JOC The Journal of Organic Chemistry

ARTICLE

pubs.acs.org/joc

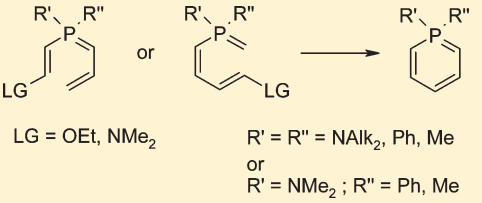
Electrocyclization of Phosphahexatrienes: An Approach to λ^5-Phosphinines

Yurii V. Svyaschenko, Bogdan B. Barnych, Dmitriy M. Volochnyuk, Nadiya V. Shevchuk, and Aleksandr N. Kostyuk*

Institute of Organic Chemistry, National Academy of Sciences of Ukraine, Murmanska 5, Kyiv-94, 02094, Ukraine

Supporting Information

ABSTRACT: We experimentally verified an assumption that the substitution of a carbon atom with a pentavalent phosphorus atom in 1-alkoxy (dialkylamino) hexatrienes will not hamper its ability to electrocyclize. A series of 1-, 3-, and 5-phosphahexatrienes were synthesized. It was shown that parent λ^5-phosphinines could be synthesized by electrocyclization of the 3- and 5-phosphahexatrienes. The resultant electrocyclization is a convenient method for the synthesis of parent λ^5-phosphinines bearing different substituents on the phosphorus atom.



INTRODUCTION

Electrocyclization of 1,3,5-hexatrienes into cyclohexadienes has been thoroughly studied and widely used in organic chemistry because the oxidation or elimination of leaving groups from the intermediate cyclohexadienes affords benzene derivatives. The method has mainly been used for the synthesis of complex natural compounds. Detailed theoretical studies of these reactions allow one to promote a slower reaction by placing proper substituents at the 1,3,5-hexatrienes.[1] Its synthetic utility has been further enhanced by finding a catalytic version of the reaction that allows the synthesis of complicated molecules under mild conditions.[2] It is also well-known that a carbon atom in hexatrienes can be replaced by a nitrogen atom, and the resulting aza-homologues undergo cyclization as well.[3] This method appears to be quite practical and has been used in many syntheses of natural compounds.[4]

In this paper we studied and analyzed whether carbon in hexatriene can be replaced by heavier atoms and still allow the molecule to keep its ability to electrocyclize. For a long time, phosphorus has been thought to mimic a carbon in many respects. Indeed, there are many examples of analogous behavior.[5] The analogy can be demonstrated on the parent λ^3-phosphinine, which possesses aromaticity comparable to that of benzene.[6] Experimentally, the parent λ^3-phosphinine was prepared by flash vacuum pyrolysis of vinyldiallylphosphine at 700 °C. Researchers claimed that it formed via electrocyclization, and the most plausible pathway was proposed based on DFT calculations.[7]

Our attention was focused on the cyclization of 1-dialkylamino-1,3,5-hexatrienes, where it was shown that the introduction of an oxygen- or nitrogen-containing substituent at C-1 has a small effect versus the parent 1,3,5-hexatriene. Also, the neutral and anionic 2-hydroxy-1,3,5-hexatrienes have been shown to have activation energies for these processes of 29.9 and 29.6 kcal/mol, respectively. The activation energy for electrocyclization is strongly dependent upon substituents in the 1-amino-1,3,5-hexatriene. The process can be made more facile by introducing a strong electron-withdrawing group at the second and fourth positions.[8] In previous work, we have already used this approach in the synthesis of λ^5-phosphinines and have shown that such cyclization is possible for 1-dialkylamino-3(and 5)-phosphahexa-1,3,5-trienes[9a] and 1-hydroxy-3-phosphahexa-1,3,5-trienes.[9b] Moreover, we have also demonstrated that cyclization of 1-dialkyl amino-3 (or 5)-phosphazahexa-1,3,5-trienes is possible.[9c]

Literature analysis of λ^5-phosphinines reveals that no general methods for their synthesis have been proposed, with λ^3-phosphinines[10] remaining as the main starting materials for the synthesis of most λ^5-phosphinines.[11] It is worth mentioning that a few known parent phosphinines are difficult to access. Summarizing these facts, we assume that electrocyclization of phosphahexa-1,3,5-trienes might be a convenient approach to synthesize parent λ^5-phosphinines. Moreover, taking into account the fact that the methods for synthesizing parent λ^3-phosphinine and λ^5-phosphinines are quite scarce, we decided to systematically study phosphahexatrienes that bear an electron-donating group such as dialkyl amino or alkoxy groups at the first position and then move the phosphorus atom from the first to sixth position as presented in Figure 1.

It was our objective to use this approach for the synthesis of previously little studied, hardly accessible parent λ^5-phosphinines **VII**. As the starting hexatrienes **I**−**VI** are unstabilized ylids, the proposed synthetic approach envisages their formation from the corresponding phosphonium salts at the final stage. In this work we have designed and tested synthetic schemes for **I**, **III**, and **V** phosphahexatrienes.

Synthesis of parent λ^5-phosphinines **VII** by electrocyclization would be of great importance because convenient approaches to these rather scarce compounds would make their further study possible.

Received: April 26, 2011
Published: June 21, 2011

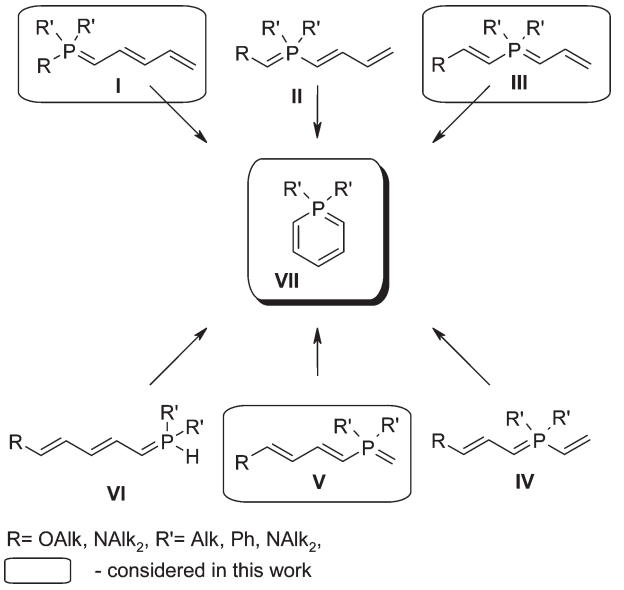
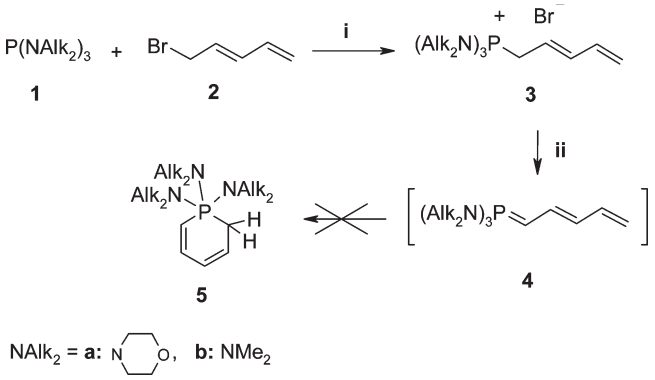


Figure 1. Types of hexatrienes studied in the cyclization.

Scheme 1. Reagents and Conditions[a]



[a] **i**, for **11a:** toluene, 40 °C, 3 h, for **11b:** hexane, 3 h; **ii**, THF, *n*-BuLi.

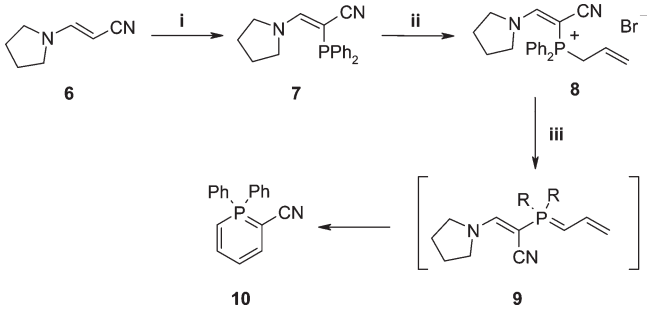
RESULTS AND DISCUSSION

In our investigation we started by synthesizing 1-phospha-1,3,5-hexatrienes. It should be noted that compounds of this type are described in the literature as extended ylides for Wittig reactions.[12] Nevertheless, no examples of cyclization are mentioned. All these compounds have only aryl (alkyl) substituents on the phosphorus atom, so our aim was to introduce dialkylamino groups on the phosphorus atom and study their cyclization.

We synthesized ylids **4** by the reaction of hexaalkylphosphorus triamides **1** with penta-2,4-dienyl bromide **2**,[13] followed by treatment with a base. Formation of ylid **4** was confirmed by ^{31}P NMR spectra of the reaction mixture, but isolation of **4** in pure state failed. Nevertheless, even on prolonged standing and heating the reaction mixture cyclization failed (Scheme 1).

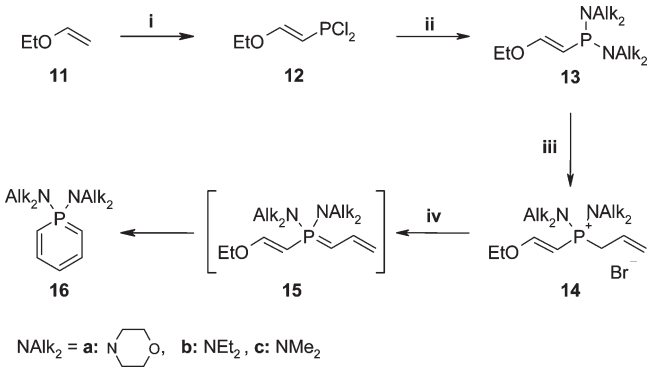
Our experience with phosphorylated enamines was applied to the synthesis of hexatrienes **III**. For further investigation we selected the stable push−pull enamine **6** bearing a nitrile group. It easily reacted with diphenyl chlorophosphine giving phosphine **7**, which is a crystalline, stable compound. Treatment of phosphine **7** with allyl bromide in boiling benzene afforded phosphonium salt

Scheme 2. Reagents and Conditions[a]



[a] **i**, Ph_2PCl, Et_3N, CH_2Cl_2, 3 days; **ii**, CH_2=$CHCH_2Br$, benzene, reflux, 7 h; **iii**, THF, *n*-BuLi, −78 °C, 1 h, rt, 1 day.

Scheme 3. Reagents and Conditions[a]



[a] **i**, PCl_3, Et_3N, CH_2Cl_2, 2 days; **ii**, hexane, $HNAlk_2$, for **a:** $HN(C_2H_4)_2O$ and Et_3N; **iii**, CH_2=$CHCH_2Br$, CH_2Cl_2; **iv**, THF, *n*-BuLi, −78 °C, 1 h.

8. It was treated with *n*-butyl lithium in THF that led directly to phosphinine **10** (Scheme 2). The reaction proceeded quickly and our attempts to register intermediate phosphahexatriene **9** by ^{31}P NMR spectroscopy of the reaction mixture failed.

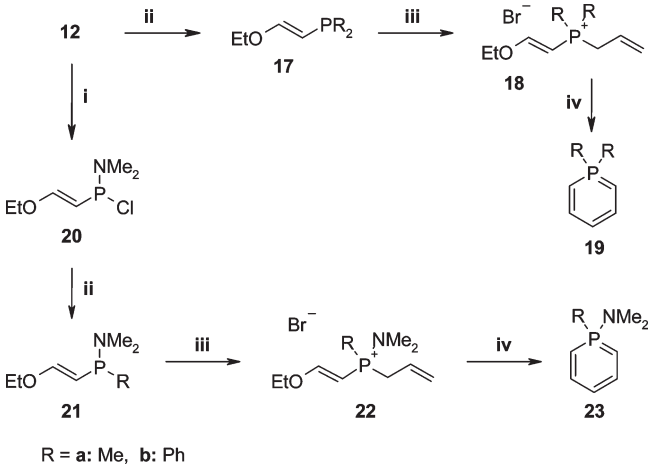
Unfortunately, the phosphorylation of enamine **6** with other phosphorylating agents, such as PCl_3, $PhPCl_2$, is quite complicated and does not lead to individual phosphorylated enamines. Thus, we were unable to extend this approach to other derivatives.

As the main object of our study is parent λ^5-phosphinines, it was logical to use *N,N*-dialkylvinylamines as the most suitable starting materials. Despite their relative availability,[14] these compounds are unstable and prone to polymerization. These enamines are generated in situ, and for a short period of time (<24 h) they can be stored at low temperature. Moreover, phosphorylation of enamines of this type has not been studied extensively, and C-phosphorylated derivatives are shown to have quite labile C−P bonds. Thus, it was impossible to use them as the starting materials. At the same time, there are well documented procedures in the literature for the synthesis of dichlorophosphine **12** from ethyl vinyl ether, which is a stable, easily available compound,[15] so it was used for further transformations (Scheme 3).

Thus, dichlorophosphine **12** easily reacted with 2-fold excess of dialkylamines, affording diamides **13**, which are stable distillable compounds. They readily reacted with allyl bromide, giving phosphonium salts **14**, precursors to 3-phosphahexatrienes. Further treatment of phosphonium salts **14** with *n*-BuLi in THF

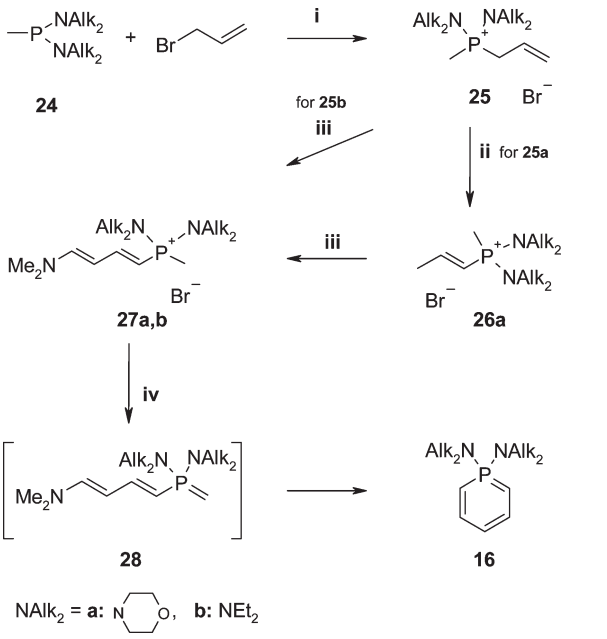
dx.doi.org/10.1021/jo200847r |*J. Org. Chem.* 2011, 76, 6125–6133

Scheme 4. Reagents and Conditions[a]



[a] **i**, 1 eqiv of **13c** neat; **ii**, RLi or RMgX, THF; **iii**, $CH_2{=}CHCH_2Br$, CH_2Cl_2; **iv**, THF, *n*-BuLi, −78 °C, 1 h.

Scheme 5. Reagents and Conditions[a]



[a] **i**, for **20a:** benzene, rt, 1 day, for **20b:** hexane, rt, 1 day; **ii**, pyridine, Et_3N, reflux, 4 h; **iii**, *i*-PrOH, DMFDMA, reflux, for **26a:** 16 h, for **26b:** 9 days; **iv**, THF, *n*-BuLi, −78 °C, 1 h, rt, 1 day.

at −78 °C led directly to the targeted phosphinines **16**. The reaction proceeded spontaneously at this low temperature, but we were unable to register signals of intermediary ylids **15** by ^{31}P spectroscopy.

This approach proved to be very convenient for the synthesis of parent λ^5-phosphinines with various substituents on the phosphorus atom. Thus, dichlorophosphine **12** readily reacted with aryl and alkyl C-nucleophiles, affording phosphines **17**, with both Grignard reagents and organo lithium compounds being highly efficient. Phosphonium salts **18** were prepared in good yields with allyl bromide. Previously known phosphinines **19a,b** were prepared by treatment of salts **18** with a strong base (Scheme 4).

It should be noted that previously these phosphinines were prepared by other methods. Thus, 1,1-dimethyl-λ^5-phosphinine was synthesized by Ashe et al. by interaction of λ^3-phosphinine with MeLi and water, followed by quaternization with methyl iodide and deprotonation with dimsyl anion.[16a,b] The synthetic approach to 1,1-diphenyl-λ^5-phosphinine by Märkl was double alkylation of potassium phosphide with 1,5-bis halogen derivatives followed by oxidation.[16c]

This approach is also very convenient for the synthesis of λ^5-phosphinines bearing different substituents at the phosphorus atom. Thus, dichlorophosphine **12** and diamide **13c** reacted neat, giving dimethyl amido chlorophosphine **20**. Unfortunately, further reaction of compound **20** with Grignard's reagents led to a mixture of **17**, **13c**, and **21** in equal ratio, so for the preparation of amides **21**, only organo lithium compounds were used as C-nucleophiles. Phosphonium salts **22** were readily prepared by alkylation with allyl bromide. As in previous cases, phosphonium salts **22** were directly transformed into the corresponding 1-R-1-*N*,*N*-dimethyl-amino-λ^5-phosphinines **23a,b** upon treatment with a strong base (Scheme 4). Thus, we have developed a new approach to parent λ^5-phosphinines allowing varying substituents at the phosphorus atom. It should be noted that parent phosphinines that bear different substituents at the phosphorus atom were described by Quin et al. These compounds were characterized but not separated as individual compounds.[17]

Previously we have reported on the cyclization of 5- and 3-phosphahexatrienes, which affords phosphinines.[9a] On the basis of these results, we assume that parent λ^5-phosphinines **16** can also be synthesized via 5-phosphahexatrienes by the route proposed in Scheme 5. Starting phosphonites **24** were alkylated with allyl bromide, affording phosphonium salts **25**. Further, it was necessary to elongate the carbon chain to access phosphahexatrienes. Salt **25a** was isomerized into salt **26a** that reacted with DMFDMA to give **27a**. The insertion of a dimethyl amino methylene group proceeded exclusively at the terminal methyl group of the propenyl substituent, leaving the methyl group on the phosphorus atom intact. Monitoring the reaction by ^{31}P NMR spectroscopy indicated the presence of only one product that was proved to be salt **27a**. We have also shown that salts **27** can be prepared directly from salts **25**. Thus, refluxing salt **25b** with DMFDMA in isopropanol led directly to salt **27b** in almost quantitative yield. Again we did not observe any products resulting from insertion of the dimethyl amino methylene group, either at the methyl group on the phosphorus atom or on the methylene group. Nevertheless, this method has the disadvantage of requiring a reaction time 10 times longer than the analogous reaction of salts **26**.

Salts **27** are precursors to 5-phosphahexatrienes. Indeed, treatment of salts **27** with *n*-BuLi led to formation of 5-phosphahexatrienes **28** that spontaneously cyclized to λ^5-phosphinines **16**.

5-Phosphahexatrienes **28** can be registered spectroscopically by ^{31}P NMR, contrary to 3-phosphahexatrienes **15**. Thus, the addition of *n*-BuLi to phosphonium salts **27** at −70 °C for 30 min results in a ^{31}P NMR spectra, which exhibits three signals that correspond to the starting salts **27** (δ_P = 57.5 ppm), the final phosphinine **16** (poorly resolved triplet at δ_P = 46.3 ppm), and the ylid **28** (broadened multiplet at 73.5−75.5 ppm) (Figure 2). Keeping the reaction mixtures at room temperature for an additional 12 h leads to disappearance of all signals, with the exception of the final phosphinines **16**. Heating the reaction mixture facilitates the reaction so that phosphinines form almost immediately.

dx.doi.org/10.1021/jo200847r |*J. Org. Chem.* 2011, 76, 6125–6133

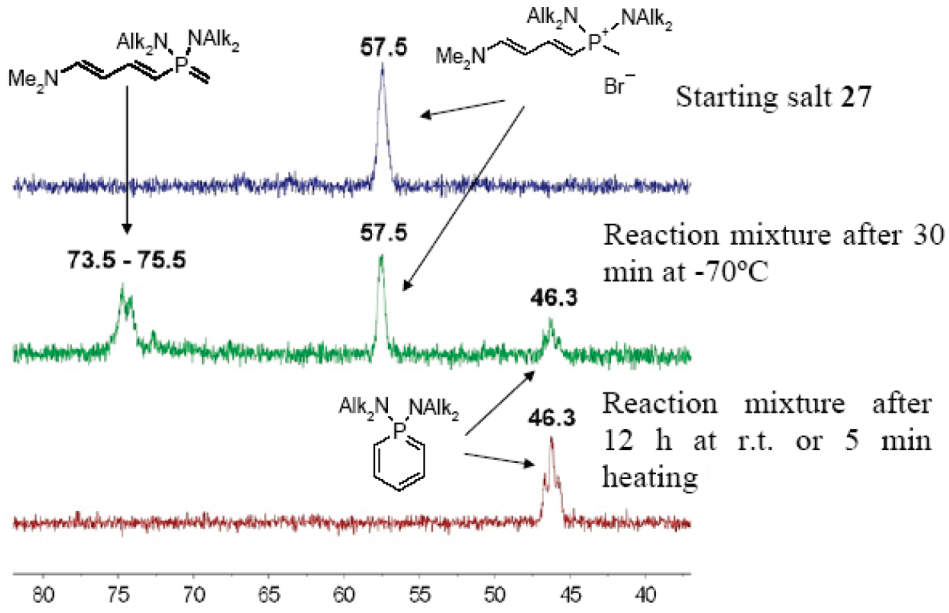


Figure 2. ^{31}P NMR studies of transformation of salt **27** into phosphinine **16** via ylid **28**.

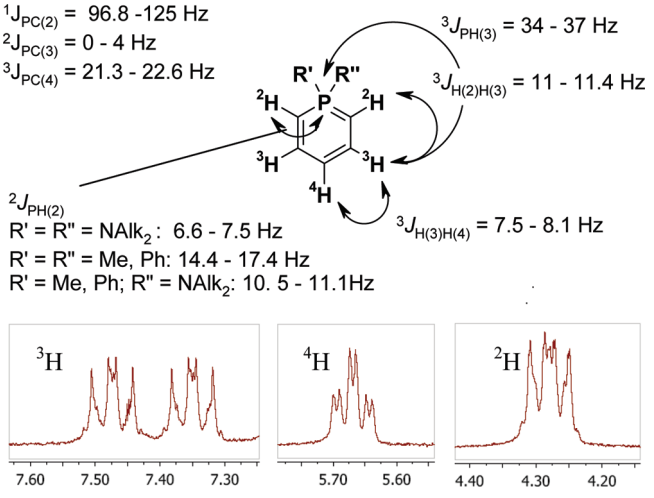


Figure 3

Despite a plethora of literature data on λ^5-phosphinines, there are only a few examples of parent λ^5-phosphinines. These are the above-mentioned 1,1-dimethyl-λ^5-phosphinine and 1,1-diphenyl-λ^5-phosphinine, as well as three unsymmetrical λ^5-phosphinines prepared by silylation of 1,6-dihydrophosphinine-l-oxides.

Parent λ^5-phosphinines are relatively stable compounds and can be exposed to air for a short time, but on longer exposure they visibly darken and decompose. Thus, they should be stored in a freezer under inert atmosphere.

^{1}H NMR spectra of parent λ^5-phosphinines (in C_6D_6) exhibited three multiplets of the heterocyclic core. Their complex multiplicity is due to spin−spin interactions of all protons with the phosphorus atom. Mean values of spin−spin coupling constants and their characteristic appearances are given in Figure 3. It is worth mentioning that substituents at the phosphorus atom markedly influence spin−spin coupling constants between the phosphorus atom and ortho protons of the phosphinine. When going from dialkylamino substituents to alkyl and aryl ones, spin−spin coupling constants increase 2−2.5 times (Figure 3); meta and para spin−spin coupling constants in all cases remain roughly the same.

Table 1. Chemical Shifts ^{1}H and ^{13}C NMR Spectra for Core of Phosphinines 16, 19, 23

	^{1}H NMR chemical shifts			^{13}C NMR chemical shifts		
R′, R″	^{2}H	^{3}H	^{4}H	^{2}C	^{3}C	^{4}C
$N(CH_2CH_2)_2O$	4.28	7.35	5.66	72.3	140.4	99.3
NEt_2 $^{(CDCl_3)}$	4.54	7.46	5.71	75.6	138.9	97.7
NMe_2	4.48	7.45	5.70	71.1	140.2	99.1
Me	3.9	7.14	5.24	66.4	140.3	96.2
Ph $^{(CDCl_3)}$	4.36	7.11	5.05	65.9	139.4	96.0
Me, NMe_2	4.41	7.39	5.64	72.4	139.6	98.6
Ph, NMe_2	4.61	7.44	5.70	70.7	139.8	99.3

The reverse tendency is observed for ^{13}C NMR spectra. Thus, the direct spin−spin coupling constants between the phosphorus and C2 and C6 atoms is ∼125 Hz for dialkylamino derivatives, which is 25−30 Hz more than for methyl and phenyl derivatives and 15 Hz more for unsymmetrical derivatives having a dialkylamino group and alkyl (aryl) group.

Chemical shifts of ortho protons at the phosphinines and chemical shifts of carbon atoms directly bound to the phosphorus atom are quite sensitive to substituents at the phosphorus atom, with dialkylamino substituents shifting them downfield (Table 1).

Besides NMR investigation, the structure of phosphinine **16a** was unambiguously proved by X-ray diffraction study. It is the first X-ray study of parent λ^5-phosphinines. The phosphinines **16a** have an almost symmetrical and planar structure of the core (the mean deviation from the plane is 0.0225 Å; Figure 4). Geometric parameters of the central core are close to the parameters of previously investigated related 1,1-(bis)dimethylamino-2,4,6-triphenylphosphinine.[18] The phosphorus−nitrogen bond lengths

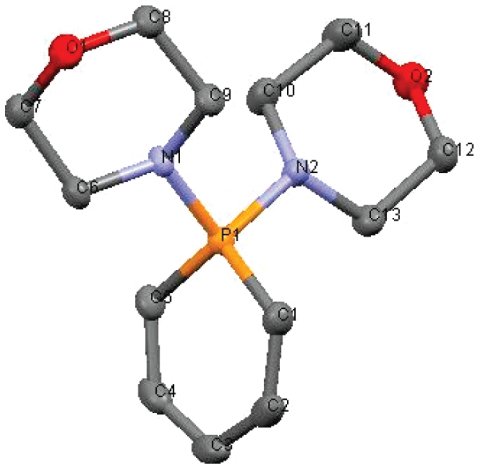


Figure 4. The X-ray crystal structure of λ^5-phosphinine **16a**. H atoms were omitted for clarity. Selected bond lengths [Å] and angles [deg]: P(1)−C(1) 1.719, C(1)−C(2) 1.385, C(2)−C(3) 1.390, C(3)−C(4) 1.392, C(4)−C(5) 1.376, C(5)−P(1) 1.718, C(5)−P(1)−C(1) 104.76, N(1)−P(1)−N(2) 99.11.

are almost equivalent: 1.6785(11) and 1.6865(11). Geometric parameters of morpholine substituents are usual.

CONCLUSIONS

In conclusion we have demonstrated that phosphahexatrienes that bear phosphorus at the 3- and 5-positions can be cyclized. The proposed method is very convenient for the synthesis of parent λ^5-phosphinines, especially starting with ethyl vinyl ether. Thus, these compounds can now be prepared in bulk quantities. It is worth continuing these synthetic efforts to synthesize other phosphahexatrienes to check their suitability for the synthesis of phosphinines.

EXPERIMENTAL SECTION

General Comments. All procedures with compounds sensitive to hydrolysis and oxidation were carried out in an atmosphere of dry argon. All solvents were purified and dried by standard methods. ^{1}H spectra were recorded at 300 or 500 MHz; C_6D_6, $CDCl_3$ or DMSO-d_6 as solvents with TMS as an internal standard; ^{31}P NMR spectra were recorded at 81 MHz with 85% H_3PO_4 as an external standard. For all compounds, phosphorus spectra were recorded in the same solvent that was used for taking up ^{1}H NMR spectra.

The peak assignments in the NMR spectra of the compounds **10** and **16a** were confirmed by COSY and HSQC 2D correlations. LC/MS (APCI MS) spectra for compounds **3b**, **7**, **8**, **10**, **18a** and **21a** were recorded using a chromatography/mass spectrometric system. Mass spectra (EI, 70 eV) for compounds **13a**, **16a**−**c**, **17b**, **19b**, **20** and **23a,b** were obtained by direct inlet. Compounds **13b,c** and **17a** were oxidized to appropriate phosphorus oxides in a mass spectrometer and mass spectra are shown for their phosphorus oxides. FAB mass spectra for **3a**, **b**, **14a**−**c**, **18b**, **22b**, **25a,b**, **26b**, **27a,b** substances were recorded. Microanalyses were obtained using elemental microanalyzers. Melting points are uncorrected. Yields refer to pure isolated products.

General Procedures. *Synthesis of Phosphonium Salts* ***3***. To a solution of pent-2,4-dien-yl bromide **2** (0.87 g, 6 mmol) in hexane (10 mL), hexa alkylphosphorus triamide **1** (6 mmol) was added with stirring. The reaction mixture was left for 3 h with stirring. The precipitated solid was collected by filtration and washed with hexane. (For **1a** toluene at 40 °C was used.)

Synthesis of Phosphonous Diamides ***13***. To a stirred solution of (2-ethoxyvinyl)phosphonous dichloride **12** (3 g, 16.8 mmol) in hexane (20 mL) was added a solution of morpholine (33.6 mmol) and Et_3N (33.6 mmol) dropwise for **13a** or the corresponding amine (67.2 mmol) for **13b,c** in hexane (20 mL) at 0−5 °C. The reaction mixture was stirred for 1 day at rt. The precipitated solid was filtered off and the filtrate was evaporated in vacuo. For **13b,c** the residue was distilled in vacuo (0.03 Torr, bp 76−81 °C for 13b, 78 °C for **13c**).

Synthesis of Phosphines ***17***. To a stirred solution of (2-ethoxyvinyl)-phosphonous dichloride **12** (5 g, 28.9 mmol) in Et_2O (20 mL) was added dropwise a solution of CH_3MgI for **17a** or PhMgBr for **17b** (57.8 mmol) in Et_2O (40 mL) at −50 °C. The reaction mixture was stirred for 3 h and was allowed to warm to rt, and then the solution of NH_4Cl (4.64 g, 86.7 mmol) in deoxygenated water (30 mL) was added. The reaction mixture was stirred for 1 day at rt. The organic layer was separated, dried (Na_2SO_4), and evaporated in vacuo.

Synthesis of Phosphinous Amides ***21***. To a stirred solution of phosphonamidous chloride **20** (1 g, 5.5 mmol) in THF (30 mL) was added a solution of CH_3Li for **21a** or PhLi for **21b** (5.5 mmol) dropwise. The reaction mixture was stirred for 1 h, allowed to warm to rt, and evaporated in vacuo. The residue was extracted with pentane; the residue was distilled using a short path vacuum distillation apparatus.

Synthesis of Allyl Phosphonium Salts ***14, 18, 22***. To a stirred solution of phosphonous diamide **13** for **14**, phosphine **17** for **18** or phosphinous amide **21** for **22** (6.6 mmol) in CH_2Cl_2 (10 mL), allyl bromide (0.8 g, 6.6 mmol) was added. The reaction mixture was stirred at rt for 3 h and evaporated in vacuo. The residue was washed with hexane.

Synthesis of Allyl Phosphonium Salts ***8, 25***. To a stirred solution of phosphine **7** or phosphonite **24** (3.3 mmol) in benzene (for **25b** hexane) (10 mL), a solution of allyl bromide (0.4 g, 3.3 mmol) was added. The reaction mixture was refluxed with stirring for 7 h for **8** or stirred for 1 day for **25**. The precipitated solid was collected by filtration and washed with an appropriate solvent.

Synthesis of Phosphonium Salts ***27***. To a solution of **26a** for **27a** or **25b** for **27b** (2.9 mmol) in isopropanol (20 mL), DMADMF (3.5 g, 3.91 mL, 0.029 mol) was added with stirring. The reaction mixture was refluxed for 16 h for **27a** or 9 days for **27b**. The solvents were evaporated and the residue was triturated with heptane. The solid was collected, washed with heptane, and dried.

Synthesis of λ^5-Phosphinines ***10, 16, 19, 23***. To a suspension of allyl phosphonium salts **8**, **14**, **18**, **22** or salt **27** (2 mmol) in THF (20 mL) cooled to −78 °C, a solution of *n*-BuLi (4 mmol, 2.5 M, 1.62 mL) was added with stirring. The reaction mixture was stirred 1 h, allowed to warm to rt, and was kept stirring for 12 h.

For **10**: The reaction mixture was evaporated and the residue was extracted with $CHCI_3$ (3 × 10 mL). The solution was evaporated and the solid was dried.

For **16**: Water (50 mL) was added to the reaction mixture and the phosphinine was extracted with benzene (3 × 20 mL). The solution was evaporated and the residue was dried and crystallized from pentane for **16a** or distilled in vacuo (0.03 Torr, bp 90−95 °C) for **16b,c**.

For **19**, **23**: Water (50 mL) was added to the reaction mixture and the phosphinine was extracted with Et_2O (3 × 20 mL). The solution was evaporated and the residue was dried.

Experimental Data. *Trimorpholin-4-yl(penta-2,4-dien-1-yl)phosphonium Bromide (**3a**).* **Yield:** 29.4%; amorphous solid (hexane−toluene); **^{1}H NMR** (300 MHz, $CDCl_3$): δ 3.32 (br t, 12H), 3.78 (br t, 12H), 4.46 (dd, $^3J_{HH}$ = 7.8 Hz, $^2J_{PH}$ = 17.4 Hz, 2H), 5.23 (d, $^3J_{HH}$ = 9.6 Hz, 1H), 5.36 (d, $^3J_{HH}$ = 18 Hz, 1H), 5.43−5.55 (m, 1H), 6.27−6.39 (m, 1H), 6.68−6.78 (m, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 28.2 (d, $^1J_{PC}$ = 99.3 Hz, CH_2−P), 45.7 (NCH_2), 66.6 (d, $^3J_{PC}$ = 5.0 Hz, OCH_2), 118.0 (d, J = 13.8 Hz, CH), 120.3 (d, $^5J_{PC}$ = 3.8 Hz, $\underline{CH_2}$=CH), 135.0 (d, J = 3.8 Hz, CH), 139.9 (d, J = 15.1 Hz, CH); **^{31}P NMR** (81 MHz, $CDCl_3$) δ 49.3; **MS-FAB**, m/z (%): 356 ([M − Br]$^+$, 100); **Anal. Calcd for**

dx.doi.org/10.1021/jo200847r |*J. Org. Chem.* 2011, 76, 6125–6133

$C_{17}H_{31}BrN_3O_3P$: C, 46.80; H, 7.16; N, 9.63; P, 7.10. Found C, 46.83; H, 7.17; N, 9.7; P, 7.15.

*Tris(dimethylamino)(penta-2,4-dien-1-yl)phosphonium Bromide (**3b**).* **Yield:** 96%; amorphous solid (hexane); **^{1}H NMR** (300 MHz, $CDCl_3$): δ 2.85 (d, $^3J_{PH}$ = 10.5 Hz, 18H), 3.86 (dd, $^3J_{HH}$ = 7.5 Hz, $^2J_{PH}$ = 17.7 Hz, 2H), 5.16 (d, $^3J_{HH}$ = 9.6 Hz, 1H), 5.28 (d, $^3J_{HH}$ = 16.8 Hz, 1H), 5.48−5.62 (m, 1H), 6.29−6.54 (m, 1H), 6.70−6.79 (m, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 28.9 (d, $^1J_{PC}$ = 104.4 Hz, CH_2−P), 37.54 (NCH_3), 118.9 (d, J_{PC} = 10.1 Hz, CH), 119.2 (d, $^5J_{PC}$ = 3.8 Hz, $\underline{CH_2}$=CH), 135.4 (d, J_{PC} = 5.0 Hz, CH), 138.8 (d, J_{PC} = 13.8 Hz, CH); **^{31}P NMR** (81 MHz, $CDCl_3$): δ 55.9; **APCI MS**: $[M - Br]^+$ = 230; **Anal. Calcd for $C_{11}H_{25}BrN_3P$:** C, 42.59; H, 8.12; N, 13.55; P, 9.98. Found C, 42.62; H, 8.11; N, 13.57; P, 10.02.

*2-(Diphenylphosphino)-3-pyrrolidin-1-ylacrylonitrile (**7**).* To a solution of Ph_2PCl (3.6 g, 16.4 mmol, 2.94 mL) in CH_2Cl_2 (10 mL) a mixture of **14** (2 g, 16.4 mmol) and Et_3N (2.16 g, 21.3 mmol, 2.96 mL) in CH_2CI_2 (30 mL) was added with stirring. The reaction mixture was kept stirring at room temperature for 3 days. Water (50 mL) was added to the reaction mixture, the reaction mixture was thoroughly shaken, and the organic layer was separated and dried over Na_2SO_4. The solvent was evaporated; the residue was recrystallized from isopropanol. **Yield:** 31.1%; **mp** 125−127 °C (2-propanol); **^{1}H NMR** (300 MHz, $CDCl_3$): δ 1.88 (br m, 2H), 1.98 (br m, 2H), 3.51 (br m, 2H), 3.85 (br m, 2H), 7.25 (d, $^3J_{PH}$ = 11.7 Hz, 1H), 7.35−7.47 (m, 6H), 7.49−7.52 (m, 4H) (this substance exists as a mixture of *Z*/*E* isomers; ^{1}H NMR spectra refer to the major isomer). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 24.6 (b, CH_2), 25.8 (b, CH_2), 47.7 (b, NCH_2), 54.1 (b, NCH_2), 67.3 (d, $^1J_{PC}$ = 11.3 Hz, C(2)), 120.7 (d, $^2J_{PC}$ = 5 Hz, CN), 128.3 (d, $^3J_{PC}$ = 7.5 Hz, PPh_2), 128.6 (PPh_2), 132.5 (d, $^2J_{PC}$ = 20 Hz, PPh_2), 137.8 (d, $^1J_{PC}$ = 6.3 Hz, PPh_2), 155.3 (d, $^2J_{PC}$ = 74.2 Hz, C(3)); **^{31}P NMR** (81 MHz, $CDCl_3$): δ 1.7; **APCI MS**: $[M^+ + 1]$ = 307; **Anal. Calcd for $C_{19}H_{19}N_2P$:** C, 74.49; H, 6.25; N, 9.14; P, 10.11. Found C, 74.61; H, 6.13; N, 9.26; P, 10.00.

*Allyl(1-cyano-2-pyrrolidin-1-ylvinyl)diphenylphosphonium Bromide (**8**).* **Yield:** 24.3%; **mp** 203−205 °C (acetone); **^{1}H NMR** (300 MHz, $CDCl_3$): δ 1.88−2.12 (m, 4H), 3.93 (t, $^3J_{HH}$ = 7.2 Hz, 2H), 4.16 (t, $^3J_{HH}$ = 7.2 Hz, 2H), 4.62 (dd, $^3J_{HH}$ = 5.69 Hz, $^2J_{PH}$ = 20.4 Hz, 2H), 5.31−5.36 (m, 1H), 5.51−5.56 (m, 2H), 7.65−7.83 (m, 6H), 7.85−7.93 (m, 4H), 8.65 (d, $^3J_{PH}$ = 11.7 Hz, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 23.6 (CH_2), 25.0 (CH_2), 27.4 (d, $^1J_{PC}$ = 51.6 Hz, CH_2−P), 48.2 (NCH_2), 55.3 (NCH_2), 117.4 (d, $^2J_{PC}$ = 7.5 Hz, CN), 119.3 (d, $^1J_{PC}$ = 90.2 Hz, PPh_2), 123.3 (d, $^2J_{PC}$ = 10 Hz, CH_2=$\underline{CH}$), 125.5 (d, $^3J_{PC}$ = 12.6 Hz, $\underline{CH_2}$=CH), 129.9 (d, $^3J_{PC}$ = 12.6 Hz, $\overline{PPh_2}$), 133.3 (d, $^2J_{PC}$ = 10 Hz, $\overline{PPh_2}$), 134.6 (d, $^4J_{PC}$ = 2.8 Hz, PPh_2), 156.2 (d, $^2J_{PC}$ = 20 Hz, C(2)), the C(1) signal is not observed; **^{31}P NMR** (81 MHz, $CDCl_3$): δ 25.1; **APCI MS**: $[M - Br]^+$ = 347; **Anal. Calcd for $C_{22}H_{24}BrN_2P$:** C, 61.84; H, 5.66; N, 6.56; P, 7.25. Found C, 61.98; H, 5.72; N, 6.40; P, 7.14.

*1,1-Diphenyl-1-λ^5-phosphinine-2-carbonitrile (**10**).* Yield: 78%; **mp** 132 °C ($CHCl_3$); **^{1}H NMR** (300 MHz, $CDCl_3$) δ 5.00 (dd, $^3J_{HH}$ = 11.4 Hz, $^3J_{PH}$ = 17.4 Hz, 1H), 5.29 (ddd, $^3J_{HH}$ = 7.2 Hz, $^3J_{HH}$ = 8.7 Hz, $^4J_{PH}$ = 1.5 Hz, 1H), 7.08 (dd, $^3J_{HH}$ = 8.7 Hz, $^3J_{PH}$ = 26.1 Hz, 1H), 7.27 (ddd, $^3J_{HH}$ = 7.2 Hz, $^3J_{HH}$ = 11.4 Hz, $^3J_{PH}$ = 36.6 Hz, 1H), 7.45−7.63 (m, 10H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 44.8 (d, $^1J_{PC}$ = 113.2 Hz, C(2)), 78.9 (d, $^1J_{PC}$ = 93 Hz, C(6)), 100.7 (d, $^3J_{PC}$ = 17.6 Hz, C(4)), 122.7 (d, $^2J_{PC}$ = 11.3 Hz, CN), 122.7 (d, $^3J_{PC}$ = 13.8 Hz, PPh_2), 130.8 (d, $^1J_{PC}$ = 90.5 Hz, PPh_2), 131.7 (d, $^2J_{PC}$ = 11.3 Hz, PPh_2), 132.1 (d, $^4J_{PC}$ = 3.8 Hz, PPh_2), 139.0 (d, $^2J_{PC}$ = 3.8 Hz, C(3)), 143.6 (C(5)); **^{31}P NMR** (81 MHz, $CDCl_3$) δ 8.48. **APCI MS**: $[M^+ + 1]$ = 276; **Anal. Calcd for $C_{18}H_{14}NP$:** C, 78.53; H, 5.13; N, 5.09; P, 11.25. Found C, 78.47; H, 5.05; N, 5.13; P, 11.4.

*4,4′-((2-Ethoxyvinyl)phosphinediyl)dimorpholine (**13a**).* **Yield:** 69%; oil; **^{1}H NMR** (300 MHz, C_6D_6): δ 1.02 (t, $^3J_{HH}$ = 6.9 Hz, 3H), 2.75−3.20 (m, 8H), 3.42−3.52 (m, 10H), 4.89 (dd, $^3J_{HH}$ = 13.8 Hz, $^2J_{PH}$ = 12 Hz, 1H), 6.60 (dd, $^3J_{HH}$ = 13.8 Hz, $^3J_{PH}$ = 5.1 Hz, 1H); **^{13}C NMR** (125 MHz, C_6D_6): δ 14.4 (CH_3), 49.1 (d, $^2J_{PC}$ = 12.6 Hz, NCH_2), 64.6 ($O\underline{CH_2}CH_3$), 68.0 (d, $^3J_{PC}$ = 7.5 Hz, OCH_2) 97.9 (d, $^1J_{PC}$ = 5 Hz, CH−P), 155.7 (d, $^2J_{PC}$ = 40.2 Hz, EtO−$\underline{CH}$=CH); **^{31}P NMR** (81 MHz, C_6D_6): δ 87.3; **MS-EI**, *m*/*z* (%): 274(M^+, 18), 189(11), 188(100), 103(26), 86(19), 85(7), 83(8), 75(12), 56(10), 42(6). **Anal. Calcd for $C_{12}H_{23}N_2O_3P$**: C, 52.55; H, 8.45; N, 10.21; P, 11.29. Found C, 52.49; H, 8.47; N 10.23; P 11.30.

*P-(2-Ethoxyvinyl)-N,N,N′,N′-tetraethylphosphonous Diamide (**13b**).* **Yield:** 69%; bp 76−81 °C (0.03 Torr); **^{1}H NMR** (300 MHz, C_6D_6): δ 0.98−1.03 (m, 15H), 2.96−3.17 (m, 8H), 3.49 (q, $^3J_{HH}$ = 6.9 Hz, 2H), 5.09 (dd, $^3J_{HH}$ = 13.5 Hz, $^2J_{PH}$ = 13.5 Hz, 1H), 6.68 (dd, $^3J_{HH}$ = 13.5 Hz, $^3J_{PH}$ = 4.5 Hz, 1H); **^{13}C NMR** (125 MHz, C_6D_6): δ 14.5 ($OCH_2\underline{CH_3}$), 14.9 (d, $^3J_{PC}$ = 3.8 Hz, CH_3), 42.4 (d, $^2J_{PC}$ = 17.6 Hz, NCH_2), 64.2 ($O\underline{CH_2}CH_3$), 101.1 (CH−P), 154.1 (d, $^2J_{PC}$ = 39 Hz, EtO−$\underline{CH}$=CH); **^{31}P NMR** (81 MHz, C_6D_6): δ 86.8; **MS-EI for P=O**, *m*/*z* (%): 262(M^+, 6), 217(17), 190(77), 136(78),100(24), 73(21), 72(100), 58(78), 44(42), 42(17). **Anal. Calcd for $C_{12}H_{27}N_2OP$:** C, 58.51; H, 11.05; N 11.37; P 12.57. Found C, 58.49; H, 11.07; N 11.41; P 12.55.

*P-(2-Ethoxyvinyl)-N,N,N′,N′-tetramethylphosphonous Diamide (**13c**).* **Yield:** 85%; 70 °C (0.05 Torr); **^{1}H NMR** (300 MHz, C_6D_6): δ 1.00 (t, $^3J_{HH}$ = 7.2 Hz, 3H), 2.63 (d, $^3J_{PH}$ = 9.3 Hz, 12H), 3.41 (q, $^3J_{HH}$ = 7.2 Hz, 2H), 5.07 (dd, $^3J_{HH}$ = 13.8 Hz, $^2J_{PH}$ = 10.8 Hz, 1H), 6.64 (dd, $^3J_{HH}$ = 13.8 Hz, $^3J_{PH}$ = 5.4 Hz, 1H); **^{13}C NMR** (125 MHz, C_6D_6): δ 14.4 (CH_3), 40.5 (d, $^2J_{PC}$ = 15.1 Hz, N−CH_3), 64.3(O−CH_2), 100.1-(CH−P), 155.3 (d, $^2J_{PC}$ = 42.8 Hz, EtO−$\underline{CH}$=CH); **^{31}P NMR** (81 MHz, C_6D_6) 92.1; **MS-EI for P=O**, *m*/*z* (%): 206(M^+, 7), 176(1), 161(30), 136(14),119(13), 108(97), 72(40), 58(12), 44(100); **Anal. Calcd for $C_8H_{19}N_2OP$:** C, 50.51; H 10.07; N, 14.73; P, 16.28. Found C, 50.48; H, 10.06; N, 14.77; P, 16.25.

*Allyl(2-ethoxyvinyl)dimorpholin-4-ylphosphonium Bromide (**14a**).* **Yield:** 88%; amorphous solid; **^{1}H NMR** (300 MHz, $CDCl_3$): δ 1.39 (t, $^3J_{HH}$ = 7.2 Hz, 3H), 3.28−3.33 (m, 8H), 3.74−3.77 (m, 8H), 4.08 (dd, 2H, $^3J_{HH}$ = 6.6 Hz, $^2J_{PH}$ = 16.8 Hz), 4.33 (q, $^3J_{HH}$ = 7.2 Hz, 2H), 5.07 (dd, $^3J_{HH}$ = 13.2 Hz, $^2J_{PH}$ = 13.2 Hz, 1H), 5.44−5.47 (m, 1H), 5.59−5.69 (m, 2H), 7.82 (dd, $^3J_{HH}$ = 13.2 Hz, $^3J_{PH}$ = 10.5 Hz, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 14.5 ($\underline{CH_3}CH_2O$), 30.1 (d, $^1J_{PC}$ = 81.7 Hz, P−CH_2), 45.4 (NCH_2), 67.2 (d, $^2J_{PC}$ = 5.1, O−CH_2), 69.6 (O−$\underline{CH_2}CH_3$), 79.5 (d, $^1J_{PC}$ = 137 Hz, CH−P), 124.4 (d, $^2J_{PC}$ = 7.5 Hz, CH_2=$\underline{CH}$), 124.5 (d, $^3J_{PC}$ = 11.3 Hz, $\underline{CH_2}$=CH), 168.3 (d, $^2J_{PC}$ = 22.6 Hz, EtO−$\underline{CH}$=CH); **^{31}P NMR** (81 MHz, $CDCl_3$) δ 53.7; **MS-FAB**, *m*/*z* (%): 315([M − Br]$^+$, 100); **Anal. Calcd for $C_{15}H_{28}N_2O_3PBr$:** C, 45.58; H, 7.14; Br, 20.21; N, 7.09; P, 7.84. Found C, 45.54; H, 7.12; Br, 20.1; N, 7.13; P, 7.87.

*Allyl(bis(diethylamino))(2-ethoxyvinyl)phosphonium Bromide (**14b**).* **Yield:** 100%; amorphous solid; **^{1}H NMR** (300 MHz, $CDCl_3$): δ 1.1 (t, $^3J_{HH}$ = 6.9 Hz, 12H), 1.28 (t, $^3J_{HH}$ = 6.9 Hz, 3H), 3.06−3.17 (m, 8H), 3.54 (dd, 2H, $^3J_{HH}$ = 6.9 Hz, $^2J_{PH}$ = 16.2 Hz), 4.21 (q, $^3J_{HH}$ = 6.9 Hz, 2H), 4.95 (dd, $^3J_{HH}$ = 13.5 Hz, $^2J_{PH}$ = 13.5 Hz, 1H), 5.31−42 (m, 1H), 5.48−5.61 (m, 1H), 5.62−5.78 (m, 1H), 7.51 (dd, $^3J_{HH}$ = 13.5 Hz, $^3J_{PH}$ = 11.1 Hz, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 14.1 (d, $^3J_{PC}$ = 2.5 Hz, $\underline{CH_3}CH_2N$), 14.5 ($\underline{CH_3}CH_2O$), 31.5 (d, $^1J_{PC}$ = 85.5 Hz, P−CH_2), 40.2 (d, $^3J_{PC}$ = 3.8 Hz, CH_2N), 69.2 (O−CH_2), 81.6 (d, $^1J_{PC}$ = 137 Hz, CH−P), 123.9 (d, $^3J_{PC}$ = 13.8 Hz, $\underline{CH_2}$=CH), 124.7 (d, $^2J_{PC}$ = 8.8 Hz, CH_2=$\underline{CH}$), 166.9 (d, $^2J_{PC}$ = 21.4 Hz, EtO−$\underline{CH}$=CH); **^{31}P NMR** (81 MHz, $CDCl_3$) δ 54.8; **MS-FAB**, *m*/*z* (%): 287([M − Br]$^+$, 100); **Anal. Calcd for $C_{15}H_{32}N_2OPBr$:** C, 49.05; H, 8.78; Br, 21.75; N, 7.63; P, 8.43. Found C, 49.00; H, 8.76; Br, 21.69; N, 7.67; P, 8.45.

*Allyl(bis(dimethylamino))(2-ethoxyvinyl)phosphonium Bromide (**14c**).* **Yield:** 100%; amorphous solid; **^{1}H NMR** (300 MHz, $CDCl_3$): δ 1.32 (t, $^3J_{HH}$ = 7.2 Hz, 3H), 2.80 (d, $^3J_{PH}$ = 10.2 Hz, 12H), 3.58 (dd, $^3J_{HH}$ = 7.2 Hz, $^2J_{PH}$ = 16.2 Hz, 2H), 4.25 (q, $^3J_{HH}$ = 7.2 Hz, 2H), 4.97 (dd, $^3J_{HH}$ = 13.8 Hz, $^2J_{PH}$ = 13.8 Hz, 1H), 5.35−5.43 (m, 1H), 5.45−5.55 (m, 1H), 5.61−5.80 (m, 1H), 7.59 (dd, $^3J_{HH}$ = 13.8 Hz, $^3J_{PH}$ = 10.5 Hz, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 14.5 (CH_3), 30.9

(d, $^1J_{PC}$ = 84.3 Hz, P−CH_2), 37.4 (N−CH_3), 69.2(O−CH_2), 80.3 (d, $^1J_{PC}$ = 137 Hz, CH−P), 123.9 (d, $^3J_{PC}$ = 12.6 Hz, $\underline{CH_2}$=CH), 124.4 (d, $^2J_{PC}$ = 8.8 Hz, CH_2=$\underline{CH}$), 167.1 (d, $^2J_{PC}$ = 20.1 Hz, EtO−$\underline{CH}$=CH); **^{31}P NMR** (81 MHz, $CDCl_3$) δ 57.4; **MS-FAB**, *m/z* (%): 231([M − Br]$^+$, 100); **Anal. Calcd for $C_{11}H_{24}N_2OPBr$:** C, 42.46; H, 7.77; Br, 25.68; N, 9.00; O, 5.14; P, 9.95. Found C, 42.43; H, 7.75; Br, 25.70; N, 8.98; P, 9.93.

1,1-Dimorpholin-4-yl-1λ^5-phosphinine (***16a***). **Yield:** 46.6%; **mp** 75−80 °C (diethyl ether); **^{1}H NMR** (300 MHz, C_6D_6): δ 2.59−2.65 (m, 8H), 3.33 (t, $^3J_{HH}$ = 4.5 Hz, 8H), 4.28 (dd, $^3J_{HH}$ = 11.1 Hz, $^2J_{PH}$ = 6.9 Hz, 2H), 5.66 (dt, $^4J_{PH}$ = 3 Hz, $^3J_{HH}$ = 7.5 Hz, 1H), 7.35 (ddd, $^3J_{HH}$ = 7.5 Hz, $^3J_{HH}$ = 11.1 Hz, $^3J_{PH}$ = 36.9 Hz, 2H); **^{13}C NMR** (125 MHz, C_6D_6): δ 44.7 (NCH_2), 66.9 (d, $^3J_{PC}$ = 8.0 Hz, OCH_2), 72.3 (d, $^1J_{PC}$ = 123 Hz, C(2), C(6)), 99.3 (d, $^3J_{PC}$ = 21.4 Hz, C(4)), 140.4 (d, $^2J_{PC}$ = 3.8 Hz, C(3), C(5)); **^{31}P NMR** (81 MHz, C_6D_6) δ 46.3. **MS-EI**, *m/z* (%): 268(M^+, 67), 211(14), 183(34), 182(100), 134(8), 126(9), 97(23), 87(99), 86(75), 56(22); **Anal. Calcd for $C_{13}H_{21}N_2O_2P$:** C, 58.20; H, 7.89; N, 10.44; P, 11.54. Found C, 58.24; H, 7.87; N, 10.42; P, 11.53.

N^1,N^1,N^1,N^1-Tetraethyl-1λ^5-phosphinine-1,1-diamine (***16b***). **Yield:** 48%; **bp** 90−95 °C (0.05 Torr); **^{1}H NMR** (500 MHz, $CDCl_3$): δ 0.87 (t, *J* = 7.2 Hz, 12H), 2.78−2.89 (m, 8H), 4.54 (dd, $^3J_{HH}$ = 11.4 Hz, $^2J_{PH}$ = 7.5 Hz, 2H), 5.71 (dt, $^4J_{PH}$ = 2.4 Hz, $^3J_{HH}$ = 7.5 Hz, 1H), 7.46 (ddd, $^3J_{HH}$ = 7.5 Hz, $^3J_{HH}$ = 11.4 Hz, $^3J_{PH}$ = 37 Hz, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 14.1 (CH_3), 38.6 (NCH_2), 75.6 (d, $^1J_{PC}$ = 124.2 Hz, C(2), C(6)), 97.7 (d, $^3J_{PC}$ = 21.3 Hz, C(4)), 138.9 (d, $^2J_{PC}$ = 3.8 Hz, C(3), C(5)); **^{31}P NMR** (81 MHz, $CDCl_3$) δ 49.26. **MS-EI**, *m/z* (%): 240(M^+, 41), 169(37), 168(100), 98(23), 97(27), 72(53), 58(32), 56(18), 44(23), 42(22); **Anal. Calcd for $C_{13}H_{25}N_2P$:** C, 64.97; H, 10.49; N, 11.66; P, 12.89. Found C, 64.96; H, 10.48; N, 11.64; P, 12.91.

N^1,N^1,N^1,N^1-Tetramethyl-1λ^5-phosphinine-1,1-diamine (***16c***). **Yield:** 44.5%; **bp** 75−80 °C (0.05 Torr); **^{1}H NMR** (300 MHz, C_6D_6): δ 2.21 (d, $^3J_{PH}$ = 11.7 Hz, 12H), 4.48 (dd, $^3J_{HH}$ = 11.4 Hz, $^2J_{PH}$ = 6.6 Hz, 2H), 5.70 (dtt, $^4J_{PH}$ = 2.4 Hz, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 0.6 Hz 1H), 7.45 (ddd, $^3J_{HH}$ = 7.8 Hz, $^3J_{HH}$ = 11.4 Hz, $^3J_{PH}$ = 36.6 Hz, 2H); **^{13}C NMR** (125 MHz, C_6D_6): δ 35.9 (d, $^2J_{PC}$ = 2.5 Hz, NCH_3), 71.1 (d, $^1J_{PC}$ = 125 Hz, C(2), C(6)), 99.1 (d, $^3J_{PC}$ = 21.4 Hz, C(4)), 140.2 (d, $^2J_{PC}$ = 4 Hz, C(3), C(5)); **^{31}P NMR** (81 MHz, C_6D_6) δ 51.9. **MS-EI**, *m/z* (%): 184(M^+, 5), 140(12), 57(3), 45(46), 44(100), 43(8), 41(6), 36(5), 30(3); **Anal. Calcd for $C_9H_{17}N_2P$:** C, 58.68; H, 9.30; N, 15.21; P, 16.18. Found C, 58.67; H, 9.32; N, 15.27; P, 16.22.

(2-Ethoxyvinyl)(dimethyl)phosphine (***17a***). **Yield:** 88%; oil; **^{1}H NMR** (300 MHz, C_6D_6): δ 0.96 (t, $^3J_{HH}$ = 6.9 Hz) 0.98 (d, $^2J_{PH}$ = 3 Hz, 6H), 3.37 (q, $^3J_{HH}$ = 6.9 Hz, 2H), 4.84 (dd, $^3J_{HH}$ = 13.5 Hz, $^2J_{PH}$ = 3.9 Hz, 1H), 6.82 (dd, $^3J_{HH}$ = 13,5 Hz, $^3J_{PH}$ = 9.9 Hz, 1H); **^{13}C NMR** (125 MHz, C_6D_6): δ 14.3 (CH_3), 16.1 (d, $^1J_{PC}$ = 10 Hz, PCH_3), 64.4 (O−CH_2), 103.6 (d, $^1J_{PC}$ = 10 Hz, CH−P), 155.7 (d, $^2J_{PC}$ = 60.4 Hz, EtO−$\underline{CH}$=CH); **^{31}P NMR** (81 MHz, C_6D_6) −57.2. **MS-EI for P=O**, *m/z* (%): 148(M^+, 11), 128(25), 87(89), 86(62), 85(37), 83(51), 72(14), 58(25), 57(100), 56(43). **Anal. Calcd for $C_6H_{13}OP$**: C, 54.54; H 9.92; P, 23.44. Found C, 54.59; H, 9.94; P, 23.38.

(2-Ethoxyvinyl)(diphenyl)phosphine (***17b***). **Yield:** 74.2%; oil; **^{1}H NMR** (300 MHz, C_6D_6): δ 0.91 (t, $^3J_{HH}$ = 6.9 Hz, 3H), 3.31 (q, $^3J_{HH}$ = 6.9 Hz, 2H), 5.35 (dd, $^3J_{HH}$ = 13.5 Hz, $^2J_{PH}$ = 4.2 Hz, 1H), 6.92 (dd, $^3J_{HH}$ = 13.5 Hz, $^3J_{PH}$ = 9.9 Hz, 1H), 7.00−7.15 (m, 6H), 7.48−7.53 (m,4H); **^{13}C NMR** (125 MHz, C_6D_6): δ 14.3 (CH_3), 64.9 (O−CH_2), 98.3 (d, $^1J_{PC}$ = 3.8 Hz, CH−P), 128.1 (PPh_2), 128.4 (d, $^3J_{PC}$ = 6.3 Hz, PPh_2), 132.5 (d, $^2J_{PC}$ = 18.9 Hz, PPh_2), 141.1 (d, $^1J_{PC}$ = 7.6 Hz, PPh_2), 155.7 (d, $^2J_{PC}$ = 69.1 Hz, EtO−$\underline{CH}$=CH); **^{31}P NMR** (81 MHz, C_6D_6) δ −19.5; **MS-EI**, *m/z* (%): 256($\overline{M^+}$, 100), 241(49), 201(58), 186(25), 183(25), 153(28), 141(31), 108(60), 77(56), 47(24); **Anal. Calcd for $C_{16}H_{17}OP$:** C, 74.99; H 6.69; P, 12.09. Found C, 75.05; H, 6.71; P, 11.99.

Allyl(2-ethoxyvinyl)dimorpholin-4-ylphosphonium Bromide (***18a***). **Yield:** 85.5%; amorphous solid; **^{1}H NMR** (300 MHz, $CDCl_3$): δ 1.28 (t, $^3J_{HH}$ = 6.9 Hz, 3H), 2.14 (d, $^2J_{PH}$ = 14.1 Hz, 6H), 3.48 (dd, $^3J_{HH}$ = 7.5 Hz, $^2J_{PH}$ = 16.8 Hz, 2H), 4.07 (q, $^3J_{HH}$ = 6.9 Hz, 2H), 5.19 (dd, $^3J_{HH}$ = 13.5 Hz, $^2J_{PH}$ = 12.3 Hz, 1H), 5.36−5.47 (m, 2H), 5.52−5.69 (m, 1H), 7.47 (dd, $^3J_{HH}$ = 13.5 Hz, $^3J_{PH}$ = 11.7 Hz, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 9.0 ($^1J_{PC}$ = 57.8 Hz, PCH_3), 14.3 (CH_3), 30.2 (d, $^1J_{PC}$ = 55.3 Hz, P−CH_2), 68.1 (O−CH_2), 80.8 (d, $^1J_{PC}$ = 96.8 Hz, CH−P), 124.2 (d, $^3J_{PC}$ = 12.6 Hz, $\underline{CH_2}$=CH), 124.3 (d, $^2J_{PC}$ = 10 Hz, CH_2=$\underline{CH}$), 164.8 (d, $^2J_{PC}$ = 16.3 Hz, EtO−$\underline{CH}$=CH); **^{31}P NMR** (81 MHz, $CDCl_3$) δ 20.5; **APCI MS**: [M − Br]$^+$ = 173; **Anal. Calcd for $C_9H_{18}OPBr$:** C, 42.71; H, 7.17; Br, 31.57; P, 12.24. Found C, 42.69; H, 7.15; Br, 31.52; P, 12.18.

Allyl(2-ethoxyvinyl)diphenylphosphonium Bromide (***18b***). **Yield:** 79.1%; amorphous solid (hexane); **^{1}H NMR** (300 MHz, $CDCl_3$): δ 1.32 (t, $^3J_{HH}$ = 6.9 Hz, 3H), 4.26 (dd, $^3J_{HH}$ = 7.2 Hz, $^2J_{PH}$ = 15.9 Hz, 2H), 4.36 (q, $^3J_{HH}$ = 6.9 Hz, 2H), 5.34−5.39 (m, 1H), 5.48−5.53 (m, 1H), 5.62−5.68 (m, 1H), 5.91 (dd, $^3J_{HH}$ = 12 Hz, $^2J_{PH}$ = 13.5 Hz, 1H), 7.15 (dd, $^3J_{HH}$ = 12 Hz, $^3J_{PH}$ = 12.6 Hz, 1H), 7.65−7.88 (m, 10H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 14.1 (CH_3), 30.0 (d, $^1J_{PC}$ = 54.1 Hz, P−CH_2), 69.3 (O−CH_2), 78.8 (d, $^1J_{PC}$ = 103 Hz, CH−P), 119.4 (d, $^1J_{PC}$ = 89.3 Hz, PPh_2), 123.8 (d, $^2J_{PC}$ = 10 Hz, CH_2=$\underline{CH}$), 125.2 (d, $^3J_{PC}$ = 13.8 Hz, $\underline{CH_2}$=CH), 130.1 (d, $^3J_{PC}$ = 11.3 Hz, PPh_2), 133.3 (d, $^2J_{PC}$ = 10 Hz, PPh_2), 134.6 (d, $^4J_{PC}$ = 2.5 Hz, PPh_2), 167.8 (d, $^2J_{PC}$ = 17.6 Hz, EtO−$\underline{CH}$=CH); **^{31}P NMR** (81 MHz, $CDCl_3$): δ 18.1; **MS-FAB**, *m/z* (%): 298([M − Br]$^+$, 42); **Anal. Calcd for $C_{19}H_{22}OPBr$:** C, 60.49; H, 5.88; Br, 21.18; P, 8.21. Found C, 60.52; H, 5.86; Br, 21.02; P, 8.25.

1,1-Dimethyl-1λ^5-phosphinine (***19a***). **Yield:** 44.5%; oil; **^{1}H NMR** (300 MHz, C_6D_6): δ 0.91 (d, $^2J_{PH}$ = 12.6 Hz, 6H), 3.9 (dd, $^3J_{HH}$ = 11.1 Hz, $^2J_{PH}$ = 17.4 Hz, 2H), 5.24 (t, $^3J_{HH}$ = 7.8 Hz, 1H), 7.14 (ddd, $^3J_{HH}$ = 7.8 Hz, $^3J_{HH}$ = 11.1 Hz, $^3J_{PH}$ = 33.9 Hz, 2H); **^{13}C NMR** (125 MHz, C_6D_6): δ 24.6 (d, $^2J_{PC}$ = 56.6 Hz, PCH_3), 66.4 (d, $^1J_{PC}$ = 96.8 Hz, C(2), C(6)), 96.2 (d, $^3J_{PC}$ = 21.4 Hz, C(4)), 140.3 (C(3), C(5)); **^{31}P NMR** (81 MHz, C_6D_6) δ −3.8. **Anal. Calcd for $C_7H_{11}P$:** C, 66.65; H, 8.79; P, 24.56. Found C, 66.69; H, 8.82; P, 24.51.

1,1-Diphenyl-1λ^5-phosphinine (***19b***). **Yield:** 61.2%; oil; **^{1}H NMR** (300 MHz, $CDCl_3$): δ 4.36 (dd, $^3J_{HH}$ = 10.8 Hz, $^2J_{PH}$ = 14.4 Hz, 2H), 5.05 (t, $^3J_{HH}$ = 8.1 Hz, 1H), 7.11 (ddd, $^3J_{HH}$ = 8.1 Hz, $^3J_{HH}$ = 10.8 Hz, $^3J_{PH}$ = 34.5 Hz, 2H), 7.43−7.50 (m, 10H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 65.9 (d, $^1J_{PC}$ = 99.4 Hz, C(2), C(6)), 96.0 (d, $^3J_{PC}$ = 21.4 Hz, C(4)), 128.6 (d, $^3J_{PC}$ = 11.3 Hz, PPh_2), 130.3 (d, $^4J_{PC}$ = 2.5 Hz, PPh_2), 131.0 (d, $^2J_{PC}$ = 11.3 Hz, PPh_2), 136.6 (d, $^1J_{PC}$ = 88.0 Hz, PPh_2), 139.4 (C(3), C(5)); **^{31}P NMR** (81 MHz, C_6D_6) δ 4.1. **MS-EI**, *m/z* (%): 250(M^+, 100), 216(35), 215(81), 202(52), 201(73), 183(35), 173(91), 77(86), 51(55), 47(44); **Anal. Calcd for $C_{17}H_{15}P$:** C, 81.58; H, 6.04; P, 12.38. Found C, 81.56; H, 6.05; P, 12.39.

P-(2-Ethoxyvinyl)-N,N-dimethylphosphonamidous Chloride (***20***). To a stirred phosphonous diamide **13c** (13.2 g, 69.4 mmol), (2-ethoxyvinyl)phosphonous dichloride **12** (12 g, 69.4 mmol) was added at 0 °C. The reaction mixture was allowed to warm to rt. **Yield:** ∼100%; oil; **bp** 102−105 °C (7 Torr); **^{1}H NMR** (300 MHz, C_6D_6): δ 0.85 (t, $^3J_{HH}$ = 6.9 Hz, 3H), 2.45 (d, $^3J_{PH}$ = 13.8 Hz, 6H), 3.19 (q, $^3J_{HH}$ = 6.9 Hz, 2H), 5.48 (dd, $^3J_{HH}$ = 13.8 Hz, $^2J_{PH}$ = 4.2 Hz, 1H), 6.77 (dd, $^3J_{HH}$ = 13.8 Hz, $^3J_{PH}$ = 9.6 Hz, 1H); **^{13}C NMR** (125 MHz, C_6D_6): δ 14.1 (CH_3), 39.2 (d, $^2J_{PC}$ = 10.0 Hz, N−CH_3), 65.3 (O−CH_2), 103.8 (d, $^1J_{PC}$ = 23.9 Hz, CH−P), 158.1 (d, $^2J_{PC}$ = 70.4 Hz, EtO−$\underline{CH}$=CH); **^{31}P NMR** (81 MHz, C_6D_6) 142.5; **MS-EI**, *m/z* (%): 181($\overline{M^+}$, 45), 146(100), 137(12), 118(20), 109(32), 92(22), 83(18), 75(12), 60(10), 44(69), 32(81).

P-(2-Ethoxyvinyl)-N,N,P-trimethylphosphinous Amide (***21a***). **Yield:** 91.3%; oil; **^{1}H NMR** (300 MHz, C_6D_6): δ 0.97 (t, $^3J_{HH}$ = 6.9 Hz, 3H), 1.16 (d, $^3J_{HH}$ = 5.4 Hz, 3H) 2.45 (d, $^3J_{PH}$ = 10.5 Hz, 6H) 3.38 (q, $^3J_{HH}$ = 6.9 Hz, 2H), 5.14 (dd, $^3J_{HH}$ = 13.8 Hz, 1H), 6.81 (dd, $^3J_{HH}$ = 13.8 Hz, $^3J_{PH}$ = 8.7 Hz, 1H); **^{13}C NMR** (125 MHz, C_6D_6): δ 14.0 (d, $^1J_{PC}$ = 10.0 Hz, PCH_3), 14.3 (CH_3), 39.6 (d, $^2J_{PC}$ = 12.6 Hz, N−CH_3), 64.5 (O−CH_2), 100.7 (d, $^1J_{PC}$ = 20.1 Hz, CH−P), 156.9

dx.doi.org/10.1021/jo200847r |*J. Org. Chem.* 2011, 76, 6125–6133

(d, $^2J_{PC}$ = 60.4 Hz, EtO−CH=CH); **^{31}P NMR** (81 MHz, C_6D_6) 38.9; **APCI MS**: [M^+ + 1] = 161; **Anal. Calcd for $C_7H_{16}NOP$:** C, 52.16; H 10.01; N, 8.69; P, 19.22. Found C, 52.13; H, 9.98; N, 8.63; P, 19.15.

*P-(2-Ethoxyvinyl)-N,N-dimethyl-P-phenylphosphinous Amide (**21b**).* **Yield:** 77%; oil; **^{1}H NMR** (300 MHz, C_6D_6): δ 0.97 (t, $^3J_{HH}$ = 7.2 Hz, 3H), 2.53 (d, $^3J_{PH}$ = 10.2 Hz, 6H), 3.40 (q, $^3J_{HH}$ = 7.2 Hz, 2H), 5.36 (dd, $^3J_{HH}$ = 13.8 Hz, $^2J_{PH}$ = 3.6 Hz, 1H), 6.95 (dd, $^3J_{HH}$ = 13.8 Hz, $^3J_{PH}$ = 9.6 Hz, 1H), 7.11 (t, $^3J_{HH}$ = 7.5 Hz, 1H), 7.24 (t, $^3J_{HH}$ = 7.5 Hz, 2H), 7.57 (dd, $^3J_{HH}$ = 7.5 Hz, $^3J_{PH}$ = 7.5 Hz, 2H); **^{13}C NMR** (125 MHz, C_6D_6): δ 14.3 (CH_3), 40.8 (d, $^2J_{PC}$ = 12.6 Hz, N−CH_3), 64.9 (O−CH_2), 98.2 (d, $^1J_{PC}$ = 17.6 Hz, CH−P), 127.3 (PPh_2), 128.1 (d, $^3J_{PC}$ = 3.8 Hz, PPh_2), 130.1 (d, $^2J_{PC}$ = 13.8 Hz, PPh_2), 143.1 (d, $^1J_{PC}$ = 2.5 Hz, PPh_2), 160.0 (d, $^2J_{PC}$ = 71.7 Hz, EtO−CH=CH); **^{31}P NMR** (81 MHz, C_6D_6) δ 54.5. **Anal. Calcd for $C_{12}H_{18}NOP$:** C, 64.56; H 8.13; N, 6.27; P, 13.87. Found C, 64.59; H, 8.15 ; N, 6.24; P, 13.90.

*Allyl(dimethylamino)(2-ethoxyvinyl)(methyl)phosphonium Bromide (**22a**).* **Yield:** 100%; amorphous solid; **^{1}H NMR** (300 MHz, $CDCl_3$): δ 1.30 (t, $^3J_{HH}$ = 7.2 Hz, 3H), 2.20 (d, $^3J_{PH}$ = 13.2 Hz, 3H), 2.76 (d, $^3J_{PH}$ = 10.8 Hz, 6H), 3.33−3.65 (m, 2H), 4.18 (q, $^3J_{HH}$ = 7.2 Hz, 2H), 5.09 (dd, $^3J_{HH}$ = 13.5 Hz, $^2J_{PH}$ = 12.3 Hz, 1H), 5.35−5.48 (m, 2H), 5.62−5.69 (m, 1H), 7.62 (dd, $^3J_{HH}$ = 13.5 Hz, $^3J_{PH}$ = 11.1 Hz, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 9.55 ($^1J_{PC}$ = 69.1 Hz, PCH_3), 14.5 (CH_3), 30.9 (d, $^1J_{PC}$ = 64.1 Hz, P−CH_2), 37.4 (N−CH_3), 68.9 (O−CH_2), 81.3 (d, $^1J_{PC}$ = 112 Hz, CH−P), 124.1 (d, $^3J_{PC}$ = 12.6 Hz, CH_2=CH), 124.4 (d, $^2J_{PC}$ = 10 Hz, CH_2=CH), 166.8 (d, $^2J_{PC}$ = 18.9 Hz, EtO−CH=CH); **^{31}P NMR** (81 MHz, $CDCl_3$) δ 52.9; **Anal. Calcd for $C_{10}H_{21}NOPBr$:** C, 42.57; H, 7.50; N, 4.96; Br, 28.32; P, 10.98. Found C, 42.59; H, 7.53; N, 4.95; Br, 28.41; P, 11.03.

*Allyl(dimethylamino)(2-ethoxyvinyl)(phenyl)phosphonium Bromide (**22b**).* **Yield:** 100%; amorphous solid; **^{1}H NMR** (300 MHz, $CDCl_3$): δ 1.38 (t, $^3J_{HH}$ = 7.2 Hz, 3H), 2.89 (d, $^3J_{PH}$ = 11.1 Hz, 6H), 4.00 (dd, $^3J_{HH}$ = 7.2 Hz, $^2J_{PH}$ = 16.5 Hz, 2H), 4.35 (q, $^3J_{HH}$ = 7.2 Hz, 2H), 5.34−5.39 (m, 1H), 5.49−5.53 (m, 2H), 5.62−5.69 (m, 1H), 7.58 (dd, $^3J_{HH}$ = 13.8 Hz, $^3J_{PH}$ = 10.8 Hz, 1H), 7.54−7.89 (m, 5H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 14.5 (CH_3), 30.9 (d, $^1J_{PC}$ = 66.6 Hz, P−CH_2), 38.4 (N−CH_3), 69.5 (O−CH_2), 79.9 (d, $^1J_{PC}$ = 112 Hz, CH−P), 120.9 (d, $^1J_{PC}$ = 104 Hz, PPh_2), 124.1 (d, $^2J_{PC}$ = 8.8 Hz, CH_2=CH), 124.5 (d, $^3J_{PC}$ = 15.1 Hz, CH_2=CH), 130.1 (d, $^3J_{PC}$ = 12.6 Hz, PPh_2), 132.5 (d, $^2J_{PC}$ = 11.3 Hz, PPh_2), 134.7 (d, $^4J_{PC}$ = 2.5 Hz, PPh_2), 168.2 (d, $^2J_{PC}$ = 18.9 Hz, EtO−CH=CH); **^{31}P NMR** (81 MHz, $CDCl_3$) δ 48.4; **MS-FAB**, *m/z* (%): 265([M − Br]$^+$, 10); **Anal. Calcd for $C_{15}H_{23}$-NOPBr:** C, 52.34; H, 6.73; Br, 23.21; N, 4.07; P, 9.00. Found C, 52.32; H, 6.77; Br, 23.10; N, 4.05; P, 9.08.

*N,N,1-Trimethyl-1λ^5-phosphinin-1-amine (**23a**).* **Yield:** 53.0%; oil; **^{1}H NMR** (300 MHz, C_6D_6): δ 1.26 (d, $^2J_{PH}$ = 14.4 Hz, 3H), 2.0 (d, $^3J_{PH}$ = 11.4 Hz, 6H), 4.41 (dd, $^3J_{HH}$ = 11.1 Hz, $^2J_{PH}$ = 12 Hz, 2H), 5.64 (dtt, $^4J_{PH}$ = 3 Hz, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 0.6 Hz, 1H), 7.39 (ddd, $^3J_{HH}$ = 7.8 Hz, $^3J_{HH}$ = 11.1 Hz, $^3J_{PH}$ = 34.2 Hz, 2H); **^{13}C NMR** (125 MHz, C_6D_6): δ 17.6 (d, $^1J_{PC}$ = 91.8 Hz, PCH_3), 35.6 (NCH_3), 72.4 (d, $^1J_{PC}$ = 108 Hz, C(2), C(6)), 98.6 (d, $^3J_{PC}$ = 22.6 Hz, C(4)), 139.6 (C(3), C(5)); **^{31}P NMR** (81 MHz, C_6D_6) δ 24.4. **MS-EI**, *m/z* (%): 155(M^+, 1), 59(1), 45(75), 44(100), 43(20), 42(20), 41(3), 38(1), 32(12), 30(3); **Anal. Calcd for $C_8H_{14}NP$:** C, 61.92; H, 9.09; N, 9.03; P, 19.96. Found C, 61.90; H, 9.13; N, 9.00; P, 20.03.

*N,N-Dimethyl-1-phenyl-1λ^5-phosphinin-1-amine (**23b**).* **Yield:** 76.0%; oil; **^{1}H NMR** (500 MHz, C_6D_6): δ 2.1 (d, $^3J_{PH}$ = 12.5 Hz, 6H), 4.61 (dd, $^3J_{HH}$ = 11 Hz, $^2J_{PH}$ = 10.5 Hz, 2H), 5.70 (dt, $^4J_{PH}$ = 2.5 Hz, $^3J_{HH}$ = 7.5 Hz, 1H), 6.99−7.09 (m, 3H), 7.44 (ddd, $^3J_{HH}$ = 7.5 Hz, $^3J_{HH}$ = 11 Hz, $^3J_{PH}$ = 34.5 Hz, 2H), 7.49−7.52 (m, 2H); **^{13}C NMR** (125 MHz, C_6D_6): δ 35.1 (d, $^2J_{PC}$ = 3.8 Hz, NCH_3), 70.7 (d, $^1J_{PC}$ = 110.7 Hz, C(2), C(6)), 99.3 (d, $^3J_{PC}$ = 21.4 Hz, C(4)), 128.5 (d, $^3J_{PC}$ = 13.8 Hz, PPh_2), 129.8 (d, $^4J_{PC}$ = 2.5 Hz, PPh_2), 131.3 (d, $^2J_{PC}$ = 10.0 Hz, PPh_2), 139.8 (C(3), C(5)), PPh_2 (i) signal are not observed; **^{31}P NMR** (81 MHz, C_6D_6) δ 30.4. **MS-EI**, *m/z* (%): 217(M^+, 32), 174(12), 173(100), 171(18), 128(12), 95(17), 83(9), 77(9), 57(11), 44(11). **Anal. Calcd for $C_{13}H_{16}NP$:** C, 71.87; H, 7.42; N, 6.45; P, 14.26. Found C, 71.81; H, 7.43; N, 6.47; P, 14.19.

*Allyl(methyl)dimorpholin-4-ylphosphonium Bromide (**25a**).* **Yield:** 58.6%; **mp** 180−185 °C (2-propanol); **^{1}H NMR** (300 MHz, $CDCl_3$): δ 2.37 (d, $^2J_{PH}$ = 13 Hz, 3H), 3.26 (br m, 8H), 3.70 (br m, 8H), 3.90 (dd, $^3J_{HH}$ = 6.6 Hz, $^2J_{PH}$ = 17 Hz, 2H), 5.39−5.47 (m, 1H), 5.60−5.71 (m, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 8.9 (d, $^1J_{PC}$ = 80.5 Hz, CH_3−P), 29.3 (d, $^1J_{PC}$ = 76.7 Hz, CH_2−P), 45.1 (NCH_2), 66.7 (d, $^3J_{PC}$ = 5.0 Hz, OCH_2), 123.8 (d, $^2J_{PC}$ = 8.8 Hz, CH_2=CH), 125.2 (d, $^3J_{PC}$ = 13.8 Hz, CH_2=CH); **^{31}P NMR** (81 MHz, $CDCl_3$): δ 60.37. **MS-FAB**, *m/z* (%): 259([M − Br]$^+$, 100). **Anal. Calcd for $C_{12}H_{24}BrN_2O_2P$:** C, 42.49; H, 7.13; N, 8.26; P, 9.13. Found C, 42.54; H, 7.12; N, 8.25; P, 9.10.

*Allyl(bis(diethylamino))methylphosphonium Bromide (**25b**).* **Yield:** 75%; amorphous solid (hexane); **^{1}H NMR** (300 MHz, $CDCl_3$): δ 1.21 (t, *J* = 6.9 Hz, 12H), 2.26 (d, *J* = 13.2 Hz, 3H), 3.11−3.29 (m, 8H), 3.65 (dd, $^3J_{HH}$ = 6 Hz, $^2J_{PH}$ = 16.8 Hz, 2H), 5.44−5.49 (m, 1H), 5.69−5.75 (m, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 10.0(d, $^1J_{PC}$ = 84.3 Hz, CH_3−P), 14.0 (NCH_2CH_3), 30.0 (d, $^1J_{PC}$ = 77.9 Hz, CH_2−P), 40.0 (NCH_2CH_3), 124.3 (d, $^2J_{PC}$ = 7.5 Hz, CH_2=CH), 124.6 (d, $^3J_{PC}$ = 13.8 Hz, CH_2=CH); **^{31}P NMR** (81 MHz, $CDCl_3$): δ 62.1. **MS-FAB**, *m/z* (%): 231([M − Br]$^+$, 100). **Anal. Calcd for $C_{12}H_{28}BrN_2P$:** C, 46.31; H, 9.07; N, 9.00; P, 9.95. Found C, 46.33; H, 9.04; N, 8.99; P, 10.0.

*Methyl(dimorpholin-4-yl)prop-1-enylphosphonium Bromide (**26a**).* To a solution of **20a** (0.88 g, 2.6 mmol) in pyridine (20 mL), 3 drops of Et_3N was added and the reaction mixture was refluxed for 4 h. The reaction mixture was evaporated; the residue was washed with ether. **Yield: 63.6%**; amorphous solid (diethyl ether); **^{1}H NMR** (500 MHz, $CDCl_3$): δ 2.05 (d, $^4J_{PH}$ = 6 Hz, 3H), 2.40 (d, $^2J_{PH}$ = 13.5 Hz, 3H), 3.19 (br m, 8H), 3.64 (br m, 8H), 6.3 (dd, $^3J_{HH}$ = 18 Hz, $^2J_{PH}$ = 21 Hz, 1H), 6.93−7.05 (m, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 10.5 (d, $^1J_{PC}$ = 85.5 Hz, CH_3−P), 21.3 (d, $^3J_{PC}$ = 21.4 Hz, CH_3), 44.9 (NCH_2), 66.6 (d, $^3J_{PC}$ = 5 Hz, OCH_2), 113.0 (d, $^1J_{PC}$ = 120.7 Hz, CH), 156.8 (d, $^2J_{PC}$ = 6.3 Hz, CH); **^{31}P NMR** (81 MHz, $CDCl_3$) δ 52.6. **MS-FAB**, *m/z* (%): 259([M − Br]$^+$, 100). **Anal. Calcd for $C_{12}H_{24}BrN_2O_2P$:** C, 42.49; H, 7.13; N, 8.26; P, 9.13. Found C, 42.50; H, 7.09; N, 8.25; P, 9.14.

*(4-(Dimethylamino)buta-1,3-dienyl)(methyl)dimorpholin-4-yl-phosphonium Bromide (**27a**).* **Yield:** 70%; amorphous solid; **^{1}H NMR** (300 MHz, $CDCl_3$): δ 2.33 (d, $^2J_{PH}$ = 12.6 Hz, 3H), 3.0 (br s, 6H), 3.21 (br s, 8H), 3.74 (br s, 8H), 4.75 (dd, $^2J_{PH}$ = 19.2 Hz, $^3J_{HH}$ = 16.5 Hz, 1H), 5.26 (t, $^3J_{HH}$ = 12 Hz, 1H), 7.39 (d, $^3J_{HH}$ = 12 Hz, 1H), 7.46−7.61 (m, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 10.6 (d, $^1J_{PC}$ = 86.3 Hz, CH_3−P), 44.8 (NCH_2), 66.7 (d, $^3J_{PC}$ = 5.0 Hz, OCH_2), 83.5 (d, $^1J_{PC}$ = 131.3 Hz, CH−P), 97.6 (d, $^3J_{PC}$ = 26.4 Hz, C(3)), 155.26 (C(4)), 157.2 (d, $^2J_{PC}$ = 12.9 Hz, C(2)), NMe_2 signals are not observed; **^{31}P NMR** (81 MHz, $CDCl_3$) δ 55.2. **MS-FAB**, *m/z* (%): 314([M − Br]$^+$, 100). **Anal. Calcd for $C_{15}H_{29}BrN_3O_2P$:** C, 45.69; H, 7.41; N, 10.66; P, 7.86. Found C, 45.67; H, 7.43; N, 10.75; P, 7.89.

*Bis(diethylamino)(4-(dimethylamino)buta-1,3-dienyl)methylphosphonium Bromide (**27b**).* **Yield:** 100%; amorphous solid; **^{1}H NMR** (300 MHz, $CDCl_3$): δ 1.12−1.21 (m, 12H), 2.10 (d, $^2J_{PH}$ = 12.9 Hz, 3H), 2.96 (br s, 6H), 3.05−3.18 (m, 8H), 4.83 (dd, $^2J_{PH}$ = 20.4 Hz, $^3J_{HH}$ = 16.2 Hz, 1H), 5.20 (t, $^3J_{HH}$ = 9 Hz, 1H), 7.29−7.41 (m, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 12.7 (d, $^1J_{PC}$ = 89.3 Hz, CH_3−P), 14.2 (CH_3), 39.9 (d, $^2J_{PC}$ = 3.8 Hz, NCH_2), 87.8 (d, $^1J_{PC}$ = 137 Hz, CH−P), 97.1 (d, $^3J_{PC}$ = 26.4 Hz, C(3)), 154.6 (C(4)), 155.3 (d, $^2J_{PC}$ = 10.1 Hz, C(2)), NMe_2 signals are not observed; **^{31}P NMR** (81 MHz, $CDCl_3$) δ 55.2. **MS-FAB**, *m/z* (%): 281([M − Br]$^+$, 100). **Anal. Calcd for $C_{15}H_{33}BrN_3P$:** C, 49.18; H, 9.08; N, 11.47; P, 8.46. Found C, 49.20; H, 9.11; N, 11.54; P, 8.55.

■ ASSOCIATED CONTENT

Supporting Information. Experimental procedures, characterization data for the compounds obtained, and crystallographic

details. This material is available free of charge via the Internet at http://pubs.acs.org

AUTHOR INFORMATION

Corresponding Author
*Email: a.kostyuk@enamine.net

REFERENCES

(1) Tang-Qing, Yu.; Yao, Fu.; Lei, L.; Guo, Q. X. *J. Org. Chem.* **2006**, *71*, 6157.
(2) Bishop, L. M.; Barbarow, J. E.; Bergman, R. G.; Trauner, D. *Angew. Chem., Int. Ed.* **2008**, *47*, 8100.
(3) (a) Nakamura, I.; Zhang, D.; Terada, M. *J. Am. Chem. Soc.* **2010**, *132*, 7884. (b) Maynard, D. F.; Okamura, W. H. *J. Org. Chem.* **1995**, *60*, 1763. (c) Palacios, F.; Herrán, E.; Alonso, C.; Rubiales, G.; Lecea, B.; Ayerbe, M.; Cossío, F. P. *J. Org. Chem.* **2006**, *71*, 6020.
(4) Beaudry, C. M.; Malerich, J.; Trauner, P. D. *Chem. Rev.* **2005**, *105*, 4757.
(5) Dillon, K. B.; Mathey, F.; Nixon, J. F. *Phosphorus. The Carbon Copy*; John Wiley & Sons: New York, 1997.
(6) Nyulászi, L. *Chem. Rev.* **2001**, *101*, 1229.
(7) (a) LeFloch, P.; Mathey, F. *J. Chem. Soc. Chem. Comm.* **1993**, 1295. (b) Mathey, F. *Tetrahedron Lett.* **1988**, *29*, 4289. (c) Piechaczyk, O.; Jean, Y.; Le Floch, P. *J. Org. Chem.* **2005**, *70* (12), 4637.
(8) Guner, V. A.; Houk, K. N.; Davies, I. W. *J. Org. Chem.* **2004**, *69*, 8024.
(9) (a) Kostyuk, A. N.; Svyaschenko, Y. V.; Volochnyuk, D. M. *Tetrahedron* **2005**, *61* (39), 9263. (b) Svyaschenko, Y. V.; Kostyuk, A. N.; Barnych, B. B.; Volochnyuk, D. M. *Tetrahedron* **2007**, *63* (25), 5656. (c) Svyaschenko, Y. V.; Volochnyuk, D. M.; Kostyuk, A. N. *Tetrahedron Lett.* **2010**, *51* (48), 6316.
(10) (a) Kollár, L.; Keglevich, G. *Chem. Rev.* **2010**, *110*, 4257. (b) Müller, C.; Vogt, D. *Dalton Trans.* **2007**, *47*, 5505. (c) Broeckx, L. E. E.; Lutz, M.; Vogt, D.; Müller, C. *Chem. Commun.* **2011**, *47*, 2003.
(11) (a) Le Floch, P. *Coord. Chem. Rev.* **2006**, *250* (5−6), 627–681. (b) Le Floch, P. *Top. Heterocycl. Chem.* **2009**, *20*, 147–184. (c) Streubel, R. *Science of Synthesis*; Thieme: New York, 2005; Vol. *15*, pp 1157−1179. (d) Müller, C.; Wasserberg, D.; Weemers, J. J. M.; Pidko, E. A.; Hoffmann, S.; Lutz, M.; Spek, A. L.; Meskers, S. C. J.; Janssen, R. A. J.; Van Santen, R. A.; Vogt, D. *Chem.—Eur. J.* **2007**, *13*, 4548–4559.
(12) (a) Leblanc, Y.; Fitzsimmons, B. J.; Zamboni, R.; Rokach, J. *J. Org. Chem.* **1988**, *53*, 267–275. (b) Hanessian, S.; Botta, M. *Tetrahedron Lett.* **1987**, *28* (11), 1151–1154.
(13) Kan, C.; Ollis, W. D.; Somanathan, R.; Sutherland, I. O. *J. Chem. Soc. Perkin Trans. 1* **1983**, *5*, 1041–1048.
(14) (a) Hall, H. K., Jr.; Abdelkader, M.; Glogowski, M. E. *J. Org. Chem.* **1982**, *47* (19), 3691. (b) Nagel, M.; Hansen, H.-J. *Synlett* **2002**, *5*, 692.
(15) (a) Trostyanskaya, I. G.; Efimova, I. V.; Kazankova, M. A.; Lutsenko, I. F. *J. Gen. Chem. USSR (Engl. Transl.)* **1983**, *53* (1), 236–237. (b) Kazankova, M. A.; Trostyanskaya, I. G.; Efimova, I. V.; Beletskaya, I. P. *Rus. J. Org. Chem.* **1996**, *32* (11), 1606–1619.
(16) (a) Ashe, A. J. *J. Am. Chem. Soc.* **1971**, *93*, 3293. (b) Ashe, A. J.; Smith, T. W. *J. Am. Chem. Soc.* **1976**, *98*, 7861. (c) Märkl, G. *Angew. Chem.* **1963**, 669. *Angew. Chem., Int. Ed. Engl.* **1963**, *2*, 479.
(17) Quin, L. D.; Kisalus, J. C.; Skolimowski, J. J.; Rao, N. S. *Phosphorus, Sulfur Silicon Relat. Elem.* **1990**, *54* (1/4), 1–7.
(18) Thewalt, U.; Bugg, C. E. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1972**, *28*, 871.