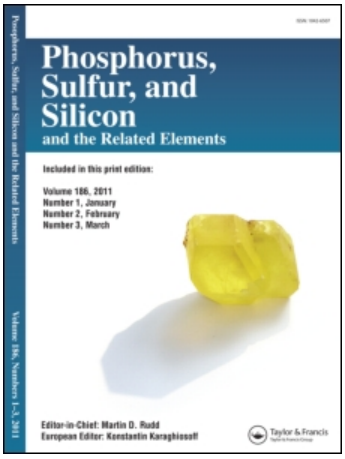

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

SYNTHESIS OF PENTADIENYLIUM IONS WITH N-SILYLATED PHOSPHAIMINES, CHARACTERIZATION AND REACTIVITY

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To cite this Article Fialon, M. P. , Maziéres, M. R. , Madaule, Y. , Payrastre, C. , Sanchez, M. , Wolf, J. G. , Gudima, A. O. and Romanenko, V. D.(1995) 'SYNTHESIS OF PENTADIENYLIUM IONS WITH N-SILYLATED PHOSPHAIMINES, CHARACTERIZATION AND REACTIVITY', Phosphorus, Sulfur, and Silicon and the Related Elements, 102: 1, 243 — 251
To link to this Article: DOI: 10.1080/10426509508042563
URL: http://dx.doi.org/10.1080/10426509508042563

Phosphorus, Sulfur, and Silicon, 1995, Vol. 102, pp. 243–251
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SYNTHESIS OF PENTADIENYLIUM IONS WITH N-SILYLATED PHOSPHAIMINES, CHARACTERIZATION AND REACTIVITY

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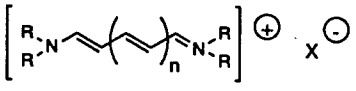
(Received January 17, 1995)

By condensation of a carboxonium salt with N-silylated phosphaimines new types of pentadienylium salts are obtained. These new compounds are characterized by NMR spectroscopy, UV and mass spectra. Their aza-Wittig reactivity towards isocyanides is described.

Key words: Cyanines dyes, pentadienylium salts, charged polyenic systems, phosphaimines, UV studies, aza-Wittig reaction.

INTRODUCTION

Polydienylium salts are organic compounds with an odd number of more or less substituted conjugated double bonds of general structure:

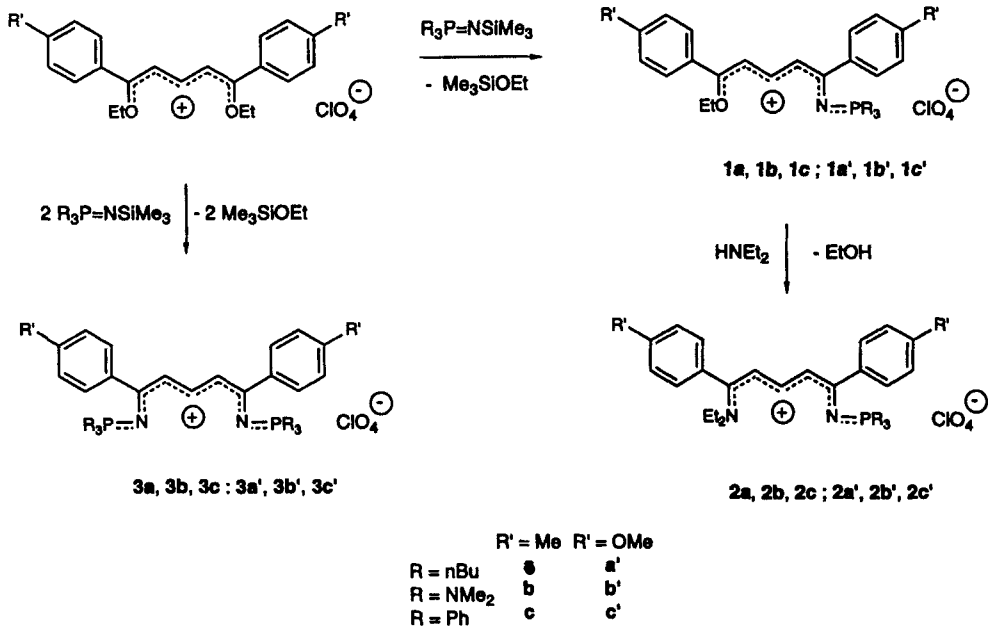


They have numerous applications mainly in chemistry and photophysics (dyes, photosensitizers, nonlinear optic) and also exhibit anthelmintic properties. We specially developed the synthesis of pentadienylium salts (n = 1).[1] The aim of our work is now to introduce some dicoordinated nitrogen like guanidines $(R_2N)_2C{=}N\text{-}SiMe_3$ and phosphaimines for it seems that extension of the conjugated system and introduction of an heteroatom like phosphorus can induce some new properties. Our interest is particularly focused on pentadienylium salts with P—N bonds; we present here the synthesis of nonsymmetric and symmetric ones with three different N-silylated phosphaimines $R_3P{=}NSiMe_3$ (R = n-butyl, N-dimethylamino, phenyl) and also with $(Me_2N)_2{-}P(Ph){=}NSiMe_3$.

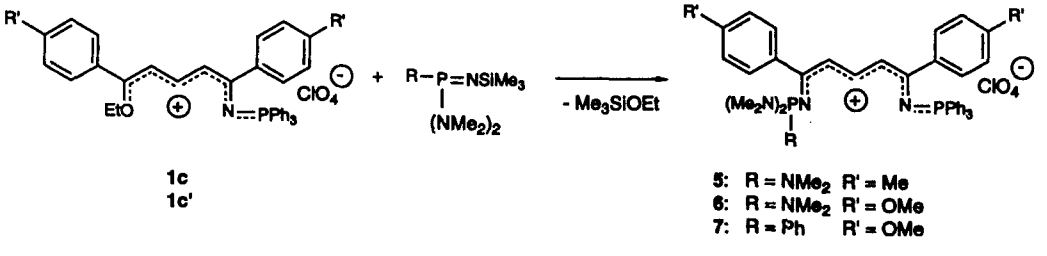
RESULTS

Pentadienylium salts with a phosphorus atom in the conjugated chain are obtained by reaction of N-silylated phosphaimines with carboxonium intermediates. We describe two kinds of nonsymmetric ones (**1a–c**, **1a′–c′**) and (**2a–c**, **2a′–c′**) and also symmetric ones (**3a–c**, **3a′–c′**) (Scheme 1).

Other nonsymmetric salts are obtained by adding different phosphaimines to **1a–c**, or **1a′–c′** compounds. Three examples are described here (Scheme 2).



SCHEME 1



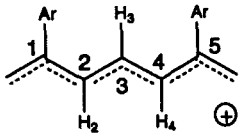
SCHEME 2

Experiments are realized at room temperature in acetonitrile and the yields are quantitative after recrystallization in ethanol (see experimental part). All products are characterized with common spectroscopic methods (^{31}P, ^{1}H, ^{13}C NMR, UV and MS) and elemental analysis.[2]

DISCUSSION

^1H and ^{13}C NMR Spectroscopy

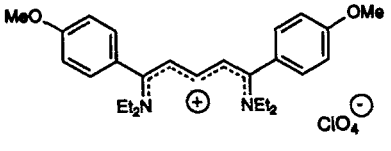
The three protons on the pentadienylium chain are coupled in a A_2X spin system for symmetric derivatives or in a ABX spin system for dissymmetric ones with, in all cases, the central proton H_3 as the most deshielded one. This fact is in agreement with the electrophilic character of the carbon C_3. Coupling constants ($^3J_{H-H} \approx 13$ Hz) between vicinal protons are in accordance with a *trans-trans* configuration whatever the nature of the terminal group (ethoxy, diethylamino, iminophosphane).



^{13}C chemical shifts show that the carbon atoms C_1, C_5 and C_3 are deshielded ($152 < \delta < 190$ ppm) whereas C_2 and C_4 are more shielded ($102 < \delta < 125$ ppm). Like in the case of dialkylaminopentadienylium salts,[3] these observations can be interpreted as an alternate charge distribution, positive for C_1, C_5 and the central carbon C_3 and negative for C_2 and C_4. In symmetrical derivatives, carbons C_2 and C_4 bear also the same negative charge and have almost identical chemical shifts.[2] Moreover C_1 and C_5 bear the same positive charge as is confirmed by molecular modeling and Ampac Mopac calculation.[4]

UV-Visible Spectroscopy

The results of the UV-Vis study (Table I) are compared with the UV parameters of pentadienylium salt **8**: its UV absorption maxima is at 444 nm with a molecular extinction coefficient of 104 900 $mol^{-1}.l.cm^{-1}$ for an electronic delocalization extended through six bonds between the two nitrogen atoms.



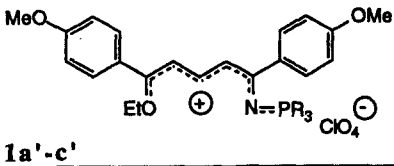
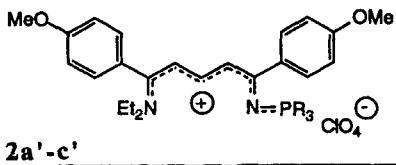
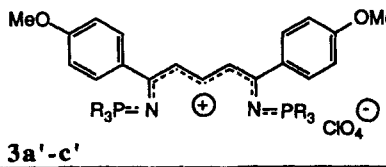
8

Factors governing the variation of the wavelength of the first absorption band are well known, i.e., the chain length, the symmetry of the system[5] and, in the case of sterically hindered compounds, the decrease of the conjugation related to the out of plane deformation. A striking example of this effect was recently described by Reichardt and coll.[6] As a result, an increase of the length of the conjugation path is associated to a bathochromic and hypochromic effect.

In our compounds, when one diethylamino group is replaced by a phosphaimino group (**2a'–c'** compounds), we observe a bathochromic effect ($460 < \delta < 475$ nm) and an hypochromic effect ($81\ 150 < \varepsilon < 69\ 000$) as compared to **8**. The same

TABLE I

^{31}P ($CDCl_3$) and UV-Vis (CH_2Cl_2, 25°C, $\pi \rightarrow \pi^*$ pentamethin chain) parameters

			R = *n*Bu	R = NMe_2	R = Ph
 **1a'-c'**	RMN ^{31}P δ		44.5	32.7	20.6
	UV	λ_{max}	423	412	439
		ε	28 000	29 000	29 600
 **2a'-c'**	RMN ^{31}P δ		32.5	27.9	14.1
	UV	λ_{max}	460	462	475
		ε	81 150	69 000	74 900
 **3a'-c'**	RMN ^{31}P δ		36.6	28.9	13
	UV	λ_{max}	489	495	515
		ε	51 860	62 900	68 150

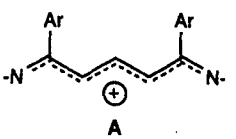
phenomena is observed when the second amino group is replaced by a phosphaimino group (**3a'–c'** compounds). These values are in agreement with an extension of the conjugation path and the electronic delocalization extension through seven (**2a'–c'**) and eight bonds (**3a'–c'**), respectively. For symmetric compounds (**3a'–c'**), each phosphorus bears the same partial charge and the positive charge is totally distributed on the chain framework (structure **A**).

The nature of the substituent R in the phosphaimino group has only a small influence of λ_{max} and ε.

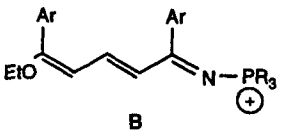
^{31}P NMR Spectroscopy

These observations are confirmed with ^{31}P NMR data. The variation of the ^{31}P chemical shifts between **1a'–c'** and **3a'–c'** is significant ($3.8 < \Delta\delta < 7.9$ ppm) and expresses a greater localization of the positive charge on the phosphorus in **1a'–c'** than in **3a'–c'**.[7]

Comparison of **1a'–c'** and **2a'–c'** leads to the same conclusion ($4.8 < \Delta\delta < 12.0$ ppm) with greater values for monophosphorylated salts **1a'–c'**. Furthermore, **1a'–c'** salts exhibit absorption maxima in the range 410–440 nm with a molecular extinction coefficient of only 30 000 which is a low value for a pentadienylium framework. This can be interpreted by the greater localization of the positive charge on the phosphorus atom; we note that ^{31}P chemical shifts are in good agreement with a phosphonium structure as shown in **B**.



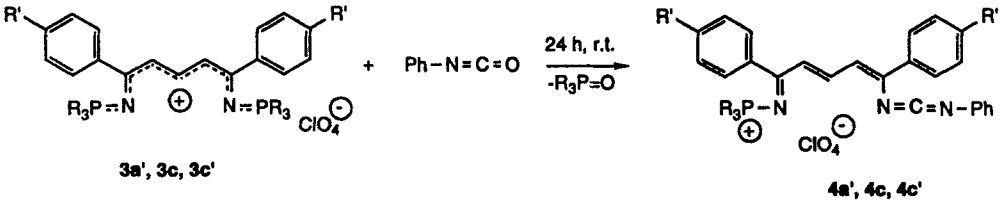
A



B

Reactivity

The aza-Wittig like reactivity of these new pentadienylium salts including a P=N bond is under investigation. Carbonyl and thiocarbonyl reagents, usually employed for this type of reaction,[5] are currently tried. We describe here the reaction of phenylisocyanide towards the symmetric compounds **3a'**, **3c'** and **3c'** and the corresponding formed products (Scheme 3).



SCHEME 3

In products **4a'**, **4c** and **4c'**, the positive charge is more localized on the phosphorus atom as shown by the ^{31}P chemical shifts in the range 27–52 ppm and UV parameters ($470 < \lambda_{max} < 475$; $15\,000 < \varepsilon < 25\,000$). That is the reason why they do not react with a second equivalent of phenylisocyanide.

The fact that the monophosphaimine salts **1a–c** and **1a'–c'** do not react with phenylisocyanide is to be related to the same observation in a phosphonium structure, the greater localization of the positive charge on P should decrease the nucleophilic character of the vicinal nitrogen atom.

CONCLUSION

The condensation between carboxonium salts and N-silylated phosphaimines is a mild method (room temperature in acetonitrile) to prepare new symmetric and nonsymmetric pentadienylium salts presenting interesting UV properties. We observed that the aza-Witting reaction with isocyanide is only possible with symmetric compounds where the delocalization is extended through N—P bonds. This reaction is, to our knowledge, an original method to prepare pentadienylium salts including the N=C=NR framework.

The products obtained are stable, beautiful colored solids. This work demonstrates the generality of the precedent synthesis described for guanidines and some phosphaimine compounds (**1c**, **1c'**, **2c**, **3c** and **3c'**).[2] The introduction of a phosphorus atom in the conjugated chain will probably induce original physical properties and this part of the work is currently under investigation.

EXPERIMENTAL

Nuclear magnetic resonance spectra were obtained on multinuclear Bruker AC 200 spectrometers operating in the Fourier transform mode at 200.13 (^1H), 81.01 (^{31}P) and 50.32 (^{13}C) MHz. Chemical shifts in $CDCl_3$ are expressed in ppm downfield from internal TMS for ^1H and ^{13}C or external 85% H_3PO_4 for ^{31}P, coupling constants are in Hertz. UV/Vis. spectra were recorded on a Perkin-Elmer Lambda-17 spectrophotometer.

The N-silylated phosphaimines used are $nBu_3P{=}NSiMe$, $(Me_2N)_3P{=}NSiMe_3$, $Ph_3P{=}NSiMe_3$ and $(Me_2N)_2P(Ph){=}NSiMe_3$. There are prepared by the Staudinger reaction[9] (80°C, argon atmosphere).

N-Silylated*tris*(nbutyl)phosphaimine: δ $^{31}P(C_6D_6$, 32.438 MHz): 9.01 ppm (s).

N-Silylated*tris*(dimethylamino)phosphaimine: δ $^{31}P(C_6D_6$, 32.438 MHz): 14.10 ppm (s).

N-Silylatedtriphenylphosphaimine: δ $^{31}P(C_6D_6$, 32.438 MHz): -1.25 ppm (s).

N-Silylated*bis*(dimethylamino)phenylphosphaimine: δ $^{31}P(C_6D_6$, 32.438 MHz): 14.50 ppm (s).

To synthesize carboxonium salts,[1] we currently avoid the use of ClO_4^- with BF_4^- or $CF_3SO_3^-$. No changes in reactivity or structures are observed.

1-Nonsymmetric pentadienylium salts with an ethoxy group: All synthesis are carried under an argon atmosphere at room temperature. Pentadienylium salts are obtained by addition of the N-silylated phosphaimine in a CH_3CN solution to the carboxonium intermediate.

To 0.295 g (0.68 mmol) of carboxonium salt in 5 ml of acetonitrile solution is added 0.196 g (0.68 mmol) of $nBu_3PNSiMe_3$. The mixture is stirred at room temperature during one day. After evaporation of the solvent and washing with pentane, the residue **1a** is crystallised in ethanol as yellow crystals. Other compounds **1a'**, **1b**, **1b'** are prepared according to the same procedure. **1c** and **1c'** are described in a precedent publication.[2]

1a: 1-ethoxy-5-*tris*(nbutyl)phosphazenyl-1,5-*bis*(4-methylphenyl) pentadienylium perchlorate.

Yield: 40%; yellow crystals; M.p. 107.5°C; MS: DCI, NH_3, M^+ = 506, 27%, 219, 100% $nBu_3PHN_3^+$. Anal. Calcd. for $C_{33}H_{49}NO_5PCl$ (606.19) C, 65.39; H, 8.15; N, 2.30; Found: C, 64.96, H, 8.16, N, 2.22. ^1H δ, J_{HH}: 0.91 (t, 6.3, 9H, Me of Bu), 1.30–1.50 (m, 15H, CH_2 of Bu and Me of Et), 2.00–2.30 (m, 6H, CH_2P), 2.33 and 2.38 (2s, 6H, Me—Ph), 4.16 (q, 6.9, 2H, CH_2 of Et), 6.13 (d, 11.7, 1H, H_2), 6.45 (d, 14.7, 1H, H_4), 6.90 (m, 1H, H_3), 7.20–7.40 (m, 8H, Ph). ^{31}P δ: 45.3 (s). ^{13}C δ J_{CP}: 13.7 (s, Me of Bu), 23.9–25.1 (m, CH_3 of Bu), 56.2 and 56.5 (2s, Me—Ph), 66.6 (s, CH_2 of Et), 102.6 (s, C_2), 124.1 (d, ^3J = 16.9, C_4); 153.6 (s, C_3), 171.0 (s, C_1), 188.0 (d, ^1J = 8.5 C_5).

1a': 1-ethoxy-5-*tris*-(nbutyl)phosphazenyl-1,5-*bis*(4-methoxyphenyl) pentadienylium perchlorate.

Yield: 50%; orange crystals; M.p. 151°C; MS: DCI, NH_3, M^+ = 538, 100%; 219, 89% $Bu_3PNH_3^+$. Anal. Calcd. for $C_{33}H_{49}NO_7PCl$ (638.19) C, 62.11; H, 21.9; N, 7.74; Found: C, 62.25; H, 2.08; N, 7.70. ^1H δ, J_{HH}: 0.92 (t, 6.9, 9H, Me of Bu), 1.30–1.70 (m, 15H, CH_2 of Bu and Me of Et), 2.00–2.30 (m, 6H, CH_2P), 3.80 and 3.84 (2s, 6H, OMe), 6.8–7.7 (m, 8H, Ph), 4.15 (q, 7.0, 2H, CH_2 of Et), 6.12 (d, 11.4, 1H, H_2), 6.4 (d, 14.5, 1H, H_4), 7.2 (m, 1H, H_3). ^{31}P δ: 44.5 and 45.7. ^{13}C δ, J_{CP}: 13.7 (s, Me of Bu), 23.9–25.1 (m, CH_2 of Bu), 56.2 and 56.5 (2s, MeO), 66.5 (s, CH_2O), 102.6 (s, C_2), 114.6 and 114.7; 132.1 and 132.4 (CH, Ph), 132.4 and 136.9 (2s, C—OMe), 142.0 and 143.7 (2s, C of Ph), 123.1 (d, ^3J = 15.8, C_4), 171 (s, C_1), 186.8 (d, ^1J = 8.7, C_5).

1b: 1-ethoxy-5-*tris*(dimethylamino)phosphazenyl-1,5-*bis*(4-methylphenyl) pentadienylium perchlorate.

Yield: 55%; yellow powder; M.p. 169°C; MS: FAB/MNBa, M^+ = 467. Anal. Calcd. for $C_{27}H_{40}N_4O_5PCl$ (605.12) C, 57.19; H, 7.06; N, 9.89; Found: C, 55.80; H, 7.04; N, 10.04. ^1H δ J_{HH}: 1.44 (t, 7, 3H, Me of Et), 2.33 and 2.39 (2s, 6H, Me—Ph), 2.77 (d, $^3J_{HP}$ = 9.6, 18H, MeN), 4.28 (q, 7.0, 2H, CH_2O), 6.25 (d, 11.7, 1H, H_2), 6.53 (d, 14.7, 1H, H_4), 7.41 (m, 9H, H_3 and Ph). ^{31}P δ: 30.85 (s). ^{13}C δ J_{CP}: 14.4 (s, Me of Et), 21.4 and 21.5 (2s, Me—Ph), 37.1 (d, ^2J = 4, MeN), 102.9 (s, C_2), 122.0 (d, ^3J = 13.5, C_4), 131.6 (s, C of Ph), 136.3 (d, ^3J = 23.2, C of Ph), 140.6 and 142.6 (2s, C—Me), 154.3 (s, C_3), 171.1 (s, C_1), 183.2 (s, C_5).

1b': 1-ethoxy-5-*tris*(dimethylamino)phosphazenyl-1,5-*bis*(4-methoxyphenyl) pentadienylium perchlorate.

Yield: 50%; yellow powder; M.p. 192.8°C; MS: DCI, NH_3, M^+ = 499, 100%. Anal. Calcd. for $C_{27}H_{40}N_4O_7PCl$ (599.07): C, 54.13; H, 6.73; N, 9.35; Found; C, 53.93; H, 6.80; N, 9.28. ^1H δ J_{HH}: 1,40 (t, 7.0, 3H, Me of Et), 3.71 (d, $^3J_{HP}$ = 10.6, 18H, MeN), 3.79 and 3.84 (2s, 6H, MeO), 4.15 (q, 7.0, CH_2 of Et), 6.90–7.02 and 7.35–7.65 (AA'BB' system, 8.9, 8H, Ph), 6.10 (d, 1H, H_2), 6.40 (d, 1H, H_4), 7.10–7.30 (m, 1H, H_3). ^{31}P δ: 32.7. ^{13}C δ J_{CP}: 14.7 (s, Me of Et), 37.3 (d, ^2J = 4.0, MeN, 66.5 (s, CH_2 of Et), 56.2 and 56.5 (s, MeO), 102.8 (s, C_2), 114.8 and 133.0 (2s, CH of Ph), 127.7 and 142.0 (2s, C of Ph), 122.8 (s, ^3J = 13.6, C_4), 153.3 (s, C_3), 162.0 (s, C—OMe), 170.4 (s, C_1), 182.5 (s, C_5).

2-Nonsymmetric pentadienylium salts (with a diethylamino group): **2a**: 1-diethylamino-5-*tris*(nbutyl) phosphazenyl-1,5-*bis*(4-methylphenyl) pentadienylium perchlorate. To 0.3 g (4.9 mmol) of **2a** is added 0.36 g (4.9 mmol) of diethylamine in acetonitrile solution at room temperature during ten hours. After recrystallisation in ethanol, orange crystals of **2a** are obtained. Other salts **2a'**, **2b**, **2b'**, **2c** and **2c'** are obtained with the same procedure.

Yield: 70%: orange crystals; M.p. 157°C; MS: DCI, NH_3, M^+ = 533. Anal. Calcd. for $C_{35}H_{54}N_2O_4PCl$

(633.26) C, 66.39; H, 8.60; N, 4.42; Found: C, 66.35; H, 8.68; N, 4.40. ^{1}H δ J_{HH}: 0.70 (t, 7.2, Me of Bu), 1.30–1.54 (m, 12H, CH_2 of Bu), 1.90–2.30 (m, 6H, CH_2P), 2.32 and 2.34 (2s, 6H, Me—Ph), 3.10–3.25 and 3.15–3.70 (m, 4H, CH_2 of Et), 6.04 (d, 12.6, 1H, H_4), 6.00 (d, 13.6, 1H, H_2), 6.55 (m, 1H, H_3), 7.00–7.25 (m, 8H, Ph). ^{31}P δ: 39.1 (s). ^{13}C δ, J_{CP}: 13.8 (s, Me of Bu), 22.9–25.7 (m, CH_2 of Bu), 103.9 (s, C_2), 114.9 (d, ^3J = 15.8, C_4), 131.9 and 136.5 (C of Ph), 140.6 and 141.3 (2s, C—Me), 158.5 (s, C_3), 168.2 (s, C_1), 182.4 (d, ^2J = 7.1, C_5).

2a': 1-diethylamino-5-*tris*(nbutyl)phosphazenyl-1,5-*bis*(4-methoxyphenyl) pentadienylium perchlorate.

Yield: 70%; orange crystals; M.p. 165°C; MS: DCI, NH_3, M^+ = 565, 13%; 219, 100% $Bu_3PHN_3^+$. Anal. Calcd. for $C_{35}H_{54}N_2O_6PCl$ (665.26) C, 63.19; H, 8.18; N, 4.21; Found: C, 63.22; H, 8.17; N, 3.98. ^{1}H δ, J_{HH}: 0.91 (t, 7.2, Me of Bu), 1.30–1.40 (m, 12H, CH_2 of Bu), 1.90–2.20 (m, 6H, CH_2P), 3.10–3.80 (m, 4H, CH_2 of Et), 6.80 and 7.10 (AB system, 8.5, 4H, Ph), 6.96 and 7.22 (AB system, 8.8 4H, Ph). ^{31}P δ: 37.2 (s). ^{13}C δ, J_{CP}: 13.8 (s, Me of Bu), 24.3–25.6 (m, CH_2 of Bu), 56.2 (s, MeO), 103.3 (s, C_2), 113.6 (d, ^3J = 15.3, C_4), 114.2 and 115.0; 131.1 and 131.8 (CH of Ph), 126.9 and 133.7 (s, C—Me), 159.2 (s, C_3), 181.8 (d, ^2J = 6.9, C_5), 167.6 (s, C_1).

2b: 1-diethylamino-5-*tris*(dimethylamino)phosphazenyl-1,5-*bis*(4-methylphenyl) pentadienylium perchlorate.

Yield: 80%; red powder; M.p. 127°C; MS: DCI, NH_3, M^+ = 494, 100%. Anal. Calcd. for $C_{29}H_{45}N_5PO_4Cl$ (594.14) C, 58.63; H, 7.63; N, 11.79; Found: C, 57.97; H, 7.62; N, 11.63. ^{1}H δ, J_{HH}: 2.31 and 2.34 (2s, 6H, Me—Ph), 2.63 (d, $^3J_{HP}$ = 9.8, 18H, MeN). ^{31}P δ: 28.3 (s). ^{13}C δ, J_{CP}: 8.0 and 9.0 (2s, Me of Et), 16.9 and 17.0 (2s, Me—Ph), 32.8 (d, ^2J = 3.9, MeN), 40.2 and 40.9 (2s, CH_2 of Et), 98.9 (s, C_2), 109.7 (d, ^3J = 14.1, C_4), 123.9 (s, CH of Ph), 154.5 (s, C_3), 132.5 (s, C_1), 174.6 (s, C_5).

2b': 1-diethylamino-5-*tris*(dimethylamino)phosphazenyl-1,5-*bis*(4-methylphenyl) pentadienylium perchlorate.

Yield: 80%; orange crystals; M.p. 143°C; MS: DCI, NH_3, M^+ = 526, 100%; 180, 11% $(Me_2N)_3PNH_3^+$. Anal. Calcd. for $C_{29}H_{45}N_5O_6PCl$ (626.14) C, 55.63; H, 7.24; N, 11.18; Found: C, 55.47; H, 7.26; N, 11.08. ^{1}H δ, J_{HH}: 1.12 (t, 7.0, Me of Et), 2.63 (d, $^3J_{HP}$ = 9.8, 18H, MeN); 3.56 and 3.57 (2q, 4H), 3.60 and 3.61 (2s, 6H, MeO), 6.82 and 7.13 (AB system, 8.8, 4H, Ph), 6.98 and 7.27 (AB system, 8.9, 4H, Ph), 5.90 (d, 13.1, H_2), 6.00 (d, 13.6, H_4), 6.74 (m, 1H, H_3). ^{31}P δ: 29.9 (s). ^{13}C δ, J_{CP}: 37.7 (d, ^2J = 3.8, MeN), 56.2 (s, MeO), 103.4 (s, C_2), 113.9 (s, C_4), 131.1 and 131.8; 114.0 and 115.0 (CH of Ph), 127.0 and 142.0 (C of Ph), 159.2 (s, C_3), 161.3 and 161.4 (2s, C—OMe), 167.8 (s, C_1), 179.1 (s, C_5).

2c: 1-diethylamino-5-triphenylphosphazenyl-1,5-*bis*(4-methylphenyl) pentadienylium perchlorate.

Yield: 55%; MS: DCI, NH_3, M^+ = 593, 100%. Anal. Calcd. for $C_{41}H_{42}N_2O_4PCl$ (693.23) C, 71.04; H, 6.11; N, 4.04; Found: C, 70.09; H, 6.06; N, 4.04 ^{1}H δ, J_{HH}: 1.06 (t, 7.0, 3H, Me of Et), 1.33 (t, 7.0, 3H, Me of Et), 2.27 (s, 3H, Me—Ph), 2.31 (s, 3H, Me—Ph), 3.22 (q, 7.0, 2H, N—CH_2), 3.64 (q, 8.7, 2H, N—CH_2), 5.75 (d, 13.0, 1H, H_2), 5.85 (d, 13.0, 1H, H_4), 6.71 (t, 13.0 1H, H_3), 6.85–7.16 (m, 8H, Ph), 7.50–7.70 (m, 15H, PPh_3). ^{31}P δ: 12.7 (s). ^{13}C δ, J_{CP}: 12.5 (s, Me of Et), 14.2 (s, Me of Et), 21.3 (s, Me—Ph), 45.1 and 48.2 (2s, CH_2 of Et), 110.2 (s, C_2), 110.5 (s, C_4), 121.5 (d, 101.1, C_{ipso} of PPh_3), 123.7, 129.2, 132.4, 132.6 (4s, CPh), 155.4 (s, C_3), 164.6 (s, C_1).

2c': 1-diethylamino-5-triphenylphosphazenyl-1,5-*bis*(4-methoxyphenyl) pentadienylium perchlorate.

Yield: 65%; red crystals; M.p. 120°C; MS: FAB M^+: = 625, 100%. Anal. Calcd. for $C_{41}H_{42}N_2O_6PCl$ (725.23) C, 67.90; H, 5.84; N, 3.86; Found: C, 68.94; H, 5.88; N, 3.74. ^{1}H δ, J_{HH}: 3.78 and 3.79 (2s, 6H, MeO), 6.62–7.21 (m, Ph—OMe), 7.52–7.66 (m, Ph—P). ^{31}P δ: 14.1 (s), ^{13}C δ, J_{CP}: 12.4 and 14.3 (2s, Me of Et), 45.7 and 46.7 (2s, CH_2 of Et), 55.5 (s, MeO), 105.1 (s, C_2), 113.3 (C_4), 159.3 (s, C_3), 168.6 (s, C_1), 178.9 (d, ^2J = 3.5, C_5).

3-Symmetric pentadienylium salts: **3b**: 1,5-*bis*(*tris*(dimethylamino)phosphazenyl)-1,5,*bis*(4-methylphenyl)pentadienylium perchlorate. 0.56 g (1.95. mmol) of $nBu_3PNSiMe_3$ dissolved in 5 ml of acetonitrile are added to 0.421 g (0.96.mmol) of carboxonium at room temperature to obtain the product **3b** which is precipitated in ethanol as a yellow powder.

Yield: 50%; yellow powder; M.p. 181°C; MS: DCI, NH_3, M^+ = 599. Anal. Calcd. for $C_{31}H_{53}N_8O_4P_2Cl$ (698) C, 53.29; H, 7.59; N, 16.04; Found: C, 52.57; H, 7.64; N, 15.58. ^{1}H δ, J_{HH}: 2.35 (s, 6H, Me—Ph), 2.64 (d $^3J_{HP}$ = 9.7, 36H, NMe_2), 5.87 (d, $X(AX_2)$, 13.2, 2H, H_2 and H_4), 7.22 (syst. AA'BB', 8H, Ph), 7.52 (t, $A(AX_2)$, 13.2, 1H, H_3). ^{31}P δ: 26.8 (s). ^{13}C δ, J_{CP}: 21.3 (Me—Ph), 37.2 (d, ^2J = 3.8, NMe), 112.6 (d, ^3J = 14.2, C_2 and C_4), 128.6 (C_{meta}), 138.6 (d, ^3J = 20.2, C_{ipso}), 139.9 (C_{ortho}), 158.1 (C_3), 176.4 (C_1 and C_5).

Other symmetric compounds **3a'** and **3b'** are prepared according to the same procedure. **3c** and **3c'** are described in a precedent publication.[2]

3a': 1,5-*bis*(*tris*(nbutyl)phosphazenyl)-1,5-*bis*(4-methoxyphenyl) pentadienylium perchlorate.

Yield: 50%; pink crystals; M.p. 120°C; MS: DCI, NH_3, M^+ = 709, 13%, 219, 100% $Bu_3PNH_3^+$. Anal. Calcd. for $C_{43}H_{71}N_2O_6P_2Cl$ (809.46) C, 63.81; H, 8.84; N, 3.46; Found: C, 63.91; H, 9.04; N, 3.3. ^1H δ, J_{HH}: 0.90 (t, 6.8, 18H, Me of Bu), 1.30–1.50 (m, 24H, CH_2 of Bu), 2.00–2.20 (m, 12H, CH_2P), 3.80 (s, 6H, Me—Ph), 6.90 and 7.40 (AB system, 8.8, 8H), 7.24 (A(AX_2), 13.0, 1H, H_3), 5.90 (X(AX_2), 13.0, 2H, H_2 and H_4). $^{31}P\delta$: 36.6 (s). ^{13}C δ, J_{CP}: 13.8 (s, Me of Bu), 24.3–25.7 (m, CH_2 of Bu), 56.2 (s, MeO), 11.7 (d, ^3J = 15, C_2 and C_4), 114.3 and 131.6 (CH of Ph), 134.7 (d, ^3J = 20.4, C of Ph), 157.1 (s, C_3), 179.6 (d, ^2J = 6.3, C_1 and C_5).

3b': 1,5-*bis*(*tris*(dimethylamino)phosphazenyl)-1,5-*bis*(4-methoxyphenyl) pentadienylium perchlorate.

Yield: 30%; orange crystals; M.p. 192°C; MS: DCI, NH_3, M^+ = 631, 100%; 180, 58% $(Me_2N)_3PNH_3^+$. Anal. Calcd. for $C_{31}H_{53}N_8O_6P_2Cl$ (731.22) C, 50.92; H, 7.31; N, 15.32; Found: C, 50.71; H, 7.28; N, 15.25. ^1H δ, J_{HH}: 2.63 (d, $^3J_{HP}$ = 9.7, 36H, MeN), 3.80 (s, 6H, MeO), 6.90 and 7.40 (AB system, 8.7, 8H, Ph), 5.94 (d, A(A_2X), 13.2, 2H, H_2 and H_4), 7.45 (m, X(A_2X), 13.2, 1H, H_3). ^{31}P δ: 28.9 (s), ^{13}C δ, J_{CP}: 37.4 (d, ^2J = 3.8, MeN), 56.2 (s, MeO), 112.5 (d, ^3J = 12.8, C_2 and C_4), 114.4 and 131.6 (CH of Ph), 134.9 (d, ^3J = 21.8, C of Ph), 156.7 (s, C_3), 176.7 (C_1 and C_5).

4-Reactivity: The aza-Wittig reaction is carried under an argon atmosphere at room temperature. Phenylisocyanide is added to pentadienylium salt in 1:1 stoichiometric ratio in CH_3CN solution. After about 20 hours stirring, the solvent is evaporated. The residue is washed with pentane and crystallised in ethanol.

4a': 1-*tris*(nbutyl)phosphazenyl-5-arylcarbodiimide-1,5-*bis*(4-methoxyphenyl) pentadienylium perchlorate.

Yield: 80%; red crystals; M.p. 69°C; MS: DCI, NH_3, M^+ = 610. Anal. Calcd. for $C_{38}H_{49}N_3O_6PCl$ (710.26) C, 64.26; H, 6.95; N, 6.51; Found: C, 64.24; H, 6.86; N, 5.92. ^1H δ, J_{HH}: 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), 6.30–7.80 (m, 15H, MeO—Ph, N—Ph, H_2, H_4), 8.10 (m, 1H, H_3). ^{31}P δ: 51.8 (s). ^{13}C δ, J_{CP}: 13.6 (s, Me of Bu), 23.8–25.0 (m, CH_2 of Bu), 56.3 and 56.6 (2s, MeO), 110.9 (s, C_2), 114.8 (d, ^3J = 6.2, C_4), 115.3–115.6 and 132.0–132.8 (m, CH of Ph—OMe), 154.5 (s, N=C=N), 156.1 (s, C_3), 163.2 and 163.5 (2s, C—OMe), 162.1 (s, C_1).

4c: 1-triphenylphosphazenyl-5-arylcarbodiimide-1,5-*bis*(4-methylphenyl) pentadienylium perchlorate.

Yield: 65%; orange crystals; M.p. 215°C; MS: DCI, NH_3, M^+ = 638, 54%; 361, 100%. Anal. Calcd. for $C_{44}H_{37}N_3O_4PCl$ (738.23) C, 71.59; H, 5.05; N, 5.69; Found: C, 71.38; H, 4.99; N, 5.54. ^1H δ, J_{HH}: 2.26 and 2.40 (2s, 6H, Me of Ph), 6.60–7.80 (m, 30H, Ph, H_2 and H_4), 7.98 (m, 1H, H_3). ^{31}P δ: 27.1 (s). ^{13}C δ, J_{CP}: 21.4 and 21.6 (2s, Me of Ph), 110.9 (s, C_2), 121.2 (s, C_4), 123.0–131.0 (CH of Ph), 113.0 and 113.7 (2s, Cq of Ph), 122.2 (d, ^1J = 101, C—P), 139.2 (s, C of Ph—Me), 141.8 (d, ^3J = 36, C of Ph—Me), 145.0 (s, C_3), 158.0 (s, N=C=N), 188.5 (d, ^2J = 17.4, C_5), 163.9 (s, C_1).

4c': 1-triphenylphosphazenyl-5-arylcarbodiimide-1,5-*bis*(4-methoxyphenyl) pentadienylium perchlorate.

Yield: 75%; red powder; M.p. 215°C; MS: DCI, NH_3, M^+ = 670, 100%. Anal. Calcd. for $C_{44}H_{37}N_3O_6PCl$ (770.23) C, 68.61; H, 4.84; N, 5.46; Found: C, 67.67; H, 4.86; N, 5.69. ^1H δ: 3.80 and 3.87 (s, 6H, MeO), 6.60–7.10 (m, AB(ABX), 2H, H_2 and H_4), 6.90–7.90 (m, 28H, Ph), 8.03 (m, X(ABX), 1H, H_3). ^{31}P δ: 27.5 (s), ^{13}C δ, J_{CP}: 56.4 and 56.6 (s, MeO), 110.8 (s, C_2), 117.6 (d, ^3J = 9, C_4), 129.0–136.0 (CH of Ph and Ph—P), 116.0, 116.4, 122.4 and 122.5 (CH of Ph—OMe), 154.2 (s, N=C=N), 112.4 (C of Ph), 142.3 (s, C_3), 160.6 and 162.8 (2s, C—OMe), 165.2 (s, C_1), 188.7 (d, 7, C_5).

5-Nonsymmetric pentadienylium salts with two different phosphaimino groups: To 1.1 g (1.65 mmol) of pentadienylium salt **1c** is added 0.42 g (1.65 mmol) of *tris*(dimethylamino)N-silylated phosphaimine. The mixture is stirred at room temperature in an acetonitrile solution during one day. ^{31}P NMR indicates the end of the reaction. After evaporation of the solvent under vacuum, the residue **5** is recrystallised in ethanol.

5: 1-triphenylphosphazenyl-5-*tris*(dimethylamino)phosphazenyl-1,5-*bis*(4-methylphenyl) pentadienylium perchlorate.

Yield: 85%; red crystals; M.p. 182°C; MS: DCI, NH_3, M^+ = 698, 100%; 279, 63% $Ph_3HNH_3^+$; 180, 8% $(Me_2N)_3PNH_3^+$. Anal. Calcd. for $C_{43}H_{50}N_5O_5P_2Cl$ (814.31) C, 64.70; H, 6.31; N, 8.77; Found: C,

65.54; H, 6.12; N, 7.21. ^{1}H δ, J_{HH}: 2.30 and 2.34 (2s, 6H, Me—Ph), 2.6 (d, 18H, ^3J = 9.8, MeN), 5.60–5.80 (m, 9H, Ph and H_3), 7.59–7.63 (m, 15H, PhP). ^{31}P δ: 13.5 and 28.9 (2s). ^{13}C δ, J_{CP}: 21.4 and 21.5 (2s, Me—Ph), 37.1 (d, ^2J = 3.9, NMe), 126.3 (d, ^1J = 101.0, Cipso of Ph_3P), 112.6 (d, ^3J = 15.0, C_4), 114.6 (d, ^3J = 15.8, C_2), 128.6–129.6 CH of Ph), 132.4–133.5 (CH of PhP), 137.4 and 137.7 (2s, (Ph—Me), 139.4 and 140.6 (2s, C of Ph), 155.7 (s, C_3).

6: 1-triphenylphosphazenyl-5-*tris*(dimethylamino)phosphazenyl-1,5-*bis*(4-methoxyphenyl) pentadienylium perchlorate.

Yield: 80%; red powder; M.p. 207°C; MS: DCI, NH_3, M^+ = 730, 20%, 279, 100% $Ph_3PHN_3^+$. Anal. Calcd. for $C_{43}H_{50}N_5O_7P_2Cl$ (846.31) C, 62.24; H, 6.03; N, 8.44; Found: C, 62.24; H, 5.89; N, 7.45. H δ, J_{HH}: 2.61 (d, 18H, $^3J_{HP}$ = 9.8, MeN), 3.79 and 3.80 (2s, 6H, MeO), 5.50–5.75 (m, 2H, H_2 and H_4), 6.70–6.85 (m, 4H, Ph—OMe), 7.30–7.70 (m, 20H, Ph—OMe, PhP and H_3). ^{31}P δ: 10.7 and 28.7 (2s). ^{13}C δ, J_{CP}: 37.1 (d, ^2J = 4.2, NMe), 55.5 (s, OMe), 112.1 (d, ^3J = 14.5, C_2, 114.1 (d, ^3J = 15.4, C_4), 113.4 (m, CH of Ph—OMe), 126.4 (d, ^1J = 100.8, C_{ipso} of PhP), 129.0–133.0 (m, CH of Ph—OMe and PhP), 155.4 (s, C_3), 160.9 and 161.7 (2s, C—OMe), 178.3 (d, C_5), 177.8 (d, ^2J = 3.9, C_1), 133.8 and 133.4 (2s, C of Ph—OMe).

7: 1-triphenylphosphazenyl-5-*tris*(dimethylamino)phenylphosphazenyl-1,5-*bis*(4-methoxyphenyl) pentadienylium perchlorate.

Yield: 80%; red powder; M.p. 160°C; MS: DCI, NH_3, M^+ = 763, 3.7%; 279, 100% $Ph_3PNH_3^+$; 213, 49.6% $(Me_2N)_3PPhNH_3^+$. Anal. Calcd for $C_{47}H_{49}N_4O_6P_2Cl$ (863.29) C, 65.43; H, 5.68; N, 6.49; Found: C, 65.40; H, 5.51; N, 6.04. ^{1}H δ, J_{HH}: 2.55 (d, ^3J = 10.2, 18H, MeN), 3.80–3.82 (2s, 6H, OMe), 5.66–5.78 (m, 2H, H_2 and H_4), 6.72–6.90 (m, 4H, Ph—OMe), 1.35 (m, 1H, H_3), 7.37–7.75 (m, 24H, Ph—OMe and PhP). ^{31}Pδ: 12.0 and 28.8 (2s). ^{13}C δ, J_{CP}: 37.1 (d, ^2J = 3.6, NMe_2), 55.5 (s, MeO), 113.5 (d, ^2J = 10.2, C_2 of PhP), 114.2 (d, ^3J = 17.8, C_2), 126.4 (d, ^1J = 101.9, Cipso of PhP), 126.8 (d, ^1J = 100.9, Cipso of Ph_3P), 129.4 (d, ^3J = 12.4, C_3 of Ph_3P), 130.6 (d, ^4J = 6.0, C_4 of Ph_3P), 132.5 (d, ^2J = 10.0, C_2 of Ph_3P), 155.9 (s, C_3), 161.2 and 161.5 (2s, C—OMe), 176.5 (C_1), 177.9 (C_5).

ACKNOWLEDGEMENTS

The authors wish to acknowledge The Centre National de la Recherche Scientifique (CNRS), The Université Paul Sabatier (France) and The State Committee of the Ukraine for Science and Technology for financial support of this research.

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