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Reactions of *N*-vinylic phosphazenes with azodicarboxylic and acetylenic esters

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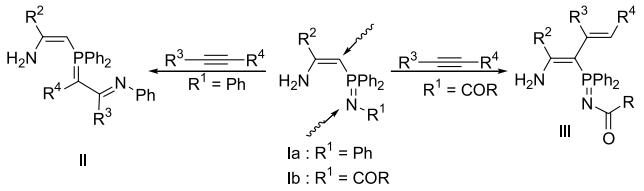
Abstract—*N*-Vinylic phosphazenes react as enamines (1,4-addition) with azodicarboxylic esters, whereas different behavior is observed when these phosphazenes react with dimethyl acetylenedicarboxylate (3,4-addition). A [2+2] cycloaddition reaction of the vinyl moiety of vinylic phosphazenes with the acetylenic triple bond of the acetylenic esters followed by a ring opening leads to the formation of functionalized conjugated phosphazenes.

1. Introduction

Phosphazenes[1,2] have been extensively used as useful tools for the construction of carbon–nitrogen double bonds (Aza-Wittig reaction)[1,3] and they are versatile precursors of acyclic[4] and heterocyclic compounds,[5] but as far as we know no reaction of phosphazenes with azodicarboxylic derivatives has been described,[1] and few examples of their reaction with acetylenic derivatives such as propargylic phosphonium salts[6] or acetylenedicarboxylic acid esters[7] are reported.

We have previously studied the [2+2] cycloaddition reaction of simple phosphazenes with acetylenic esters involving a formal insertion of the triple bond into the phosphazene linkage (1,2-addition).[7] However, when P-functionalized phosphazenes such as β-enamino phosphazenes **I** were used, the presence of a new functional group offered new reactive centres towards the acetylenic triple bond and the reaction may have taken place either through the phosphazene linkage or through the enamine moiety, depending on the reactivity of the phosphazene. *N*-Aryl β-enamino phosphazenes **Ia** (R^1=Ph) reacted with acetylenic esters through the phosphazene group to give conjugated phosphorus ylides **II**.[8a] However, when the reactivity of the phosphazene group decreased with the introduction of electron-withdrawing substituent in the nitrogen atom such as *N*-benzoyl-[8b] **Ib** (R^1=COPh) or *N*-ethoxycarbonyl β-enamino phosphazenes[8c] **Ib** (R^1=COOR) the reaction with acetylenic esters took place through the enamine moiety to give functionalized enamines **III** (Scheme 1), without altering the phosphazene group. Following on from our previous studies on the reactivity and the synthetic utility of phosphazenes, here, we aim to explore the reaction of *N*-vinylic phosphazenes with well known electrophilic reagents widely used in cycloaddition reactions[9] such as azodicarboxylic and acetylenic esters, in order to test whether the introduction in the nitrogen atom of a new functional group (a double bond) conjugated with the phosphazene group could drive the process through the vinyl carbon atom.



Scheme 1.

2. Results and discussion

2.1. Reaction of *N*-vinylic phosphazenes with diethyl azodicarboxylate

N-Vinylic phosphazenes **1** were easily obtained by reaction of phosphorus ylides and nitriles.[10] The treatment of phosphazene **1** (R=Ph), derived from triphenylphosphine, with diethyl azodicarboxylate **2** in $CHCl_3$ at room temperature gave functionalized hydrazino derivatives **3**, in good yields (Scheme 2, Table 1, entries 1–5). Compounds **3** were characterized on the basis of spectroscopic data. A ^{31}P NMR spectrum of compound **3a** showed

Keywords: Phosphazenes; Acetylenic esters; Azodicarboxylates; [2+2] Cycloaddition reactions.
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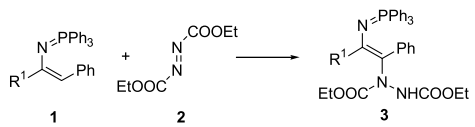


Scheme 2.

Table 1. Conjugated phosphazenes **3** obtained

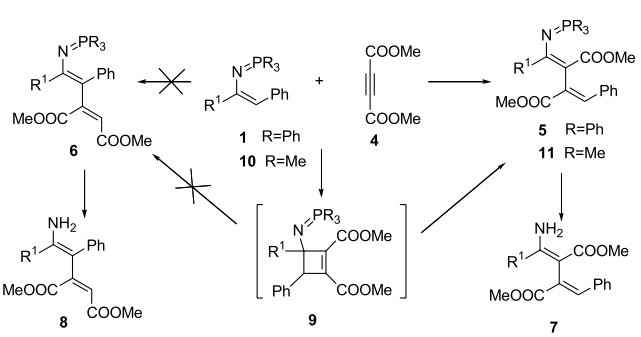
Entry	Compound	R^1	Yield (%)[a]	Mp (°C)
1	**3a**	2-Pyridyl	85	149–150
2	**3b**	Ph	80	180–181
3	**3c**	2-Furyl	67	59–60
4	**3d**	2-Thienyl	87	128–129
5	**3e**	3-Pyridyl	81	103–105

[a] Yield after purification by flash chromatography.

absorption at δ_P=8.09 ppm, while ^{13}C NMR displayed singlets at δ_C=148.2 ppm for the enamine double carbon atom attached to the azo substituent and δ_C=157.8 and 158.2 ppm for the carboxylate esters. The GC–MS spectrometry of **3a** shows the molecular ion peak (*m*/*z* 630, 24%) which is in agreement with the structure of compounds **3**. The formation of conjugated phosphazenes **3** could be explained by conjugative addition of the γ-C-atom (1,4-addition) of phosphazenes **1** to the azo moiety of diethyl azodicarboxylate **2** in a similar way to that observed of *N*-vinylic phosphazenes to simple[3c,d] and unsaturated carbonyl compounds.[11] A similar way was observed when enamines react with diethyl azodicarboxylate.[12]

2.2. Reaction of *N*-vinylic phosphazenes with acetylenic esters

Different behavior is observed in the reaction of *N*-vinylic phosphazenes with acetylenic compounds. Treatment of phosphazene **1a**, derived from triphenylphosphine (R=Ph, R^1=2-pyridyl), with dimethyl acetylenedicarboxylate **4** in $HCCl_3$ at room temperature gave an 1:1 adduct in good yield (Scheme 3). This adduct was characterized on the basis of spectroscopic data and the structure could be initially consistent with both conjugated phosphazenes **5a** or **6a**. Mass spectrometry showed the molecular ion peak (*m*/*z* 599, 50%). A ^{31}P NMR spectrum of adduct **5a** or **6a** showed absorption at δ_P=7.52 ppm, characteristic of conjugated phosphazenes.[3] ^1H NMR showed absorptions in the region of 6.45–7.60 ppm for the aromatic and the vinyl protons and two singlets at 3.74 and 3.77 ppm for the methoxy groups of carboxylic esters, while the ^{13}C NMR displayed



Scheme 3.

singlets at δ_C=147.5 ppm for the enamine carbon bonded to the nitrogen atom and at δ_C=168.2 and 170.5 ppm for carboxylate esters. However, given that the vinyl proton signal appeared with the aromatic protons, it is not easy to use NMR experiments (NOE, HMBC…) in order to distinguish between both structures **5a** and **6a**, the hydrolysis of the phosphazene linkage of the adduct **5a** or **6a** was carried out to give primary enamines **7a** or **8a** (Scheme 3, Table 2, entry 4). The primary enamine obtained (**7a** or **8a**) shows a vinylic proton separated from the aromatic signals which could be used to establish whether the phenyl group in **7a** or the carboxylate group in **8a** is vicinal to the vinyl proton by NMR experiments.

Table 2. Compounds **5** and **7** obtained

Entry	Compound	R^1	Yield (%)[a]
1	**5a**	2-Pyridyl	60
2	**5b**	Ph	93[b]
3	**5c**	2-Furyl	80[c]
4	**7a**	2-Pyridyl	86[d]
5	**7b**	Ph	93[b]/88[e]
6	**7c**	2-Furyl	80[c]/79[e]
7	**7d**	2-Thienyl	54

[a] Yield after purification by flash-chromatography.
[b] Proportion **5b/7b**, 67:33.
[c] Proportion **5c/7c**, 90:10.
[d] Obtained from phosphazenes **5**.
[e] Obtained from phosphazenes **10**.

HMBC experiments corroborated the structure **7a** and, therefore, the formation of compound **5a** with exclusion of the other possible structure **6a**. A correlation between the olefinic proton and aromatic =CH indicated that the phenyl group was the substituent more closely situated to the olefinic proton. In addition, in the case of conjugated β-enamino ester **7a** the presence of an ester group would stabilize the primary enamine, since it is known that primary enamines are very unstable unless conjugated with an electron-withdrawing group in the β-carbon atom.[13]

The formation of conjugated phosphazene **5a** (Scheme 3, Table 2, entry 1) could be explained by [2+2] cycloaddition reaction of the vinyl moiety of the phosphazene with the triple carbon–carbon bond of the acetylenic ester after redistribution of bonds in the four-membered intermediate cycle **9**, although a different cleavage of the same intermediate **9** could also explain the formation of isomeric **6a**. When the reaction was performed with phosphazenes **1b** (R^1=Ph) and **1c** (R^1=2-furyl), not only conjugated phosphazenes **5b**,**c** but also primary enamines **7b**,**c**, as minor components (Scheme 3, Table 2, entries 2, 3, 5, and 6) were isolated, due to the easy hydrolysis of the phosphazene, and in the case of phosphazene **1d** (R^1=2-thienyl) only primary enamine **7d** (Scheme 3, Table 2, entry 7) was obtained. An X-ray diffraction analysis for primary enamine **7d** (R^1=2-thienyl) was performed and confirmed the structure proposed for **7d** (Fig. 1).[14]

In order to test whether the reaction of *N*-vinylic phosphazenes with dimethyl acetylenedicarboxylate could be driven to the phosphazene linkage in a similar way to that observed in simple phosphazenes,[15] *N*-vinylic phosphazenes **10** (R=Me), derived from trimethylphosphine were

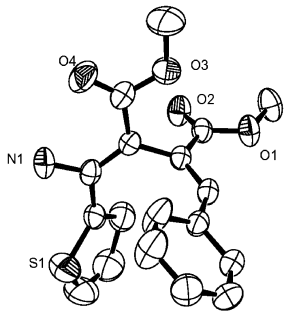


Figure 1. ORTEP for compound **7d**.

prepared, given that it is known that the substitution in the phosphorus atom of phosphazenes of aryl by alkyl substituents increases the reactivity of the phosphazene in a similar way to that observed in the isosteric phosphorus ylides.[3c,d,15] However, a similar result was obtained when *N*-vinylic phosphazenes **10** (R=Me), derived from aliphatic phosphines, were treated with dimethyl acetylenedicarboxylate **4**, affording in this case the enamine derivatives **7** exclusively (Scheme 3, Table 2, entries 5 and 6), without detection of conjugated phosphazene intermediate **11** derived from trimethylphosphine. The higher hydrolysis sensibility to the nucleophilic attack of water to the phosphazene derived from trimethylphosphine, more reactive than that derived from triphenylphosphine, could favor the formation of the primary enamine **7**. As before, the formation of conjugated enamines **7** could be explained by [2+2] cycloaddition reaction followed by ring opening of intermediate **9** and subsequent hydrolysis of the unstable phosphazenes derived from trimethylphosphine **11**.

3. Conclusion

In conclusion, the presence of an olefinic group in conjugation with the phosphazene group in *N*-vinylic phosphazenes opens new synthetic pathways. *N*-Vinylic phosphazenes derived from triphenyl phosphine react like enamines (1,4-addition) with diethylazodicarboxylate. However, different behavior is observed in the reaction with acetylenic esters. *N*-Vinylic phosphazenes derived from triphenyl **1** or trimethyl phosphine **10** gave [2+2] cycloaddition reaction through the vinylic double bond with diacetylenic esters such as dimethyl acetylendicarboxylic ester to afford conjugated phosphazenes **5** and **11**.

4. Experimental

4.1. General

Chemicals were purchased from Aldrich Chemical Company. Solvents for extraction and chromatography were technical grade. All solvents used in reactions were freshly distilled from appropriate drying agents before use. All other reagents were recrystallized or distilled as necessary. All reactions were performed under an atmosphere of dry nitrogen. Analytical TLC was performed with Merck silica gel 60 F_{254} plates. Visualization was accomplished by UV light. Flash chromatography was carried out using Merck silica gel 60 (230–400 mesh ASTM). Melting points were determined with an Electrothermal IA9100 Digital Melting Point Apparatus and are uncorrected. ^{1}H (400, 300, 250 MHz), ^{13}C (100, 75 MHz) and ^{31}P NMR (120 MHz) spectra were recorded on a Bruker Avance 400 MHz, a Varian VXR 300 MHz and a Bruker AC 250 MHz spectrometer using $CDCl_3$ or CD_3OD solutions with TMS as an internal reference (δ=0.00 ppm) for ^{1}H and ^{13}C NMR spectra and phosphoric acid (85%) (δ=0.0 ppm) for ^{31}P NMR spectra. Chemical shifts (δ) are reported in ppm. Coupling constants (J) are reported in Hertz. Low-resolution mass spectra (MS) were obtained at 50–70 eV by electron impact (EIMS) on a Hewlett–Packard 5971 or 5973 spectrometer. Data are reported in the form m/z (intensity relative to base=100). Infrared spectra (IR) were taken on a Nicolet IRFT Magna 550 spectrometer, and were obtained as solids in KBr or as neat oils. Peaks are reported in cm^{-1}. Elemental analyses were performed in a LECO CHNS-932 apparatus.

4.2. General procedure for the reaction of *N*-vinylic phosphazenes and diethylazodicarboxylate

To a 0 °C solution of *N*-vinylic phosphazene (5 mmol) in $CHCl_3$ under a nitrogen atmosphere, diethylazodicarboxylate (0.8 ml, 5 mmol) was added. The mixture was stirring at room temperature until TLC indicated the disappearance of phosphazene. Evaporation of solvent under reduced pressure and chromatographic purification by flash column chromatography with hexane/AcOEt afforded the corresponding derivatives.

4.2.1. 1,1,1,4-Tetraphenyl-3-(2-pyridyl)-2-aza-4-(*N*,*N*′-diethoxycarbonylhydrazono)-1,λ^5-phosphabuta-1,3-diene (3a). The general procedure was followed using 1,1,1,4-tetraphenyl-3-(2-pyridyl)-2-aza-1,λ^5-phosphabuta-1,3-diene (2.28 g, 5 mmol) and the mixture was stirred at room temperature for 1 h. Chromatographic purification (1:1, hexane/diethyl ether) gave 2.680 g (85%) of compound **3a**; mp 149–150 °C (ethyl acetate); ^{1}H NMR (250 MHz, $CDCl_3$): δ 1.01–1.24 (m, 6H), 1.52 (s, 1H), 4.06–4.15 (m, 4H), 6.63–7.80 (m, 24H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.4, 14.5, 61.2, 62.0, 121.0–135.2 (m), 138.5, 148.2, 157.8, 158.2; ^{31}P NMR (120 MHz, $CDCl_3$): δ 8.09; IR (KBr) ν_{max} 3355, 1740, 1719, 1367; MS (EI): m/z 630 (M^+, 24). Anal. Calcd for $C_{37}H_{35}N_4O_4P$: C, 70.46; H, 5.59; N, 8.88. Found: C, 70.31; H, 5.52; N, 8.81.

4.2.2. 1,1,1,3,4-Penthaphenyl-2-aza-4-(*N*,*N*′-diethoxycarbonylhydrazono)-1,λ^5-phosphabuta-1,3-diene (3b). The general procedure was followed using 1,1,1,3,4-pentaphenyl-2-aza-1,λ^5-phosphabuta-1,3-diene (2.28 g, 5 mmol) and the mixture was stirred at room temperature for 1 h. Chromatographic purification (1:1, hexane/ethyl acetate) gave 2.517 g (80%) of compound **3b**; mp 180–181 °C (ethyl acetate); ^{1}H NMR (250 MHz, $CDCl_3$): δ 1.03–1.24 (m, 6H), 4.00–4.12 (m, 4H), 5.82 (s, 1H), 6.73–7.57 (m, 25H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.4, 14.8, 61.5, 62.2, 124.0–132.6 (m), 138.0, 141.3, 156.8; ^{31}P NMR (120 MHz, $CDCl_3$): δ 3.9; IR (KBr) ν_{max} 3361, 1765, 1729, 1394; MS (EI): m/z 629 (M^+, 100). Anal. Calcd for $C_{38}H_{36}N_3O_4P$: C, 72.48; H, 5.76; N, 6.67. Found: C, 71.99; H, 5.70; N, 6.63.

4.2.3. 1,1,1,4-Tetraphenyl-3-(2-furyl)-2-aza-4-(*N*,*N*′-diethoxycarbonylhydrazono)-1,λ^5-phosphabuta-1,3-diene (3c). The general procedure was followed using 1,1,1,4-tetraphenyl-3-(2-furyl)-2-aza-1,λ^5-phosphabuta-1,3-diene (2.22 g, 5 mmol) and the mixture was stirred at room temperature for 30 min. Chromatographic purification (4:1, hexane/diethyl ether) gave 2.076 g (67%) of compound **3c**; mp 59–60 °C (ethyl acetate); ^{1}H NMR (250 MHz, $CDCl_3$): δ 1.09–1.29 (m, 6H), 4.04–4.20 (m, 4H),5.50 (d, $^3J_{HH}$=2.9 Hz, 1H), 5.80 (s, 1H) 6.69–7.63 (m, 22H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.4, 14.5, 61.3, 62.1, 109.8, 110.6, 125.1–132.7 (m), 140.2, 158.0; ^{31}P NMR (120 MHz, $CDCl_3$): δ 8.56; IR (KBr) ν_{max} 3247, 1720, 1328; MS (EI): *m*/*z* 620 (M^+, 100). Anal. Calcd for $C_{36}H_{34}N_3O_5P$: C, 69.78; H, 5.53; N, 6.78. Found: C, 70.00; H, 5.48; N, 6.80.

4.2.4. 1,1,1,4-Tetraphenyl-3-(2-thienyl)-2-aza-4-(*N*,*N*′-diethoxycarbonylhydrazono)-1,λ^5-phosphabuta-1,3-diene (3d). The general procedure was followed using 1,1,1,4-tetraphenyl-3-(2-thienyl)-2-aza-1,λ^5-phosphabuta-1,3-diene (2.30 g, 5 mmol) and the mixture was stirred at room temperature for 30 min. Chromatographic purification (1:1, hexane/diethyl ether) gave 2.765 g (87%) of compound **3d**; mp 128–129 °C (ethyl acetate); ^{1}H NMR (250 MHz, $CDCl_3$): δ 1.06–1.30 (m, 6H), 4.06–4.18 (m, 4H), 6.26–7.63 (m, 23H), 8.25 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.5, 14.7, 62.1, 62.3, 124.6–132.6 (m), 138.5, 142.6, 156.0, 156.7; ^{31}P NMR (120 MHz, $CDCl_3$): δ 4.51; IR (KBr) ν_{max} 3356, 1725, 1723, 1335; MS (EI): *m*/*z* 636 (M^+, 10). Anal. Calcd for $C_{36}H_{34}N_3O_4PS$: C, 68.02; H, 5.39; N, 6.61. Found: C, 67.89; H, 5.32; N, 6.59.

4.2.5. 1,1,1,4-Tetraphenyl-3-(3-pyridyl)-2-aza-4-(*N*,*N*′-diethoxycarbonylhydrazono)-1,λ^5-phosphabuta-1,3-diene (3e). The general procedure was followed using 1,1,1,4-tetraphenyl-3-(3-pyridyl)-2-aza-1,λ^5-phosphabuta-1,3-diene (2.28 g, 5 mmol) and the mixture was stirred at room temperature for 3 h. Chromatographic purification (1:10, hexane/diethyl ether) gave 2.552 g (81%) of compound **3e**; mp 103–105 °C (ethyl acetate); ^{1}H NMR (250 MHz, $CDCl_3$): δ 1.11–1.25 (m, 6H), 1.75 (s, 1H), 4.00–4.12 (m, 4H), 6.51–7.56 (m, 22H) 8.05–8.18 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.2, 14.3, 61.6, 62.1, 122.5, 127.2–132.4 (m), 137.0, 141.8, 147.1, 149.0, 157.2; ^{31}P NMR (120 MHz, $CDCl_3$): δ 4.55; IR (KBr) ν_{max} 3361, 1767, 1716, 1329; MS (EI): *m*/*z* 630 (M^+, 43). Anal. Calcd for $C_{37}H_{35}N_4O_4P$: C, 70.46; H, 5.59; N, 8.88. Found: C, 70.36; H, 5.51; N, 8.86.

4.3. General procedure for the reaction of phosphazenes 1, 10 and acetylenic ester 4

To a solution of phosphazene **1** or **10** (5 mmol) in chloroform (20 ml) was added dimethyl acetylendicarboxylate (0.67 ml, 5 mmol), and the mixture was stirred at room temperature in an atmosphere of nitrogen until TLC indicated the disappearance of phosphazene. Evaporation of solvent under reduced pressure afforded an oil that was chromatographied on silica gel to give compounds **5** and/or **7**.

4.3.1. 4,5-Bis(methoxycarbonyl)-1,1,1,6-tetraphenyl-3-(2-pyridyl)-2-aza-1,λ^5-phosphahexa-1,3,5-triene (5a). The general procedure was followed using 1,1,1,4-tetraphenyl-3-(2-pyridyl)-2-aza-1,λ^5-phosphabuta-1,3-diene **1a** (2.28 g) for 20 h. Chromatographic separation (1:1, hexane/ethyl acetate) gave **5a** (1.80 g, 60%) as a yellow solid; mp 171–172 °C (hexane/dichloromethane); ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.74 (s, 3H), 3.77 (s, 3H), 6.45–6.97 (m, 3H), 7.18 (s, 1H), 7.20–7.60 (m, 21H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 50.7, 53.0, 122.0 (d, J_{PC}=75 Hz), 127.8–134.4 (m), 136.4, 139.7, 147.5, 157.6, 162.3, 168.2, 170.5; ^{31}P NMR (120 MHz, $CDCl_3$): δ 7.52; IR (KBr) ν_{max} 1694, 1241. MS (EI): *m*/*z* 599 (M^+, 50). Anal. Calcd for $C_{37}H_{31}N_2O_4P$: C, 74.24; H, 5.22; N, 4.68. Found: C, 74.33; H, 5.28; N, 4.63.

4.3.2. 1-Amino-2,3-dimethoxycarbonyl-4-phenyl-1-(2-pyridyl)buta-1,3-diene (7a). To a solution of phosphazene **5a** (1 mmol) in toluene (20 ml), HCl 6 N (2 ml) was added and the mixture was stirred at reflux temperature under inert atmosphere. The reaction was monitored by ^{31}P NMR and after 24 h the total disappearance of phosphazene was observed. Evaporation under reduced pressure afforded a solid which was chromatographied (5:1, hexane/ethyl acetate) giving **7a** (0.29 g, 86%) as a yellow solid; mp 137–138 °C (hexane/dichloromethane). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.52 (s, 3H), 3.94 (s, 9H), 7.29–7.48 (m, 7H), 7.60 (s, 2H), 7.72 (dd, *J*=4.2, 1.7 Hz, 1H), 8.81 (d, *J*=8.5, 1.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 51.7, 52.0, 101.4, 123.9–149.1 (m), 167.7, 169.4.; IR (KBr) ν_{max} 3456, 3330, 1732, 1679, 1235. MS (EI): *m*/*z* 338 (M^+, 15). Anal. Calcd for $C_{19}H_{18}N_2O_4$: C, 67.44; H, 5.36; N, 8.28. Found: C, 67.33; H, 5.28; N, 8.43.

4.3.3. 4,5-Bis(methoxycarbonyl)-1,1,1,3,6-pentaphenyl-2-aza-1,λ^5-phosphahexa-1,3,5-triene (5b) and 1-amino-2,3-dimethoxycarbonyl-1,4-diphenyl-buta-1,3-diene (7b). The general procedure was followed using 1,1,1,3,4-pentaphenyl-2-aza-1,λ^5-phosphabuta-1,3-diene **1b** (2.28 g) for 7.5 h. Chromatographic separation (5:1, hexane/ethyl acetate) gave **5b** (1.67 g, 56%) as a yellow solid; mp 107–108 °C (hexane/dichloromethane) and **7b** (0.62 g, 37%) as a yellow solid; mp 120–121 °C (hexane/dichloromethane). For compound **5b**: ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.33 (s, 3H), 3.81 (s, 3H), 6.75–7.83 (m, 26H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 50.4, 52.0, 126.2–132.8 (m), 137.1, 138.4, 142.7, 168.1, 170.2; ^{31}P NMR (120 MHz, $CDCl_3$): δ 7.78; IR (KBr) ν_{max} 1705, 1407; MS (EI): *m*/*z* 597 (M^+, 100). Anal. Calcd for: $C_{38}H_{32}NO_4P$: C, 76.37; H, 5.40; N, 2.34. Found: C, 76.33; H, 5.38; N, 2.33. For **7b**: ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.65 (s, 3H), 3.73 (s, 3H), 4.75 (s, 2H, NH_2), 6.86–7.26 (m, 11H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 50.9, 52.0, 91.4, 127.0–140.5 (m), 161.1, 169.9, 170.1; IR (KBr) ν_{max} 3424, 1710, 1690; MS (EI): *m*/*z* 337 (M^+, 100). Anal. Calcd for $C_{20}H_{19}NO_4$: C, 71.20; H, 5.68; N, 4.15; Found: C, 71.33; H, 5.70; N, 4.13.

When the general procedure was followed using 1,1,1-trimethyl-3,4-phenyl-2-aza-1,λ^5-phosphabuta-1,3-diene **10b** (5 mmol) generated 'in situ',[7a] the mixture was stirred at room temperature for 3 h. Chromatographic separation (5:1, hexane/ethyl acetate) gave **7b** (1.47 g, 88%).

4.3.4. 4,5-Bis(methoxycarbonyl)-3-(2-furyl)-1,1,1,6-tetraphenyl-2-aza-1,λ^5-phosphahexa-1,3,5-triene (5c) and

1-amino-2,3-dimethoxycarbonyl-1-(2-furyl)-4-phenyl-buta-1,3-diene (7c). The general procedure was followed using 1,1,1,4-tetraphenyl-3-(2-furyl)-2-aza-1,λ^5-phospha-buta-1,3-diene **1c** (2.22 g) for 18 h. Chromatographic separation (5:1, hexane/ethyl acetate) gave **5c** (2.05 g, 70%) as a yellow solid; mp 128–129 °C (hexane/dichloro-methane) and **7c** (0.16 g, 10%) as a yellow solid; mp 143–144 °C (hexane/dichloromethane). For compound **5c**: ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.35 (s, 3H), 3.61 (s, 3H), 5.90 (s, 2H), 6.82 (s, 1H), 7.22–7.74 (m, 21H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 50.7, 51.9, 109.3, 110.3, 128.0–140.4 (m), 152.4, 168.0, 170.0; ^{31}P NMR (120 MHz, $CDCl_3$): δ 8.59; IR (KBr) ν_{max} 1694, 1406; MS (EI): *m/z* 587 (M^+, 100). Anal. Calcd for $C_{36}H_{30}NO_5P$: C, 73.58; H, 5.15; N, 2.38. Found: C, 73.53; H, 5.18; N, 2.33. For compound **7c**: ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.54 (s, 3H), 3.72 (s, 3H), 6.33 (dd, J_{HH}=1.7, 3.5 Hz, 1H), 6.69 (d, J_{HH}=3.5 Hz, 1H), 7.25–7.77 (m, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 50.7, 51.9, 109.3, 110.3, 128.0–148.1 (m), 169.5, 169.8; IR (KBr) ν_{max} 3509, 1705, 1665; MS (EI): *m/z* 327 (M^+, 100). Anal. Calcd for $C_{18}H_{17}NO_5$: C, 66.05; H, 5.23; N, 4.28. Found: C, 66.10; H, 5.20; N, 4.20.

When the general procedure was followed using 1,1,1-trimethyl-4-phenyl-3-(2-furyl)-2-aza-1,λ^5-phosphabuta-1,3-diene **10c** (5 mmol) generated in situ,[7a] the mixture was stirred at room temperature for 2 h. Chromatographic separation (5:1, hexane/ethyl acetate) gave **7c** (1.29 g, 79%).

4.3.5. 1-Amino-2,3-dimethoxycarbonyl-4-phenyl-1-(2-thienyl)buta-1,3-diene (7d). The general procedure was followed using 1,1,1,4-tetraphenyl-3-(2-thienyl)-2-aza-1,λ^5-phosphabuta-1,3-diene **1d** (2.30 g) for 22.5 h. Chromatographic separation (5:1, hexane/ethyl acetate) gave **7d** (0.93 g, 54%) as a brown solid; mp 122–124 °C (hexane/dichloromethane); ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.60 (s, 3H), 3.72 (s, 3H), 6.80–7.49 (m, 11H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 51.1, 52.2, 92.4, 126.8–141.7 (m), 153.4, 169.6, 169.8; IR (KBr) ν_{max} 3425, 1711, 1680; MS (EI): *m/z* 343 (M^+, 100). Anal. Calcd for $C_{18}H_{17}NO_4S$: C, 62.96; H, 4.99; N, 4.08. Found: C, 63.02; H, 5.00; N, 4.10.

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References and notes

1. For reviews see: (a) Steiner, S. J. H.; Zacchini, S.; Richards, P. I. *Coord. Chem. Rev.* **2002**, *227*, 193–216. (b) Wamhoff, H.; Richardt, G.; Stölben, S. *Adv. Heterocycl. Chem.* **1995**, *64*, 159–249. (c) Molina, P.; Vilaplana, M. J. *Synthesis* **1994**, 1197–1218. (d) Eguchi, S.; Matsushita, Y.; Yamashita, K. *Org. Prep. Proced.* **1992**, *24*, 209–243. (e) Gololobov, Y. G.; Kaskhin, L. F. *Tetrahedron* **1992**, *48*, 1353–1406. (f) Barluenga, J.; Palacios, F. *Org. Prep. Proced.* **1991**, *23*, 1–59.
2. For recent contributions see: (a) Lemieux, G. A.; de Graffenried, C. L.; Bertozzi, C. R. *J. Am. Chem. Soc.* **2003**, *125*, 4708–4709. (b) Alajarin, M.; López, C.; Llamas, P. *Synlett* **2003**, 801–804. (c) García, J.; Peralta, E.; Forcen, A.; García, S.; López, F. *Chem. Commun.* **2003**, 856–857. (d) Bell, S. A.; Meyer, T. Y.; Geib, S. J. *J. Am. Chem. Soc.* **2002**, *124*, 10698–10705. (e) Andujar, C.; Pérez, I.; López, F. *Tetrahedron* **2002**, *58*, 2569–2575.
3. (a) Palacios, F.; Ochoa de Retana, A. M.; Martínez de Marigorta, E.; Rodríguez, M.; Pagalday, J. *Tetrahedron* **2003**, *56*, 2617–2623. (b) Palacios, F.; Alonso, C.; Amezua, P.; Rubiales, G. *J. Org. Chem.* **2002**, *67*, 1941–1946. (c) Palacios, F.; Herrán, E.; Rubiales, G. *J. Org. Chem.* **1999**, *64*, 6239–6246. (d) Palacios, F.; Aparicio, D.; de los Santos, J. M. *Tetrahedron* **1996**, *52*, 4857–4866.
4. (a) Molina, P.; Aller, E.; Lorenzo, A. *Synlett* **2003**, 714–716. (b) Saaby, S.; Bayón, P.; Aburel, P. S.; Jorgensen, K. A. *J. Org. Chem.* **2002**, *67*, 4352–4361. (c) Katritzky, A. R.; Nair, S. R.; Silina, A. *J. Org. Chem.* **2002**, *67*, 7530–7532.
5. (a) Hoesl, C.; Nefti, A.; Houghten, R. A. *J. Comb. Chem.* **2003**, *5*, 155–160. (b) Biao, J.; Yang, C. G.; Wang, J. *J. Org. Chem.* **2002**, *67*, 1396–1398. (c) Bonini, C.; D'Auria, M.; Funucello, M.; Romaniello, G. *Tetrahedron* **2002**, *58*, 3507–3512. (d) Chezal, J. M.; Moreau, E.; Chavignon, O.; Gaumet, V.; Metin, J.; Blache, Y.; Diez, A.; Fradera, X.; Lique, J.; Teulade, J. C. *Tetrahedron* **2002**, *58*, 295–307.
6. Barluenga, J.; Merino, I.; Palacios, F. *Tetrahedron Lett.* **1989**, *30*, 5493–5496.
7. (a) Palacios, F.; Alonso, C.; Pagalday, J.; Ochoa de Retana, A. M.; Rubiales, G. *Org. Biomol. Chem.* **2003**, *1*, 1112–1118. (b) Palacios, F.; Ochoa de Retana, A. M.; Pagalday, J. *Tetrahedron* **1999**, *55*, 14451–14458. (c) Barluenga, J.; López, F.; Palacios, F.; Sánchez-Ferrando, F. *Tetrahedron Lett.* **1988**, *29*, 381–384. (d) Barluenga, J.; López, F.; Palacios, F. *J. Organomet. Chem.* **1990**, *382*, 61–67.
8. (a) Barluenga, J.; López, F.; Palacios, F. *Chem. Commun.* **1985**, 1681–1682. (b) López, F.; Pelaez, E.; Palacios, F.; Barluenga, J.; García, S.; Tejerina, B.; García, A. *J. Org. Chem.* **1994**, *59*, 1984–1992. (c) Barluenga, J.; López, F.; Palacios, F. *J. Chem. Soc., Perkin Trans. 1* **1989**, 2273–2277.
9. (a) Baldwin, J. E. *Comprehensive organic synthesis*; Trost, B. M., Fleming, I., Paquette, L. A., Eds.; Pergamon: Oxford, 1991; Vol. 5, pp 63–84. (b) Oppolzer, W. *Comprehensive organic synthesis*; Trost, B. M., Fleming, I., Paquette, L. A., Eds.; Pergamon: Oxford, 1991; Vol. 5, pp 315–398. (c) Weinreb, S. M. *Comprehensive organic synthesis*; Trost, B. M., Fleming, I., Paquette, L. A., Eds.; Pergamon: Oxford, 1991; Vol. 5, pp 401–449.
10. Palacios, F.; Alonso, C.; Rubiales, G. *J. Org. Chem.* **1997**, *62*, 1146–1152.
11. (a) Oikawa, T.; Kanomata, N.; Tada, M. J. *J. Org. Chem.* **1993**, *58*, 2046–2051. (b) Nitta, M.; Iino, Y.; Sugiyama, T.; Akagi, A. *Tetrahedron Lett.* **1993**, *34*, 831–834. (c) Kanomata, N.; Kawagi, H.; Nitta, N. *J. Org. Chem.* **1992**, *57*, 618–625. (d) Nitta, M.; Ohnuma, M.; Iino, Y. *J. Chem. Soc., Perkin Trans. 1* **1991**, 1115–1118.
12. (a) Cheng, Y.; Zhao, M.; Wang, M.-X.; Wang, L.-B.; Huang, Z.-T. *Synth. Commun.* **1995**, *25*, 1339–1351. (b) Fatutta, S.; Pitacco, G.; Valentin, E. *J. Chem. Soc., Perkin Trans. 1* **1983**,

2735–2738. (c) Colona, F. P.; Forchiassin, M.; Pitacco, G.; Risaliti, A.; Valentin, E. *Tetrahedron* **1970**, *26*, 5289.
13. (a) Palacios, F.; Pascual, S.; Oyarzabal, J.; Ochoa de Retana, A. M. *Org. Lett.* **2002**, *4*, 769–772. (b) Palacios, F.; Ochoa de Retana, A. M.; Pascual, S.; López de Munain, R. *Tetrahedron Lett.* **2002**, *43*, 5917–5919. (c) Palacios, F.; Ochoa de Retana, A. M.; Oyarzabal, J. *Tetrahedron Lett.* **1996**, *37*, 4577–4580. (d) Erker, G.; Riedel, M.; Kch, S.; Jödicke, T.; Würthwein, E. H. *J. Org. Chem.* **1995**, *60*, 5284–5290.
14. CCDC-223311 contains the supplementary crystallographic data for this paper. These data can by obtained free of charge at http://www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (internat) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].
15. Johnson, A. W.; Kahsa, W. C.; Starzewski, K. A. O.; Dixon, D. A. In *Ylides and imines of phosphorus*; Johnson, A. W., Ed.; Wiley: New York, 1993.