Reaction of Dihydrodiazaphosphinines with Acetylenic Diesters: A Direct Synthesis of the λ^5-Diazaphosphaazulene Skeleton

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1,2-Dihydro-1,3,2-diazaphosphinine **2** reacts with acetylenedicarboxylic acid esters to give chemoselectively the adducts **5** or **6a**, **b**, depending on the reaction conditions. Compound **6a** is alternatively synthesized by treatment of equimolecular amounts of the previously described monoadduct **3**(**3′**) and dimethyl acetylenedicarboxylate. A reaction pathway is proposed based primarily on i) the isolation and characterization of intermediate **8**(**8′**) and ii) the reactivity of **3**(**3′**) towards electrophiles, in particular with tetracyanoethylene (compound **10**).

Introduction

A few years ago we reported the synthesis of 1,2-dihydro-1,3,2-diazasilines and -germines and their potential as valuable precursors for 1,4-diazepine derivatives[1]. At that moment we became intrigued by the particular behaviour of trivalent phosphorus-containing substrates in heterocycloaddition processes where the phosphanyl substituent can act as a reactive peripherial functional group in cycloaddition reactions. For instance, it has been shown that *N*-phosphanyl imines[2] and *N*- and *C*-phosphanyl 1,3-dipoles[3] behave as 1,3- and 1,4-dipoles, respectively, leading to five- and six-membered rings.

Accordingly, we studied next the behaviour of the related 1,2-dihydro-1,3,2-diazaphosphinines **2**, readily available from 4-amino-1-azadienes **1** and dichloro(diisopropylamino)phosphane, and found that they displayed an interesting reactivity pattern towards dimethyl acetylenedicarboxylate (DMAD) (Scheme 1)[4]. Thus, heterocycles **2** reacted with DMAD in stoichiometric amounts to furnish the complex heteropolycyclic structure **3(3′)**. Moreover, this adduct was protonated and methylated through the valence isomer **3′** affording **4a**, **b** by treatment with difluorochloroacetic acid and methyl iodide, respectively. At this point we thought about the possibility that a second equivalent of DMAD would act as electrophile. The complex zwitterionic species formed in this case could delineate new stabilization pathways leading eventually to novel structures.

Therefore, reported herein is the formation of λ^5-diazaphosphaazulene derivatives either by reaction of **2** with 2 equivalents of dimethyl and diethyl acetylenedicarboxylate or by treatment of **3(3′)** with an additional equivalent of DMAD.

Results and Discussion

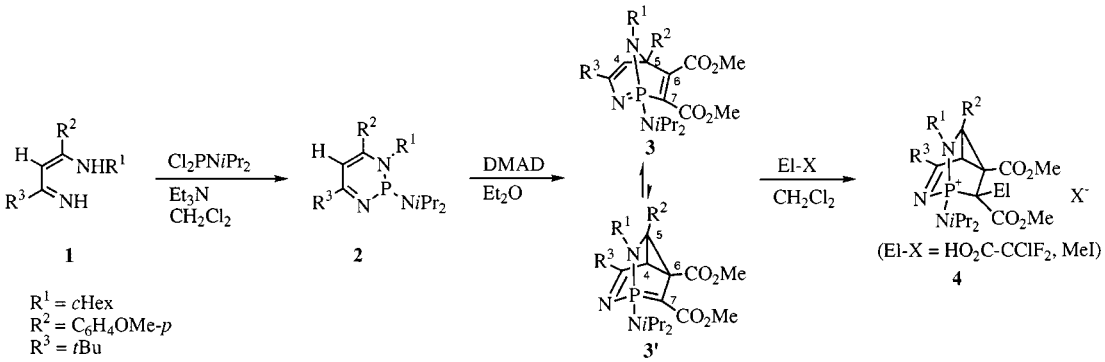
First, 1,2-dihydro-1,3,2-diazaphosphinine **2** was formed by condensation of the corresponding 4-amino-1-azadiene **1** with dichloro(diisopropylamino)phosphane following a previously described procedure[5]. Then a solution of **2** in ether was stirred with excess of dimethyl acetylenedicarboxylate (DMAD) (molar ratio 1:3; −20°C to room temperature) at −20°C for 12 h; removal of the solvent followed by flash column chromatography and crystallization from methylene chloride/hexane allowed to isolate the 1:2 adduct **5** as the major reaction product (yield 70%; ^{31}P NMR: δ = 36.2) (Scheme 2).

This result is in accordance with the reaction of triphenylphosphane with DMAD described by Tebby in 1969 though the resulting adduct was never characterized crystalographically[6]. Therefore, crystals of the λ^5-diazaphosphinine derivative **5** were grown from diethyl ether/hexane and an X-ray determination performed[7].

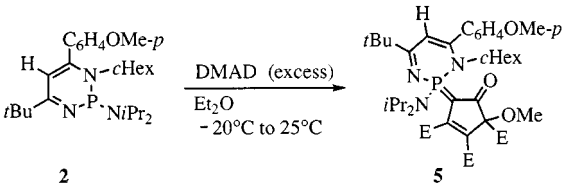
Since the structure **5** unexpectedly does not arise from the 1:1 adduct **3(3′)** we turned our attention to the reaction conditions. To our delight, we found that treatment at −20°C of a diluted solution (*c* ca. 0.05 M) of diazaphosphinine **2** with dimethyl and diethyl acetylenedicarboxylate (molar ratio 1:2.4) in diethyl ether for 72 h and slowly rising the temperature from −20°C to room temperature resulted in the formation of a reaction product different from **5**, namely λ^5-dihydrodiazaphosphaazulene derivative **6** (**6a**: E=CO_2Me, ^{31}P NMR: δ = 36.8; **6b**: E=CO_2Et, ^{31}P NMR: δ = 36.2), in yields of 89% (**6a**) and 85% (**6b**) of isolated compounds (Scheme 3). It could be confirmed that **3(3′)** was actually an intermediate in the process by treating it with DMAD (molar ratio 1:1.1) under the same reaction

  1434−193X/98/0707−1425 $ 17.50+.50/0

Scheme 1. Formation of heterocycles **3** by [5+2] Cycloaddition of diazaphosphinines **2** with dimethyl acetylenedicarboxylate and their reaction with electrophiles

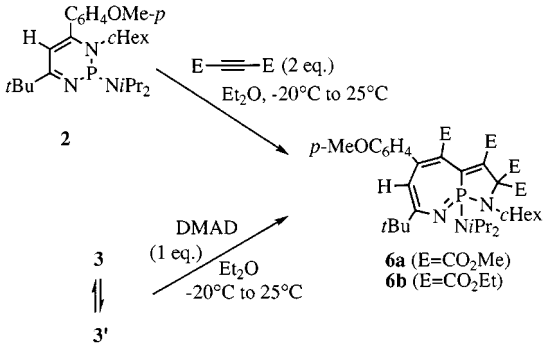


Scheme 2. Formation of diazaphosphinine derivative **5** from **2** and dimethyl acetylenedicarboxylate



conditions leading cleanly to compound **6a**. This compound exhibited an extraordinary thermal stability and could be heated up to 300°C in air without appreciable alteration. In addition, the yluric charge is well stabilized as no protonation took place with weak acids (e.g. acetic acid).

Scheme 3. Formation of diazaphosphaazulene derivatives **6** from **2** or **3** and acetylenedicarboxylic acid esters

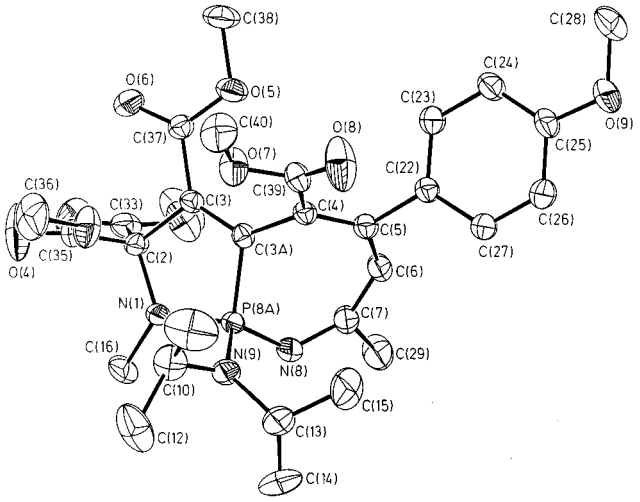


Because of the profound structural changes that had occurred in this transformation and of the unique phosphorus-containing bicyclic framework, good quality crystals of **6a** were obtained from diethyl ether/THF and its structure unambiguously confirmed by an X-ray analysis (Figure 1)[8].

The bicyclic system is not flat but consists of two planar subsystems. The first plane is formed by the phosphorus atom, N8, C7, C6, and C5 while the second is formed by phosphorus, N1, C2, C3, C3A, and C4.

Endocyclic double- and single bonds are enlarged respectively shortened by mesomeric effects, especially in the seven-membered ring moiety. Anyhow they still can be

Figure 1. Crystal structure of **6a**[a]

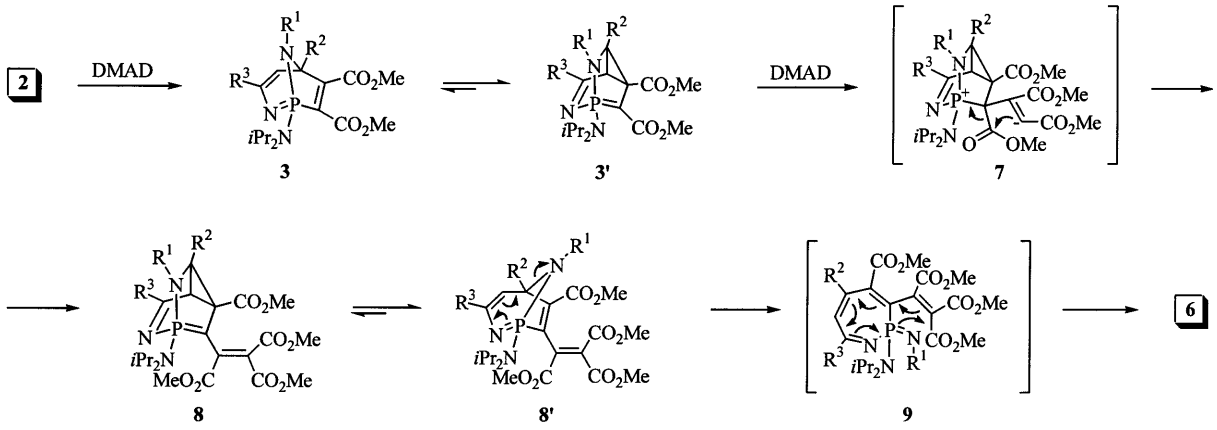


[a] Selected bond lengths [pm] and bond angles [°]: N1−C2: 148.0(3); N1−P8a: 165.7(2); P8a−N8: 156.1(3); P8a−N9: 163.6(3); P8a−C3a: 178.1(3); N8−C7: 134.6(4); C2−C3: 152.9(4); C3−C3a: 134.0(4); C3a−C4: 147.0(4); C4−C5: 136.6(4); C5−C6: 143.5(4); C6−C7: 137.3(4); C2−N1−P8a: 113.8(2); N8−P8a−N1: 117.5(2); N8−P8a−C3a: 110.9(1); N1−P8a−C3a: 94.6(1); C7−N8−P8a: 129.8(2); N1−C2−C3: 105.7(2); C3a−C3−C2: 116.1(2); C3−C3a−C4: 131.7(3); C3−C3a−P8a: 109.5(2); C4−C3a−P8a: 118.6(2); C5−C4−C3a: 120.5(2); C4−C5−C6: 127.8(3); C7−C6−C5: 133.2(3); N8−C7−C6: 128.1(3).

found in concordance with the structural formula. All other geometric parameters are in the range of expectation.

Concerning the mechanism involved in this complex transformation, we propose a reaction pathway which accounts for the skeletal rearrangement and the [1,3]-CO_2Me shift (Scheme 4). First, nucleophilic attack of the yluric valence isomer **3′** onto the activated carbon-carbon triple bond would lead to the zwitterionic intermediate **7**. Intramolecular nucleophilic attack from the alkenyl carbanion onto the ester function followed by a retroaldol-type carbon−carbon bond cleavage would afford the intermediate **8** in equilibrium with its valence isomer **8′**. Finally, the retro-Michael reaction of **8′** leading to **9** followed by a formal anionic [1,10]-electrocyclic ring closure can be invoked to rationalize the last step of the reaction sequence.

Scheme 4. Mechanistic proposal for the formation of diazaphosphaazulene derivatives **6**

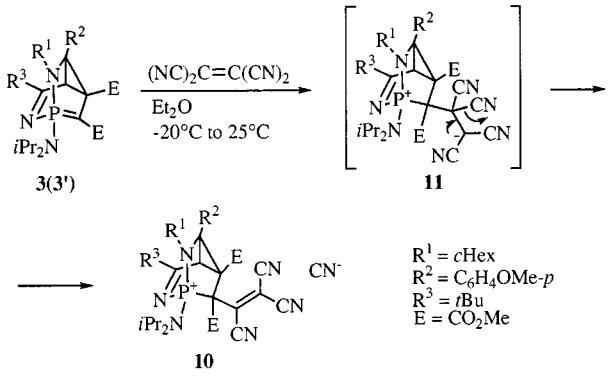


Great mechanistic support stems from the isolation and spectroscopic characterization of intermediate **8(8′)** (see Experimental Section). Thus, its ^{13}C- and ^{31}P-NMR spectra perfectly match those of the analogous precursor **3(3′)**. For instance, the ^{13}C-NMR resonances of the seven-membered ring carbon atoms of **8(8′)** are found at δ = 164.3, 142.1, 112.2, 87.0, and 62.2 [for **3(3′)**: δ = 167.1, 137.5, 96.5, 84.6, and 67.2] and the ^{31}P-NMR signal of **8(8′)** appears at δ = 44.1 [for **3(3′)**: 48.2]. Left at room temperature in solution **8(8′)** disappears within 12 h yielding **6** as the only product according to NMR spectroscopy. The ring-opening of **8(8′)** leading to **9** has precedent in the room temperature rearrangement of bicyclo[3,2,1]-1-phospha-2,8-diaza-1,3,6-octatriene **3(3′)** into its isomer bicyclo[3,2,1]-1-phospha-7,8-diaza-1,3,6-octatriene[4].

Moreover, support of the first step could be obtained by using an appropriate substrate, instead of DMAD, so as the first non-isolated intermediate could be stabilized, and therefore isolable, without framework disruption. To verify this hypotesis TCNE was chosen and found that its reaction with **3(3′)** (molar ratio 1:1.05) in diethyl ether (−20°C to room temperature) led exclusively to the phosphonium cyanide salt **10** (Scheme 5). The formation of such a compound should imply again an initial nucleophilic attack to form **11**, which is analogous to **7**, followed by cyanide displacement to give the final adduct.

In summary, it is shown that the readily available 1,2-dihydro-1,3,2-diazaphosphinines **2** are excellent precursors for the efficient synthesis of novel phosphorus heterocycles which can be seen as heteroanalogues of biologically important systems by reaction with acetylenedicarboxylic acid esters. The reaction involves a complex mechanism and unconventional intermediate structures. A mechanistic proposal based on the reactivity of the monoadduct **3(3′)** and on the characterization of intermediate **8(8′)** is outlined. It should be pointed out that ester migrations are seemingly rare processes, particularly the present [1,3]-shift that occurs below room temperature and that has no precedent in the literature to the best of our knowledge. In this context, Bertrand and co-workers have noted a [1,2]-CO_2Me shift at 80°C and have rationalized it by a similar pathway[2b].

Scheme 5. Formation of phosphonium salt **10** from **3** and tetracyanoethylene



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Experimental Section

General: All reactions were carried out under nitrogen. Solvents were purified by standard methods[9]. Chemicals were of reagent grade. Compounds **1** were prepared according to the literature reports[10]. − Flash column chromatography was carried out on silica gel 60 (230−400 mesh). − Melting points were obtained on a Büchi-Tottoli apparatus using open capillary tubes and are uncorrected. − NMR spectra were run in $CDCl_3$ on Bruker AC 200 and AC300 spectrometers. − Mass spectra were determined on HP 5987A (EIMS) spectrometer.

Synthesis of λ^5-Diazaphosphinine **5**: To a well stirred solution of diazadihydrophosphinine **2** (0.57 g, 1.3 mmol) in 10 ml of CH_2Cl_2 at −20°C was added a solution of DMAD (0.84 g, 6 mmol) in 5 ml of CH_2Cl_2. The mixture was slowly warmed to room temperature and the solvent and excess of ester removed under reduced pressure. The residue was subjected to flash chromatography (SiO_2; eluent: CH_2Cl_2 and then CH_2Cl_2/ether) to afford **5** (0.64 g, 70%),

yellow crystals, m.p. 240°C (dec.). − IR: $\tilde{\nu}_{max}$ = 1766 cm^{-1}, 1751, 1689, 1631, 1605, 1548, 1492, 1344, 1255, 1236, 1207, 1176, 1159, 1120, 1103, 1012, 852, 831, 821. − ^{31}P NMR: δ = 36.2. − ^{1}H NMR: δ = 7.5 (b, 2 H), 6.9 (m, 2 H), 6.2 (s, 1 H), 3.8−3.3 (m, 14 H, 4 H), 3.0 (s, 3 H), 2.5 (m, 1 H), 1.4−1.1 (m, 31 H). − ^{13}C NMR: δ = 194.2 [d, ^{3}J(P,C) = 7.6 Hz, CN], 192.0 [d, ^{2}J(P,C) = 7.6 Hz, *C*C_{ar}], 168.3 (s), 166.2 (s), 162.2 [d, *J*(P,C) < 2 Hz, CO], 161.1 (s, $C_{ar}O$), 160.4 [d, *J*(P,C) = 20.1 Hz, CO], 158.5 [d, *J*(P,C) = 4.2 Hz, CO], 132.0 (b, CH_{ar}), 128.8 [d, ^{2}J(P,C) = 6.2 Hz], 113.8 [d, ^{3}J(P,C) = 29.1 Hz, CH], 113.0 (s, CH_{ar}), 104.5 [d, ^{3}J(P,C) = 13.2 Hz, C(CO_2CH_3)=*C*-CO_2CH_3], 86.6 [d, ^{3}J(P,C) = 14.6 Hz, *C*-OCH_3], 78.4 [d, ^{1}J(P,C) = 174.1 Hz, PC], 59.0 (s, CH), 55.0 (s, OCH_3), 52.1 (s, OCH_3), 51.9 (s, OCH_3), 51.5 (s, OCH_3), 50.6 (s, OCH_3), 48.5 [d, ^{2}J(P,C) = 6.2 Hz, CH], 40.4 [d, ^{3}J(P,C) = 20.1 Hz, *C*(CH_3)$_3$], 34.7 (s, CH_2), 33.0 (s, CH_2), 28.0 (s, CH_3), 26.4 (s, CH_2), 24.7 (s, CH_2), 23.2 (s, CH_2), 22.1 [d, ^{3}J(P,C) = 2.1 Hz, CH_3]. − MS (EI, 70 eV); *m*/*z*: 727 [M^+]; 644 [$M^+ - C_6H_{11}$].

Synthesis of λ^5*-Diazaphosphaazulene* **6a**. − *Method A:* To a well stirred solution of 2.2 g (5 mmol) of diazadihydrophosphinine **2** in 10 ml CH_2Cl_2 at −20°C were added 1.7 g (12 mmol) of dimethyl acetylenedicarboxylate (DMAD) in 5 ml of CH_2Cl_2. The mixture was left overnight allowing it to reach slowly room temperature. Then it was left for an additional two days at room temperature, the solution filtered through SiO_2 and the solvent evaporated. Crystallization from ether/CH_2Cl_2 afforded 3.1 g of **6a**: 3.1 g (89%). − *Method B:* Compound **3(3′)** (1.5 g, 2.5 mmol) was dissolved at −20°C in 15 ml of CH_2Cl_2 and 0.38 g (2.7 mmol) of DMAD in 5 ml of CH_2Cl_2 were added. The mixture was stirred overnight and allowed to warm slowly to room temperature. After filtration through SiO_2, the product was crystallized in CH_2Cl_2 and the solvent evaporated to furnish 1.7 g of **6a** (90%), red crystals, m.p. 235°C. − IR ν_{max}: 1784 cm^{-1}, 1765, 1767, 1729, 1703, 1605, 1506, 1478, 1407, 1243, 1175, 1120, 1040, 803. − ^{31}P NMR: δ = 36.8. − ^{1}H NMR: δ = 7.2−7.1 (m, 2 H); 6.9−6.8 (m, 2 H); 5.1 (m, 1 H); 4.0−3.5 (m, 3 H); 3.8 (s, 3 H); 3.8 (s, 3 H); 3.7 (2s, 6 H); 3.3 (s, 3 H); 2.2−0.9 (m, 25 H). − ^{13}C NMR: δ = 172.5 [d, ^{3}J(P,C) = 2.8 Hz, *C*O_2CH_3]; 167.5 [d, ^{3}J(P,C) = 3.5 Hz, *C*O_2CH_3]; 167.3 [d, ^{3}J(P,C) = 3.5 Hz, *C*O_2CH_3]; 164.0 [d, ^{2}J(P,C) = 20.1 Hz, CN]; 158.2 (s, $C_{ar}O$); 154.8 (s, *C*C_{ar}); 139.2 (s, C*C*$_{ar}$); 134.5 [d, ^{1}J(P,C) = 96.4 Hz, PC]; 128.4 (s, CH_{ar}); 126.1 [d, ^{2}J(P,C) = 22.8 Hz, PC*C*]; 112.8 (s, CH_{ar}); 104.7 [d, ^{2}J(P,C) = 11.8 Hz, PC*C*]; 104.0 [d, ^{3}J(P,C) = 5.5 Hz; CH]; 73.1 [d, ^{2}J(P,C) = 22.2 Hz, *C*(CO_2CH_3)$_2$]; 56.7 [d, ^{2}J(P,C) = 2.1 Hz, CN]; 54.9 (s, ArO*C*H_3); 52.8 (s, OCH_3); 52.7 (s, OCH_3); 51.8 (s, OCH_3); 50.5 (s, OCH_3); 46.9 [b, *C*H(CH_3)$_2$]; 40.5 [d, ^{2}J(P,C) = 22.2 Hz, *C*(CH_3)$_3$]; 32.9 (s, CH_2); 30.8 (s, CH_2); 30.2 (s, CH_3); 26.9 (s, CH_2); 26.4 (s, CH_2); 25.2 (s, CH_2); 23.1 (s, CH_3). − MS (EI, 70 eV); *m*/*z*: 727 [M^+], 685 [$M^+ - C_3H_7$], 668 [$M^+ - CO_2CH_3$]. − $C_{38}H_{54}N_3O_9P$ (727.8): calcd. C 62.71, H 7.48, N 5.77; found C 62.55, H 7.28, N 5.69.

Synthesis of λ^5*-Diazaphosphaazulene* **6b**. − *Method A:* The above procedure was followed using 2.2 g (5 mmol) of diazadihydrophosphinine **2** and 2.0 g (12 mmol) of diethyl acetylenedicarboxylate. Yield 3.2 g (85%), red oil. − ^{31}P NMR: δ = 36.2. − ^{1}H NMR: δ = 7.1 [d, 2 H, *J*(H,H) = 8.9 Hz]; 6.8 [d, 2 H, *J*(H,H) = 8.9 Hz]; 5.1 [d, 1 H, ^{4}J(P,H) = 1.9 Hz]; 4.3−3.4 (m, 11 H); 3.77 (s, 3 H); 2.1−0.9 (m, 37 H). − ^{13}C NMR: δ = 172.0 [d, ^{3}J(P,C) < 2.5 Hz, *C*$O_2C_2H_5$]; 167.0 [d, ^{3}J(P,C) = 3.1 Hz, *C*$O_2C_2H_5$]; 166.8 [d, ^{3}J(P,C) = 3.1 Hz, *C*$O_2C_2H_5$]; 165.7 [d, ^{3}J(P,C) = 9.4 Hz, *C*$O_2C_2H_5$]; 163.7 [d, ^{2}J(P,C) = 20.3 Hz, CN]; 158.1 (s, $C_{ar}O$); 154.9 (s, *C*C_{ar}); 139.6 (s, C_{ar}); 133.4 [d, ^{1}J(P,C) = 96.3 Hz, PC]; 128.4 (s, CH_{ar}); 112.6 (s, CH_{ar}); 104.9 [d, ^{3}J(P,C) = 11.0 Hz, PC*C*]; 103.8 [d, ^{3}J(P,C) = 5.3 Hz, CH]; 74.5 [d, ^{2}J(P,C) = 21.9 Hz, *C*($CO_2C_2H_5$)$_2$]; 61.8 (s, CH_2); 61.8 (s, CH_2); 60.6 (s, CH_2); 59.1 (s, CH_2); 57.1 (s, CH); 54.9 (s, OCH_3); 46.8 [b, *C*H(CH_3)$_2$]; 40.4 [d, ^{3}J(P,C) = 21.9 Hz, C(CH_3)$_3$]; 33.1 (s, CH_3); 31.5 (b, CH_2); 30.2 (s, CH_3); 27.0 (s, CH_2); 26.4 (s, CH_2); 25.3 (s, CH_3); 23.2 (s, CH_3); 13.9 (s, CH_3); 13.7 (s, CH_3). − MS (EI, 70 eV); *m*/*z*: 783 [M^+]; 740 [$M^+ - C_3H_7$]; 710 [$M^+ - CO_2C_2H_5$]. − $C_{42}H_{62}N_3O_9P$ (783.9): calcd. C 64.35, H 7.97, N 5.36; found C 63.95, H 7.93, N 5.09.

Intermediate **8(8′)**: To a well stirred mixture of 0.4 g (0.68 mmol) of **3(3′)** in 10 ml of CH_2Cl_2 were added 0.1 g (0.8 mmol) of DMAD in 10 ml of CH_2Cl_2 at −70°C. Then the mixture was left overnight allowing it to warm up to −20°C. It was rapidly concentrated to 3−4 ml at reduced pressure between −20 and 0°C and 5−10 ml of hexane added. Crystallization occurred on standing at −30°C affording **8(8′)**, orange solid (decomposes on warming). − ^{31}P NMR: δ = 44.4. − ^{1}H NMR: δ = 7.8−7.6 (m, 1 H); 7.3−7.1 (m, 1 H); 7.0−6.8 (m, 2 H); 5.0 (s, 1 H); 4.5−4.3 (m, 1 H); 3.9 (s, 6 H); 3.8 (s, 3 H); 3.6 (s, 3 H); 3.3 (s, 3 H); 3.7−3.3 (m, 2 H); 2.9−2.8 (m, 1 H); 1.7−0.8 (m, 30 H). − ^{13}C NMR: δ = 164.7 (b, *C*O_2CH_3); 164.3 [d, *J*(P,C) = 18.5 Hz, CN]; 163.6 [d, ^{3}J(P,C) = 18.5 Hz, *C*O_2CH_3]; 162.3 (b, *C*O_2CH_3); 158.3 (s, $C_{ar}O$); 142.1 (b, PC*C*); 133.2 [d, ^{3}J(P,C) = 9.8 Hz, *C*C_{ar}]; 131.3 (b, C=C); 130.2 (s, CH_{ar}); 129.7 (b, C=C); 127.6 (s, CH_{ar}); 113.9 (s, CH_{ar}); 112.2 [d, ^{1}J(P,C) = 132.2 Hz, PC]; 87.0 [d, ^{3}J(P,C) = 17.6 Hz, CN]; 62.8 [d, ^{2}J(P,C) = 13.2 Hz, CN]; 55.0 (s, CN); 54.2 (s, OCH_3); 52.9 (s, OCH_3); 52.6 (s, OCH_3); 51.3 (s, OCH_3); 46.1 (s, NCH); 45.6 [d, ^{2}J(P,C) = 9.81 Hz, NCH]; 38.0 [d, ^{3}J(P,C) = 23.4 Hz, C(CH_3)$_3$]; 34.5 (b, CH_2); 31.5 (s, CH_2); 31.0 (s, CH_2); 29,0 (s, CH_3); 28.9 (s, CH_2); 27.5 (s, CH_2); 27.1 (s, CH_2); 26.7 (s, CH_2); 25.1 (s, CH_2); 25.0 (s, CH_3); 24.0 (s, CH_3); 21.6 (s, CH_3); 20.4 (s, CH_3). − MS (EI, 70 eV); *m*/*z*: 727 (M^+); 684 ($M^+ - C_3H_7$); 668 ($M^+ - CO_2CH_3$).

Synthesis of the Phosphonium Cyanide **10**: Compound **3(3′)** (0.5 g, 0.85 mmol) was dissolved in 20 ml of CH_2Cl_2 at −20°C and 0.12 g (0.9 mmol) of tetracyanoethylene in 20 ml CH_2Cl_2 were added. The well stirred mixture was left overnight allowing it to reach room temperature. Then the solvent was removed under reduced pressure and the residue crystallized from CH_2Cl_2/Et_2O. Yield 0.55 g (90%), colorless crystals. − ^{31}P NMR: δ = 46.3. − ^{1}H NMR: δ = 7.4−7.3 (m, 2 H); 7.0−6.8 (m, 2 H); 4.4 (s, 1H); 3.9−3.4 (m and 3s, 11 H); 3.3−3.1 (m, 1 H); 1.8−0.9 (m and s, 31 H). − ^{13}C NMR: δ = 206.1 [d, ^{2}J(P,C) = 8.6 Hz, C=N]; 164.0 [d, ^{3}J(P,C) = 11.0 Hz, *C*O_2CH_3]; 162.7 (s, *C*O_2CH_3); 160.5 (s, $C_{ar}O$); 134.9 (s); 132.6 (s); 130.5 (s, CH_{ar}); 121.7 (s); 120.5 [d, ^{3}J(P,C) = 8.6 Hz, C*C*$_{ar}$]; 116.1 (s); 115.0 (s); 113.3 (s, CH_{ar}); 113.2 [d, ^{2}J(P,C) = 10.2 Hz, PC*C*=C]; 110.4 (s); 108.3 (s); 57.2 [d, ^{2}J(P,C) = 2.4 Hz, *C*C_{ar}]; 56.0 (s, NCH); 54.8 (s, OCH_3); 53.4 (s, OCH_3); 53.0 (s, OCH_3); 48.2 (b, NCH); 44.0 [d, ^{3}J(P,C) = 19.6 Hz, C(CH_3)$_3$]; 35.9 (s, PC*C*); 33.0 [d, ^{3}J(P,C) = 18.8 Hz, CH]; 31.4 (s, CH_2); 30.7 (s, CH_2); 26.8 (s, CH_3); 25.8 (s, CH_2); 25.4 (s, CH_2); 23.9 (s, CH_2); 23.3 (b, CH_3); 20.2 (b, CH_3).

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