Dehydrochlorination of α-Chlorophosphines, a Simple and General Route to Phosphaalkenes

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Primary and secondary α-chlorophosphines **2a**−**g** are prepared in *ca*. 70% yield by chemoselective reduction of the corresponding phosphonic and phosphinic esters with $AlHCl_2$ and are characterized by ^{31}P, ^{13}C, and ^{1}H NMR and by HMRS. They can be kept several weeks in the refrigerator after purification. They lead then to the corresponding phosphaalkenes **3a**−**g** by HCl elimination. For the volatile α-chlorophosphines **2a**−**e** HCl elimination occurs *in the gas phase* on solid potassium carbonate under VGSR conditions (vacuum gas−solid reactions); the corresponding phosphaalkenes **3a**−**e** are characterized by real time HRMS analysis of the gaseous flow (VGSR/HRMS coupling) and by solid-phase IR spectroscopy after condensation of the gaseous flow on a KBr window cooled to 77 K. The decomposition of phosphaalkenes at this temperature is monitored by IR spectroscopy. The α-chlorophosphines **2a**−**g** undergo a HCl elimination *in the liquid phase* in the presence of a Lewis base; the formation of the transient phosphaalkenes is monitored by ^{31}P FT-NMR. The temperature of HCl elimination is dependent both upon the P−H acidity of the phosphine precursors and the nature of the base. The ^{31}P NMR data of the simple phosphaalkenes **3a**−**g** are for the first time reported. They are consistent with the proposed structure. The stereochemistry of the (*Z*)- and (*E*)-isomers is established according to the "*cis*-rule". Phosphaalkenes **3a**−**g** are also characterized by chemical trapping in solution with various dienes, dipoles, or thiols. All of these experiments confirm the transient character of these species. The synthetic potential of this route is evaluated.

Introduction

Considerable efforts have been devoted during the past decade to the development of the P−C multiple bond derivatives.[1,2] Numerous compounds stabilized by bulky substituents have been isolated and characterized. Their reactivity was also studied. It was thus shown that phosphaalkenes react under mild conditions with various dienes or dipoles yielding to the corresponding [4 + 2] and [3 + 2] cycloadducts and with nucleophiles giving the corresponding adducts at the phosphorus atom. The non-sterically hindered structures are generally considered as transient species and consequently have been much less studied. Some of them have been generated in the gas phase using flash vacuum thermolysis (FVT) or vacuum gas−solid reaction (VGSR) techniques and characterized in real time by microwave and photoelectron spectroscopy or by mass spectrometry.[2] A possible application of these derivatives in organophosphorus chemistry mainly depends upon the development of efficient synthetic methods which would notably allow the introduction of any kind of substituent both at the carbon and the phosphorus centers. This problem has been solved in the case of simple phosphaalkynes for which efficient synthetic approaches have been recently described. They involve either elimination of hexamethyldisiloxane from the stable P-silylated phosphaalkene precursors,[3] the bis(dehydrochlorination) of α-dichlorophosphines,[4] or the base-induced rearrangement of primary ethynylphosphines.[5] While most of the phosphaalkynes are fairly stable in solution at room temperature,[3−5] simple phosphaalkenes are highly unstable and undergo self-condensation reactions even at low temperature.[6] This high reactivity probably accounts from the fact that only a few IR and NMR data have been reported to date and that synthetic applications of such compounds remains challenging. The formation of the C-nonsubstituted derivatives $H_2C{=}P{-}CH_3$ and $H_2C{=}P{-}Ph$

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have been reported. It involves a retro-Diels−Alder reaction from their corresponding 2-phosphabicyclo[2.2.2]octa-5,7-diene precursors in toluene at 40−50 °C followed by chemical trapping of the intermediates by [4 + 2] cycloadditions in the presence of dienes.[8] However, the synthesis of the corresponding precursors is convoluted and thus limits the synthetic applicability of this approach. We have recently prepared these two compounds by another approach which involves the base-induced rearrangement of secondary vinylphosphines, readily obtained by a chemoselective reduction of the corresponding phosphinates.[9a] The corresponding [4 + 2] cycloadducts have been isolated in high yield when the rearrangement was carried out in the presence of dienes.[9b] However, under these conditions, the phosphaalkene intermediate could not be detected by low-temperature ^{31}P NMR.

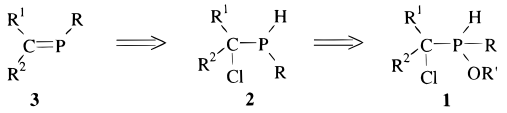
The dehydrohalogenation of *P*-halophosphines was one of the first methods used to prepare the P−C multiple bond derivatives.[10] Such a reaction occurs under mild conditions only with compounds that display an activated C−H bond in position α to the phosphorus.[11] However, when the leaving group is bonded to the carbon atom, the HX elimination (X = Cl, F) is favored. We[4a,6,12,14] and others[7a,13] have used this approach to prepare different phosphaalkenes and phosphaalkynes. In this paper we report a general preparation of primary and secondary α-chlorophosphines and the subsequent formation of simple phosphaalkenes by dehydrochlorination of these compounds either in the gas phase or in the liquid phase. In the former approach, phosphaalkenes are characterized by HRMS and IR, whereas in the latter they are identified by low-temperature ^{31}P NMR and by chemical trapping with dienes, dipoles, or nucleophiles. These reactions further provide useful insight into the synthetic potential of the P═C double bond species.

Results

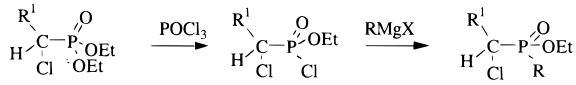
The synthesis of phosphaalkenes **3** involves, as a key step, the dehydrochlorination of α-chlorophosphines **2** which were previously obtained by a chemoselective reduction of the corresponding phosphonic or phosphinic esters **1** (retrosynthesis, Scheme 1).

The α-chlorophosphonate precursors **1a**−**c** have been prepared according to literature procedures.[15] We have synthesized

Scheme 1



Scheme 2

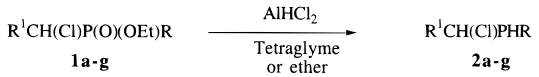


1a-b **1d-g**

1a : R^1 = H
1b : R^1 = Me

1d : R^1 = H ; R = Me
1e : R^1 = Me ; R = Me
1f : R^1 = H ; R = Ph
1g : R^1 = Me ; R = Ph

Scheme 3



2a : R = H; R^1 = H
2b: R = H ; R^1 = Me
2c: R = H ; R^1 = Et
2d: R = Me ; R^1 = H
2e: R = Me ; R^1 = Me
2f: R = Ph ; R^1 = H
2g: R = Ph ; R^1 = Me

the α-chlorophosphinates **1d**−**g** by use of the reported route[16] outlined in Scheme 2. It involves the formation of the phosphonochloridate intermediates by treatment of the phosphonic esters with $POCl_3$ followed by a selective P-alkylation with a Grignard reagent.[17]

Synthesis of α-Chlorophosphines 2. The preparation of the nonsubstituted α-chlorophosphine (**2a**) by thermal disproportionation of the chloromethylphosphinic acid has been previously reported.[18] We synthesized this phosphine in a more efficient manner by a chemoselective reduction of the chloromethylphosphonate with AlH_3 and used this approach for the synthesis of the primary α-chlorophosphines **2b,c**.[15a] However, the extension of this procedure to the preparation of the secondary α-chlorophosphines **2d**−**g**, which involves the reduction of the corresponding chlorophosphinic esters **1d**−**g**, was accompanied by the formation of byproducts resulting from P−C or C−Cl bond cleavages. We thought to enhance the selectivity by increasing the electrophilic character of the phosphorus with a Lewis acid. Thus, the secondary α-chlorophosphines **2d**−**g** were obtained in good yield with only small amounts of byproducts (<5%) by reduction of the phosphinates **1d**−**g** at low temperature with $AlHCl_2$ as an electrophilic reducing agent.[15b] These results encouraged us to revisit our initial work and to extend the use of this reagent for the preparation of primary α-chlorophosphines **2a**−**c** from their corresponding phosphonates: a chemoselectivity, better than that previously reported by using AlH_3,[15a] was in each case observed (Scheme 3 and Table 1).

The reduction conditions are dependent upon the nature of the products. The volatile phosphines **2a**−**e** are reduced at −10 °C in tetraglyme. This high-boiling solvent allows one to work under vacuum, to continuously evacuate the phosphines from the reducing mixture as soon as they are formed, and to condense them on a cold finger (77 K). The purification is performed by standard vacuum line techniques (yields *ca*. 80%).

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Table 1. NMR Data and Yields of α-Chlorophosphines **2**[a]

products	R	R^1	$\delta^{31}P$ (ppm)	$^1J_{PH}$ (Hz)	$^1J_{CP}$[b] (Hz)	ν_{PH} (cm^{-1})	yield (%)
2a	H	H	−105	201	22	2310	80[c]
2b	H	Me	−98	198	15	2305	88[c]
2c	H	Et	−104	198	15.6	2285	92[c]
2d	Me	H	−60.8	206	26.6	2295	74[c]
2e	Me	Me	−40.0	199	20.9	2300	73[c]
			−50.1	198	20.9	2300	73[c]
2f	Ph	H	−36.7	214	26.6	2300	80[d]
2g	Ph	Me	−23.6	215	20.6	2300	80[d]
			−25.6	213			

[a] All the phosphines were prepared by reduction of esters with $AlHCl_2$ in tetraglyme for the volatile phosphines **2a**−**e** or in ether or THF for the *P*-phenylphosphines **2f**−**g**. [b] Coupling constant between P and C(Cl). [c] Yield in distillated product. [d] Measured by NMR.

This method cannot, however, be applied to the heavier *P*-phenylphosphines **2f,g**. These are synthesized in a low-boiling solvent (ether or THF); at the end of the reaction the suspension is filtered on celite to remove aluminium salts, and the filtrate is concentrated and distilled under reduced pressure. The lower yields (*ca*. 45%) observed in these experiments are due to an important decomposition occurring during the distillation. Consequently, the crude solutions are used directly after filtration for the following step of the sequence (*ca*. 90% yields, purity higher than 90% as determinated by ^{31}P NMR).

Chlorophosphines **2a**−**g** are characterized by ^{31}P, ^{13}C, and ^1H NMR as well as by HRMS and by IR spectroscopy. The two diastereoisomers **2e** and **2g** are differentiated by NMR. The spectroscopic data, partially listed in Table 1, are in good agreement with the proposed structure. The chlorophosphines are not very stable and slowly polymerize at room temperature. The *P*-alkylphosphines **2a**−**e** can be kept in solution for several weeks in the refrigerator. *P*-Phenylphosphines **2f,g** present a lower stability and consequently must be rapidly used in the following step.

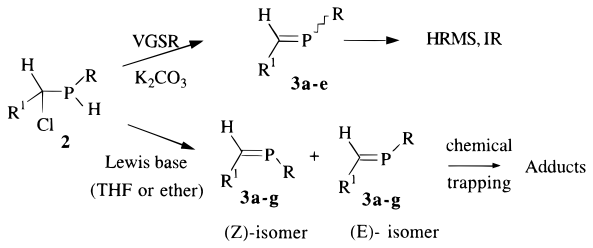
Caution: All of the reactions and handling of phosphines should be carried out under an inert atmosphere in a well-ventilated hood.

HCl Elimination. In 1966 Goldwhite and co-workers postulated the formation of the phosphaethene **3a** as a transient species in the dehydrochlorination of chlorophosphine **2a** in an aqueous hydroxylic media.[18] However, only their corresponding nucleophilic adducts have been isolated. In the present study we have generated the phosphaalkenes **3** by dehydrohalogenation of the α-chlorophosphines **2**, both *in the gas phase* on potassium carbonate (VGSR, procedure A) and *in the liquid phase* in the presence of a Lewis base (procedure B). Only the volatile derivatives **3a**−**e** can be formed by the former technique; all of the phosphaalkenes **3a**−**g** can be generated by the second approach.

Gas-phase HCl Elimination (VGSR) of the Volatile α-Chlorophosphines 2a−e. HRMS and IR Analysis of the Phosphaalkenes 3a−e and Photoelectron Spectroscopy of 3a,b (Procedure A). The transient phosphaalkenes **3a**−**e** are formed in the gas phase by using the vacuum gas−solid reaction technique (VGSR),[19] and the dehydrochlorination of the volatile α-chlorophosphine precursors **2a**−**e** takes place on solid potassium carbonate (Scheme 4).

HRMS Analysis. The HCl elimination conditions are first optimized by coupling the VGSR apparatus with a high-resolution mass spectrometer and by real time analysis of the gaseous flow (VGSR/HRMS coupling).[14b,20] When the temperature of the reactor is progressively raised, a decrease of the intensity of both the molecular ion (M^-) and the base peak of the chlorophosphine precursor is observed for all of the species, whereas the intensity of the peak corresponding to the desired phosphaalkene simultaneously increases ($M^+ - 36$, loss of HCl as confirmed by HRMS and MS/MS analysis) (Table 2). An almost total dehydrochlorination of the primary phosphines **2a**−**c** is observed at approximately 150 °C, whereas that of the secondary phosphines **2d,e** occurs at higher temperatures (150−200 °C). Attempts to extend this study to the phosphaalkenes **3f** and **3g** were unsuccessful, the *P*-phenylchlorophosphine precursors **2f** and **2g** being too unstable to be vaporized under the experiment conditions.

Scheme 4



Solid Phase IR Analysis. The gaseous flow exiting from the VGSR device can also be condensed on a KBr window cooled to 77 K, and the IR spectra of the phosphaalkenes **3a**−**e** can thus be immediately recorded at this temperature in order to minimize the decomposition of the species (see below). From theoretical calculations,[21] the large band at 850 cm^{-1}, initially attributed to the $\nu_{C=P}$ stretching frequencies of **3a**,[6] must be reassigned to the CH_2 bending frequency which has a very strong intensity. After reexamination of the IR spectra,[22] we attributed the weak band at 1012 cm^{-1} to the C═P stretching frequency. This value is in good agreement with the calculations[21] and the experimental data determinated by Ohno and co-workers for CH_2═P−Cl.[23] The data of the $\nu_{P=C}$ mode of phosphaalkenes **3a**−**e** are listed in Table 3 along with the ν_{P-H} absorptions of **3a**−**c** and those of their chlorophosphine precursors **2a**−**e** observed at the same temperature (77 K). The $\nu_{P=C}$ stretching frequencies thus assigned are very sensitive to substituent modifications on the P═C core. For example the replacement of the hydrogen atom on the phosphorus by a methyl group leads to a shift toward longer wavenumbers of *ca*. 100 cm^{-1} (**3a**, 1012 cm^{-1}; **3d**, 1115 cm^{-1}). A similar but less important shift (±88 cm^{-1}) is observed when the carbon atom in the position α is methylated. The ν_{P-H} frequencies of **3a**−**c** are less sensitive to the change of substituent on the carbon atom. They are observed at shorter wavenumbers than those of the chlorophosphine precursors **2a**−**c** (shift of *ca*. 40 cm^{-1}).

Phosphaalkenes are not stable in the solid state at 77 K. A self-condensation on the KBr window is observed which results in a decrease of the intensity of the ν_{P-H} and $\nu_{P=C}$, peaks a total disappearence occurring after *ca*. 30 mn.

Attempts to transfer the phosphaalkenes **3a**−**e** by trap to trap distillation from the cold trap (77 K) to an NMR tube (solvent

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Table 2. Mass Spectrometry Data for α-Chlorophosphines **2** and Phosphaalkenes **3**[a]

			3 ($M^{\bullet+}$ − HCl)[b]		
chlorophosphines **2**	$M^{\bullet+}$ (molecular ion of **2**)	phosphaalkenes **3**	calcd	found (HRMS)	MS/MS fragmentation
2a	82	H_2C═PH	45.9972	45.9975	
2b	96	Me(H)C═PH	60.0129	60.0127	45 (−CH_3)
2c	110	(Et)HC═PH	74.0285	74.0287	
2d	96	H_2C═PMe	60.0129	60.0124	45 (−CH_3)
2e	110	Me(H)C═PMe	74.0285	74.0291	59 (−CH_3)

[a] Determinated by a VGSR/MS sequence. The temperature of the oven was optimized by real time analysis of the gaseous flow. [b] Molecular ion of **3**.

Table 3. Selected Infrared Data of Chlorophosphines **2a**−**c** and Phosphaalkenes **3a**−**e**[a,b]

α-chlorophosphines		phosphaalkenes			
compd	ν_{P-H} (cm^{-1})	compd	ν_{P-H} (cm^{-1})	compd	$\nu_{P=C}$ (cm^{-1}) (calcd)
2a	2310 (s)	**3a**	2260 (s)	**3a**	1012 (w) (1017)[c]
2b	2305 (s)	**3b**	2250 (s)	**3b**	1100 (w)
2c	2280 (s)	**3c**	2240 (s)	**3c**	1140 (w)
				3d	1115 (w)
				3e	1120 (w)
				CH_2═P−Cl	979.7[d,e] (w) (980.2)[e]

[a] Solid phase; 77 K. [b] Intensity: (s) strong, (w) weak. [c] Reference 21. [d] Gas phase. [e] Reference 23.

$CD_2Cl_2/CFCl_3$, $T < -120$ °C) or a Schlenk flask were unsuccessful; the self-condensation occurred either on the cold trap or during the transfer, which required a rise in temperature to *ca*. −120 °C. Therefore, NMR measurements nor chemical trapping experiments could be performed on the phosphaalkenes prepared by VGSR. In comparison, it is notable that H_2C═P−Cl appeared to be a more stable species or at least a less reactive one since its transfer under the same conditions, after it was formed by HCl elimination from CH_3PCl_2 under flash vacuum thermolysis conditions, has been successful, allowing low-temperature NMR measurements and chemical trapping.[10d]

Photoelectron Spectra of 3a and 3b. The PE spectra of phosphaalkenes **3a** and **3b** have been recorded by the use of the VGSR/PE technique described above. This work has been previously published.[14a] Attribution of the vertical $\pi_{P=C}$ and n_P ionization energies (10.3 and 10.7 eV, respectively) were correlated with those of the corresponding imines and with substituted phosphaalkenes and were confirmed by theoritical calculations.

In conclusion of this section, the tandem VGSR/MS, VGSR/IR, and VGSR/PES are efficient techniques for generating the transient phosphaalkenes **3a**−**e** by HCl elimination of the corresponding α-chlorophosphines under high-dilution conditions and for characterizing them by real time analysis. Yet these species are too reactive to be transferred by classical trap to trap distillation. The chemical trapping experiments are consequently unfeasible by this technique.

Liquid-Phase HCl Elimination of α-Chlorophosphines. NMR Analysis and Chemical Trapping Experiments of Phosphaalkenes 2a−g (Procedure B). The dehydrohalogenation of the α-chlorophosphines **2a**−**g** occurs in solution in the presence of a Lewis base (Scheme 4). The conditions for the elimination are dependent upon both the structure of the phosphine and the strength of the base. They may also vary with the purpose of the reaction. Thus, for NMR experiments, a strong Lewis base is usually chosen so that the reactive species can be generated at a temperature as low as possible in order to minimize the self-condensation processes. However, for chemical trapping, the generation of the phosphaalkenes at a temperature consistent with the reactivity of the species toward the reagent is required.

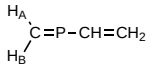
NMR Analysis. As we have reported above, the simple phosphaalkenes are unstable in solution even at low temperature. They can however be detected by NMR under special conditions. The NMR tube containing a solution of the chlorophosphine precursor and the Lewis base is introduced into the probe at a temperature lower than that of the elimination reaction. Under continuous scanning, the temperature of the NMR probe is slowly raised and then finally stabilized to a value corresponding to the beginning of elimination. The signals of the phosphaalkenes are only observed during the course of the dehydrochlorination. This experiment along with IR monitoring (slow decomposition of the species on the KBr window at 77 K) confirms the transient character of free simple phosphaalkenes.

The HCl-elimination conditions of the chlorophosphines **2a**−**g** are summarized in Table 4, along with the observed ^{31}P NMR data of the corresponding phosphalkenes **3a**−**g**. For comparison we have added the data concerning the chlorophosphine (CH_2═CH)P(H)CH_2Cl (**2h**) and those of the corresponding 2-phosphabutadiene CH_2═CHP═CH_2 (**3h**).[14b] The temperature of elimination is closely related to the P−H acidity of the chlorophosphine precursors and to the strength of the Lewis base. HCl elimination of the primary phosphines **2a**−**c** occurs at low temperature (<25 °C) in the presence of DABCO (Table 4, entries 1−3). For the secondary *P*-methyl(chloromethyl)-phosphines (**2d,e**), a strong Lewis base such as DBU is required to perform the HCl elimination (−25 °C for **2d** (entry 4) and −80 °C for **2e** (entry 5)). For phosphine **2d**, a rapid self-condensation is observed at the elimination temperature (−25 °C), confirming the high instability of these structures. In relation with the higher P−H acidity, the HCl elimination of the *P*-phenyl- and *P*-vinylchlorophosphines (**2f**−**h**) occurs as expected at low temperature (*ca*. −80 °C) and even in the presence of a weak Lewis base (Et_3N).

The observed ^{31}P chemical shift of the parent compound **2a** ($\delta = +231$ ppm) is relatively close to the one determined by calculations using the IGLO method ($\delta = +269$ ppm).[24] A complex ABCX splitting pattern is expected due to the nonequivalence of the two olefinic protons H_A, H_B and a larger coupling constant $^2J_{PH_A}$ for the proton in the *cis* position relative to the lone pair of phosphorus (*cis*-rule)[25] (Figure 1). The

(24) Fleischer, U.; Kutzelnigg, W. Phosphorus, Sulfur Silicon *Relat. Elem.* **1993**, *77*, 105−108.
(25) Quin, L. D. *Phosphorus 31 NMR Spectroscopy in Stereochemical Analysis*; VCH Publishers Inc.: Deerfield Beach, FL, 1987.

Table 4. Conditions for HCl Elimination of Chlorophosphines **2a**−**h** and ^{31}P NMR Data of Phosphaalkenes **3a**−**h**

entry	chlorophosphines **2a**−**h**	Lewis base (elimination temp (°C))	phosphaalkenes **3a**−**h**	δ ^{31}P (stereo)[a] (ppm)	$^{1}J_{PH}$ (Hz)	$^{2}J_{PH}$ (Hz)
1	**2a**	DABCO (−50)	H_2C═P−H	231[b]	130	29
2	**2b**	DABCO (−50)	(Me)CH═P−H	192 (*Z*)	130	36
				186 (*E*)	136	20
3	**2c**	DABCO (−25)	(Et)CH═P−H	179 (*Z*)	131	39
				181 (*E*)	135	17
4	**2d**	DBU (+25)	H_2C═P−Me	285[c]		*c*
5	**2e**	DBU (−80)	Me(H)C═P−Me	238 (*Z*)		>20
				224 (*E*)		<20
6	**2f**	Et_3N (−80)		266[d]		31[e]; 29[f]
7	**2g**	Et_3N (−80)	Me(H)C═P−Ph	236 (*Z*)[g]		≥30[g]
				241 (*E*)[g]		<20[g]
8	**2h**[h]	Et_3N (−10)		268[h]		29.3[e]; 29.2[f]

[a] Stereochemistry established according to the "*cis*-rule"[25]. [b] Calculated 231 ppm.[24] [c] A self-condensation is mainly observed. [d] Calculated 336 ppm.[24] [e] $^{2}J_{B}$. [f] $^{2}J_{PH_A}$. [g] Values in good agreement with those obtained by rearrangement of the *P*-phenylvinylphosphine.[9b] [h] Reference 14b.

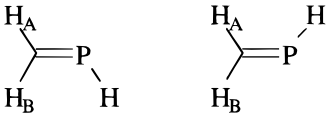


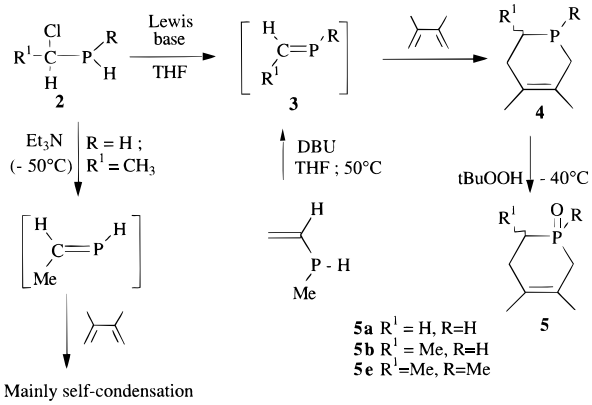
Figure 1.

deceptively simple spectrum (two triplets, $^{1}J_{PH}$ = 130 Hz, $^{2}J_{PH}$ = 29 Hz) can be hardly explained by a rapid inversion at phosphorus since the calculated inversion barrier is too high (106.6 kJ).[26] A mechanism involving a base-induced deprotonation/reprotonation of the acidic P−H (too fast to be observed on the NMR time scale) is proposed.[5] By this exchange process, the two olefinic protons are expected to be equivalent, in good agreement with the observed triplet splitting. However, identical vinylic $^{2}J_{PH}$ coupling constants cannot be ruled out, since similar coupling constants have already been observed in the literature for the 2-phosphabutadiene **3h** (Table 4, entry 8).[14b]

Other interesting information can be obtained from the NMR data of phosphaalkenes **3a**−**h** (Table 4). The chemical shifts for the two *P*-phenyl isomers **3f** (δ = 236 ppm (*Z*-isomer) and δ = 241 ppm (*E*-isomer)) are in good agreement with the value reported in the literature for an authentic sample obtained by the base-induced rearrangement of the *P*-phenylvinylphosphine (only one isomer is formed in this process, δ = 268 ppm).[9b] At the elimination temperature of phosphine **2d** (25 °C), the self-condensation is very fast. The chemical shift of the corresponding phosphaalkene **3d** (δ = 285 ppm) was consequently detected with difficulty. On the other hand, the proximity of the chemical shifts for **2f** and **2h** show the similar effects of substitution at the phosphorus atom by a vinyl or a phenyl group (entries 6 and 8). The presence of a methyl group in the position α to the phosphorus induces a shielding effect of *ca*. 40 ppm for the C═P derivatives whatever the substituent at phosphorus. The determination of the stereochemistry of the phosphaalkene isomers **3b**, **3c**, **3e**, and **3g** is based on the $^{2}J_{PH}$ values in relation with the *cis*-rule.[25]

Chemical Trapping. Stabilized phosphaalkenes are known to react with various dienes, dipoles, and nucleophiles. By carrying out the HCl-elimination reactions in solution in the presence of some of these trapping agents, we have successfully obtained the cycloadducts or nucleophilic adducts of the phosphaalkenes **3**, giving thus additional evidence of their formation as transient intermediates. In general, the reaction conditions were not optimized. Owing to their easy oxidizability, most of the new free phosphines are only analyzed by ^{31}P NMR. The structural assignment is established by the formation and the complete characterization of their phosphine oxide or methiodide phosphonium salt derivatives.

Scheme 5



[4 + 2] Cycloadditions. The dehydrochlorination of **2a** with DABCO in THF occurs at −50 °C.[6] The tetrahydrophosphinine adduct **4a** (δ ^{31}P −88 ppm, $^{1}J_{PH}$ 190 Hz) is obtained when the elimination reaction occurs in the presence of a large excess (5 equiv) of 2,3-dimethylbutadiene (DBD). Compound **4a** is then oxidized to the corresponding phosphine oxide **5a** (δ ^{31}P = 22 ppm, $^{1}J_{PH}$ 460 Hz; overall yield, 12% after chromatography on silica). Under nearly identical experimental conditions, the formation of self-condensed products is mainly observed in the case of the chloroethylphosphine **2b**. However, the two expected cycloadduct isomers **4b** are observed by the use of pyridine both as solvent and reagent at 80 °C. The higher elimination temperature allows enhancement of the reactivity of the phosphaalkene toward the diene (Scheme 5). By this method, the phosphine oxides **5b** can be isolated by chromatography on silica. The overall yield is however very poor (9%). The stereochemistry of the two isomers has not been determined (Table 5). Compounds **5a** and **5b** are characterized by NMR and mass spectrometry. The phosphinine oxides **5a** and **5b** are slowly oxidized in air into their corresponding cyclic phosphinic acid.

As was already mentioned above, the dehydrohalogenation of the *P*-methylchlorophosphine **2e** only occurs with a strong

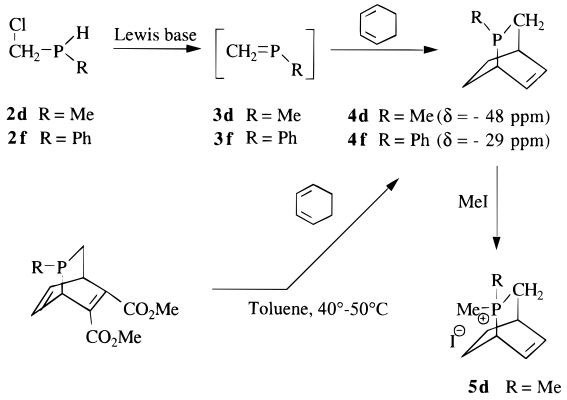
(26) Francl, M. M.; Pellow, R. C.; Allen, L. C. *J. Am. Chem. Soc*. **1988**, *110*, 3723−3728.

Table 5. [4 + 2] Cycloadditions: Experimental Conditions for HCl Elimination and Selected ^{31}P NMR Data of the Corresponding Phosphines **4** and **5**

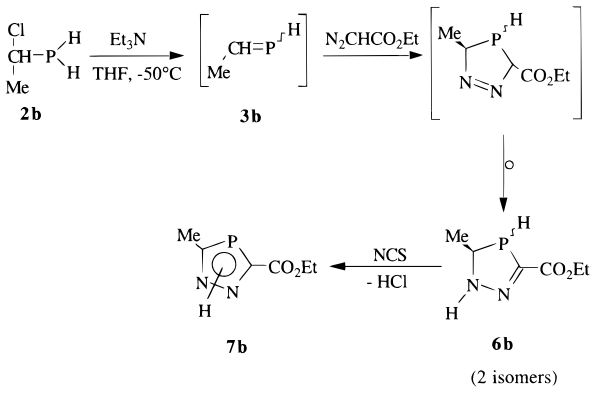
					δ_P ($^1J_{PH}$)		
chlorophosphines **2**	Lewis base (solvent)	temp[a] (°C)	phosphaalkenes **3**	reagent	**4**[b]	**5**	yield[e] (%) (ref)
2a	DABCO (THF)	−50	**3a**	DBD	−86 (190)	22[c] (460)	15
2b	pyridine (pyridine)	+80	**3b**	DBD	−75 (188)[f]	25[c] (443)[f]	9
					−65 (185)[f]	33[c] (449)[f]	
2e	DBU (THF)	+20	**3e**	DBD	−49[f]	38[c]	<5 (75)[g]
2d	DBU (THF)	+20	**3d**	CHD	−48	28[d]	27 (quant.)[h]
2f	Et_3N (THF)	−80	**3f**	CHD	−29		

[a] Temperature of HCl elimination. [b] Chemical shift of the free cycloadducts. [c] Chemical shift of phosphine oxides. [d] Chemical shift of the methiodide salts. [e] Yield of the phosphine oxide or methiodide salt derivatives. [f] Mixture of the two stereoisomers; stereochemistry non-established. [g] Route involving the formation of **3e** by a base-induced rearrangement of vinylphosphine.[9b] [h] Route involving the formation of **3d**, **3f** by a retro[4 + 2] cycladdition; the overall yields were claimed to be virtually quantitative.[8]

Scheme 6



Scheme 7

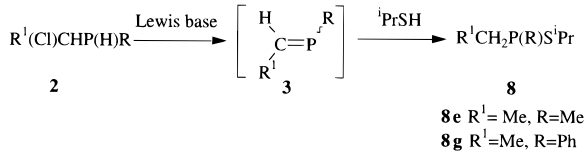


base (DBU) at ca. 20 °C. The phosphaalkene intermediate **3e** is trapped with DBD to afford the phosphine adducts **4e**. The tetrahydrophosphinine oxide isomers **5e** are finally isolated after oxidation of **4e** with BuOOH at −40 °C. The NMR data of these adducts are similar to those of authentic samples obtained when the same transient phosphaalkene is formed by a base-induced rearrangement of the *P*-methylvinylphosphine in THF at 50 °C.[9b] The yields are, however, dramatically lower in the HCl-elimination sequence (yields for **4e** <5% by the HCl elimination *vs* 75% by rearrangement).

The transient phosphaalkenes **3d** and **3f** are formed by HCl elimination from the chlorophosphines **2d** and **2f** with DABCO (20 °C) and Et_3N (−80 °C), respectively, and are trapped *in situ* by cyclohexadiene (2 equiv). The free phosphine adduct **4d** is then transformed into their methiodide derivative **5d**. The NMR data are identical to those of an authentic sample[8] formed by a route involving a retro[4 + 2] cycloaddition carried out under mild conditions (50 °C) (Scheme 6). The observed overall yields are, however, lower in the HCl-elimination route (27% starting from **2d**) as compared with the virtually quantitative yields claimed by Quin and co-workers.[8] Experimental conditions for HCl elimination and ^{31}P NMR data of the free phosphines and their derivatives are shown in Table 5.

[3 + 2] Cycloadditions. The [3 + 2] cycloadditions have been widely used in the literature for the phosphaalkenes trapping. Therefore we tested the reactivity of the transient 1-phosphapropene **3b** toward ethyl diazoacetate (EDA). The HCl elimination of (chloroethyl)phosphine **2b** was induced by Et_3N at −50 °C in the presence of an excess of EDA (Scheme 7). The two cycloadduct isomers **6b$_1$** and **6b$_2$** formed by a spontaneous hydrogen migration from the primary adducts[27] are first detected and are characterized without purification by ^1H, ^{13}C, and ^{31}P NMR. The stereochemistry is assigned by use of the *cis*-rule[25] (*Z*-isomer **6b$_1$**, $^2J_{PH}$ = 29.5 Hz, $^3J_{PH}$ = 10 Hz; *E*-isomer **6b$_2$**, $^2J_{PH}$ = 7 Hz, $^3J_{PH}$ = 18 Hz). The regioselectivity is determined by ^{13}C NMR: the vinylic carbon C_1 is directly bonded to the phosphorus atom since the $^1J_{C1P}$ is large (**6b$_1$**, δ_{C_1} = 167 ppm, $^1J_{C1P}$ = 52 Hz; **6b$_2$**, δ_{C_1} = 174 ppm, $^1J_{C1P}$ = 56 Hz).

Scheme 8



Aromatization to the azaphosphole **7b** is achieved by a P-chlorination/dehydrochlorination sequence with NCS at −30 °C (Scheme 7) in a 17% overall yield (determined after purification by chromatography on silica). The analoguous nonmethylated compound has already been obtained by a [3 + 2] cycloaddition of HC≡P with ethyl diazoacetate.[12a] Consequently, the chlorophosphine **2b** can be considered as a synthetic equivalent of $CH_3C{\equiv}P$.

Nucleophilic Additions. The nucleophilic addition of a thiol in the presence of a Lewis base is one of the most efficient procedures for phosphaalkene chemical trapping. The adducts **8e** and **8g** are thus obtained when phosphaalkenes **3e** and **3g** are generated in the presence of ^{i}PrSH (4 equiv). The temperature of the reaction is dependent on the P—H acidity. The adducts are characterized by NMR and HRMS. Compound **8e** has been identified by comparison of the NMR data with an authentic sample[9b] (Scheme 8). Oxidation of the free phosphines **8e** and **8g** (^{t}BuOOH) in mild conditions (−10 °C) gave a complex mixture.

Discussion and Conclusion

α-Chlorophosphines. We have previously developed an efficient route to α-chlorophosphonates and α-chlorophosphi-

(27) Zurmülhen, F.; Röschs, M.; Regitz, M. *Z. Naturforsch. B* **1995**, *40*, 1077.

nates that allows us to control the nature of both the C- and the P-substituents.[15,16] We show in the present study that these compounds can be efficiently used as precursors of primary and secondary α-chlorophosphines by a chemoselective reduction using $AlHCl_2$ as an electrophilic reducing agent. These two new classes of phosphines are obtained in good yields and are characterized by different spectroscopic methods. Only some representative derivatives have been chosen as precursors of phosphaalkenes in the present work.

Transient Phosphaalkenes. Phosphaalkenes are obtained by dehydrochlorination of their corresponding α-chlorophosphines in basic media both in the gas phase on solid potassium carbonate (VGSR) or in solution in the presence of a Lewis base. The gas-phase approach concerns only the volatile α-chlorophosphines. The corresponding phosphaalkenes have been characterized by HRMS/VGSR coupling and by solid-phase IR spectroscopy after condensation of the gaseous flow on a KBr window cooled at 77 K. The dehydrohalogenation in solution with a Lewis base is general. We have obtained by this procedure the first ^{31}P NMR data of simple phosphaalkenes. The chemical trapping experiments (Diels−Alder and dipolar cycloadditions or nucleophilic additions) provided additional evidence of these intermediates. The overall yields of the adducts are moderated (<30%), and it is clear that further synthetic developments would require an optimization of reaction conditions to increase the yield. Recent literature results[8,9] give some reasons to be optimistic. It was chosen that the yields of adducts are strongly dependent on the experimental conditions. Thus, when the transient phosphaalkenes can be formed in high-dilution conditions at a temperature which allows a rapid cycloaddition, the self-condensation can be almost avoided and the yields are good and sometimes excellent. The P—H acidity of the chlorophosphine precursors of phosphaalkenes depends on the nature of substituents. The HCl-elimination conditions are consequently modified for each species. Optimization should be found mainly by changing the strength of the Lewis base. The present route would play an interesting role in phosphorus chemistry in the future if good control of these conditions can be obtained.

Experimental Section

General Procedure. All of the manipulations were performed with standard Schlenck techniques under an atmosphere of dried argon or nitrogen. The volatile phosphines were distilled and transferred by standard vacuum line techniques. Solvents were purified by distillation from an appropriate drying agent. IR spectra of phosphaalkenes were recorded on a Perkin-Elmer Model 157 G spectrometer using a KBr window cooled with liquid nitrogen. ^1H, ^{31}P, and ^{13}C NMR spectra were recorded on a Brucker AC 300P. Chemical shifts are given in parts per million relative to internal $SiMe_4$ for ^1H and ^{13}C spectra and H_3PO_4 for ^{31}P NMR spectra. Chemical shifts upfield from standard are defined as negative. High-resolution mass spectra were recorded on a Varian MAT 311 spectrometer. Elemental analyses were obtained by the Service de Microanalyse du CNRS (Solaize). All of the experiments have been conducted under neutral and dried atmosphere. Compounds **2a**−**c** were prepared by modification of the literature procedure.[15] $AlHCl_2$ was used instead of AlH_3.

Preparation of Volatile α-Chlorophosphines 2a−2e. General Procedure. The apparatus already described for the reduction of α-chlorophosphonates with AlH_3 was used.[15] Tetraglyme was dried by refluxing over sodium/benzophenone and then distilled under reduced pressure (10^{-2} hPa). The solution of $AlHCl_2$ in tetraglyme was prepared according to the recently reported procedure.[28] The flask containing the reducing mixture (4.6 g, 4.6×10^{-2} mol of $AlHCl_2$ in 20 mL of tetraglyme) was fitted on the vacuum line, degassed, and then cooled at −10 °C. The chlorophosphonate (10^{-2} mol in 5 mL of tetraglyme) was slowly added (10 min) through a flex needle. The phosphine was continuously evacuated from the reducing mixture and condensed on a cold trap cooled at 77 K. At the end of the transfer, the phosphine was purified by classical trap to trap distillation. The product was collected in a Schlenk and characterized by spectroscopy. The purity is higher than 90%. The product was stored in a refrigerator.

***P*-Methyl(chloromethyl)phosphine (2d).** Yield, 74%. ^1H NMR (300 MHz, $CDCl_3$): 1.28 ($^2J_{PH}$ = 3.2 Hz), 3.56 (the $^1J_{PH}$ coupling constant was not observed in $CDCl_3$), 3.71 ($^2J_{PH}$ = 7 Hz). ^{31}P NMR (32.38 MHz, ether/C_6D_6): −61.30 ($^1J_{PH}$ = 206 Hz). ^{13}C NMR (75.5 MHz, $CDCl_3$): 1.91 ($^1J_{CH}$ = 130.2 Hz), 38.22 ($^1J_{CH}$ = 150 Hz). IR (cm^{-1}): ν_{P-H} 2300 (F), ν_{C-Cl} 670 (F). HRMS. Calcd for C_2H_6ClP: 95.9896. Found: 95.9899. Rel intens (%): 98 (25), 96 (7), 83 (30), 61 (56), 45 (100).

***P*-Methyl(2-Chloroethyl)phosphine (2e).** Mixture of 2 diastereoisomers (yield 73%). ^1H NMR (300 MHz, $CDCl_3$): 1.24 ($^2J_{PH}$ = 3 Hz, 1.8 Hz, $^3J_{HH}$ = 7.1 Hz), 3.65 (the $^1J_{PH}$ coupling constant was not observed in $CDCl_3$), 4.22 ($^2J_{PH}$ = 5.3 Hz, $^3J_{HH}$ = 7.1 Hz). ^{31}P NMR (32.8 MHz, ether/C_6D_6): −40.0 and −50.1 ($^1J_{PH}$ = 198 Hz). ^{13}C NMR (75.5 MHz, $CDCl_3$): 2.39 ($^1J_{CH}$ = 130.1 Hz), 24.22 ($^1J_{CH}$ = 129.2 Hz), 52.24 ($^1J_{CH}$ = 151.4 Hz). IR (cm^{-1}): ν_{P-H} 2295 (F), ν_{P-CHCl} 1455 (F, ν_{C-Cl}) 652 (F). HRMS. Calcd for C_3H_8ClP: 110.00521. Found: 110.0056.

Preparation of the α-Chlorophosphines 2f,g. General Procedure. The ethereal solution of $AlHCl_2$ was prepared according to the literature procedure.[28] The flask containing the reducing mixture (0.46 g, 4.6×10^{-3} mol) in 10 mL of solvent was cooled at −80 °C and the chlorophosphinate (2×10^{-3} mol in 5 mL of ether) was slowly added through a flex needle. After addition, the mixture was slowly warmed to room temperature and then filtered on dried celite. The yields of crude product (^{31}P NMR) are higher than 80%. The *P*-phenylphosphines are not very stable, even in solution, and must be rapidly used without further purification. For spectroscopic analysis, a sample was rapidly purified by washing the ethereal solution with degassed water. The solution was dried, and the product was purified by trap to trap distillation *in vacuo*. The ^{31}P, ^{13}C, and ^1H NMR and mass spectra were recorded. The spectroscopic data are consistent with the structure.

***P*-Phenylmethylphosphine (2f).** Yield, *ca*. 80% (determined by ^{31}P NMR on the crude product) and 46% after trap to trap distillation *in vacuo* (40 °C under 10^{-2} hPa). ^1H NMR (300 MHz, $CDCl_3$): 3.81 ($^2J_{PH}$ = 6.3 Hz), 4.52 (the $^1J_{PH}$ coupling constant was not observed in $CDCl_3$), 7.35, 7.56. ^{31}P NMR (32.38 MHz, ether/C_6D_6): −36.7 ($^1J_{PH}$ = 214 Hz). ^{13}C NMR (75.5 MHz, $CDCl_3$): 37.9 ($^1J_{CH}$ = 151.9 Hz), 128.62 ($^1J_{CH}$ = 163 Hz), 129.31 ($^1J_{CH}$ = 161 Hz), 131.75, 134.41 ($^1J_{CH}$ = 161.7 Hz). IR (cm^{-1}): 2300 (f, ν_{P-H}), 685 (f, ν_{C-Cl}). HRMS. Calcd for C_7H_8ClP: 158.0052. Found: 158.0058. Rel intens (%): 158 (100), 159 (7.99), 160 (32.25), 161 (2.56), 162 (0.09).

***P*-Phenyl(2-chloroethyl)phosphine (2g).** Mixture of 2 diastereoisomers; yield, *ca*. 80% (determined by ^{31}P NMR) and 42% after trap to trap distillation (50 °C under 10^{-2} hPa). ^1H NMR (300 MHz, $CDCl_3$): 1.63 ($^3J_{PH}$ = 12.5 Hz, $^3J_{HH}$ = 7 Hz), 4.15 (the $^1J_{PH}$ coupling constant was not observed in $CDCl_3$), 4.36 ($^2J_{PH}$ = 3.4 Hz, $^3J_{HH}$ = 7 Hz), 7.36 7.55. ^{31}P NMR (32.38 MHz, ether/C_6D_6): −23.6 ($^1J_{PH}$ = 215 Hz) and −25.6 ($^1J_{PH}$ = 213 Hz). ^{13}C NMR (75.5 MHz, $CDCl_3$): 24.04 ($^1J_{CH}$ = 129.5 Hz), 51.81 ($^1J_{CH}$ = 154.9 Hz), 128.55 ($^1J_{CH}$ = 162 Hz), 129.2 ($^1J_{CH}$ = 161.8 Hz), 131.25, 135.16 ($^1J_{CH}$ = 162 Hz). IR (cm^{-1}): 2295 (f, ν_{P-H}), ν_{C-Cl} 690 (F). HRMS. Calcd for $C_8H_{10}ClP$: 172.0209. Found: 172.0213.

Formation of the Phosphalkenes 3a−e by Gas-Phase HCl Elimination (VGSR) and Characterization by VGSR/HRMS and VGSR/IR Experiments. General Procedure (Procedure A). The VGSR apparatus has been already described in preceding papers.[19] Powdered and dried K_2CO_3 (15 g) was introduced into the VGSR reactor (l = 25 cm; i.d. = 2.5 cm) and then horizontally distributed between two pads of glass wool 20 cm distant from each other. The reactor was then fitted onto the ionization chamber of a mass spectrometer (VGSR/HRMS coupling) or onto a vacuum line equipped with a KBr window cooled at 77 K (VGSR/IR coupling). Chloro-

(28) Guillemin, J. C.; Le Guennec, M.; Denis, J. M. *J. Chem. Soc., Chem. Commun*. **1989**, 989.

phosphines **2a**−**e** were slowly vaporized *in vacuo* through the reactor.

VGSR/HRMS Experiments. In the VGSR/HRMS experiments, the gaseous flow coming out of the reactor was analyzed in real time by mass spectrometry. The temperature of the elimination was optimized by continuous gas flow analysis. The peak corresponding to the loss of HCl ($M^{\bullet+} - 36$) increases with the temperature of the solid base. The temperature was finally maintained until the total disappearance of the molecular ion of the chlorophosphine precursor was observed. The HRMS and MS/MS experiments were then performed.

VGSR/IR Experiments. In the VGSR/IR experiments, the gaseous flow was condensed on a KBr window cooled at 77 K. The VGSR/HRMS coupling has been previously described.[20] The temperature of elimination is that determined by VGSR/HRMS experiments. The IR spectra of the starting material are first recorded and the self-condensation of the phosphaalkenes is then monitored. Selected IR data are collected in Table 3.

Phosphaethene (3a). Temperature of K_2CO_3 for MS and IR experiments: 150 °C MS, *m*/*z* (%): 46 (100), 45 (59), 44 (49), HRMS. Calcd for CH_3P: 45.9972. Found: 45.9965, IR (77 K, cm^{-1}): 815 (w), 990 (s), 1012 (w, $\nu_{C=P}$), 1410 (s), 2260 (s, ν_{P-H}), 2990 (w).

1-Phosphapropene (3b). Temperature of K_2CO_3 for MS and IR experiments: 150 °C, MS, *m*/*z* (%): 60 (70), 58 (55), 57 (100), 56 (21). HRMS. Calcd for C_2H_5P: 60.0130. Found: 60.0127. IR (77 K, cm^{-1}): 700 (w), 750−850 (s), 880 (F), 1100 (w, $\nu_{C=P}$), 1445 (s), 2260 (w, ν_{P-H}), 2940 (w), 2960 (w).

1-Phosphabutene (3c). Temperature of K_2CO_3 for MS and IR experiments: 150 °C. MS, *m*/*z* (%): 74 (64), 57 (40), 48 (25), 46 (25), 44 (46), 41 (100), 39 (30). HRMS. Calcd for C_3H_7P: 74.0285. Found: 74.0287. IR, (77 K, cm^{-1}): 730 (w), 750−900 (s), 1140 (w, $\nu_{C=P}$), 1450 (s), 2240 (s, ν_{P-H}), 2880 (w), 2960 (w).

***P*-Methyl-1-phosphaethene (3d).** Temperature of K_2CO_3 for MS and IR experiments: 200 °C. MS, *m*/*z* (%): 44 (100), 60 (40), 96 (12). HRMS ($M^{\bullet+}$). Calcd for C_2H_5P: 60.012 89. Found: 60.0124. MIKE spectrum (*m*/*z* 60): 58. CAD-MIKE spectrum (*m*/*z* 60): 58, 45. IR (77 K, cm^{-1}): 1260 (f), 1115 (w, $\nu_{C=P}$), 862 (vs), 810 (s).

***P*-Methyl-1-phosphapropene (3e).** Temperature of K_2CO_3 for MS and IR experiments: 200 °C. MS *m*/*z* (%): 74 (15), 64, (90), 60 (54), 57 (36), 49 (26), 44 (20), 43 (46), 27 (100). HRMS ($M^{\bullet+}$). Calcd for C_3H_7P: 74.0285. Found: 74.0284. MIKE spectrum (*m*/*z* 74): 73, 72. CAD-MIKE spectrum (*m*/*z* 74): 73, 72, 71, 59, 57, 15. IR (77 K, cm^{-1}): 1120 (w, $\nu_{C=P}$), 860 (vs), 810 (vs).

Liquid-Phase HCl Elimination of α-Chlorophosphines. ^{31}P NMR Analysis and Chemical Trapping Experiments of Phosphaalkenes 3a−g (Procedure B). ^{31}P NMR Analysis, General Procedure. A solution of the chlorophosphine precursor (0.2 mmol, solvent THF/C_7D_8 (3:1 ratio)) was added into a 5 mm NMR tube sealed with a rubber septum and cooled at −80 °C. The required Lewis base (0.2 mmol) was then slowly introduced. The NMR tube was rapidly shaken and then introduced into a previously cooled NMR probe (−80 °C). The probe was slowly warmed up and the temperature corresponding to the formation of the phosphaalkene was established by monitoring the appearance of the characteristic ^{31}P NMR low-field signal. The temperature was then maintained, and the ^{31}P NMR spectra were recorded.

Phosphaethene (3a). Prepared according to procedure B. Elimination temperature: −50 °C (DABCO). ^{31}P NMR (THF/C_7D_8): 231.0 ($^1J_{PH}$ = 130 Hz, $^2J_{PH}$ = 29 Hz).

1-Phosphapropene (3b). Prepared according to procedure B (two isomers). Elimination temperature: −50 °C (DABCO). ^{31}P NMR (THF/C_7D_8): *Z*-isomer, 192 (d, $^1J_{PH}$ = 130 Hz, $^2J_{PH}$ = 36 Hz, $^3J_{PH}$ = 14 Hz); *E*-isomer, 186 (d, $^1J_{PH}$ = 136 Hz, $^2J_{PH}$ = 20 Hz, $^3J_{PH}$ = 20 Hz).

1-Phosphabutene (3c). Prepared according to procedure B (two isomers). Elimination temperature: −25 °C (DABCO). ^{31}P NMR (THF/C_7D_8): *Z*-isomer, 179 (d, $^1J_{PH}$ = 131 Hz, $^2J_{PH}$ = 39 Hz); *E*-isomer, 181 (d, $^1J_{PH}$ = 135 Hz, $^2J_{PH}$ = 17 Hz).

***P*-Methyl-1-phosphaethene (3d).** Prepared according to procedure B. Elimination temperature: 25 °C (DBU). ^{31}P NMR (THF/C_7D_8): 285.

***P*-Methyl-1-phosphapropene (3e).** Prepared according to procedure B (two isomers). Elimination temperature: −80 °C (DBU). ^{31}P NMR (THF/C_7D_8): *Z*-isomer, 238 ($^2J_{PH}$ > 20 Hz); *E*-isomer, 224 ($^2J_{PH}$ < 20 Hz).

***P*-Phenyl-1-phosphaethene (3f).** Prepared according to procedure B. Elimination temperature: −80 °C (Et_3N). ^{31}P NMR (THF/C_7D_8): 266 ($^2J_{PHB}$ = 31 Hz, $^2J_{PH_A}$ = 29 Hz).

***P*-Phenyl-1-phosphapropene (3g).** Prepared according to procedure B (two isomers). Elimination temperature: −80 °C (Et_3N). ^{31}P NMR (THF/C_7D_8): *Z*-isomer, 236 ($^2J_{PH}$ > 20 Hz); *E*-isomer, 241 ($^2J_{PH}$ < 20 Hz).

Chemical Trapping. General Procedure. For the trapping experiments, the THF or ethereal solution containing α-chlorophosphines **2** and the reagent in a large excess (>4 equiv) were cooled at a temperature lower than that corresponding to the temperature of elimination. The Lewis base was then introduced, and the temperature was slowly allowed to warm to room temperature. In most cases, the free phosphines were only analyzed by ^{31}P NMR. The corresponding oxides were fully characterized.

1,2,5,6-Tetrahydro-3,4-dimethylphosphinine (4a) and Phosphine Oxide (5a). To a THF/C_7D_8 solution (90:10, 5 mL) of (chloromethyl)-phosphine **2a** (0.14 g, 1.70 mmol) cooled at −50 °C was added 0.22 g (2.67 mmol) of dimethylbutadiene and 0.2 g (1.78 mmol) of diazabicyclooctane (DABCO). The reaction mixture was stirred at this temperature for 2 h and then warmed to room temperature and analyzed by ^{31}P NMR. The observed data are consistent with the proposed structure **4a** (δ_P −87 ppm, $^1J_{PH}$ = 190 Hz). After oxygen bubbling for 2 h, the solvents were evaporated *in vacuo*, and the oily residue chromatographed on silica gel with ethanol as eluent. The pure phosphine oxide **5a** was isolated (15% overall yield). ^{31}P NMR (C_5D_5N: 22 ($^1J_{PH}$ = 4.59 Hz). HRMS. Calcd for $C_7H_{13}PO$; 144.0702. Found: 144.0704.

6-Methyl-1,2,5,6-tetrahydro-3,4-dimethylphosphinines (4b) and Phosphine Oxides (5b). The dehydrochlorination of the phosphine **2b** (0.48 g, 3.4 mmol) was performed in pyridine as solvent and reagent. The mixture containing **2b** and dimethylbutadiene was refluxed for 2 h and cooled at room temperature. The crude free phosphine isomers **4b$_1$** and **4b$_2$** were identified by ^{31}P NMR (THF/C_7D_8): −75 ($^1J_{PH}$ = 188 Hz), −64.6 ($^1J_{PH}$ = 187.5 Hz). The mixture was then cooled to −30 °C, and a solution of ^{t}BuOOH was added. The pyridine was then distillated *in vacuo*. After filtration on celite, the oily residue was chromatographed on silica gel. The mixture of the two phosphine oxides isomers **5b$_1$** and **5b$_2$** was isolated in 9% overall yield. The stereochemistry was not precise. ^{31}P NMR: isomer **5b$_1$**, 25 (d, $^1J_{PH}$ = 443 Hz); isomer **5b$_2$**, 33 ($^1J_{PH}$ = 449 Hz). ^{1}H NMR ($CDCl_3$) of the mixture: 1−1.3, 1.67, 1.5−2.5, 6.5 ($^1J_{PH}$ = 450 Hz). HRMS. Calcd for $C_8H_{15}OP$: 158.085. Found: 158.085. Calcd for $C_8H_{15}O_2P$: 174.0801. Found: 174.080.

***P*-Methyl-1,2,5,6-tetrahydro-3,4-dimethylphosphinines (4e) and Phosphine Oxides (5e).** By use of the standard protocol, the elimination reaction of the phosphine **2e** occurred in ether at 20 °C, in the presence of DBU. Phosphine oxides **5e** were isolated in *ca*. 9% yield. The free phosphine isomers **4e** and the corresponding oxides derivatives **5e** were identified by comparison of the NMR data with authentic samples.[9b]

2-Methyl-2-phosphabicyclo[2.2.2]octa-5-ene (4d) and Phosphine Oxide (5d). By use of the standard protocol, the transient phosphaalkene **3d** was formed by HCl elimination from the chlorophosphine **2d** with DABCO (20 °C) as the Lewis base and was trapped *in situ* by an excess (2 equiv) of cyclohexadiene (CHD). The free bicyclic phosphines **4d**, **4f** were characterized by their methiodide derivatives **5d**, **5f** (overall yield 27%). The NMR spectra of these adducts were identical with those of authentic samples.[8]

2-(Ethoxycarbonyl)-5-methyl-3,4-diazaphosphole (7b). By application of the standard protocol, the HCl elimination of (chloroethyl)-phosphine **2b** was induced by Et_3N at −50 °C. At the end of the reaction, the solution was filtered and the solvent evaporated *in vacuo*. The stereochemistries of the free phosphine isomers **6b$_1$** and **6b$_2$** were established by ^{31}P and ^{13}C NMR of the mixture.

Dihydrophosphole 6b$_1$ (*Z*-isomer). ^{31}P NMR (THF/C_7D_8): −69 (d, $^1J_{PH}$ = 181 Hz, $^2J_{PH}$ = 29.5 Hz, $^3J_{PH}$ = 10 Hz). ^{13}C NMR ($CDCl_3$): 14 (q, $^1J_{CH}$ = 127 Hz), 16.4 (q, $^1J_{CH}$ = 129 Hz, $^2J_{PC}$ = 4 Hz), 60 (d, $^1J_{CH}$ = 147 Hz, $^1J_{CP}$ = 12 Hz), 61 (d, $^1J_{CH}$ = 145 Hz), 62 (t, $^1J_{CH}$ = 145 Hz), 164 (s), 167 (d, $^1J_{CP}$ = 52 Hz).

Dihydrophosphole 6b$_2$ (*E*-isomer). ^{31}P NMR (THF/C_7D_8): −77 (d, $^1J_{PH}$ = 168 Hz, $^2J_{PH}$ = 7 Hz, $^3J_{PH}$ = 18 Hz). ^{13}C NMR ($CDCl_3$): 14 (q, $^1J_{CH}$ = 127 Hz), 19.5 (d, $^1J_{CH}$ = 129 Hz, $^2J_{PC}$ = 34 Hz), 56 (d, $^1J_{CH}$ = 152 Hz, $^1J_{CP}$ = 10 Hz), 62 (t, $^1J_{CH}$ = 145 Hz), 164 (s), 174 (d, $^1J_{CP}$ = 56 Hz).

The aromatization of the dihydrophospholes **6b** was achieved by low-temperature (−30 °C) P-chlorination with *N*-chlorosuccimide followed by a spontaneous HCl elimination. The reaction mixture was then allowed to warm to room temperature, and the organic layer was filtered off. The solvent was distillated *in vacuo* and the oily residue chromatographed on silica gel. Phosphole **7b** was obtained in a 17% overall yield (four step sequence). ^{31}P NMR (THF/C_6D_6): 96 (q). ^{1}H NMR ($CDCl_3$/tms): 1.3 (t, 3H, $^3J_{HH}$ = 7 Hz), 2.67 (d, 3H, $^3J_{HP}$ = 10 Hz), 4.35 (q, 2H). HRMS. Calcd for $C_6H_9O_2N_2P$: 172.04016. Found: 172.0391. Anal. Calcd: C, 41.86; H, 5.23; P, 18.02. Found: C, 41.44; H, 5.11; P, 17.68.

Ethylmethyl(isopropylthio)phosphine (8e). By application of the standard protocol, the HCl elimination of (chloroethyl)phosphine **2e** was induced by DBU in THF, in the presence of 2-propanethiol (4 equiv) at −30 °C. The reaction mixture was then stirred at 20 °C for 48 h; adduct **8e** was separated by trap to trap distillation (40% yield) and identified by comparison with an authentic sample.[9b]

Ethylphenyl(isopropylthio)phosphine (8g). By application of the standard protocol, the HCl elimination of chlorophosphine **2g** was induced by Et_3N in THF, in the presence of 2-propanethiol (4 equiv) at −80 °C. The reaction mixture was then stirred at 20 °C for 72 h; the adduct **8g** was separated by trap to trap distillation and obtained in 32% yield. ^{31}P NMR ($CDCl_3$): 22.2. ^{1}H NMR ($CDCl_3$): 1.1 (t, 3H, $^3J_{HH}$ = 23 Hz, $^3J_{HH}$ = 6.9 Hz), 1.2 (d, 6H, $^3J_{HH}$ = 6.5 Hz, 1.23 (d, 3H, $^3J_{HH}$ = 6.5 Hz), 1.7 (m, 2H), 2.95 (oct, 1H, $^3J_{HH} \approx {}^3J_{PH}$ = 6.5 Hz), 7.2 (m, 3H), 7.5 (m, 2H). ^{13}C NMR ($CDCl_3$): 6.3 (qdt, $^1J_{CH}$ = 127.2 Hz, $^2J_{CP}$ = 14 Hz, $^2J_{CH}$ = 4.2 Hz), 24.2 (tdq, $^1J_{CH}$ = 126.2 Hz, $^1J_{CP}$ = 15.7 Hz, $^2J_{CH}$ = 4.2 Hz), 25.5 (qd, $^1J_{CH}$ = 124.7 Hz, $^3J_{CP}$ = 12.8 Hz), 25.65 (qd, $^1J_{CH}$ = 124.2 Hz, $^3J_{PC}$ = 12.2 Hz), 37.9 (ddhept, $^1J_{CH}$ = 142 Hz, $^2J_{CP}$ = 20.9 Hz, $^2J_{CH}$ = 4.6 Hz), 128.3 (ddm, $^1J_{CH}$ = 158.9 Hz, $^2J_{PC}$ = 6.5 Hz), 128.5 (dm, $^1J_{CH}$ = 167 Hz), 131.5 (ddm, $^1J_{CH}$ = 154 Hz, $^3J_{CP}$ = 20.1 Hz), 139.6 (dm, $^1J_{CP}$ = 25 Hz). HRMS. Calcd for $C_{11}H_{17}SP$: 212.0789. Found: 212.0782.

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