REACTION OF (VINYLIMINO)PHOSPHORANES WITH ELECTRON-DEFICIENT ACETYLENES: SYNTHESIS AND REACTIVITY OF 1,2λ^5-AZAPHOSPHININES[1]

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Abstract--The reactions of trimethoxy(1-phenylvinylimino)phosphorane and methoxydiphenyl(1-phenylvinylimino)phosphorane with electron-deficient acetylenes result in the formation of 1,2λ^5-azaphosphinines (**7a,b**) and (**9a,b**), while those of triphenyl(1-phenylvinylimino)phosphorane and trimethoxy(vinylimino)phosphorane with dimethyl acetylenedicarboxylate (DMAD) proceeds *via* formal [2+2] cycloadducts to give functionalized butadienes. Thermal rearrangement of **7a,b** and the preparation of HBF_4 salts of **9a,b** are studied. Reactions of compounds **7a,b** and **9a** with DMAD leading to λ^5-phosphinine derivatives are studied as well.

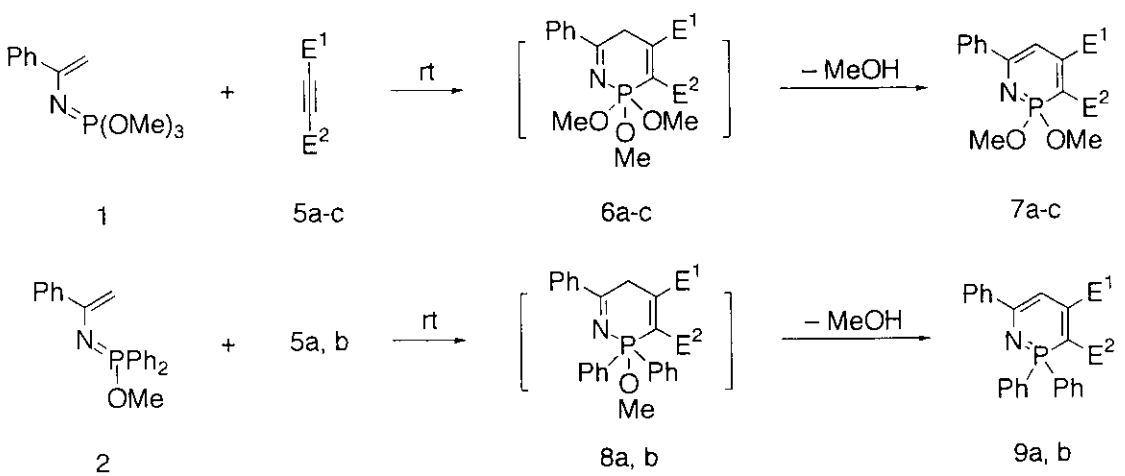
The synthesis of λ^3-azaphosphinines has received recent attention,[2,3] but there are few reports on the preparation and synthetic applications of λ^5-azaphosphinines. 4,4-Diphenyl-1,4λ^5-azaphosphinines,[4] 3,3-diethoxy-1,3λ^5-azaphosphinines,[5] 2,2-dialkoxy-1,2λ^5-azaphosphinines,[6] 1,4λ^5-azaphosphinine,[7] and a series of 3,5-dialkyl-substituted 1,2λ^5-azaphosphinines and their reactivity have been reported.[8] In relation to the synthetic utility of (vinylimino)phosphoranes,[9] we have also reported the synthesis of 1,2λ^5-azaphosphinine derivatives by using the reaction of trimethoxy(vinylimino)phosphorane with electron-deficient acetylenes.[10] We would like to describe herein the synthesis and the spectroscopic and chemical properties of 1,2λ^5-azaphosphinine derivatives.

The (vinylimino)phosphoranes (**1**, **2**, **3**),[9,10,11] and (**4**) were readily prepared by the Staudinger reaction of the corresponding azidoethylenes with trivalent-phosphorus compounds, respectively. Compound (**3**) is known, and the spectroscopic properties of **1**, **2**, and **4** are satisfactory for their structures. The compound (**2**) is not stable and it decomposes gradually under storage; thus the analytical data obtained, except for the HRMS

data, were not satisfactory.

The reaction of **1** with dimethyl acetylenedicarboxylate (DMAD) (**5a**) in benzene at room temperature afforded 2,2-dimethoxy-3,4-dimethoxycarbonyl-6-phenyl-1,2λ^5-azaphosphinine (**7a**). Similarly, the reaction of **1** with methyl propiolate (MP) (**5b**) and dibenzoylacetylene (**5c**) resulted in the formation of 1,2λ^5azaphosphinines (**7b**) and (**7c**), respectively. When the (vinylimino)phosphorane (**2**), which has a methoxy group and two phenyl groups on the phosphorus atom was allowed to react with acetylenes (**5a**) and (**5b**) in a similar manner, 1,2λ^5-azaphosphinines (**9a**) and (**9b**) were isolated, respectively (Scheme 1). The reaction conditions and the yields of the products are summarized in Table 1 (Entries 1-5). The structure of the 1,2λ^5-azaphosphinines (**7a-c**) and (**9a,b**) was determined by ^{1}H NMR spectra, as well as ^{31}P and ^{13}C NMR spectra (Table 2). According to their NMR spectra, particularly the large high-field shifts of C3 and C5 and the large values of the J_{PC3}, the 1,2λ^5-azaphosphinines (**7a-c**) and (**9a,b**) can be classified as six π-electron phosphorus ylides.[8b,12] In the ^{31}P NMR spectra, the signals appearing at δ 38.1-39.4 for **7a-c** and δ 25.1-23.6 for **9a,b** are consistent with the values of the 3,3-diethoxy-1,2λ^5-azaphosphinine derivative[6] and 3-methyl-3-phenyl-1,2λ^5azaphosphinine derivatives,[8] respectively. It is known that 3-methyl-3-phenyl-1,2λ^5-azaphosphinines derivatives are unstable and readily undergo oxidation and hydrolysis on exposure to air to give functionalized phosphine oxides.[8] In sharp contrast, compounds (**7a-c**) and (**9a,b**), which have electron-withdrawing substituent(s), are stable on exposure to air and under storage.

The formation of **7a-c** and **9a,b** is explained by formal (stepwise) [4 + 2] cycloaddition reaction of **1** and **2**



a: E^1=E^2=CO_2Me; b: E^1=H, E^2=CO_2Me; c: E^1=E^2=COPh

Scheme 1.

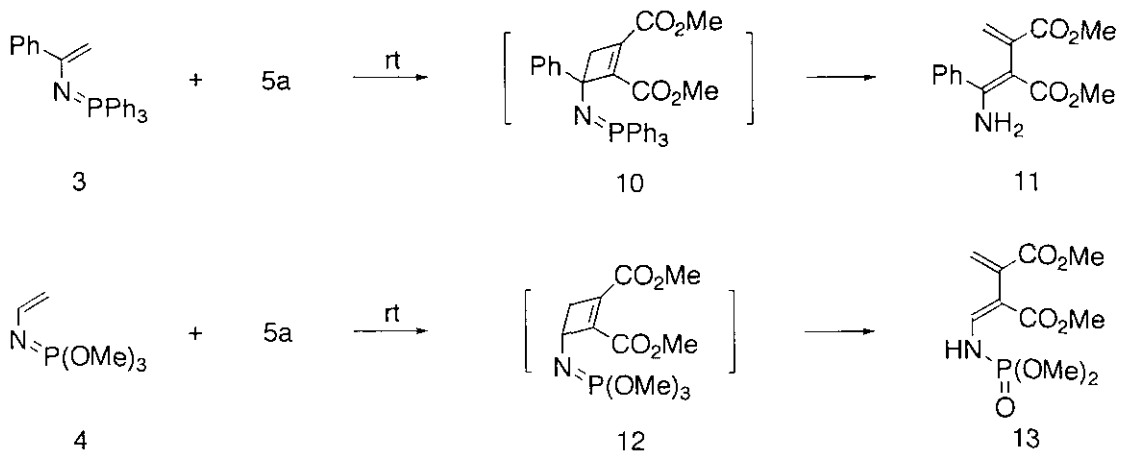
with acetylenes (**5a-c**) to give the intermediate (**6a-c**) and (**8a,b**) and subsequent elimination of MeOH. Regioselective formation of **7b** and **9b** bearing a methoxycarbonyl group at C3 would be ascribed to the ylide character of (vinylimino)phosphoranes (**1**) and (**2**), the anionic β-carbon atom in which connects with the β-carbon atom of MP to result in the formation of [4 + 2] cycloadducts (**7b**) and (**9b**) in a stepwise fashion.

Table 1. Results for the reaction of (vinylimino)phosphoranes (**1**) and (**2**) and 1,2λ^{5}azaphosphinines (**7**) and (**9**) with electron-deficient acetylenes (**5**)

			Molar ratio	Reaction Conditions			
Entry	Compd	Acetylene	of **5a-c**/Compd	Solvent	Time/h	Product (Yield/%)	
1	**1**	**5a**	1.2	Benzene	24[a]	**7a**	(58)
2	**1**	**5b**	1.2	Benzene	24[a]	**7b**	(57)
3	**1**	**5c**	1.0	Benzene	24[a]	**7c**	(17)
4	**2**	**5a**	1.2	Benzene	36[a]	**9a**	(36)
5	**2**	**5b**	2.0	Benzene	150[a]	**9b**	(27)
6	**7a**	**5a**	2.0	Xylene	69[b]	**17a**	(72)
7	**7b**	**5a**	2.0	Xylene	48[b]	**17b**	(60)
8	**9a**	**5a**	3.0	Xylene	16[b]	**19a**	(24)

a. Reactions were carried out at room temperature. b. Reactions were carried out under refluxing.

It is well known that (vinylimino)triphenylphosphoranes react with DMAD on the α- and β-positions of their nitrogen atom to afford functionalized cyclobutenes.[13] An attempted reaction of (vinylimino)phosphorane (**3**), which has no eliminating substituent on the phosphorus atom, with DMAD at room temperature failed to give a formal [4 + 2] cycloadduct, and resulted in the formation of functionalized butadiene (**11**) (Scheme 2). The reaction is clearly explained by the formation of [2 + 2] cycloadduct (**10**) and subsequent ring opening, followed by hydrolysis of the (imino)phosphorane moiety. Thus the (vinylimino)phosphoranes (**1**) and (**2**), both of which have an eliminating substituent such as a methoxy group on the phosphorus atom, apparently provide a new aspect of the reaction, serving as a formal diene unit leading to 1,2λ^5-azaphosphinine derivatives. However, an attempted reaction of (vinylimino)phosphorane (**4**) with DMAD also failed to give the expected 1,2λ^5-azaphos-phinine, but resulted in the formation of the functionalized butadiene (**13**) possibly *via* a [2 + 2] cycloadduct as in the case of (imino)phosphorane (**3**). Thus, the generality of the present reaction affording

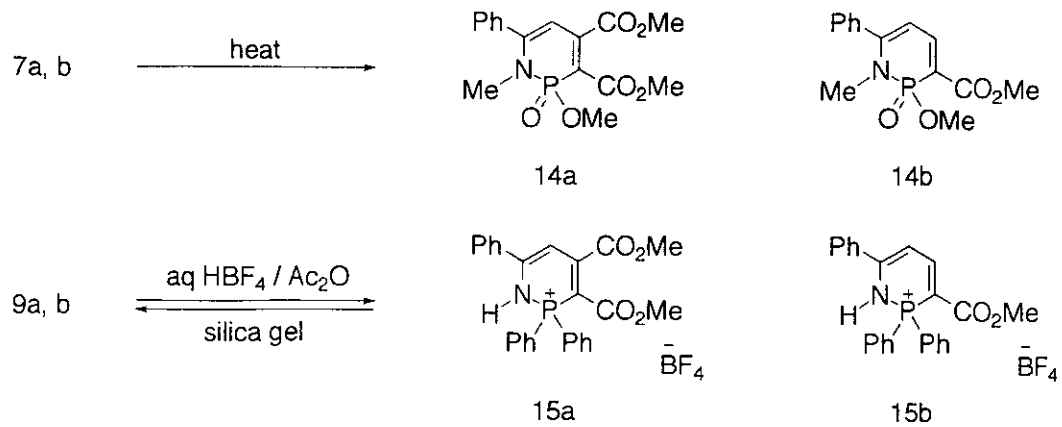


Scheme 2.

[4 + 2] cycloadducts, 1,2λ^5-azaphosphinines, is unclear here.

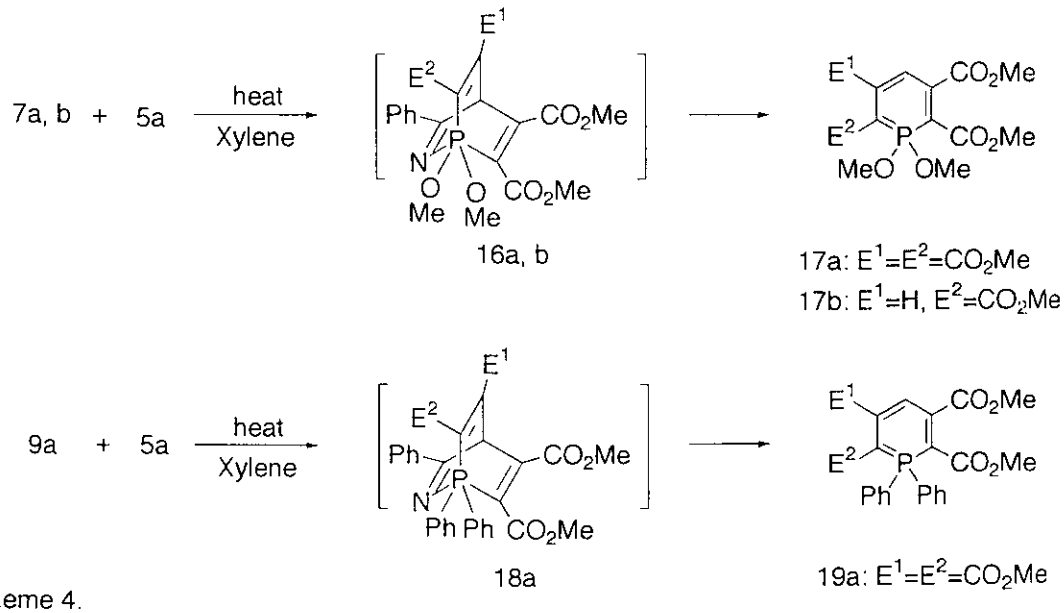
Thermal rearrangements of some methyl phosphorimidates to phosphoramidates [$R_2P(OMe)$=NMe to $R_2P(O)NMe_2$] have been observed.[14] In addition, the 2,2-dimethoxy-1,2λ^5-azaphosphinine derivative undergoes elimination of the methyl group in the presence of water to give 1,2-dihydro-2-methoxy-2-oxo-1,2-λ^5-azaphosphinine.[6] When compounds (**7a,b**) were heated at 180 ℃ in neat for 30 min, complete methyl group migration was observed to give 1,2-dihydro-2-oxo-1,2λ^5-azaphosphinines (**14a**) and (**14b**) in 74 and 85% yields, respectively (Scheme 3). Thermal rearrangement of (**7a,b**) proceeded very slowly in 1,2,4-trichlorobenzene solution at 180 ℃, and gave mixtures of **7a/14a** (86/14) and **7b/14b** (82/18), respectively, after heating for 20 h. Thus, the methyl-migration of **7a,b** affording **14a,b**, respectively, seems to proceed in an intermolecular process, and not in an intramolecular process. The structure of **14a,b** was determined on the basis of ^{1}H NMR as well as ^{31}P NMR and ^{13}C NMR spectral data (Table 2). According to the ^{13}C NMR spectra, the low-field shifts of C3 and C6, as compared to those of **7a,b** in particular, were observed. Furthermore, the large high-field shifts of the ^{31}P signal as compared to those of **7a,b** are consistent with the reported data of similar compounds.[6] When compounds (**9a**) and (**9b**), both of which have no alkoxy group on the phosphorus atom, were treated with aqueous HBF_4 solution in Ac_2O, fairly stable 1,2λ^5-azaphosphininium tetrafluoroborates (**15a**) and (**15b**) in quantitative yield, respectively, were obtained (Scheme 3). Compound (**15a**) was not crystallized from usual solvent such as CH_3CN, AcOEt, EtOH, and benzene, while that is crystallized easily from a mixture of CH_3Cl-Et_2O (1/1) to give a 1 : 1 complex containing Et_2O in the crystal lattice. The salts (**15a**) and (**15b**) regenerated compounds (**9a**) and (**9b**) in 95 and 98% yields, respectively, through TLC on silica gel (hexane-AcOEt : 1/1). The structures of **15a,b** were also characterized

on the basis of the elemental analyses, ^{1}H NMR, ^{31}P NMR, and ^{13}C NMR spectral data (Table 2).



Scheme 3.

The 1,2λ^5azaphosphinines (**7a-c**) and (**9a,b**) also have a (vinylimino)phosphorane moiety, respectively. Although (vinylimino)phosphoranes, (imino)phosphoranes[9,13,15] and 3,4,5,6-tetrahydro-1,2λ^5-aza-phosphinine[16] undergo aza-Wittig reaction, compound (**7a**) did not react with benzaldehyde in refluxing xylene, and **7a** was recovered. On the other hand, when compounds (**7a,b**) and (**9a**) were allowed to react with DMAD in refluxing xylene, λ^5-phosphinines (**17a,b**) and (**19a**) were isolated (Scheme 4). The reaction



Scheme 4.

conditions and the yields of the products are also summarized in Table 1 (Entries 6-8). The formation of the

Table 2. Selected NMR spectral data of 1,2λ^5-azaphosphinines (**7a-c**) and (**9a,b**), and their related compounds (**14a,b**) and (**15a,b**)

Compd.	δ^{31}P	δC3 (J_{PC})	δC4 (J_{PC}; J_{CH})	δC5 (J_{PC}; J_{CH})	δC6 (J_{PC})	Remaining signals
7a	38.1	78.5 (155.0)	155.3 (12.8)	99.7 (25.0; 164.8)	138.4 (22.0)	51.4, 52.3, 53.5, 126.9, 127.0, 128.0, 130.3, 165.6, 169.1
7b	39.4	83.1 (153.2)	151.1 (10.4; 157.5)	100.4 (24.4; 163.0)	139.1 (22.6)	51.1, 53.1, 126.9, 127.0, 127.9, 129.8, 167.0
7c	38.3	90.7 (146.5)	160.2 (11.0)	101.5 (26.2; 163.6)	138.6 (22.0)	53.7, 127.1, 127.4, 127.8, 127.9, 128.2, 128.6, 130.5, 131.1, 132.7, 136.0, 136.1, 139.9, 193.1, 196.0
9a	25.1	69.0 (93.4)	153.2 (8.9)	97.2 (24.2; 165.1)	166.4 (10.5)	51.0, 52.7, 127.4, 128.3, 128.4, 130.5, 131.2, 132.0, 132.4, 139.8, 169.3, 170.2
9b	23.6	74.9 (93.4)	149.0 (6.4; 157.0)	97.5 (24.2; 164.3)	168.0 (11.7)	50.9, 127.3, 128.2, 128.3, 130.0, 131.7, 132.0, 132.2, 140.5, 168.8,
14a	20.3	103.2 (171.7)	151.0 (7.3)	101.2 (13.9)	157.8 (0)	33.0, 52.7 , 52.9 , 55.2, 128.0, 128.8, 130.0, 134.9, 164.7, 168.0
14b	20.2	106.2 (172.4)	148.0 (5.1)	101.8 (13.9)	158.0 (0)	32.6, 52.3, 55.1, 128.0, 128.7 129.6, 135.4, 166.1
15a	32.6	88.4 (110.8)	155.1 (2.2)	99.6 (11.7)	156.1 (4.4)	52.9, 53.7, 121.6, 127.7, 129.8, 129.8, 132.3, 133.2, 133.7, 135.6 162.5, 166.6,
15b	32.2	92.9 (110.8)	152.5 (2.2)	99.9 (11.7)	153.8 (5.9)	52.7, 122.2, 127.5, 129.6, 129.7, 132.7, 132.7, 133.6, 135.3, 164.0

λ^5-phosphinine (**17a,b**) and (**19a**) is explained by the site-selective cycloaddition giving [4 + 2] cycloadducts (**16a,b**) and (**18a**) and subsequent elimination of benzonitrile, which was detected by GLC analysis. The structures of compounds (**17a,b**) and (**19a**) were determined on the basis of the ^{1}H NMR, ^{31}P NMR, ^{13}C

NMR, (Table 2), as well as IR and UV spectral data. Especially, the ^{13}C NMR spectra (Table 3) are instructive of the ring system. The chemical shifts of C2 and C4 are considerably shifted to higher field as compared with those of C3, and the coupling constant J_{PC4} is larger than J_{PC3}. These features are similar to those of λ^5-azaphosphinines[17] and acyclic ylides.[12a]

Table 3. Selected NMR spectral data of λ^5-phosphinines (**17a,b**) and (**19a**)

Compd.	$\delta^{31}P$	δC2 (J_{PC})	δC3 (J_{PC})	δC4 (J_{PC}; J_{CH})	δC5 (J_{PC}; J_{CH})	δC6 (J_{PC})	Remaining signals
17a	57.2	84.9	150.2	101.9	---	---	51.8, 52.4, 55.5,
		(148.3)	(10.6)	(18.3; 167.9)	---	---	164.8, 168.5
17b	58.5	(91.7)	150.4	101.8	146.3	85.4	51.1, 51.3, 51.9,
		(146.5)	(9.8)	(18.3; 166.6)	(8.5; 159.3)	(143.4)	60.0,164.9, 165.5,
							168.9
19a	9.1	79.8	149.7	100.8	---	---	51.4, 52.7, 127.1,
		(101.2)	(5.9)	(12.5)	---		128.3, 131.8, 133.5,
							165.3, 169.6

In conclusion, we have developed a convenient route to stable 1,2λ^5-azaphosphinines through the reaction of readily available (vinylimino)phosphoranes with electron-deficient acetylenes. The stable 1,2λ^5-azaphosphinines underwent the reaction with DMAD to result in the formation of λ^5-phosphinines. 2,2-Dimethoxy-substituted 1,,2λ^5-azaphosphinines underwent thermal migration of the methyl group from the oxygen to the nitrogen atom to give 1,2-dihydro-2-oxo-1,2λ^5-azaphosphinines. 2,2-Diphenyl-substituted 1,2λ^5-azaphosphinines afforded stable 1,2λ^5-azaphosphininium tetrafluoroborates, which regenerated 1,2λ^5-azaphosphinines through TLC on silica gel.

EXPERIMENTAL

IR spectra were taken on a Shimadzu IR-400, a Perkin-Elmer FT-IR1640, or a JASCO FT/IR-260 spectrophotometer. Electronic spectra were measured on a Shimadzu UV-240, or a UV-3101PC spectrophotometer. MS spectra were obtained on a Shimadzu GCMS-QP1000, or a JEOL JMS-

AUTOMASS150 spectrometer. HRMS spectra were run on a JEOL JMS-DX300 or a JMS-SX102A spectrometer. ^{1}H NMR spectra were recorded on a Hitachi R-24 (60 MHz), a R-90H (90 MHz), a JEOL JNM-GSX400 (400 MHz), and a JNM-LA500 (500 MHz) spectrometers and chemical shifts are given relative to internal $SiMe_4$ standard. ^{13}C NMR spectra were recorded on a JEOL JNM-FX90Q (22.6 MHz), a JNM-GSX400 (100.4 MHz), and a JNM-LA500 (125.7 MHz) spectrometers and chemical shifts are given relative to internal $SiMe_4$ standard. ^{31}P NMR spectra were recorded on a Varian XL-200 (80.9 MHz), or a JEOL JNM-EX270 (109.3 MHz) spectrometer and chemical shifts are given relative to external 85% H_3PO_4 standard. J-Values are given in Hz. Microanalyses were performed at the Materials Characterization Central Laboratory of Waseda University. Mps were recorded on a Büchi, or a Yamato MP-21 apparatus and are uncorrected. All the reactions except for the formation of HBF_4 salts were carried out under anhydrous conditions and dry nitrogen atmosphere.

Preparation of trimethoxy(1-phenylvinylimino)phosphorane (1). To a solution of 1-azido-1-phenylethylene (1.45 g, 10 mmol) in benzene (20 mL) was added a solution of trimethyl phosphite (1.24 g, 10 mmol) in benzene (10 mL) dropwise at rt, and the mixture was stirred for 24 h. After evaporation of the solvent, the residue was distilled under reduced pressure to give **1** (2.02 g, 84%): oil; bp 114 ℃/1 Torr; ^{1}H NMR (CCl_4, 60 MHz) δ 3.76 (6H, d, J_{PH}=12.1 Hz), 4.32 (1H, d, J=2.6 Hz), 4.78 (1H, d, J=2.6 Hz), 7.12-7.40 (3H, m), 7.68-7.85 (2H, m); IR (film) 1597, 1567, 1449, 1404, 1331, 1216, 1182, 1098, 1031 cm^{-1}; MS (*m/z*) 241 (M^+, 100%). HRMS Calcd for $C_{11}H_{16}NO_3P$: 241.0867. Found: 241.0873.

Preparation of methoxydiphenyl(1-phenylvinylimino)phosphorane (2). To a stirred solution of 1-phenyl-1-azidoethylene (1.45 g, 10 mmol) in benzene (5 mL) was added a solution of methyl diphenylphosphinite (2.16 g, 10 mmol) in benzene (5 mL) dropwise at 0 ℃, and the mixture was stirred for 2 h. After evaporation of the solvent, the residue was crystallized from benzene-hexane to give **2** (3.06 g, 92%): pale yellow prisms; mp 85-86 ℃ (from benzene-hexane); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.76 (3H, d, J_{PH}=11.4 Hz), 4.24 (1H, d, J=2.6 Hz), 4.77 (1H, d, J=2.6 Hz), 7.26 (1H, tt, J=7.9, 1.4 Hz), 7.34 (2H, td, J=7.9, 1.4 Hz), 7.41 (4H, ddd J_{PH}=3.7 Hz, J=7.9, 7.0 Hz), 7.46 (2H, tq, J=7.3, 1.5 Hz), 7.91 (4H, ddt, J_{PH}=12.1 Hz, J=7.0, 1.5 Hz), 7.94 (2H, dt, J=7.9, 1.4 Hz); ^{13}C NMR ($CDCl_3$, 125.7 MHz) δ 51.0 (J_{PC}=5.6 Hz), 93.1 (J_{PC}=12.9 Hz), 126.1 (J_{PC}=1.6 Hz), 127.1, 127.7, 128.5 (J_{PC}=12.9 Hz), 129.9 (J_{PC}=136.9 Hz), 131.7 (J_{PC}=2.4 Hz), 132.2 (J_{PC}=9.7 Hz), 142.5 (J_{PC}=22.5 Hz), 150.9 (J_{PC}=3.2 Hz); ^{31}P NMR ($CDCl_3$,

109.3 MHz) δ 21.6; IR ($CHCl_3$) 1588, 1563, 1489, 1438, 1397, 1328, 1306, 1291 cm^{-1}; MS (*m/z*) 333 (M^+ 100%). HRMS Calcd for $C_{21}H_{20}NOP$: 333.1283. Found: 333.1309. *Anal.* Calcd for $C_{21}H_{20}NOP$: C, 75.65; H, 6.05; N, 4.20. Found: C, 75.31; H, 5.99; N, 4.64.

Preparation of trimethoxy(vinylimino)phosphorane (4). To a stirred solution of azidoethylene (480 mg, 7 mmol) in ether (10 mL) was added a solution of trimethyl phosphite (620 mg, 5 mmol) in ether (10 mL) dropwise at 0 ℃, and the mixture was stirred for 2 h. After evaporation of the solvent, the residue was distilled under reduced pressure to give **4** (523 mg, 63%): oil; bp 37 ℃/0.6 Torr; ^1H NMR ($CDCl_3$, 90 MHz) δ 3.76 (9H, d, J_{PH}=11.2 Hz), 4.06 (1H, ddd, J_{PH}=5.5 Hz, *J*=7.3, 1.3 Hz), 4.41 (1H, ddd, J_{PH}1.1 Hz, *J*= 15.0, 1.3 Hz), 6.54 (1H, ddd, J_{PH}=24.0 Hz, *J*=15.0, 7.3 Hz); ^{13}C NMR ($CDCl_3$, 100.4 MHz) δ 54.2 (J_{PC}=6.9 Hz), 96.1 (J_{PC}=26.9 Hz), 138.3 (J_{PC}=2.1 Hz); IR ($CHCl_3$) 1611, 1449, 1409, 1322, 1273, 1183 cm^{-1}. HRMS Calcd for $C_5H_{12}NO_3P$: 165.0554. Found: 165.0593.

General procedures for the reaction of 1 and 2 with electron-deficient acetylenes (5a-c). A solution of (vinylimino)phosphorane (2 mmol) and acetylene (2.4 mmol) in benzene (3 mL) was stirred for 24 h at rt. The reaction mixture was concentrated under reduced pressure, and the residue was purified through column chromatography on silica gel using CH_2Cl_2 as the eluent to give the product. The reaction conditions and the yields of the products are summarized in Table 1.

For **7a** (410 mg, 58%): yellow prisms; mp 85-86 ℃ (from MeOH); ^1H NMR (CCl_4, 60 MHz) 3.63 (6H, d, J_{PH}=12.1 Hz), 3.79 (3H, s), 3.87 (3H, s), 6.37 (1H, d, J_{PH}=1.4 Hz), 7.30-7.57 (3H, m), 7.85-8.20 (2H, m); IR ($CHCl_3$) 1733, 1696, 1278 cm^{-1}; UV (MeCN) (log ε) 265 (3.96), 384 (4.34) nm; MS (*m/z*) 351 (M^+, 100%). *Anal.* Calcd for $C_{16}H_{18}NO_6P$: C, 54.71; H, 5.16; N, 3.99. Found: C, 54.61; H, 4.96; N, 3.94.

For **7b** (334 mg, 57%): yellow oil; bp 130 ℃ (bath temperature) / 0.5 Torr; ^1H NMR (CCl_4, 60 MHz) δ 3.52 (6H, d, J_{PH}=12.4 Hz), 3.71 (3H, s), 6.35 (1H, dd, J_{PH}=1.7 Hz, *J*=8.0 Hz), 7.20-7.42 (3H, m), 7.75-8.03 (2H, m), 8.09 (1H, dd, J_{PH}=36.0 Hz, *J*=8.0 Hz); IR ($CHCl_3$) 1696, 1683 1277 cm^{-1}; UV (MeCN) (log ε) 259 (4.06), 389 (4.37) nm; MS (*m/z*) 293 (M^+, 100%). *Anal.* Calcd for $C_{14}H_{16}NO_4P$: C, 57.34; H, 5.50; N,4.77. Found: C, 57.50; H, 5.33; N, 4.99.

For **7c** (148 mg, 17%): yellow prisms; mp 142-143 ℃ (from MeOH); ^1H NMR ($CDCl_3$, 60 MHz) δ 3.71 (6H, d, J_{PH}=13.1 Hz), 6.46 (1H, d, J_{PH}=1.1 Hz), 7.10-8.05 (15H, m); IR ($CHCl_3$) 1667 cm^{-1}; UV (MeCN) (log ε) 226 (4.39), 259 (4.24), 414 (4.14) nm; MS (*m/z*) 443 (M^+, 100). *Anal.* Calcd for $C_{26}H_{22}NO_4P$: C,

70.42; H, 5.00; N, 3.16. Found: C, 70.26; H, 4.67; N, 3.44.

For **9a** (319 mg, 36%): yellow prisms, mp 139-140 ℃ (from ether); ^{1}H NMR ($CDCl_3$, 90 MHz) δ 3.51 (3H, s), 3.92 (3H, s), 6.03 (1H, s), 7.27-8.03 (1H, m); IR ($CHCl_3$) 1729, 1682 cm^{-1}; UV (MeCN) (log ε) 219 (4.44), 275 (4.20), 450 (4.20) nm; MS (*m/z*) 443 (M^+, 78%), 201 (100). *Anal.* Calcd for $C_{26}H_{22}NO_4P$: C, 70.42; H, 5.00; N, 3.16. Found: C, 70.54; H, 5.07; N, 3.29.

For **9b** (208 mg, 27%): yellow prisms; mp 129-130 ℃ (from Et_2O); ^{1}H NMR ($CDCl_3$, 90 MHz) δ 3.61 (3H, s), 6.06 (1H, dd, *J*=8.8 Hz), 7.30-8.03 (15H, m), 8.04 (1H, dd, J_{PH}=26.2 Hz, *J*=8.8 Hz); IR ($CHCl_3$) 1663 cm^{-1}; UV (MeCN) (log ε) 219 (4.46), 266 (4.24), 441 (4.13) nm; MS (*m/z*) 385 (M^+, 100%). *Anal.* Calcd for $C_{24}H_{20}NO_2P$: C, 74.80; H, 5.23; N, 3.63. Found: C, 75.02; H, 5.26; N, 3.80.

Reaction of triphenyl(1-phenylvinylimino)phosphorane (3) with DMAD (5a). A solution of (vinylimino)phosphorane (**3**) (376 mg, 1 mmol) and DMAD (**5a**) (142 mg, 1 mmol) in benzene (5 mL) was stirred for 24 h at rt. The reaction mixture was concentrated under reduced pressure, and the residue was purified by TLC on silica gel using $CHCl_3$ as the eluent to give triphenylphosphine oxide (201 mg, 72%) and **11** (162 mg, 62%): bp 150 ℃ (bath temperature) / 0.5 Torr ; ^{1}H NMR (CCl_4, 60 MHz) δ 3.58 (3H, s), 3.61 (3H, s), 5.01 (1H, d, *J*=2.2 Hz), 5.84 (1H, d, *J*=2.2 Hz), 7.32 (5H, s) ; IR ($CHCl_3$) 3484, 3311, 2985, 1718, 1663, 1600, 1265, 1124 cm^{-1} ; MS (*m/z*) 261 (M^+, 36%), 170 (100). HRMS Calcd for $C_{14}H_{15}NO_4$: 261.1001. Found: 261.1009.

Reaction of trimethoxy(vinylimino)phosphorane (4) with DMAD (5a). A solution of (imino)phosphorane (**4**) (340 mg, 2.1 mmol) and DMAD (341 mg, 2.40 mmol) in benzene (2 mL) was stirred for 39 h at rt. The reaction mixture was concentrated under reduced pressure, and the residue was purified by TLC on silica gel (hexane-AcOEt: 1/4) to give **13** (441 mg, 73%): pale yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.71 (3H, s), 3.75 (3H, s), 3.81 (6H, d, J_{PH}=11.5 Hz), 5.62 (1H, d, *J*=1.4 Hz), 6.12 (1H, d, *J*=1.4 Hz), 7.01 (1H, dd, J_{PH}=12.5 Hz, *J*=8.8 Hz), 8.85-9.00 (1H, bt); ^{13}C NMR ($CDCl_3$, 100.4 MHz) δ 51.6, 52.2, 53.9 (J_{PC}=5.1 Hz), 105.7 (J_{PC}=10.3 Hz), 126.2, 137.5, 143.7 (J_{PC}=4.4 Hz), 167.4, 168.6 (J_{PC}=1.5 Hz); ^{31}P NMR ($CDCl_3$, 109.3 MHz) δ 6.34; IR ($CHCl_3$) 1728, 1687 cm^{-1} ; MS (*m/z*) 293 (M^+, 76%), 261 (100). HRMS Calcd for $C_{16}H_{18}NO_6P$: 293.0664. Found: 293.0662.

Thermal rearrangement 1,2λ^5-azaphosphinines (7a,b). Azaphosphinine (**7a,b**) (1 mmol) was

heated in neat at 180 ℃ for 30 min. The reaction mixture was purified by TLC on silica gel (AcOEt) to give the products (**14a**) and (**14b**) in 87 and 85% yields, respectively.

For **14a** (306 mg, 87%): pale yellow oil; ^1H NMR $CDCl_3$, 400 MHz) δ 3.12 (3H, d, J_{PH}=6.5 Hz), 3.87 (3H, s), 3.88 (3H, s), 3.92 (3H, d, J_{PH}=12.0 Hz), 5.49 (1H, d, J_{PH}=1.6 Hz), 7.26-7.35 (2H, m), 7.43-7.47 (3H, m); IR ($CHCl_3$) 1738, 1710, 1268 cm^{-1}; UV (MeCN) (log ε) 246 (sh, 3.66), 372 (4.17) nm; MS (*m/z*) 351 (M^+, 84%), 118 (100). HRMS Calcd for $C_{16}H_{18}NO_6P$: 351.0872. Found: 351.0869.

For **14b** (249 mg, 85%): pale yellow prisms; mp 135-136 ℃ (from MeOH); ^1H NMR ($CDCl_3$, 90 MHz) δ 3.11 (3H, d, J_{PH}=6.4 Hz), 3.87 (3H, s), 3.89 (3H, d, J_{PH}=12.1 Hz), 5.52 (1H, dd, J_{PH}=2.0 Hz, *J*=7.7 Hz) 7.20-7.55 (5H, m), 7.94 (1H, dd, J_{PH}=36.2 Hz, *J*=7.7 Hz); IR ($CHCl_3$) 1707, 1266 cm^{-1}; UV (MeCN) (log ε) 237 (sh, 3.81), 364 (4.34) nm; MS (*m/z*) 293 (M^+, 99%), 262 (100). *Anal.* Calcd for $C_{14}H_{16}NO_4P$: C, 57.34; H, 5.50; N, 4.78. Found: C, 57.23; H, 5.72; N, 4.83.

Preparation of 1,2λ^5-azaphosphininium tetrafluoroborate (15a,b). To a stirred solution of **9a** or **9b** (1 mmol) in Ac_2O (1.5 mL) was added 42% aqueous HBF_4 (0.3 mL) at 0 ℃, and the mixture was stirred at rt for 1 h. To the reaction mixture was added ether (10 mL), and the precipitates were collected by filtration to give **15a** (490 mg, 92%) or **15b** (460 mg, 97%).

For **15a**: yellow powder; mp 61-112 ℃ (decomp) (from $CHCl_3$-Et_2O); ^1H NMR ($CDCl_3$, 90 MHz) δ 3.60 (3H, s), 3.99 (3H, s), 6.08 (1H, s), 7.40-8.10 (15H, m); IR (KBr) 1727, 1687, 1117-1036 cm^{-1}; UV (MeCN) (log ε) 221 (4.49), 268 (3.93), 316 (sh, 3.22), 474 (4.28) nm. *Anal.* Calcd for $C_{30}H_{33}NO_5BF_4P$: C, 59.52; H, 5.49; N,. 2.31. Found: C, 59.47; H, 5.44; N, 2.32.

For **15b**: yellow powder; mp 181-182 ℃ (from $CHCl_3$-Et_2O); ^1H NMR ($CDCl_3$, 400 MHz) δ 3.72 (3H, s), 6.20 (1H, d, *J*=8.3 Hz), 7.46-7.55 (3H, m), 7.62-7.71 (4H, m), 7.73-7.81 (4H, m), 7.89 (4H, dd, J_{PH}=14.7 Hz, *J*=7.7 Hz), 8.40 (1H, dd, J_{PH}=31.1 Hz, *J*=8.3 Hz); IR (KBr) 1683, 1140-1035 cm^{-1}; UV (MeCN) (log ε) 226 (4.41), 266 (4.08), 395 (4.22) nm. *Anal.* Calcd for $C_{24}H_{21}NO_2BF_4$: C, 60.92; H, 4.47; N, 2.96. Found: C, 60.77; H, 4.61; N,.2.91.

General procedure for the reaction of 1,2λ^5-azaphosphinines (9a,b and 11a) with DMAD (5a). A solution of 1,2λ^5-azaphosphinines (**9a,b** and **11a**) (1 mmol) and DMAD (**5a**) (284 mg, 2 mmol) in xylene (3 mL) was heated under reflux for the period indicated in Table 1. After the reaction mixture was concentrated under reduced pressure, the resulting residue was purified by TLC on silica gel ($CHCl_3$) to give

the products (**17a,b**) and (**19a**), respectively. The reaction conditions and the yields of the products are summarized in Table 1.

For **17a** (281 mg, 72%): yellow prisms, mp 146-147 ℃ (from MeOH); ^{1}H NMR ($CDCl_3$, 60 MHz) δ 3.65 (6H, d, J_{PH}=10.5 Hz), 3.75 (6H, s), 3.79 (6H, s), 5.60 (1H, d, J_{PH}=2.6 Hz); IR ($CHCl_3$) 1729, 1700 cm^{-1}; UV (MeCN) (log ε) 259 (3.73), 399 (4.42) nm; MS (*m/z*) 390 (M^+, 53%), 93 (100). *Anal.* Calcd $C_{15}H_{19}O_{10}P$: C, 46.16; H, 4.91. Found: C, 46.33; H, 5.02.

For **17b** (199 mg, 60%): yellow oil, bp 105 ℃ (bath temperature) / 1 Torr; ^{1}H NMR ($CDCl_3$, 60 MHz) δ 3.68 (6H, d, J_{PH}=12.5 Hz), 3.80 (3H, s), 3.81 (3H, s), 3.83 (3H, s), 5.71 (1H, dd, J_{PH}=3.2 Hz, *J*=8.9 Hz), 8.10 (1H, dd, J_{PH}=38.0 Hz, *J*=8.9 Hz); IR ($CHCl_3$) 1740 1681 cm^{-1}; UV (MeCN) (log ε) 250 (3.68) 395 (4.15) nm; MS (*m/z*) 332 (M^+, 48%), 93 (100). HRMS Calcd for $C_{13}H_{17}O_8P$: 332.0661. Found: 332.0654.

For **19a** (114 mg, 24%): orange prisms, mp 160-161 ℃ (from MeOH); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.42 (6H, s), 3.85 (6H, s), 5.39 (1H, d, J_{PH}=1.4 Hz), 7.26-7.55 (6H, m), 7.79 (4H, ddd, J_{PH}=14.0, *J*=7.9, 1.8 Hz); IR (CCl_4) 1742, 1706 cm^{-1}; UV (MeCN) (log ε) 221 (4.49), 268 (3.93), 316 (sh, 3.22), 474 (4.28) nm; MS (*m/z*) 482 (M^+, 86%), 185 (100). *Anal.* Calcd for $C_{25}H_{23}O_8P$: C, 62.24; H 4.81. Found : C, 61.90; H, 5.02.

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Received, 18th May, 1998