (t), $^2J_{CP}$ = 23.4 Hz (d)). IR (cm^{-1}): ν_{PH} 2280 (s), $\nu_{C=C}$ 1605 (w), ν_{CCl} 655 (s). MS, *m/z* (%): 110 (10.8), 108 (30.8), 82 (68.7), 59 (42.6), 57 (84.5), 41 (100). HRMS: calcd for $C_3H_6{}^{35}ClP$, 107.9896; found, 107.990.

3-Chloro-1-propenylphosphine (13a) (yield 57%). ^{1}H NMR (300 MHz, $CDCl_3$): 3.47 (d, 2H, $^1J_{PH}$ = 203 Hz), 4.05 (m, 2H, $^3J_{HH}$ = 2.8 Hz, $^4J_{HH}$ = 2.8 Hz, $^4J_{PH}$ = 2.0 Hz), 6.19–6.26 (m, 2H). ^{31}P NMR (121 MHz, $CDCl_3$): −138.3. ^{13}C NMR (75.5 MHz, $CDCl_3$): 45.2 ($^1J_{CH}$ = 151 Hz (t), $^3J_{CP}$ = 9.7 Hz (d)), 121.6 ($^1J_{CH}$ = 164 Hz (d), $^2J_{CP}$ = 13.1 Hz (d)), 139.9 ($^1J_{CH}$ = 160 Hz (d), $^1J_{CP}$ = 20.8 Hz (d)). IR (film, 77K) (cm^{-1}): 3020 (w) 2960 (w), 2930 (w), 2890 (w), ν_{PH} 2300 (s), $\nu_{C=C}$ 1640 (m), 1430 (s), 1300 (s), 1270 (s), 1240 (s), 1200 (s), 1140 (s), 1105 (s), 1070 (s), 970 (s), 840 (s), 780 (s), 760 (s), 660 (s). MS, *m/z* (%): 108 (1.7), 73 (3.3), 72 (9.1), 71 (5.7), 57 (8.2), 45 (16.2). HRMS: calcd for $C_3H_6{}^{35}ClP$, 107.9895; found, 107.990.

Phosphadienes 1a,b and 3a. Phosphadienes **1a** and **3a** are formed by HCl-elimination of chlorophosphines **13a** and **8** respectively. ^{31}P and ^{1}H NMR spectra of **3a** were recorded when the reaction occurs in a solvent in the presence of a Lewis base. IR (77 K) and mass spectra of **1a** and **3a** were obtained from samples synthesized by dehydrochlorination of **8** and **13a** under VGSR conditions. IR (77 K) and mass spectra of **1a,b** were obtained by using a retro-ene reaction (FVT) starting from **15a,b**. Chemical trapping with 2-propanethiol has been performed by addition of the thiol to the solvent or by condensation on the cold trap (77 K) of the phosphadiene with the thiol as cosolvent.

Procedure Used for Recording ^{31}P or ^{1}H NMR Data for 3a. Into a 5-mm NMR tube sealed with a rubber septum and cooled at −50 °C were introduced with a flexible needle syringe the phosphine **8** (0.3 mmol), the solvent (CD_2Cl_2-CCl_3F (1:3 ratio) (0.5 cm^3)), and the triethylamine (0.3 mmol). The NMR tube was rapidly shaked and then introduced into the previously cooled probe (−50 °C) of a ^{1}H 300-MHz NMR spectrometer. The tube then was slowly warmed up to −10 °C and ^{1}H and ^{31}P NMR spectra of **3a** were recorded.

2-Phosphabuta-1,3-diene (3a). ^{1}H NMR (300 MHz, CD_2Cl_2, CCl_3F, −10 °C): 5.60–5.80 (m, 2H), 7.09 (ddd, 1H, $^2J_{PH}$ = 6.5 Hz, $^3J_{HHtrans}$ = 18.9 Hz; $^3J_{HHcis}$ = 11.7 Hz), 7.35 (dd, 1H, $^2J_{PH}$ = 29.3 Hz, $^2J_{HH}$ = 5.2

Hz), 7.82 (dd, 1H, $^2J_{PH}$ = 29.2 Hz, $^2J_{HH}$ = 5.2 Hz). ^{31}P NMR (121 MHz, CD_2Cl_2, CCl_3F, −10 °C): 268.1 (m, 22 peaks are observed).

Procedure Used for Recording IR and Mass Spectra of 1a and 3a from 13a and 8 (VGSR Conditions).[19] Powdered and dried K_2CO_3 (15 g) was introduced into a VGSR reactor (l = 25 cm; id = 2.5 cm pyrex tube) and then horizontally distributed between two pads of glass wool 20 cm distant from each other. This reactor was fitted onto a vacuum line equipped with a KBr window cooled at 77 K (IR analysis) or onto the ionization chamber of a mass spectrometer.[22a] (Chloroalkenyl)phosphine **13a** or **8** (0.1–1 mmol) was slowly vaporized in vacuo through the reactor heated at 200 °C, and the gaseous flow was condensed on the KBr window (IR) or directly analyzed (MS).

Procedure Used for Recording IR and Mass Spectra of 1a,b by FVT of 15a,b.[22a] A quartz tube (l = 20 cm; id = 2.0 cm) was fitted onto a vacuum line equipped with a KBr window cooled at 77 K (IR analysis) or onto the ionization chamber of the mass spectrometer. Diallylphosphines **15a,b** (0.1–1 mmol) were slowly vaporized *in vacuo* through the reactor heated at 700 °C, and the gaseous flow was condensed on the KBr window (IR) or directly analyzed (MS).

1-Phosphabuta-1,3-diene (1a). IR (film, 77 K, cm^{-1}): ν_{P-H} 2260 (s), $\nu_{C=C}$ 1610 (m), 1410 (m), 1090 (m), ν_{C-P} 968 (m). MS, m/z (%): 72 (21.1), 71 (10.1), 57 (16.8), 45 (12.6), 44 (7.2). HRMS: calcd for C_3H_5P, 72.0129; found, 72.0124 (VGSR), 72.0131 (FVT). MIKE spectrum of m/z 72: 71, 57. CAD-MIKE spectrum of m/z 72: 71, 70, 69, 57, 45.

***P*-Methyl-1-phosphabuta-1,3-diene (1b).** IR (film, 77 K, cm^{-1}): ($\nu_{C=C}$) 1591 (m), 1020 (m), (ν_{C-P}) 968 (m). MS, m/z (%) 86 (16.6), 85 (7.4), 71 (13.0), 59 (14.8). HRMS: calcd for C_4H_7P, 86.0285; found, 86.0290. MIKE spectrum of m/z 86: 85, 84, 71. CAD-MIKE spectrum of m/z 86: 85, 84, 83, 71, 69.

2-Phosphabuta-1,3-diene (3a). IR (film, 77 K, cm^{-1}): $\nu_{C=C}$ 1578 (m), 1390 (m), 1102 (s), ν_{C-P} 978 (s), 942 (s), 910 (s), 795 (s). MS, m/z (%): 72 (100), 71 (24.0), 57 (58.8), 46 (48.1), 45 (57.2), 44 (74.5). HRMS: calcd for C_3H_5P, 72.0129; found, 72.0131. MIKE spectrum of m/z 72: 71, 70. CAD-MIKE spectrum of m/z 72: 71, 70, 57, 15.

Chemical Trapping of Phosphadiene 1a or 3a Formed in Solution (Method a). Into a two-necked 25-mL flask, sealed with rubber septa and cooled at −50 °C, were introduced with a flex-needle syringe the phosphine **8** or **13a** (1 mmol), the solvent (6 cm^3 of THF), 2-propanethiol (10 mmol), and the Lewis base (1.1 mmol of triethylamine for **8** or 1.1 mmol of DABCO for **13a**). The solution is slowly allowed to warm to room temperature under magnetical stirring. The flask was then fitted on a vacuum line and the adduct **16** or **17a** was purified by trap-to-trap distillation (the U-tube was cooled at −60 °C to remove the low boiling derivatives (THF, *i*-PrSH), then allowed to warm to −20 °C; the volatile phosphine **8** or **13a** was condensed on a cold finger (77K)).

Chemical Trapping of Phosphadiene 1a or 3a Synthesized in Gaseous Phase (Method b). The reactor (VGSR or FVT) was fitted onto a cold finger equipped with a 5-mm NMR tube and then evacuated (10^{-2} HPa). The phosphadiene (**1a** or **3a**) ($\approx$ 0.2 mmol) formed in the gaseous phase by dehydrochlorination of the corresponding phosphine (**13a** or **8**) or by FVT of the diallylphosphines **15a,b** was condensed with 2-propanethiol (2 mmol) and C_6D_6 (50 μL) on the finger cooled at 77 K. The solution was then transferred to the 5-mm NMR tube and analyzed by ^{31}P NMR at room temperature.

Methylethenylisopropylthiophosphine (16) (yield: 65% (method A), 37% (method B)). ^{1}H NMR (300 MHz, $CDCl_3$): 1.22 (dd, 6H, $^4J_{PH}$ = 1.8 Hz, $^3J_{HH}$ = 6.7 Hz), 1.25 (d, 3H, $^2J_{PH}$ = 6.7 Hz), 2.93 (dsept, 1H, $^3J_{PH}$ = $^3J_{HH}$ = 6.7 Hz), 5.47 (ddd, 1H, $^3J_{PH}$ = 26 Hz, $^3J_{HH}$ = 11.7 Hz, $^2J_{HH}$ = 1.7 Hz), 5.58 (ddd, 1H, $^3J_{PH}$ = 12 Hz, $^3J_{HH}$ = 18.2 Hz, $^2J_{HH}$ = 1.7 Hz), 6.34 (ddd, 1H, $^2J_{PH}$ = 20.6 Hz, $^3J_{HH}$ = 18.2 Hz, $^3J_{HH}$ = 11.7 Hz). ^{31}P NMR (121 MHz, $CDCl_3$): 3.2. ^{13}C NMR (75.5 MHz, $CDCl_3$): 16.0 ($^1J_{CH}$ = 130.0 Hz (q), $^1J_{CP}$ = 19.3 Hz (d)), 27.1 ($^1J_{CH}$ = 126 Hz (q), $^3J_{CP}$ = 3.0 Hz (d)), 39.1 ($^1J_{CH}$ = 142 Hz (d), $^2J_{CP}$ = 20.6 Hz (d)), 125.4 ($^1J_{CP}$ = 17.2 Hz (d), $^1J_{CH}$ = 157.5 Hz (d)), 142.5 ($^1J_{CH}$ = 150 Hz (t), $^2J_{CP}$ = 25.9 Hz (d)). IR (cm^{-1}): 2965 (vs), 2927 (s), 1610 (w), 1450 (s), 1362 (s), 1250 (m), 1095 (s). MS, m/z (%): 148 (6.3), 107 (4.4), 106 (35.0), 105 (7.2), 91 (4.4), 80 (6.3), 79 (4.7), 78 (10.7), 63 (11.5). HRMS: calcd for $C_6H_{13}PS$, 148.0476; found, 148.047.

(Prop-1-enyl)-2-propylthiophosphine (17a) (yield: 65% (method A), 3% (method B starting from **13a** or **15a**)). ^{1}H NMR (300 MHz, $CDCl_3$): 1.32 (dd, 6H, $^3J_{HH}$ = $^4J_{PH}$ = 6.8 Hz), 2.50 (m, 1H, $^2J_{PH}$ = $^3J_{HH}$ = 7.3 Hz), 2.99 (d sept, 1H, $^3J_{PH}$ = 8.3 Hz, $^3J_{HH}$ = 6.8 Hz), 4.37 (dtd, 1H, $^1J_{PH}$ = 208 Hz, $^3J_{HH}$ = 6.6 Hz, $^4J_{HH}$ = 0.8 Hz), 5.00–5.15 (m, 2H), 5.72–5.90 (m, 2H). ^{31}P NMR (121 MHz, $CDCl_3$): −37.4. ^{13}C NMR (75.5 MHz, $CDCl_3$): 25.1 ($^1J_{CH}$ = 126.9 Hz (q), $^4J_{CP}$ = 7.7 Hz (d)), 30.6 ($^1J_{CH}$ = 132.0 Hz (q), $^1J_{CP}$ = 18.4 Hz (d)), 37.8 ($^1J_{CH}$ = 141.8 Hz (d), $^2J_{CP}$ = 18.7 Hz (d)), 116.5 ($^1J_{CH}$ = 154.3 Hz (d), $^3J_{CP}$ = 7.5 Hz (d)), 134.2 ($^1J_{CH}$ = 159.3 Hz (d), $^2J_{CP}$ = 4.7 Hz (d)). IR (cm^{-1}): 2980 (vs), 2945 (vs), ν_{PH}: 2230 (s), $\nu_{C=C}$ 1637 (s), 1420 (s), 1247 (s), 1153 (s), 1051 (s). MS, m/z (%): 148 (9.3), 107 (7.5), 106 (25.4), 105 (1), 76 (35.1), 73 (8.5), 72 (14), 59 (35.4). HRMS: calcd for $C_6H_{13}PS$, 148.0476; found, 148.048.