Synthesis of phosphinyl, thiophosphinyl and phosphonio guanidines

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Abstract

Sodium diphenylcyanamidophosphinates $Na[Ph_2P(X)NCN]$ (X = O, S) react with alkyl or aryl ammonium chlorides $[RNH_3]Cl$ to give the corresponding ammonium salts. These rearrange into phosphinyl or thiophosphinyl guanidines, with the nitrogen atoms not linked to the phosphorus non-, mono- or disubstituted. ^1H NMR and ^{31}P NMR investigations show that these molecules are present in solution under only one tautomeric form, for which two isomers are detectable at low temperatures. The extension to the synthesis of phosphonio guanidines, starting from N-cyanophosphinimines Ph_3PNCN or $Ph_2(RNH)PNCN$, show the broad application field of the method. Moreover, these guanidines, for which the few known examples described are essentially N-disubstituted phosphorus guanidines, present interesting potentialities in the agricultural and medicinal fields.

Keywords: Sodium diphenylcyanamidophosphinates; N-cyanophosphinimines; Phosphinyl guanidines; Thiophosphinyl guanidines; Phosphonio guanidines

1. Introduction

Phosphorus substituted guanidines are interesting compounds, which can find agricultural and medicinal applications [1,2], or can be used as tools in organic synthesis. Indeed, in these molecules the phosphorus part is a potential amino protective group, the deprotection being realizable by acid hydrolysis [3]. Until now only a few examples of phosphorus guanidines have been described, and mainly with disubstituted nitrogens. Thus the literature reports the reaction of phosphorylated isothiourea with medium basic amines giving the corresponding guanidines [4], the amination of N-diphenylphosphinyl N'-alkyl-carbodiimide affording the N-diphenylphosphinyl N',N''-alkyl(aryl)guanidines [5], or the synthesis of guanidyl phosphonium chlorides by reaction of N-chloroguanidines with trivalent phosphorus compounds [6]. Besides, azidoformamidium chloride reacts with triphenylphosphine to give the triphenyphosphonioformamidium chloride [7], and recently, the synthesis of N-diphenylthiophosphinyl N',N',N'',N''-tetramethylguanidine has also been performed by reaction of the corresponding phosphine with elemental sulphur [8].

We describe here a direct and general synthetic way to new phosphinylguanidines and related compounds, obtained by the reaction of phosphorus cyanamides with alkyl or aryl ammonium chlorides. The method, using stable synthons and affording a very broad variety of phosphorus guanidines, even those for which the terminal nitrogen atoms are non- and monosubstituted, is interesting in comparison with synthetic procedures of related molecules described in the literature.

2. Results and discussion

Sodium oxo- or thiodiphenylcyanamidophosphinates 1, which we have synthesized by cyanamidolysis of the corresponding diphenylphosphinyl chlorides in water [9], react with alkyl- or arylammonium or morpholinium chlorides, leading to the formation of the corresponding phosphinyl or thiophosphinyl guanidines 3 and 4 (Scheme 1) (Table 1).

As already reported for diphenylcyanamidothiophosphinate, the phosphorus cyanamides 1 exhibit different behaviour in the presence of aryl- and alkylammonium chlorides [10]. Thus, on the one hand, the mixture of 1 with arylammonium chloride leads directly, after 1 h in
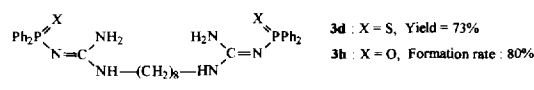
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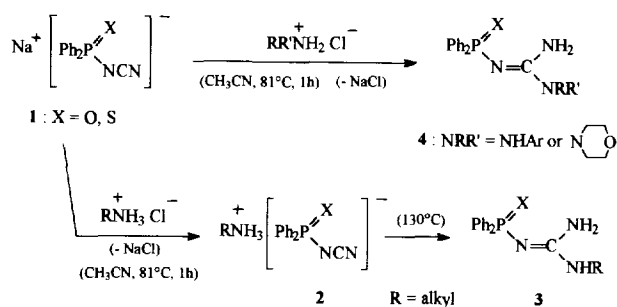
Scheme 1. Synthesis of alkylammonium cyanamidophosphinates 2 and of phosphinyl or thiophosphinyl guanidines 3 and 4.

dry refluxing acetonitrile or 24 h stirring in dry methanol at room temperature, to the formation of phosphinyl or thiophosphinyl guanidines 4. These compounds can be isolated in 36 to 80% yield after recrystallization. On the other hand, alkylammonium chlorides react in dry acetonitrile with sodium diphenylcyanamidophosphinates 1 to form the corresponding alkylammonium diphenylcyanamidophosphinates 2. After isolation, these new fully characterized compounds rearrange completely, at about 130 °C, to guanidines 3 obtained in 40 to 80% yield after recrystallization. In the particular case of morpholin, whose basicity is intermediate between that of primary alkyl and aryl amines, the corresponding guanidines can be directly obtained almost quantitatively, after 2–3 h in refluxing acetonitrile.

This method enables us to isolate with moderate to good yields a new class of phosphinyl and thiophosphinyl guanidines, whose two nitrogen atoms not linked to the phosphorus present different substitution degrees. Moreover, the method affords a large application field, not limited to the monoguanidines, as shown by the synthesis of symmetrical diguanidines 3d and 3h, start-

Table 1
Isolated yields after recrystallization for phosphinyl or thiophosphinyl guanidines 3 and 4 (Scheme 1)

Compound	R	R'	X	Yield (%)
3a	^{n}Bu	—	S	63
3b	^{i}Bu	—	S	82
3c	^{c}Hex	—	S	73
3e	^{n}Bu	—	O	45
3f	^{i}Bu	—	O	38
3g	^{c}Hex	—	O	76
4i	C_6H_5	H	S	80
4j	4-MeC$_6$H$_4$	H	S	62
4k	2-MeC$_6$H$_4$	H	S	40
4l	4-ClC$_6$H$_4$	H	S	64
4m	4-BrC$_6$H$_4$	H	S	56
4n	C_6H_5	H	O	61
4o	4-ClC$_6$H$_4$	H	O	38
4p	4-BrC$_6$H$_4$	H	O	36
4q	—N◯O		S	55
4r	—N◯O		O	55

ing from octamethylene diammonium salts $[(H_3N(CH_2)_8NH_3)Cl_2]$.

3d : X = S, Yield = 73%
3h : X = O, Formation rate : 80%

The likely mechanism involves first a protonation of the cyanamido group followed by a second step in which the free amine attacks the carbon atom of the cyano group. In accordance with our results, the limiting factor of the reaction seems to be the former step, since the strong acidic ammonium chlorides (arylammonium chlorides: $pK_a \approx 5$) react more easily than the weak ones (alkylammonium chlorides: $pK_a \approx 10$) with phosphorylated cyanamides 1, the morpholin hydrochloride ($pK_a = 8$) showing an intermediate reactivity.

As shown in Scheme 2, for each of the guanidines 3, 4, several tautomeric forms can be considered. In order to determine their structure in solution, low temperature ^{31}P NMR and ^{1}H NMR for 3a, 4i and 4n were undertaken.

It is known, in the case of N-aryl-N'-cyanoguanidines, that the tautomer containing the stronger electron withdrawing substituents at the imino nitrogen atom predominates [11]. Moreover, in the case of N,N'-diarylguanidines the concentration of the tautomer with the hydrogen at the imino nitrogen atom is very small, and in some cases undetectable [12].
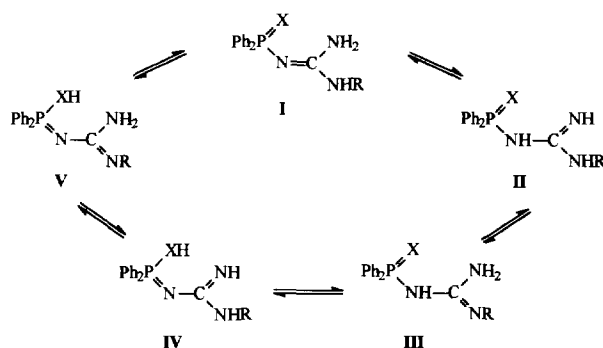
On the basis of the literature, the most likely tautomeric form for guanidines 3, 4, in solution, corresponds then to the tautomer I. This prediction is in good accordance with our NMR experiments, which lead to the same conclusion.

Indeed, the ^{1}H NMR spectra at room temperature of the compounds 3, 4 exhibit, for the protons bonded to the nitrogen, oxygen or sulphur atoms, one signal corresponding to the NH_2 group (integration 2H) and another one corresponding to an NH, OH or SH group

Scheme 2. Possible tautomeric structures for guanidines 3 and 4.

Scheme 3. Syn / anti isomers of phosphinyl or thiophosphinyl guanidines **3** and **4**.

(integration 1H). From this result, it is possible to discard the tautomeric forms **II** and **IV**, the forms **I**, **III** and **V** remaining possible.

Moreover, the chemical shift of the proton (integration 1H) depends strongly on the nature of the nitrogen substituent ($\delta = 8-9$ in the case of aryl substituted guanidines and $\delta = 4.8-6.5$ for the alkylguanidines). This information suggests that this proton and the substituents are bonded to the same nitrogen atom and, among the three remaining forms, allows us to eliminate the tautomers **III** and **V**.

Dismissing the tautomers **III** and **V** is also possible on the basis of irradiation experiments performed in the particular case of **3a** ($R = {}^nBu$, $X = S$). Indeed, the methylen group bonded to the nitrogen atom appears as a doublet of triplets ($\delta = 3.1$), which is simplified into only one triplet after irradiation of the frequency of the NH or XH proton ($\delta = 5.7$) (Table 3). This result shows that this frequency corresponds to the NH group, and that this one and the methylen group are bonded together, thus excluding the structures **III** and **V**.

^{1}H NMR experiments and the results of the literature are then in good accordance, with the presence in solution of the phosphinyl or thiophosphinyl guanidines as the tautomeric form **I**. For this structure, two isomers (**Ia** and **Ib**) can be taken into consideration (Scheme 3). In order to confirm their possible formation in solution, we performed low temperature NMR experiments for compounds **3a**, **4i** and **4n** (Tables 2 and 3).

In the case of the N-phenyl-N'-diphenyl-thiophosphinyl guanidine **4i** ($R = Ph$, $R' = H$, $X = S$), the ^{1}H NMR investigations show that, at temperatures lower than $-10\,°C$, the signal of the NH_2 protons ($\delta = 6.2$) is split into two peaks ($\Delta_{1/2} = 12\,Hz$), one at high field ($-80\,°C$, 1H, $\delta = 6.5$) and one at low field ($-80\,°C$, 1H, $\delta = 7.6$). The signal of the NH proton is not split, but shifted (from $\delta = 8.5$ to $\delta = 9.2$). This result suggests the existence of two different protons for the NH_2 group.

Table 2
^{1}H NMR low temperature studies for the thiophosphinyl guanidine **4i** and the phosphinyl guanidine **4n** (acetone-d_6)

Guanidine	$\delta\ NH_2$		$\delta\ NH$	
	25 °C	−80 °C	25 °C	−80 °C
4i	6.2 bs	6.5 s, 7.6 s	8.5 d	9.2 d
4n	6.6 bs	6.7 s, 7.2 s	8.4 d	8.9 d

s, Singlet; bs, broad singlet; d, doublet.

Table 3
^{1}H NMR low temperature studies for the N-n-butyl N'-diphenyl-thiophosphinyl guanidine **3a** ($CDCl_3$); bs, broad singlet; dt, doublet of triplets

Guanidine	$\delta\ NH_2$		$\delta\ NH$		$\delta\ NH-CH_2$	
	25 °C	−50 °C	25 °C	−50 °C	25 °C	−50 °C
3a	5.9 bs	a	5.7 bs	a	3.1 dt [b]	2.7 dt, 3.2 dt

[a] Six broad singlets are obtained for the NH and NH_2 protons at $\delta = 4.60$, 4.85, 5.96, 6.70, 6.92, 7.03 (because of poor resolution of certain amino signals, the distinction between the NH and NH_2 protons has not been realized with good reliability).
[b] The ^{1}H NMR signal of the protons, which appears as a doublet of triplets, is simplified after irradiation of the NH proton, in only one triplet.

The explanation for this phenomenon could be the formation of a hydrogen bond between one of the NH_2 protons of the isomer **Ia** and the sulphur atom, this bond being more stable by cooling at $-80\,°C$. It is interesting to notice that the literature reports a similar intramolecular hydrogen bond for the thiophosphorylated isothioureas [13] $(RO)_2P(S)N=C(NH_2)SR'$. A second hypothesis related to the isomer **Ib** can also be advanced. Indeed, the observed differentiation of the two amino protons could disclose that, for **Ib** at $-80\,°C$, the free rotation between the imino carbon and the NH_2 group is limited because of a mesomeric effect.

The parallel ^{31}P NMR investigations for **4i** show at room temperature a single resonance ($\delta = 43$), the spectra being unchanged until $-60\,°C$. But, at $-80\,°C$, a second peak discloses the presence this time of the two isomers **Ia** and **Ib**, the latter appearing at $\delta = 40.1$ and the ratio between the two signals being 15:1. Surprisingly, we did not observe in the ^{1}H NMR spectrum at $-80\,°C$ any peaks corresponding to this second, albeit minor, ^{31}P NMR signal.

In the case of the corresponding oxo compound, the N-phenyl-N'-diphenylphosphinyl guanidine **4n** ($R = Ph$, $R' = H$, $X = O$), the ^{1}H NMR spectra show, as for **4i**, the presence of one of the two isomers **Ia** or **Ib**. At low temperature, the ^{31}P NMR spectrum confirms the presence of only one (one peak at $-80\,°C$, $\delta = 22$), in opposition to the result observed for **4i**. This difference in the ^{31}P NMR data between **4i** and **4n** seems to indicate that the presence of the two isomers **Ia** or **Ib** depends on X (O or S) at low temperature.

With N-alkyl N'-thiophosphinyl guanidines, slightly different behaviour can be noticed (Table 3). Thus, in the case of compounds **3a** ($R = {}^nBu$, $R' = H$, $X = S$), the ^{1}H NMR spectra show a decoalescence, at $-10\,°C$, for the doublet of triplets corresponding to the protons of the methylen group bonded to the nitrogen atom ($\delta = 3.1$; $HN-CH_2-CH_2-$). Indeed, this signal is observed, at $-50\,°C$, as a pair of doublets of triplets (ratio 90:10) with the same coupling constant ($^3J_{HNCH} = 6.3\,Hz$) at $\delta = 2.7$ and $\delta = 3.2$. Thus, in the case of
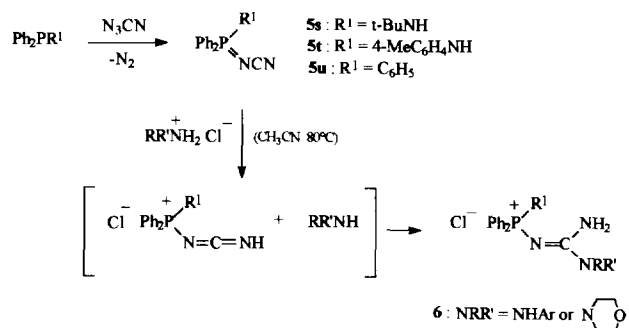
Scheme 4. Synthesis of alkyl- and arylamino N-cyano-diphenylphosphinimines 5s, 5t, of N-cyanotriphenylphosphinimine 5u, and of the corresponding phosphonioguanidines 6.

alkyl substituted guanidines, both isomers Ia and Ib are then present in solution. This result is also confirmed by the splitting, at $-10\,°C$, of the two amino group signals in six broad singlets, as expected, taking into account the differentiation between the two NH_2 protons.

3. Generalization of the reaction starting from cyanophosphinimines 5

In order to extend the application field of the reaction, we prepared the new N-cyanodiphenylphosphini-mines 5s and 5t by oxidation of the corresponding phosphines with cyanazide (Scheme 4).

These compounds react in analogy to 1 with arylammonium chloride or morpholinium chloride in boiling acetonitrile to form the corresponding phosphonioguani-dines 6 (Scheme 4) (Table 4). However, it was not possible, even using hard conditions, to perform the same reaction with primary alkyl ammonium chlorides. This method was applicable as well, starting from N-cyanotriphenylphosphinimine 5u [14], the guanidines obtained being limited, as for 5s and 5t, to the aryl and morpholino substituted phosphonioguanidines 6.

Table 4
Isolated yields after recrystallization [a] for alkyl- and arylamino N-cyanodiphenylphosphinimines 5s, 5t, and for the phosphonioguanidines 6

Compound	R^1	R	R′	Yield (%)
5s	^{t}BuNH			40
5t	4-MeC$_6$H$_4$NH			55
6s	^{t}BuNH	H	C$_6$H$_5$	87
6t	4-MeC$_6$H$_4$NH	H	C$_6$H$_5$	77
6u	C$_6$H$_5$	H	C$_6$H$_5$	81
6s′	^{t}BuNH	—N◯O		81
6u′	C$_6$H$_5$	—N◯O		76

[a] The formation rates, monitored by ^{31}P NMR, reach 100% for all the compounds 6 synthesized.
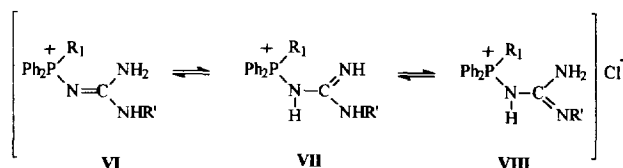
Scheme 5. Possible tautomeric structures for phosphonioguanidines 6s, 6t, 6u.

It was not our goal to realize an exhaustive tautomeric study of all the types of guanidine synthesized. However, in the case of aryl substituted guanidines 6s–u, among the three possible tautomeric forms (Scheme 5), it seems reasonable to discard the form VII, on the basis of ^{1}H NMR results, obtained at room temperature, which show the presence of one NH and one NH_2 groups. In the case of morpholino substituted guanidines 6s′–u′, the tautomer equivalent to VI is the only one possible.

4. Conclusion

Sodium diphenylcyanamidophosphinates 1 ($X = O$, S) react in the presence of aryl-, primary and secondary alkylammonium chlorides, and also alkyldiammonium dichlorides, to form the corresponding phosphinyl or thiophosphinyl guanidines 3 and 4. Spectroscopic results suggest for these molecules that only the tautomer I, in which the imino group is bonded to the phosphorus atom, is present in solution. Moreover, the NMR results show for the tautomer I, the presence of $syn/anti$ isomers at low temperature. The method which permits us to obtain a great variety of phosphinyl and thiophosphinyl guanidines with different substitution degrees on the nitrogen atoms is generalizable, via the new N-cyanophosphinimines 5, to the synthesis of phosphonioguanidines 6. All these molecules, because they combine a phosphorus and a guanidine part, could find agricultural and medicinal applications. At the present time they are tested in agrochemistry by Rhône-Poulenc.

Work is now in progress to synthesize precursors which could allow the extension of this method to the synthesis of derivatives, having two guanidine moieties attached to the phosphorus.

5. Experimental part

IR spectra: Carl-Zeiss Specord IR 75 Spectrometer. All IR spectra were taken as thin film in Nujol or in KBr tablets (ν(cm^{-1})). ^{1}H NMR spectra: AM-200 Bruker and Bruker 250 (for low temperature NMR) instruments (δ, external reference Me$_4$Si). ^{13}C$\{^1$H$\}$ NMR spectra: AM-200 Bruker (external reference

Me$_4$Si; s, singlet; bs, broad singlet; d, doublet; dt, doublet of triplets). ^{31}P{^{1}H} NMR spectra: Bruker AC-80 (external reference H$_3$PO$_4$ 80%).

Sodium diphenylcyanamidophosphinate **1a** and sodium diphenylcyanamidothiophosphinate **1b** [9], cyanazides [15] and the aminophosphines were prepared using known procedures, and their structures have been verified through NMR and IR spectra.

5.1. General method for the preparation of alkylammonium diphenylcyanamidophosphinates or alkylammonium diphenylcyanamidothiophosphinates 2

A mixture of **1a** (2.64 g, 10 mmol) or **1b** (2.80 g, 10 mmol) and alkylammonium chloride (10 mmol) in dry acetonitrile (20 ml) was refluxed for 1 h or stirred for 24 h at 20 °C. After warm filtration of the sodium chloride, the solvent was concentrated in vacuo, and oil or crystals obtained. Almost all oils were crystallized by addition of hexan or ether. The compounds thus obtained are pure and do not need recrystallization.

5.1.1. n-Butylammonium diphenylcyanamidothiophosphinate 2a
Yield 3.0 g (90%); oil. IR (capillary): ν = 2080, 2130 (CN). ^{31}P NMR (methanol): δ = 52.3. Anal. Found: P, 9.40. C$_{17}$H$_{22}$N$_3$PS (331.4) Calc.: P, 9.35%.

5.1.2. t-Butylammonium diphenylcyanamidothiophosphinate 2b
Yield 2.5 g (75%); m.p. 148 °C (methanol). IR (Nujol): ν = 2085, 2135 (CN). ^{31}P NMR (methanol): δ = 52.3. Anal. Found: P, 9.48. C$_{17}$H$_{22}$N$_3$PS (331.4) Calc.: P, 9.35%.

5.1.3. c-Hexylammonium diphenylcyanamidothiophosphinate 2c
Yield 3.4 g (95%); m.p. 119 °C (hexane–ether). IR (Nujol): ν = 2080, 2120 (CN). ^{31}P NMR (methanol): δ = 52.3. Anal. Found: P, 9.01. C$_{19}$H$_{24}$N$_3$PS (357.4) Calc.: P, 8.67%.

5.1.4. 1-8-Octamethylendiammonium bis(diphenylcyanamidothiophosphinate) 2d
Yield 1.4 g (42%); m.p. 154–155 °C (water). IR (Nujol): ν = 2090, 2160 (CN). ^{31}P NMR (methanol): δ = 53.6. Anal. Found: P, 9.43. C$_{34}$H$_{42}$N$_6$P$_2$S$_2$ (660.8) Calc.: P, 9.37%.

5.1.5. n-Butylammonium diphenylcyanamidophosphinate 2e
Yield 2.64 g (84%); m.p. 122 °C (methanol). IR (Nujol): ν = 2085, 2135 (CN). ^{31}P NMR (methanol): δ = 22.7. Anal. Found: P, 9.80. C$_{17}$H$_{22}$N$_3$OP (315.4) Calc.: P, 9.82%.

5.1.6. t-Butylammonium diphenylcyanamidophosphinate 2f
Yield 2.42 g (77%); m.p. 93 °C (methanol). IR (Nujol): ν = 2090, 2140 (CN). ^{31}P NMR (methanol): δ = 22.7. Anal. Found: P, 9.86. C$_{17}$H$_{22}$N$_3$OP (315.4) Calc.: P, 9.82%.

5.1.7. c-Hexylammonium diphenylcyanamidphosphinate 2g
Yield 3.20 g (95%); m.p. 130–131 °C (ether). IR (Nujol): ν = 2080, 2145 (CN). ^{31}P NMR (methanol): δ = 22.7. Anal. Found: P, 9.85. C$_{19}$H$_{24}$N$_3$OP (341.4) Calc.: P, 9.07%.

5.1.8. Octamethylendiammonium-1-8-bis(diphenylcyanamidophosphinate) 2h
Yield 2.89 g (46%); m.p. 150–151 °C (water/acetone). IR (Nujol): ν = 2095, 2160 (CN). ^{31}P NMR (methanol): δ = 24.07. Anal. Found: P, 9.74. C$_{34}$H$_{42}$N$_6$O$_2$P$_2$ (628.7) Calc.: P, 9.85%.

5.2. General method for the preparation of N-alkylphosphinyl or N-alkyl-thiophosphinyl guanidines 3

Alkylammonium diphenylcyanamido- or diphenylcyanamidothiophosphinates **2** (5 mmol) were heated to 10 °C above their respective melting points during 5–20 min. After cooling, the brown glass was dissolved in 50 ml chloroform, and the organic layer washed with 2 × 20 ml water. The organic layer was dried on sodium sulphate and concentrated in vacuo, affording an oil corresponding to phosphinyl or thiophosphinyl guanidines **3**. **3a** was crystallized from 5 ml methanol and recrystallized in n-hexan/toluene 1:1. **3d** was precipitated from acetone/water and recrystallized in 10 ml dry acetonitrile. **3f** was precipitated from acetone/water and recrystallized in dichloromethane (5 ml)/c-hexane (15 ml). **3e** is an oil. **3b** was recrystallized from 10 ml toluene. **3c** and **3g** were recrystallized from 5 ml dry methanol.

5.2.1. N-n-butyl N'-diphenylthiophosphinyl guanidine 3a
M.p. 102 °C (toluene/hexane). IR (Nujol): ν = 3415, 3280 (NH$_2$), 1615 (C:N). ^{31}P NMR (CHCl$_3$): δ = 40.2. ^{1}H NMR (CDCl$_3$): δ = 0.9 (t, 3H, CH_3CH$_2$), 1.2–1.5 (m, 2H, CH$_3$CH_2), 1.5–1.7 (m, 2H, CH$_2$CH_2CH$_2$), 3.1 (dt, $^3J_{HNCH}$ = 6.2 Hz, 2H, CH_2NH), 5.7 (bs, 1H, CH$_2$NH), 5.9 (bs, 2H, NH$_2$), 7.3 (m, 6H, aromatic), 7.8–8.0 (m, 4H, aromatic). ^{13}C NMR (CDCl$_3$): δ = 158.4 (s, C=N), 138.5 (d, $^1J_{PC}$ = 108.6 Hz, i-C), 130.6 (d, $^2J_{PC}$ = 10.9 Hz, o-C), 128.0 (d, $^3J_{PC}$ = 12.9 Hz, m-C), 130.4 (s, p-C), 41.3 (s, CH_2NH), 31.5 (s, CH_2CH$_2$NH), 20.0 (s, CH$_3$CH_2), 13.8 (s, CH_3CH$_2$). Anal. Found: C, 61.9; H, 6.65; N, 12.30; P, 9.31. C$_{17}$H$_{22}$N$_3$PS (331.4) Calc.: C, 61.61; H, 6.69; N, 12.68; P, 9.35%.

5.2.2. N-t-butyl N'-diphenylthiophosphinyl guanidine 3b

M.p. 159–160 °C (toluene). IR (Nujol): $\nu = 3380$, 3265 (NH$_2$), 1605 (C:N). ^{31}P NMR (CHCl$_3$): $\delta = 42.9$. ^{1}H NMR (CDCl$_3$): $\delta = 1.4$ (s, 9H, (CH_3)$_3$), 4.8 (bs, 1H, (CH$_3$)$_3$CNH), 5.8 (bs, 2H, NH_2), 7.4 (m, 6H, aromatic), 7.8–8.0 (m, 4H, aromatic). ^{13}C NMR (CDCl$_3$): $\delta = 157.6$ (s, $C = N$), 138.5 (d, $^1J_{PC} = 108.9$ Hz, i-C), 130.7 (d, $^2J_{PC} = 10.9$ Hz, o-C), 127.5 (d, $^3J_{PC} = 12.9$ Hz, m-C), 130.4 (d, $^4J_{PC} = 2.7$ Hz, p-C), 51.4 (s, C(CH$_3$)$_3$), 29.5 (s, C(CH_3)$_3$). Anal. Found: C, 61.75; H, 6.82; N, 12.55; P, 9.23. C$_{17}$H$_{22}$N$_3$PS (331.4) Calc.: C, 61.61; H, 6.69; N, 12.68; P, 9.35%.

5.2.3. N-c-hexyl N'-diphenylthiophosphinyl guanidine 3c

M.p. 172–173 °C (methanol). IR (Nujol): $\nu = 3360$, 3245 (NH$_2$), 1605 (C:N). ^{31}P NMR (CHCl$_3$): $\delta = 41.3$. ^{1}H NMR (CDCl$_3$): $\delta = 1.0$–1.4 (m, 5H, c-hexyl), 1.5–2.0 (m, 5H, c-hexyl), 3.5 (bs, 1H, CHNH), 6.2 (bs, 2H, NH_2), 6.5 (bs, 1H, CHNH), 7.4 (m, 6H, aromatic), 7.7–7.9 (m, 4H, aromatic). ^{13}C NMR (CDCl$_3$): $\delta = 151.3$ (s, $C = N$), 132.6 (d, $^1J_{PC} = 108.7$ Hz, i-C), 124.5 (d, $^2J_{PC} = 10.8$ Hz, o-C), 122.1 (d, $^3J_{PC} = 12.9$ Hz, m-C), 124.3 (s, p-C), 44.3 (s, HNCH<), 26.9 (s, HNCHCH$_2$), 19.4 (s, HNCHCH$_2$$CH_2$), 18.6 (s, HNCHCH$_2CH_2$$CH_2$). Anal. Found: C, 63.38; H, 6.71; N, 11.62; P, 9.25. C$_{19}$H$_{24}$N$_3$PS (357.4) Calc.: C, 63.84; H, 6.77; N, 11.76; P, 8.67%.

5.2.4. 1,8-N^1,N^2-octamethylene bis(N'^{1},N'^{2}-diphenyl-thiophosphinyl) guanidine 3d

M.p. 161–162 °C (acetonitrile). IR (Nujol): $\nu = 3415$, 3280 (NH$_2$), 1620 (C:N). ^{31}P NMR (CHCl$_3$): $\delta = 39.7$. ^{1}H NMR (CDCl$_3$): $\delta = 1.25$–1.5 (m, 12H, NHCH$_2$(CH_2)$_6$CH$_2$NH), 3.2 (dt, $^3J_{HNCH} = 5.2$ Hz, 4H, NHCH_2(CH$_2$)$_6$CH_2NH), 5.7 (bs, 6H, CH$_2$NH, NH_2), 7.2–7.4 (m, 12H, aromatic), 7.7–7.9 (m, 8H, aromatic). ^{13}C NMR (CDCl$_3$): $\delta = 158.3$ (s, $C = N$), 138.7 (d, $^1J_{PC} = 108.7$ Hz, i-C), 130.6 (d, $^2J_{PC} = 10.8$ Hz, o-C), 128.0 (d, $^3J_{PC} = 12.9$ Hz, m-C), 130.4 (d, $^4J_{PC} = 2.9$ Hz, p-C), 41.4 (s, NHCH$_2$(CH$_2$)$_6$$CH_2$NH), 28.9 (s, NHCH$_2$$CH_2$(CH$_2$)$_4$$CH_2CH_2$NH), 28.5 (s, (C$H_2$)$_2CH_2$(C$H_2$)$_2CH_2$(C$H_2$)$_2$), 26.2 (s, (CH$_2$)$_3$(C$H_2$)$_2$(CH$_2$)$_3$). Anal. Found: C, 61.69; H, 6.34; N, 12.61; P, 9.53. C$_{34}$H$_{42}$N$_6$P$_2$S$_2$ (660.8) Calc.: C, 61.80; H, 6.41; N, 12.72; P, 9.37%.

5.2.5. N-n-butyl N'-diphenylphosphinyl guanidine 3e

Oil. IR (capillary): $\nu = 3300$, 3250 (NH$_2$), 1615 (C:N). ^{31}P NMR (methanol): $\delta = 20.8$.

5.2.6. N-t-butyl N'-diphenylphosphinyl guanidine 3f

M.p. 179–180 °C (CH$_2$Cl$_2$/c-hexane). IR (Nujol): $\nu = 3440$, 3265 (NH$_2$), 1605 (C:N). ^{31}P NMR (CHCl$_3$): $\delta = 20.8$. ^{1}H NMR (CDCl$_3$): $\delta = 1.3$ (s, 9H, (CH_3)$_3$), 5.6 (d, $^4J_{PH} = 5.3$ Hz, 1H, PN:CNH), 5.8 (bs, 2H, NH_2), 7.3 (m, 6H, aromatic), 7.8–7.9 (m, 4H, aromatic).

^{13}C NMR (CDCl$_3$): $\delta = 158.1$ (s, $C = N$), 137.4 (d, $^1J_{PC} = 131.3$ Hz, i-C), 131.0 (d, $^2J_{PC} = 9.5$ Hz, o-C), 129.0 (d, $^3J_{PC} = 12.3$ Hz, m-C), 130.4 (d, $^4J_{PC} = 2.5$ Hz, p-C), 50.7 (s, C(CH$_3$)$_3$), 29.4 (s, C(CH_3)$_3$). Anal. Found: C, 64.43; H, 6.89; N, 12.95; P, 10.06. C$_{17}$H$_{22}$N$_3$OP (315.4) Calc.: C, 64.75; H, 7.03; N, 13.32; P, 9.82%.

5.2.7. N-c-hexyl N'-diphenylphosphinyl guanidine 3g

M.p. 188–189 °C (methanol). IR (Nujol): $\nu = 3360$, 3245 (NH$_2$), 1605 (C:N). ^{31}P NMR (CHCl$_3$): $\delta = 21$. ^{1}H NMR (CDCl$_3$): $\delta = 1.0$–1.5 (m, 5H, c-hexyl), 1.4–1.7 (m, 3H, c-hexyl), 1.7–2.1 (m, 2H, c-hexyl), 3.6 (bs, 1H, NHCH<), 5.9 (bs, 2H, NH_2), 6.1 (bs, 1H, CHNH), 7.3 (m, 6H, aromatic), 7.7–7.9 (m, 4H, aromatic). ^{13}C NMR (CDCl$_3$): $\delta = 157.9$ (s, $C = N$), 137.5 (d, $^1J_{PC} = 131.2$ Hz, i-C), 131.0 (d, $^2J_{PC} = 9.4$ Hz, o-C), 128.0 (d, $^3J_{PC} = 12.3$ Hz, m-C), 130.4 (d, $^4J_{PC} = 2.7$ Hz, p-C), 49.8 (s, HNCH <), 33.0 (s, HNCHCH$_2$), 25.6 (s, HNCHCH$_2$$CH_2$), 24.9 (s, HNCHCH$_2CH_2$$CH_2$). Anal. Found: H, 7.01; N, 12.03; P, 9.11. C$_{19}$H$_{24}$N$_3$OP (341.4) Calc.: C, 66.85; H, 7.09; N, 12.31; P, 9.07%.

5.3. General method for the preparation of N-morpholino, N-aryl phosphinyl guanidines and N-aryl thiophosphinyl guanidines 4

A mixture of sodium diphenylcyanamido- and diphenylcyanamidothiophosphinate 1 (X = O 2.64 g, 10 mmol; X = S 2.80 g, 10 mmol) and the appropriate morpholinium or arylammonium chloride (10 mmol) was refluxed, for 1 h in acetonitrile (20 ml) in the case of the synthesis of N-arylphosphinyl guanidines 4i, 4j, 4k, 4l, 4m, 4n, 4o, 4p, and for 2–3 h in acetonitrile in the case of N-morpholinophosphinyl guanidines 4q, 4r. In both cases, after warm filtration of the sodium chloride, the solvent was concentrated in vacuo. The guanidines 4 crystallized after addition of ether on the oils obtained. The compounds 4i, 4n, 4q, 4r were recrystallized from dry acetonitrile and all the others from methanol.

5.3.1. N-phenyl N'-diphenylthiophosphinyl guanidine 4i

M.p. 126 °C (acetonitrile). IR (Nujol): $\nu = 3440$, 3260, 3180 (NH$_2$), 1615 (C:N). ^{31}P NMR (methanol): $\delta = 43.0$. ^{1}H NMR (acetone-d_6): $\delta = 6.2$ (bs, 2H, NH_2), 7.1 (t, $^3J_{HH} = 7$ Hz, 1H, aromatic), 7.3–7.4 (m, 8H, aromatic), 7.6 (d, $^3J_{HH} = 10$ Hz, 2H, aromatic), 7.9–8 (m, 4H, aromatic), 8.5 (d, $^4J_{PH} = 5.8$ Hz, 1H, PN:CNH). ^{13}C NMR (CDCl$_3$): $\delta = 156.7$ (s, $C = N$), 137.4 (d, $^1J_{PC} = 108.5$ Hz, i-C), 130.7 (d, $^2J_{PC} = 10.9$ Hz, o-C), 128.2 (d, $^3J_{PC} = 13.0$ Hz, m-C), 130.7 (d, $^4J_{PC} = 2.9$ Hz, p-C), 137.0 (d, $^4J_{PC} = 1.3$ Hz, i-C of NC_6H$_5$), 123.9 (s, o-C of NC_6H$_5$), 129.5 (s, m-C of NC_6H$_5$), 125.8 (s, p-C of NC_6H$_5$). Anal. Found: C, 64.47; H, 5.05; N, 11.85; P, 8.90. C$_{19}$H$_{18}$N$_3$PS (351.4) Calc.: C, 64.94; H, 5.16; N, 11.96; P, 8.81%.

5.3.2. N-(p-tolyl) N'-diphenylthiophosphinyl guanidine 4j

M.p. 112 °C (methanol). IR (Nujol): $\nu = 3455$, 3300, 3235 (NH_2), 1600 (C:N). ^{31}P NMR ($CHCl_3$): $\delta = 42.1$. ^1H NMR ($CDCl_3$): $\delta = 2.3$ (s, 3H, CH_3), 5.8 (bs, 2H, NH_2), 7.0 (d, $N = 8$ Hz, 2H, aromatic), 7.1 (d, $N = 8$ Hz, 2H, aromatic) 7.3–7.4 (m, 6H, aromatic), 7.8–8.0 (m, 5H, aromatic and NH). ^{13}C NMR ($CDCl_3$): $\delta = 157.1$ (s, $C = N$), 138.2 (d, $^1J_{PC} = 108.6$ Hz, i-C), 130.8 (d, $^2J_{PC} = 10.9$ Hz, o-C), 128.2 (d, $^3J_{PC} = 12.9$ Hz, m-C), 130.6 (s, p-C), 134.2 (d, $^4J_{PC} = 1.2$ Hz, i-C: NC_6H_4Me), 124.5 (s, o-C: NC_6H_4Me), 130.1 (s, m-C: NC_6H_4Me), 135.9 (s, p-C: NC_6H_4Me), 20.9 (s, CH_3). Anal. Found: C, 65.22; H, 5.41; N, 11.50; P, 8.23. $C_{20}H_{20}N_3PS$ (368.4) Calc.: C, 65.74; H, 5.52; N, 11.50; P, 8.48%.

5.3.3. N-(o-tolyl) N'-diphenylthiophosphinyl guanidine 4k

M.p. 114–115 °C (methanol). IR (Nujol): $\nu = 3440$, 3300, 3250 (NH_2), 1615 (C:N). ^{31}P NMR ($CHCl_3$): $\delta = 43.0$. ^1H NMR ($CDCl_3$): $\delta = 2.2$ (s, 3H, CH_3), 5.5 (bs, 2H, NH_2), 7.2 (m, 4H, aromatic), 7.4–7.6 (m, 6H, aromatic), 7.8–8.0 (m, 4H, aromatic), 8.2 (bs, 1H, NH). ^{13}C NMR ($CDCl_3$): $\delta = 157.7$ (s, $C = N$), 138.1 (d, $^1J_{PC} = 108.1$ Hz, i-C), 130.8 (d, $^2J_{PC} = 10.8$ Hz, o-C), 128.1 (d, $^3J_{PC} = 13.3$ Hz, m-C), 130.7 (d, $^4J_{PC} = 2.8$ Hz, p-C), 135.5 (d, $^4J_{PC} = 1.7$ Hz, C_1), 137.2 (s, C_2), 131.3 (s, C_3), 127.1 (s, C_4), 127.6 (s, C_5), 127.1 (s, C_6), 22.6 (s, CH_3). Anal. Found: C, 65.43; H, 5.49; N, 11.38; P, 8.57. $C_{20}H_{20}N_3PS$ (368.4) Calc.: C, 65.74; H, 5.52; N, 11.50; P, 8.48%.

5.3.4. N-(4-chloro-phenyl) N'-diphenylthiophosphinyl guanidine 4l

M.p. 137–138 °C (methanol). IR (Nujol): $\nu = 3435$, 3300, 3250 (NH_2), 1615 (C:N). ^{31}P NMR ($CHCl_3$): $\delta = 43.0$. ^1H NMR ($CDCl_3$): $\delta = 5.9$ (bs, 2H, NH_2), 7.1 (d, $N = 8.8$ Hz, 2H, aromatic), 7.2 (d, $N = 8.8$ Hz, 2H, aromatic), 7.3–7.4 (m, 6H, aromatic), 7.8–8.0 (m, 5H, aromatic and NH). ^{13}C NMR ($CDCl_3$): $\delta = 156.2$ (s, C=N), 137.4 (d, $^1J_{PC} = 108.7$ Hz, i-C), 130.7 (d, $^2J_{PC} = 11.1$ Hz, o-C), 128.2 (d, $^3J_{PC} = 13.0$ Hz, m-C), 130.9 (d, $^4J_{PC} = 2.9$ Hz, p-C), 135.9 (d, $^4J_{PC} = 0.9$ Hz, i-C of NC_6H_4Cl), 130.4 (s, o-C of NC_6H_4Cl), 139.2 (s, m-C of NC_6H_4Cl), 130.4 (s, p-C of NC_6H_4Cl). Anal. Found: C, 58.89; H, 4.34; N, 10.85; P, 7.89. $C_{19}H_{17}ClN_3PS$ (385.9) Calc.: C, 59.14; H, 4.44; N, 10.89; P, 8.03%.

5.3.5. N-(4-bromo-phenyl) N'-diphenylthiophosphinyl guanidine 4m

M.p. 156–157 °C (methanol). IR (Nujol): $\nu = 3440$, 3300, 3240 (NH_2), 1615 (C:N). ^{31}P NMR ($CHCl_3$): $\delta = 43.8$. ^1H NMR ($CDCl_3$): $\delta = 5.9$ (bs, 2H, NH_2), 7.1 (d, $N = 8.8$ Hz, 2H, aromatic), 7.3–7.4 (m, 8H,

aromatic), 7.8–8.0 (m, 5H, aromatic and NH). ^{13}C NMR ($CDCl_3$): $\delta = 156.0$ (s, $C = N$), 137.6 (d, $^1J_{PC} = 108.7$ Hz, i-C), 130.6 (d, $^2J_{PC} = 11.1$ Hz, o-C), 128.2 (d, $^3J_{PC} = 13.0$ Hz, m-C), 130.9 (d, $^4J_{PC} = 3.1$ Hz, p-C), 136.3 (d, $^4J_{PC} = 1.1$ Hz, i-C of NC_6H_4Br), 132.3 (s, o-C of NC_6H_4Br), 124.9 (s, m-C of NC_6H_4Br), 118.4 (s, p-C of NC_6H_4Br). Anal. Found: C, 52.91; H, 3.94; N, 9.81; P, 6.95. $C_{19}H_{17}BrN_3PS$ (430.3) Calc.: C, 53.03; H, 3.98; N, 9.76; P, 7.10%.

5.3.6. N-phenyl N'-diphenylphosphinyl guanidine 4n

M.p. 193–194 °C (acetonitrile). IR (Nujol): $\nu = 3455$, 3315, 3200 (NH_2), 1650 (C:N). ^{31}P NMR (methanol): $\delta = 21.9$. ^1H NMR ($CDCl_3$): $\delta = 6.6$ (bs, 2H, NH_2), 7.1 (t, $^3J_{HH} = 6.5$ Hz, 1H, aromatic), 7.2–7.4 (m, 10H, aromatic), 7.8–7.9 (m, 4H, aromatic), 8.4 (d, $^4J_{PH} = 5.1$ Hz, 1H, NH). ^{13}C NMR ($CDCl_3$): $\delta = 156.4$ (s, $C = N$), 136.3 (d, $^1J_{PC} = 131.8$ Hz, i-C), 131.1 (d, $^2J_{PC} = 9.7$ Hz, o-C), 128.3 (d, $^3J_{PC} = 12.5$ Hz, m-C), 130.8 (d, $^4J_{PC} = 2.7$ Hz, p-C), 139.1 (d, $^4J_{PC} = 1.4$ Hz, i-C: NC_6H_5), 121.2 (s, o-C: NC_6H_5), 128.8 (s, m-C: NC_6H_5), 123.4 (s, p-C: NC_6H_5). Anal. Found: N, 12.28; P, 9.40. $C_{19}H_{18}N_3OP$ (335.3) Calc.: N, 12.53; P, 9.24%.

5.3.7. N-(4-chloro-phenyl) N'-diphenylphosphinylguanidine 4o

M.p. 178–179 °C (methanol). IR (Nujol): $\nu = 3425$, 3315, 3195 (NH_2), 1655 (C:N). ^{31}P NMR ($CHCl_3$): $\delta = 22.9$. ^1H NMR ($CDCl_3$): $\delta = 6.4$ (bs, 2H, NH_2), 6.9–7.5 (m, 10H, aromatic), 7.7–8.0 (m, 4H, aromatic), 9.1 (bs, 1H, NH). ^{13}C NMR ($CDCl_3$): $\delta = 156.2$ (s, C=N), 135.9 (d, $^1J_{PC} = 132.3$ Hz, i-C), 130.9 (d, $^2J_{PC} = 9.8$ Hz, o-C), 128.4 (d, $^3J_{PC} = 12.3$ Hz, m-C), 131.1 (d, $^4J_{PC} = 3.2$ Hz, p-C), 138.2 (s, i-C of NC_6H_4Cl), 121.6 (s, o-C of NC_6H_4Cl), 128.6 (s, m-C of NC_6H_4Cl), 127.7 (s, p-C of NC_6H_4Cl). Anal. Found: C, 61.68; H, 4.56; N, 11.30; P, 8.50. $C_{19}H_{17}ClN_3OP$ (369.8) Calc.: C, 61.71; H, 4.63; N, 11.36; P, 8.38%.

5.3.8. N-(4-bromo-phenyl) N'-diphenylphosphinyl guanidine 4p

M.p. 196–197 °C (methanol). IR (Nujol): $\nu = 3425$, 3315, 3195 (NH_2), 1655 (C:N). ^{31}P NMR ($CHCl_3$): $\delta = 22.9$. ^1H NMR ($CDCl_3$): $\delta = 6.4$ (bs, 2H, NH_2), 7.2–7.4 (m, 10H, aromatic), 7.7–8.0 (m, 4H, aromatic), 9.1 (d, $^4J_{PH} = 4.1$ Hz, 1H, NH). ^{13}C NMR ($CDCl_3$): $\delta = 156.2$ (s, $C = N$), 135.9 (d, $^1J_{PC} = 132.4$ Hz, i-C), 130.9 (d, $^2J_{PC} = 9.8$ Hz, o-C), 128.5 (d, $^3J_{PC} = 12.6$ Hz, m-C), 131.2 (d, $^4J_{PC} = 3.4$ Hz, p-C), 138.7 (s, i-C of NC_6H_4Br), 131.5 (s, o-C of NC_6H_4Br), 121.9 (s, m-C of NC_6H_4Br), 115.3 (s, p-C of NC_6H_4Br). Anal. Found: C, 55.08; H, 4.14; N, 9.96; P, 7.55. $C_{19}H_{17}BrN_3OP$ (414.1) Calc.: C, 55.09; H, 4.14; N, 10.14; P, 7.48%.

5.3.9. (Morpholino)-N-(diphenylthiophosphinyl) amidine 4q

M.p. 209–210 °C (acetonitrile). IR (Nujol): $\nu = 3440$, 3380 (NH$_2$), 1625 (C:N). ^{31}P NMR (CHCl$_3$): $\delta = 41.1$. ^{1}H NMR (CDCl$_3$): $\delta = 3.5$ (t, 4H, CH_2NCH_2), 3.7 (t, 4H, CH_2OCH_2), 6.3 (bs, 2H, NH_2), 7.3 (m, 6H, aromatic), 7.8–8.0 (m, 4H, aromatic). ^{13}C NMR (CDCl$_3$): $\delta = 157.6$ (s, $C = N$), 138.7 (d, $^1J_{PC} = 116.7$ Hz, i-C), 130.6 (d, $^2J_{PC} = 10.9$ Hz, o-C), 128.1 (d, $^3J_{PC} = 12.9$ Hz, m-C), 130.5 (d, $^4J_{PC} = 2.8$ Hz, p-C), 44.3 (d, $^4J_{PC} = 1.7$ Hz, CH$_2$NCH$_2$), 66.3 (s, CH$_2$OCH$_2$). Anal. Found: C, 59.11; H, 5.99; N, 12.17; P, 8.65. C$_{17}$H$_{20}$N$_3$OPS (345.4) Calc.: C, 59.12; H, 5.84; N, 12.17; P, 8.97%.

5.3.10. (Morpholino)-N-(diphenylphosphinyl) amidine 4r

M.p. 225–227 °C (acetonitrile). IR (Nujol): $\nu = 3365$, 3305 (NH$_2$), 1660 (C:N). ^{31}P NMR (CHCl$_3$): $\delta = 21.9$. ^{1}H NMR (CDCl$_3$): $\delta = 3.5$ (t, 4H, CH_2NCH_2), 3.7 (t, 4H, CH_2OCH_2), 6.3 (bs, 2H, NH_2), 7.3 (m, 6H, aromatic), 7.8–8.0 (m, 4H, aromatic). ^{13}C NMR (CDCl$_3$): $\delta = 157.9$ (s, $C = N$), 137.2 (d, $^1J_{PC} = 131.5$ Hz, i-C), 130.9 (d, $^2J_{PC} = 9.3$ Hz, o-C), 128.0 (d, $^3J_{PC} = 12.4$ Hz, m-C), 130.6 (d, $^4J_{PC} = 2.7$ Hz, p-C), 41.5 (d, $^4J_{PC} = 1.7$ Hz, CH$_2$NCH$_2$), 66.4 (s, CH$_2$OCH$_2$). Anal. Found: C, 62.07; H, 6.00; N, 12.77; P, 9.35. C$_{17}$H$_{20}$N$_3$O$_2$P (329.3) Calc.: C, 62.00; H, 6.12; N, 12.76; P, 9.40%.

5.4. General method for the preparation of alkyl- and arylamino N-cyano-diphenylphosphinimines 5s, 5t

To a stirred solution of diphenylaminophosphine (10 mmol) in 50 ml dry acetonitrile was added dropwise a solution of cyanogen azide (10 mmol) in 10 ml dry acetonitrile under nitrogen. After the exothermic addition was complete, the mixture was allowed to stir at room temperature for 2 h more. After one night at room temperature, the product crystallized from the mother solution. After filtration, a recrystallization was performed in 30 ml dry acetonitrile.

5.4.1. Diphenyl-t-butylamino-N-cyanophosphinimine 5s

M.p. 208–209 °C (acetonitrile). IR (Nujol): $\nu = 2175$, 2165 (CN), 1260 (P=N). ^{31}P NMR (CHCl$_3$): $\delta = 21.9$. ^{1}H NMR (CDCl$_3$): $\delta = 1.3$ (s, 9H, CH_3), 3.0 (d, $^2J_{PH} = 7.8$ Hz, 1H, NH), 7.4–7.5 (m, 6H, aromatic), 7.8–8.0 (m, 4H, aromatic). ^{13}C NMR (CDCl$_3$): $\delta = 32.0$ (d, $^3J_{PC} = 4.3$ Hz, CH$_3$), 54.1 (d, $^2J_{PC} = 3.4$ Hz, C(CH$_3$)$_3$), 118.7 (s, NCN), 129.7 (s, $^1J_{PC} = 131.7$ Hz, i-C), 131.1 (d, $^2J_{PC} = 10.2$ Hz, o-C), 128.7 (d, $^3J_{PC} = 13.4$ Hz, m-C), 132.8 (d, $^4J_{PC} = 2.9$ Hz, p-C). Anal. Found: N, 13.84; P, 10.2. C$_{17}$H$_{20}$N$_3$P (297.34) Calc.: N, 14.13; P, 10.42%.

5.4.2. Diphenyl-p-tolylamino-N-cyanophosphinimine 5t

M.p. 208–209 °C (acetonitrile). IR (Nujol): $\nu = 2180$, 2165 (CN), 1280 (P=N). ^{31}P NMR (CHCl$_3$): $\delta = 19.72$. ^{1}H NMR (CDCl$_3$): $\delta = 2.2$ (s, 3H, CH_3), 6.2 (d, $^2J_{PH} = 10.2$ Hz, 1H, NH), 6.9 (s, 4H, aromatic), 7.4–7.6 (m, 6H, aromatic), 7.8–8 (m, 4H, aromatic). ^{13}C NMR (CDCl$_3$): $\delta = 20.7$ (s, CH_3), 118.7 (s, NCN), 134.2 (s, $^1J_{PC} = 172.7$ Hz, i-C), 132.1 (d, $^2J_{PC} = 10.5$ Hz, o-C), 129.1 (d, $^3J_{PC} = 13.7$ Hz, m-C), 129.9 (s, p-C), 128.2 (s, i-C: C_6H$_4$), 120.0 (d, $^3J_{PC} = 6.6$ Hz, o-C: C_6H$_4$), 133.2 (d, $^3J_{PC} = 2.9$ Hz, m-C: C_6H$_4$), 125.6 (s, p-C: C_6H$_4$). Anal. Found: N, 12.65; P, 9.36. C$_{20}$H$_{18}$N$_3$P (331.36) Calc.: N, 12.68; P, 9.40%.

5.5. General method for the preparation of N-morpholino- or N-arylphosphonioguanidines 6

N-cyano-diphenylphosphinimines 5 (2.5 mmol) were refluxed for seven days in acetonitrile (20 ml) in the presence of the morpholinium or arylammonium chloride (2.5 mmol). After concentration of the solvent in vacuo, the oily residues obtained were dissolved in CHCl$_3$ (40 ml), washed three times with water (20 ml), and the organic layer was dried on Na$_2$SO$_4$. After concentration, the guanidines 6 were isolated by crystallization from acetonitrile.

5.5.1. N-phenyl N'-(tertiobutylamino-diphenyl-phosphonio)guanidine chloride 6s

M.p. 235–236 °C (acetonitrile). IR (KBr): $\nu = 3300$, 3180, 3120 (NH$_2$), 1645 (C:N) 1170. ^{31}P NMR (CHCl$_3$): $\delta = 13.7$. ^{1}H NMR (CDCl$_3$): $\delta = 1.25$ (s, 9H, (CH_3)$_3$C), 6.32 (d, $^2J_{PH} = 4.4$ Hz, 1H, PNH), 7.14 (t, $^3J_{HH} = 7.2$ Hz, 1H, aromatic), 7.2 (s, 2H, NH_2), 7.35 (d, $J = 7.4$ Hz, 2H, aromatic), 7.42 (m, 6H, aromatic), 7.65 (d, $J = 7.8$ Hz, 2H, aromatic), 7.95 (m, 4H, aromatic), 9.6 (d, $^4J_{PH} = 7.5$ Hz, 1H, C$_6$H$_5$NH). ^{13}C NMR (CDCl$_3$): $\delta = 156.5$ (s, $C = N$), 129.6 (d, $^1J_{PC} = 133.3$ Hz, i-C), 132.3 (d, $^2J_{PC} = 10.2$ Hz, o-C), 128.8 (d, $^3J_{PC} = 13.2$ Hz, m-C), 132.6 (d, $^4J_{PC} = 4.2$ Hz, p-C), 138.6 (s, i-C of NC_6H$_5$), 122.1 (s, o-C of NC_6H$_5$), 128.5 (s, m-C of NC_6H$_5$), 123.8 (s, p-C of NC_6H$_5$), 54.7 (d, $^2J_{PC} = 3.9$ Hz, (CH$_3$)$_3$$C$), 31.8 (d, $^3J_{PC} = 4.7$ Hz, (CH_3)$_3$C). Anal. Found: C, 64.25; H, 6.83; N, 12.95. C$_{23}$H$_{28}$ClN$_4$P (426.93) Calc.: C, 64.71; H, 6.61; N, 13.12%. Molar mass 391 (FAB$^+$).

5.5.2. N-phenyl N'-diphenyl-p-tolylamino-phosphonioguanidine chloride 6t

M.p. 223–225 °C (acetonitrile). IR (KBr): $\nu = 3300$, 3180, 3060 (NH$_2$), 1635 (C:N) 1180. ^{31}P NMR (CHCl$_3$): $\delta = 13.7$. ^{1}H NMR (CDCl$_3$): $\delta = 2.15$ (s, 3H, CH_3), 6.75 (d, $N = 8.3$ Hz, 2H, aromatic), 6.95 (d, $N = 8.4$ Hz, 2H, aromatic), 7.06 (s, 2H, NH_2), 7.13 (t, $J = 7.2$ Hz, 1H, aromatic), 7.31 (d, $J = 8.1$ Hz, 2H, aromatic), 7.39 (m, 6H, aromatic), 7.54 (d, $J = 7.6$ Hz,

2H, aromatic), 7.89 (m, 4H, aromatic), 9.13 (d, $^2J_{PH}$ = 8.0 Hz, 1H, PNH), 9.61 (d, $^4J_{PH}$ = 7.2 Hz, 1H, C$_6$H$_5$NH). ^{13}C NMR (CDCl$_3$): δ = 156.4 (s, C = N), 124.8 (d, $^1J_{PC}$ = 135 Hz, i-C), 132.2 (d, $^2J_{PC}$ = 10.5 Hz, o-C), 129.2 (d, $^3J_{PC}$ = 13.7 Hz, m-C), 133.2 (d, $^4J_{PC}$ = 2.8 Hz, p-C), 138.3 (s, i-C of NC$_6$H$_5$), 122.2 (s, o-C of NC$_6$H$_5$), 128.6 (s, m-C of NC$_6$H$_5$), 124.2 (s, p-C of NC$_6$H$_5$), 136.2 (d, $^2J_{PC}$ = 2.0 Hz, i-C of C$_6$H$_4$Me), 120.4 (d, $^3J_{PC}$ = 7.2 Hz, o-C of C$_6$H$_4$Me), 129.8 (s, m-C of C$_6$H$_4$Me), 132.4 (s, p-C of C$_6$H$_4$Me), 20.65 (s, CH_3). Anal. Found: C, 67.82; H, 5.83; N, 12.13. C$_{26}$H$_{26}$ClN$_4$P (460.95) Calc.: C, 67.75; H, 5.69; N, 12.15%. Molar mass 425 (FAB$^+$).

5.5.3. N-phenyl N'-triphenylphosphonioguanidine chloride 6u

M.p. 162–163 °C (THF). IR (KBr): ν = 3470, 3270, 3110 (NH$_2$), 1620 (C:N) 1180. ^{31}P NMR (CHCl$_3$): δ = 17.6. ^{1}H NMR (CDCl$_3$): δ = 6.2 (bs, 2H, NH_2), 7.1 (t, 1H, aromatic), 7.3 (t, 3H, aromatic), 7.8 (m, 16H, aromatic), 10.7 (d, $^4J_{PH}$ = 7.6 Hz, 1H, NH). ^{13}C NMR (CDCl$_3$): δ = 156.9 (s, C = N), 126.9 (d, $^1J_{PC}$ = 105 Hz, i-C), 132.3 (d, $^2J_{PC}$ = 10.8 Hz, o-C), 129.8 (d, $^3J_{PC}$ = 11.9 Hz, m-C), 134.0 (d, $^4J_{PC}$ = 2.8 Hz, p-C), 137.7 (s, i-C of NC$_6$H$_5$), 122.7 (s, o-C of NC$_6$H$_5$), 128.5 (s, m-C of NC$_6$H$_5$), 124.6 (s, p-C of NC$_6$H$_5$). Anal. Found: C, 69.56; H, 5.35; N, 9.64. C$_{25}$H$_{23}$ClN$_3$P (431.9) Calc.: C, 69.52; H, 5.37; N, 9.73%.

5.5.4. C-(morpholino)-N-(diphenyl-tertiobutylamino-phosphonio)-amidine chloride 6s'

M.p. 203–204 °C (acetonitrile). IR (KBr): ν = 3300, 3100 (NH$_2$), 1640 (C:N). ^{31}P NMR (CHCl$_3$): δ = 12.6. ^{1}H NMR (CDCl$_3$): δ = 1.15 (s, 9H, (CH_3)$_3$C), 3.73 (t, $^3J_{HH}$ = 4.5 Hz, 4H, CH_2-N-CH_2), 3.84 (t, $^3J_{HH}$ = 4.5 Hz, 4H, CH_2-O-CH_2), 6.88 (d, $^2J_{PH}$ = 3.4 Hz, 1H, NH), 7.35 (bs, 2H, NH_2), 7.42 (m, 6H, aromatic), 7.8 (m, 4H, aromatic). ^{13}C NMR (CDCl$_3$): δ = 156.8 (d, $^2J_{PC}$ = 2.3 Hz, C =NP), 130.3 (d, $^1J_{PC}$ = 134.2 Hz, i-C), 132.0 (d, $^2J_{PC}$ = 9.9 Hz, o-C), 128.8 (d, $^3J_{PC}$ = 13.2 Hz, m-C), 132.2 (d, $^4J_{PC}$ = 2.8 Hz, p-C), 54.3 (d, $^2J_{PC}$ = 3.9 Hz, (CH$_3$)$_3$C), 31.7 (d, $^3J_{PC}$ = 4.9 Hz, (CH$_3$)$_3$C), 46.0 (s, CH$_2$-N-CH$_2$), 66.7 (s, CH$_2$-O-CH$_2$). Anal. Found: C, 59.90; H, 6.99; N, 12.97. C$_{21}$H$_{30}$ClN$_4$OP (420.92) Calc.: C, 59.92; H, 7.18; N, 13.31%. Molar mass 385 (FAB$^+$).

5.5.5. C-(morpholino)-N-(triphenylphosphonio)-amidine chloride 6u'

M.p. 196–197 °C (acetonitrile). IR (KBr): ν = 3450, 3180 (NH$_2$), 1660 (C:N). ^{31}P NMR (CHCl$_3$): δ = 15.9. ^{1}H NMR (CDCl$_3$): δ = 3.73 (t, 4H, $^3J_{HH}$ = 4.3 Hz, CH_2-N-CH_2), 3.93 (t, 4H, $^3J_{HH}$ = 4.5 Hz, CH_2-O-CH_2), 6.85 (bs, 2H, NH_2), 7.68 (m, 15H, aromatic). ^{13}C NMR (CDCl$_3$): δ = 156.3 (d, $^2J_{PC}$ = 4.0 Hz, C =NP), 125.6 (d, $^1J_{PC}$ = 103.8 Hz, i-C), 131.0 (d, $^2J_{PC}$ = 10.7 Hz, o-C), 129.7 (d, $^3J_{PC}$ = 12.8 Hz, m-C), 133.8 (d, $^4J_{PC}$ = 2.9 Hz, p-C), 66.2 (s, CH$_2$-O-CH$_2$), 46.0 (s, CH$_2$-N-CH$_2$). Anal. Found: C, 64.79; H, 5.88; N, 9.78. C$_{23}$H$_{25}$ClN$_3$OP (425.90) Calc.: C, 64.86; H, 5.92; N, 9.87%. Molar mass 390 (FAB$^+$).

Acknowledgements

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