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New Diaza Pentadienylium Salts (Cyanine dyes) derived from N-Silylated Phosphinimines and Guanidines

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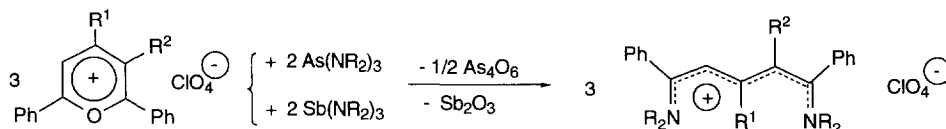
Abstract: New synthetic methods for the preparation of pentadienylium cations (cyanine dyes) are developed in our laboratories. In particular the reaction of carboxonium derivatives on various primary and secondary amines is to be emphasized. This method is remarkably versatile to lead to new dyes hardly obtainable otherwise. It is applied here to the synthesis of previously unknown derivatives of N-silylated phosphinimines and guanidines where the conjugated polyenic system can be extended over the nitrogen atom on the phosphinimine or guanidine moiety. Spectrochemical results, mainly ³¹P, ¹³C NMR and UV are in accordance with these assumptions opening thus a new field of investigation for the reactivity of the aza-Wittig compounds and more generally for the physical applications (ie in optical devices).

1,5-Dialkoxypentadienylium salts (carboxonium ions), transient intermediates in pyrylium synthesis, can be stabilized by substitution on 1- and 5- positions and their isolation was achieved by Mezheritskii and Coll.¹ Another isolable carboxonium salt stabilised by oxasubstituents was recently described by Lüning and Coll.²

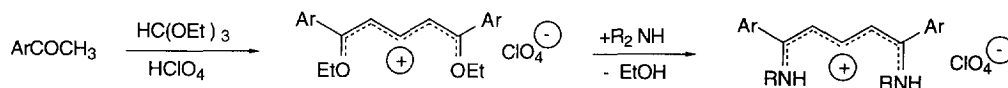
In contrast to carboxonium ions, cyanine dyes are highly stable compounds widely used in industry. Numerous applications mainly in chemistry and photophysics are described and about 500 papers are published every year on these subjects. The most interesting features are actually found in colour photography with photosensitizers and in optical memories like erasable laser disks.

Owing to this practical application interest, the use of new methods of synthesis is expected to lead to dyes with an enhanced pattern of physical properties.

During the last three years, we discovered and developed two new cyanine dyes synthesis based on pyrylium salts chemistry: first we described a new reaction of *tris*(dialkylamino)arsanes and stibanes with pyrylium salts leading to the formation of symmetrically aminated and highly substituted pentamethinium salts.³



In a second stage we demonstrated that arylcarboxonium ions are key compounds in pentamethinium synthesis: we were thus able to synthesize new dyes hardly obtainable otherwise.⁴



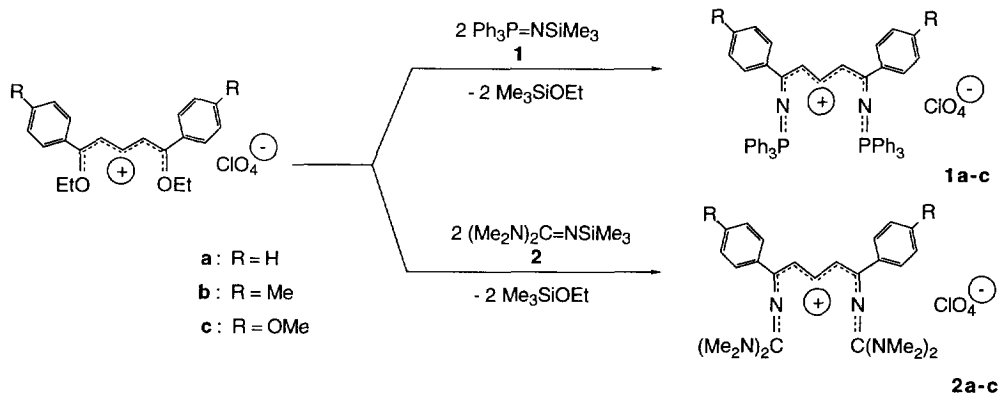
For instance, the use of various primary and secondary alkyl amines, diamines or aminoalcohols like ephedrine lead to dissymmetric, macrocyclic and/or optically active compounds.

The aim of the work presented here is to describe the results obtained by generalisation of the carboxonium based method to other nucleophiles. To synthesize new pentadienylium dyes with extended electronic delocalisation and further reactivity, the choice of phosphinimines and guanidines reagents seemed the most suitable.

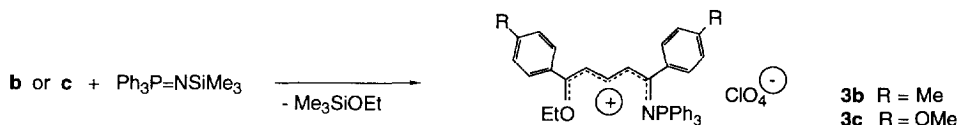
RESULTS AND DISCUSSION

Intermolecular elimination of silylether between alkoxyated and silylated compounds is a classical reaction leading to a variety of substituted species in organic and organometallic chemistry. Numerous phosphorus compounds with various coordination types were also obtained using this method.⁵

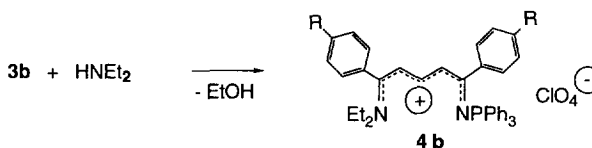
We took advantage of such reaction to prepare new diaza pentadienylium salts by adding the N-silylated phosphinimine **1** or the N-silylated guanidine **2** to the carboxonium ions (**a-c**) yielding the symmetrical diazapentadienylium salts **1a-c** and **2a-c**.



Moreover starting from a 1:1 stoichiometric ratio, we are able to isolate the stable monosubstituted derivatives **3b-c** according to the next scheme.

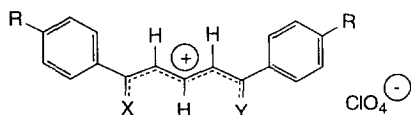


The **3b** derivative can react in a second step with dialkylamine to obtain a new nonsymmetrically substituted compound **4b**.



We note that these results are comparable to those obtained with aminoalcohols⁴. In the case of the guanidine moiety, the reaction seems to be an equilibrium between the different components and it is most difficult to prepare the monosubstituted compound. Only the disubstituted species can be obtained pure.

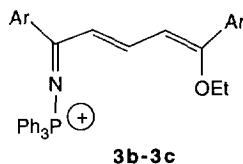
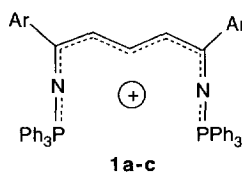
Due to the high reactivity of the carboxonium ions **a-c**, and the "good leaving group" ability of the silylether, pure diazapentadienylium salts **1a-c**, **2a-c**, **3b-c** and **4b** are formed in good yields. The reaction is realized at room temperature in acetonitrile as solvent. The crude product is recrystallized from ethanol. All the new compounds are fully characterized with common spectroscopic methods (³¹P, ¹H, ¹³C, NMR, UV and MS) and by elemental analyses (see Experimental Section).



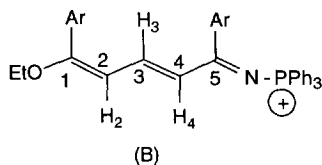
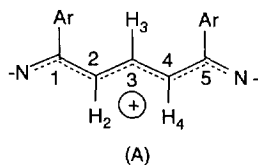
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|---|---|---|---------|
| 1 | X = Y = NPh ₃ | a | R = H |
| 2 | X = Y = N(CNMe ₂) ₂ | b | R = Me |
| 3 | X = OEt, Y = NPh ₃ | c | R = OMe |
| 4 | X = NEt ₂ , Y = NPh ₃ | | |

NMR spectra

The ³¹P NMR signals of **1a-c** (symmetrical derivatives) are centred at ca 13 ppm, whereas those of the monosubstituted **3b** and **3c** are situated near 20 ppm. These values show first, that the nature of the substituent R (H, Me or OMe) on the phenyl group has only a minor influence on the ³¹P chemical shifts, and secondly that the variation of the $\delta(^{31}\text{P})$ between **1a-1c** and **3b-3c** ($\Delta\delta = 7$ ppm) is significant and express a greater localisation of the positive charge on the phosphorus in **3b** and **3c** than in **1a-1b** and **1c**. It suggests that in the disubstituted pentamethinium salts (**1a-c**) the positive charge is completely delocalized on the chain framework, each phosphorus atom bearing the same partial positive charge whereas in the monosubstituted compounds **3b-3c**, the positive charge is located in greater part on the phosphorus atom.⁶



We have also characterized all compounds by their ¹H NMR data (Experimental Part). The three protons on the chain are coupled in a A₂X spins system for the symmetrical derivatives **1a-1c** and **2a-c** and in a ABX spins system for the unsymmetric ones (**3b-c** and **4c**). In agreement with the electrophilic character of the carbon C-3, the central proton H-3 is the most deshielded ($6.7 < \delta_3 < 7.5$). For all the types of compounds, the coupling constants between vicinal protons are on the range $11.8 \text{ Hz} < {}^3J_{\text{HH}} < 14.5 \text{ Hz}$ (Table 1 and Experimental Part). These values are in accordance with a *trans-trans* configuration (A) or (B).



Effectively, one can note that ${}^3J_{\text{H-H}}$ values are equal to $13 \text{ Hz} \pm 0.1$ in (A) configuration assigned to compounds **1a-c**, **2a-c** and **4b** whereas the two ${}^3J_{\text{H-H}}$ coupling constants are well differentiated in nonsymmetrical systems like (B) as it appears in compound **3b** ($J_{2,3} = 14.4$ and $J_{4,3} = 11.8$ Hz) or **6**. Table 1 summarizes these ${}^1\text{H}$ NMR data in the case of compounds with the p-tolyl group ($-\text{C}_6\text{H}_4\text{-Me}$) and also allow the comparison with the starting carboxonium **b** and the diethylamino pentamethinium salts **5** and **6**. Undoubtedly the ${}^3J_{\text{HH}}$ coupling constants are identical ($13 \text{ Hz} \pm 0.1$) for all symmetrical derivatives confirming the trans delocalized configuration (A) of the chain whatever the nature of the terminal group: ethoxy (**b**), diethylamino **5**, guanidino **2b** and iminophosphane **1b**. The consistency of this assumption is evidenced by the ${}^3J_{\text{HH}}$ values on the unsymmetrical derivatives. The two different coupling constants obtained for **6** and **3b** become accidentally equal in **4b**, and their average value (13.1 Hz) is the one observed for the symmetrical compounds. Moreover the solid state X ray determination of **5** ensures this structure to be trans planar.⁶

Finally, the ${}^{13}\text{C}$ NMR data confirm all the structural observations related with ${}^{31}\text{P}$ and ${}^1\text{H}$ NMR parameters. Firstly the ${}^{13}\text{C}$ chemical shifts are independent of the substitution on the phenyl ring. Secondly the carbon atoms C-1, C-5 and C-3 are deshielded ($150 < \delta < 190$) whereas C-2 and C-4 are more shielded ($102 < \delta < 117$); these observations can be interpreted as an alternate charge distribution: positive for C-1, C-3 and C-5 and negative for C-2 and C-4.

The comparison between the ${}^{13}\text{C}$ chemical shifts for the seven derivatives reported in table 1 shows a large variation range for C-1, C-5 ($165 < \delta < 190$) and C-3 ($150 < \delta < 175$). The chemical shifts of these carbons (C-1, C-5 and C-3) increase with the inductive effect of the terminal group on the pentamethine chain going, for example, from guanidine **2b** ($\delta_1 = 165.5$, $\delta_3 = 150.7$) to iminophosphine **1b** ($\delta_1 = 180.0$, $\delta_3 = 157.5$) and to carboxonium **b** ($\delta_1 = 190.4$, $\delta_3 = 175.4$).

The values of the chemical shifts of C-2 or C-4 carbons are almost identical for symmetrical derivatives i.e. 111.2 (**2b**); 112.1 (**b**); 114.6 (**1b**) respectively. This is consistent with the presence of an equal negative charge on these carbon atoms.

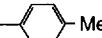
U.V./Vis. spectra

Our compounds belong to the cyanine dyes family: they absorb in the U.V and visible regions. Table 2 presents the U.V/Vis. data for some of these salts. The spectra are recorded in dichloromethane at 25°C . We have only considered the $\pi \rightarrow \pi^*$ transition of the electrons of the pentamethine chain. The λ_{max} is located between 423 nm and 528 nm and the molar extinction coefficient is in the area:

$$3 \cdot 10^4 < \epsilon_{\text{max}} < 11 \cdot 10^4 \text{ mol}^{-1} \cdot \text{l} \cdot \text{cm}^{-1}.$$

We note that for the phosphinimine **1c** and the guanidine **2a** the λ_{max} value are greater than the value obtained for pentamethinium **5** (bearing two diethylamino substituents), this fact is connected with an extension of the conjugation increasing from **5** to **1c** and **2a**.

We obtained a bathochromic effect in going from **5** to **1c** and **2a** and in the same time, the molar extinction coefficient diminishes (hypochromic effect). These observations confirm the charge delocalization on all the framework related with a greater number of bonds going from **5** to **1c** and **2a**.

Table 1: ^1H and ^{13}C NMR Parameters of Pentadienylium Salts in CDCl_3 δ (ppm), J (Hz), * Ar = 

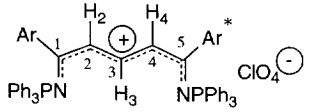
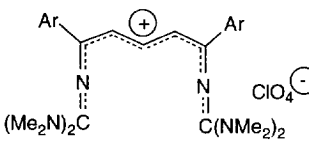
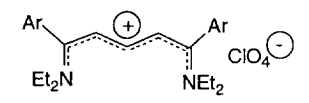
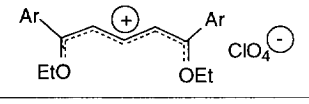
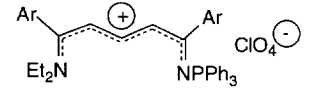
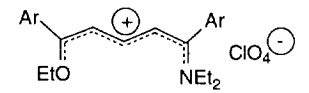
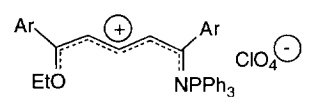
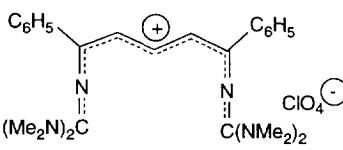
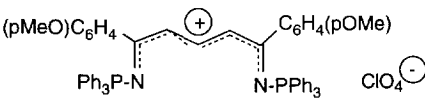
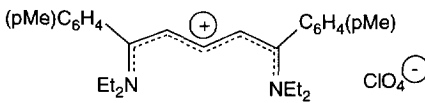
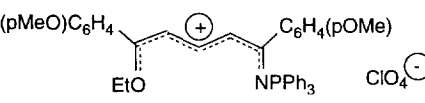
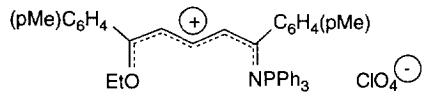
Compounds	H-2/H-4 $^3J_{\text{H-H}}$	H-3	C-1/C-5	C-3	C-2/C-4
 1b	5.46 13.1	7.31	180.0 $^2J_{\text{CP}} = 4.7$	157.5	114.6 $^3J_{\text{CP}} = 15.1$
 2b	6.12 13.1	7.48	165.5	150.7	111.2
 5	5.98 12.9	6.12	170.3	162.9	106.0
 b	6.93 13	8.0	190.4	175.4	112.1
 4b	5.85/5.75 13	6.71	164.6	155.4	110.2/110.5
 6	6.77/6.24 13.8/12	6.83	176.6/175.4	162.3	117.1/104.3
 3b	6.31/5.77 11.8/14.4		172.8/187.9 $^2J_{\text{CP}} = 6.8$	155.9	102.9/123.1 $^3J_{\text{CP}} = 16$

Table 2: UV/ Vis. maxima of the pentadienylium perchlorates **1c**, **2a**, **3b-c**, **5**, measured in dichloromethane at 25°C

Compounds	λ_{\max} ($\pi \rightarrow \pi^*$) in nm	ϵ_{\max} in $\text{mol}^{-1} \cdot \text{l} \cdot \text{cm}^{-1}$
 2a	528	35963
 1c	515	68153
 5	443	107400
 3c	439	29600
 3b	423	36025

CONCLUSION

In conclusion, we have been able to synthesize a series of new diazapentadienylium salts based on guanidines and phosphinimines presenting the new properties to extend of the conjugated framework in contrast with the previously described dialkylamino derivatives. This procedure is advantageous, the reactions proceed under mild conditions and with good yields. The new salts are obtained under well crystallized compounds and have beautiful and bright colours: green, red, yellow or violet. Finally the aza-Wittig like reactivity of the new diazapentadienylium salts is under investigation.

EXPERIMENTAL SECTION

General Methods

Nuclear magnetic resonance spectra were obtained on multinuclear Bruker AC 80 and AC 250 spectrometers operating in the Fourier transform mode at 80 (^1H), 32.44 (^{31}P) MHz for AC 80 and at 250.133 (^1H), 62.896

(^{13}C) MHz for AC 250. 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.

U.V./Vis. spectra were recorded on a Perkin-Elmer Lambda-17 spectrophotometer. Mass spectra were obtained on a Nermag R10 spectrometer with chemical ionisation by NH_3 ; surprisingly in these conditions the higher peak observed always correspond to the M^+ mass of the cationic part of the molecule. Microanalysis were performed in the "Service de Microanalyses" ENSCT Toulouse.

General experimental procedure

All synthesis were carried out under an argon atmosphere at room temperature. Very dangerous explosions were recently reported with perchlorates salts handling. However in our case, owing to the fact that experiments are performed in limited scale, we never observed any problem. Nevertheless, we are currently avoiding the use of ClO_4^- by substitution by CF_3SO_3^- .

The phosphorus compound $\text{Ph}_3\text{PNSiMe}_3$ **1** has been prepared according to literature procedure with the Staudinger reaction⁸ between triphenylphosphine and trimethylsilylazide. The three carboxonium ions **a**, **b**, **c** are obtained with the protocol of Mezheritzkii and al.¹

The 2-trimethylsilylguanidine **2** is obtained according to the procedure given by Romanenko and al.⁹

A - Reactions of the N-trimethylsilyltriphenyl phosphinimine **1**

*1- Synthesis of symmetrical pentamethinium salts **1a**, **1b**, **1c**.*

The preparation was identical for the three symmetrical compounds. We thus describe only the synthesis of a characteristic compound **1b**.

0.680g (1.94.mmol) of N-trimethylsilyltriphenyl phosphinimine **1**, dissolved in 5 ml of acetonitrile (uncoloured solution), are added dropwise to 0.421 g (0.97.mmol) of carboxonium **b** in 10 ml of acetonitrile (orange solution) at room temperature. We observe the formation of a deep red colour in solution. The reaction mixture is stirred during one day and controlled by ^{31}P NMR to follow the disparition of the starting phosphinimine **1**. After evaporation of the solvent under vacuum we obtain a pink oil, which is dried under vacuum. A pink powder is crystallised from ethanol in a quantitative yield. The two other pentamethinium salts **1a** and **1c** have been prepared according to the same procedure.

1a: 1,5-bis(triphenylphosphazeny)-1,5-bis(phenyl)pentadienylium perchlorate

Yield: 60%; fuschia solid; M.p. 180°C; MS (FAB, M^+ = 769,49%)

Anal. Calcd. for $\text{C}_{53}\text{H}_{43}\text{N}_2\text{P}_2\text{O}_4\text{Cl}$ (869.35) C, 73.23; H, 4.99; N, 3.22; Found: C, 73.56; H, 5.09; N, 2.85.

^1H δ (ppm), J (Hz): 5.58 (d, 13.1, (A_2), 2H, H_2 and H_4); 6.6 < δ < 7.4 (m, 10H, H_{Ph}); 7.5 < δ < 7.9 [m, 30H, $\text{Ph}(\text{PPh}_3)$]; 8.37 (t, 13.1, X, 1H, H_3)

^{31}P δ (ppm): 13.7 (s)

^{13}C δ (ppm), $\text{J}_{\text{P-C}}$ (Hz): 114.8 (d, 16.8, C_2 and C_4); 126.1 (d, 100.9, $\text{C}_{\text{ipso}}\text{PPh}_3$); 128.0, 128.7 (2s, C_{Ph}); 129.5 (d, 12.6, C_{Ph}); 130.1 (s, C_{Ph}); 132.5 (d, 10.2 C_{Ph}); 133.5 (d, 2.6, C_{Ph}); 140.0 (d, 18.7, C_{Ph}); 156.7 (s, C_3); 179.2 (d, 4.9, C_1 and C_5)

1b: 1,5-bis(triphenylphosphazeny)-1,5-bis(4-methylphenyl)pentadienylium perchlorate.

Yield: 60%; pink powder; MS (DCI, NH_3 , M^+ = 797, 6.6%; 279, 100% $\text{Ph}_3\text{PNH}_3^+$)

Anal. Calcd. for $\text{C}_{55}\text{H}_{47}\text{N}_2\text{P}_2\text{O}_4\text{Cl}$ (897.40) C, 73.61; H, 5.28; N, 3.12; Found: C, 71.8; H, 5.17; N, 2.83.

^1H δ (ppm), J (Hz): 2.3 (s, 6H, Me); 5.46 (d, 13.1, (A₂), 2H, H₂ and H₄); 7.07 (d, 8, (AB), 4H, H_{Ph}); 7.29 (d, 8, (AB), 4H, H_{Ph}); 7.31 (t, 13.1, X, 1H, H₃); 7.5 < δ < 7.7 [m, 30H, Ph(PPh₃)].

^{31}P δ (ppm): 13.0 (s).

^{13}C δ (ppm), J_{P-C} (Hz): 21.4 (s, Me); 114.6 (d, 15.1, C₂ and C₄); 127.1 (d, 100.6, C_{ipso}PPh₃); 129.7, 130.0 (2s, C_{arom}); 130.5 (d, 12.7, C_{Ph}); 133.6 (d, 10.2, C_{Ph}); 134.5 (d, 2.7, C-C=); 138.4 (s, C_{Ph}); 141.7 (s, C₁-Me); 157.5 (s, C₃); 180.0 (d, 4.7, C₁ and C₅).

1c: 1,5-bis(triphenylphosphazeny)-1,5-bis(4-methoxyphenyl)pentadienylium perchlorate.

Yield: 55%; M.p. 220°C; MS (DCI, NH₃, M⁺ = 829, 2.6%; 279, 100% Ph₃PNH₃⁺)

Anal. Calcd. for C₅₅H₄₇N₂P₂O₆Cl (929.40) C, 71.08; H, 5.10; N, 3.01; Found: C, 70.86; H, 4.99; N, 2.77.

^1H δ (ppm), J (Hz): 1.78 (s, 6H, Me); 5.51 (d, 13.1, 2H, H₂ and H₄); 6.73 (d, 8.8, 4H, H_{Ph}); 7.35 (d, 8.8, 4H, H_{Ph}); 7.37 (t, 13.1, 1H, H₃); 7.5 < δ < 7.7 [m, 30H, Ph(PPh₃)].

^{31}P δ (ppm): 13.0 (s).

^{13}C δ (ppm), J_{P-C} (Hz): 55.5 (s, OMe); 113.4 (s, C_{Ph}); 114.1 (d, 15.4, C₂ and C₄); 126.4 (d, 100.9, C_{ipso}PPh₃); 129.4 (d, 12.6, C_{Ph}); 130.7 (s, C_{Ph}); 132.6 (d, 10.2, C_{Ph}); 133.4 (d, 2.8, C_{Ph}); 158.0 (s, C₃); 161.5 (s, C-OMe); 177.9 (d, 4.1, C₁ and C₅).

2 - Synthesis of nonsymmetrical compounds

The following process described for **3b** was also applied to **3c**.

We treat 0.295 g (0.67.mmol) of carboxonium **b** in 5 ml of acetonitrile with 0.236 g (0.67.mmol) of **1** (Ph₃PNSiMe₃). The mixture is stirred at room temperature during one day. After evaporation of the solvent under vacuum, ^{31}P NMR confirms the disappearance of the starting phosphinimine **1**. The residue is a green powder. The product is recrystallized in ethanol and precipitated in the form of greenish crystals.

3b: 1-ethoxy 5-(triphenylphosphazeny)-1,5-bis(4-methylphenyl)pentadienylium perchlorate.

Yield: 50%; M.p. 190°C; MS: DCI, NH₃, M⁺ = 570, 100%; 279, 14% Ph₃PNH₃⁺.

Anal. Calcd. for C₃₉H₃₇NPO₅Cl (666.16) C, 70.32; H, 5.60; N, 2.10; Found: C, 70.05; H, 5.64; N, 2.00.

^1H δ (ppm), J (Hz): 1.41 (t, 7.0, 3H, Me of Et); 2.32 (s, 3H, Me); 2.35 (s, 3H, Me); 4.13 (q, 7.0, 2H, CH₂ of Et); 5.77 (d, 11.8, 1H, H₄); 6.31 (d, 14.4, 1H, H₂); 7.1 < δ < 7.4 (m, 9H, Ph and H₃); 7.5 < δ < 7.8 (m, 15H, Ph).

^{31}P δ (ppm): 20.3 (s).

^{13}C δ (ppm), J_{P-C} (Hz): 14.3 (s, Me of Et); 21.4, 21.5 (2s, Me-Ph); 66.3 (s, CH₂ of Et); 102.9 (s, C₂); 123.1 (d, 16.7, C₄); 123.4 (d, 100.9, C_{ipso} of PPh₃); 128.9, 129.2, 129.4, 129.5 (4s, C_{Ph}); 130.1 (d, 12.9, C_{ortho}Ph); 132.9 (d, 10.8, C_{meta}Ph); 134.5 (d, 2.9, C_{para}Ph); 141.4, 143.1 (2s, C-Me); 155.9 (s, C₃); 172.8 (s, C₁); 187.3 (d, 6.8, C₅).

3c: 1-ethoxy 5-(triphenylphosphazeny)-1,5-bis(4-methoxyphenyl)pentadienylium perchlorate.

Yield: 55%; M.p. 175°C; MS: DCI, NH₃, M⁺ = 598, 56%.

Anal. Calcd. for C₃₉H₃₇NPO₇Cl (698.16) C, 67.10; H, 5.34; N, 2.01; Found: C, 66.90; H, 5.33; N, 2.04.

^1H δ (ppm), J (Hz): 1.39 (t, 6.98, 3H, Me of Et); 3.79 (s, 3H, OMe); 3.84 (s, 3H, OMe); 4.07 (q, 7, 2H, CH₂ of Et); 5.62 (d, 11.7, 1H, H₄); 6.20 (d, 14.4, 1H, H₂); 6.8 < δ < 7.3 (m, 9H, Ph et H₃); 7.5 < δ < 7.7 (m, 15H, Ph).

^{31}P δ (ppm): 20.6 (s).

^{13}C δ (ppm), J_{P-C} (Hz): 14.3 (s, Me of Et); 55.5; 55.8 (2s, OMe on Ph); 66.0 (s, CH₂ of Et); 102.3 (s, C₂); 113.9 (d, 17.9, C₄); 123.6 (d, 100.8, C_{ipso} of PPh₃); 130.1 (d, 12.9, C_{ortho}); 132.8 (d, 10.8, C_{meta}); 134.5 (d, 3, C_{para}); 161.6 (s, C₃); 163.6 (s) 172.0 (s, C₁); 185.8 (d, 6.3, C₅).

Synthesis of **4b**: To 0.200 g (0.3.mmol) of **3b** in 3 ml of acetonitrile were added at room temperature 0.022 g (0.3.mmol) of diethylamine in 2 ml of acetonitrile. After crystallization in ethanol, we obtain an orange powder.

4b: 1-diethylamino 5-(triphenylphosphazeny)-1,5-bis(paramethylphenyl)pentadienylium perchlorate.

Yield: 55%; MS: DCI, NH₃, M⁺ = 593, 100%.

Anal. Calcd. for C₄₁H₄₂N₂PO₄Cl (693.23) C, 71.04; H, 6.11; N, 4.04; Found: C, 70.09; H, 6.06; N, 4.04.

¹H δ (ppm), J (Hz): 1.06 (t, 7.0, 3H, Me of Et); 1.33 (t, 7.0, 3H, Me of Et); 2.27 (s 3H, Me-Ar); 2.31 (s, 3H, Me-Ar); 3.22 (q, 7, 2H, N-CH₂); 3.64 (q, 8.7, 2H, N-CH₂); 5.75 (d, 13, 1H, H₂); 5.85 (d, 13, 1H, H₄); 6.71 (t, 13, 1H, H₃); 6.85 < δ < 7.16 (m, 8H, Ph); 7.5 < δ < 7.7 (m, 15H, PPh₃).

³¹P δ (ppm): 12.7 (s).

¹³C δ (ppm), J_{P-C} (Hz): 12.5 (s, Me of Et); 14.2 (s, Me of Et); 21.3 (s, Me-Ph); 45.1 and 48.2 (2s, CH₂ of Et) 110.2 (s, C₂); 110.5 (s, C₄); 121.5 (d, 101.1, C_{ipso} of PPh₃); 123.7, 129.2, 132.4, 132.6 (4s, CPh); 155.4 (s, C₃); 164.6 (s, C₁).

B - Reactions of the N trimethylsilyl guanidine **2**

Synthesis of symmetrical derivatives 2a, 2b, 2c

We describe only the procedure for **2b**.

To 0.503 g (1.15.mmol) of carboxonium **b** in 10 ml of acetonitrile we add dropwise 0.445 g (2.37.mmol) of the N-trimethylsilylguanidine **2** at room temperature. We observe a change in the coloration of the mixture. Stirring is continued 12 h at room temperature. After removal of the solvent the residue is dried in vacuo during three hours. The compound **2b** is then recrystallized in ethanol and is obtained as a red powder.

The other compounds **2a** and **2c** have been prepared according to the same procedure.

2a: 1,5-bis(dimethylguanidino)-1,5-bis(phenyl)pentadienylium perchlorate.

Yield: 55%; powder; M.p. 200°C; MS: DCI, NH₃, M⁺ = 445, 1% ; 116, 100% (Me₂N)₂CNH₂⁺.

Anal. Calcd. for C₂₇H₃₇N₆O₄Cl (545.09) C, 59.50; H, 6.84; N, 15.42; Found: C, 58.98; H, 7.08; N, 14.81.

¹H δ (ppm), J (Hz): 2.9 (s, 24H, NMe₂); 6.15 (d, 13.1, (A₂), 2H, H₂ and H₄); 7.45 (m, 10H, Ph); 7.5 (t, 13.1, (X), 1H, H₃)

¹³C δ (ppm): 40.3 (s, NMe₂); 111.2 (C₂ and C₄); 127.9; 128.6; 130.5; 138.6 (s, aromatic C); 151.5 (s, C₃); 165.6 (s, C₁ and C₅); 171.0 (s, C(N)₃)

2b: 1,5-bis(dimethylguanidino)-1,5-bis(4-methylphenyl)pentadienylium perchlorate.

Yield: 60%; powder; M.p. 180°C; MS: DCI, NH₃, M⁺ = 473, 2.5%; 116, 100% (Me₂N)₂CNH₂⁺.

Anal. Calcd. for C₂₉H₄₁N₆O₄Cl (573.14) C, 60.77; H, 7.21; N, 14.66. Found: C, 60.68; H, 7.11; N, 14.38.

¹H δ (ppm), J (Hz): 2.37 (s, 6H, Me); 2.6 (s, 24H, NMe₂); 6.12 (d, 13.1, (A₂), 2H, H₂ and H₄); 7.21 (d, 8, (AB), 4H, Ph); 7.42 (d, 8, (AB), 4H, Ph); 7.48 (t, 13.1, X, 1H, H₃).

¹³C δ (ppm): 21.4 (s, Me); 40.3 (s, NMe₂); 111.2 (s, C₂ and C₄); 127.9, 129.3 (s, C_{arom.}); 135.7 (s, C_{ar.-C}); 141.1 (s, C_{ar-Me}); 150.7 (s, C₃); 165.5 (s, C₁ and C₅); 170.9 (s, C(N)₃).

2c: 1,5-bis(dimethylguanidino)-1,5-bis(4-methoxyphenyl)pentadienylium perchlorate.

yield: 60%; powder; M.p. 160°C; MS: DCI, NH₃, M⁺ = 505, 35%; 116, 100% (Me₂N)₂CNH₂⁺.

Anal. Calcd. for C₂₉H₄₁N₆O₆Cl (605.14) C, 57.56; H, 6.83; N, 13.89; Found: C, 56.35; H, 6.73; N, 13.78.

^1H δ (ppm), J (Hz): 2.86 (s, 24H, NMe₂); 3.86 (s, 6H, OMe); 6.18 (d, 13.1, (A₂), 2H, H₂ and H₄); 6.95 (d, 8.9, (AB), 4H, H_{Ph}); 7.53 (d, 8.9, (AB), 4H, H_{Ph}); 7.54 (t, 13.1, (X), 1H, H₃).
 ^{13}C δ (ppm): 40.3 (s, NMe₂); 55.6 (s, OMe); 111.0 (s, C₂ and C₄); 114.0; 129.7 (2s, C_{Ph}); 130.8 (s, C_{Ph-C}); 150.3 (s, C₃); 161.8 (s, C_{ar-OMe}); 165.5 (s, C₁ and C₅); 170.3 (s, -C(N)₃)

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