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Unexpected Staudinger Reaction of α-Azidoacetonitriles α-Phenyl Substituted with Triphenylphosphine. Preparation, X-Ray Crystal and Molecular Structures of a Phosphazine, an Aminophosphonium Carbanion Salt and a Phosphazide, with (Z)-Configuration

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Abstract: Staudinger reaction of α-azidophenylacetonitrile with triphenylphosphine in 1:2 molar ratio provides the triphenylphosphazine **4** derived from α-diazophenylacetonitrile, whereas in 2:1 molar ratio the final product is found to be the aminotriphenylphosphonium salt of phenylmalononitrile **6**. However, the Staudinger reaction of α-azidodiphenylacetonitrile with triphenylphosphine affords the corresponding (Z)-phosphazide **17**. The crystal and molecular structures of compounds **4**, **6**, and **17** have been determined by X-ray analysis. Compound **17** is the first isolated phosphazide which presents the (Z)-configuration with respect to the central N-N bond of the PN_3C moiety (P-N-N-N= 0.0(3)°).

The reaction of a tertiary phosphine with an organic azide to produce an iminophosphorane after nitrogen evolution is known as the Staudinger reaction.[1] In a few instances the primary imination products, phosphazides, have been isolated,[2] or can be trapped via an intramolecular reaction[3] but most such phosphazides lose nitrogen at room temperature or even at lower temperature to give the corresponding iminophosphorane compound in practically quantitative yields.

Isolable phosphazides have been formed from sterically hindered components or the electronic effects of substituents have been such as to increase the electron density on phosphorus atom or decrease it on the Nα atom of the azide. X-ray structural data of six phosphazides[4] revealed that the phosphorus atoms are approximately tetrahedral, the P-N-N-N-C framework is nearly planar, and the orientation of substituents about the N_α-N_β and N_β-N_γ is *E*. The geometry in the isolable phosphazides probably accounts for their stability by making more difficult ring closure to the four-membered trasition state necessary for nitrogen elimination and iminophosphorane formation.

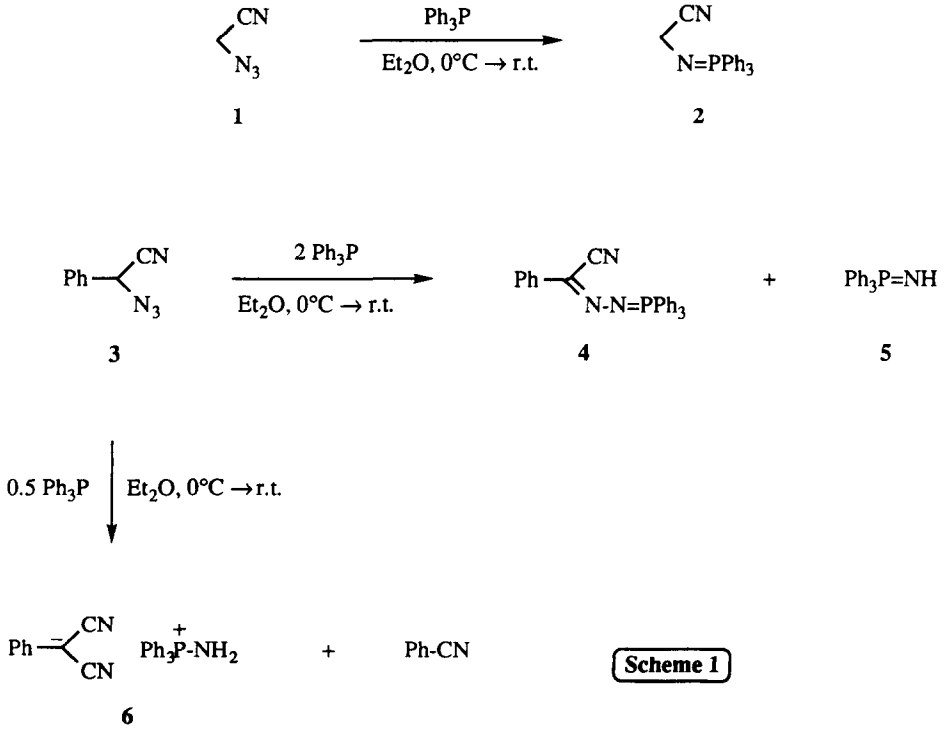
An inmense variety of azides have been employed in the Staudinger reaction, with the only limits apparently being the availability of the requisite azide but also the thermal and shock stability of azides. Aromatic, aliphatic, heterocyclic, olefinic, carbonyl, carbalkoxy, carbamido, tosyl, bisazides and metallic azides have been used.[5] However, the Staudinger imination of trivalent phosphorus compounds with azides containing a CH-acidic group has not been investigated. It has only been briefly reported[6] that the most acid azides reacted with tertiary phosphines to form phosphorus-substituted betaines.

We wish to report here the Staudinger reaction of α-azidoacetonitriles α-phenyl substituted with triphenylphosphine. In one case, the intra- or intermolecular protonation of the initially formed phosphazide is of special interest since the resulting betaine is capable of undergoing various conversions. In other case, the isolated phosphazide presents unprecedent structural features.

The parent azidoacetonitrile[7] **1** reacts with 1 equiv of triphenylphosphine in dry diethyl ether at room temperature to give the expected iminophosphorane **2** in excellent yield (91%) (Scheme 1). The introduction of aryl group into compound **1** strongly affected the nature of the reaction product.

An earlier communication described the formation of the α-azidophenylacetonitrile **3** from 5-amino-4-phenyl-1,2,3-thiadiazole by diazotization, reaction with sodium azide and further heating.[8] However, a recent report[9] has shown than the only reaction product is found to be the α-chlorophenylacetonitrile, and a mixture of compound **3**, α-acetoxyphenylacetonitrile and benzonitrile in the ratio 85:10:5 was obtained from the reaction of α-(methanesulfonyloxy)phenylacetonitrile with sodium azide. In our hands, compound **3** was easily prepared by the two-step sequence: a) reaction of phenylacetonitrile with *N*-bromosuccinimide in the presence of dibenzoyl peroxide (75%) and b) bromine-azide exchange using a polymeric quaternary ammonium azide[10] (89%).

When compound **3** was allowed to react with 2 equiv of triphenylphosphine in diethyl ether at room temperature for 2 h a precipitate **4** (82%) with m.p. 176-178 °C was formed and from the filtrate triphenylphosphinimine **5** was obtained. The IR spectrum of **4** showed a characteristic band due to the cyano group at 2206 cm^{-1} and in the ^{31}P-NMR spectrum appeared only one signal at δ 22.3 ppm. Both ^{1}H- and ^{13}C-NMR spectra indicated that the α-methine group in **4** is now a quaternary carbon atom (Scheme 1).



Scheme 1

In order to identify unambigouosly the structure of the reaction product X-ray structure determination of crystalline compound **4** was performed[11] (Fig. 1). These results indicate that a certain degree of electron delocalization in the N(9)-C(8)-C(1)-N(10)-N(11)-P(12) fragment is observed (Table 1) when compared with data retrieved from the CSD,[12] the averaged values for the 6 structures containing the Ph-C(CN)-N moiety are: 1.133(13), 1.443(35), 1.286(15) Å and 119(4)° for the N≡Csp, Csp-Csp^2, Csp^2-N distances and Csp-Csp^2-N angle (hereinafter, in the statistical analyses, the values in parenthesis correspond to the standard deviation of the sample). The N-P bond (Fig. 1) is greater than the PPh_3=N bond of 1.595(24) Å and it is consistent with the values reported for PPh_3=N^+ distance of 1.623(13) Å, 50 and 10 structures respectively, and even greater than the value found in compound **6** (Fig. 2). The internal angle at C(2) reflects the influence of the substituent giving rise to Δα= -1.3(2)° in agreement with the tabulated values for CH=NR[13] one. The N(10) atom is almost trans to the C(13) atom which shows the shortest P-C length.

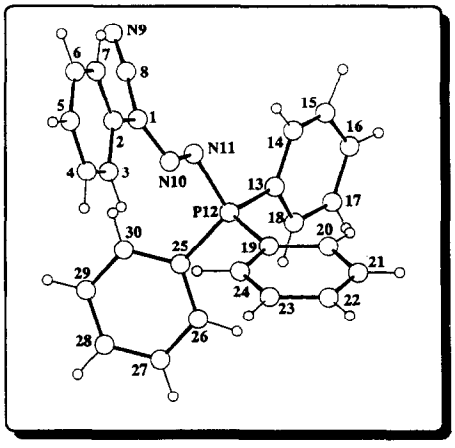


Fig. 1: Molecular structure of **4** showing 30% probability ellipsoids for the non-hydrogen atoms.

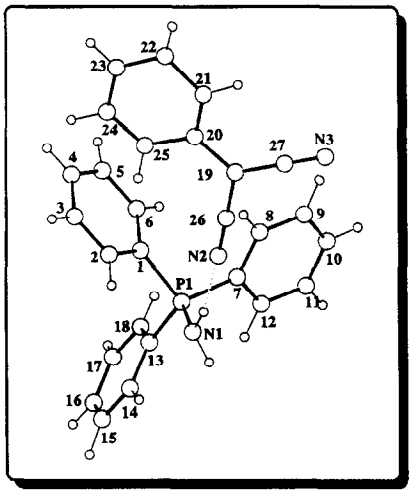


Fig. 2: Molecular structure of **6** (ellipsoids at 30% probability level). Dotted lined stand for hydrogen bonds.

A literature survey performed via the CSD revealed that 119 structures well refined (R < 0.050) are involved in C-H...N≡C interactions (C...N < 3.4 Å) with mean values of 3.33(5), 2.51(10) Å and 143 ° for the C...N, H...N and C-H...N parameters. As ilustrated in Fig. 3, the crystal packing is mainly due to C-H...N≡C weak interactions as compared with the statistical analysis. These interactions through symmetry centers and two-fold axis along c and by translations along b form sheets that are then joined by C-H...phenyl interactions.

When the reaction between **3** and triphenylphosphine was carried out in 2:1 molar ratio under the same conditions, nitrogen was evolved and the metal-free carbanion salt **6** (87%) was isolated as crystalline product m.p. 164-166 °C and from the filtrate benzonitrile was isolated. Staudinger reaction between **3** and triphenylphosphine in 1:1 molar ratio provided **4** as minor product and **6** as major product (Scheme 1). This compound is stable at room temperature for months and can also be handled without problems. Its IR spectrum showed two bands in the region of the cyano group and the ^{31}P-NMR spectrum displayed a signal at δ 35.8 ppm. The ^{13}C-NMR spectrum showed a signal at δ 27.2 ppm due to a quaternary carbon atom.

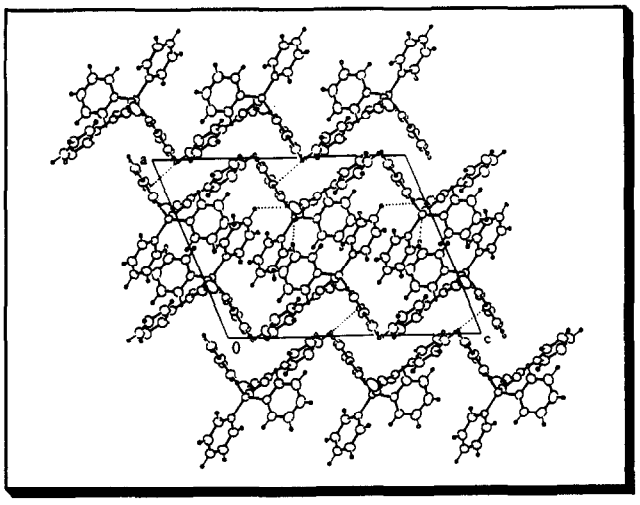


Fig. 3: Crystal packing of **4** as projected along the b axis.

In the molecular structure of compound[11] **6**, the shortening of the C(19)-C(26)/C(27) and the lengthening of the C(26)-N(2) and C(27)-N(3) bonds (Table 1) are associated with some degree of charge delocalization (1.414(15) and 1.143(38) Å for 34 structures containing charged dicyano groups without hydrogen interactions and with R < 0.050). The P=N$^+$ bond do not deviate significantly from the averaged value retrieved for the aminotriphenylphosphonium bromide and chloride compounds.[12] The C(21)-C(20)-C(25) angle, as in **4**, appears to be affected by the cyano groups substituents,[13] $\Delta\alpha$ = -2.6(2)°.

The anions and cations linked by N-H...N bonds form chains parallel to the b axis, (Fig. 4). The unit cell accommodates two centrosymmetrically chains held together by C-H...electronic π cloud (phenyl rings) interactions, Table 1.

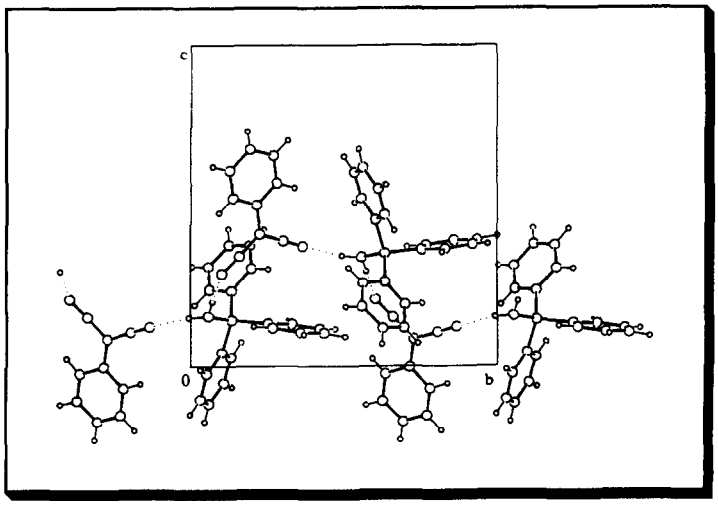


Fig. 4: Chains of ions alongs the b axis, compound **6**. Only one chain has been plotted for clarity purposes.

Table 1. Selected geometrical parameters (Å,°). $C(A_1)$ stands for the centroid of the C(25)...C(30) ring in compound **4** and $C(A_2)$, $C(A_3)$ for the centroids of the C(7)...C(12) and C(20)...C(25) rings in **6** and $C(A_4)$, $C(A_5)$ for those of the C(32)..C(37) and C(2)...(7) rings in **17**.

Compound **4**			
C(1)-C(2)	1.469(3)	C(1)-C(8)	1.428(3)
C(1)-N(10)	1.301(3)	C(8)-N(9)	1.143(4)
N(10)-N(11)	1.356(2)	N(11)-P(12)	1.637(2)
P(12)-C(13)	1.792(2)	P(12)-C(19)	1.801(3)
P(12)-C(25)	1.805(3)		
C(3)-C(2)-C(7)	118.7(2)	C(1)-C(8)-N(9)	175.3(3)
C(1)-N(10)-N(11)	115.4(2)	C(8)-C(1)-N(10)	121.9(2)
C(3)-C(2)-C(1)-N(10)	-19.6(4)	C(2)-C(1)-N(10)-N(11)	-175.2(2)
C(1)-N(10)-N(11)-P(12)	-175.4(2)	N(10)-N(11)-P(12)-C(13)	-161.9(2)
N(10)-N(11)-P(12)-C(19)	-40.6(2)	N(10)-N(11)-P(12)-C(25)	79.7(2)

Hydrogen interactions	X-H	X...Y	H...Y	X-H...Y
C(16)-H(16)...N(9)(1-x,y+1/2,3/2-z)	1.05(3)	3.445(4)	2.76(4)	123(3)
C(21)-H(21)...N(9)(1-x,-y,1-z)	0.95(5)	3.362(5)	2.58(5)	139(4)
C(26)-H(26)...N(9)(x,1+y,z)	0.98(3)	3.368(4)	2.52(3)	144(3)
C(5)-H(5)...$C(A_1)$(-x,y-1/2,1/2-z)	1.00(4)	3.746(6)	2.81(4)	156(3)

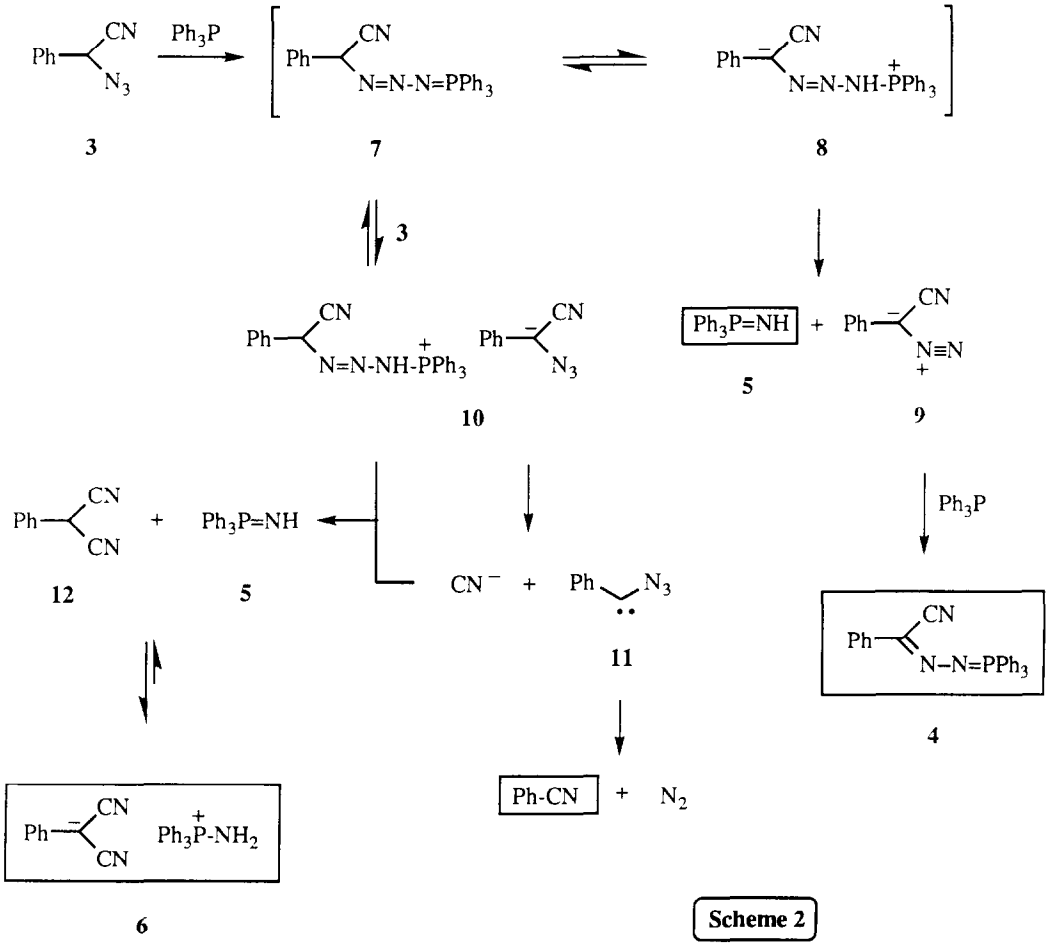
Compound **6**			
P(1)-N(1)	1.622(2)	C(19)-C(20)	1.456(3)
C(19)-C(26)	1.392(4)	C(19)-C(27)	1.393(4)
C(26)-N(2)	1.158(4)	C(27)-N(3)	1.155(4)
C(26)-C(19)-C(27)	116.9(2)	C(21)-C(20)-C(25)	117.4(2)
C(19)-C(26)-N(2)	178.9(3)	C(19)-C(27)-N(3)	178.6(3)
P(1)-N(1)-H(111)	114(2)	P(1)-N(1)-H(112)	116(2)
H(111)-N(1)-H(112)	116(3)		
C(13)-P(1)-N(1)-H(111)	-169(2)	C(13)-P(1)-N(1)-H(112)	52(2)

Hydrogen interactions	X-H	X...Y	H...Y	X-H...Y
C(16)-H(16)...N(9)(1-x,y+1/2,3/2-z)	1.05(3)	3.445(4)	2.76(4)	123(3)
N(1)-H(112)...N(3)(1-x,y+1/2,1/2-z)	0.93(3)	3.050(3)	2.13(3)	171(3)
N(1)-H(111)...N(2)	0.92(4)	2.927(3)	2.02(3)	167(3)
C(16)-H(16)...$C(A_2)$(1-x,y+1/2,1/2-z)	1.02(4)	3.596(3)	2.83(3)	113(2)
C(6)-H(6)...$C(A_3)$(2-x,1-y,1-z)	0.99(4)	3.574(3)	2.79(3)	136(2)
C(15)-H(15)...$C(A_3)$(1-x,1-y,1-z)	1.06(5)	3.922(4)	2.95(5)	153(3)

Compound **17**			
P(19)-N(18)	1.641(2)	N(17)-N(18)	1.339(3)
N(16)-N(17)	1.262(3)	C(1)-N(16)	1.488(3)
C(1)-C(14)	1.488(3)	C(14)-N(15)	1.140(3)
P(19)...N(16)	2.800(2)	C(3)-C(2)-C(7)	118.9(2)
C(9)-C(8)-C(13)	118.6(2)	C(1)-N(16)-N(17)	111.1(1)
N(16)-N(17)-N(18)	117.8(2)	N(17)-N(18)-P(19)	121.5(1)
C(14)-C(1)-N(16)-N(17)	-11.2(2)	C(1)-N(16)-N(17)-N(18)	-177.2(2)
N(16)-N(17)-N(18)-P(19)	0.0(3)	N(17)-N(18)-P(19)-C(26)	-170.3(2)

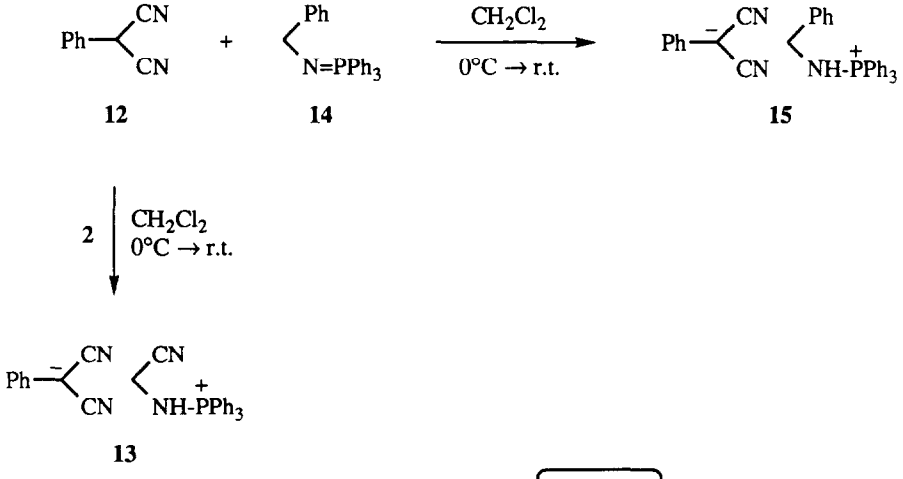
Hydrogen interactions	X-H	X...Y	H...Y	X-H...Y
C(4)-H(4)...N(15)(1-x,-y,2-z)	1.00(5)	3.489(5)	2.61(4)	147(3)
C(28)-H(28)...N(17)(1-x,-y,1-z)	0.99(4)	3.543(4)	2.59(5)	162(3)
C(36)-H(36)...N(17)(-x,-y,1-z)	0.97(3)	3.351(2)	2.62(3)	132(3)
C(9)-H(9)...$C(A_4)$	1.00(4)	3.590(4)	2.66(4)	154(4)
C(29)-H(29)...$C(A_5)$(x,y,-1+z)	0.93(4)	3.700(3)	2.92(4)	142(3)

A rational mechanism for the formation of the unexpected phosphinazide **4** and the metal-free carbanionic salt **6** is depicted in Scheme 2 and involves the formation of the phosphazide **7** in the first step of the reaction. This intermediate may undergo either intramolecular or intermolecular protonation on the nitrogen atom adjacent to the phosphorus.[14] The intramolecular protonation leads to the betaine **8** which by elimination of triphenylphosphinimine **5** provided the diazo compound **9**. Further reaction of **9** with a second equivalent of triphenylphosphine yields the phosphinazine **4**. The reaction between diazodiarylmethanes and triphenylphosphine to give phosphinazides has been recently reported.[15] The intramolecular protonation of the initially formed phosphazide **7** by the action of the CH-acidic group of **3** affords the aminophosphonium salt **10**. The carbanionic moiety undergoes loss of the cyanide anion to give the azidocarbene **11** which is then transformed into benzonitrile after extrusion of nitrogen.[16] Finally, nucleophilic attack of the cyano anion on the aminophosphonium cation **10** with concomitant elimination of nitrogen and triphenylphosphinimine **5** provides the phenylmalononitrile **12**, which undergoes proton abstraction by the action of the strong base **5** to give the salt **6** (Scheme 2).



Scheme 2

Metal-free carbanion salts type **6** can also be prepared from phenylmalononitrile[17] **12** and different iminophosphoranes, which by the way confirms the proposed final step of the compound **6** formation. Thus, the reaction of phenylmalononitrile **12** and the iminophosphorane **2** or *N*-(benzyl)triphenyliminophosphorane **14** in dry dichloromethane at 0 °C and then at room temperature afforded the salts **13** (74%) and **15** (69%) respectively (Scheme 3).



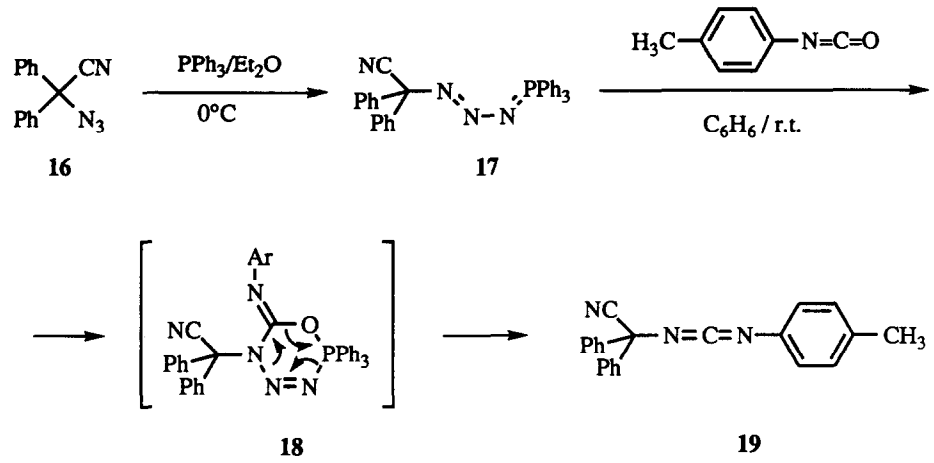
Scheme 3

Recent examples on the preparation of related metal-free carbanion salts namely tetraalkylammonium of malonic dialkyl esters[18] carbazole and dibenzoazepine[19] and their application as initiators for the quantitative anionic polymerization of α-activated olefins at room temperature have been described. In all cases this type of salts have been prepared under strong basic conditions.

This result shows for the first time the preparation, *via* an unexpected Staudinger reaction under extremely mild condition, and the isolation as a crystalline solid of an aminophosphonium salt of phenylmalononitrile, which is not a truly "naked" carbanion. Rather, the anion and the cation interact with one another *via* hydrogen bonds in a highly ordered manner.

On the other hand, α-azidodiphenylacetonitrile **16** was prepared from diphenylacetonitrile in 86% overall yield by sequential treatment with *N*-bromosuccinimide in the presence of dibenzoyl peroxide and further treatment with sodium azide. When compound **16** was allowed to react with 1 equiv. of triphenylphosphine in diethyl ether at 0 °C for 10 min. the phosphazide **17** (78%) with m.p. 121-123 °C was formed (Scheme 4). Compound **17** can be stored for a several months without any signs of decomposition. Its IR spectrum showed a band in the region of the cyano group at 2234 cm^{-1} and the ^{31}P-NMR spectrum displayed a signal at δ 25.3 which is in good agreement with previously reported values for this type of compounds.[20] The ^{13}C NMR spectrum showed a signal at 74.5 due to the quaternary carbon atom.

Slow recrystallization of compound **17** from dichloromethane / diethyl ether afforded crystals suitable for X-ray structural analysis (Fig.5). The P=N is significantly elongated as compared to the values retrieved from CSD and mentioned before. The most striking feature deals with the (*Z*)-configuration of the PN_3R fragment which is the first example where the *cis*- position with respect to the N-N central bond is reported



Scheme 4

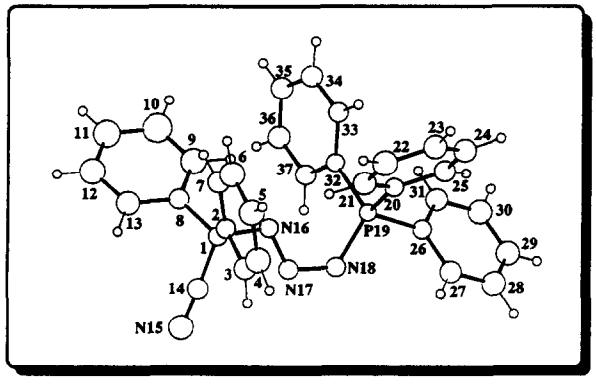


Fig. 5: Molecular structure of **17** (ellipsoids at 30% probability level)

(Table 2). The other main differences with respect to the previous phosphazides are those concerning the angles at the N atoms (121.5(1), 117.8(2)°) which are even greater than those presented by DILDEH (119.1, 112.0°) and YEDPIG (114.7, 112.5°) compounds with bulkier substituents at the P atom. All bonds lengths in the P=N-N=N fragment show that there is an extensive electronic delocalization as in the analogous phosphazide derivatives. The (*Z*)-configuration has also found in the only two reported 1-methylthiotriazenes derivatives (MABTRZ, MTMORT) which show N-N and N=N distances of 1.375 and 1.245 Å (C=N-N=N-S *vs.* P=N-N=N-Csp^3) longer and shorter than the average values for the phosphazides derivatives of 1.341 and 1.273 Å.

The influence of the -C≡N subtituent[13] is reflected in the *ipso* angles at C(2) and C(8) atoms showing $\Delta\alpha$ values of -1.1(2) and -1.4(2)° respectively. The bond distances are close to the average values retrieved for the Csp^3-C≡N (R < 0.050) fragment of 1.134(23) and 1.470(19) Å.

In order to find out the difference in energy corresponding to the *Z* versus the *E* configuration and due to the complexity of the present molecule, *ab initio* calculations at HF/6-31G** level[21] on the hypothetical $PH_3N_3CH_3$ molecule were carried out. The *Z* configuration is 1.6 Kcal mol^{-1} more stable than the *E* one

presented by the phosphazides reported so far. While the P-N bond, in the *E* configuration, exhibits a double bond character (see above) an elongation of this bond and a shortening of the contiguous N(1)-N(2) bond (Table 2) together with and opening of the angle at the N atoms is observed in the *Z* one.

Table 2. Selected X-ray structural data for phosphazides: $R(R')_2P$=N1-N2=N3-R", τ= P-N1-N2-N3.

CSD code	P-N1	N1-N2	N2-N3	P-N1-N2	N1-N2-N3	N2-N3-R"	τ
BEYKEV#	1.672(5)	1.364(6)	1.279(6)	112.9(4)	103.8(4)	116.3(4)	172.4
DILDEH	1.638(5)	1.298(7)	1.316(7)	119.1(4)	111.9(5)	112.1(5)	175.6
GIJMIV	1.615(1)	1.375(2)	1.256(2)	111.7(1)	112.1(1)	111.2(19	-170.6
PIPHEB	1.620(2)	1.376(2)	1.261(2)	107.5(1)	112.6(2)	111.9(2)	170.5
VEZDUZ	1.651(1)	1.328(1)	1.279(1)	109.5(7)	113.0(9)	114.8(9)	178.2
YEDPIG	1.623(1)	1.342(2)	1.273(2)	114.8(9)	112.6(1)	112.3(1)	178.0
Present work	1.641(2)	1.339(3)	1.262(3)	121.5(1)	117.8(2)	112.1(1)	0.0
**ab initio*	1.582	1.373	1.213	111.2	113.1	111.9	180.0
***ab initio*	1.618	1.338	1.227	112.8	115.3	114.0	0.0

#W phosphazide complex. Energy: *= -136.32343, **= -136.32603 Hartrees.

Mechanistic studies of the Staudinger reaction involving kinetic studies[22] revealed that nucleophilic attack of the tertiary phosphine on the azide occurs with the formation of a *E*-phosphazide (only six of them have been isolated) having zwitterionic character, and this reaction is the rate-determining step. After $E \rightarrow Z$ isomerization, nitrogen is evolved via a four-center intermediate. Apart from steric factors, avoided in the hypothetical molecule, this compound can be considered as an intermediate product between an acyclic and cyclic compound where the tetrahedral environment of phosphorus atom appears to be distorted towads a trigonal bipyramid with C(26) and N(16) in axial positions (see Fig. 5), in a similar way to other compounds[23] which were intermediate between open-chain betaines and ring-chain 1,3,2-diazaphosphetidines. The P(19)....N(16) distance (2.800(2)Å) is longer than those already mentioned (2.592(7)-2.741(7)Å) and than the value (2.519Å) obtained in the *ab initio* calculation.

The crystal packing (Fig. 6) is governed by weak C-H...N interactions and by C-H...electronic π cloud (phenyl rings) interactions, Table 1.

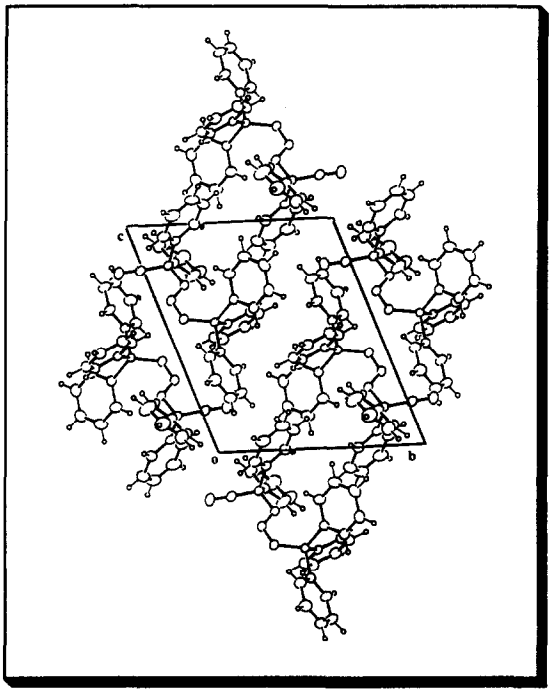


Fig. 6: Crystal packing of **17** as projected along the a axis.

When the phosphazide **17** was heated in benzene at reflux temperature a complex mixture was obtained from which the expected iminophosphorane could not be detected. However, compound **17** reacted with 4-tolylisocyanate in dry benzene at room temperature to give the carbodiimide **19**. This result clearly show that the phosphazide **17** itself reacts with the isocyanate to give the six-membered intermediate **18** which by loss of triphenylphosphine oxide leads to the carbodiimide **19** (Scheme 4). This assumption is in agreement with the zwetterionic character of phosphazides[1] in which the phosphorus atoms have partial phosphonium character and the negative charge is on the Nα nitrogen atom.

Experimental.

All melting points were determined on a Kofler hot-plate melting point apparatus and are uncorrected. IR spectra were obtained as Nujol emulsions or films on a Nicolet Impact 400 spectrophotometer. NMR spectra were recorded on a Bruker AC-200 and Varian UNITY-300 spectrometers. Chemical shifts refer to signals of tetramethylsilane in the case of ^{1}H and ^{13}C spectra and to 85% aqueous phosphoric acid in the case of ^{31}P spectra. The mass spectra were recorded on a Hewlett-Packard 5993C spectrometer. Microanalyses were performed on a Perkin-Elmer 240C instrument.

X-Ray Crystallography. Compound **17**: $C_{32}H_{25}N_4P$, triclinic, P-1, a= 9.9684(6), b= 11.9198(12), c= 13.3598(10) Å, α= 101.00(1), β= 105.27(1)°, g= 114.34(1)°, *V*= 1311.8(2) Å^3, D_c= 1.257 g cm^{-3}, Z= 2, μ= 11.381 cm^{-1}, crystal dimensions 0.43x0.33x0.20mm, 4326 independent reflections were recorded up to θ_{max}= 65° on a Philips PW1100, four cicle diffractometer with Cu-Kα radiation and graphite monochromator. Semi-empirical ψ-scan absorption correction was applied. The structure was solved by Patterson and the refinement was carried by least-squares methods on *Fo* with full matrix. Anisotropic thermal model for the non-hydrogen atoms while H atoms, obtained unambiguously from difference Fourier synthesis were refined isotropically. *R(Rw)*= 0.040(0.046) for 3871 [$I>2\sigma(I)$] observed reflections. The max. final Δ*F* peak 0.27 eÅ^{-3}.

Most of the calculations were performed using the XTAL System[24] on a VAX6410 computer. The atomic scattering factors were taken from the *International Tables for X-Ray Crystallography*, Vol. IV.[25] The weighting scheme was established as to give no trends in $<\omega\Delta^2F>$ vs $<F_o>$ and $<\sin\theta/\lambda>$.

(Triphenylphosphoranylidene)aminoacetonitrile 2. To a solution of azidoacetonitrile **1** (0.56 g, 6.8 mmol) in dry diethyl ether (10 ml) was added dropwise a solution of triphenylphosphine (1.79 g, 6.8 mmol) in the same solvent (15 ml) at 0 °C under nitrogen. The reaction mixture was allowed to warm at room temperature and stirring was continueded for 1h. The precipitated solid was collected by filtration, dried and recrystallized from dichloromethane / diethyl ether to give (triphenylphosphoranylidene)aminoacetonitrile **2**: (91%), m.p. 142-144 °C (colourless prisms); (Found: C, 76.03; H, 5.28; N, 8.80. $C_{20}H_{17}N_2P$ requires: C, 75.94; H, 5.42; N, 8.86; IR (Nujol): 2240 (m), 1589 (m), 1438 (vs), 1334 (s), 1307 (m), 1260 (s), 1213 (s), 1112 (s), 998 (m), 857 (s), 756 (s), 729 (vs), 696 (vs) cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ: 4.01 (d, 2H, $^{3}J_{P-C}$ = 26.5 Hz, CH_2), 7.28-7.70 (m, 15H, H_{arom}); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ: 34.05 (d, $^{2}J_{P-C}$ = 5.0 Hz, CH_2), 120.88 (d, $^{3}J_{P-C}$ = 11.5 Hz, CN), 128.48 (d, $^{3}J_{P-C}$ = 12.1 Hz, C_m), 129.36 (d, $^{1}J_{P-C}$ = 97.7 Hz, C_i), 131.74 (d, $^{4}J_{P-C}$ = 2.5 Hz, C_p), 132.26 (d, $^{2}J_{P-C}$ = 9.1 Hz, C_o); ^{31}P-NMR ($CDCl_3$, 121 MHz) δ: 19.11; m/z: 316 (M^+, 11), 315 (25), 287 (22), 262 (33), 183 (100), 108 (32).

α-Azidophenylacetonitrile 3. A mixture of *N*-bromosuccinimide (0.89 g, 5 mmol), dibenzoyl peroxide (0.048 g, 0.2 mmol) and carbon tetrachloride (5 ml) was heated at reflux temperature. A solution of phenylacetonitrile (0.59 g, 5 mmol) in carbon tetrachloride (3 ml) was added dropwise. The reaction mixture was refluxed with stirring for 6 h. After cooling, the white precipitated solid was separated by filtration and the filtrate was washed whit aqueose sodium bicarbonate (3 x 10 ml). The organic layer was dried over anhydrous magnesium sulfate, filtered and concentrated to dryness. The crude product was chromatographied on a silica gel column using diethyl ether / n-hexane 1:4 es eluent to give α-bromophenylacetonitrile (75%), as a yellow oil; (Found: C, 48.89; H 2.93; N, 7.01. C_8H_6NBr requires: C, 49.01; H, 3.08; N, 7.14); IR (film): 2249 (w), 1501 (m), 1459 (m), 1189 (m), 770 (m), 701 (vs), 658 (s), 627 (s) cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ: 5.49 (s, 1H, CH), 7.40-7.55 (m, 5H, H_{arom}); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ: 27.53 (CH), 116.32 (CN), 127.75 (C_o or C_m), 129.47 (C_o or C_m), 130.33 (C_p), 133.42 (C_i); m/z: 197 (M^++2, 4), 195 (M^+,4), 117 (32), 116 (100), 90 (15), 89 (65), 76 (9), 63 (46). To a solution of sodium azide (11.8 g) in water (47 ml) Amberlite IRA-400 (60 g) was added. The mixture was stirred at room temperature for 15 min and the filtered. The polymer was washed with water (10 ml), methanol (10 ml), chloroform (10 ml), diethyl ether (10 ml) and dried. A mixture of the polymeric azide (4.9 g), α-bromophenylacetonitrile (0.21 g, 1.06 mmol) and dry dichloromethane (10 ml) was stirred at room temperature for 2 h, and then filtered. The filtrate was concentrated to dryness and the residual material was chromatographed on a silica gel column using as eluent diethyl ether / n-hexane 3:7 to give α-azidophenylacetonitrile **3** (89%), as a yellow oil; (Found: C, 60.83; H, 3.85; N, 35.52. $C_8H_6N_4$ requires: C, 60.75; H, 3.82; N, 35.42); IR (film): 2231 (w), 2118 (vs), 1460 (m), 1228 (s), 1190 (m), 755 (m), 716 (m), 709 (s) cm^{-1}; ^{1}H-NMR ($CDCl_3$, 200 MHz) δ: 5.23 (s, 1H, CH), 7.46 (s, 5H, H_{arom}); ^{13}C-NMR ($CDCl_3$, 50 MHz) δ: 54.27 (CH), 115.47 (CN), 127.32 (C_o or C_m), 129.46 (C_o or C_m), 130.31 (C_p), 130.92 (C_i); m/z: 158 (M^+, 14), 129 (18), 116 (100), 77 (96).

Triphenylphosphinazine derived from α-diazophenylacetonitrile 4. To a cooled at 0 °C solution of α-azidophenylacetonitrile **3** (0.2 g, 1.3 mmol) in 15 ml of dry diethyl ether was added all at once triphenylphosphine (0.66 g, 2.6 mmol) under nitrogen. The reaction mixture was allowed to warm at rom temperature and stirred for 2 h. Afterwards the precipitated solid was collected by filtration and recrystallized from dichloromethane / diethyl ether to give **4** (82%), m.p. 176-178 °C (yellow prisms); (Found: C, 77.15; H, 4.84; N, 10.30. $C_{26}H_{20}N_3P$ requires: C, 77.02; H, 4.97; N, 10.36); IR (Nujol): 3049 (m), 2206 (m), 1501 (m), 1485 (m), 1443 (s), 1135 (vs), 1114 (s), 891 (m), 780 (m), 748 (m), 721 (m), 701 (s) cm^{-1}. ^{1}H-NMR ($CDCl_3$, 300 MHz) δ: 7.17-7.76 (m, H_{arom}); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ: 113.65 (d, $^4J_{P-C}$ = 2.0 Hz, CN), 124.43 (C_o), 126.15 (d, $^3J_{P-C}$ = 49.9 Hz, Ph(CN)C=N), 127.17 (d $^1J_{P-C}$ = 94.7 Hz, C_i), 127.36 (C_p), 128.35 (C_m), 128.83 (d, $^3J_{P-C}$ = 11.6 Hz, C_m), 132.66 (d, $^4J_{P-C}$ = 3.0 Hz, C_p), 133.35 (d, $^2J_{P-C}$ = 9.6 Hz, C_o), 134.92 (C_i); ^{31}P-NMR ($CDCl_3$, 121 MHz) δ: 22.2; m/z: 262 (15), 183 (100), 157 (10), 152 (15), 115 (24), 108 (34). (In the filtrate triphenylphosphinimine **5** was detected by ^{31}P-NMR[26]).

Aminotriphenylphosphonium salt derived of phenylmalononitrile 6. To a cooled at 0 °C solution of α-azidophenylacetonitrile **3** (0.2 g, 1.3 mmol) in 15 ml of dry diethyl ether was added triphenylphosphine (0.17 g, 0.65 mmol) under nitrogen. A white precipitated was immediatly formed and the resultant mixture was allowed to warm at room temperature and stirred until evolution of nitrogen was finished (6 h). The final brown solid was separated by filtration and recrystallized from dichloromethane / diethyl ether to give **6** (87%), m.p. 164-166 °C (brown prisms); (Found: 77.22; H, 5.20; N, 10.15. $C_{27}H_{22}N_3P$ requires: C, 77.31; H, 5.29; N, 10.02); IR (Nujol): 3208 (m), 3160 (m), 3033 (m), 2169 (s), 2121 (vs), 1597 (m), 1496 (m), 1448

(m), 1305 (m), 1252 (m), 1119 (s), 961 (m), 764 (m), 749 (m), 732 (m), 700 (s) cm^{-1}; ^1H-NMR ($CDCl_3$, 200 MHz) δ: 6.48 (tt, 1H, J = 0.8, 7.5 Hz, H_p), 6.71 (dd, 2H, J = 0.8, 7.5 Hz, H_o), 6.73 (bs, 2H, NH_2), 6.99 (t, 2H, J = 7.5 Hz, H_m), 7.68-7.9 (m, 15H, H_{arom}); ^{13}C-NMR ($CDCl_3$, 50 MHz) δ: 27.21 (C^-), 116.76 (C_p), 117.97 (C_o), 123.14 (d, $^1J_{P-C}$ = 103.3 Hz, C_i), 126.31 (CN), 128.07 (C_m), 129.80 (d, $^3J_{P-C}$ = 13.3 Hz, C_m), 132.66 (d, $^2J_{P-C}$ = 11.4 Hz, C_o), 134.66 (d, $^4J_{P-C}$ = 2.9 Hz, C_p), 141.37 (C_i); ^{31}P-NMR ($CDCl_3$, 121 MHz) δ: 35.84; m/z: 303 (5), 277 (18), 276 (61), 200 (38), 198 (50), 183 (91), 122 (30), 115 (100), 77 (53). (From the filtrate benzonitrile was detected by GC-MS).

Reaction of phenylmalononitrile with iminophosphoranes. Preparation of the salts 13 and 15. To a solution of phenylmalononitrile **12**[17] (0.14 g, 1 mmol) in dry dichloromethane (15 ml) was added dropwise a solution of the corresponding iminophosphorane **2** or **14** (1 mmol). The mixture was allowed to warm at room temperature and stirred for 15 h. The solvent was removed under reduced pressure and the residual material was washed with dry diethyl ether (3 x 15 ml) and dried to give the corresponding salt **13** or **15**. All attempts to purified these compound by recrystallization led a complex mixture from which only the triphenylphosphine oxide could be detected.

Salt **13**: (74%); (Found: 75.90; H, 5.20; N, 12.15. $C_{29}H_{23}N_4P$ requires 75.97; H, 5.06; N, 12.22); IR (Nujol): 3057 (m), 2171 (vs), 2109 (vs), 1593 (m), 1492 (m), 1441 (s), 1301 (m), 1239 (m), 1116 (s), 1094 (m), 1004 (m), 763 (m), 723 (m), 701 (m) cm^{-1}; ^1H-NMR ($CDCl_3$, 200 MHz) δ: 3.89 (d, 2H, $^3J_{P-H}$ = 16.0 Hz, CH_2), 6.45 (s, 1H, NH), 6.70 (t, 1H, J = 6.8 Hz, H_p), 6.88 (d, 2H, J = 6.8 Hz, H_o), 7.03 (t, 2H, J = 6.8 Hz, H_m), 7.66-7.74 (m, 15H, H_{arom}); ^{13}C-NMR ($CDCl_3$, 50 MHz) δ: 27.97 (C^-), 30.43 (CH_2), 116.25 (d, $^3J_{P-C}$ = 3.6 Hz, CH_2-$\underline{C}N$), 119.68 (C_p), 119.98 (d, $^1J_{P-C}$ = 102.4 Hz, C_i), 120.32 (C_o), 127.05 (2CN), 128.37 (C_m), 130.24 (d, $^3J_{P-C}$ = 13.4 Hz, C_m), 133 (d, $^2J_{P-C}$ = 11.2 Hz, C_o), 135.42 (d, $^4J_{P-C}$ = 2.9 Hz, C_p), 138.12 (C_i); ^{31}P-NMR ($CDCl_3$, 121 MHz) δ: 34.03; m/z: 316 (43), 315 (100), 287 (51), 277 (19), 262 (59), 183 (38).

Salt **15**: (69%); (Found: 80.01; H, 5.40; N, 8.38. $C_{34}H_{28}N_3P$ requires: C, 80.14; H, 5.54; N, 8.25); IR (Nujol): 3062 (m), 2169 (vs), 2115 (vs), 1590 (s), 1493 (s), 1433 (s), 1303 (m), 1119 (s), 1071 (m), 751 (m), 735 (s), 692 (s) cm^{-1}; ^1H-NMR ($CDCl_3$, 200 MHz) δ: 4.17 (d, 2H, $^3J_{P-H}$ = 13.1 Hz, CH_2), 6.60 (t, 1H, J = 7.1 Hz, H_p), 6.87 (d, 2H, J = 7.1 Hz, H_o), 6.95 (t, 2H, J = 7.1 Hz, H_m), 7.11-7.75 (m, 21H, NH + H_{arom}); ^{13}C-NMR ($CDCl_3$, 50 MHz) δ: 28.18 (C^-), 46.05 (CH_2), 118.06 (C_p), 119.55 (C_m), 120.73 (d, $^1J_{P-C}$ = 102.6 Hz, C_i), 127.60 (C_p), 127.66 (C_o or C_m), 127.78 (CN), 128.07 (C_m), 128.68 (C_o or C_m), 130.02 (d, $^3J_{P-C}$ = 13.3 Hz, C_m), 133.33 (d, $^2J_{P-C}$ = 11.0 Hz, C_o), 135.08 (d, $^4J_{P-C}$ = 3.0 Hz, C_p), 137.49 (d, $^3J_{P-C}$ = 4.8 Hz, C_i), 140.06 (C_i); ^{31}P-NMR ($CDCl_3$, 121 MHz) δ: 38.12; m/z: 368 (9), 367 (45), 366 (100), 262 (60), 183 (25).

α-Azidodiphenylacetonitrile 16: This compound was prepared from diphenylacetonitrile by bromination with *N*-bromosuccinimide in the presence of dibenzoyl peroxide according with the method described for the preparation of α-azidophenylacetonitrile **3** followed by bromine-azide exchange with sodium azide in acetone[27]: (overall yield 86%); m.p. 41 °C[27]; IR (Nujol): 2237 (w), 2175 (m), 2107 (vs), 1495 (s), 1450 (s), 1223 (s), 1183 (m), 1030 (m), 1013 (m), 951 (m), 940 (m), 917 (m), 905 (m), 770 (s), 753 (s), 730 (m), 696 (vs), 674 (s), 640 (s) cm^{-1}; ^{13}C-NMR ($CDCl_3$, 75 MHz) δ: 68.30 (C-N_3), 117.51 (CN), 126.37 (C_o), 128.98 (C_m) 129.50 (C_p), 136.59 (C_i).

(*Z*)-Triphenylphosphazide 17 derived from 16 and triphenylphosphine. To a solution of α-azidodiphenylacetonitrile **16** (0.24 g, 1 mmol) in dry diethyl ether (6 ml) was added once triphenylphosphine (0.26 g, 1 mmol). Efter a few minutes a white solid was formed, and the mixture was stirred at room temperature for additional 1 h. The solid was collected by filtration, dried and recrystallized from

dichloromethane / diethyl ether to give **17**: (78%), p.f. 121-123 °C (yellow prisms); (Found: 77.53; H, 5.17; N, 11.17. $C_{32}H_{25}N_4P$ requires: C, 77.40; H, 5.07; N, 11.28); IR (Nujol): 2234 (w), 1491 (s), 1433 (vs), 1384 (m), 1312 (m), 1271 (s), 1190 (m), 1114 (vs), 1056 (m), 1033 (m), 1004 (m), 940 (s), 905 (m), 731 (s), 696 (s), 650 (m) cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ: 7.24-7.72 (m, H_{arom}); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ: 74.54 ($Ph_2(CN)\underline{C}$-N), 120.25 (CN), 126.67 (d, $^1J_{P-C}$ = 95.2 Hz, C_i), 127.66 (C_o), 127.80 (C_p), 128.18 (C_m), 128.69 (d, $^3J_{P-C}$ = 11.6 Hz, C_m), 132.62 (d, $^4J_{P-C}$ = 2.5 Hz, C_p), 133.24 (d, $^2J_{P-C}$ = 8.6 Hz, C_o), 140.47 (C_i) ppm; ^{31}P-NMR ($CDCl_3$, 121 MHz) δ: 25.32; m/z: 391 (7), 262 (100), 183 (67), 108 (32), 77 (15).

***N*-(Cyanodiphenylmethyl),*N'*-(4-tolyl)carbodiimide 19**: To a stirred solution of the phosphazide **17** (0.5 g, 1 mmol) in dry benzene (15 ml) was added dropwise a solution of 4-tolylisocyanate (0.13 g, 1 mmol) in the same solvent (5 ml) at room temperature under nitrogen. The mixture was stirred at room temperature for 24 h, and the solvent removed under reduced pressure. The crude product was chromatographed on a silica gel column using ethyl acetate / diethyl ether 1:9 as eluent to give the carbodiimide **19** (87%), as colourless oil; (Found: C, 81.80; H, 5.18; N, 13.12. $C_{22}H_{17}N_3$ requires: C, 81.71; H, 5.30; N, 12.99); IR (film): 2226 (w), 2135 (vs), 2107 (vs), 1512 (s), 1489 (m), 1450 (m), 1144 (m), 1019 (m), 815 (m), 753 (m), 725 (m), 696 (s) cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ: 2.27 (s, 3H, CH_3), 6.84 (d, 2H, J = 8.1 Hz, H-3), 7.03 (d, 2H, *J* = 8.1 Hz, H-2), 7.36-7.56 (m, 10H, H_{arom}); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ: 21.02 (CH_3), 65.64 ($Ph_2(CN)\underline{C}$-N), 119.58 (CN), 124.26 (C-2), 126.29 (C_o), 129.01 (C_m), 129.14 (C_p), 130.09 (C-3), 133.94 (C-4), 136.27 (C-1), 138.23 (-N=C=N-), 139.62 (C_i); m/z: 323 (M^+, 100), 297 (23), 208 (7), 131 (31), 105 (15), 91 (37), 77 (40).

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