Synthesis and X-ray structural studies of new spiro-cyclotriphosphazenes

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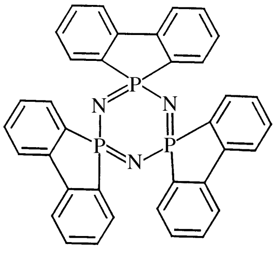
The series of four cyclotriphosphazenes containing biphenyl and phenyl groups, $[N_3P_3(C_{12}H_8)_{3-n}Ph_{2n}]$, where $n = 0$–3, (1–4 respectively), has been completed by the synthesis of two new C-bonded spirocyclotriphosphazenes, $[N_3P_3(C_{12}H_8)_2Ph_2]$ 2 and $[N_3P_3(C_{12}H_8)Ph_4]$ 3. They have been fully characterised and X-ray structural analysis shows that both compounds have a planar cyclotriphosphazene ring with less overall molecular rigidity compared to the trispirocyclic analogue, 1.

Trispirocyclotriphosphazenes have attracted attention in the past because many of them have exhibited the ability to form inclusion adducts with water and organic solvents.[1] This phenomenon occurs because of the unusual 'paddle wheel' conformation adopted by the molecule that permits the formation of channels or tunnels within the crystal lattice into which these guest molecules can be absorbed.[2] Most tunnel inclusion adducts have been formed by molecules where the rigid substituents were attached to the cyclotriphosphazene ring at the phosphorus atoms through P–X bonds, where X = N, O or S. The tris(biphenyl) compound **1** was the first trispirocyclotriphosphazene compound with carbon-bonded substituents on the cyclotriphosphazene ring.[3] It forms an inclusion adduct with chloroform as the guest molecule in tunnels of approximately 5.7 Å in diameter running throughout the crystal.

We have now extended the work on the *C*-bonded spirocyclotriphosphazenes by a new, relatively simple, two-step synthesis of two new compounds, **2** and **3**, the dispiro- and monospiro-cyclic derivatives respectively, and which also gave traces of the previously reported[4] hexaphenyl derivative **4**. These compounds complete a series of four cyclotriphosphazenes with biphenyl and/or phenyl ring substituents, $[N_3P_3(C_{12}H_8)_{3-n}Ph_{2n}]$, where $n = 0$–3, **1**–**4** respectively. This series of *C*-bonded cyclotriphosphazenes provides a unique progression in decreasing overall molecular rigidity as the number of phenyl groups is increased.



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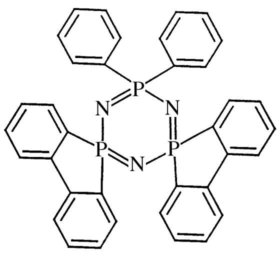

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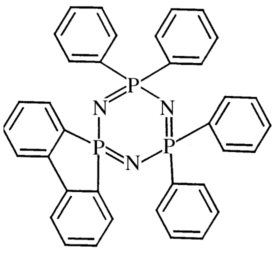

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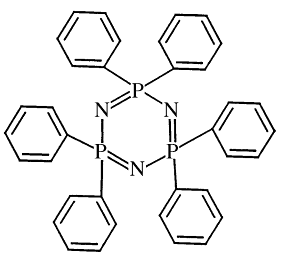


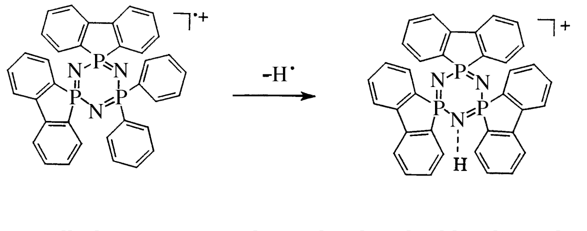
4

Synthesis and characterisation of the spirocyclotriphosphazenes

The dispirocyclotriphosphazene, **2**, and the monospirocyclotriphosphazene, **3**, were prepared from an equimolar mixture of diphenylphosphinic amide and biphenyl-2,2′-diylphosphinic amide using the triphenylphosphine–carbon tetrachloride reagent described by Appel.[5] Although we were expecting all four phosphazenes, **1**–**4**, only **2** and **3** were isolated as pure samples by chromatographic separation.

Compounds **2** and **3** were characterised by elemental analysis and mass spectrometry, and their structures were determined using ^{31}P, ^{13}C, ^{1}H NMR spectroscopy and X-ray crystallography with diffraction-quality crystals being obtained from chloroform.

Some peculiarities were observed in the EI mass spectra of the cyclotriphosphazene compounds **1**, **2** and **3**. For the trispirocyclic compound, **1**, the base peak is $[M]^{\cdot+}$ but for compounds **2** and **3**, the base peak is the molecular ion $[M-1]^{+}$. The elimination of $H^{\cdot}$ could be compared to that observed for hexaphenoxycyclotriphosphazene[6] in which an intramolecular cyclization is associated with nitrogen protonation.



For all these compounds, molecular doubly charged ions $[M]^{2+}$ are also detected as controlled by the 'Profile' method.

Crystal structures of compounds 2 and 3

The molecular structures of compounds **2** and **3**, depicted in Figs. 1(*a*) and 1(*b*), each consist of a central six-membered ring

Table 1 Comparison of selected bond lengths (Å) and angles (°) for $[N_3P_3(C_{12}H_8)_{3-n}Ph_{2n}]$, where n = 0–3, compounds **1**–**4**, respectively

Compound	**1**[a]	**2**	**3**	**4**[b]
n	0	1	2	3
P(1)–N(1)	1.579(8)	1.599(7)	1.603(6)	1.610(6)
P(1)–N(3)	1.574(8)	1.607(8)	1.600(4)	1.600(7)
P(2)–N(1)	1.597(7)	1.615(7)	1.600(6)	1.599(6)
P(2)–N(2)	1.602(8)	1.594(8)	1.600(4)	1.584(6)
P(3)–N(2)	1.591(8)	1.603(7)	1.585(5)	1.592(6)
P(3)–N(3)	1.592(8)	1.595(8)	1.591(5)	1.599(6)
P(1)–C(11)	1.790(10)	1.805(9)	1.806(6)	1.811(7)
P(1)–C(112)	1.788(10)	1.807(10)	1.797(5)	1.806(7)
P(2)–C(21)	1.805(10)	1.816(10)	1.806(5)	1.800(7)
P(2)–C(212)	1.792(10)	1.807(10)	1.790(6)	1.799(7)
P(3)–C(31)	1.814(10)	1.798(10)	1.803(5)	1.804(7)
P(3)–C(312)	1.792(10)	1.816(9)	1.799(5)	1.801(7)
N(1)–P(1)–N(3)	116.5(4)	118.4(4)	117.0(3)	118.2(3)
N(1)–P(2)–N(2)	115.9(4)	117.2(4)	117.5(3)	117.4(3)
N(2)–P(3)–N(3)	116.6(4)	117.6(4)	117.3(2)	117.8(3)
P(1)–N(1)–P(2)	123.4(5)	121.7(5)	122.1(2)	122.0(4)
P(2)–N(2)–P(3)	122.3(5)	123.1(5)	122.7(3)	123.0(4)
P(1)–N(3)–P(3)	123.2(5)	121.7(5)	123.0(3)	121.3(4)
C(11)–P(1)–C(112)	92.0(5)	106.1(4)	104.8(3)	103.4(3)
C(21)–P(2)–C(212)	91.4(5)	91.0(4)	103.5(3)	103.5(3)
C(31)–P(3)–C(312)	91.7(5)	92.0(4)	91.6(2)	104.4(3)

[a] From ref. 3. [b] From ref. 4. Renumbered for comparison purposes.

of alternating phosphorus and nitrogen atoms. In **2**, the phosphorus atoms, P(2) and P(3), each bond to a biphenyl unit, to give a dispirocyclic compound, and in **3** only one phosphorus atom, P(3), is bonded to a biphenyl unit, to give the monospirocyclic derivative. The remaining phosphorus atoms are each bonded to two phenyl groups. The nitrogen–phosphorus bond lengths in the cyclotriphosphazene (N_3P_3) ring are approximately equivalent and are in the range 1.594(8)–1.615(7) Å in **2** and 1.585(5)–1.603(6) Å in **3** with mean bond lengths of 1.602(8) and 1.596(5) Å, respectively. All the bond angles within the N_3P_3 ring are equal within experimental error with a mean N–P–N value of 117.7(4)° for **2** and 117.3(3)° for **3**, and mean P–N–P values of 122.2(5)° and 122.6(3)° for **2** and **3**, respectively.

The phosphorus–carbon bond lengths are all very similar and vary from 1.798(10)–1.816(9) Å with a mean of 1.808(10) Å for **2** and 1.790(6)–1.806(6) Å with a mean of 1.800(5) Å for **3**. The main difference in the two structures lies in the carbon–phosphorus–carbon (C–P–C) angles and can be related to the nature of the substituent. The C–P–C angles for the biphenyl groups are 91.0(4)° and 92.0(4)° for **2** and 91.6(3)° for **3** and are significantly smaller than the corresponding C–P–C angles for the phenyl groups whose values are 106.1(4)° for **2** and 104.8(3)° and 103.5(3)°, at P(1) and P(2) respectively, for **3**. This pattern is also evident in the trispiro compound, **1**, and the non-spiro compound **4**, shown in Table 1, and it can be seen that there is a remarkable similarity between the four structures. The smaller size of the C–P–C angles from the biphenyl substituents is a consequence of the bond between the two rings and illustrates the extra rigidity imparted by these substituents. The trispiro compound **1**, reported earlier, has shorter P–N bonds [mean P–N = 1.589(8) Å] than the other compounds [mean P–N = 1.602(8) **2**; 1.596(8) **3**; 1.597 Å **4**] but the difference is of low significance and the N_3P_3 ring shows the greatest deviation from planarity (maximum deviation = 0.096 Å). In both compounds, **2** and **3**, the cyclotriphosphazene rings are approximately planar with maximum deviations from the least-squares plane of 0.038 for **2** and 0.039 Å for **3**.

The planes of the biphenyl units are almost perpendicular to the plane of the cyclotriphosphazene rings with dihedral angles of 89.12° and 88.58° [at P(2) and P(3) respectively] in **2**, and 88.87° in **3**. This was also seen in the trispiro analogue **1**, where the dihedral angles varied from 83.1–89.7° and which resulted in the rigid ‘paddle wheel’ conformation. The packing arrangement of compound **1** favoured coplanar interactions between the biphenyl groups of adjacent molecules that resulted in voids or tunnels in the crystal lattice into which a chloroform molecule was absorbed.[3] For compounds **2** and **3**, the situation is markedly different because the phenyl groups are able to adopt random orientations where this flexibility leads to a more efficient molecular packing and no large voids in the crystal lattice. Consequently, this space-saving arrangement in **2** and **3** explains why, unlike trispiro species,[2] inclusion adducts are not observed for these molecules. The conformations of **2** and **3** could be described as being intermediate to those of **1** and **4**. The dihedral angles between the plane of the cyclotriphosphazene ring and the phenyl groups were 66.84° and 54.47° in **2** and 60.64° and 67.52° at P(1) and 57.12° and 58.40° at P(2) in **3** which were similar to the range of 51.7–63.0° reported for **4**.[4]

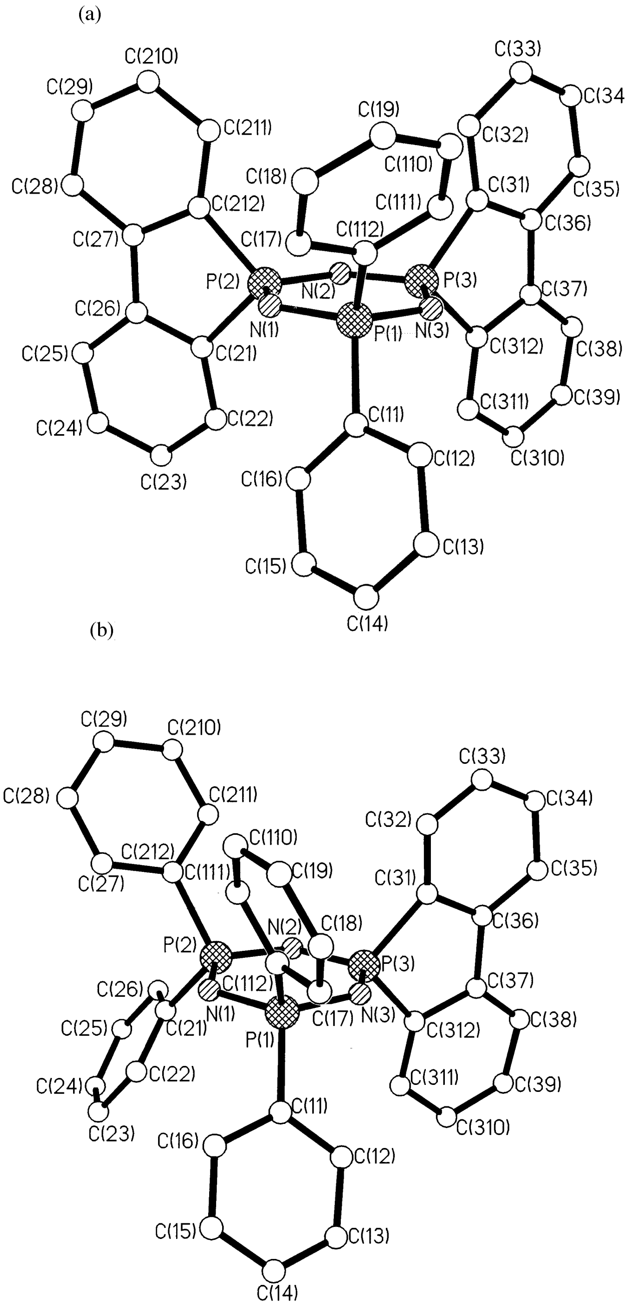


Fig. 1 (a) Molecular structure of the dispiro compound showing the relative orientation of the aromatic substituents (b) Molecular structure of the monospiro compound showing the relative orientation of the aromatic substituents

Experimental

The ^1H, ^{13}C and ^{31}P NMR spectra were recorded on a Bruker AC 200 Spectrometer at 200, 50 and 81 MHz respectively. Infrared spectra were recorded as KBr pellets using a Perkin-Elmer 377. Mass spectra were recorded using a JEOL JMS-DX 300 and elemental analyses were carried out in the Central Department of Elemental Analysis of ENSCM at the University of Montpellier.

Preparations

Diphenylphosphinic amide, [(O)PNH$_2$(Ph)$_2$]. The synthesis of diphenylphosphinic amide was adapted from a literature method[7] and gave a 90% yield.[8]

Biphenyl-2,2′-diylphosphinic amide, [(O)PNH$_2$(C$_{12}$H$_8$)]. A mixture of 9-hydroxy-9-phosphafluorene 9-oxide (3.88 g, 18 mmol) (prepared according to a method described in the literature[7]) and phosphorus pentachloride (3.75 g, 18 mmol) was heated to 180 °C for 30 min. After distillation of the formed phosphorus oxychloride, the residue was dissolved in chloroform (15 cm^3) and added dropwise under nitrogen gas to a 1:1 solution of diethyl ether–ammonia (28%) cooled to 0 °C. The mixture was stirred for 1 h at 0 °C allowed to increase to 20 °C and then stirred at this temperature for a further 12 h. The aqueous layer was then extracted with methylene chloride (2 × 30 cm^3) and the combined organic layers were washed with water (30 cm^3), dried using $MgSO_4$ and filtered. The solvent was removed at reduced pressure and the residue was recrystallized to leave a white solid; mass = 2.55 g (66%). Mp 179 °C (Found: C, 66.8; H, 4.7; N, 6.4. $C_{12}H_{10}NOP$ requires C, 66.97; H, 4.65; N, 6.51%); ν_{max}/cm^{-1} 1180 (P=O), 750 (P–N); δ_H(CDCl$_3$; 200 MHz) (J values in Hz) 7.39 (2 H, ddt, $^3J_{23}$ 7.5; $^3J_{21}$ 7.5; $^4J_{24}$ 0.8; $^4J_{2P}$ 3.7, 2-H), 7.54 (2 H, tt, $^3J_{32}$ 7.5, $^3J_{34}$ 7.7, $^4J_{31}$ 1.3, $^5J_{3P}$ 1.4, 3-H), 7.73 (2 H, ddt, $^3J_{34}$ 7.7, $^4J_{24}$ 0.8, $^5J_{14}$ 0.8, $^4J_{4P}$ 3.3, 4-H , 7.81 (2 H, dddd, $^3J_{12}$ 7.5, $^4J_{13}$ 1.3, $^5J_{14}$ 0.8, $^3J_{1P}$ 10.4, 1-H); δ_C Table 2; δ_P(CDCl$_3$, 81 MHz) 34.8; *m/z* (IE) 215 (M$^+$, 86%), 199 (100), 168 (18), 152 (40), 139 (6), 126 (5), 77 (3).

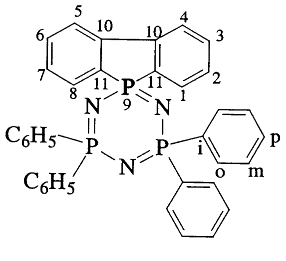
Dispiro, [N$_3$P$_3$(C$_{12}$H$_8$)$_2$Ph$_2$] 2, and monospiro, [N$_3$P$_3$(C$_{12}$H$_8$)Ph$_4$] 3, cyclotriphosphazene compounds. A solution of diphenylphosphinic amide (2.21 g, 10.2 mmol), biphenyl 2,2′-diylphosphinic amide (2.19 g, 10.2 mmol), carbon tetrachloride (3.14 g, 20.4 mmol), triethylamine (2.06 g, 20.4 mmol) and triphenylphosphine (6.42 g, 24.5 mmol) was refluxed in methylene chloride (40 cm^3) for 5 h. The solvent was removed and the residue was put through a chromatographic column (silica gel, 1:1 methylene chloride–hexane) to isolate the two spirocyclotriphosphazenes.

[N$_3$P$_3$(C$_{12}$H$_8$)$_2$Ph$_2$] 2. Yield 15%. (Column $R_f = 0.25$); mp 343 °C (chloroform) (Found: C, 72.8; H, 4.6; N, 7.0. $C_{36}H_{26}N_3P_3$ requires C, 72.85; H, 4.38; N, 7.08%); ν_{max}/cm^{-1}: 1195 (P=N), 1180 (P=N); δ_H(CDCl$_3$; 200 MHz) 7.39 (m, 14 H), 7.64 (m, 8 H), 7.95 (m, 4 H); δ_C: Table 2; δ_P(CDCl$_3$; 81 MHz) 18.3 [(C$_6$H$_5$)$_2$P], 25.6 [(C$_{12}$H$_8$)P]$_2$; *m/z* (IE) 593 [M$^{\cdot+}$, 62%], 592 [(M − 1)$^+$, 100], 516 (45), 471 (6), 440 (15), 395 (6), *296 [M^{2+}, 14], 274 (7), 198 (14), 183 (28), 122 (2), 77 (3). (*The use of ‘Profile’ method gives M^{2+} = 296.794.)

[N$_3$P$_3$(C$_{12}$H$_8$)Ph$_4$] 3. Yield 33%. (Column $R_f = 0.4$); mp 359 °C (chloroform) (Found: C, 72.7; H, 4.4; N, 7.0. $C_{36}H_{28}N_3P_3$ requires C, 72.60; H, 4.70; N, 7.05%); ν_{max}/cm^{-1}: 1190 (P=N), 1170 (P=N); δ_H(CDCl$_3$; 200 MHz) 7.32 (m, 8 H), 7.67 (m, 4 H), 7.85 (m, 16 H); δ_C: Table 2; δ_P(CDCl$_3$; 81 MHz) 17.0 [(C$_6$H$_5$)$_2$P]$_2$; 24.4 [(C$_{12}$H$_8$)P]; *m/z* (IE) 595 (M$^{\cdot+}$, 60%), 594 [(M − 1)$^+$; 100], 518 (73), 442 (14), 395 (9), 319 (6), *298 [M^{2+}, 14], 274 (17), 259 (7), 198 (24), 183 (37), 152 (5), 122 (12), 77 (8). (*The use of ‘Profile’ method gives M^{2+} = 297.72.)

Trispiro [N$_3$P$_3$(C$_{12}$H$_8$)$_3$] 1 cyclotriphosphazene. A solution of 9-amino-9-phosphafluorene 9-oxide (9.18 g, 42.7 mmol), carbon tetrachloride (6.57 g, 42.7 mmol), triethylamine (4.31 g, 42.7 mmol) and triphenylphosphine (13.41 g, 51.2 mmol) was refluxed in methylene chloride (110 cm^3) for 5 h. The solvent was removed at reduced pressure. The residue was washed by methanol (250 cm^3) and filtered. The filtrate was concentrated (100 cm^3), then hexane (20 cm^3) was added. After 3 h at 5 °C, the formed precipitate was filtered, $m = 1.17$ g (14%). Elemental analyses, ^1H and ^{31}P NMR, mass spectrometry and X-ray diffraction results have already been published.[3]

The numbering scheme employed for the compounds is shown below for compound **3** and applies to the other compounds when assigning $^1H/^{13}C$ NMR data. The ^{13}C data of biphenyl-2,2′-diylphosphinic amide and compounds **1**, **2** and **3** are reported in Table 2.



3

X-Ray crystallography

Crystal data for 2. $C_{36}H_{26}N_3P_3$ $M_r = 593.54$, monoclinic, space group $P2_1/n$ (No. 14), $a = 30.709(6)$, $b = 9.744(3)$, $c = 10.213(3)$ Å, $\beta = 97.55(2)°$, $U = 3029.5$ Å^3, $Z = 4$, $F(000) = 1232$, $D_c = 1.301$ g cm^{-3}, $\lambda = 0.710\,69$ Å, μ(Mo-Kα) = 0.22 mm^{-1}.

Crystal data for 3. $C_{36}H_{27}N_3P_3$, $M_r = 595.56$, orthorhombic, space group $Pna2_1$ (No. 33), $a = 19.037(2)$, $b = 10.5186(12)$, $c = 15.343(2)$ Å, $U = 3072.3$ Å^3, $Z = 4$, $F(000) = 1240$, $D_c = 1.287$ g cm^{-3}, $\lambda = 1.541\,78$ Å, μ(Cu-Kα) = 2.007 mm^{-1}.

Data collection. Data were collected on colourless crystals of dimensions 0.40 × 0.34 × 0.24 mm for **2** and 0.50 × 0.34 × 0.28 mm for **3** using Mo-Kα radiation on a Philips PW1100 and using Cu-Kα radiation on a Siemens P4 four-circle diffractometer respectively. Lorentz and polarisation corrections were applied and merged giving 3487 unique reflections ($R_{int} = 0.0659$) for **2**, and 2185 unique reflections ($R_{int} = 0.0511$) for **3**.

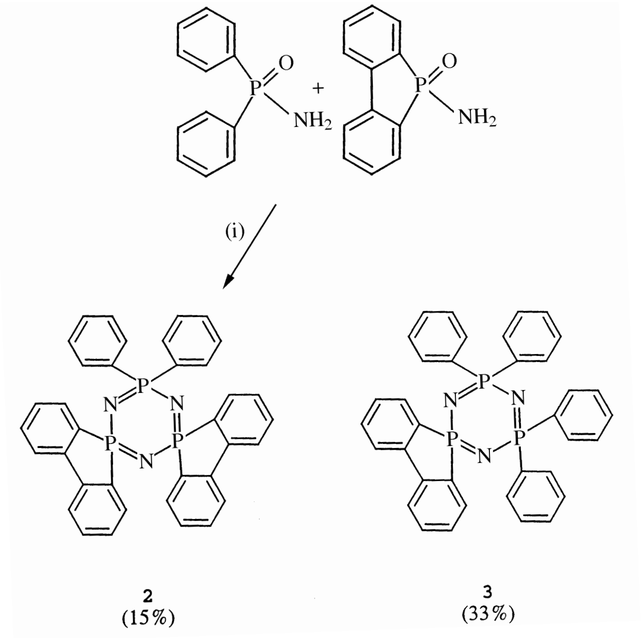
Structure solution and refinement. Both structures were solved by direct methods (SHELXS 86 for **2**,[10] and SHELXTL for **3**[11]) giving the positions of all the non-hydrogen atoms. The hydrogen atoms were included at idealised geometrical positions [C–H 1.08 (**2**) and 0.93 Å (**3**)] with fixed isotropic thermal parameters of 0.08 Å^2 for **2**,[12] and an isotropic thermal parameter 1.2 × U_{eq}C for **3**. The range of values for the isotropic thermal parameters, U_{iso} for the phenyl groups of **2** was 0.033(3)–0.093(4) Å^2 whereas for **3** was 0.037(2)–0.143(5) Å^2. Anisotropic thermal parameters could only be assigned to the nitrogen and phosphorus atoms in **2** owing to a lack of data but were assigned to all the non-hydrogen atoms in **3**. Some of the components of the anisotropic thermal parameters for the phenyl carbon atoms furthest from the N$_3$P$_3$ ring in **3** were high with a range of *ca.* 0.105(6)–0.236(14) Å^2. This was consistent with the greater flexibility associated with the larger number of freely rotable phenyl rings of **3** compared to **2** and indicated a degree of disorder in the crystal lattice. Full-matrix least-squares refinement on F converged at $R = 0.0668$, $R_w = 0.0662$, for 1583 reflections with $F_o/\sigma(F_o) > 4$ and 199 parameters, for **2**, and at $wR2 = 0.1144$ (all data) for 2184 reflections $\{R1 = 0.0404$, $[F_o/\sigma(F_o) > 4]$, goodness-of-fit (S) on $F^2 = 1.030\}$ and 380 parameters. Weights of $1/[\sigma(F_o)]$ and of $1/[\sigma^2(F_o)^2 + (0.0613P)^2 + 1.01P]$, where $P = \{\max[(F_o)^2, 0] + 2(F_c)^2]\}/3$ were assigned to the individual reflections for **2** and **3**, respectively.

Atomic coordinates, bond lengths and angles, and thermal

Table 2 $\delta_C(CDCl_3$; 50 MHz) chemical shift (ppm) and coupling constant (Hz)

	bppa	**1**[a]	**2**	**3**
C-*i*			138.05 (121.8)	138.18 (132.3)
C-*o*			130.98 (10.4)	130.80 (11.7)
C-*m*			128.21 (13.2)	128.01 (13.5)
C-*p*			130.94	130.77 (2.8)
C-11	132.12 (126.8)	135.24 (136.8)	135.51 (138.3)	135.79 (135.5)
C-10	140.21 (26.7)	140.29 (26.3)	140.45 (26.3)	140.45 (25.9)
C-4	120.91 (11.6)	120.65 (12.5)	120.65 (12.3)	120.57 (11.9)
C-3	133.18 (2.1)	132.51	132.32	132.09 (2.2)
C-2	129.30(11.5)	129.25 (12.3)	129.13 (12.2)	128.92 (12.1)
C-1	128.51 (9.0)	127.33 (10.1)	127.73 (10.0)	127.95 (7.8)

[a] Chemical shift and coupling constants were determined after a correlation spectrum $^1H-^{13}C$.



Scheme 1 A general synthetic route for the preparation of **2** and **3** (*i*) triphenylphosphine, triethylamine, tetrachloromethane in dichloromethane

parameters for **2** and **3** have been deposited at the Cambridge Crystallographic Data Centre (CCDC). For details of the deposition scheme, see ‘Instructions for Authors’, *J. Chem. Soc., Perkin Trans. 2*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 188/46.

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