

[2+2] Cycloaddition and ring expansion reactions of cyclic phosphonium and aminophosphonium salts: synthesis and structure of the first eight-membered ylides-type heterocycles

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A series of new eight-membered heterocycles, **4** and **6**, was isolated from the reactions of simple six-membered aza-ylides with acetylene and nitrile derivatives. These structures were elucidated by X-ray crystal analysis. On the other hand, the reactions of five-membered ylides and aza-ylides with nitrile derivatives formed seven-membered ylides, which were hydrolyzed immediately during aqueous work-up to give phosphine oxide derivatives.

Cyclic ylides and cyclic aza-ylides generated from cyclic phosphonium and aminophosphonium salts are very useful reagents for the synthesis of unsymmetrical unconjugated dienes¹ and nitrogen containing heterocycles.² Because their Wittig and aza-Wittig reactions provide alkenylphosphine oxides, they can be subjected to further reaction by the Horner–Wittig reaction. Furthermore the reaction of cyclic ylides with α,β -unsaturated carbonyl compounds does not give simple Wittig products, but instead a tandem Michael intramolecular Wittig reaction takes place to provide cycloheptenyl- or cyclooctenyl-diphenylphosphine oxide.³ On the other hand, reactions of acyclic aza-ylides with multiple-bonded compounds were reported by Brown, Barluenga, and Ciganek *et al.*⁴ They found that iminophosphoranes are reactive to dimethylacetylene dicarboxylate (DMAD) to form phosphonium ylides. Few cyclic aza-ylides have been reported,^{5a} although we have reported the properties of several examples.^{3,6} Recently, Barluenga^{5b} reported the synthesis of a seven-membered iminophosphorane. The reactions of cyclic aza-ylides with triple-bonded compounds, however, are still unknown. We report herein the first isolation of novel eight-membered phosphaheterocycles from the reactions of simple six-membered cyclic aza-ylides with DMAD and Cl_3CCN .

Results and discussion

The reaction of aza-ylide **2** with DMAD at 0 °C in THF proceeded in a [2+2] cycloaddition manner followed by ring expansion to give aza-ylide **4** in 50% yield (Scheme 1). The structure of **4** was determined by spectral data and confirmed by X-ray structural analysis (Fig. 1 and Tables 1–3).

Similarly, a [2+2] cycloaddition reaction of **2** with Cl_3CCN at –78 °C gave a four-membered bicyclic intermediate **5**, which underwent ring expansion to give stable eight-membered aza-ylide derivative **6** in 58% yield as pale yellow crystals (Scheme 2). The structure of **6** was determined by spectral data and confirmed by X-ray structural analysis (Fig. 2 and Tables 4–6).

These are the first examples of eight-membered ylides being isolated.⁷ We were surprised at the abnormal stability of these cyclic ylides, which can be recrystallized from isopropyl alcohol. The torsion angle P(1)–C(1)–C(2)–N(1) in compound **4** is 50(1)°, which might mean that the P=C and C=N double bonds are not conjugated. The P=C bond length, however, is 1.727(8) Å and this value is similar to that of a P–C single bond (1.79 Å)

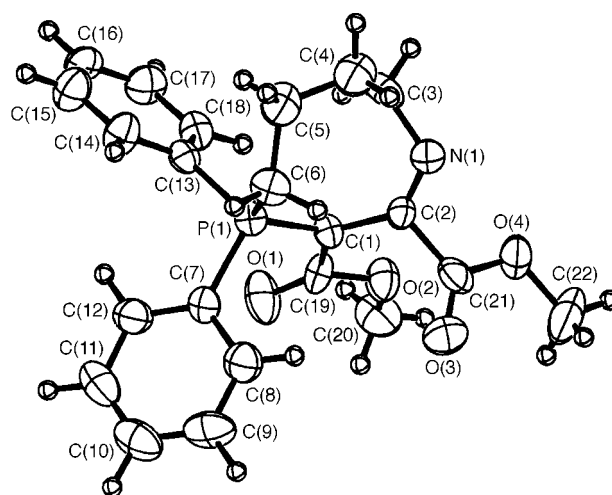
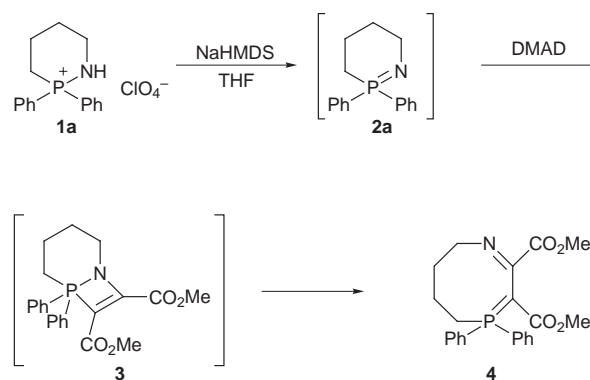


Fig. 1 X-Ray crystal structure of **4**.



Scheme 1

found in 1,2-azaphosphinan-2-ium salt **1a**.^{6a} Furthermore, the bond length C(1)–C(2) (1.46(1) Å) indicates some double bond character. These observations suggest that the P=C bond has an ylide structure rather than an ylene structure, and the ylide carbanion conjugates to the C=N double bond. In addition, the torsion angle P(1)–C(1)–C(19)–O(1) is 4(1)°, which is nearly coplanar. These results would explain the stability of compound **4**.

Table 1 Selected bond distances for **4**^a

Atoms	Distance/Å
P(1)–C(1)	1.727(8)
N(1)–C(2)	1.273(9)
C(1)–C(2)	1.46(1)
C(2)–C(21)	1.52(1)
C(4)–C(5)	1.51(1)
P(1)–C(6)	1.818(8)
N(1)–C(3)	1.460(9)
C(1)–C(19)	1.42(1)
C(3)–C(4)	1.52(1)
C(5)–C(6)	1.54(1)

^a Estimated standard deviations to the last significant figure are given in parentheses.

Table 2 Selected bond angles for **4**^a

Atoms	Angle (°)
C(1)–P(1)–C(6)	112.7(4)
P(1)–C(6)–C(5)	118.1(6)
P(1)–C(1)–C(2)	123.1(6)
C(2)–C(1)–C(19)	120.9(8)
N(1)–C(2)–C(21)	112.2(8)
N(1)–C(3)–C(4)	113.6(7)
O(3)–C(21)–C(2)	124(1)
O(1)–C(19)–C(1)	127.3(9)
C(4)–C(5)–C(6)	115.9(8)
C(2)–N(1)–C(3)	119.1(7)
P(1)–C(1)–C(19)	114.9(6)
N(1)–C(2)–C(1)	133.2(8)
C(1)–C(2)–C(21)	114.5(8)
C(3)–C(4)–C(5)	117.0(8)
O(4)–C(21)–C(2)	113.0(8)
O(2)–C(19)–C(1)	111.3(8)

^a The sign is positive if, when looking from atom 2 to atom 3, a clockwise motion of atom 1 would superimpose it on atom 4.

Table 3 Selected torsion or conformation angles for **4**^a

Atoms	Angle (°)
P(1)–C(1)–C(2)–N(1)	–50(1)
P(1)–C(1)–C(2)–C(21)	126.2(7)
P(1)–C(1)–C(19)–O(1)	4(1)
P(1)–C(6)–C(5)–C(4)	–81.4(9)
C(3)–N(1)–C(2)–C(21)	176.4(7)
C(5)–C(6)–P(1)–C(7)	–155.8(7)
O(1)–C(19)–C(1)–C(2)	172.3(9)
O(3)–C(21)–C(2)–N(1)	126(1)
O(3)–C(21)–C(2)–C(1)	–51(1)
O(4)–C(21)–C(2)–C(1)	127.1(8)
N(1)–C(3)–C(4)–C(5)	–93(1)
C(1)–C(2)–N(1)–C(3)	–8(1)
C(2)–N(1)–C(3)–C(4)	105.6(9)
C(2)–C(1)–P(1)–C(6)	–4.3(9)
P(1)–C(1)–C(19)–O(2)	179.3(5)
C(2)–C(21)–O(4)–C(22)	–173.6(7)
C(3)–C(4)–C(5)–C(6)	54(1)
C(6)–P(1)–C(1)–C(19)	164.2(6)
O(2)–C(19)–C(1)–C(2)	–12(1)
C(6)–P(1)–C(13)–C(18)	133.1(6)
O(4)–C(21)–C(2)–N(1)	–56(1)
N(1)–C(2)–C(1)–C(19)	143(1)
C(1)–P(1)–C(6)–C(5)	84.4(7)
C(1)–C(19)–O(2)–C(20)	–174.5(7)

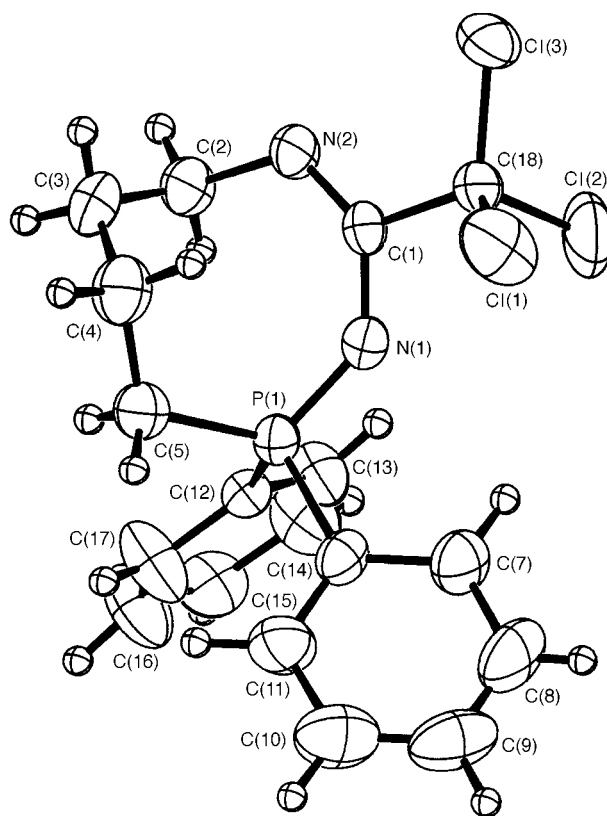
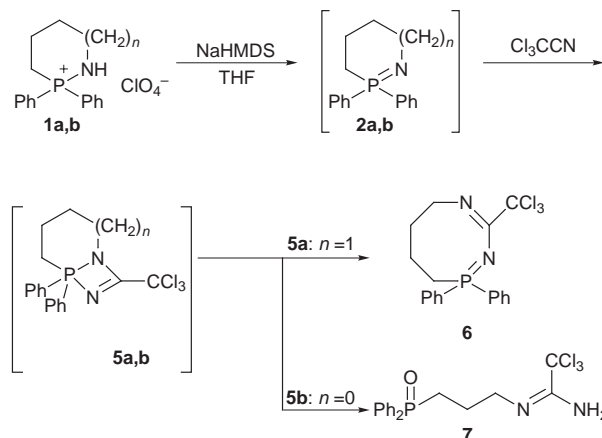
^a The sign is positive if when looking from atom 2 to 3, a clockwise motion of atom 1 would superimpose it on atom 4.

On the other hand, the bond length P=N in compound **6** is 1.560(3) Å, which is shorter than those of typical aza-ylides and indicates an ylene structure,^{4d} but the N(1)–C(1) bond is 1.354(4) Å, which suggests a conjugated length. Furthermore,

Table 4 Selected bond distances for **6**^a

Atoms	Distance/Å
P(1)–N(1)	1.560(3)
P(1)–C(5)	1.816(4)
N(1)–C(1)	1.354(4)
N(2)–C(1)	1.262(4)
N(2)–C(2)	1.455(4)
C(1)–C(18)	1.554(4)
C(2)–C(3)	1.525(6)
C(3)–C(4)	1.509(6)
C(4)–C(5)	1.503(6)

^a Estimated standard deviations to the last significant figure are given in parentheses.

**Fig. 2** X-Ray crystal structure of **6**.**Scheme 2**

the torsion angle P(1)–N(1)–C(1)–N(2) is –30.5(7)°, which might allow a small degree of conjugation. Generally, aza-ylides are more stable than phosphorus ylides, and sometimes

Table 5 Selected bond angles for **6**^a

Atoms	Angle (°)
N(1)–P(1)–C(5)	117.7(2)
P(1)–N(1)–C(1)	137.0(2)
C(1)–N(2)–C(2)	116.9(3)
N(1)–C(1)–N(2)	134.3(3)
N(1)–C(1)–C(18)	110.2(3)
N(2)–C(1)–C(18)	115.5(3)
N(2)–C(2)–C(3)	112.4(4)
C(2)–C(3)–C(4)	115.3(4)
C(3)–C(4)–C(5)	116.6(4)
P(1)–C(5)–C(4)	116.6(3)

^a The sign is positive if, when looking from atom 2 to atom 3, a clockwise motion of atom 1 would superimpose it on atom 4.

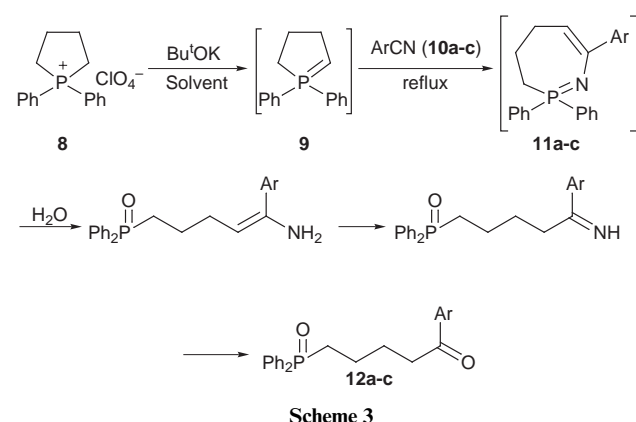
Table 6 Selected torsion or conformation angles for **6**^a

Atoms	Angle (°)
P(1)–N(1)–C(1)–N(2)	–30.5(7)
P(1)–N(1)–C(1)–C(18)	150.9(3)
P(1)–C(5)–C(4)–C(3)	74.6(5)
N(1)–P(1)–C(5)–C(4)	5.6(4)
N(1)–C(1)–N(2)–C(2)	–0.7(6)
N(2)–C(2)–C(3)–C(4)	–58.8(6)
C(1)–N(1)–P(1)–C(5)	–21.5(5)
C(1)–N(1)–P(1)–C(6)	–143.0(4)
C(1)–N(1)–P(1)–C(12)	104.4(4)
C(1)–N(2)–C(2)–C(3)	93.0(4)
C(2)–N(2)–C(1)–C(18)	178.0(3)
C(2)–C(3)–C(4)–C(5)	–61.7(6)
C(4)–C(5)–P(1)–C(6)	126.7(4)
C(4)–C(5)–P(1)–C(12)	–122.0(4)

^a The sign is positive if when looking from atom 2 to 3, a clockwise motion of atom 1 would superimpose it on atom 4.

they can be isolated. The stability of compound **6** might be due to the above observations.

On the other hand, a reaction of five-membered aza-ylide **2b** with trichloroacetonitrile gave amidine **7** in 60% yield. Furthermore, reactions of cyclic phosphonium ylide **9** with benzonitriles **10a–c** gave ketone derivatives **12a–c** in 50–63% yield (Scheme 3, Table 7). In these cases, seven-membered aza-ylides could not be isolated. The synthetic applications of the seven- and eight-membered cyclic ylides are under active investigation.



Experimental

4,4-Diphenyl-2,3-bis(methoxycarbonyl)-5,6,7,8-tetrahydro-1,4-azaphosphocine **4**

A solution of NaHMDS (2 ml, 2 mmol) was added to a suspension of 2,2-diphenyl-1,2-azaphosphinan-2-ium perchlorate (0.71 g, 2 mmol) in dry THF (15 ml), and the mixture stirred for

Table 7 Isolated yields of phosphino ketone derivatives

Ar	Solvent	t/h	Compound	Yield (%)
Ph (10a)	Toluene	20	12a	60
<i>p</i> -ClPh (10b)	Toluene	20	12b	50
<i>p</i> -CNPh (10c)	THF	40	12c	63

30 min at room temperature. After cooling to 0 °C, a solution of dimethyl acetylenedicarboxylate (0.28 g, 2 mmol) in dry THF (5 ml) was added dropwise to this mixture, and stirred for 20 h and then allowed to warm to room temperature. Water (10 ml) and dichloromethane (50 ml) were added to the mixture, and the organic layer was separated. Then the aqueous layer was extracted with dichloromethane (2 × 50 ml). The combined organic extracts were washed with brine (2 × 50 ml), dried over anhydrous sodium sulfate, and concentrated under reduced pressure to afford the crude product. This crude product was purified by column chromatography on 120 g of silica gel using ethyl acetate–ethanol (8:2) as eluent to give pale crystals (0.40 g, 50%): mp 227–230 °C (from ethyl acetate) (Found: C, 66.17; H, 6.07; N, 3.46. C₂₂H₂₄O₄P₁N₁ requires C, 66.49; H, 6.08; N, 3.53%); $\nu_{\max}/\text{cm}^{-1}$ (KBr) 3040, 2950, 1730, 1620, 1600; δ_{H} (90 MHz, CDCl₃) 1.33–2.46 (m, 6H, –CH₂–), 3.34 (s, 3H, –OCH₃), 3.55–3.61 (m, 2H, –CH₂–), 3.90 (s, 3H, –OCH₃) and 7.57–7.89 (m, 10H, Ph); δ_{C} (22.5 Hz, CDCl₃) 21.17 (d, ³J_{PC} 4.88 Hz, –CH₂–), 25.45 (d, ¹J_{PC} 57.37 Hz, –CH₂–), 28.36 (s, –CH₂–), 49.89 (s, –CH₃), 52.58 (s, –CH₃), 53.44 (d, ²J_{PC} 1.22 Hz, –CH₂–), 124.76 (s, –P=C–) 161.41 (d, ²J_{PC} 7.32 Hz, –C=N–), 168.59–169.65 (m, 4 peaks, C=O) and 132.94–128.66 (m, 7 peaks, Ph).

2,2-Diphenyl-8-trichloromethyl-3,4,5,6-tetrahydro-1,7,2-diazaphosphocine **6**

A solution of NaHMDS (2 ml, 2 mmol) was added to 2,2-diphenyl-1,2-azaphosphinan-2-ium perchlorate (0.71 g, 2 mmol) in dry THF (15 ml) and stirred for 30 min at room temperature. After cooling to –78 °C, a solution of trichloroacetonitrile (0.29 g, 2 mmol) in dry THF (5 ml) was added dropwise to this mixture at –78 °C and stirred for 3 h. Water (10 ml) and dichloromethane (50 ml) were added to the mixture, and the organic layer was separated. Then the aqueous layer was extracted with dichloromethane (2 × 50 ml). The combined organic extracts were washed with brine (2 × 50 ml), dried over anhydrous sodium sulfate, and concentrated under reduced pressure to afford the crude product. This crude product recrystallized from propan-2-ol to give yellow crystals (0.47 g, 58%): mp 194–197 °C (Found: 398.0281 (M⁺). C₁₈H₁₈N₂P₁³⁵Cl₃ (M) requires 398.0273); $\nu_{\max}/\text{cm}^{-1}$ (KBr) 2950, 2940, 2850, 1650 (–C=N–), 1600, 1440, 1280, 1180, 1090, 1010 and 970; δ_{H} (90 MHz, CDCl₃) 1.83–2.02 (m, 4H, –CH₂–), 2.59–2.70 (m, 2H, –CH₂–), 3.42–3.31 (m, 2H, –CH₂–) and 7.97–7.48 (m, 10H, Ph); δ_{C} (22.5 MHz, CDCl₃) 18.97 (d, ³J_{PC} 12.81 Hz, –CH₂–), 29.13 (d, ¹J_{PC} 49.44 Hz, –CH₂–), 32.15 (s, –CH₂–), 45.72 (s, –CH₂N–), 98.92 (s, –CCl₃), 160.68 (s, N=C–N) and 135.06–128.61 (m, 22 peaks, Ph); m/z (70 eV) 398 (M⁺, ³⁵Cl₃).

Diphenyl [3-(1-amino-2,2,2-trichloroethylideneamino)propyl]-phosphine oxide **7**

A solution of NaHMDS (2 ml, 2 mmol) was added to 2,2-diphenyl-1,2-azaphosphinan-2-ium perchlorate (0.68 g, 2 mmol) in dry THF (15 ml) and stirred for 30 min at room temperature. After cooling to –78 °C, a solution of trichloroacetonitrile (0.29 g, 2 mmol) in dry THF (5 ml) was added dropwise to this mixture at –78 °C and stirred for 3 h. Water (10 ml) and dichloromethane (50 ml) were added to the mixture, and the organic layer was separated. Then the aqueous layer was extracted with dichloromethane (2 × 50 ml). The combined organic extracts were washed with brine (2 × 50 ml), dried over anhydrous sodium sulfate, and concentrated under reduced

pressure to afford the crude product. This crude product was purified by column chromatography on 120 g of silica gel using ethyl acetate–ethanol (8:2) as eluent (0.41 g, 51%) (Found: 402.0242 (M^+). $C_{17}H_{18}N_2O_1P_1^{35}Cl_3$ (M^+) requires 402.0222; $\nu_{\max}/\text{cm}^{-1}$ (CHCl_3) 3350 ($-\text{NH}_2$), 2960, 2340, 1730, 1675, 1640 ($-\text{C}=\text{N}$), 1530, 1440, 1180 ($\text{P}=\text{O}$), 1130, 1080 and 910; δ_{H} (90 MHz, CDCl_3) 1.83–3.50 (m, 6H, $-\text{CH}_2-$), 5.87 (s, 2H, $-\text{NH}_2$) and 7.31–7.85 (m, 10H, Ph); δ_{C} (22.5 MHz, CDCl_3) 21.67 (d, $^2J_{\text{PC}}$ 3.66 Hz, $-\text{CH}_2-$), 27.01 (d, $^1J_{\text{PC}}$ 72.03 Hz, $-\text{CH}_2-$), 44.82 (d, $^3J_{\text{PC}}$ 10.38 Hz, $-\text{CH}_2-$), 94.81 (s, $-\text{CCl}_3$), 157.57 (s, $-\text{C}=\text{N}$) and 135.11–128.69 (m, 7 peaks, Ph); m/z (70 eV) 402 (M^+ , $^{35}\text{Cl}_3$).

1-Phenyl-5-diphenylphosphinoylpentan-1-one 12a

A mixture of Bu^tOK (0.22 g, 2 mmol) and 1,1-diphenylphospholanium perchlorate (0.68 g, 2 mmol) in dry toluene (15 ml) was stirred for 30 min at room temperature. After a solution of benzonitrile (0.21 g, 2 mmol) in dry toluene (10 ml) was added, the resulting mixture was refluxed for 20 h. Water (10 ml) and dichloromethane (50 ml) were added to the mixture, and the organic layer was separated. Then the aqueous layer was extracted with dichloromethane (2×50 ml). The combined organic extracts were washed with brine (2×50 ml), dried over anhydrous sodium sulfate, and concentrated under reduced pressure to afford the crude product. This crude product recrystallized from ethyl acetate to give white crystals (0.40 g, 56%); mp 148–150 °C (Found: 362.1434 (M^+). $C_{23}H_{23}P_1O_2$ (M^+) requires 362.1406; $\nu_{\max}/\text{cm}^{-1}$ (KBr) 2940, 1670 ($\text{C}=\text{O}$), 1425, 1220, 1175 ($\text{P}=\text{O}$) and 1100; δ_{H} (90 MHz, CDCl_3) 1.51–2.31 (m, 8H, $-\text{CH}_2-$) and 7.29–7.94 (m, 15H, Ph); δ_{C} (22.5 MHz, CDCl_3) 21.75 (d, $^2J_{\text{PC}}$ 3.66 Hz, $-\text{CH}_2-$), 25.58 (d, $^3J_{\text{PC}}$ 7.94 Hz, $-\text{CH}_2-$), 29.94 (d, $^1J_{\text{PC}}$ 67.75 Hz, $-\text{CH}_2-$), 38.38 (s, $-\text{CH}_2-$), 199.96 (s, $\text{C}=\text{O}$) and 137.33–116.10 (m, 18 peaks, Ph); m/z (70 eV) 362 (M^+).

1-*p*-Chlorophenyl-5-diphenylphosphinoylpentan-1-one 12b

Prepared as above (0.40 g, 50%); mp 154–158 °C (Found: 396.1063 (M^+). $C_{23}H_{22}O_2P_1^{35}Cl_1$ (M) requires 396.1045; $\nu_{\max}/\text{cm}^{-1}$ (KBr) 2950, 2330, 1680 ($\text{C}=\text{O}$), 1585, 1380, 1180 ($\text{P}=\text{O}$) and 970; δ_{H} (90 MHz, CDCl_3) 1.57–2.47 (m, 6H, $-\text{CH}_2-$), 2.84–2.99 (m, 2H, $-\text{CH}_2-$) and 7.33–7.88 (m, 14H, Ph); δ_{C} (22.5 MHz, CDCl_3) 21.72 (d, $^2J_{\text{PC}}$ 3.66 Hz, $-\text{CH}_2-$), 25.66 (d, $^3J_{\text{PC}}$ 14.04 Hz, $-\text{CH}_2-$), 31.42 (d, $^1J_{\text{PC}}$ 71.42 Hz, $-\text{CH}_2-$), 38.27 (s, $-\text{CH}_2-$), 198.44 (s, $\text{C}=\text{O}$) and 139.61–128.58 (m, 14 peaks, Ph); m/z (70 eV) 396 (M^+).

1-*p*-Cyanophenyl-5-diphenylphosphinoylpentan-1-one 12c

Prepared as above (0.49 g, 63%); mp 154–158 °C (Found: 387.1386 (M^+). $C_{24}H_{22}O_2P_1N_1$ (M) requires 387.1386; $\nu_{\max}/\text{cm}^{-1}$ (KBr) 2950, 2230, 1685 ($\text{C}=\text{O}$), 1425, 1400, 1220, 1170 ($\text{P}=\text{O}$), 1110 and 820; δ_{H} (90 MHz, CDCl_3) 1.57–2.14 (m, 4H, $-\text{CH}_2-$), 2.19–2.47 (m, 2H, $-\text{CH}_2-$), 2.90–3.05 (m, 2H, $-\text{CH}_2-$) and 7.29–8.03 (m, 14H, Ph); δ_{C} (22.5 MHz, CDCl_3) 21.72 (d, $^2J_{\text{PC}}$ 3.66 Hz, $-\text{CH}_2-$), 25.48 (d, $^3J_{\text{PC}}$ 14.04 Hz, $-\text{CH}_2-$), 30.05 (d,

$^1J_{\text{PC}}$ 71.42 Hz, $-\text{CH}_2-$), 38.65 (s, $-\text{CH}_2-$), 198.39 (s, $\text{C}=\text{O}$), 116.77 (s, $-\text{CN}$) and 139.61–128.58 (m, 14 peaks, Ph); m/z (70 eV) 387 (M).

X-Ray crystal analysis †

Compound 4. $C_{22}H_{24}NO_4P$, $M = 397.41$, orthorhombic, $a = 16.97(1)$, $b = 17.10(1)$, $c = 14.20(1)$ Å, $V = 4119(1)$ Å³ (by least-squares refinement on diffractometer angles for 24 automatically centered reflections with $13.04 \leq \theta \leq 17.06$, $\lambda = 0.71069$ Å, $T = 293$ K), space group $Pbca$ (#61), $Z = 8$, $D = 1.282$ g cm⁻³, pale prism $0.180 \times 0.280 \times 0.800$ mm, $\mu(\text{Mo-K}\alpha) = 1.5$ cm⁻¹, Residuals: R , R_w 0.083, 0.066. The structure was solved by direct methods.

Compound 6. $C_{18}H_{18}N_2PCl_3$, $M = 399.69$, orthorhombic, $a = 15.773(5)$, $b = 20.40(2)$, $c = 11.627(7)$ Å, $V = 3741(8)$ Å³ (by least-squares refinement on diffractometer angles for 25 automatically centered reflections with $15.3 \leq \theta \leq 18.4$, $\lambda = 0.71069$ Å, $T = 293$ K), space group $Pbca$ (#61), $Z = 8$, $D = 1.419$ g cm⁻³, yellow prism, $0.340 \times 0.380 \times 1.000$ mm, $\mu(\text{Mo-K}\alpha) = 5.78$ cm⁻¹, Residuals: R , R_w 0.056, 0.062. The structure was solved by direct methods.

† CCDC reference number 207/322.

References

- (a) I. Yamamoto, T. Fujimoto, K. Ohta and K. Matsuzaki, *J. Chem. Soc., Perkin Trans. 1*, 1987, 1537; (b) I. Yamamoto, S. Tanaka, T. Fujimoto and K. Ohta, *J. Org. Chem.*, 1989, **54**, 747; (c) T. Fujimoto, Y. Hotei, H. Takeuchi, S. Tanaka, K. Ohta and I. Yamamoto, *J. Org. Chem.*, 1991, **56**, 4799.
- T. Sakai, K. Ida, T. Uchiyama, T. Fujimoto, K. Ohta and I. Yamamoto, *Heterocycl. Commun.*, 1996, **2**, 233.
- (a) T. Fujimoto, Y. Takeuchi, K. Kai, Y. Hotei, K. Ohta and I. Yamamoto, *J. Chem. Soc., Chem. Commun.*, 1992, 1263; (b) T. Fujimoto, Y. Uchiyama, Y. Kodama, K. Ohta and I. Yamamoto, *J. Org. Chem.*, 1993, **58**, 7322; (c) T. Fujimoto, Y. Kodama, I. Yamamoto and A. Kakehi, *J. Org. Chem.*, 1997, **62**, 6627.
- (a) G. W. Brown, R. C. Cookson, I. D. R. Stevens, T. C. W. Mak and J. Trotter, *Proc. Chem. Soc.*, 1964, 87; (b) E. M. Briggs, G. W. Brown, W. T. Dawson and J. Jirny, *J. Chem. Soc., Chem. Commun.*, 1975, 641; (c) J. Barluenga, F. Lopez and F. Palacios, *J. Chem. Soc., Perkin Trans. 1*, 1989, 2273; (d) A. W. Johnson, W. C. Kaska, K. A. O. Starzewski and D. A. Dixon, *Ylides and Imines of Phosphorus*, John Wiley & Sons, N. Y., Chichester, Brisbane, Toronto, Singapore, 1993, pp. 442–443 and references cited therein.
- Some examples of five-, six- and seven-membered iminophosphoranes are known; (a) ref. 4, pp. 412–413; (b) J. Barluenga, Miguel Tomas and Klaus Bieger, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 897.
- (a) T. Sakai, T. Kodama, T. Fujimoto, K. Ohta, I. Yamamoto and K. Kakehi, *J. Org. Chem.*, 1994, **59**, 7144; (b) T. Sakai, T. Fujimoto, K. Ohta and I. Yamamoto, *Phosphorus, Silicon Sulfur*, 1996, **108**, 99.
- Ref. 4(d), p. 415.

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