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Reactivity of a 1,3,2-Diazaphosphinine Toward Propargyl-Phosphine Derivatives and Activated Alkenes

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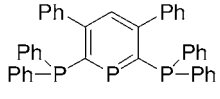
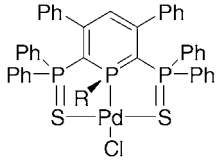
ABSTRACT: *2,5-Diphenylphosphole and diphenylphosphino derivatives* **2, 3** *of 1-phenylpropargyl were prepared by reacting the corresponding diphenylphosphinolithium and 2,5-diphospholyl lithium salts with (3-bromo-prop-1-ynyl)-benzene in THF at low temperature. Sulfurization of these propargyl derivatives was then carried out with elemental sulfur in toluene at 90°C to yield the corresponding phosphole* **8** *and phosphino* **9** *derivatives. Reaction of 3,5-di-*tert*-butyl-1,3,2-diazaphosphinine* **1** *with the free phosphole derivative led to a mixture of diazaphosphinines* **4** *and* **5** *that were converted to the corresponding phosphinines* **6** *and* **7** *upon treatment with trimethylsilylacetylene in excess. Reaction of* **1** *with 1-phenylpropargyl derivatives of diphenylphosphine* **8** *and phosphole* **9** *afforded 7,8-dihydro-1-phospha-2,6-diazabarrelenes* **10** *and* **11** *having an exocyclic double bond. Formation of these compounds results from a (1,3)-shift of a hydrogen atom from the methylene carbon atom to the bridge of the barrelene moiety. Depending on the nature of the phosphine group, the sulfur atom can also be displaced to the P atom of the barrelene moiety. The X-ray structure of the phosphole derivative* **10** *was recorded. Three 6,7-dihydro-1-phospha-2,6-diazabarrelenes bearing two (***16***) or one ester (***17a,b***), or one cyano group (***18a,b***) on the bridge were also synthesized through the reaction of* **1** *with ethyl acrylate, dimethyl fumarate, and acrylonitrile. The X-ray structure of the cyano derivative* **18a** *is also presented.* © 2003 Wiley Periodicals, Inc. Heteroatom Chem 14:326–333, 2003; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.10152

INTRODUCTION

Diels–Alder reactions of 1,3,2-diazaphosphinines with alkynes prove to be a powerful and versatile method for the synthesis of phosphinines [1]. Over the last few years we exploited this approach in the elaboration of different polyfunctional phosphinine-based structures such as bi-/tridentate, tripodal ligands and macrocycles having different cavity sizes [2]. Some of these ligands have found interesting applications in coordination chemistry because of their strong π-acceptor capacity [3]. Recently, we showed that 2,6-bis(diphenylphosphino)phosphinines could be used as precursor in the synthesis of a new class of S—P—S based pincer ligands featuring a central σ^4,λ^5-phosphorus atom. Palladium(II) complexes of these ligands, such as those depicted in the following scheme, showed an interesting catalytic activity in the formation of C—B bonds through the Myaura-catalyzed process [4].





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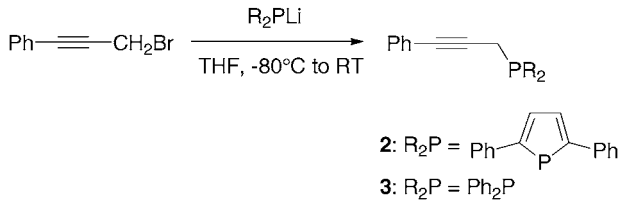
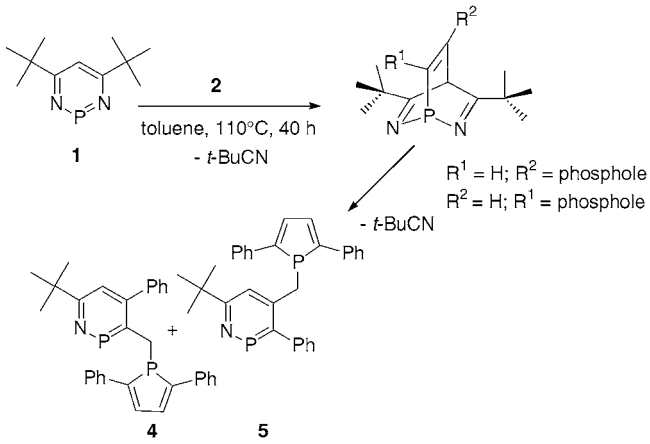
As a logical extension, we recently explored the synthesis of extended pincer ligands featuring a methylene group between the phosphinine ring and the pendant phosphine ligands. Following a similar strategy, we thus explored the reactivity of 1,3,2-diazaphosphinines toward phosphine derivatives of propargyl. This study led to unexpected results that prompted us to explore the reactivity of activated alkenes toward 1,3,2-diazaphosphinines. Herein we report on these results.

RESULTS AND DISCUSSION

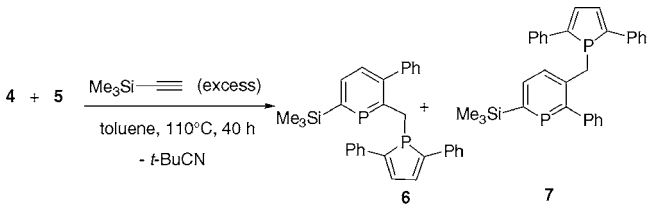
The reactivity of diazaphosphinine **1** toward propargylphosphines was tested using the phosphole **2** and the phosphine **3** derivatives. Syntheses of these two compounds were achieved by reacting 1-phenylethynyl-lithium [5] and the 2,5-diphenylphospholyl-lithium [6] derivatives with (3-bromo-prop-1-ynyl)-benzene in THF at low temperature [7]. Compounds **2** and **3** were isolated in good yields. Phosphole **2** was characterized by NMR spectroscopy, mass spectrometry, and elemental analysis. The phosphine derivative **3** proved to be highly oxygen-sensitive and was characterized by ^{31}P NMR exclusively. As seen later, **3** was fully characterized as its P-sulfide derivative.



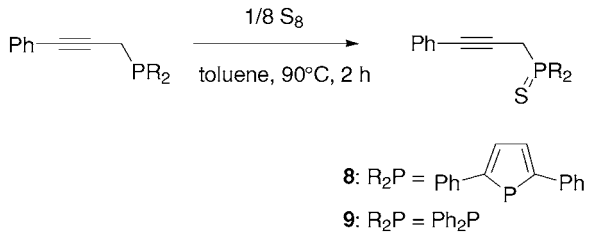
Thermal reaction of **1** with **2** and **3** did not yield the expected result and, whatever the experimental conditions used (temperature, concentration), the cycloaddition of 1 equiv. of alkyne led to a mixture of two 1,2-azaphosphinines (**4** and **5**). As reported in precedent studies, formation of these two diazaphosphinines occurs through a [4 + 2] cycloaddition/cycloreversion sequence that involves the transient formation of diazaphosphaberrelenes, followed by the release of one molecule of pivalonitrile. Thus, the reaction of phosphole **2** with 1 equiv. of **1** in toluene at 110°C for 40 h afforded 1,2-azaphosphinines **4** and **5**, which were identified by ^{31}P NMR exclusively. On the basis of ^{31}P NMR data, compounds **4** and **5** are formed in a 4:1 ratio. The formulation of compound **4** was evidenced by a $^{3}J_{PP} = 24.26$ Hz coupling constant.



In order to definitively establish the formulation of 1,2-azaphosphinines **4** and **5**, the crude mixture was reacted with trimethylsilylacetylene to yield phosphinines **6** and **7**, which, according to ^{31}P NMR spectroscopy, were formed in a 4:1 ratio, respectively. The mechanism of these transformations involves a mechanism similar to that depicted in the following scheme for the formation of diazaphosphinines **4** and **5**. A cycloaddition of 1 equiv. of trimethylsilyl acetylene takes place to yield an azaphosphabarrelene that eliminates 1 equiv. of pivalonitrile. Unfortunately, the separation of **6** and **7** could not be achieved by column chromatography and these two phosphinines were characterized as a mixture. The presence of a $^{3}J_{PP} = 20.64$ Hz coupling constant in **6** confirms the presence of the methylenephosphole group at the α-positions of phosphorus. These two phosphinines were only characterized by ^{1}H NMR spectroscopy and mass spectroscopy. The use of propargylphosphine **2** in place of **3** yielded a similar result.



In view of these results, we anticipated that the steric bulk around the phosphine group could enhance the regioselectivity in favor of the formation of the α-substituted phosphinine. Indeed, previous studies have clearly showed that alkynyl carbon atoms bearing bulky susbtituents are usually bound to phosphorus in the final compound [1,2]. Thus, **2** and **3** were reacted with elemental sulfur to form sulfides **8** and **9**, which were isolated as stable yellow solids and successfully characterized by NMR techniques and elemental analyses.



Reaction of **1** with **8** and **9** led to a surprising result. Contrary to what is usually observed when alkynes are reacted with diazaphosphinines, the formation of 1,2-azaphosphinines was not observed. Thus, reaction of **1** with **8** cleanly afforded compound **10**, which is characterized by an AB spin system in ^{31}P NMR spectroscopy. The formulation of **10** could not be directly established on ^{1}H and ^{13}C NMR data. Fortunately, single crystals could be grown and the X-ray structure could be recorded. An ORTEP view of one molecule of **10** is presented in Fig. 1 and the most significant bond lengths and bond angles are also listed. As can be seen, the structure of **10** results from the cycloaddition of 1 equiv. of **8** on the diazaphosphinine skeleton but the expected 2,6-diaza-1-phosphabarrelene structure has been isomerized into a 7,8-dihydro-2,6-diaza-1-phosphabarrelene through a (1,3)-shift of one methylene proton. Another surprising feature is the transfer of the sulfur atom from the phosphole ring to the phosphorus atom of the dihydrophosphabarrelene unit.

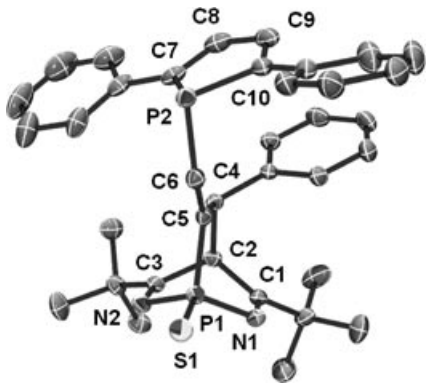
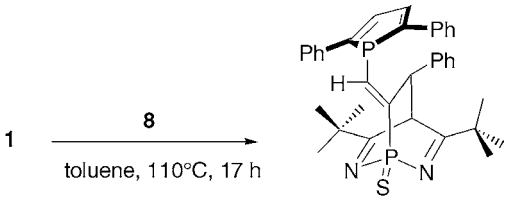


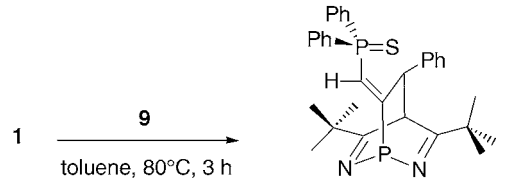
FIGURE 1 ORTEP drawing of one molecule of **10** (50% ellipsoid probability). Hydrogen atoms are omitted for clarity. Relevant bond lengths (Å) and angles (deg) data: S(1)–P(1), 1.9186(6); P(1)–N(1), 1.697(1); P(1)–N(2), 1.709(1); P(1)–C(5), 1.818(2); P(2)–C(7), 1.805(2); P(2)–C(10), 1.815(2); P(2)–C(6), 1.823(2); N(1)–C(1), 1.289(2); N(2)–C(3), 1.286(2); C(1)–C(2), 1.527(2); C(2)–C(4), 1.589(2); C(4)–C(5), 1.517(2); C(5)–C(6), 1.334(2); C(2)–C(3), 1.525(2); C(7)–C(8), 1.359(3); C(8)–C(9), 1.436(3); C(3)–C(15), 1.521(2); N(1)–P(1)–N(2), 104.54(7); N(1)–P(1)–C(5), 100.59(7); N(2)–P(1)–C(5), 97.66(7); N(1)–P(1)–S(1), 116.27(5); N(2)–P(1)–S(1), 115.97(5); C(5)–P(1)–S(1), 118.94(6); C(1)–N(1)–P(1), 113.3(1); N(1)–C(1)–C(2), 118.4(1); C(3)–C(2)–C(1), 109.4(1); C(3)–C(2)–C(4), 106.0(1); C(1)–C(2)–C(4), 108.0(1); N(2)–C(3)–C(2), 119.1(1); C(6)–C(5)–C(4), 130.0(2); C(6)–C(5)–P(1), 119.1(1); C(5)–C(6)–P(2), 131.0(1).



10

The formation of **10** resulted from the reaction of the corresponding 1-(2,5-diphenylphospholyl)-3-phenyl-allene with **1**. However, the formation of this allene as intermediate can be ruled out. Several experiments, carried out under the experimental conditions used for the synthesis of **10**, showed that no isomerization of compound **8** occurs even at high temperature (150°C). Therefore, we must admit that the formation of **10** results from a two-step process that involves first the cycloaddition then the rearrangement. On the basis of this result, it is very difficult to establish whether this rearrangement is promoted by the transfer of the sulfur atom or not.

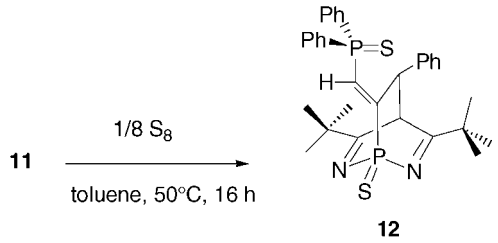
Reaction of **1** with the phosphine sulfide **9** led to a slightly different result and shed some light on the role played by the transfer of the sulfur atom. For example, heating equimolar amounts of the two compounds in toluene at 80°C for 3 h resulted in the formation of compound **11** that exhibited an AB spin system in ^{31}P NMR spectroscopy. However, chemical shifts of the two phosphorus moieties (δ (toluene) = 27.70 and 28.60 ppm with $^{3}J_{PP}$ = 39.0 Hz) were found to be rather different from that recorded for compound **10**. Indeed, a similar rearrangement such as that observed in the synthesis of **10** should lead to a structure incorporating a dihydrobarrelene sulfide (δ (toluene) = −51.40 ppm in **10**) moiety and a free diphenylphosphino group (δ (toluene) = −13.10 ppm in **3**).



11

Unfortunately, several attempts to purify by column chromatography resulted in the isolation of

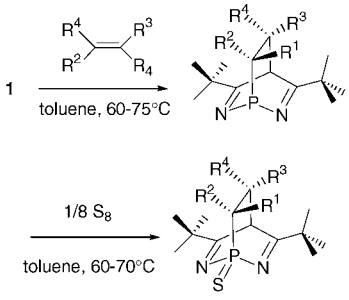
many unidentified compounds. Suspecting that the oxygen sensitivity of the diphenylphosphino group could be responsible for of this failure, we investigated the sulfurization of **11**. Disulfide **12** was easily synthesized by reacting **11** with elemental sulfur in toluene at 50°C for 16 h. On the basis of ^{31}P NMR chemical shifts, we propose that the compound **11** features a diphenylphosphinosulfide group and a free dihydro-1,3,2-diazaphosphabarrelene. Indeed, the sulfurization of phosphorus atom of the barrelene subunit is evidenced by a characteristic downfield shift (δ ($CDCl_3$) = 50.50 ppm) as observed in **10**. Disulfide **12** was successfully characterized by NMR techniques, mass spectroscopy, and elemental analyses. The presence of the exocyclic double bond was easily evidenced by a characteristic signal at δ ($CDCl_3$) = 7.81 ppm in the ^1H NMR spectrum. This signal appears as a characteristic AMX spin system with two important coupling constants with the two P atoms ($^2J_{HP}$ = 27.70 Hz, $^3J_{HP}$ = 20.18 Hz) and a small ($^4J_{HH}$ = 2.49 Hz) coupling constant with the hydrogen located on the saturated bridge.



12

It is still difficult to rationalize why the isomerization of the internal double bond takes place in these reactions. We first supposed that the transfer of the sulfur atom, from the phosphine to the P atom of barrelene, could prevent the retrocycloaddition process. However, the synthesis of **11**, in which the sulfur atom has not been displaced, demonstrates that the transfer of the sulfur atom is not a prerequisite to the (1,3)-shift of hydrogen. One may propose that the displacement of this sulfur atom occurs in a second step as the result of the difference of basicity between the two P atoms.

Beyond this, the synthesis of dihydrophosphabarrelene derivatives is interesting and, to the best of our knowledge, this type of backbone is still unknown. Supposing that diazaphosphinine could undergo cycloaddition with activated alkenes, we explored the reactivity of **1** toward ethyl acrylate, dimethyl fumarate, and acrylonitrile. In all cases, cycloadditions took place in toluene (between 60 and 75°C) to afford the corresponding diazaphosphabarrelenes **13–15**. In the synthesis of **14** and **15**, the cycloaddition was not regioselective and ^{31}P NMR spectroscopy indicated that two isomers (**a** and **b**) are formed. Compounds **14a** (δ (toluene) = 24.80 ppm) and **14b** (δ (toluene) = 24.30 ppm) were formed in a 9:1 ratio and **15a** (δ (toluene) = 41.90 ppm) and **15b** (δ (toluene) = 46.50 ppm) in a 5:1 ratio. Unfortunately, compounds **13–15** were found to be too oxygen-sensitive to be purified by conventional chromatographic separation. Therefore, they were sulfurized prior to purification. Sulfides **16–18** were isolated as colorless solids and fully characterized by conventional NMR techniques, mass spectrometry, and elemental analyses.



13: $R^1 = R_4 = CO_2Me$; $R^2 = R^3 = H$
14a: $R^1 = CO_2Et$; $R^2 = R^3 = R^4 = H$
14b: $R^3 = CO_2Et$; $R^1 = R^3 = R^4 = H$
15a: $R^1 = CN$; $R^2 = R^3 = R^4 = H$
15b: $R^3 = CN$; $R_1 = R^3 = R^4 = H$

16: $R^1 = R^4 = CO_2Me$; $R^2 = R^3 = H$
17a: $R^1 = CO_2Et$; $R^2 = R^3 = R^4 = H$
17b: $R^3 = CO_2Et$; $R^1 = R^3 = R^4 = H$
18a: $R^1 = CN$; $R_2 = R^3 = R^4 = H$
18b: $R^3 = CN$; $R^1 = R^3 = R^4 = H$

Despite many attempts, isomers of **17** and **18** could not be separated by chromatography on silica gel. Fortunately, crystallization using a mixture of dichloromethane and methanol afforded the major isomers **17a** and **18a** as microcrystals. Their formulation was unambiguously ascribed by combination of ^{31}P NMR spectroscopy and X-ray crystallography. Only the structure of **18a** is reported here. An ORTEP view of one molecule of **18a** is presented in Fig. 2 and relevant bond distances and angles are also listed. As can be seen, the cyano group is located on the C7 carbon atom at the α-position of phosphorus. This is in good agreement with a theoretical study, that showed that the outcome of these cycloadditions depends on the polarity of the two partners [8]. Accordingly, in many examples, it was shown that the carbon atom that bears the more attractive functional group is regiospecifically grafted at the α-position at phosphorus in the C2 position.

In conclusion, we have showed that a diazaphosphinine such as **1** reacts with propargyl phosphines in an unusual way to yield the corresponding 7,8-dihydrobarrelenes with an exocyclic double bond. A theoretical study aimed at understanding the factors that govern this surprising reactivity is currently underway in our laboratories. This finding also prompted us to investigate a more rationale approach to such structures by using the reactivity of these diazaphosphinines toward activated alkenes. Various polyfunctional structures can now be anticipated by varying the substitution scheme of

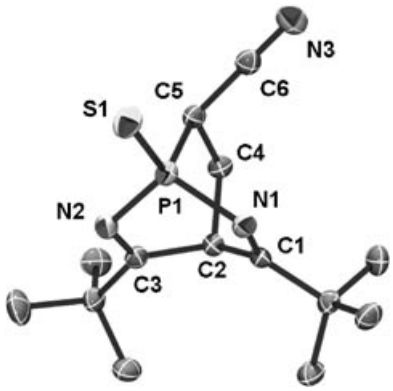


FIGURE 2 ORTEP drawing of one molecule of **18a** (50% ellipsoid probability). Hydrogen atoms are omitted for clarity. Relevant bond lengths (Å) and angles (deg) data: S(1)–P(1), 1.9168(6); P(1)–N(1), 1.686(1); P(1)–N(2), 1.696(1); P(1)–C(5), 1.857(2); N(1)–C(1), 1.289(2); N(2)–C(3), 1.290(2); N(3)–C(6), 1.141(2); C(1)–C(2), 1.524(2); C(2)–C(3), 1.522(2); C(2)–C(4), 1.570(2); C(4)–C(5), 1.549(2); C(5)–C(6), 1.464(2); N(1)–P(1)–N(2), 105.96(7); N(1)–P(1)–C(5), 100.30(7); N(2)–P(1)–C(5), 97.70(7); N(1)–P(1)–S(1), 116.10(5); N(2)–P(1)–S(1), 116.27(5); C(5)–P(1)–S(1), 117.79(6); C(1)–N(1)–P(1), 113.0(1); C(3)–N(2)–P(1), 112.9(1); N(1)–C(1)–C(2), 119.1(2); C(3)–C(2)–C(1), 110.1(1); C(3)–C(2)–C(4), 106.0(1); C(1)–C(2)–C(4), 106.6(1); N(2)–C(3)–C(2), 119.0(1); C(5)–C(4)–C(2), 111.2(1); C(6)–C(5)–C(4), 112.7(1); C(6)–C(5)–P(1), 111.2(1); C(4)–C(5)–P(1), 107.7(1); N(3)–C(6)–C(5), 178.9(2).

the alkene moiety and the substitution scheme of the phosphinine ring.

EXPERIMENTAL

All reactions were routinely performed under an inert atmosphere of argon or nitrogen by using Schlenk and glove-box techniques and dry, deoxygenated solvents. Dry THF and hexanes were obtained by distillation from Na/benzophenone and dry CH_2Cl_2 and $CDCl_3$ from P_2O_5. Dry CD_2Cl_2 was distilled and stored, like $CDCl_3$, on 4 Å Linde molecular sieves. NMR spectra were recorded on a Bruker Avance 300 spectrometer operating at 300 MHz for ^1H, 75.5 MHz for ^{13}C, and 121.5 MHz for ^{31}P NMR. Solvent peaks are used as internal reference relative to Me_4Si for ^1H and ^{13}C chemical shifts (ppm); ^{31}P chemical shifts are relative to a 85% H_3PO_4 external reference and coupling constants are expressed in hertz. The following abbreviations are used: b, broad; s, singlet; d, doublet; t, triplet; m, multiplet; p, pentuplet; sext, sextuplet; sept, septuplet; v, virtual. Mass spectra were obtained at 70 eV with an HP 5989B spectrometer coupled to an HP 5980 chromatograph by the direct inlet method. Elemental analyses were performed by the "Service d'analyses du CNRS," at Gif sur Yvette, France.

*2,5-Diphenyl-1-(3-phenyl-prop-2-ynyl)-1H-phosphole (**2**)*

To a solution of the 2,5-diphenylphospholide anion (4.7 mmol) in THF (25 ml) was added 1 equiv. of 3-bromo-1-phenyl-propyne (915 mg, 4.7 mmol). The reaction mixture was stirred for 15 min at 50°C and checked by ^{31}P NMR. After addition of celite, the solvent was evaporated and the coated gel obtained was deposited onto the top of a silica gel packed-column for chromatography and eluted with a mixture of hexane and toluene (70/30). After the evaporation of solvents the product was obtained as a yellow powder (690 mg, 42%). ^{31}P NMR ($CDCl_3$): δ 4.45. ^1H NMR ($CDCl_3$): δ 2.80 (d, 2H, $^2J_{HP} = 2.0$ Hz, CH_2), 6.90–7.50 (m, 17H, CH of C_6H_5 and H of phosphole). ^{13}C NMR ($CDCl_3$): δ 16.60 (s, CH_2), 77.60 (s, $\equiv C{-}C_6H_5$), 83.50 (d, $^2J_{PC} = 18.0$ Hz, $\equiv C{-}CH_2P$), 125.0–140.0 (m, C_6H_5), 136.80 (d, $^1J_{PC} = 17.15$ Hz, Cα of phosphole), 151.20 (d, $^2J_{PC} = 5.0$ Hz, CH of phosphole). MS *m/z*: 350 (M^+). Anal. Calcd for $C_{25}H_{19}P$: C, 85.69; H, 5.47. Found: C, 85.55; H, 5.40.

*Diphenyl-(3-phenyl-prop-2-ynyl)-phosphine (**3**)*

Lithium (18.5 mmol, 130 mg) was added to a solution of chlorodiphenyl phosphine (7.5 mmol, 1.65 g) in THF at room temperature. After 2 h, a control by ^{31}P NMR indicated the end of the reaction. The solution was canulated into a solution of 3-chloro-1-phenyl-propyne (7.5 mmol, 1.10 g) in THF (10 ml) at −78°C. After addition, the mixture was allowed to warm slowly to room temperature and the progress of the reaction was monitored by ^{31}P NMR. After evaporation of the solvent, hexane (50 ml) was added and the resulting solution was filtered. Phosphine **3** was recovered as a colorless oxygen-sensitive oil (1.35 g, 60%). ^{31}P NMR ($CDCl_3$): δ −13.10. MS *m/z*: 300 (M^+).

*2-[(2,5-Diphenylphospholyl)methyl]-3-phenyl-6-trimethylsilylphosphinine (**6**) and 3-[(2,5-Diphenylphospholyl)methyl]-2-phenyl-6-trimethylsilylphosphinine (**7**)*

A solution of diazaphosphinine **1** (1.26 mmol) in toluene (16 ml) was heated with phosphole **2** at 110°C for 40 h. A control by ^{31}P NMR spectroscopy indicated the formation of monoazaphosphinines **4** and **5**. Monoazaphosphinines **4** and **5**, which are reactive intermediates, were characterized by their ^{31}P NMR chemical shift exclusively. For **4**: ^{31}P NMR (toluene):

δ 273.90 (d, AB system, $^3J_{PP} = 18.30$, azaphosphinine) and –0.25 (d, phosphole); for **5**: ^{31}P NMR (toluene): δ 265.50 (s, azaphosphinine) and −1.10 (s, phosphole). Trimethylsilylacetylene (7 mmol, 0.7 g) was then added and the resulting mixture was heated at 90°C for 17 h. After addition of celite, the solvent was evaporated and the coated gel obtained was deposited onto the top of a silica gel packed-column for chromatography. Elution with a mixture of hexane and toluene (60/40) yielded a fraction containing **6** and **7**. After evaporation of hexane, **6** and **7** were recovered as a yellow viscous oil (250 mg, 40%). For **6**: ^{31}P NMR ($CDCl_3$): δ 237.70 (d, AB system, $^3J_{PP} = 20.64$, phosphinine) and 0.24 (d, phosphole). ^{1}H NMR ($CDCl_3$): δ 0.13 (s, 9H, $SiMe_3$), 3.40 (d, 2H, $^3J_{HP} = 16.85$ Hz, CH_2), 6.85–7.70 (m, 19H, H of C_6H_5, phosphole and phosphinine). For **7**: ^{31}P NMR ($CDCl_3$): δ 229.45 (s, phosphinine) and −0.46 (s, phosphole). ^{1}H NMR ($CDCl_3$): δ 0.25 (s, 9H, $SiMe_3$), 3.00 (s, 2H, $^3J_{HP} = 16.85$ Hz, CH_2), 6.85–7.70 (m, 19H, H of C_6H_5, phosphole and phosphinine). MS *m/z*: 492 (M^+).

*2,5-Diphenyl-1-(3′-phenyl-prop-2′-ynyl)-1H-phosphole Sulfide (**8**)*

S_8 (0.35 mmol, 90 mg) was added to a solution of **2** (1.86 mmol , 650 mg) in THF(10 ml). The reaction was stirred at 80°C for 2 h. After evaporation of the solvent, celite was added and the coated silica gel was then deposited onto the top of a silica gel packed-column for chromatography. Elution was carried out with dichloromethane. After evaporation of the solvent, the product was recovered as a yellow viscous oil (476 mg, 67%). ^{31}P NMR ($CDCl_3$): δ 51.25. ^{1}H NMR ($CDCl_3$): δ 3.30 (d, 2H, $^2J_{HP} = 15.05$ Hz, CH_2), 6.90–7.75 (m, 17H, CH of C_6H_5 and H of phosphole). ^{13}C NMR ($CDCl_3$): δ 27.60 (d, $^1J_{PC} = 43.9$ Hz, CH_2), 79.70 (d, $^2J_{PC} = 13.2$ Hz, $\equiv C_{2'}$), 85.20 (d, $^3J_{PC} = 8.8$ Hz, $\equiv C_{3'}$), 125.0–140.0 (m, C_6H_5), 137.70 (s, Cα of phosphole), 139.30 (s, CH of phosphole). MS *m/z*: 382 (M^+). Anal. Calcd for $C_{25}H_{19}PS$: C, 78.51; H, 5.01. Found: C, 78.45; H, 5.12.

*Diphenyl-(3-phenyl-prop-2-ynyl)-phosphine Sulfide (**9**)*

S_8 was added to a solution of **3** (4.33 mmol, 1.30 g) in toluene (10 ml) and the resulting mixture was heated at 80°C for 1 h. After addition of celite (1 g), the powder obtained was deposited onto the top of a silica gel packed-column for chromatography and eluted with a mixture of pentane and toluene (75/25).After evaporation of solvents the product was obtained as a yellow powder (0.935 g, 65%). ^{31}P NMR ($CDCl_3$): δ 40.45. ^{1}H NMR ($CDCl_3$): δ 3.55 (d, 2H, $^2J_{HP} = 15.25$ Hz, CH_2), 7.01–8.00 (m, 15H, CH of C_6H_5). ^{13}C NMR ($CDCl_3$): δ 29.40 (d, $^1J_{PC} = 54.30$ Hz, CH_2), 81.70 (d, $^2J_{PC} = 12.9$ Hz, $\equiv C_2$), 86.20 (d, $^3J_{PC} = 8.7$ Hz, $\equiv C_3$), 128.0–135.0 (m, C_6H_5). MS *m/z*: 332 (M^+). Anal. Calcd for $C_{21}H_{17}PS$: C, 75.88; H, 5.15. Found: C, 75.70; H, 5.37.

*7-[(2,5-Diphenyl-phosphole)-methylen]-7,8-dihydro-1,3-diaza-2-phosphabarrelene Sulfide (**10**)*

To a solution of diazaphosphinine **1** (0.8 mmol) in toluene (10 ml) was added 1 equiv. of alkyne **8** (0.8 mmol, 306 mg) and the resulting mixture was warmed at 110°C for 17 h. When the reaction was completed, celite (1 g) was added and the solvent was evaporated. The powder obtained was deposited onto the top of a silica gel packed-column for chromatography and eluted with dichloromethane. The product was recovered as a yellow powder (200 mg, 42%). ^{31}P NMR (C_6D_6): δ −15.05 (d, $^3J_{PP} = 23.3$ Hz, P phosphole), 50.15 (d, $^3J_{PP} = 23.3$ Hz, P=S). ^{1}H NMR (C_6D_6): δ 0.49 (s, 9H, CH_3), δ 0.87 (s, 9H, CH_3), 3.62 (m, 1H, H_8), 4.77 (ABX, 1H, $^4J_{HP} = 3.18$ Hz, $^3J_{HH} = 4.9$ Hz, H_5), 6.89–7.29 (m, 17H, CH of C_6H_5 and CH of phosphole), 7.75 (ddd, 1H, $^2J_{HP} = 25.6$ Hz,$^3J_{HP} = 18.06$ Hz, $^4J_{HH} = 2.24$ Hz, CH—P). ^{13}C NMR (C_6D_6): δ 27.96 (s, CH_3), δ 28.12 (s, CH_3), 42.40 (d, $^3J_{PC} = 15.5$ Hz, CMe_3), 45.66 (m, C—P and C_8), 54.00 (d, $^3J_{PC} = 62.7$ Hz, C_5), 54.11 (m, C_7), 127–149 (m, C_6H_5 and Cβ of phosphole), 145.52 (d, $^1J_{CP} = 9.1$ Hz, Cα of phosphole), 147.00 (d, $^1J_{CP} = 8.9$ Hz, Cα of phosphole), 192.04 (d, $^2J_{CP} = 15.3$ Hz, C_4), 192.04 (d, $^2J_{CP} = 15.2$ Hz, C_6). MS *m/z*: 592 (M^+). Anal. Calcd for $C_{36}H_{38}N_2P_2S$: C, 72.95; H, 6.46. Found: C, 73.09; H, 6.69.

*7-[(Diphenylphosphine sulfide)-methylen]-7,8-dihydro-1,3-diaza-2-phosphabarrelene Sulfide (**12**)*

Alkyne **9** (1.0 mmol, 332 mg) was added to a solution of diazaphosphinine **1** (1.0 mmol) in toluene (10 ml). The resulting solution was warmed at 80°C for 3 h. After checking the formation of compound **11**, S_8 (0.31 mmol, 80 mg) was added and the mixture was stirred at 50°C for 16 h. Celite (1 g) was added and the solvent was evaporated. The solid obtained was deposited onto the top of a silica gel packed-column for chromatography and eluted with a mixture of dichloromethane and methanol (1/10). The product was recovered as yellow needles (310 mg, 54%).^{31}P NMR ($CDCl_3$): δ 29.55 (d, $^3J_{PP} = 56.18$ Hz, P phosphine), 50.54 (d, $^3J_{PP} = 56.18$ Hz, P_2). ^{1}H NMR

($CDCl_3$): δ 0.60 (s, 9H, CH_3), δ 1.27 (s, 9H, CH_3), 4.83 (m, 1H, H_8), 5.16 (AMX, 1H, H_5), 6.82–7.53 (m, 15H, C_6H_5), 7.82 (ddd, 1H, $^2J_{HP} = 27.70$ Hz, $^3J_{HP} = 20.18$ Hz, $^4J_{HH} = 2.49$ Hz, CH—P). ^{13}C NMR ($CDCl_3$): δ 26.44 (s, CH_3), δ 27.31 (s, CH_3), 40.95 (d, $^3J_{PC} = 14.9$ Hz, CMe_3), 41.15–41.96 (m, C_7, C_8, and C—P), 52.96 (d, $^3J_{PC} = 63.7$ Hz, C_5), 126.61–150.35 (m, C_6H_5), 192.98 (d, $^2J_{CP} = 15.6$ Hz, C_4), 196.14 (d, $^2J_{CP} = 15.6$ Hz, C_6). MS *m/z*: 574 (M^+). Anal. Calcd for $C_{32}H_{36}N_2P_2S_2$: C, 66.87; H, 6.31. Found: C, 67.10; H, 6.63.

*7,8-(Methylcarboxylate)-7,8-dihydro-1,3-diaza-2-phosphabarrelene Sulfide (**16**)*

To a solution of diazaphosphinine (1.0 mmol) in toluene (10 ml) was added 1.8 equiv. of methyl fumarate (1.8 mmol, 260 mg). The resulting mixture was warmed at 75°C for 20 h. When the reaction completed, S_8 (0.38 mmol, 97 mg) was added and the mixture was stirred at 70°C for 3 h. Celite (1 g) was added and the solvent was evaporated. The solid obtained was deposited onto the top of a silica gel packed-column for chromatography and eluted with a mixture of dichloromethane and ethyl acetate (80/20). The product was recovered as a white powder (127 mg, 33%). ^{31}P NMR ($CDCl_3$): δ 46.00. ^{1}H NMR ($CDCl_3$): δ 1.10 (s, 9H, CH_3), δ 1.28 (s, 9H, CH_3), 3.07 (m, 1H, H_8), 3.36 (dd, 1H, $^2J_{HP} = 16.20$ Hz,$^3J_{HH} = 6.11$ Hz, H_7), 3.68 (s, 3H, OMe), 3.74 (s, 3H, OMe), 5.23 (dd, 1H, $^4J_{HP} = 8.82$ Hz,$^3J_{HH} = 1.80$ Hz, H_5). ^{13}C NMR ($CDCl_3$): δ 26.10 (s, CH_3), δ 26.23 (s, CH_3), 40.8 (d, $^3J_{PC} = 15.4$ Hz, CMe_3), 41.34 (d, $^3J_{PC} = 15.2$ Hz, CMe_3), 42.71 (d, $^3J_{PC} = 70.5$ Hz, C_5), 46.05 (d, $^2J_{PC} = 45.10$ Hz, C_8), 46.60 (d, $^1J_{PC} = 5.2$ Hz, C_7), 52.03 (s, OMe), 52.16 (s, OMe), 166.51 (d, $^2J_{PC} = 4.3$ Hz, CO—C_7), 168.17 (d, $^3J_{PC} = 6.61$ Hz, CO—C_8), 194.63 (d, $^2J_{CP} = 15.84$ Hz, C_6), 194.82 (d, $^2J_{CP} = 15.09$ Hz, C_4). MS *m/z*: 386 (M^+). Anal. Calcd for $C_{17}H_{27}N_2O_4PS$: C, 52.84; H, 7.04. Found: C, 53.01; H, 7.42.

*7-(Ethylcarboxylate)-7,8-dihydro-1,3-diaza-2-phosphabarrelene Sulfide (**17a**) and 8-(Ethylcarboxylate)-7,8-dihydro-1,3-diaza-2-phosphabarrelene Sulfide (**17b**)*

Ethyl acrylate (2.40 mmol, 240 mg) was added to a solution of diazaphosphinine **1** (1.0 mmol) in toluene (10 ml). The resulting mixture was heated at 60°C for 1 h. When the reaction completed, S_8 (0.31 mmol, 80 mg) was added and the mixture was stirred at 60°C for 15 h. The crude product was purified by chromatography and eluted with a solution of dichloromethane and ethyl acetate (90/10). Compounds **17a** and **17b** were recovered as white solids (129 mg, 38%). Compound **17a** was obtained as a white solid after crystallization in a mixture of dichloromethane–methanol (1/1). Data of only **17a**, which was obtained in a pure form, are given. Compound **17a**: ^{31}P NMR ($CDCl_3$): δ 25.70. ^{1}H NMR ($CDCl_3$): δ 1.14 (s, 9H, CH_3), δ 1.18 (s, 9H, CH_3), 1.25 (m, 4H, H_8 and Me), 1.64 (m, 1H, H_8), 2.64 (m, 1H, H_7), 4.09 (q, 2H, $^3J_{HC} = 6.7$ Hz, OCH_2), 5.13 (m, 1H, H_5). ^{13}C NMR ($CDCl_3$): δ 14.87 (s, Me), 23.71 (s, C_8), 28.23 (s, CH_3), δ 28.37 (s, CH_3), 41.99 (b s, CMe_3), 42.59 (d, $^1J_{PC} = 13.69$ Hz, C_7), 45.26 (d, $^3J_{PC} = 29.23$ Hz, C_5), 61.89 (s, OCH_2), 171.89 (d, $^3J_{PC} = 12.75$ Hz, C═O), 194.24 (d, $^2J_{CP} = 18.07$ Hz, C_4), 194.82 (d, $^2J_{CP} = 16.95$ Hz, C_6). MS *m/z*: 342 (M^+). Anal. Calcd for $C_{16}H_{27}N_2O_2PS$: C, 56.12; H, 7.95. Found: C, 56.45; H, 7.79.

*7-Cyano-7,8-dihydro-1,3-diaza-2-phosphabarrelene Sulfide (**18a**) and 8-Cyano-7,8-dihydro-1,3-diaza-2-phosphabarrelene Sulfide (**18b**)*

Acrylonitrile (3.0 mmol, 159 mg) was added to a solution of diazaphosphinine **1** (1.0 mmol) in toluene (10 ml). The resulting mixture was heated at 65°C for 2 h. When the reaction completed, S_8 (0.38 mmol, 97 mg) was added and the mixture was stirred at 60°C for 2 h. Celite (1 g) was added and the solvent was evaporated. The solid obtained was purified by chromatography and eluted with ethyl acetate. The mixture of **18a** and **18b** was recovered as a white powder (115 mg, 39%). Compound **18a** was obtained in a pure form after crystallization in a mixture of dichloromethane–methanol (1/1). Data of only **18a** are reported. Compound **18a**: ^{31}P NMR (CD_2Cl_2): δ 42.50. ^{1}H NMR (CD_2Cl_2): δ 1.02 (s, 9H, CH_3), δ 1.07 (s, 9H, CH_3), 1.62 (m, 1H, H_8), 1.96 (m, 1H, H_8), 2.75 (m, 1H, H_7), 4.82 (m, 1H, H_5). ^{13}C NMR (CD_2Cl_2): δ 26.91 (s, CH_3), δ 27.05 (s, CH_3), 29.61 (d, $^2J_{PC} = 51.69$ Hz, C_8), 32.64 (d, $^1J_{PC} = 6.12$ Hz, C_7), 42.06 (d, $^3J_{PC} = 72.21$ Hz, C_5), 42.61 (d, $^3J_{PC} = 16.1$ Hz, CMe_3), 42.70 (d, $^3J_{PC} = 15.5$ Hz, CMe_3), 116.32 (d, $^3J_{PC} = 14.5$ Hz, C≡N), 197.60 (d, $^2J_{CP} = 19.25$ Hz, C_4), 197.86 (d, $^2J_{CP} = 19.21$ Hz, C_6). MS *m/z*: 295 (M^+). Anal. Calcd for $C_{14}H_{22}N_3PS$: C, 56.93; H, 7.51. Found: C, 57.09; H, 7.72.

X-ray Crystallographic Studies

Single crystals of compounds **10** and**18a** suitable for X-ray crystallography were obtained by diffusing methanol into a dichloromethane solution of the compounds at room temperature in a 5-mm NMR tube. Data were collected at 150 K on a Nonius Kappa

TABLE 1 Crystal Data and Structural Refinement Details for Structures of Compounds **10** and **18a**

	10	***18a***
Empirical formula	$C_{36}H_{38}N_2P_2S$	$C_{14}H_{22}N_3PS$
Formula weight	592.68	295.38
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
a (Å)	21.0309(3)	9.9570(10)
b (Å)	15.46550(10)	9.5630(10)
c (Å)	19.8127(2)	17.3020(10)
β (deg)	95.308(5)	105.5060(10)
V (Å^3)	6416.51(12)	1587.5(2)
Z	8	4
D_{calcd} (g/cm^3)	1.227	1.236
μ (cm^{-1})	0.228	0.296
h, k, l ranges	−27 27; −20 20; −25 25	−13 14; −13 11; −24 24
Crystal size (mm^3)	0.22 × 0.22 × 0.18	0.20 × 0.20 × 0.12
Crystal color and habit	Lemon yellow plate	Colorless plate
$2\Theta_{max}$ (deg)	27.48	30.02
No. of reflections measured	28061	8149
No. of independent reflections	14675	4635
No. of reflections used	11924	3358
$R1^a[I > 2\sigma(I)]$	0.0409	0.0443
$wR2^b[I > 2\sigma(I)]$	0.1189	0.1394
Goodness of fit on F^2	1.045	1.097
Largest diff. peak (eÅ^{-3})	2.058 (0.056)/−0.331 (0.056)	0.730 (0.090)/−0.431 (0.090)

[a] $R1 = \Sigma||F_0| - |F_c||/\Sigma|F_0|$.
[b] $wR2 = (\Sigma w||F_0| - |F_c||^2/\Sigma w|F_0|^2)^{1/2}$.

CCD diffractometer using an Mo Kα (λ = 0.71069 Å) X-ray source and a graphite monochromator. Experimental details are described in Table 1. The crystal structures were solved using SIR 97 [9] and SHELXL-97 [10]. ORTEP drawings were made using ORTEP III for Windows [11].

SUPPLEMENTARY DATA

CCDC 198870 (compound **10**) and CCDC 198871 (compound **18a**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/const/retrieving.html (or from Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 336033; or deposit@ccdc.cam.ac.uk).

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