Reaction of α-Metallated *N*-Acyl-λ⁵-Phosphazenes with Aryl Cyanides

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Metallated *N*-acyl-λ⁵-phosphazenes react with aryl cyanide to give imino-λ⁵-phosphazenes (**6**) and (**7**), in which nitrile insertion into the phosphorus–carbon bond of *N*-acyl-λ⁵-phosphazenes (**2**) and (**3**) takes place. Subsequent reactions of the imino- and enamino-*N*-ethoxycarbonyl-λ⁵-phosphazenes (**7**) and (**9**) afford the phosphine oxide derivatives (**13**) and (**11**), through a cyclocondensation and hydrolysis sequence.

λ⁵-Phosphazenes were first prepared in 1919.[1] Applications of these species have attracted growing interest in recent years because of their widespread utility; *i.e.*, as organic semiconductors,[2] as backbone polymer precursors,[3] and as ligands in transition-metal complexes;[4] they have also been used in natural product[5] and phosphorus-containing heterocycle[6] synthesis. However, most reactions of these compounds involve the phosphorus–nitrogen double bond.[5,6]

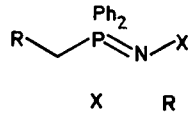
Previously, we have reported on the the ability of α-metallated *N*-aryl-λ⁵-phosphazenes to react with electrophiles, affording acyclic[7] and heterocyclic[8] derivatives. In this context, *C*-functionalised λ⁵-phosphazenes are valuable intermediates in organic synthesis.[9,10] However, though a new synthetic method for *N*-functionalised λ⁵-phosphazenes was recently reported,[11] very little is known about their reactivity. Continuing our interest in the chemistry of λ⁵-phosphazenes, we describe here the reaction of α-metallated *N*-acyl derivatives with aryl cyanides.

Results and Discussion

Primary (*Z*)-β-enamino-λ⁵-phosphazenes (**5**) were obtained through α-lithiation of *N*-aryl derivatives (**1**) followed by reaction with nitriles,[7] in a similar way to that recently reported for reactions of metallated 1,3-dithianes.[12] However, λ⁵-phosphazenes with electron-withdrawing substituents (**2**) and (**3**), obtained through the classical Staudinger reaction[1] using alkyldiphenylphosphines and *N*-acyl azides in ether, show different reactivity. Thus, when compounds (**2**) and (**3**) were treated with lithium di-isopropylamide (LDA) followed by addition of aryl cyanides and aqueous work-up, β-enamino compounds (**8**) and (**9**) were not obtained, but imino-λ⁵-phosphazenes (**6**) and (**7**) were isolated instead (see Table and Scheme 1).

The decreasing P–H and P–C coupling constants[13] for the methyl group observed in the ^1H and ^{13}C n.m.r. spectra of (**6a**) ($^4J_{PH}$ 1.6 Hz, $^3J_{PC}$ 13.8 Hz) relative to those of the starting *N*-benzoyl-λ⁵-phosphazene (**2a**) ($^2J_{PH}$ 13.2 Hz, $^1J_{PC}$ 63 Hz), is consistent with a shift of the methyl group from the α- to the γ-position with respect to the phosphorus atom and, thus, with nitrile insertion into the phosphorus–carbon single bond. The isolation of the fragmentation products of (**6a**) (aminodiphenylphosphine oxide, acetophenone, and benzamide) by acid hydrolysis confirmed the structure of compounds (**6**). In the case of *P*-benzyl *N*-acyl derivatives (**2b**) and (**3c**) (R = Ph), however, no reaction products were observed, probably due to the lower reactivity of the corresponding anion.

$$\text{(6a)} \xrightarrow{2M\ H_2SO_4} Ph_2PONH_2 + PhCONH_2 + PhCOMe$$



	X	R
(2b)	COPh	Ph
(3c)	CO_2Et	Ph

These results could be explained through rearrangement[14] of the metallated intermediate (**4**), which probably involves formation of an unstable cyclic adduct[15] containing pentavalent phosphorus, to give product (**6**) after treatment with water. The conjugation of electron-withdrawing substituents on λ⁵-phosphazenes (X = COPh, CO_2Et) could stabilise the proposed intermediates.

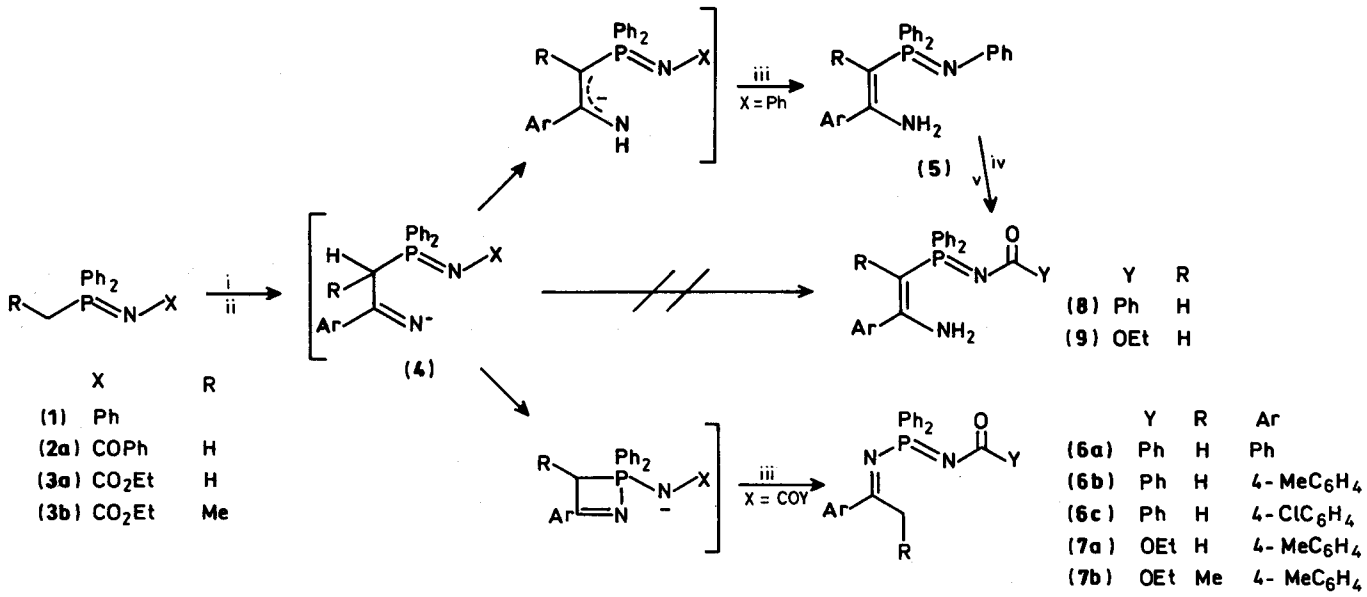
This new behaviour observed in λ⁵-phosphazenes allows the isolation of new imino-λ⁵-phosphazene species resulting from nitrile insertion into acyclic phosphorus–carbon single bonds. A related reaction has been previously reported involving cyclic phosphine oxides.[14]

Primary (*Z*)-β-enamines derived from *N*-acyl-λ⁵-phosphazenes (**8**) and (**9**) are not available from α-metallated

Table. *N*-Acyl-λ⁵-phosphazenes (**2**) and (**3**) and rearrangement products (**6**) and (**7**)

Compound	R	Ar	Y	Yield (%)[a]	M.p. (°C)
(**2a**)	H			94	95–96
(**2b**)	Ph			95	138–139
(**3a**)	H			93	76–77
(**3b**)	Me			96	80–81
(**3c**)	Ph			93	95–96
(**6a**)	H	Ph	Ph	78	132–133
(**6b**)	H	4-MeC_6H_4	Ph	80	184–185
(**6c**)	H	4-ClC_6H_4	Ph	83	183–184
(**7a**)	H	4-MeC_6H_4	OEt	82	125–126
(**7b**)	Me	4-MeC_6H_4	OEt	76	117–118

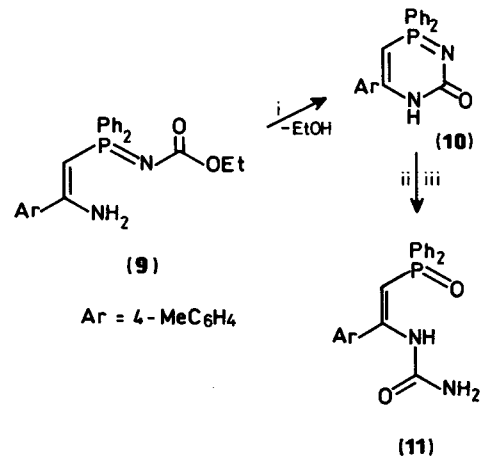
[a] Isolated yields.



Scheme 1. *Reagents and conditions:* i, LDA–THF, −70 °C; ii, ArCN; iii, water; iv, $LiAlH_4$–THF; v, N_3COY–ether

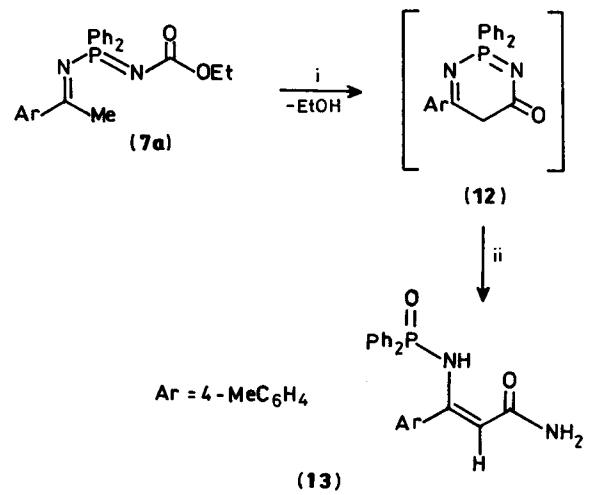
compounds (**2**) and (**3**) with nitriles, but they were prepared by lithium aluminium hydride (LAH) reduction of intermediate (**5**) followed by treatment with acyl azides.[9] Spectral data of compounds (**8**) are markedly different from those observed for the isomer (**6b**). Thus, in the ^1H n.m.r. spectrum, the vinyl hydrogen of (**8**) resonates at δ 4.31 as a doublet with a coupling constant of 17.3 Hz, while the ^{13}C n.m.r. spectrum shows an absorption at 73.0 ($^1J_{PC}$ 107.1 Hz) assignable to the carbon bonded to phosphorus. These values are similar to those previously reported for primary β-enamino-λ^5-phosphazenes.[7,9]

The multifunctional character of *N*-ethoxycarbonyl β-enamino-λ^5-phosphazenes (**9**) was shown by thermal intramolecular cyclocondensation[9] under anhydrous conditions to give 1,3,4-diaza-λ^5-phosphinin-2-ones (**10**). However, the treatment of compounds (**9**) with base (KH) at 60 °C followed by methanolysis and aqueous work-up afforded the corresponding acyclic phosphine oxide (**11**). This result suggests that the cyclic derivative (**10**) undergoes hydrolysis under the reaction conditions, leading to (**11**); in fact, reaction of compound (**10**) with KH under similar reaction conditions afforded the product (**11**) (Scheme 2).



Scheme 2. *Reagents and conditions:* i, 150 °C; ii, KH–THF, 60 °C; iii, MeOH–water

The C_α-hydrogen of the imino moiety is known to be labile towards Lewis acids[16] and, therefore, cyclocondensation of imino-λ^5-phosphazenes (**7**) by means of aluminium chloride was also attempted. Thus, the reaction of compound (**7a**) with aluminium chloride and aqueous work-up gave the amino phosphine oxide derivative (**13**), resulting probably by electrocyclisation process of the $AlCl_3$–imino-λ^5-phosphazene complex followed by hydrolysis of the cyclic compound (**12**) (Scheme 3).



Scheme 3. *Reagents and conditions:* i, $AlCl_3$–THF, 80 °C; ii, water

In conclusion, we have shown that aryl cyanides were inserted into the phosphorus–carbon single bond of α-metallated *N*-acyl-λ^5-phosphazenes. This method allowed us to obtain imino-λ^5-phosphazenes for the first time, to the best of our knowledge. It is also worth noting that phosphorylated imines show oncolitic activity.[17] On the other hand, the multifunctional character of *C*- and *N*-functionalised λ^5-phosphazenes is reported. Thus, intramolecular cyclisation of *P*-imino and β-enamino-λ^5-phosphazenes (**7**) and (**9**) affords the acyclic phosphine oxide isomers (**13**) and (**11**) respectively.

Experimental

General.—M.p.s were taken on samples in open capillary tubes using a Büchi melting-point apparatus and are uncorrected. N.m.r. spectra were obtained using a Varian FT-80 n.m.r. spectrometer with deuteriated chloroform as solvent; chemical shifts are reported in p.p.m. downfield from internal $SiMe_4$ for ^1H and ^{13}C n.m.r. or from H_3PO_4 85% in the case of ^{31}P n.m.r. I.r. spectra were recorded in KBr on a Perkin-Elmer 298 spectrophotometer. Microanalyses were performed on a Perkin-Elmer model 240 instrument and mass spectra were obtained using a Hewlett-Packard 5930A spectrometer. Compounds (**5**) and (**9**) were obtained according to the literature methods.[7,9]

Synthesis of N-*Acyl Alkyldiphenyl-*λ^5*-phosphazenes* (**2**) *and* (**3**). *General Procedure.*—N-*Benzoyl*-P-*methyldiphenyl-*λ^5*-phosphazene* (**2a**). In a dried, argon-filled round-bottomed flask, a solution of benzoyl azide (2.9 g, 20 mmol) in dry ether was added dropwise to a cooled (0 °C) solution of methyldiphenyl phosphine (20 mmol) in ether. After being stirred for 1 h, the mixture was left to reach room temperature and was then stirred until N_2 evolution ceased. The solvent was evaporated off and the resulting oil was taken up in ether (10 ml) until formation of a crystalline solid, which was recrystallised from hexane–methylene dichloride to give *compound* (**2a**) (6.0 g, 94%), m.p. 95—96 °C (Found: C, 74.9; H, 5.6; N, 4.2. $C_{20}H_{18}NOP$ requires C, 75.22; H, 5.68; N, 4.39%); $\nu_{max.}$(KBr) 1 340 (P=N) and 1 610 cm^{-1} (C=O); $\delta_H(CDCl_3)$ 2.31 (3 H, d $^2J_{PH}$ 13.2 Hz, Me) and 7.12—8.31 (15 H, m, Ph); $\delta_C(CDCl_3)$ 11.4 (d, $^1J_{PC}$ 63.0 Hz, Me), 125.5—137.7 ($C_{arom.}$), and 175.8 (CO); $\delta_P(CDCl_3)$ 21.5.

N-*Benzoyl*-P-*benzyldiphenyl-*λ^5*-phosphazene* (**2b**). M.p. 138—139 °C (Found: C, 79.1; H, 5.8; N, 3.7. $C_{26}H_{22}NOP$ requires C, 78.97; H, 5.61; N, 3.54%); $\nu_{max.}$(KBr) 1 340 (P=N) and 1 600 cm^{-1} (C=O); $\delta_H(CDCl_3)$ 4.22 (2 H, d, $^2J_{PH}$ 14.1 Hz, CH_2) and 6.81—8.35 (20 H, m, Ph); $\delta_C(CDCl_3)$ 31.7 (d, $^1J_{PC}$ 51.2 Hz, CH_2), 125.6—138.4 ($C_{arom.}$), and 177.3 (CO); $\delta_P(CDCl_3)$ 27.2.

N-*Ethoxycarbonyl*-P-*methyldiphenyl-*λ^5*-phosphazene* (**3a**). M.p. 76—77 °C (Found: C, 66.7; H, 6.2; N, 4.7. $C_{16}H_{18}NO_2P$ requires C, 66.89; H, 6.31; N, 4.87%); $\nu_{max.}$(KBr) 1 280 (P=N) and 1 620 cm^{-1} (C=O); $\delta_H(CDCl_3)$ 1.22 (3 H, t, $^3J_{HH}$ 6.9 Hz, Me), 2.20 (3 H, d, $^2J_{PH}$ 13.2 Hz, Me), 4.0 (2 H, q, CH_2), and 7.24 – 7.84 (10 H, m, Ph); $\delta_C(CDCl_3)$ 10.9 (d, $^1J_{PC}$ 65.4 Hz, Me), 13.0 (Me), 58.8 (d, $^4J_{PC}$ 3.3 Hz, CH_2), 125.2—130.3 ($C_{arom.}$), and 160.5 (CO); $\delta_P(CDCl_3)$ 22.5.

N-*Ethoxycarbonyl*-P-*ethyldiphenyl-*λ^5*-phosphazene* (**3b**). M.p. 80—81 °C (Found: C, 67.6; H, 6.5; N, 4.6. $C_{17}H_{20}NO_2P$ requires C, 67.76; H, 6.69; N, 4.65%); $\nu_{max.}$(KBr) 1 280 (P=N) and 1 590 cm^{-1} (C=O); $\delta_H(CDCl_3)$ 1.14 (3 H, dt, $^3J_{PH}$ 15.7 Hz, $^3J_{HH}$ 7.9 Hz, Me), 1.24 (3 H, t, $^3J_{HH}$ 6.9 Hz, Me), 2.63 (2 H, dd, $^2J_{PH}$ 12.6 Hz, $^3J_{HH}$ 7.9 Hz, CH_2), and 7.24—7.87 (10 H, m, Ph); $\delta_C(CDCl_3)$ 4.5 (Me), 13.6 (Me), 17.7 (d, $^1J_{PC}$ 63 Hz, CH_2), 59.6 (d, $^4J_{PC}$ 2.6 Hz, OCH_2), 126.7—130.8 ($C_{arom.}$), and 161.0 (CO); $\delta_P(CDCl_3)$ 28.2.

P-*Benzyldiphenyl*-N-*ethoxycarbonyl-*λ^5*-phosphazene* (**3c**). M.p. 95—96 °C (Found: C, 72.5; H, 5.9; N, 3.8. $C_{22}H_{22}NO_2P$ requires C, 72.72; H, 6.10; N, 3.85%); $\nu_{max.}$(KBr) 1 280 (P=N) and 1 600 cm^{-1} (C=O); $\delta_H(CDCl_3)$ 1.26 (3 H, t, $^3J_{HH}$ 6.9 Hz, Me), 4.08 (2 H, q, CH_2), 4.20 (2 H, d, $^2J_{PH}$ 13.2 Hz, CH_2), and 6.67—7.89 (15 H, m, Ph); $\delta_C(CDCl_3)$ 13.6 (Me), 31.3 (d, $^1J_{PC}$ 53.5 Hz, CH_2), 59.7 (d, $^4J_{PC}$ 2.1 Hz, OCH_2), 123.6—130.9 ($C_{arom.}$), and 161.0 (CO); $\delta_P(CDCl_3)$ 23.9.

Synthesis of N-*Acyl*-P-*iminodiphenyl-*λ^5*-phosphazenes* (**6**) *and* (**7**). *General Procedure.*—1-*Benzoyl*-2,2,4-*triphenyl*-1,3-*diaza*-2λ^5-*phosphapenta*-1,3-*diene* (**6a**). In a dried, argon-filled round-bottomed flask, a solution of *N*-benzoyl-*P*-methyldiphenyl-λ^5-phosphazene (**2a**) (1.6 g, 5 mmol) in tetrahydrofuran (THF) (20 ml) was added to a solution of LDA (5 mmol) in THF at −20 °C and the mixture was stirred for 0.5 h. The reaction mixture was cooled at −70 °C and then a solution of benzonitrile (5 mmol) in THF (10 ml) was added. When the mixture had attained room temperature it was stirred for 12 h and then poured into ice–water, extracted with methylene dichloride (100 ml), and the extract was dried (Na_2SO_4). Evaporation of the solvent afforded a crude solid, which was recrystallised from hexane–CH_2Cl_2 to yield *compound* (**6a**) (1.6 g, 78%), m.p. 132—133 °C (Found: C, 76.5; H, 5.3; N, 6.7. $C_{27}H_{23}N_2OP$ requires C, 76.76; H, 5.49; N, 6.63%); $\nu_{max.}$(KBr) 1 330 (P=N), 1 600 (C=N), and 1 630 cm^{-1} (C=O); $\delta_H(CDCl_3)$ 2.70 (3 H, d, $^4J_{PH}$ 1.6 Hz, Me) and 7.16—8.28 (20 H, m, Ph); $\delta_C(CDCl_3)$ 22.6 (d, $^3J_{PC}$ 13.8 Hz, Me), 127.4—139.4 ($C_{arom.}$), 176.3 (d, $^2J_{PC}$ 7.9 Hz, CO), and 183.5 (d, $^2J_{PC}$ 7.2 Hz, C=N); $\delta_P(CDCl_3)$ 15.2; *m/z* 422 (M^+, 2%), 345 (20), 319 (51), and 201 (100).

1-*Benzoyl*-2,2-*diphenyl*-4-(p-*tolyl*)-1,3-*diaza*-2λ^5-*phosphapenta*-1,3-*diene* (**6b**), m.p. 184—185 °C (Found: C, 76.9; H, 5.8; N, 6.5. $C_{28}H_{25}N_2OP$ requires C, 77.05; H, 5.77; N, 6.42%); $\nu_{max.}$ 1 330 (P=N), 1 600 (C=N), and 1 630 cm^{-1} (C=O); $\delta_H(CDCl_3)$ 2.39 (3 H, s, *p*-Me), 2.75 (d, $^4J_{PH}$ 1.6 Hz, Me), and 7.00—8.47 (19 H, m, ArH); $\delta_C(CDCl_3)$ 21.3 (*p*-Me), 22.3 (d, $^3J_{PC}$ 13.8 Hz, Me), 127.4—143.3 ($C_{arom.}$), 176.0 (d, $^2J_{PC}$ 7.6 Hz, CO), 183.2 (d, $^2J_{PC}$ 7.2 Hz, C=N); $\delta_P(CDCl_3)$ 15.2; *m/z* 436 (M^+, 3%), 359 (100), and 333 (53).

1-*Benzoyl*-4-(p-*chlorophenyl*)-2,2-*diphenyl*-1,3-*diaza*-2λ^5-*phosphapenta*-1,3-*diene* (**6c**). M.p. 183—184 °C (Found: C, 70.9; H, 4.75; N, 6.0. $C_{27}H_{22}ClN_2OP$ requires C, 70.98; H, 4.85; N, 6.13%); $\nu_{max.}$(KBr) 1 330 (P=N), 1 600 (C=N), and 1 630 cm^{-1} (C=O); $\delta_H(CDCl_3)$ 2.69 (3 H, d, $^4J_{PH}$ 1.7 Hz, Me), and 7.34—8.30 (19 H, m, ArH); $\delta_C(CDCl_3)$ 22.4 (d, $^3J_{PC}$ 13.6 Hz, Me), 127.6—138.9 ($C_{arom.}$), 176.3 (d, $^2J_{PC}$ 7.8 Hz, CO), 182.0 (d, $^2J_{PC}$ 7.0 Hz, C=N); $\delta_P(CDCl_3)$ 16.0; *m/z* 457 (M^+, 2%), 355 (9), 353 (28), and 201 (100).

1-*Ethoxycarbonyl*-2,2-*diphenyl*-4-(p-*tolyl*)-1,3-*diaza*-2λ^5-*phosphapenta*-1,3-*diene* (**7a**). M.p. 125—126 °C (Found: C, 71.4; H, 6.35; N, 7.05. $C_{24}H_{25}N_2O_2P$ requires C, 71.21; H, 6.23; N, 6.93%); $\nu_{max.}$(KBr) 1 280 (P=N), 1 600 (C=N), and 1 620 cm^{-1} (C=O); $\delta_H(CDCl_3)$ 1.16 (3 H, t, $^3J_{HH}$ 7.9 Hz, Me), 2.41 (3 H, s, *p*-Me), 2.79 (3 H, d, $^4J_{PH}$ 1.6 Hz, Me), 4.04 (2 H, q, CH_2), and 7.08—8.12 (14 H, m, ArH); $\delta_C(CDCl_3)$ 13.6 (Me), 20.3 (*p*-Me), 21.5 (d, $^3J_{PC}$ 14.5 Hz, Me), 59.7 (d, $^4J_{PC}$ 1.6 Hz, OCH_2), 127.0—142.5 ($C_{arom.}$), 160.4 (CO), and 182.4 (d, $^2J_{PC}$ 7.3 Hz, C=N); $\delta_P(CDCl_3)$ 15.3; *m/z* 404 (M^+, 2%) and 359 (100).

1-*Ethoxycarbonyl*-2,2-*diphenyl*-4-(p-*tolyl*)-1,3-*diaza*-2λ^5-*phosphahexa*-1,3-*diene* (**7b**). M.p. 117—118 °C (Found: C, 71.6; H, 6.4; N, 6.5. $C_{25}H_{27}N_2O_2P$ requires C, 71.74; H, 6.51; N, 6.70%); $\nu_{max.}$(KBr) 1 280 (P=N), 1 610 (C=N), and 1 630 cm^{-1} (C=O); $\delta_H(CDCl_3)$ 1.16 (6 H, t, 2Me), 2.43 (3 H, s, p-Me), 3.24 (2 H, dq, $^3J_{HH}$ 6.3 Hz, $^4J_{PH}$ 1.5 Hz, CH_2), 4.0 (2 H, q, OCH_2), and 6.85—8.16 (14 H, m, ArH); $\delta_C(CDCl_3)$ 11.4 (Me), 13.5 (Me), 20.1 (*p*-Me), 28.4 (d, $^3J_{PC}$ 12.6 Hz, CH_2), 59.6 (d, $^4J_{PC}$ 1.5 Hz, OCH_2), 126.9—142.2 ($C_{arom.}$), 160.3 (CO), and 187.5 (d, $^2J_{PC}$ 7.1 Hz, C=N); $\delta_P(CDCl_3)$ 14.0; *m/z* 418 (M^+, 20%), 373 (74), 201 (59), and 153 (100).

Hydrolysis of Compound (**6a**). *Fragmentation Products.*—A solution of compound (**6a**) (2.1 g, 5 mmol) in a mixture of dioxane (30 ml) and 2M H_2SO_4 (30 ml) was heated 6 h at 50 °C. After aqueous work-up and extraction with methylene dichloride, the organic phase afforded aminodiphenylphosphine oxide (0.9 g), m.p. 190—191 °C (lit.,[18] 190—192 °C) and acetophenone (0.4 g). The remaining aqueous phase was treated with 3M KOH until it became alkaline and was then extracted with CH_2Cl_2; evaporation of the extract led to benzamide (0.5 g), m.p. 128—129 °C.

Synthesis of 1-*Benzoyl*-2,2-*diphenyl*-4-(p-*tolyl*)-1,5-*diaza*-2λ^5-*phosphapenta*-1,3-*diene* (**8**).—This compound was prepared by

the same method as derivatives (**2**) with solutions of benzoyl azide (0.75 g, 5 mmol) in ether (10 ml) and (β-amino-β-tolylvinyl)diphenylphosphine[9] (1.6 g, 5 mmol) in ether (10 ml) and gave *compound* (**8**) (2.0 g, 92%), m.p. 162—163 °C (from hexane–methylene dichloride) (Found: C, 76.9; H, 5.6; N, 6.4. $C_{28}H_{25}N_2OP$ requires C, 77.05; H, 5.77; N, 6.42%); $\nu_{max.}$(KBr) 1 360 (P=N), 1 650 (C=C–N), and 3 200 and 3 380 cm^{-1} (NH_2); δ_H($CDCl_3$) 2.35 (3 H, s, *p*-Me), 4.31 (1 H, d, $^2J_{PH}$ 17.3 Hz, CH=), 6.67 (1 H, s, NH), and 7.04—8.39 (20 H, m, ArH + NH); δ_C-($CDCl_3$) 20.6 (*p*-Me), 73.0 (d, $^1J_{PC}$ 107.1 Hz, C-1), 126.2—140.3 ($C_{arom.}$), 162.7 (C-2), and 176.6 (d, $^2J_{PC}$ 6.3 Hz, CO); δ_P($CDCl_3$) 13.4; *m/z* 436 (M^+, 22%), 359 (43), 332 (52), and 185 (100).

Synthesis of Diphenyl[2-(p-*tolyl*)-2-*ureidovinyl*]*phosphine Oxide* (**11**).—To a suspension of KH (5 mmol) in THF (10 ml) was added dropwise, under argon, compound (**9**)[9] or (**10**)[9] (5 mmol) in THF (10 ml). The mixture was heated for 6 h at 60 °C and quenched with MeOH (20 ml) and water (20 ml). After extraction with methylene dichloride (100 ml), drying (Na_2SO_4) and evaporation of the extract gave crude *compound* (**11**) (1.5 g, 81%), m.p. 226—227 °C (from MeOH) (Found: C, 70.4; H, 5.7; N, 7.3. $C_{22}H_{21}N_2O_2P$ requires C, 70.20; H, 5.62; N, 7.44%); $\nu_{max.}$(KBr) 1 180 (P=O), 1 600, 1 720 (C=O), and 3 200, 3 320, 3 400 cm^{-1} (NH); δ_H($CDCl_3$) 2.3 (3 H, s, *p*-Me), 5.14 (1 H, d, $^2J_{PH}$ 20 Hz, CH=), 5.4 (2 H, m, NH_2), 7.05—7.80 (14 H, m, ArH), and 9.78 (1 H, s, NH); δ_C($CDCl_3$) 21.2 (*p*-Me), 96.9 (d, $^1J_{PC}$ 104.0 Hz, =CHP), 126.7—139.3 ($C_{arom.}$), 155 (CO), and 158.1 (CH=C); δ_P($CDCl_3$) 21.1; *m/z* 376 (M^+, 3%), 333 (85), 332 (90), and 77 (100).

Synthesis of 3-(*Diphenylphosphoramido*)-3-(p-*tolyl*)*acrylamide* (**13**).—To a solution of compound (**7a**) (2.0 g, 5 mmol) in THF (20 ml) was added aluminium chloride (5 mmol) and the mixture was heated for 12 h at 80 °C. After aqueous work-up and extraction with methylene dichloride, the extract was evaporated to give *compound* (**13**) (1.54 g, 82%), m.p. 182—183 °C (from hexane–CH_2Cl_2) (Found: C, 70.0; H, 5.5; N, 7.3. $C_{22}H_{21}N_2O_2P$ requires C, 70.20; H, 5.62; N, 7.44%); $\nu_{max.}$(KBr) 1 220 (P=O), 1 630, 1 730 (C=O), 3 280, and 3 410 cm^{-1} (NH); δ_H[$(CD_3)_2SO$] 2.2 (3 H, s, *p*-Me), 5.1 (1 H, d, $^4J_{PH}$ 2.0 Hz, CH=), 6.80—7.80 (10 H, m, ArH + NH_2), and 11.61 (1 H, d, $^2J_{PH}$ 12.5 Hz, NH); δ_C[$(CD_3)_2SO$] 21.0 (*p*-Me), 97.6 (d, $^3J_{PC}$ 4.9 Hz, CH=), 126.7—138.0 ($C_{arom.}$), 154.9 (d, $^2J_{PC}$ 1.2 Hz, C), and 169.8 (CO); δ_P($CDCl_3$) 20.1; *m/z* 376 (M^+, 30%), 333 (70), 332 (70), and 201 (100).

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