Notes

A Simple Route to Kinetically Unstabilized Phosphaalkynes

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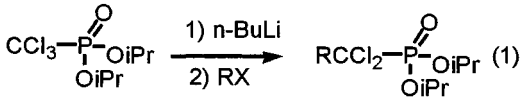
Introduction

Kinetically stabilized phosphaalkynes R−C≡P are readily available by base-induced elimination of hexamethyldisiloxane from $Me_3SiO(R)C{=}PSiMe_3$[1] As a result of the presence of both the triple bond and the phosphorus lone pair electrons, such compounds were intensively used as partners and ligands for a variety of transition metals and for the synthesis of numerous oligomers of controlled structure.[2,3] In organic chemistry, they are interesting starting materials for addition and cycloaddition reactions.[3] By contrast, the development of the chemistry of kinetically nonstabilized phosphaalkynes remains dramatically poor. That is mainly due to their relative instability and to the lack of simple and efficient synthetic approaches.[4] In 1991, we described the preparation of various phosphaalkynes by bis-dehydrohalogenation of volatile α-dichlorophosphines under vacuum gas−solid reactions conditions (VGSR technique).[5,6] Thus, simple derivatives such as HC≡P, CH_3−C≡P, or TMS−C≡P and new compounds such as Cl−C≡P have been prepared. Nevertheless, this approach needs special equipment and furthermore is rather restrictive, especially with regard to its analytical relevance. To consider such phosphaalkynes as potentially useful synthons in organophosphorus chemistry, more conventional approaches are required. The feasibility of a preparation in solution under standard conditions was reinforced by the unexpected stability of these compounds. As an example, a solution of Et−C≡P can be kept several days at room temperature without appreciable alteration.[5] We have shown several years ago that simple phosphaalkynes can be synthesized in liquid phase by rearrangement at low temperature of the corresponding 1-alkynylphosphines in the presence of catalytic amounts of Lewis base.[7] This efficient approach was however limited by the small number of easily available primary 1-alkynylphosphines. Herein we report that phosphaalkynes, substituted as well by primary or secondary alkyl groups, can be synthesized under classical conditions in a sequence involving the chemoselective reduction of an ethereal solution of α-dichlorophosphonates with $AlHCl_2$ followed by the bis-dehydrohalogenation of the resulting α-dichlorophosphines by a strong Lewis base. Scalability of the process is demonstrated by the preparation of 0.4 mol of $CH_3C{\equiv}P$.

Results and Discussion

α-Dichlorophosphonates. α-Dichlorophosphonic acid, dialkyl esters **1b**−**f**,**h** were prepared starting from the easily available trichloromethylphosphonate **1a**[8] by halogen/metal exchange followed by reaction of the resulting anion with the corresponding alkyl halide.[9−11] Compounds **1g,i** were synthesized by a similar approach starting from (2-bromoethyl)benzene and 4-bromobutene respectively (eq 1).



1a **1b-1i**

b: R = H, **c**: R = Me, **d**: R = Et, **e**: R = n-Bu,
f: R = TMS, **g**: R = $PhCH_2CH_2$,
h: R = $H_2C{=}CHCH_2$, **i**: R = $H_2C{=}CHCH_2CH_2$

The phenyl- and cyclohexyl derivatives **1j**,**k** were synthesized in a three-step sequence involving the condensation on alumina of the corresponding aldehyde with diethyl phosphite,[12] chlorination of the resulting hydroxydiethyl ester by thionyl chloride, and reaction of the formed product with BuLi and then CCl_4 (Scheme 1).[10,13]

Reduction of phosphonates **3** to phosphines **4** and dehydrochlorination of the resulting α-chlorophosphines **4** to phosphalkynes **5** are presented in the following text. For both steps, the choice of the solvent is critical and

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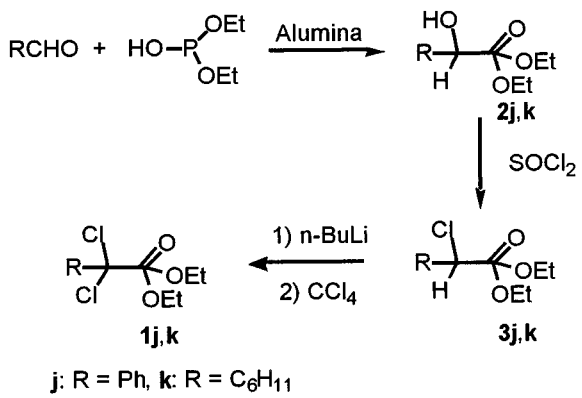
Table 1. Yields and ^{31}P NMR Data of Dichlorophosphines 4a−k and Phosphaalkynes 5a−k

phosphonate	dichlorophosphine	δ_P [ppm] ($^1J_{PH}$) [Hz]	yield [%][a]	phosphaalkyne	δ_P [ppm] ($^3J_{PH}$) [Hz]	yield [%][a]
1a	Cl_3CPH_2, **4a**	−12 (200)	71	ClC≡P, **5a**	*b*	*b*
1b	$HCCl_2PH_2$, **4b**	−78 (199)	86	HC≡P, **5b**	−32, (44.0)[c]	20
1c	$MeCCl_2PH_2$, **4c**	−46 (196)	91	CH_3C≡P, **5c**	−61, (15.0)	75
1d	$EtCCl_2PH_2$, **4d**	−56 (197)	91	EtC≡P, **5d**	−62, (15.0)	77
1e	n-$BuCCl_2PH_2$, **4e**	−53 (198)	94	*n*-BuC≡P, **5e**	−59, (14.7)	81
1f	$TMSCCl_2PH_2$, **4f**	−79 (196)	85	TMSC≡P, **5f**	*b*	*b*
1g	$PhCH_2CH_2CCl_2PH_2$, **4g**	−55 (197)	85[d]	$PhCH_2CH_2C$≡P, **5g**	−56.8, (14.9)	60[d]
1h	H_2C=$CHCH_2CCl_2PH_2$, **4h**	−57 (198)	85	H_2C=$CHCH_2C$≡P, **5h**	−52, (15.3)	75
1i	H_2C=$CH(CH_2)_2CCl_2PH_2$, **4i**	−53 (198)	85	H_2C=$CH(CH_2)_2C$≡P, **5i**	−57, (15.2)	72
1j	$PhCCl_2PH_2$, **4j**	−30 (198)	55[d]	PhC≡P, **5j**	*b*	*b*
1k	$C_6H_{11}CCl_2PH_2$, **4k**	−55 (201)	84[d]	$C_6H_{11}C$≡P, **5k**	−62 (14.9)	73[d]

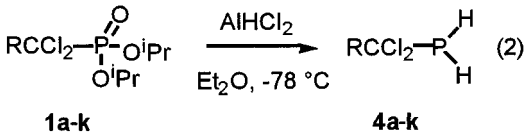
[a] Determined by ^1H or/and ^{31}P NMR spectroscopy with an internal reference. [b] Decomposition in the elimination step. [c] $^2J_{PH}$. [d] Crude product.

Scheme 1



depends on how the products (neat or in solution) have to be obtained.

α-Dichlorophosphines. The chemoselective reduction of phosphonates **1a**−**k** to the corresponding phosphines **4a**−**k** was performed in a cooled ethereal solution of dichloroalane ($AlHCl_2$) (eq 2).[14] Volatile solvents such as



diethyl ether or THF and high boiling diglymes having a melting point lower than −60 °C such as diethylene glycol dibutyl ether can be commonly used. Excess of the reducing agent was then hydrolyzed with degassed water, and the resulting solution was filtered off on Celite under a nitrogen pressure. Ethereal solutions of the low boiling phosphines **4a**−**f**,**h**,**i**, completely free of alane residues, can be obtained by trap-to-trap distillation of both volatile solvents and products from the crude mixture. In these conditions, the solutions can be kept several weeks in a freezer (−20 °C) in the presence of duroquinone as radical inhibitor. If needed, volatile phosphines can also be obtained in pure form by selective trapping on a vacuum line. The best conditions for purification of **1b**−**c** were obtained by trapping the solvent of reduction (diglyme for this purpose) at low temperature (−40 °C) and then the pure phosphines on a trap cooled at −80 °C. For **1a**,**d**−**f**,**h**,**i**, diethyl ether should be used as solvent, the dichlorophosphines being selectively trapped at −70 °C.

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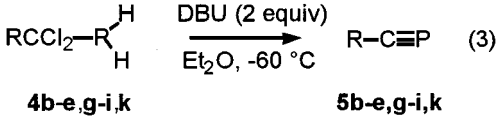
The crude nonvolatile phosphines **4g**,**j**,**k** were obtained by removing in vacuo (10^{-1} mbar) the volatile solvent at low temperature (−40 °C). In the absence of solvent, the dichlorophosphines **4a**−**k** are not stable at room temperature and consequently have to be used as formed.

Structures of phosphines **4a**−**k** were determined by ^1H, ^{31}P, and ^{13}C NMR spectroscopy. The phosphorus chemical shift range from δ_P −12 (**4a**) to −79 ppm (**4f**). All the coupling constants $^1J_{PH}$ observed by ^1H and ^{31}P NMR spectroscopy are of 198 ± 3 Hz (Table 1). The high-resolution mass spectra (HRMS) of phosphines **4a**−**i**,**k** were also recorded and are in very good agreement with the assigned structures. Attempts to get the mass spectrum of **4j** were unsuccessful, the product being too unstable in the experimental conditions. Yields determined by ^1H or by ^{31}P NMR spectroscopy with an internal reference range between 55% and 94% (Table 1).

Phosphaalkynes. For the elimination step, ethereal solutions of α-chlorophosphines **4a**−**k** are commonly used. When other solvents such as toluene are employed, they should be added to the neat phosphines **4a**−**k** after the reduction step (vide supra). The choice of the base was critical. The use of weak Lewis bases such as pyridine or triethylamine gave a complex mixture of products probably resulting from a partial HCl-elimination and in situ oligomerization of the corresponding transient phosphaalkene intermediates. The best results were obtained with a strong Lewis base. Thus, the phosphaalkynes **5b**−**e**,**g**−**i**,**k** are formed by low-temperature elimination (−60 °C) of **4b**−**e**,**g**−**i**,**k** with DBU (2.1 equiv) (eq 3). A clear solution was obtained after precipi-



tation of the salts with pentane followed by filtration on Celite under a nitrogen pressure. The low boiling phosphaalkynes **5b**−**e**,**h**,**i**, free of Lewis base, were obtained in solution by trap-to-trap distillation in vacuo and condensation on a cold trap of both volatile solvents and phosphaalkynes. Under these conditions, these solutions can be kept several days at room temperature or several months in a freezer (−20 °C) in the presence of a radical inhibitor (duroquinone). The yields determined by ^{31}P NMR spectroscopy with internal reference range from 60% to 81%. Even the very unstable parent compound **5b** (HC≡P) was prepared by this way but in a lower yield (20%). The syntheses of 3-butenylphosphaalkyne **5i** and

phenylethylphosphaalkyne **5g** are unprecedented. The presented process was extended to the preparation of the phosphaalkyne **5k** substituted by a secondary carbon, a compound usually considered as kinetically stabilized.[15] However, we failed in the attempts to prepare the more unstable derivatives ClC≡P **5a**, TMSC≡P **5f** or PhC≡P **5j**, which are accessible by bis-dehydrochlorination of the corresponding α-dichlorophosphines in gas-phase under VGSR conditions.[5]

Volatile phosphaalkynes **5b**−**e**,**h**,**i** were easily purified on the vacuum line, diglyme being in this case chosen as solvent both in the reduction and elimination steps. The boiling points of the phosphaalkynes **5g,k** are too high to allow their purification by distillation in good conditions. Consequently, crude samples of these products were obtained by removing the solvent at low temperature (−40 °C) in vacuo (10^{-1} mbar). In the absence of solvent, the phosphaalkynes **5b**−**e**,**g**−**i**,**k** are unstable at room temperature (eq 3).

Structures of the phosphaalkynes **5b**−**e**,**h** were determined by ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy and compared with the reported data.[4,5,7] The IR and mass spectra of compounds **5b**−**e** were also recorded. The structures of compounds **5g**,**i**,**k** were attributed on the basis of their NMR data. On the ^{31}P NMR spectra, the signals of phosphaakynes **5b**−**e**,**g**−**i**,**k** were observed between −32 (**5b**) and −62 (**5c**) ppm. The chemical shift and $^{3}J_{PH}$ coupling constants for **5c**−**e**,**g**−**i**,**k** (15.0 ± 0.3 Hz) are characteristic of these compounds. The signals of the ^{13}C NMR chemical shifts of the *sp* carbon atoms were observed at 158.0 ppm (HC≡P) and at 176 ± 4 ppm for all the substituted derivatives (Table 1).

The scalability of the process was demonstrated by the preparation of $CH_3C{\equiv}P$ **5c** on a 0.4 molar scale starting from the corresponding dichlorophosphonate **1c**. The general protocol was used without any modification. The overall yield (66%) was on the same order as that obtained on the analytical scale. The distilled ethereal solution (concentration ≈8%) was kept for few months in the freezer (−20 °C). Samples of this solution were drawn from time to time for various experiments. After 3 months, the decomposition was estimated to be lower than 10% (^{13}P NMR analysis).

Conclusion

A two-step sequence allowing the preparation of kinetically unstabilized phosphaalkynes under standard synthetic conditions has been presented. This process can be extended to the preparation of kinetically stabilized phosphaalkynes. The scalability is well demonstrated. This approach should contribute to the use of unstabilized phosphaalkynes in organic and organometallic chemistry. As a result of the intrinsic reactivity of these compounds, the reactions that can be performed at room temperature or below and in diluted concentration have the best opportunity to work.

Experimental Section

Caution! Phosphines and phosphaalkynes are highly oxidizable and potentially toxic molecules. All reactions should be carried out under an inert atmosphere in a well-ventilated hood.

Materials. LAH, aluminum chloride, DBU, and triisopropyl phosphite were purchased from Acros and used as received. Diethyl ether and diethylene glycol dibutyl ether (diglyme) were dried by distillation on Na/benzophenone.

General. ^{1}H (300 MHz), ^{13}C (100 MHz), and ^{31}P (121 MHz) NMR spectra were recorded on a Bruker AC-300P spectrometer, and HRMS (high-resolution mass spectrometry) experiments were performed on a Varian MAT 311 instrument. To record the mass spectra, dichlorophosphines **4** and phosphaalkynes **5** were directly introduced from a cell into the ionization chamber of the spectrometer. *All dichlorophosphines and phosphaalkynes were kept at low temperature under neutral gas in the presence of small amounts of duroquinone.*

Preparation of Dichlorophosphines (4a−k). General Procedure. A suspension of $LiAlH_4$ (0.53 g, 14 mmol) in the desired freshly distilled solvent (diethyl ether or diglyme, 30 mL) was cooled to −70 °C, and $AlCl_3$ (5.60 g, 42 mmol) was quickly added. After warming up this suspension to −10 °C and then cooling it to −80 °C, the phosphonate **1a**−**k** (10 mmol) in diethyl ether or diglyme (10 mL) was added dropwise at a rate to maintain the temperature under −60 °C. The solution was allowed to warm to −30 °C, and degassed water (5 mL) was slowly added. The mixture was then heated to 0 °C, transferred in a flask containing about 20 g of $MgSO_4$, filtered on Celite under a nitrogen pressure, and kept at low temperature (<−30 °C).

Purification of the Ethereal Solution of Low Boiling Dichlorophosphines (4a−f,h,i). When diethyl ether was used as solvent, the residual high boiling impurities contained in the crude solution of the phosphines **4a**−**f,h,i**, such as aluminum derivatives, were removing by trap-to-trap distillation in vacuo (10^{-1} mbar) of both the solvent and product. Thus, the flask was fitted on a vacuum line, and all of the low boiling compounds were evaporated and then condensed in a cold trap (77 K). Under these conditions, the solutions of dichlorophosphines **4a**−**f,h,i** can be kept for several weeks in a freezer under nitrogen.

Preparation of Pure Low Boiling Dichlorophosphines (4b,c). To obtain pure samples of phosphines **4b,c**, diglyme should be used as solvent. The filtrated mixture, prepared as reported above, was fitted on a vacuum line equipped with two cold traps. The first trap was cooled at −40 °C, and the second one, equipped with two stopcocks, was immersed in a bath cooled at −80 °C. The mixture was degassed, and the low boiling compounds were distilled in vacuo (10^{-1} mbar). The phosphines **4b,c** were selectively condensed in the second trap. At the end of the distillation, this trap was disconnected from the vacuum line, and the pure phosphines **4b,c** thus obtained were kept at low temperature (−20 °C)

Preparation of Pure Low Boiling Dichlorophosphines (4a,d−f,h,i). To obtain pure samples of phosphines **4a**,**d**−**f**,**h**,**i**, diethyl ether should be used as solvent. The flask containing the crude or the distilled ethereal solution was fitted on a vacuum line equipped with two traps. The low boiling compounds were distilled, and the phosphines **4a**,**d**−**f**,**h**,**i** were selectively condensed on the first trap cooled at −70 °C. To get a very pure compound, the procedure was repeated by cooling the second trap at −70 °C and removing the cold bath from the first one. Pure phosphines **4a**,**d**−**f**,**h**,**i** should be kept at low temperature (−20 °C).

Preparation of Crude Dichlorophosphines (4g,j,k) in the Absence of Solvent. Dichlorophosphines **4g**,**j**,**k** decompose on heating. Consequently, their boiling points are too high to allow their purification by distillation in good conditions. Ethereal solutions were concentrated by cooling the solution at −40 °C and removing the solvent in vacuo. These resulting crude products should be kept at low temperature (< −50 °C).

Trichloromethylphosphine (4a). Yield: 71%. ^{31}P NMR ($CDCl_3$) δ: −12 ($^{1}J_{PH}$ = 200 Hz). ^{1}H NMR ($CDCl_3$) δ: 5.06 (d, 2H, $^{1}J_{PH}$ = 200 Hz). ^{13}C NMR ($CDCl_3$) δ: 89.8 ($^{1}J_{CP}$ = 42.0 Hz). HRMS calcd for CH_2Cl_3P: 149.8960; found 149.895.

Dichloromethylphosphine (4b). Yield: 86%. ^{31}P NMR ($CDCl_3$) δ: −78 ($^{1}J_{PH}$ = 199 Hz). ^{1}H NMR ($CDCl_3$) δ: 4.06 (dd, 2H, $^{1}J_{PH}$ = 199 Hz, J = 4.7 Hz), 6.18 (dt, 1H, $^{2}J_{PH}$ = 7.3 Hz, J = 4.7 Hz). ^{13}C NMR ($CDCl_3$) δ: 61.6 ($^{1}J_{CP}$ = 25.7 Hz). HRMS calcd for CH_3Cl_2P: 115.9349; found 115.935. *m/z* (%): 118 (15.7), 116 (23.4), 103 (6.5), 101 (13.2), 85 (63.9), 83 (100), 80 (35.9), 45 (50.5).

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1,1-Dichloroethylphosphine (4c). Yield: 91%. ^{31}P NMR ($CDCl_3$) δ: −46 ($^1J_{PH}$ = 196 Hz). ^{1}H NMR ($CDCl_3$) δ: 2.45 (dt, 3H, $^3J_{PH}$ = 6.7 Hz, J = 0.5 Hz), 4.33 (dq, 2H, $^1J_{PH}$ = 196 Hz, J = 0.5 Hz). ^{13}C NMR ($CDCl_3$) δ: 42.0 ($^2J_{CP}$ = 8.0 Hz), 80.3 ($^1J_{CP}$ = 25.3 Hz). HRMS calcd for $C_2H_5Cl_2P$: 129.9506; found 129.951. *m/z* (%): 132 (6.8), 131 (2.0), 130 (12.0), 129 (4.7), 128 (1.6), 99 (50.0), 97 (100), 95 (35.9), 79 (9.2), 67 (22.9).

1,1-Dichloropropylphosphine (4d). Yield: 91%. ^{31}P NMR ($CDCl_3$) δ: −56 ($^1J_{PH}$ = 197 Hz). ^{1}H NMR ($CDCl_3$) δ: 1.23 (t, 3H, J = 7.1 Hz), 2.44 (qd, 2H, J = 7.1 Hz, $^3J_{PH}$ = 4.1 Hz), 4.20 (d, 2H, $^1J_{PH}$ = 197 Hz). ^{13}C NMR ($CDCl_3$) δ: 10.9 ($^3J_{CP}$ = 3.7 Hz), 45.4 ($^2J_{CP}$ = 8.0 Hz), 86.2 ($^1J_{CP}$ = 26.0 Hz). HRMS calcd for $C_3H_7Cl_2P$: 143.9662; found 143.967. *m/z* (%): 146 (2.9), 144 (4.1), 143 (12.0), 131 (33.9), 129 (47.8), 113 (23.9), 11 (54.5), 83 (17.7), 81 (26.8), 77 (25.7), 70 (90.5).

1,1-Dichloropentylphosphine (4e). Yield: 94%. ^{31}P NMR ($CDCl_3$) δ: −53.5 ($^1J_{PH}$ = 198 Hz). ^{1}H NMR ($CDCl_3$) δ: 0.96 (t, 3H, J = 7.3 Hz), 1.40 (qt, 2H, J = 7.3, 7.3 Hz), 1.69 (tt, 2H, J = 7.2,7.3 Hz), 2.41 (m, 2H, J = 7.2 Hz, $^3J_{PH}$ = 5.4 Hz), 4.24 (d, 2H, $^1J_{PH}$ = 198 Hz). ^{13}C NMR ($CDCl_3$) δ: 13.9, 22.0, 28.5, 51.7, 85.1 ($^1J_{CP}$ = 27.9 Hz). HRMS calcd for $C_5H_{11}ClP$ (M − Cl)$^+$: 137.0287; found 137.028. *m/z* (%): 146 (2.9), 144 (4.1), 143 (12.0), 131 (33.9), 129 (47.8), 113 (23.9), 11 (54.5), 83 (17.7), 81 (26.8), 77 (25.7), 70 (90.5).

1,1-Dichloro-1-trimethylsilylmethylphosphine (4f). Yield: 85%. ^{31}P NMR ($CDCl_3$) δ: −79 ($^1J_{PH}$ = 196 Hz). ^{1}H NMR ($CDCl_3$) δ: 0.32 (s, 9H), 4.05 (d, 2H, $^1J_{PH}$ = 196 Hz). ^{13}C NMR ($CDCl_3$) δ: −3.62, 73.9 ($^1J_{CP}$ = 29.8 Hz). HRMS calcd for $C_4H_{11}Cl_2PSi$: 187.9745; found 187.974. *m/z* (%): 147 (1.2), 115 (3.6), 113 (4.5), 101 (1.3), 95 (9.9), 93 (28.6), 65 (4.4), 45 (11.3).

1,1-Dichloro-3-phenylpropylphosphine (4g). Yield: 85%. ^{31}P NMR ($CDCl_3$) δ: −55 ($^1J_{PH}$ = 197 Hz). ^{1}H NMR ($CDCl_3$) δ: 2.65 (t, 2H, J = 7.9 Hz), 3.06 (m, 2H, J = 7.9 Hz), 4.30 (d, 2H, $^1J_{PH}$ = 197 Hz), 7.16−7.21 (m, 2H), 7.24−7.28 (m, 3H). ^{13}C NMR ($CDCl_3$) δ: 32.8 ($^3J_{CP}$ = 3.6 Hz), 53.8 ($^2J_{CP}$ = 6.5 Hz), 84.4 ($^1J_{CP}$ = 26.5 Hz), 126.5, 126.6, 126.6, 128.8. HRMS calcd for $C_9H_{11}Cl_2P$: 219.9975; found 219.997.

1,1-Dichloro-1-but-3-enylphosphine (4h). Yield: 85%. ^{31}P NMR ($CDCl_3$) δ: −57 ($^1J_{PH}$ = 198 Hz). ^{1}H NMR ($CDCl_3$) δ: 3.14 (tm, 2H, J = 5.7 Hz), 4.28 (d, 2H, $^1J_{PH}$ = 198 Hz), 5.30 (dm, 1H, J = 17.0 Hz), 5.32 (dm, 1H, J = 9.3 Hz), 5.95 (ddt, 1H, J = 17.0, 9.3, 5.7 Hz). ^{13}C NMR ($CDCl_3$) δ: 55.8 ($^2J_{CP}$ = 11.6 Hz), 83.1 ($^1J_{CP}$ = 25.3 Hz), 121.1 ($^3J_{CP}$ = 5.7 Hz), 131.6. HRMS calcd for $C_4H_7Cl_2P$: 155.9662; found 155.966.

1,1-Dichloro-1-pent-3-enylphosphine (4i). Yield: 85%. ^{31}P NMR ($CDCl_3$) δ: −53 ($^1J_{PH}$ = 198 Hz). ^{1}H NMR ($CDCl_3$) δ: 2.52 (m, 4H), 4.28 (d, 2H, $^1J_{PH}$ = 198 Hz), 5.07 (d, 1H, J = 10.2 Hz), 5.13 (d, 1H, J = 17.5 Hz), 5.86 (ddt, 1H, J = 17.5, 10.2, 5.9 Hz). ^{13}C NMR ($CDCl_3$) δ: 30.5 ($^3J_{PC}$ = 4.0 Hz), 50.9 ($^2J_{PC}$ = 7.2 Hz), 84.6 ($^1J_{PC}$ = 26.4 Hz), 116.0, 135.9. HRMS calcd for $C_5H_8Cl_2P$ (M − H)$^+$: 168.9741; found 168.975.

1,1-Dichloro-1-phenylmethylphosphine (4j). Yield: 55%. ^{31}P NMR ($CDCl_3$) δ: −30 ($^1J_{PH}$ = 198 Hz). ^{1}H NMR ($CDCl_3$) δ: 4.59 (d, 2H, $^1J_{PH}$ = 198 Hz), 7.04−7.21 (m, 3H), 7.80−7.84 (m, 2H). ^{13}C NMR ($CDCl_3$) δ: 83.0 ($^1J_{PC}$ = 27.6 Hz), 125.6 ($^3J_{PC}$ = 6.9 Hz), 127.6 ($^2J_{PC}$ = 17.1 Hz) 128.4, 129.1.

1,1-Dichloro-1-cyclohexylmethylphosphine (4k). Yield: 84%. ^{31}P NMR ($CDCl_3$) δ: −55 ($^1J_{PH}$ = 201 Hz). ^{1}H NMR ($CDCl_3$) δ: 1.10−2.22 (m, 11H), 4.23 (d, 2H, $^1J_{PH}$ = 201 Hz). ^{13}C NMR ($CDCl_3$) δ: 25.7, 25.9, 28.9 ($^3J_{PC}$ = 5.1 Hz), 54.7($^2J_{PC}$ = 9.9 Hz), 90.4 ($^1J_{PC}$ = 31.7 Hz). HRMS calcd for $C_7H_{12}Cl_2P$ (M − H)$^+$: 197.0054; found 197.006.

Preparation of Phosphaalkynes (5b−e,g−i,k). General Procedure. The solution of α-dichlorophosphines **5b**−**e**,**g**−**i**,**k** (50 mmol in Et_2O, diglyme or toluene) cooled to −40 °C was added dropwise through a flex needle to a cooled (−60 °C) solution of DBU (1.2 10^{-1} mol) diluted in the desired solvent (200 ml) at a rate to maintain the temperature under −60 °C. A part of the DBU−HCl salt precipitated. At the end of the addition, the mixture was allowed to warm to −10 °C. Dry and degassed pentane (100 mL) was added to the solution to precipitate all the ammonium salts. The mixture was filtrated on Celite under nitrogen and kept at low temperature (−50 °C).

Purification of the Ethereal Solutions of Low Boiling Phosphaalkynes (5b−e,h,i). When diethyl ether was used as solvent, the impurities contained in the crude ethereal solution of the phosphaalkynes **5b**−**e**,**h**,**i** (excess of DBU and residual salts) were removing by trap-to-trap distillation in vacuo (10^{-1} mbar) of both the solvents and products. Thus, the flask cooled at −10 °C was fitted on a vacuum line, the low boiling compounds were evaporated and then condensed in a cold trap (−196 °C). Thus prepared, the ethereal solutions of phosphaalkynes can be kept for several months in a freezer (−20 °C) under nitrogen.

Preparation of Pure Low Boiling Phosphaalkynes (5c−e,h,i). To obtain pure samples of phosphaalkynes **5c**−**e**,**h**,**i**, diglyme should be used as solvent both in the reduction and elimination steps. The filtered mixture was fitted on a vacuum line equipped with two cold traps. The first one was cooled at −40 °C to remove the solvent, and the second one cooled at −120 °C allowed the trapping of the phosphaalkynes **5c**−**e**,**h**,**i** selectively. The mixture was degassed, and the low boiling compounds were distilled in vacuo (10^{-1} mbar). At the end of the distillation, this trap was disconnected from the vacuum line. In these conditions, the pure phosphaalkynes **5c**−**e,h**,**i** should be kept at low temperature (< −80 °C).

Preparation of Crude Phosphaalkynes (5g,k) in Absence of Solvent. Phosphaalkynes **5g**,**k** decompose on heating, their boiling point being too high to allow their purification by distillation in good conditions. When diethyl ether or toluene are used as solvent, solutions of dichlorophosphines **5g**,**k** can be concentrated by cooling the solution at −40 °C and removing the solvent in vacuo. Crude products **5g**,**k** should be kept at low temperature (< −80 °C).

Methylidynephosphine (5b). Yield: 20%. ^{31}P NMR ($CDCl_3$) δ: −32 ($^2J_{PH}$ = 44.0 Hz). ^{1}H NMR ($CDCl_3$) δ: 2.90 (d, $^2J_{PH}$ = 44.0 Hz). ^{13}C NMR ($CDCl_3$) δ: 158.0 ($^1J_{PC}$ = 56.0 Hz). HRMS calcd for CHP: 43.98159; found 43.9818. IR (neat, 77 K): 1267 cm^{-1} ($\nu_{C\equiv P}$).

Ethylidynephosphine (5c). Yield: 75%. ^{31}P NMR ($CDCl_3$) δ: −61 ($^3J_{PH}$ = 15.0 Hz). ^{1}H NMR ($CDCl_3$) δ: 2.44 (d, 3H, $^3J_{PH}$ = 15.0 Hz). ^{13}C NMR ($CDCl_3$) δ: 15.6 ($^2J_{PC}$ = 20 Hz), 170.8 ($^1J_{PC}$ = 49.0 Hz). HRMS calcd for C_2H_3P: 57.99724; found 57.9972. IR (neat, 77 K): 1559 cm^{-1} ($\nu_{C\equiv P}$).

Propylidynephosphine (5d). Yield: 77%. ^{31}P NMR ($CDCl_3$) δ: −62 ($^3J_{PH}$ = 15.0 Hz). ^{1}H NMR ($CDCl_3$) δ: 1.17 (t, 3H, J = 7.5 Hz), 2.34 (dq, 2H, $^3J_{PH}$ = 15.0 Hz, J = 7.5 Hz). ^{13}C NMR ($CDCl_3$) δ: 14.8 ($^3J_{PC}$ = 7.6 Hz), 19.4 ($^2J_{PC}$ = 19.4 Hz), 177.0 ($^1J_{PC}$ = 44.3 Hz). HRMS calcd for C_3H_5P: 72.01289; found 72.0131. IR (neat, 77 K): 1552 cm^{-1} ($\nu_{C\equiv P}$).

Pentylidynephosphine (5e). Yield: 81%. ^{31}P NMR ($CDCl_3$) δ: −59 ($^3J_{PH}$ = 14.7 Hz). ^{1}H NMR ($CDCl_3$) δ: 0.91 (t, 3H, J = 7.3 Hz), 1.45 (tq, 2H, J = 7.3, 7.3 Hz), 1.53 (tt, 2H, J = 7.3, 6.8 Hz), 2.37 (td, 2H, $^3J_{PH}$ = 14.7 Hz, J = 6.8 Hz). ^{13}C NMR ($CDCl_3$) δ: 13.6, 21.6, 29.3 ($^2J_{PC}$ = 19.6 Hz), 31.7 ($^3J_{PC}$ = 6.6 Hz), 176.4 ($^1J_{PC}$ = 43.0 Hz). HRMS calcd for C_5H_9P: 100.0442; found 100.044. IR (neat, 77 K): 1545 cm^{-1} ($\nu_{C\equiv P}$).

3-Phenylpropylidynephosphine (5g). Yield: 60%. ^{31}P NMR ($CDCl_3$) δ: −56.8 ($^3J_{PH}$ = 14.9 Hz). ^{1}H NMR ($CDCl_3$) δ: 2.60 (m, 2H, J = 6.6 Hz), 3.08 (m, 2H, J = 6.6 Hz), 7.15−7.28 (m, 5H). ^{13}C NMR ($CDCl_3$) δ: 29.9 ($^3J_{PC}$ = 7.0 Hz), 35.3 ($^2J_{PC}$ = 7.0 Hz), 126.4, 128.4, 128.6, 140.1, 174.0 ($^1J_{PC}$ = 45.3 Hz).

But-3-enylidynephosphine (5h). Yield: 75%. ^{31}P NMR ($CDCl_3$) δ: −52 ($^3J_{PH}$ = 15.3 Hz). ^{1}H NMR ($CDCl_3$) δ: 2.73 (ddt, 2H, $^3J_{PH}$ = 15.3 Hz, J = 5.4, 1.7 Hz), 4.92 (ddt, 1H, J = 9.9, 1.7, 1.7 Hz), 5.12 (ddt, 1H, J = 17.0, 1.7, 1.7 Hz), 5.50 (ddtd, 1H, J = 17.0, 9.9, 5.4 Hz, $^4J_{PH}$ = 0.9 Hz). ^{13}C NMR ($CDCl_3$) δ: 33.3 ($^2J_{PC}$ = 19.5 Hz), 116.4, 132.0 ($^3J_{PC}$ = 6.9 Hz), 170.2 ($^1J_{PC}$ = 46.3 Hz). HRMS calcd for C_4H_5P: 84.01289; found 84.0128.

Pent-4-enylidynephosphine (5i). Yield: 72%. ^{31}P NMR ($CDCl_3$) δ: −57 ($^3J_{PH}$ = 15.2 Hz). ^{1}H NMR ($CDCl_3$) δ: 2.31 (m, 2H, J = 6.5 Hz), 2.46 (m, 2H, J = 6.5, 6.6 Hz), 5.03 (m, 1H, J = 10.3 Hz), 5.08 (m, 2H, J = 17.0 Hz), 5.82 (m, 1H, J = 6.6, 10.3, 17.0 Hz). ^{13}C NMR ($CDCl_3$) δ: 28.7 ($^2J_{PC}$ = 19.7 Hz), 33.0 ($^3J_{PC}$ = 7.2 Hz), 115.4, 135.6, 173.8 ($^1J_{PC}$ = 45.0 Hz). HRMS calcd for C_5H_7P: 98.02854; found 98.0284.

1-Cyclohexylmethylidynephosphine (5k). Yield: 73%. ^{31}P NMR ($CDCl_3$) δ: −62 ($^3J_{PH}$ = 14.9 Hz). ^{1}H NMR ($CDCl_3$) δ: 1.12−1.67 (m, 10H), 2.25 (m, 1H). ^{13}C NMR ($CDCl_3$) δ: 24.4, 25.4, 33.1, 38.8 ($^2J_{PC}$ = 18.9 Hz), 129.1 ($^3J_{PC}$ = 6.6 Hz), 180.4 ($^1J_{PC}$ = 35.5 Hz).

Preparative Synthesis of (5c). A suspension of $LiAlH_4$ (22.8 g, 0.6 mol) in freshly distilled diethyl ether (400 mL) was cooled to −70 °C, and $AlCl_3$ (240 g, 1.8 mol) was added in several portions. After warming up to −10 °C, then cooling to −80 °C, the phosphonate **1c** (157.2 g, 0.6 mol) in diethyl ether (200 mL)

was added dropwise at a rate to maintain the temperature under −70 °C. The mixture was then allowed to warm to −10 °C. To remove the aluminum salts, purification of the ethereal solution of **4c** was performed by distillation in vacuo and condensation of the low boiling compounds in a 1 L three-necked flask immersed in a liquid nitrogen bath. This solution cooled to −40 °C was then added dropwise through a flex needle to a cooled (−90 °C) solution of DBU (192 g, 1.26 mol) in Et_2O (200 mL) at a rate to maintain the temperature under −60 °C. A salt (DBU−HCl) precipitated. At the end of the addition, the mixture was allowed to warm to −10 °C and purified by distillation in vacuo and condensation of the volatile products at low temperature (−196 °C). The overall yield was estimated to be 66% (0.4 mol of CH3C≡P) by ^{1}H and ^{31}P NMR spectroscopy with two 200 μL samples of solution using respectively 5 μL of dichloromethane and 5 μL of Bu_3P as internal reference. Solutions of **5c** were kept several months in a freezer.

Supporting Information Available: 400-MHz ^{1}H, 100-MHz ^{13}C and 121-MHz ^{31}P NMR spectral data of phosphonates **1g**,**i**,**k**, **2k**, **3k**. Copies of ^{1}H and ^{13}C NMR spectra for compounds **1g**, **1i**, **1k**, **2k** and **3k**. This material is available free of charges via the Internet at http://pubs.acs.org.

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