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Reaction of *m*-Terphenyldichlorophosphanes with Sodium Azide: Synthesis and Characterization of Stable Azidocyclophosphazenes

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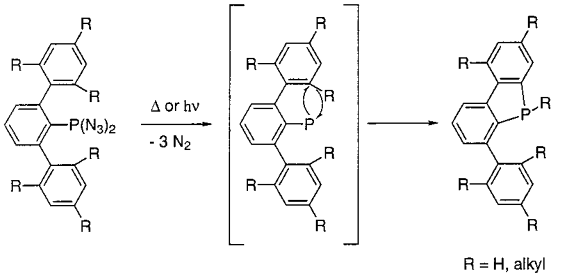
Reaction of the *m*-terphenyldichlorophosphanes 2,6-(2-MeC$_6$H$_4$)$_2$C$_6$H$_3$PCl$_2$ (**1**), 2,6-(4-*t*-BuC$_6$H$_4$)$_2$C$_6$H$_3$PCl$_2$ (**2**), or 2,6-Mes$_2$C$_6$H$_3$PCl$_2$ (**3**) with excess NaN$_3$ in acetonitrile at room temperature afforded the corresponding bisazidophosphanes 2,6-(2-MeC$_6$H$_4$)$_2$C$_6$H$_3$P(N$_3$)$_2$, 2,6-(4-*t*-BuC$_6$H$_4$)$_2$C$_6$H$_3$P(N$_3$)$_2$ (**5**), or 2,6-Mes$_2$C$_6$H$_3$P(N$_3$)$_2$ (**6**) (Mes = 2,4,6-Me$_3$C$_6$H$_2$), respectively. These compounds are thermally labile and decompose into a number of azidophosphazenes. The azidocyclophosphazenes [NP(N$_3$)(C$_6$H$_3$(4-*t*-BuC$_6$H$_4$)$_2$-2,6)]$_3$ (**4**) and [NP(N$_3$)C$_6$H$_3$Mes$_2$-2,6]$_2$ (**8**) have been isolated from these mixtures. All compounds were characterized by ^{1}H, ^{13}C, ^{31}P NMR and IR spectroscopy. Crystal structures of **2**, **4**, and **8** were determined.

Introduction

During the past few years it has been reported by two groups that the reduction of various *m*-terphenyl-substituted main group halides (ArBX$_2$, Ar = 2,6-Mes$_2$C$_6$H$_3$, 2,6-Trip$_2$C$_6$H$_3$, X = Cl, Br, Mes = 2,4,6-Me$_3$C$_6$H$_2$, Trip = 2,4,6-*i*-Pr$_3$C$_6$H$_2$;[1] ArSiF$_3$, Ar = 2,6-Mes$_2$C$_6$H$_3$, 2,6-Trip$_2$C$_6$H$_3$;[2] 2,6-Trip$_2$C$_6$H$_3$PCl$_2$[3]) readily leads to unsymmetrical 9-heterofluorenes. The most remarkable feature in these reactions is the facile insertion of the main group element into a C−C bond of the *m*-terphenyl substituent (i.e., C−C activation). So far, the mechanism of these reactions is unknown, but it has been suggested that highly reactive, low oxidation state species such as boranediyl ArB, silanediyl ArSiF, or phosphanediyl ArP might be the intermediates.

We have recently initiated a study of the coordination properties of some of these heterofluorenes and have so far focused on 9-borafluorenes.[4] Intrigued by the possibility that unsymmetrical 9-phosphafluorenes (dibenzophospholes) could be used as potentially bidentate chiral ligands in asymmetric synthesis and given that the published reductive procedure is limited to 2,6-Trip$_2$C$_6$H$_3$PCl$_2$,[3] we were interested in developing a general route to the unsymmetrical 9-phosphafluorenes. Assuming that a phosphanediyl ArP is the reactive intermediate, we investigated the potential of *m*-terphenyl-substituted bisazidophosphanes ArP(N$_3$)$_2$ as precursors for unsymmetrical 9-phosphafluorenes via thermolytic or photolytic N$_2$ elimination and subsequent C−H or C−C activation by the intermediate phosphanediyl ArP (eq 1).

Precedent for the formation of a phosphanediyl by photolysis of bisazidophosphanes has been reported by Cowley et al. for Ar = Mes or Mes* (Mes* = 2,4,6-*t*-Bu$_3$C$_6$H$_2$).[5]



(1)

On the other hand, azidophosphazenes R$_2$PN$_3$ have been reported to undergo thermal or photolytic rearrangement to phosphazenes (R$_2$P=N−)$_n$.[6−8] An analogous reaction for bisazidophosphanes ArP(N$_3$)$_2$ would then lead to azidophosphazenes (Ar(N$_3$)P=N−)$_n$, a class of compounds currently of interest as cross-linking or branching reagents for organic polymers.[9,10] The reported synthesis of azidophosphazenes is a multistep procedure, the last step being the reaction of chlorophosphazenes with NaN$_3$ for 1 to 7 days depending on the solvent system employed.[9] Azidophosphazene formation from readily available bisazidophosphane precursors would thus constitute a considerable synthetic shortcut.

Here, we report the synthesis of rare *m*-terphenyl-substituted bisazidophosphanes, their unexpectedly low thermal stability despite the steric protection by the large *m*-terphenyl substituent, and their facile transformation into azidophosphazenes.

Experimental Section

General Procedures. All work was performed under anaerobic and anhydrous conditions by using either modified Schlenk techniques or an Innovative Technologies drybox. Solvents were freshly distilled

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under N_2 from Na/K alloy and degassed twice prior to use. 2-Bromotoluene, *m*-dichlorobenzene, *n*-butyllithium, (1.6 M in hexanes), PCl_3, and NaN_3 were obtained from commercial suppliers. 2,6-Mes$_2$C$_6$H$_3$-PCl$_2$ (**3**),[11] 2,6-Mes$_2$C$_6$H$_3$I, and 2,6-(4-*t*-BuC$_6$H$_4$)$_2$C$_6$H$_3$Br[12,13] were synthesized by following modified literature procedures. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded on a Varian Unity Plus 400 spectrometer. ^{1}H NMR chemical shift values were determined relative to the residual protons in C_6D_6 or $CDCl_3$ as internal reference ($\delta = 7.15$ or 7.26 ppm). ^{13}C NMR spectra were referenced to the solvent signals ($\delta = 128.0$ or 77.0 ppm). ^{31}P NMR spectra were referenced to an 85% H_3PO_4 solution as external standard. Infrared spectra were recorded in the range 4000−400 cm^{-1} as a Nujol mull between KBr or CsI plates using either a Bio-Rad FT-155 or a Nicolet Nexus 470 FTIR spectrometer. FAB mass spectra were measured with a VG ZAB-E mass spectrometer using 3-nitrobenzyl alcohol as the matrix material, and electrospray mass spectra were measured with a Micromass Q-ToF spectrometer. Melting points were determined in Pyrex capillary tubes (sealed under nitrogen where appropriate) with a Mel-Temp apparatus and are uncorrected. Elemental analyses were performed by Complete Analyis Laboratories Inc. in Parsippany, NJ.

2,6-(2-MeC$_6$H$_4$)$_2$C$_6$H$_3$I was synthesized according to a modification of the literature procedure[12] allowing for large scale syntheses as described by Power et al.[13] as a colorless crystalline solid (99.86 g, 61% yield), mp 95−100 °C. ^{1}H NMR (400 MHz, $CDCl_3$): *syn*:*anti* mixture ≈ 44:56; 7.43 (t, *p*-H, 1H, *anti*), $^3J_{HH} = 7.6$ Hz, 7.42 (t, *p*-H, 1 H, *syn*), $^3J_{HH} = 7.4$ Hz, 7.29 (m, 6H), 7.18 (d, *m*-H, 2H, *syn*), 7.17 (d, *m*-H, 2H, *anti*), 7.16 (s, broad, 1H), 7.14 (s, broad, 1H), 2.13 (s, *o*-Me, 6H, *syn*), 2.12 (s, *o*-Me, 6H, *anti*). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): *syn*:*anti* mixture ≈ 44:56; 147.70, 147.60, 145.25, 135.62, 135.57, 129.84, 129.80, 129.26, 128.96, 127.95, 127.93, 127.86, 127.71, 125.58, 125.50, 106.10 (*i*-C, *anti*), 105.67 (*i*-C, *syn*), 20.06 (*o*-Me, *syn*), 19.94 (*o*-Me, *anti*). MS (EI, 70 eV): *m*/*z* 384.0 (M$^+$, 100).

2,6-(2-MeC$_6$H$_4$)$_2$C$_6$H$_3$PCl$_2$ (1). A solution of 2,6-(2-MeC$_6$H$_4$)$_2$C$_6$H$_3$I (4.38 g, 11.4 mmol) in hexanes (80 mL) was treated with *n*-butyllithium (4.6 mL, 12.0 mmol, 1.6 M in hexanes) at 0 °C, immediately after which a fine colorless solid began to precipitate. The reaction mixture was warmed to room temperature, stirred overnight (ca. 12 h), and cooled to −78 °C, and freshly distilled PCl_3 (1.2 mL, 1.89 g, 13.7 mmol) was added via syringe. After 30 min the reaction mixture was slowly warmed to room temperature and stirred for an additional 4 h. After filtration through a medium porosity glass frit, the yellow filtrate was concentrated to 3−4 mL under reduced pressure and cooled to −28 °C for 3 days to give a sticky, crystalline, yellow solid (2.78 g). Recrystallization from hexanes (5 mL) at −28 °C for 1 week afforded **1** as pale yellow needles (1.94 g, 47% yield), mp 58−60 °C. Anal. Calcd for $C_{20}H_{17}Cl_2P$: C, 66.87; H, 4.77. Found: C, 66.99; H, 4.84. ^{1}H NMR (400 MHz, C_6D_6): *syn*:*anti* mixture ≈ 35:65; 7.41 (dd, 2H), $J = 7.2$, 1.8 Hz, 7.28 (dd, 1H), $J = 7.2$, 1.2 Hz, 7.09 (m, 10H), 6.98 (t, 1H), $J = 7.2$ Hz, 6.86 (m, 3.5H), 2.09 (s, *o*-Me, 3H, *syn*), 2.03 (s, *o*-Me, 6H, *anti*). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6): 147.54, 147.25, 139.63, 139.54, 136.67, 136.26 (d), $J_{CP} = 2.3$ Hz, 131.72, 131.11, 131.09, 131.05, 130.96, 130.10, 130.05, 128.65, 128.58, 125.47, 125.29, 20.83. ^{31}P{^{1}H} NMR (161.9 MHz, C_6D_6): *syn*:*anti* mixture ≈ 35:65; 157.6 (s, *anti*), 157.2 (s, *syn*).

2,6-(4-*t*-BuC$_6$H$_4$)$_2$C$_6$H$_3$Li. A solution of 2,6-(4-*t*-BuC$_6$H$_4$)$_2$C$_6$H$_3$Br (3.26 g, 7.7 mmol) in hexanes (80−90 mL), cooled in an ice bath, was treated with *n*-butyllithium (5.3 mL, 8.5 mmol, 1.6 M in hexanes). The reaction mixture was slowly warmed to room temperature. After about 1.5 h, a fine colorless solid precipitated, which was redissolved by gentle heating with a heatgun. Stirring was halted, and after 1 h a microcrystalline solid began to precipitate. The mixture was kept at room temperature for a further 12 h and subsequently cooled to −28 °C for 24 h to afford a colorless, crystalline solid (2.13 g, 79% yield). ^{1}H NMR(C_6D_6, 400 MHz): 7.56 (d, *o*- or *m*-H (4-*t*-BuC$_6$H$_4$), 4H), $^3J_{HH} = 8.0$ Hz, 7.38 (s, broad, *m*-H, 2H), 7.25 (s, broad, *o*- or *m*-H (4-*t*-BuC$_6$H$_4$), 4H), 1.12 (s, Me, 18H). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6): 174.6 (br, *i*-C), 151.2, 149.9, 144.0 (br), 127.3, 126.3, 124.7, 34.3 (*C*(CH$_3$)$_3$), 31.3 (CH$_3$).

2,6-(4-*t*-BuC$_6$H$_4$)$_2$C$_6$H$_3$PCl$_2$ (2). Freshly distilled PCl_3 (0.92 mL, 1.44 g, 10.5 mmol) was added via syringe to a stirred suspension of 2,6-(4-*t*-BuC$_6$H$_4$)$_2$C$_6$H$_3$Li (3.27 g, 9.4 mmol) in hexanes (100 mL) at −78 °C. The reaction mixture was kept at −78 °C for 1 h, slowly warmed to room temperature, and stirred overnight. The fine precipitated solid was separated by filtration, and the clear colorless filtrate was concentrated to ca. 40 mL under reduced pressure. The precipitated crystalline solid was redissolved by warming with a heatgun. After 1 h at room temperature, large colorless crystals (plates) of sufficient quality for X-ray diffraction studies began to form (1.49 g). Concentration of the mother liquor afforded a second crop (3.01 g, 74% yield), mp softens at 120 °C, melts at 138−140 °C. ^{1}H NMR(C_6D_6, 400 MHz): 7.53 (d, *o*- or *m*-H (4-*t*-BuC$_6$H$_4$), 4H), $J = 8.4$ Hz,): 7.34 (d, *o*- or *m*-H (4-*t*-BuC$_6$H$_4$), 4H), $J = 8.4$ Hz, 7.15 (d, *m*-H, 2H), $J = 8.4$ Hz, 7.07 (t, *p*-H, 1H), $J = 8.4$ Hz, 1.23 (s, *p*-C(C*H*$_3$)$_3$. ^{13}C{^{1}H} NMR (100 MHz, C_6D_6): 151.33, 149.13 (d), $J_{CP} = 28.2$ Hz, 138.12 (d), $J_{CP} = 8.4$ Hz, 131.78, 131.20, 130.38 (d), $J_{CP} = 3.8$ Hz, 125.19, 34.64 (*C*(CH$_3$)$_3$), 31.40 (C(*C*H$_3$)$_3$). ^{31}P{^{1}H} NMR (C_6D_6, 161.9 MHz): 157.3 (s).

*Caution: Phosphonous azides $R_nP(N_3)_{3-n}$ are potentially explosive,[8] in fact, $(CF_3)_2PN_3$[6] has been reported to explode without obvious reasons. Furthermore, the azidophosphazene $[NP(N_3)_2]_3$ is a violent detonator.[14] Apparently, these compounds are very susceptible to shock, and the appropriate precautions, such as working with small amounts only, blast shields, and leather gloves, should be taken. However, we have not experienced any explosions or even milder decompositions, which we believe is due to the relatively low nitrogen content, 22.57% maximum in 2,6-(2-MeC$_6$H$_4$)$_2$C$_6$H$_3$P(N$_3$)$_2$. A minimum nitrogen content of 25% has been reported as the lower limit for the explosivity of covalent azides.[15] Shock tests (hammer) of **4**, **6**, and **8** did not indicate any sensitivity.*

Reaction of 2 with NaN$_3$ (Method A). Synthesis of [NP(N$_3$)(C$_6$H$_3$-(4-*t*-BuC$_6$H$_4$)$_2$-2,6)]$_3$ (4). A slurry of NaN_3 (1.30 g, 20 mmol) in MeCN (20 mL) was added to a slurry of **2** (0.88 g, 2.0 mmol) in MeCN (15 mL) at room temperature, and the reaction mixture was stirred for 12 h. After removal of the solvent under reduced pressure, the resulting off-white solid was extracted with hexanes (60 mL). The pale yellow extract was concentrated to ca. 15 mL under reduced pressure. Large (1 mm) colorless crystals of **4**·C$_6$H$_{14}$ deposited during 3 days at room temperature (0.24 g, 26% yield): mp turns opaque at 195 °C, slowly changes color to dark red, melts at 241−2 °C with gas evolution. Anal. Calcd for $C_{84}H_{101}N_{12}P_3$ (**4**): C, 73.55; H, 7.42; N, 12.25. Found: C, 73.74; H, 7.34; N, 12.30. ^{1}H NMR (C_6D_6, 400 MHz): 7.16 (m, broad), 6.76 (s, broad, 2H), 6.68 (td, 2H), $J = 7.4$, 2.4 Hz, 1.47 (s, broad, 18H), 1.33 (s, 36H), 1.23 (m, broad, *C*H$_2$(hexane), 8H), 0.88 (t, *C*H$_3$(hexane), 6H), $J = 7.0$ Hz. ^{31}P{^{1}H} NMR (C_6D_6, 161.9 MHz): 15.3 (d, 2P), $J_{PP} = 21.7$ Hz, 13.5 (t, 1P). IR (KBr, Nujol): $\nu(N_3) =$ 2127 (vs), 2142 (vs), 2151 (vs) cm^{-1}. MS (FAB): *m*/*z* 1285.6 (M + H$^+$, 19.2%), 1257.5 (M − N$_2$ + H$^+$, 76.6%).

Method B. Solid NaN_3 (1.30 g, 20 mmol) was added to a slurry of **2** (0.48 g, 1.1 mmol) in MeCN (15 mL) at room temperature, and the reaction mixture was stirred for 70 min with careful exclusion of light. After removal of the solvent under reduced pressure, the resulting pale yellow solid was extracted with cold Et$_2$O (20 mL, 0 °C). The solvent was removed under reduced pressure to give a “fluffy” yellowish solid (0.18 g). This solid was shown by ^{31}P{^{1}H} NMR spectroscopy to consist of a number of phosphorus-containing compounds with 2,6-(4-*t*-BuC$_6$H$_4$)$_2$C$_6$H$_3$P(N$_3$)$_2$ (**5**) as one of them. The spectrum was collected immediately after sample preparation. ^{31}P NMR (C_6D_6, 161.9 MHz): 133.5 (s, **5**, 26%), 105.4 (d, 6%), $J_{PP} = 130.0$ Hz, 21.2 (s, 2%), 17.6 (s, 4%), 15.5 (d, 21%), $J_{PH} = 594.2$ Hz, 15.3 (d, **4**, 20%), $J_{PP} = 21.7$ Hz, 13.5 (t, **4**, 10%), 10.9 (d, 6%), $J_{PP} = 130.0$ Hz, −67.1 (d, 5%), $J_{PH} = 199.1$ Hz.

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Reaction of 1 with NaN_3 (Method A). A slurry of NaN_3 (1.30 g, 20 mmol) in MeCN (20 mL) was added to a solution of **1** (0.72 g, 2.0 mmol) in MeCN (15 mL) at room temperature, and the reaction mixture was stirred for 20 h. After removal of the solvent under reduced pressure, the resulting off-white solid was extracted with hexanes (60 mL). The pale yellow extract was concentrated to ca. 5−7 mL under reduced pressure and cooled to −28 °C for 2 weeks to afford a pale yellow microcrystalline solid (0.05 g), mp 80−81 °C with gas evolution. The ^1H NMR spectrum (C_6D_6, 400 MHz) displayed broad signals at 7.6−6.5 and 2.4−1.8 ppm. The $^{31}P\{^1H\}$ NMR spectrum (C_6D_6, 161.9 MHz) showed overlapping multiplets in the region of 20−5 ppm. IR (KBr, Nujol): $\nu(N_3) = 2153$ (vs) cm^{-1}. A second crop was obtained after concentration of the mother liquor followed by cooling to −28 °C for 1 month (0.03 g).

Reaction of 3 with NaN_3 (Method A). Solid NaN_3 (1.30 g, 20 mmol) was added to a slurry of **3** (0.92 g, 2.2 mmol) in MeCN (20 mL) at room temperature, and the reaction mixture was stirred for 20 h. After removal of the solvent under reduced pressure, the resulting yellow-orange solid was extracted with hexanes (50 mL). The yellow extract was concentrated to ca. 7−10 mL under reduced pressure and allowed to stand at room temperature for 2 days. As no crystals had formed, the yellow solution was further concentrated to 1−2 mL and cooled to −28 °C for 2 days. No crystalline material was obtained, and the remaining solvent was removed under reduced pressure to give a yellow-orange solid. The ^1H NMR spectrum (C_6D_6, 400 MHz) displayed broad signals at 7.1−6.6 and 2.4−1.9 ppm. The $^{31}P\{^1H\}$ NMR spectrum (C_6D_6, 161.9 MHz) showed a multitude of signals, doublets ($J = 6.8{-}18.3$ Hz) and singlets, in the region of 19 to −10 ppm. IR (KBr, Nujol): $\nu(N_3) = 2148$ (vs) cm^{-1}.

Method B. Synthesis of 2,6-$Mes_2C_6H_3P(N_3)_2$ (6). Solid NaN_3 (1.30 g, 20 mmol) was added to a slurry of **3** (0.51 g, 1.2 mmol) in MeCN (15 mL) at room temperature, and the reaction mixture was stirred for 2 h with careful exclusion of light. After removal of the solvent under reduced pressure, the resulting pale yellow solid was extracted with cold Et_2O (20 mL, 0 °C). The solvent was removed under reduced pressure, and the remaining yellow oil was cooled to −30 °C for 2 days to give some small, very thin plates embedded in a sticky solid (0.48 g). This solid was shown by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy to consist of a mixture of five phosphorus-containing compounds with **6** as the major product (63% according to $^{31}P\{^1H\}$ NMR). The spectra were collected immediately after sample preparation. ^1H NMR data for **6** (C_6D_6, 400 MHz): 7.08 (t, *p*-H, 1H), $J = 7.6$ Hz, 6.87 (s, *m*-H(Mes), 4H), 6.77 (dd, *m*-H, 2H), $J_{HH} = 7.6$ Hz, $J_{HP} = 3.0$ Hz, 2.18 (s, *p*-Me, 6H), 2.07 (s, *o*-Me, 12H). $^{31}P\{^1H\}$ NMR (C_6D_6, 161.9 MHz): 129.8 (s, **6**, 63%), 111.0 (d, 10%), $J_{PP} = 28.4$ Hz, 18.9 (s, 4%), 11.4 (s, 8%), −3.9 (d, 9%), $J_{PP} = 28.4$ Hz, −6.3 (s, 6%).

2,6-$Mes_2C_6H_3P(O)(N_3)NH_2$ (7·0.25 Et_2O). A portion of crude **6** (0.15 g) was washed with cold hexanes (0 °C, 4 mL). The remaining thin colorless plates were dried under reduced pressure (ca. 5 mg). ^1H NMR (C_6D_6, 400 MHz): 7.07 (dt, *p*-H, 1H), $J_{HH} = 7.6$ Hz, $J_{HP} = 2.0$ Hz, 6.825 (s, *m*-H(Mes), 2H), 6.817 (s, *m*-H(Mes), 2H), 6.77 (dd, *m*-H, 2H), $J_{HH} = 7.6$ Hz, $J_{HP} = 4.4$ Hz, 3.26 (q, OCH_2, 1H), $J = 6.8$ Hz, 2.27 (s, NH, 2H), 2.18 (s, Me, 6H), 2.154 (s, Me, 6H), 2.147 (s, Me, 6H), 1.11 (t, OCH_2CH_3, 1.5H). $^{31}P\{^1H\}$ NMR (C_6D_6, 161.9 MHz): 19.2 (s).). IR (CsI, Nujol): $\nu(NH) = 3436$ (m), $\nu(CH) = 3159$ (m), $\nu_{asym}(N_3) = 2163$ (st), 2144 (st), $\nu(P{=}O) = 1284$ (st), $\nu_{sym}(N_3) = 1243$ (st) cm^{-1}; tentative assignments.[16,17] MS (electrospray, CH_3CN solution): *m*/*z* 441.2 ($M + Na^+$), 419.2 ($M + H^+$).

$[NP(N_3)C_6H_3Mes_2\text{-}2,6]_2$ (8). The hexane washings of **7** were kept at room temperature under exclusion of light for 2 weeks, during which time large colorless crystals formed (0.048 g): mp changes color to deep red at 195−220 °C, melts with gas evolution at 330−340 °C. Anal. Calcd for $C_{48}H_{50}N_8P_2$: C, 71.98; H, 6.29; N, 13.99. Found: C, 72.11; H, 6.42; N, 13.92. Crystalline **8** is only sparingly soluble in C_6D_6. ^1H NMR (C_6D_6, 400 MHz): 6.98 (t, *p*-H, 2H), $J = 7.6$ Hz, 6.88 (s, *m*-H(Mes), 8H), 6.74 (dt, *m*-H, 4H), $J_{HH} = 7.6$ Hz, $J_{HP} = 2.4$ Hz, 2.40 (s, *p*-Me, 12H), 2.03 (s, *o*-Me, 24H). $^{31}P\{^1H\}$ NMR (C_6D_6, 161.9 MHz): 56.5 (s). IR (CsI, Nujol): $\nu(N_3) = 2136$ (st) cm^{-1}.

Table 1. Crystal Data and Structural Refinement Details for **2**, **4**·C_6H_{14}, and **8**

	2	**4**·C_6H_{14}	**8**
emp formula	$C_{26}H_{29}Cl_2P$	$C_{84}H_{101}N_{12}P_3$	$C_{48}H_{50}N_8P_2$
fw	443.36	1371.68	800.90
temp, K	173(2)	163(2)	173(2)
wavelength, Å	0.710 73	0.710 73	0.710 73
crystal system	triclinic	triclinic	monoclinic
space group	*P*-1	*P*-1	*P*2(1)/*n*
a, Å	11.9310(10)	11.4044(11)	10.874(3)
b, Å	12.135(2)	13.1141(15)	10.767(3)
c, Å	17.230(2)	27.954(3)	18.868(4)
α, deg	104.920(10)	99.744(8)	90
β, deg	96.180(10)	91.285(8)	101.555(12)
γ, deg	93.330(10)	102.586(8)	90
V, $Å^3$	2386.9(5)	4013.8(7)	2164.2(9)
Z	4	2	2
D_{calcd}, Mg/m^3	1.234	1.135	1.229
μ(Mo Kα), mm^{-1}	0.349	0.124	0.144
F(000)	936	1468	848
cryst size, mm^3	0.50 × 0.56 × 0.52	0.46 × 0.42 × 0.4	00.52 × 0.44 × 0.42
cryst color and habit	colorless plates	colorless plates	colorless plates
$2\Theta_{max}$, deg	25.00	24.99	24.99
no. of obsns	8255	13 998	3785
no. of variables	536	973	268
R1[a] $[I > 2\sigma(I)]$	0.0416	0.0626	0.0713
wR2[b] $[I > 2\sigma(I)]$	0.1040	0.1525	0.2015
GOF on F^2	1.029	1.020	1.028
largest diff. peak, e $Å^{-3}$	0.460	0.505	0.793

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR2 = (\Sigma w||F_o| - |F_c||^2/\Sigma w|F_o|^2)^{1/2}$.

Thermolysis of 6. A solution of **6** (0.02 g) in C_6D_6 (0.5 mL) in an NMR tube was placed into a preheated oil bath (70 °C). Gas evolution commenced after 1 min and stopped after an additional 2 min. Heating was continued for another 25 min. $^{31}P\{^1H\}$ NMR (C_6D_6, 161.9 MHz): 56.5 (s, **8**, 60%), 55.4 (s, 15%), 21.4 (s, 1%), 18.9 (d, 3%) $J_{PP} = 18.6$ Hz, 18.4 (s, 1%), 16.2 (d, 7%) $J_{PP} = 7.3$ Hz, 12.7 (d, 7%), $J_{PP} = 7.3$ Hz, 11.7 (d, 3%), $J_{PP} = 18.6$ Hz, −27.2 (s, 3%).

Photolysis of 6. A solution of **6** (0.017 g) in C_6D_6 (0.5 mL) in a quartz NMR tube was photolyzed at room temperature for 35 min using a high-pressure mercury lamp. $^{31}P\{^1H\}$ NMR (C_6D_6, 161.9 MHz): 111.0 (d, 6%) $J_{PP} = 26.6$ Hz, 64.0 (d, 10%), $J_{PP} = 93.0$ Hz, 56.5 (s, **8**, 24%), 52.7 (d, 10%), $J_{PP} = 93.0$ Hz, 18.8 (d, 4%), $J_{PP} = 17.5$ Hz, 17.9 (s, 9%), 16.2 (d, 11%), $J_{PP} = 7.3$ Hz, 12.7 (d, 11%), $J_{PP} = 7.3$ Hz, 11.7 (d, 4%), $J_{PP} = 17.5$ Hz, 3.9 (d, 6%), $J_{PP} = 26.6$ Hz, −6.3 (s, 5%).

X-ray Crystallography. Crystals were removed from the Schlenk tube under a stream of N_2 gas and immediately covered with a layer of hydrocarbon oil. A suitable crystal was selected, attached to a glass fiber, and immediately placed in the low-temperature nitrogen stream.[18] The data for **2**, **4**·C_6H_{14}, and **8** were collected at 173(2) or 163(2) K on a Siemens P4 diffractometer using Mo Kα (λ = 0.710 73 Å) radiation. The data were corrected for Lorentz and polarization effects. An absorption correction was not applied since it was judged to be insignificant. The structures were solved by direct methods and refined by full-matrix least-squares procedures on F^2 using all reflections. The crystallographic programs employed were those of the SHELXTL program suite, Vers. 5.03[19] for **2** and 5.1[20] for **4**·C_6H_{14}, and **8.** In the final refinement cycles of the structures of **2** and **8**, all the non-hydrogen

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(19) SHELXTL Version 5.03, Siemens Analytical X-ray Instrument Inc., 1994.

(20) SHELXTL Version 5.1, Bruker AXS, 1997.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for **2**

Cl(1)−P(1)	2.0612(9)	Cl(3)−P(2)	2.0619(9)
Cl(2)−P(1)	2.0723(9)	Cl(4)−P(2)	2.0753(9)
P(1)−C(16)	1.837(2)	P(2)−C(42)	1.833(2)
C(16)−P(1)−Cl(1)	101.93(7)	C(42)−P(2)−Cl(3)	103.44(7)
C(16)−P(1)−Cl(2)	104.53(7)	C(42)−P(2)−Cl(4)	103.48(7)
Cl(1)−P(1)−Cl(2)	100.11(4)	Cl(3)−P(2)−Cl(4)	99.68(4)
C(11)−C(16)−P(1)	111.4(2)	C(41)−C(42)−P(2)	128.2(2)
C(15)−C(16)−P(1)	128.2(2)	C(37)−C(42)−P(2)	111.59(14)
C(11)−C(16)−C(15)	118.9(2)	C(41)−C(42)−C(37)	119.2(2)

Table 3. Selected Bond Lengths (Å) and Angles (deg) for **4**

P(1)−N(3)	1.5840(19)	P(3)−N(2)	1.594(2)
P(1)−N(1)	1.588(2)	P(3)−N(10)	1.705(2)
P(1)−N(4)	1.700(2)	P(3)−C(68)	1.820(2)
P(1)−C(16)	1.810(2)	N(4)−N(5)	1.228(4)
P(2)−N(1)	1.587(2)	N(5)−N(6)	1.125(4)
P(2)−N(2)	1.588(2)	N(7)−N(8)	1.141(5)
P(2)−N(7)	1.712(2)	N(8)−N(9)	1.130(6)
P(2)−C(42)	1.808(2)	N(10)−N(11)	1.235(3)
P(3)−N(3)	1.586(2)	N(11)−N(12)	1.133(3)
N(3)−P(1)−N(1)	116.75(11)	N(10)−P(3)−C(68)	102.40(10)
N(4)−P(1)−C(16)	105.18(11)	N(5)−N(4)−P(1)	116.6(2)
P(2)−N(1)−P(1)	118.36(12)	N(6)−N(5)−N(4)	173.9(3)
N(1)−P(2)−N(2)	117.96(11)	N(8)−N(7)−P(2)	119.2(3)
N(7)−P(2)−C(42)	103.48(12)	N(9)−N(8)−N(7)	173.3(6)
P(2)−N(2)−P(3)	119.94(13)	N(11)−N(10)−P(3)	116.94(17)
N(3)−P(3)−N(2)	116.23(10)	N(12)−N(11)−N(10)	174.6(3)

Table 4. Selected Bond Lengths (Å) and Angles (deg) for **8**

P(1)−N(1)	1.639(3)	P(1)−C(15)	1.798(3)
P(1)−N(1A)	1.631(3)	N(2)−N(3)	1.226(4)
P(1)−N(2)	1.687(3)	N(3)−N(4)	1.121(5)
N(1)−P(1)−N(1A)	95.52(14)	N(2)−P(1)−C(15)	99.69(15)
N(1A)-P(1)−N(2)	114.18(17)	P(1A)−N(1)−P(1)	84.48(14)
N(1)−P(1)−N(2)	114.41(17)	N(3)−N(2)−P(1)	117.1(3)
N(1A)−P(1)−C(15)	117.23(15)	N(4)−N(3)−N(2)	174.2(4)
N(1)−P(1)−C(15)	116.88(15)		

atoms were refined anisotropically and all the hydrogen atoms were included in the refinement with idealized parameters. The structure of **4**·C_6H_{14} had several disorder problems. The azide group N(7)−N(9) was found in two orientations and the nitrogen atoms N(8), N(9) and N(8A), N(9A) were modeled using split occupancies of 0.60 and 0.40. Similarly, several *tert*-butyl groups (C(27)−C(29), C(49)−C(52), C(53)−C(55)) displayed rotational disorder and were modeled using split occupancies of 0.60 and 0.40. The cocrystallized hexane solvent molecule was found to be severely disordered and was also modeled using split occupancies of 0.60 and 0.40. All the non-hydrogen atoms were refined anisotropically except for C79 to C84 (atoms belonging to the disordered *n*-hexane solvent). For the disordered solvent, these atoms were refined isotropically in initial cycles of refinement and included in the final cycles of the refinement with fixed positional and thermal parameters. All hydrogen atoms were included with idealized parameters. Further details are provided in Tables 1-4 and the Supporting Information.

Results and Discussion

Starting Materials. Phosphonous azides $R_nP(N_3)_{3-n}$ (n = 1, 2) can be synthesized by the metathesis reaction of the appropriate R_nPCl_{3-n} with NaN_3 in a polar solvent such as acetonitrile (eq 2). An alternative approach involves the reaction of Me_3SiN_3 with phosphonous chlorides and subsequent Me_3SiCl elimination (eq 3).[5,8]

$$RPCl_2 + 2NaN_3 \rightarrow RP(N_3)_2 + 2NaCl \qquad (2)$$

$$RPCl_2 + 2Me_3SiN_3 \rightarrow RP(N_3)_2 + 2Me_3SiCl \qquad (3)$$

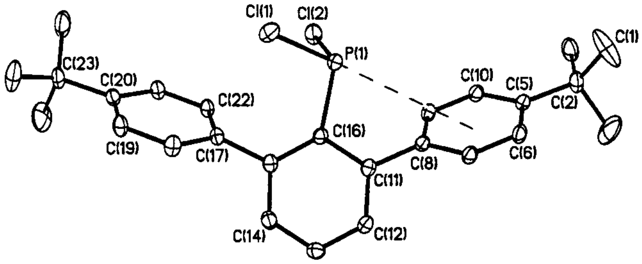

Figure 1. Thermal ellipsoid plot (30% probability ellipsoids) showing the molecular structure of one of the two independent molecules of **2**. H atoms are omitted for clarity.

As both methods require phosphonous chlorides as starting materials, we prepared three *m*-terphenyl phosphonous dichloride compounds, the new species 2,6-$(2\text{-}MeC_6H_4)_2C_6H_3PCl_2$ (**1**) and 2,6-(4-*t*-$BuC_6H_4)_2C_6H_3PCl_2$ (**2**) and the known 2,6-$Mes_2C_6H_3PCl_2$ (**3**),[11] by following standard literature procedures (eq 4).[21,22]

$$Ar^*Li + PCl_3 \xrightarrow[\text{hexanes}]{-78\ °C\ \text{to rt}} Ar^*PCl_2 + LiCl \qquad (4)$$

All three compounds are pale yellow to colorless crystalline solids and sensitive toward oxidation and hydrolysis upon exposure to air. Compounds **1** and **2** were characterized by ^1H, ^{13}C, and ^{31}P NMR spectroscopy and **2** also by X-ray crystallography (Figure 1). Interestingly, according to a search of the Cambridge Structural Database (CSD, Version 519)[23] **2** is only the second aryldichlorophosphane to be characterized by X-ray diffraction.[24]

Compounds **1**−**3** are readily identified by their characteristic ^{31}P NMR chemical shift around 158 ppm. Because of hindered rotation around the $C_{aryl}-C_{aryl}$ bonds of the unsymmetrical terphenyl substituent 2,6-$(2\text{-}MeC_6H_4)_2C_6H_3$ in **1**, two isomers, *syn* and *anti*, are observed for **1** in solution at room temperature, giving rise to two ^{31}P NMR resonances in a ca. 35:65 ratio.

Reactions with NaN_3. Stirring a solution of **2** in acetonitrile with excess NaN_3 for 1 h, followed by removal of the solvent and extraction with hexanes, afforded large colorless crystals of **4** in 26% yield. The FTIR spectrum of these crystals showed strong bands in the azide region (2151, 2142, 2127 cm^{-1}). However, the ^{31}P NMR spectrum displayed two signals, a doublet and triplet at 15.3 and 13.5 ppm in a 2:1 ratio with a J_{PP} coupling constant of 21.7 Hz, indicating that **4** was not the bisazidophosphane 2,6-(4-*t*-$BuC_6H_4)_2C_6H_3P(N_3)_2$ (**5**), for which a singlet at about 130 ppm was expected.[5] The structure of **4** was then determined by Xray crystallography and shown to be the rare *trans*-trisazidocyclotriphosphazene, $[NP(N_3)(C_6H_3(4\text{-}t\text{-}BuC_6H_4)_2\text{-}2,6)]_3$ (Figures 2 and 3). There are only a few polyazidocyclotriphosphazenes described in the literature, $[NP(N_3)_2]_3$,[14] $[NP(N_3)Cl]_3$,[25] $[NP(N_3)(OC_6H_5)]_3$, and $[NP(N_3)(NEt_2)]_3$,[9] and **4** (*vide infra*) is the first to be characterized by X-ray crystallography.

Interestingly, when the phosphonous dichloride compounds **1** and **3** were reacted with NaN_3 under the same conditions as those used for **2**, no crystalline product was obtained. ^1H and ^{31}P NMR spectra of the crude products showed the formation of a number of products. On the basis of the chemical shift of the ^{31}P NMR resonances (in the 20 to −10 ppm range) and the presence of strong bands in the azide region of the IR spectra

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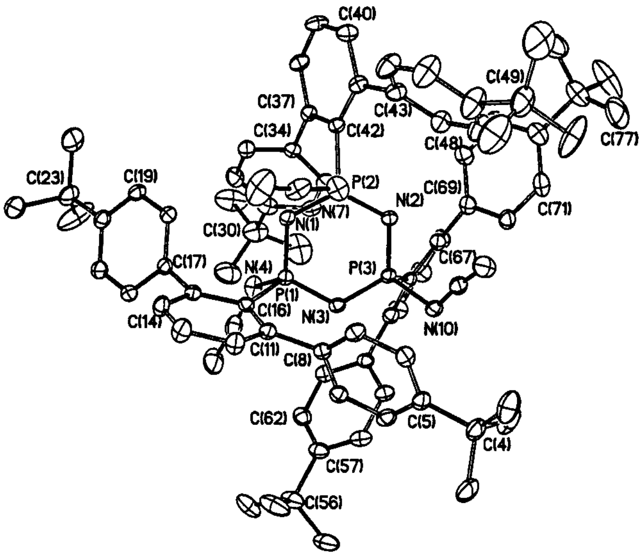

Figure 2. Thermal ellipsoid plot (30% probability ellipsoids) showing the molecular structure of **4**. H atoms are omitted for clarity.

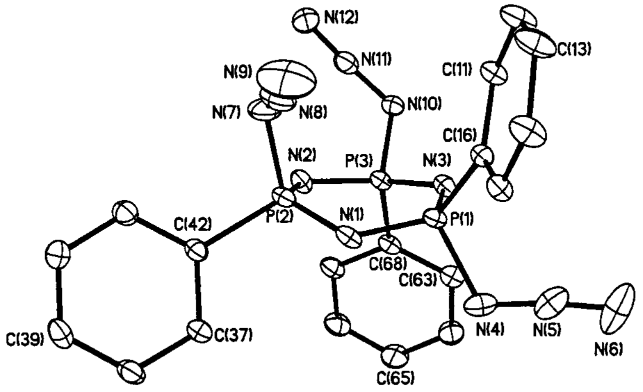

Figure 3. Thermal ellipsoid plot (30% probability ellipsoids) showing the $[C_6H_3P(N_3)N]_3$ core of **4**. H atoms are omitted for clarity.

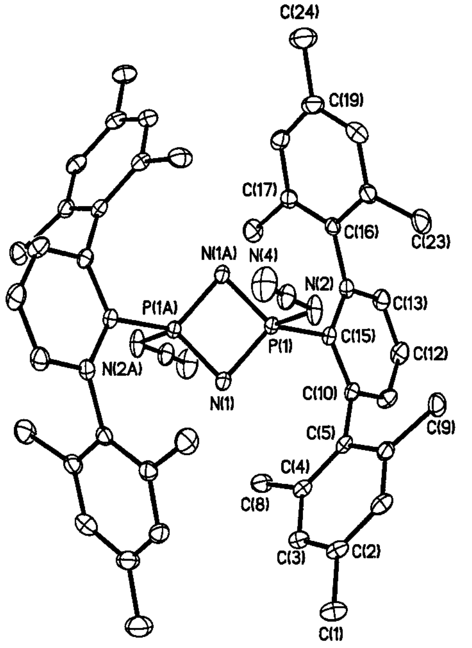

Figure 4. Thermal ellipsoid plot (30% probability ellipsoids) showing the molecular structure of **8**. H atoms are omitted for clarity.

(ca. 2150 cm^{-1}), these compounds were tentatively identified as mixtures of azide-substituted phosphazenes $[ArP(N)_3N]_n$.

A ^{31}P NMR experiment of the reaction of **3** with NaN_3 in C_6D_6/CD_3CN showed the formation of the bisazide 2,6-$Mes_2C_6H_3P(N_3)_2$ (**6**) after 1 h at room temperature ($\delta_P = 129.8$ ppm). Encouraged, we repeated this reaction on a larger scale with careful exclusion of light and a reaction time of only 2 h (method B). During workup, the crude product was kept at 0 °C and then stored at −30 °C. The resulting sticky solid was shown by NMR spectroscopy to consist of roughly 63% **6**.[26] We were also able to isolate the bisazide 2,6-(4-*t*-$BuC_6H_4)_2C_6H_3P(N_3)_2$ (**5**) ($\delta_P = 133.5$ ppm) under similar conditions, albeit in only 36% purity. Both **5** and **6** are stable in the solid state at −30 °C for at least 1 month, where as they decompose in C_6D_6 solution within 24 h at room temperature.

The crude sticky solid from the reaction of **3** with NaN_3 (method B) contained a few very thin colorless plates, which could be isolated by removal of **6** and other side products with cold hexanes. ^1H and ^{31}P NMR and FTIR spectroscopic data and an electrospray mass spectrum are in agreement with the formulation 2,6-$Mes_2C_6H_3P(O)(N_3)(NH_2)$ (**7**). The hexane washings were kept at room temperature under exclusion of light for 2 weeks, during which time large (1−2 mm) colorless plates deposited. These crystals were identified as the dimeric azidophosphazene $[NP(N_3)(C_6H_3Mes_2\text{-}2,6)]_2$ (**8**) by X-ray crystallography (Figure 4). It is worth mentioning that cyclodiphosphazenes are also rare: only one compound of this type has been characterized by X-ray crystallography,[27] and it has been suggested that bulky substituents favor the formation of cyclodiphosphazenes versus cyclotriphosphazenes and higher oligomers.[8,28]

Structure Descriptions. (a) Structure of 2. The dichlorophosphane **2** crystallizes in the triclinic space group *P*-1 with two independent molecules in the asymmetric unit. There are no significant differences between the structures of both molecules (Table 2). The geometry at the phosphorus atom is clearly pyramidal ($\sum$(angles) = 306.5(2)° (molecule 1), 306.6(2)° (molecule 2)). The P−Cl distances with values of 2.0612(9), 20619(9), 2.0723(9), and 2.0753(9) Å are within the range observed for other dichlorophosphanes such as $(Me_2PhSi)_3CPCl_2$[29] and Ph_3CPCl_2[30] with average P−Cl distances of 2.089 and 2.061 Å, respectively. Similarly, the P−C distances with values of 1.837(2) and 1.833(2) Å are consistent with those found for other terphenyl-substituted phosphines such as 2,6-$Mes_2C_6H_3P(O)(OH)H$ (1.812(2) Å) or $(2,6\text{-}Mes_2C_6H_3P)_2$ (1.842(3) Å).[11]

A quite interesting feature is found in the different $C_{ortho}-C_{ipso}-P$ angles with values of 111.4(2) and 128.2(2)° (111.6(2) and 128.2(2)°, molecule 2) leading to weak interactions of the phosphorus with one of the ortho aromatic rings. The distance from the phosphorus to the centroid of the C(5)−C(10) ring is 3.821 Å (P(2)···centroid (C(31)−C(36)) = 3.863 Å). This so-called Menshutkin interaction[31] was observed originally for complexes of antimony or bismuth halides with aromatic

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[26] Professor Protasiewicz informed us that his group had also synthesized 2,6-$Mes_2C_6H_3P(N_3)_2$ (**6**) using the same method. C_6D_6 solutions of the crude product decomposed within a few hours. Shah, S.; Protasiewicz, J. D. Personal communication, 2000.

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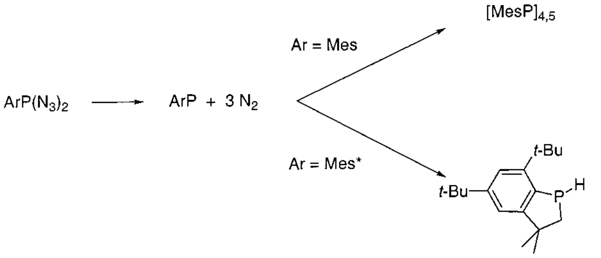
compounds, but it now appears to be a common feature of terphenyl-substituted group 15 dihalides[3] or group 14 monohalides.[32]

(b) Structure of 4. As is typical for cyclotriphosphazenes,[33] the central P−N six-membered ring is slightly puckered and adopts a boat conformation. The essentially equidistant P−N bond lengths (Table 3) fall in the narrow range of 1.584(2)−1.594(2) Å. The endocyclic N−P−N and P−N−P angles average 117.0 and 120.3°, respectively. Each phosphorus is also bound to one terphenyl and one azide substituent in a trans arrangement that has two of the terphenyl substituents above and one below the P_3N_3 plane, presumably to minimize the steric interactions between the bulky terphenyl groups. Despite the steric crowding, the average P−C bond distance with 1.813 Å is only slightly elongated compared to those in $[NPPh_2]_3$[34] or 2,2-$N_3P_3Ph_4Me_2$[35] with values of 1.804 or 1.807 Å. Similarly, the P−N(azide) distances (1.706 Å average) are practically unaffected (see P−N(azide) = 1.711(6) Å in $Me_2(S)PN_3$, the only other λ^4,σ^5-phosphorus azide, for which crystallographic information is available[36]). The P−N−N angles average 117.7° and the azide units are almost linear with N−N−N angles of 173.3(6)−174.6(3)°.

(c) Structure of 8. The centrosymmetric molecules of **8** feature an almost square-planar P_2N_2 core with a trans arrangement of the substituents. The P−N bond distances are 1.639(3) and 1.631(3) Å and the internal P−N−P and N−P−N angles are 84.48(14) and 95.52(14)°, respectively. Compared to **4**, the internal P−N bond distances are longer by 0.04 Å, whereas the exocyclic P−C and P−N(azide) distances are shorter with values of 1.781(3) and 1.669(2) Å. The exocyclic C−P−N angle is also quite small, 99.76(12)°, giving rise to a distorted tetrahedral environment at the phosphorus. A similar core geometry was also observed for the cyclodiphosphazene $[NP(N\textit{i}\text{-}Pr_2)_2]_2$ with P−N−P and N−P−N angles of 85.0(5) and 95.0(5)° and P−N bond distances of 1.651(8) and 1.648(8) Å.[27] The almost linear azide substituents (N−N−N = 174.4(3)°) are rotated away from the neighboring terphenyl substituent by 180° and are positioned above (or below) the phosphorus atom to which they are bound. Interestingly, the N(2)N(3)P(1)C(15) torsion angle is 177.5(3)°.

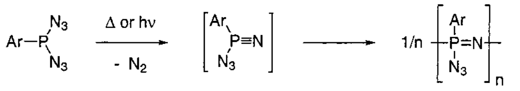
Thermolysis and Photolysis of 6. Thermolysis or photolysis of trivalent phosphorus monoazides, R_2PN_3, has been investigated by a number of groups as a synthetic route to a variety of phosphazenes, $[R_2PN]_n$.[8] The synthesis and investigation of phosphorus bisazides, however, is limited to one report by Cowley et al.[5] which describes the synthesis of three aryl-substituted phosphorus bisazides, $PhP(N_3)_2$, $MesP(N_3)_2$ (Mes = 2,4,6-$Me_3C_6H_2$), and Mes*$P(N_3)_2$ (Mes* = 2,4,6-t-$Bu_3C_6H_2$). Of these three compounds, only the latter is thermally stable, whereas the former two compounds decompose at room temperature. The decomposition products were not investigated further. Nevertheless, photolysis of $MesP(N_3)_2$ or Mes*$P(N_3)_2$ led to $[MesP]_{4,5}$ or the phosphaindane 4,6-t-$Bu_2C_6H_2$-2-CMe_2CH_2PH, respectively, which was viewed as being consistent with the formation of a transient phosphanediyl ArP (eq 5).



(5)

Interestingly, the terphenyl-substituted bisazidophosphanes **5** and **6** described here are only marginally stable in solution at room temperature and decompose into a series of presumably azide-substituted phosphazenes. The crystalline species **4** and **8** have been isolated from these mixtures. Furthermore, rapid heating of a C_6D_6 solution of crude **6** to 70 °C resulted in gas evolution and the almost exclusive formation of **8** within a few minutes. Assuming that the thermal stability of Cowley's Mes*$P(N_3)_2$ is due to steric effects, we were surprised about the comparably low stability of **5** and **6**, both of which feature large terphenyl substituents. However, a similarly clear difference between the steric protection offered by the Mes* and the terphenyl substituents 2,6-$Mes_2C_6H_3$- and 2,6-$Trip_2C_6H_3$- was recognized for primary alanes.[37]

Photolysis of C_6D_6 solutions of crude **6** at room temperature led to a product mixture whose ^{31}P NMR spectrum was very similar to that of a 1 day old solution of **6**, which had been kept at room temperature under exclusion of light. In addition, this mixture contains the cyclodiphosphazene **8** with ca. 30% of the P-containing compounds. No evidence for the formation of a phosphanediyl was obtained. Instead, it may be speculated that the bulky m-terphenyl-substituted bisazidophosphanes react in a manner similar to azidophosphanes with small substituents and rearrange via reactive phosphonitrile intermediates (eq 6).[8]



(6)

Ar = 2,6-(4-t-$BuC_6H_4)_2C_6H_3$; n = 3, **4**

Ar = 2,6-$Mes_2C_6H_3$; n = 2, **8**

Summary

m-Terphenyl-substituted dichlorophosphanes can be transformed into bisazidophosphanes $ArP(N_3)_2$ by reaction with NaN_3 in acetonitrile at room temperature. These bisazidophosphanes are thermally labile and, when in solution, decompose into a variety of azidophosphazenes at room temperature within a day. From hexane solutions of the bisazidophosphanes **5** and **6**, the rare, crystalline azidocyclophosphazenes **4** and **8** have been isolated and completely characterized. The mechanism of the azidophosphazene formation is unclear and is currently under investigation. Preliminary thermolysis and photolysis reactions of **6** indicate that **6**, unlike Mes*$P(N_3)_2$, does not decompose under formation of the phosphanediyl 2,6-$Mes_2C_6H_3P$ but rather via a possible 2,6-$Mes_2C_6H_3(N_3)PN$ intermediate to afford phosphazenes. Finally, it should be pointed out that the thermal decomposition of m-terphenyl-substituted bisazidophosphanes provides an easy access to azide-substituted cyclophosphazenes, a class of compounds that is currently of interest as cross-linking or branching agents for organic polymers.[10]

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Supporting Information Available: Three X-ray crystallographic files in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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