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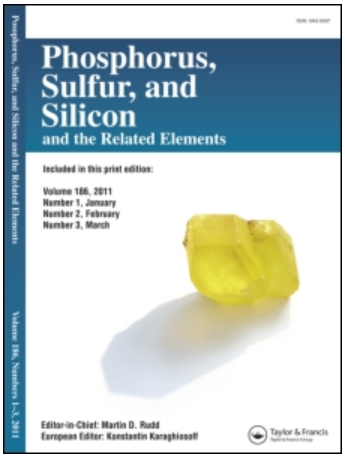

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REACTIVITY OF PHOSPHORYLATED PENTADIENYLIUM SALTS TOWARDS ISOCYANIDES: SYNTHESIS OF AMINOPYRIDINE PHOSPHONIUM SALTS

M. P. Fialon[a]; M. R. Mazieres[a]; C. Payrastre[a]; V. D. Romanenko[b]; Y. Madaule[a]; J. G. Wolf[a]; M. Sanchez[a]
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REACTIVITY OF PHOSPHORYLATED PENTADIENYLIUM SALTS TOWARDS ISOCYANIDES: SYNTHESIS OF AMINOPYRIDINE PHOSPHONIUM SALTS

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New cyanines dyes with phosphaimino substituents though engaged in delocalized system react with mono or diisocyanides in an aza-Wittig like reaction to give α-aminopyridines with phosphonium side chain. The final structure was determined by X ray.

Keywords: Cyanines dyes; Pentadienylium salts; Charged polyenic systems; Phosphaimines; Aza-Wittig reaction; Phosphonium salts

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INTRODUCTION

In the course of our work on charged polyenic systems[1], we recently obtained a new series of pentadienylium salts with enhanced conjugation pathway through the nitrogen atoms. These results confirm the selective reactivity of the carboxonium salts, our starting products, with amines[2] and imines reactants (amidine, guanidine, phosphaimine).[3]

Furthermore, the introduction of an iminophosphorane moiety in our structures offers an attractive alternative with their aza-Wittig like reactivity towards carbonyl compounds[3b,4]. This type of reaction has received considerable attention and has been applied to the synthesis of C=N

* Corresponding author

bonds.[5] Moreover, intramolecular reactions are useful ways for the synthesis of heterocycles.[6] A striking example in the recent literature is the iminophosphorane mediated synthesis of heterocycles developped by Molina et al.[7] The reaction of isocyanides with iminophosphoranes leads to C=C conjugated carbodiimides, which undergo an electrocyclic ring closure to give 2-aminopyridine derivatives.[8]

The aim of the work presented here is to describe the specific changes produced by the use of charged polyenic compounds in aza-Wittig reactions. In spite of the limited reaction pattern of the P=N bond engaged in this environment where only isocyanides were found to react, we obtained an access to a large range of phenylmethaneiminophosphonium salts with various 2-aminopyridine substituents. In the following, we shall describe the synthesis of mono and dicationic phosphonium salts containing one or two pyridine rings.

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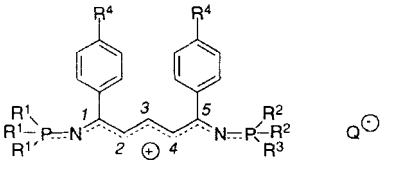
RESULTS AND DISCUSSION

I – Phosphorylated pentadienylium salts

1,5-pentadienylium salts are organic cations with conjugated double bonds in a *trans-trans* configuration. We introduced the phosphazenyl group ($R_3P{=}N$-) in both terminal group, thus lengthening the conjugation pathway.[3a]

Our synthetic scheme allows to obtain symmetrical **(1–4)** and non symmetrical **(5, 6)** phosphacyanines dyes[3b] (Scheme 1).

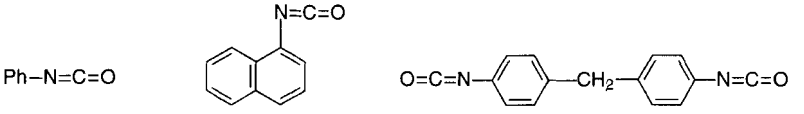


1	$R^1 = R^2 = R^3 = Ph$	$R^4 = OMe$	$Q = ClO_4$
2	$R^1 = R^2 = R^3 = Ph$	$R^4 = OMe$	$Q = CF_3SO_3$
3	$R^1 = R^2 = R^3 = Ph$	$R^4 = Me$	$Q = ClO_4$
4	$R^1 = R^2 = R^3 = nBu$	$R^4 = OMe$	$Q = ClO_4$
5	$R^1 = Ph \quad R^2 = R^3 = NMe_2$	$R^4 = OMe$	$Q = ClO_4$
6	$R^1 = R^3 = Ph \quad R^2 = NMe_2$	$R^4 = OMe$	$Q = ClO_4$

SCHEME 1

The spectroscopic parameters[3b] show that these derivatives are in *trans* configuration. The positive charge is strongly delocalized through the chain with a partial positive charge on phosphorus and a negative one on nitrogen and an alternate charge distribution on the pentamethine chain, positive for the odd carbons and negative for the even ones.

We have developped the reactivity of the salts **1–6** with isocyanides **a** and **b** and bis-isocyanide **c** (Scheme 2).



a **b** **c**

SCHEME 2

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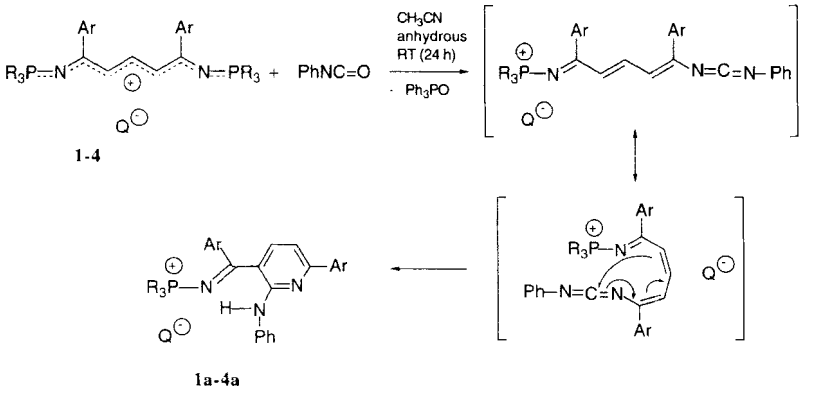
II –Reactivity of phosphorylated pentadienylium salts towards phenylisocyanide and naphtylisocyanide

II.1 Symmetrical pentadienylium salts 1–4

The 1,5-bis(iminophosphazenyl)pentadienylium salts **(1–4),** in acetonitrile solution, reacts at room temperature with one equivalent of phenylisocyanide to afford the α-aminopyridine phosphonium salts **(1a-4a).**

The reaction proceeds via an aza-Wittig reaction. The mechanism involves after elimination of phosphine oxyde, a carbodiimide intermediate formation. This intermediate undergoes an intramolecular cyclization in *cis* conformation followed by an hydrogen migration, leading to the formation of a trisubstituted pyridino phosphonium salt (Scheme 3). This reaction was previously described in a preliminary preceeding paper[3b] and at this stage, owing to the NMR spectroscopic data, we thought to have isolated the linear intermediate. In fact the latter isomerizes easily to give the pyridine ring as it was further demonstrated by an X ray structure determination presented hereafter.

It is noteworthy to observe that the second aminophosphazenic group is unreactive towards another equivalent of phenyl isocyanide. This is due to the aromatization of the chain in the pyridine ring. The positive charge is then located on the remaining phosphorus atom giving an unreactive ami-



SCHEME 3

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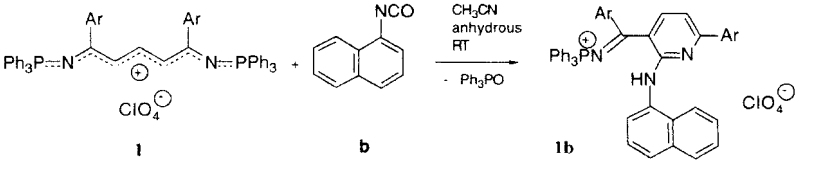
nophosphonium environment. Neverthless it is possible to take advantage of this situation in using the charged system to transport or solubilize the biologically active aminopyridine moiety (this group is the active part of the niflumic acid, used as an antiinflammatory compound).

When the reaction of the pentadienylium **1** is carried out with the naphtylisocyanide **b** we obtained, as expected, the α-aminophosphonium salt **1b** (Scheme 4).



SCHEME 4

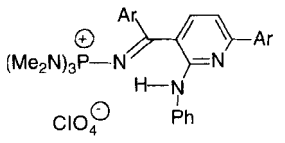
II.2 Non symmetrical pentadienylium salts

For compounds **5** and **6** the two different phosphazenyl groups are well distinguished by ^{31}P NMR; their spectra present two signals at the following respective chemical shifts:

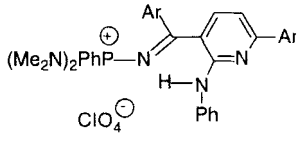
5: Ph_3P $\delta = 10.7$ $(Me_2N)_3P$ $\delta = 28.7$

6: Ph_3P $\delta = 2.0$ $(Me_2N)_2PhP$ $\delta = 28.8$

It was interesting to observe the relative reactivity of the two phosphazenyl groups. In fact, due to the greater extend of the delocalization on the nitrogen substituents than on the phenyl groups, the reaction is regiospecific, and we observed that the aza-Wittig reaction takes place only with the triphenylphosphazenyl group. After elimination of $Ph_3P(O)$ we isolate unambiguously the aminopyridine phosphonium salts **5a** and **6a** (Scheme 5).



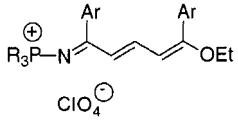
5a



6a

SCHEME 5

No reaction with phenylisocyanide is observed with phosphorylated hemicarboxonium salts like **7.** These compounds are characterized by a greater localization of the positive charge on the phosphorus atom which induce a localized polyene system in the chain. These results are in agreement with those obtained with the phosphonium salts **1a-4a.**



7

III – Reactivity towards bis-isocyanide c

Taking into account the good reactivity of phenylisocyanide **a,** the synthesis of symmetrical and non symmetrical bis-cations appears possible with bis-isocyanide. For this purpose we used the commercial 4, 4′-methylenebis-phenylisocyanide **c.**

III.1 Symmetrical bis-cations

The reaction, with pentadienylium **1,** is realized in the usual conditions with a stoichiometric ratio 2/1 and followed by ^{31}P NMR (Scheme 6). We observe the disappearence of the signal belonging to **1** ($\delta = 13$) and the appearence of two signals due to the formation of the expected phosphine

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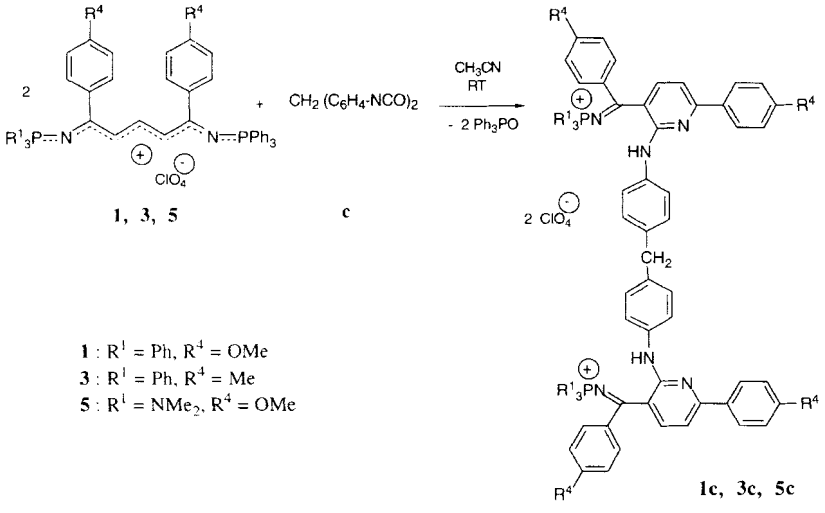
oxide (δ = 29.4) and bis-cation **1c** (δ = 26.3). After 24 hours the signal corresponding to the starting compound **1** disappears. Purification of **1c** is difficult. It needs several washing with pentane to eliminate the neutral phosphine oxide and further precipitation in ethanol. The *bis*-cations **3c** and **5c** are synthesized with the same procedure (Scheme 6).

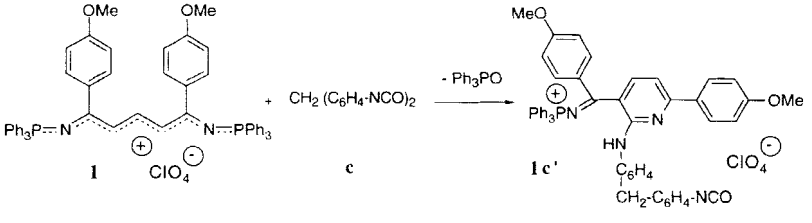


1 : R^1 = Ph, R^4 = OMe
3 : R^1 = Ph, R^4 = Me
5 : R^1 = NMe_2, R^4 = OMe

SCHEME 6

III.2 Non symmetrical bis-cations

In a first step we realized the synthesis of the monocation **1c'** in a 1:1 stoichiometric ratio of the reagents; only one isocyanide function could react. The ^{31}P NMR spectra shows that it is difficult to avoid the formation of the bis-cations **1c,** always present in a few percent (3 to 5%) (Scheme 7).



SCHEME 7

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In a second step compound **1c'** can then react with different pentadienylium moeties to give non symmetrical phosphonium salts. For example **1c'** react with **3** to give compound **8c** (see experimental part).

IV – Physicochemical studies

All compounds were identified by spectroscopic methods: NMR (^{1}H, ^{31}P, ^{13}C), Mass and UV-visible spectroscopies and finally for **3a** the solid crystalline structure was determined by X ray diffraction .

IV.1 NMR data

For clarity reasons, we will discuss here only NMR parameters of the pentadienylium **3** and those of the corresponding phosphonium salt **3a** (Table I). The same observations are made for all compounds described in this paper (cf experimental part).

As compared with the NMR data of the linear pentamethine chain of reagent **3**, the ^{31}P, ^{1}H and ^{13}C NMR data (Table I) are in good agreement with the the aza-Wittig reactivity leading to a cyclic aminopyridine structure of the phosphonium salt **3a**. The more significant changes are:

- the deshielding of the ^{31}P nucleus ($\Delta\delta^{31}P = 13.6$); the chemical shift (27.1 ppm) is characteristic of the phosphonium salt with a P-N bond.[9]
- the two protons H_3 and H_4 on the cycle, are coupled (AB system) with a constant of $^{3}J_{HH}$= 8.5 Hz due to their ortho position; the proton H_2 in 3 disappears whereas a NH is formed in **3a** (11.45 ppm). Moreover the methyl protons of the aryl substituents became unequal.
- in **3a**, like in linear cyanine systems, we observe two groups of carbons in ^{13}C NMR; the odd ones are deshielded whereas the even ones are shielded. Differences between **3** and **3a** are the particular deshielding of C_1, the shielding of C_3, C_5 due to their respective para and ortho position in the pyridine ring and the new environment of C_2which became an aromatic cyclic sp^2 carbon coupled with phosphorus ($^{3}J_{C2P}$ = 20 Hz).

For the non symmetrical compounds **5a** and **6a,** more complete proton NMR studies (2D ^{1}H-^{1}H Cosy correlation spectrum) were very helpful to assign all the NMR parameters.

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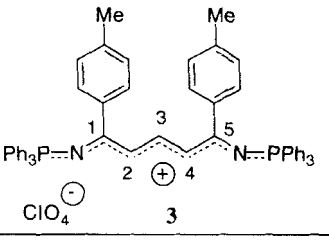
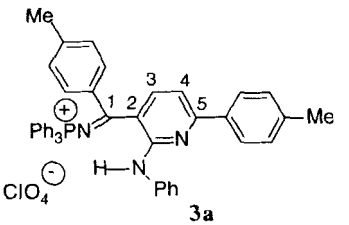
TABLE I ^{1}H, ^{13}C, ^{31}P NMR parameters of *pentadienylium* **3** and phosphonium salts **3a** in $CDCl_3$ δ (ppm), J (Hz)



3



3a

	δ	$^{(J)}HH$ or CP	δ	$^{(J)}HH$ or CP
Me	2.00 (s)		2.26 (s) 2.40 (s)	
H_3	7.31 (t)	(13.1)	7.14 (d)	(8.5)
H_4	5.58 (d)	(13.1)	7.29 (d)	(8.5)
H_2	5.58 (d)	(13.1)	-	
NH	-		11.45 (s)	
C_1	178.9 (d)	(4.4)	188.5 (d)	(7.2)
C_2	114.6 (d)	(15.0)	113.5 (d)	(20.0)
C_3	156.5 (s)		146.0 (s)	
C_4	114.6 (d)	(15.0)	110.9 (s)	
C_5	178.9 (d)	(4.4)	163.9 (s)	
NCN	-		156.0 (s)	
^{31}P	13.5 (s)		27.1 (s)	

IV.2 UV/visible spectroscopy

The phosphonium salts are coloured materials which strongly absorb in the UV/visible spectra (Table II). Their spectra present two maxima with almost the same intensity (ε = 20 000) at λ = 350–380 and λ = 450–475 nm corresponding to the π→π* transitions.

The comparison between the linear pentadienylium salts (489 < λ < 537) and their cyclic homologues prove that the ring closure implies an hypsochromic effect of about 30 to 70 nm for the highest wavelength, assessing that the delocalization of the positive charge on the conjugated chain, which is effective in the trans-pentadienylium chain, is switched by the pyridine ring.

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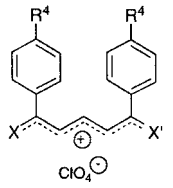
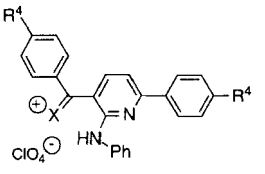
TABLE II UV/visible spectroscopy (CH_2Cl_2, 25 °C): λmax (nm), ε_{max} ($mol.l^{-1}.cm^{-1}$)





		λ_{max}	ε_{max}	λ_{max}	ε_{max}
1a	R^4 = OMe	515	68 200	472	14 500
	X = X' = Ph_3PN			371	14 700
3a	R^4 = Me	508	68 000	471	21 100
	X = X' = Ph_3PN			361	26 100
4a	R^4 = OMe	489	51 900	460	18 400
	X = X' = nBu_3PN			376	16 900
5a	R^4 = OMe	511	89 000	457	21 200
	X = Ph_3P			357	21 150
	X' = $(Me_2N)_3PN$				
6a	R^4 = OMe	537	58 200	463.5	21 200
	X = Ph_3P			371.5	25 200
	X' = $(Me_2N)_2PhPN$				

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V – Crystal and molecular structure of 3a

X Ray structure of compound **3a** confirms the cyclization of the pentadienylium chain to a 2-aminopyridine ring. Figure 1 shows a perspective view of cation with labelling scheme (H atoms are omitted for clarity), and tables III and IV present the main geometrical parameters.

The central $N_1N_2C_{19}C_{27-37}$ bond system is approximately planar (deviations from the best least-squares plane do not exceed 0.151(4) Å). The C_{39-44} benzene ring is almost orthogonal to the central plane. The phosphorus atom has a distorted tetrahedral coordination. The bond lengths distribution in the Ph_3P^+-N_1-C_{19} moiety of the cation is similar to those observed in cation Ph_3P^+-N=$C(Ph)_2$. The bond conformation for the N_3

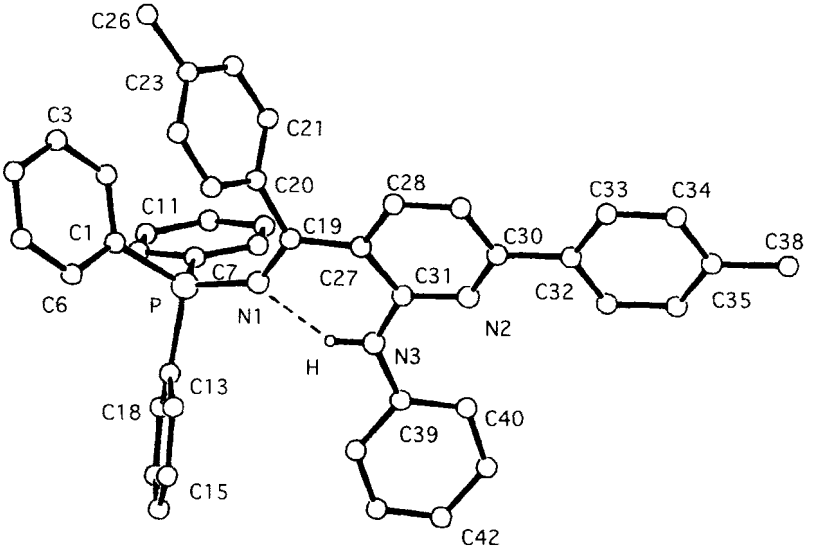

FIGURE 1 X Ray structure of compound **3a**

atom is trigonal planar (the sum of the bond angles is 358(4) Å). The N_3-C_{31}(1.354 Å) and N_3-C_{39} (1.413 Å) bonds are noticeably shortened in comparison to the value of 1.45 Å which is characteristic for a purely single N(sp^2)-C(sp^2) bond reflecting mainly n-π conjugation. A special feature of the molecular structure of this cation is the intramolecular N_3-H(N)...N_1 hydrogen bond (the geometrical parameters of this bond are : N_1...N_3 2.660 (4). N_3-H(N) 0.89 (4). N_1...H(N) 1.91(4) Å. N_3-H(N)...N_1 141(3°)). The value of N_1...N_3 distance is noticeably shorter than the average statistical value of 2.98 Å typical for the hydrogen bridges of this type and this is most likely evidence for its strength. Cations and anions are kept within the crystal by means of normal van der Waals interactions.

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TABLE III Principal interatomic distances (Å)

Bonds	*Distances*	*Bonds*	*Distances*
$P\text{-}C_1$	1.795	$C_{28}\text{-}C_{29}$	1.365
$P\text{-}C_7$	1.787	$C_{29}\text{-}C_{30}$	1.403
$P\text{-}C_{13}$	1.797	$C_{31}\text{-}N_2$	1.336
$P\text{-}N_1$	1.634	$N_2\text{-}C_{30}$	1.332
$N_1\text{-}C_{19}$	1.307	$C_{31}\text{-}N_3$	1.354
$C_{19}\text{-}C_{27}$	1.447	$N_3\text{-}C_{39}$	1.413
$C_{27}\text{-}C_{31}$	1.438	$N_3\text{-}H_{N3}$	0.89
$C_{27}\text{-}C_{28}$	1.412		

TABLE IV Principal angles (°)

Atoms	*Angles*	*Atoms*	*Angles*
$P\text{-}N_1\text{-}C_{19}$	135.4	$C_8\text{-}C_{29}\text{-}C_{30}$	119.2
$N_1\text{-}P\text{-}C_1$	120.1	$C_{29}\text{-}C_{30}\text{-}N_2$	122.1
$N_1\text{-}P\text{-}C_7$	107.2	$C_{27}\text{-}C_{31}\text{-}N_2$	122.7
$N_1\text{-}P\text{-}C_{13}$	101.5	$C_{31}\text{-}N_2\text{-}C_{30}$	119.6
$C_1\text{-}P\text{-}C_7$	108.1	$N_2\text{-}C_{31}\text{-}N_3$	118.3
$C_1\text{-}P\text{-}C_{13}$	110.6	$C_{31}\text{-}N_3\text{-}C_{39}$	131.3
$C_{19}\text{-}C_{27}\text{-}C_{28}$	119.4	$C_{31}\text{-}N_3\text{-}H_{N3}$	112
$C_{19}\text{-}C_{27}\text{-}C_{31}$	125.1	$C_{39}\text{-}N_3\text{-}H_{N3}$	115
$C_{27}\text{-}C_{28}\text{-}C_{29}$	120.7		

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CONCLUSION

The aza-Wittig reactivity of the phosphaimino cyanines dyes, though less general than with uncharged compounds, proved its interest in the reaction with isocyanides leading to new mono or di α-aminopyridines with a phosphonium side chain. Their usefulness like vectors for biologically active moieties, synthetic intermediates or bicephalic bolaform sur-

factants, i.e. compounds with two polar ends separated by a lipophilic chain, for the dicationic systems together with their properties in non linear optics are currently tested.

EXPERIMENTAL

Crystal data collection

All crystallographic measurements were made at ambient temperature (20° C) using Enraf Nonius CAD-4 diffractometer operating in the $\omega/2\theta$ scan mode (the ratio of the scanning rates $\omega/\theta = 1.2$). The intensity data were collected within the range $1 \leq \theta \leq 58°$ using graphite monochromated Cu-K_α radiation ($\lambda = 1.54184$ Å). Unit cell parameters were calculated from the setting angles of 24 strong, high-angle carefully-centered reflections. Three reflections were chosen as intensity standards and were measured every 3600 s of X ray exposure time, and three orientation control reflection were measured every 150 reflection. Neither significant crystal decay nor movement was noted. Intensities of 5405 (5240 unique) reflections were measured. All data were corrected for Lorentz, polarisation and extinction effects. The structure was solved by direct methods and refined by full-matrix least-squares techniques in the anisotropic approximation. In the refinement 4060 reflections with $I > 3\sigma$ (I) were used. All hydrogen atoms were located in the difference Fourier maps and included in the final refinement with the fixed positional and thermal parameters (only atom $H(N_3)$ was refined isotropically). Convergence was obtained at $R = 0.064$ and $R_w = 0.067$, GOF = 2.13 (unit weighting scheme: 482 refined parameters: largest shift/esd after final cycle 0.67). All crystallographic calculations were performed using the SDP-PLUS program package on a PDP-11/23+ computer. Full crystallographic data have been deposited at the Cambridge Crystallographic Data Centre.

Spectroscopies

Nuclear magnetic resonance spectra were obtained on multinuclear Bruker AC 200 spectrometer operating in the Fourier transform mode at 200.13 (^{1}H), 81.01 (^{31}P) and 50.32 (^{13}C) MHz. Chemical shifts in $CDCl_3$ or CD_3CN are expressed in ppm downfield from internal TMS for ^{1}H and

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^{13}C or external 85% H_3PO_4 for ^{31}P, coupling constants are in Hertz. UV/visible spectra were recorded on a Perkin-Elmer Lambda-17 spectrophotometer.

We note A_1, B_1 and A_2, B_2 the protons of the p(alkyl)phenyl substituents in the 1 and 5 positions respectively. However in some cases they are very close and it was difficult to assign unambiguously these positions. Anilino protons are indicated by PhNH and their position on the cycle is symbolized by Ci (ipso), Co (ortho), Cm (meta) and Cp (para).

Synthesis of monocations 1a-4a, 1b, 1c′:

The aza-Wittig reaction is carried under an argon atmosphere at room temperature. Isocyanide (**a** or **b** or **c**) is added to pentadienylium salt **(1–6)** in 1:1 stoechiometric ratio in CH_3CN solution. After few hours stirring, the solvent is evaporated. The residue is washed with pentane and crystallized in ethanol.

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1a: 2-N-anilino-6-paramethoxyphenyl-3-(methaniminotriphenylphosphoniumparamethoxyphenyl)- pyridine perchlorate

Yield: 75%; red crystals; m.p. 215 °C; **MS**: (DCI, NH_3), M^+ = 670, (100%).

$C_{44}H_{37}N_3O_6PCl$ (770.23), Calcd.: C, 68.61; H, 4.84; N, 5.46; Found: C, 67.67; H, 4.86; N, 5.69. **^{1}H** (CD_3CN) δ (ppm): 3.84 and 3.85 (s, 6H, MeO), 6.65 (d, 9.0, 2H, B_1), 7.02 (d, 9.0, 2H, B_2), 7.06 (d, 8.2, 1H, H_3), 7.20–7.40 (m, 6H, Cp, H_4, A_2, Cm), 7.94 (d, 9.0, 2H, A_1), 7.50–7.80 (m, 16H, PhP and Co), 8.80 (s, 1H, NH).

^{31}P (CD_3CN) δ (ppm): 27.5 (s).

^{13}C (CD_3CN) δ (ppm), J_{CP} (Hz) 56.2 and 566 (2s, MeO); 110.8 (s, C_4); 115.3 and 115.5 (2s, PhOMe); 116.2 (d, 15.8, C_2); 122.6 (s, Co PhNH); 124.4 (s, Cm PhNH); 124.5 (s, Cp PhNH); 129.6 and 130.1 (2s, PhOMe); 130.4 (s, Cq PhOMe); 130.8 (d, 13.3, Co PhP); 134.4 (d, 10.8, Cm PhP); 135.5 (Cp PhP); 140.2 (s, Ci PhNH); 142.9 (s, C_3); 154.2 (s, $C(N)_2$); 160.6, and 162.8 (2s, COMe); 165.2 (s, C_5) ; 188.7 (d, ^{2}J=7, C_1).

2a: 2-N-aniline-6-paramethoxyphenyl-3-(methaniminotriphenylphosphoniumparamethoxyphenyl)- pyridine trifluoromethanesulfonate

Yield: 60 %; orange crystals; m.p. 136 °C; **MS:** (DCI, NH_3), M^+ = 670 (100%)

$C_{47}H_{37}N_3O_5PF_3Sl$ (819.85), Calcd.: C, 65.93; H, 4.55; N, 5.13; Found: C, 65.45; H, 4.84; N, 4.71.

^{1}H ($CDCl_3$) b (ppm), J_{HH} (Hz): 3.85 and 3.87 (2s, 6H, MeO), 6.60 (d, 9.0, 2H, B_1), 7.00 (d, 9.0, 2H, B_2), 7.09 (d. 8.2, 1H, H_3), 7.10 (t, 7.0, 1H, Cp of PhNH), 7.30–7.80 (m, 22H, PhP, Co and Cm of PhNH, A_2 and H4), 8.10 (d, 9.0, 2H, A_1), 10.60 (s, 1H, NH).

^{31}P ($CDCl_3$) δ (ppm): 26.4 (s).

^{13}C ($CDCl_3$) δ (ppm), J_{CP} (Hz): 55.6 and 55.8 (s, MeO); 110.3 (s, C_4); 113.7 (d, ^{3}J=18.5, C_2); 114.3 and 114.5 (2s, PhOMe); 122.1 (s, Co PhNH); 122.4 (d, ^{1}J=101.3, Ci PhP); 124.4 (s, Cm PhNH); 128.5 (d, 12.9, Cq PhOMe); 128.3 (s, Cp PhNH); 128.8 and 128.9 (2s, PhOMe); 129.8 (s, Cp PhNH); 129.9 (s, Cq of PhOMe); 130.2 (d, ^{2}J=13.3, Co de PhP) . 133.1 (d, ^{3}J=10.8, Cm de PhP); 134.8 (d, 2.5, Cp PhP); 138.3 (s, Ci PhNH); 144.6 (s, C3); 155.3 (s, $C(N)_2$); 162.3 and 162.4 (2s, COMe), 162.5 (s, C5); 188. 1(C_1).

3a: 2-N-anilino-6-paramethylphenyl-3-(methaniminotriphenylphosphoniumparamethylphenyl)- pyridine perchlorate

Yield: 65%; orange crystals; m.p. 215 °C; **MS**: (DCI, NH_3), $M^+ = 638$ (54%); 361(100%) $C_{44}H_{37}N_3O_4PCl$ (738.23), Calcd: C, 71.59; H, 5.05; N, 5.69; Found: C, 71.38; H, 4.99; N, 5.54. **^{1}H** δ (ppm), J_{HH} (Hz): 2.26 and 2.40 (s, 6H, Me-Ph); 6.62 (m, 4H, PhMe); 7.14 (d, 8.5, 1H, H_3); 7.15 (m, 1H, PhNH); 7.29 (d, 8.5, 1H, H_4); 7.20–7.65 (m, 6H, PhMe and PhNH); 7.65–7.80 (m, 15H, PhP).

^{31}P δ (ppm): 27.1 (s).

^{13}C δ (ppm), J_{CP} (Hz): 221.4 and 21.6 (2s, MePh); 110.9 (s, C_4); 113.5 (d, ^{3}J=20.0, C_2); 122.2 (d, ^{1}J=100.0, Ci PhP); 122.3 (s, Co PhNH); 124.6 (s, Cm PhNH). 128.9 (s, Cp PhNH); 127.1, 128.9, 129.4 and 129.8 (4s, PhMe); 130.3 (d, ^{2}J=13.1, Co PhP); 133.1 (d, 3J=10.8, Cm PhP); 134.7 (d, ^{4}J=2.5, Cp PhP); 133.4 (s, Cq PhMe); 138.2 (s, Ci PhNH); 141.4 and 142.1 (2s, CMe); 163.9 (s, C_5); 146.0 (s, C_3); 156.0 (s, NCN); 188.5 (d, ^{2}J=17.4, C_1).

X ray: crystal data for $C_{44}H_{37}N_3P^+ClO^{4-}$, M = 738.2, monoclinic, a = 11.660 (9), b = 20.388 (7), c = 16.161 (6) Å, β = 100.95 (5)°, V = 3771.9 Å^3, Z = 4, d^c = 1.30 g.cm^{-3}, space group $P2^{1/c}$, μ = 16.8 cm^{-1}, F (000) = 1548.

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4a: 2-N-anilino-6-paramethoxyphenyl-3-(methaniminotris(nButylphosphonium) paramethoxyphenyl)-pyridine perchlorate

Yield: 80%; red crystals; m.p. 69 °C; **MS:** (DCI, NH3), M^+ = 610.(100%)

$C_{38}H_{49}N_3O_6PCl$ (710.26), Calcd.: C, 64.26; H, 6.95; N, 6.51; Found: C, 64.24; H, 6.86; N, 5.92. **^{1}H** (CD_3CN) δ (ppm), J_{HH} (Hz): 0.85 (t, 7.2, 9H, Me of Bu), 1.20–2.20 (m, 18H, CH_2 of Bu), 3.67 and 3.91 (2s, 6H, MeO), 7.04 (d, 9.0, 2H, B_1), 7.15 (d, 9.0, 2H, B_2), 7.20–7.65 (m, 7H, A_2, C3, C4, Cp, Cm), 7.70 (dd, 8.5, 2H, Co), 8.05 (d, 9.0, 2H, A_1).

^{31}P (CD_3CN) δ (ppm): 51.8 (s).

^{13}C (CD_3CN) δ (ppm), J_{CP} (Hz): 13.6 (d, ^4J = 7, Me of Bu), 24.8–25.8 (m, CH_2 (Bu)); 56.3 and 56.7 (2s, MeO); 110.9 (s, C_4); 114.8 (d, 6.2, C_2); 114.7, 114.9, 115,4 et 115,6 (4s, PhOMe); 123,3 (s, Co PhNH), 125,1 (s, Cm PhNH), 130,0 (s, Cp PhNH), 131.0 (s, Cq PhOMe); 130.4, 132.1, 132.1 et 132.8 (4s, PhOMe), 140.0 (s, Ci PhNH); 145.8 (s, C_3); 156.0 (s, NCN); 162.1 et 163.2 (2s, COMe); 163.5 (s, C_5); 180.0 (C_1).

5a: 2-N-anilino-6-paramethoxyphenyl-3-(methaniminotris(dimethylamino)phosphonium)- paramethoxyphenyl)pyridine perchlorate

Yield: 70 %; orange crystals; m.p. 225 °C, **MS:** (DCI, NH_3), M^+ = 571 (100%).

$C_{32}H_{40}N_6O_6PCl$ (671.14), Calcd: C, 57.27; H, 6.01; N, 12.52; Found C, 57.65; H, 6.02; N, 12.55.

^{1}H ($CDCl_3$) δ(ppm), J_{HH} (Hz): 2.65 (d, 10.00, 18H, MeN), 3.86 and 3.91 (2s, 6H, MeO), 6.97 (d, 8.9, 2H, B_1), $^3J_{PH}$ = 7.13 (d, 8.9, 2H, B_2), 7.15 (d, 8.5, 1H, H_3), 7.17 (t, 7.3, 1H, Cp of PhNH), 7.33 (d, 8.5, 1H, H_4), 7.39 (d, 8.9, 2H, A_2), 7.41 (dd, 8.4 and 7.3, 2H, Cm of PhNH), 7.65 (d, 8.4, 2H, Co of PhNH), 8.03 (d, 8.9, 2H, A_1), 10.46 (s, NH, 1H).

^{31}P ($CDCl_3$) δ(ppm): 32.2 (s).

^{13}C ($CDCl_3$) δ(ppm), J_{CP} (Hz): 37.7 (d, 3.32, MeN), 55.5 and 55.7 (2s, MeO), 110.0 (s, C_4), 113.5 (d, 15.0, C_2), 114.4 and 114.8 (2s, CH of PhOMe), 122.2 (s, Co of PhNH), 124.3 (s, Cm of PhNH), 129.8 and 130.1 (Cq of PhOMe), 129.1 and 129.5 (2s, CH of PhOMe), 138.5 (s, Ci of PhNH), 144.8 (s, C_3), 155.0 (s, NCN), 161.4, 162.0 and 162.1 (m, COMe and C_5), 183.1 (C_1).

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6a: 2-N-anilino-6-paramethoxyphenyl-3-(methanimino-bis(dimethyl-amino)phenylphosphoniumparamethoxyphenyl)pyridine perchlorate

Yield: 70 %; red powder; m.p. 202° C; **MS,** (DCI, NH_3), M^+ = 604 (64%), 212 (100%) $Me_2NP(Ph)NH_2^+$.

$C_{36}H_{39}N_5O_6PCl$ (704.17), Calcd: C, 61.41; H, 5.58; N, 9.95; Found C, 61.72; H, 5.47; N, 9.71.

^{1}H (CD_3CN) δ(ppm), J_{HH}, J_{HP}(Hz) : 2.60 (d, $^3J_{HP}$ = 10.3, 12H, MeN), 3.67 and 3.69 (2s, 6H, MeO), 7.00 (d, 9.0, 2H, B_1), 7.09 (d, 9.0, 2H, B_2), 7.10–7.15 (m, 2H, H_3 and Cp of PhNH), 7.33 (d, 1H, H_4), 7.35 (d, 9.0, 2H, A_2), 7.36 (m, 2H, Cm of PhNH), 7.52 (d, 8.5, 2H, Co of PhNH), 7.60–7.90 (m, 5H, PhP), 8.07 (d, 9.0. 2H, A_1), 10.80 (s, 1H, NH).

^{31}P (CD_3CN) δ(ppm): 35.7 (s).

^{13}C (CD_3CN) δ(ppm), J_{CP} (Hz): 37.5 (d, ^{2}J=4.0, NMe); 55.6 and 55.9 (2s, MeO); 110.2 (s, C_4); 114.4 and 114.9 (2s, CH PhOMe); 113.4 (d, 20.1, C_2); 122.0 (s, Co PhNH); 124.3 (s, Cm PhNH); 129.4 (s, Cp PhNH); 125.1 (s, Ci PhP); 129.9 and 130.0 (2s, Cq PhOMe); 130.3 (d, 13.8, Co PhP); 132.4 (d, 10.1, Cm PhP); 134.4 (d, 2.5, Cp PhP); 138.4 (s, Ci PhNH); 145.2 (s, C_3); 155.3 (s, NCN); 162.0 and 162.1 (2s, COMe); 162.3 (s, C_5), 184.4 (d, ^{2}J=4.2, C_1).

1b: 2-N-aminonaphtyl-6-paramethoxyphenyl-3-(methaniminotriphenyl-phosphoniumparamethoxyphenyl)pyridine perchlorate

Yield: 70 %; red powder; m.p. 145.5 °C; **MS,** (DCI, NH_3), M^+ = 720 (100%).

$C_{48}H_{39}N_3O_6PCl$ (820.29), Calcd: C, 70.28; H, 4.79; N, 5.12; Found: C, 69.17; H, 4.69; N, 4.94.

^{1}H ($CDCl_3$) δ(ppm), J_{HH} (Hz): 3.79 and 3.80 (2s, 6H, MeO), 6.64 (d, 8.9, 2H, B_1), 6.85 (d, 9.0, 2H, B_2), 7.04–7.80 (m, 25H, H_3, H_4, A_2, PhP and Naphtyl), 7.85 (d, 8.9, 2H, A_1), 8.01 (d, 1H), 11.2 (s, 1H, NH).

^{31}P ($CDCl_3$) δ(ppm): 27.3 (s).

^{13}C ($CDCl_3$) 6(ppm), J_{CP} (Hz): 55.5 and 55.8 (2s, MeO), 110.4 (s, C_4), 113.5 (d, ^3J = 19.3, C_2), 114.3 and 114.4 (2s, CH of PhOMe), 122.4 (d, ^1J = 101.1, Ci PhP), 121.5, 122.2, 125.6, 126.0, 126.1, 128.6 (6s, CH of Naphtyl), 128.2 and 128.5 (2s, Cq of PhOMe), 129.8 and 129.9 (2s, CH of PhOMe), 130.1 (d, ^2J = 13.2, Co of PhP), 133.1 (d, ^3J = 10.7, Cm of PhP), 145.2 (s, C_3), 157.0 (s, N=C-NH), 162.0, 162.4 and 162.6 (3s, COMe and C_5), 187.6 (d, ^2J = 6.9, C_1).

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1c': Methylphenylene-4-isocyanide-4'-(2-N-amino, 6-paramethoxy-phenyl, 3-methanimino-triphenyl-phosphonium)pyridine perchlorate

Yield: 30 %; red powder; m.p. 180° C; **MS**: (FAB, MNBA), $M^+ = 801$, (5%).

$C_{52}H_{42}N_4O_7PCl$ (901.36), Calcd.; C, 69.29; H, 4.70; N, 6.22; Found C, 70.18; H, 5.13; N, 5.05.

^{1}H ($CDCl_3$), J_{HH} (Hz): 3.77 and 3.83 (2s, 6H, MeOPh); 3.95 (m, 2H, CH_2); 6.60 (d, 2H, 9.0, B_1); 6.94 (d, 2H, 9, 0, B_2); 7.05 (d, 2H, 9.0, A_2); 7.17 (d, 1H, 8.5, H_3); 7.38 (d, 1H, 8.5, H_4); 7.00–7.10 (m, 4H, PhN); 7.20–7.50 (m, 4H, PhN); 7.52–7.70 (m, 15H, PhP); 8.05 (d, 2H, 9.0, A1); 10.70 (s, 1H, NH).

^{31}P ($CDCl_3$) δ (ppm): 26.4.

^{13}C ($CDCl_3$) δ (ppm), J_{CP} (Hz): 40.9 (s, CH_2); 55.6 and 55.8 (2s, MeOPh); 110.2 (s, C_4); 113.7 (d, 18.6, C_2); 114.4 and 114.5 (2s, CH PhOMe); 122.0, 129.3 and 129.7 (3s, CH diiso); 122.4 (d, 101.3, Ci PhP); 129.3 and 129.7 (2s, CH PhOMe); 130.2 (d, 13.0, Co PhP); 133.0 (d, 10.7, Cm PhP); 134.7 (d, 2.8, Cp PhP); 136.5 and 137.2 (2s, Cq diiso); 144.6 (s, C_3); 155.2 (s, NCN); 162.2 and 162.3 (2s, C-OMe); 162.5 (s, C_5); 187.5 (d, ^2J=7.0, C_1).

Synthesis of bis-cations 1c, 3c, *5c, 8c*

The aza-Wittig reaction is carried under an argon atmosphere at room temperature. 4,4'-methylenebis(phenylisocyanide) **c** is added to pentadienylium salt **(1, 3, 5)** in 1:2 stoechiometric ratio in CH_3CN solution. After few hours stirring, the solvent is evaporated. The residue is washed with pentane and crystallised in ethanol. For **8c, c** is added to **1c'** in 1:1 stoechiometric ratio.

1c: 4,4-methylphenylenebis(2-N-amino, 6-paramethoxy- phenyl, 3-methaniminotriphenyl-phosphonium)pyridine) diperchlorate

Yield: 75 %; orange powder; m.p. 205° C; **MS:** (FAB, MNBA), $M^{2+} = 676$ (100%). $C_{89}H_{74}N_6O_{12}P_2Cl_2$ (1552.47), Calcd.: C, 68.86; H, 4.80; N, 5.41; found C, 67.26; H, 4,.72; N, 5.42.

^{1}H ($CDCl_3$) δ(ppm), J_{HH} (Hz): 3.77 and 3.83 (2s, 12H, MeOPh); 3.90 (m, 2H, CH_2) ; 6.62 (d, 4H, 8.9, B_1); 6.96 (d, 4H, 8.9, B_2); 7.10 (d, 4H, 8.9, A_2); 7.10–7.40 (m, 4H, H_3 and H_4); 7.50–7.70 (m, 30H, PhP); 6.09–

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7.10 (m, 4H, PhN); 7.20–7.50 (m, 4H, PhN); 8.02 (d, 4H, 8.9, A_1); 10.70 (s, 2H, NH).

^{31}P (CDC_{l3}) δ (ppm): 26.3 (s).

^{13}C ($CDCl_3$) δ (ppm), J_{CP} (Hz): 40.9 (s, CH_2); 55.6 and 55.7 (2s, MeOPh); 110.2 (s, C_4); 113.7 (d, 18.8, C_2); 114.4 and 114.5 (2s, CH PhOMe); 122,.0 (s, Co diiso); 128.4, 128.7, 132.0 and 132.2 (4s, Ph); 129.3 and 129.7 (2s, PhOMe); 122.4 (d, 101.12, Ci PhP); 130.2 (d, 13.2, Co PhP); 133.0 (d, 10.7, Cm PhP); 134.8 (d, Cp PhP); 136.5 and 137.2 (2s, Cq diiso); 144.6 (s, C_3); 155.2 (s, NCN); 162.2 and 162.4 (2s, C-OMe); 162.5 (s, C_5); 187.5 (d, 7.1, C_1).

3c: 4,4-methylphenylenebis(2-N-amino,6-paramethyl- phenyl, 3-methaniminotriphenylphosphonium) pyridine diperchlorate

Yield: 60 %; red powder; m.p. 185° C; **MS**: (FAB, MNBA), M^{2+} = 644 (100%).

$C_{89}H_{74}N_6O_8P_2Cl_2$ (1488.47), Calcd.; C, 71.82; H, 5.01; N, 5.65; found C, 70.80; H, 4.98; N, 6.15.

^{1}H ($CDCl_3$) δ (ppm), J_{HH} (Hz): 2.24 and 2.37 (2s, 12H, MePh); 3.95 (m, 2H, CH_2); 6.60 (m, 8H, PhMe); 7.00–7.50 (m, 16H, PhMe, PhNH, H_3 and H_4); 7.50–7.70 (m, 30H, PhP); 7.97 (d, 9.0, 4H, PhMe); 11.47 (s, 2H, NH).

^{31}P ($CDCl_3$) δ (ppm): 26.9 (s).

^{13}C ($CDCl_3$) δ (ppm), J_{PC} (Hz): 41.2 (s, CH_2); 21.4 and 21.6 (2s, PhMe); 110.8 (s, C_4); 113.4 (d, 20.1, C_2); 127.2, 128.1, 129.4 and 129.8 (4s, CH PhMe); 122.2 (d, 100.9, Ci PhP); 128.4, 128.7, 132.0 and 132.2 (4s, Ph); 130.2 (d, 13.3, Co PhP); 133.0 (d, 10.4, Cm PhP); 134.8 (d, 2,3, Cp PhP); 122.1, 122.4 and 124.2 (3s, CH diiso); 141.3 and 142.1 (2s, C-Me); 145.9 (s, C_3); 156.0 (s, NCN); 163.5(s, C_5); 188.4 (C_1).

5c: 4,4′-methylphenylenebis(2-N-amino, 6-paramethoxyphenyl, 3-methaniminotris(dimethylamino)-phosphonium) pyridine diperchlorate

Yield: 50 %; orange powder; **MS**: (FAB, MNBA), M^{2+} = 661 (100%).

$C_{65}H_{80}N_{12}O_{12}P_2Cl_2$ (1354.29);Calcd.: C, 70.31; H, 4.91; N, 5.53; found C, 70.20; H, 4.96; N, 5.65.

^{1}H ($CDCl_3$) δ (ppm), J_{HH} (Hz): 2.62 (d, 36H, 10.0, NMe); 3.62 and 3.66 (2s, 12H, OMe); 4.00 (m, 2H, CH_2); 6.95 (d, 4H, 8.9, B_1); 7.10 (d, 4H, 8.9, B_2); 7.11 (d, 2H, H_3); 7.27 (d, 2H, H_4); 7.29 (d, 4H, 8.5, PhN); 7.35 (d,

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4H, 8.9, A_1) ; 7.61 (d, 4H, 8.5, PhN); 8.01 (d, 4H, 8.9, A_2); 10.6 (s, 2H, NH).

^{31}P ($CDCl_3$) δ (ppm): 32.1 (s).

^{13}C ($CDCl_3$) δ (ppm), J_{CP} (Hz): 37.6 and 37.7 (2s, NMe); 42.0 (s, CH_2); 55.5 and 5.8 (2s, MeO); 109.9 (s, C_4); 113.1 (d, 21.0, C_2); 114.4 and 114.8 (2s, CH PhOMe); 122.2 (s, CH PhNH); 129.4, 129.6, 129.9 (3s, CH PhOMe and PhNH); 130.0 (d, 13.1, Cq PhOMe); 130.1 (s, Cq PhOMe); 136.6 and 137.1 (2s, Cq PhNH); 145.0 (s, C_3); 155.1 (s, NCN); 161.5 and 161.9 (2s, C-OMe); 162.1 (s, C_5); 182.9 (s, C_1).

8c: Methylphenylene-4(2-N-amino, 6-paramethoxyphenyl, 3-methaniminotris(dimethylamino)-phosphonium)pyridine, 4'(2-N-amino, 6-paramethylphenyl, 3-methaniminotriphenylphosphonium) pyridine diperchlorate

Yield: 30 %; red powder; m.p. 185 °C; **MS:** (FAB, MNBA), M^{2+} = 661 (100%).

$C_{89}H_{74}N_6O_{10}P_2Cl_2$(1520.47), Calcd.: C, 70.31; H, 4.91; N, 5.53; found C, 70.20; H, 4.96; N, 5.65.

^{1}H ($CDCl_3$) δ (ppm), J_{HH} (Hz): (2s, 12H, MeOPh); 2.24 and 2.37 (2s, 6H, MePh); 3.76 and 3.82 (2s, 6H, MeO); 3.90–4.05 (m, 2H, CH_2); 6.61 (d, 9.0, 2H, PhOMe); 6.81 (m, 4H, PhMe); 6.90- 7.20 (m, 14H, PhOMe, PhNH, H_3 and H_4); 7.35-7.70 (m, 34H, PhNH and PhP); 7.80–8.00 (m, 4H, PhMe and PhOMe).

^{31}P ($CDCl_3$) δ (ppm): 26.3 and 26.9 (2s).

^{13}C ($CDCl_3$) δ(ppm), J_{CP} (Hz): 21.4 and 21.6 (2s, MePh); 40.9 (s, CH2); 55.6 and 55.8 (2s, MeOPh); 110.2 and 110.9 (2s, C'_4 and C_4); 113.2 and 113.7 (2d, 18.8, C'_2, 19.0, C_2); 114.4 and 114.5 (2s, CH PhOMe); 122.2 and 122.4 (2d, 101.2, Ci PhP); 127.1 and 128,.1 (2s, CH PhMe); 129.8 and 130.0 (2s, Ph); 130.2 (d, 13.2, Co PhP); 133.0 (d, 10.6, Cm PhP); 134.8 (s, Cp PhP); 141.1 and 141.3 (2s, C-Me); 144.6 and 145.9 (2s, C_3 and C'_3); 155.3 and 156.0 (2s, NCN); 162.2 and 162.4 (2s, C-OMe); 162.5 and 164.0 (2s, C_5 and C'_5) ; 187.5 (d, 7, 2, C_1); 188.2 (s, C'_1).

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