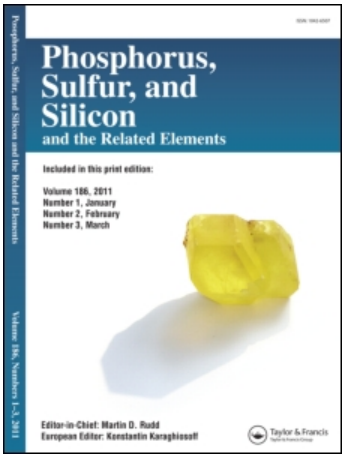

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ADDITIONS ON CYANINE DYES: A SIMPLE APPROACH TO THE SYNTHESIS OF BIS(γ-AMINOALLYL)PHOSPHINES AND PHOSPHONATES

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The nucleophilic addition of phosphine lithium derivatives on the C3 carbon of pentamethine cyanines dyes leads in one step to bis(γ-aminoallyl)phosphines. Furthermore, extension of this reaction to the phosphonate homologues affords the new bis(γ-aminoallyl)phosphonates.

Keywords: cyanine dyes; nucleophilic addition; lithium reagents; bis(γ-aminoallyl)phosphines; bis(γ-aminoallyl)phosphonates

INTRODUCTION

The cyanine dyes, charged polyenic systems containing a delocalized π-electron backbone, are considered as the basic structure within the conjugated cationic organic compounds. Their application range is rather large, from biology to physics. Some striking examples will be found in recent papers or reviews, i.e. association with DNA or PNA for molecular recognition[1], photochemistry and photochromic systems[2], non-linear optics[3], organised systems and use as fluorescent sensors[4]. Nevertheless, in the literature, there are few publications about the reactivity of the pentamethine chain and the reactions with nucleophiles are little developed.[5] Owing to the fact that these systems present an alternate charge delocaliza-

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tion, positive on the odd carbons and negative on the even ones, the regioselectivity of such attack is to be studied. In a previous development, we first explored the nucleophilic addition of lithium organo metallates in the cyanine dyes series[6] leading to new podands.

In catalysis, there is a great interest in combining the strong co-ordination via phosphorus with a hemilabile donor to obtain transient stabilisation of intermediates during the reaction pathway.[7]

Thus, the generalisation of the addition of phosphorus derivatives to cyanine moieties may open a new synthetic route to hardly obtainable trifunctional NPN, NPO or OPO complexing compounds. In our first attempt, the addition of diphenylphosphine was achieved in a tandem type reaction.[8] Though the efficiency of this reaction was high with good yields, it was limited to phosphines.

The aim of the work presented here is to describe a decisive improvement which overcomes this drawback, a new one pot synthesis of tridentate NPN ligands. This new way can be extended to the phosphonate series.

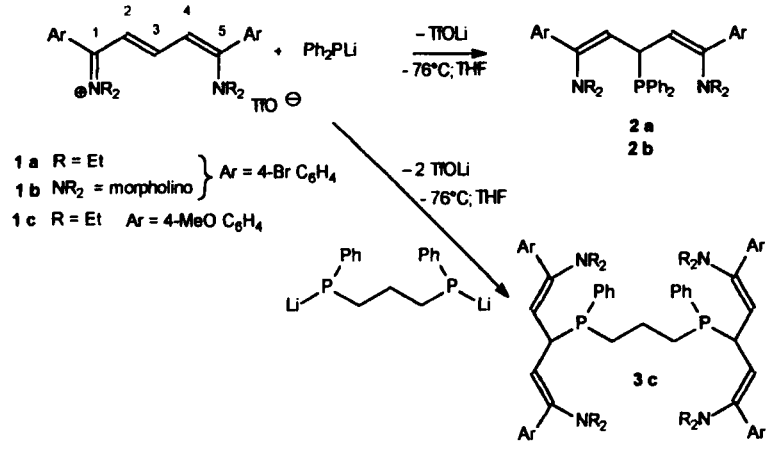
RESULTS AND DISCUSSION

The basis of the enhancement was to consider the polymethine chain as a soft electrophile owing to its delocalized positive charge. Thus, the use of the soft lithium derivatives of phosphines and phosphonates instead of the harder phosphines or phosphonates offers a better fit between the reagents.[9]

Phosphine reagents: Ph_2PLi and $PhPLi(CH_2)_3PLiPh$

The reactions are carried out by addition of the phosphine lithium derivative at −76°C in a THF solution of symmetrical cyanine **1a** and **1b** (Ph_2PLi) or **1c** ($PhPLi(CH_2)_3PLiPh$) (Scheme 1).

The directly obtained neutral NPN ligands **2a** and **2b** are characterised by spectroscopic methods. In $^{31}P\{^1H\}$ NMR we observe a single signal at 4.2 (**2a**) and 2.2 ppm (**2b**) in the range of phosphine chemical shift.[10] Furthermore the ^1H and ^{13}C NMR data indicates that the products are symmetric. If we compare the data of the starting cyanines with those of the



SCHEME 1

phosphines, we observe that the loss of the positive charge induces a shielding of the odd carbons C1, C3 and C5 in the two phosphines **2a** and **2b**. Finally, these results are in accordance with our previous ones [Ar = C_6H_5; R = morpholino) with $\delta\ ^{31}P = 6.3$ ppm and an unambiguous X-ray structure determination].[8] Furthermore, compound **3** ($\delta\ ^{31}P = -3.5$ ppm in THF) was synthesised to demonstrate the planed extensions to hexadentates or polydentates ligands.

According to a semi empirical PM3 calculations,[11] we determined the repartition of the charges along the pentamethine chain. These calculations are in good agreement with the $\delta^{13}C$ NMR chemical shifts; the odd carbons (C1, C3, C5) bearing a partial positive charge are deshielded whereas the even negatively charged carbons (C2, C4) are shielded. To take into account the effect of the electronegative bromine group, new semi empirical charge calculations were performed after geometry optimisation of the structures **1a** and **1b** with AM1 force field (program Hyperchem 5.01; 1996). (Figure 1) The results presented here show no discrepancy with the previous ones. It is to notice that the largest positive charges (0.250 *[1.6 10^{-19}C]) are localised on C1 and C5 whereas the C3 corresponds only to 0.125.

Thus the question of the regioselectivity of the phosphine addition which is preferred on C3 cannot be treated only in terms of the most electrophilic

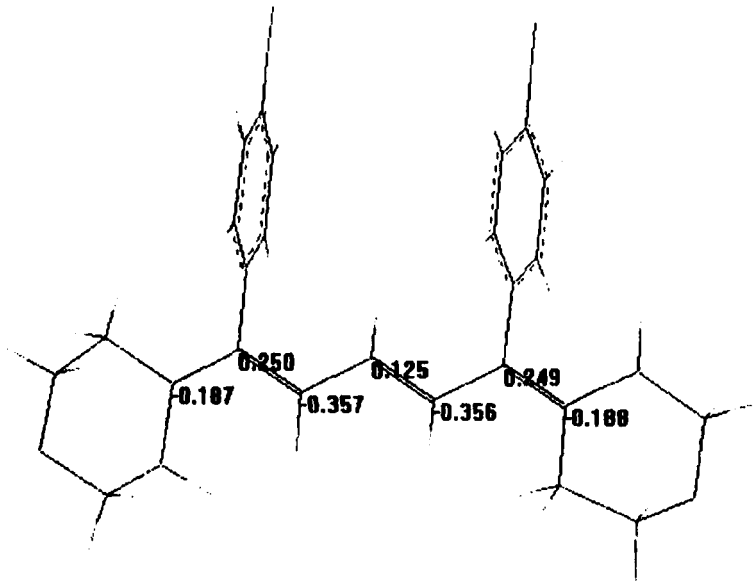


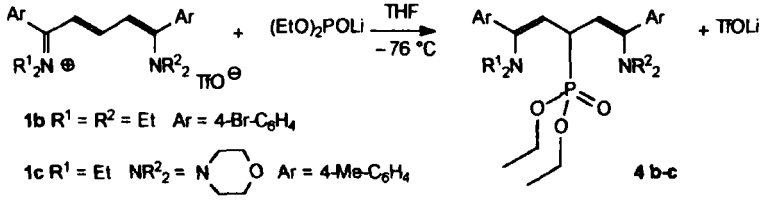
FIGURE 1 Calculated charges for cyanine **1b**

carbon but also with steric interactions and mainly in the best fit between the reagents in the Pearson theory. In fact, as exemplified by the nucleophilic cleavage of the terminal amino groups by the hard OH^- base,[12] the cyanine moiety present both soft (C3) and harder (C1 and C5) electrophilic sites which direct the regioselectivity.

Furthermore it offers the possibility to extend this synthesis to other phosphaanions like the dialkoxy phosphonates $(RO)_2 PO^-$.

Phosphonate reagent $(EtO)_2$ POLi

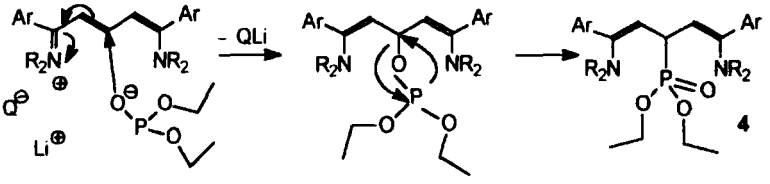
The deprotonation of the diethylphosphite is realised by addition of butyllithium in THF solution at −76°C. The phosphaanion is not isolated but added dropwise to an equimolecular amount of the cyanine in THF at −76°C. The solution temperature is raised to room temperature, and the phosphonates **4b-c** are isolated as yellow solids. (Scheme 2)



SCHEME 2

In the case of **4c**, the use of a dissymmetric cyanine **1c** render the C3 carbon atom chiral, thus this compound is a racemic mixture of enantiomers.

One of the likely mechanism is represented in Scheme 3. The oxaanion, reactive lithium derivative, can be rearranged after addition following the well known Michaelis – Becker – Nylen process leading to the formation of the phosphonates **4**.[13] It corresponds to a transformation $P^{III} \rightarrow P^{V}$. On the other hand, a similar reaction was published by Mikolajczyk and al.[14] by action of lithium or sodium salts of dialkyl and diamido phosphites on sulfinimines, where the reactivity may be explained by a direct phosphanion addition.



SCHEME 3

The most interesting feature is the easy formation of the phosphonates **4** which could not be accessed by our previous tandem method.[8] In this former case, the addition of an equimolar amount of triflic acid and diethylphosphite to the solution of the cyanine does not lead to the expected dicationic addition intermediate but to the corresponding phosphonium triflate. Thus, the nucleophilic attack of the diethylphosphonate lithium salt on the C3 carbon of the pentamethine chain is a unique way to

prepare compounds like **4**, the addition on the cyanine dye corresponding to the formation of a P-C bond without the necessity of a leaving group on the concerned carbon.[15]

In conclusion the newly synthesised products, bis(γ-aminoallyl)phosphine or phosphonate derivatives may be used as ligands in coordination chemistry, and also reduced to give bis(γ-amino)phosphorus derivatives (work in progress) and also as reactive intermediates.[16] Following the literature, the carbanions generated in the allylic position, stabilised by the phosphorus atom, are involved in reactions with aromatic aldehydes,[17] cyclic enones,[18] in the stereoselective synthesis of substituted alkenes[19] and allyl amines.[20]

EXPERIMENTAL

All reactions were carried out under a dry argon atmosphere. The solvents are dried and freshly distilled prior to use.

Cyanines

2 ml (19 10^{-3} mol) of diethylamine were added to 5.82 g (9.4 10^{-3} mol) of carboxonium salt in solution in 25 ml acetonitrile at room temperature. After three hours, the solvent is eliminated under vacuum. The product is crystallized from ethanol

Cyanine Ia

Yield 80%. mp 202°C., UV $\lambda = 466$ nm, $\varepsilon = 80810$ $mol^{-1}dm^3cm^{-1}$ Mass Spectrometry (ES, CH_3CN) m/z = 519.1 (M^+)

Anal. calcd for $C_{26}H_{31}Br_2F_3N_2O_3S$: C, 46.74; H, 4.74; N, 4.20; S, 4.19. Found C, 46.72; H, 4.99; N, 4.08; S, 4.41.

^{1}HNMR($CDCl_3$, 300.133 MHz)

δ 1.0 (t, 6H, J=7, $CH_2\underline{CH_3}$), 1.3 (t, 6H, J=7, $CH_2\underline{CH_3}$) 3.1 (q, 4H, J=7, $\underline{CH_2}CH_3$), 3.7 (q, 4H, J=7, $\underline{CH_2}CH_3$) 5.8 (t, 1H, J=14.8, H-3), 6.3 (d, 2H, J=14.8, H-2, H-4) 6.8 – 7.4 (m, 8H, H arom).

^{13}C NMR ($CDCl_3$, 75.469MHz) δ 12.5(s, CH_3), 14.3(s, CH_3), 45.4(s, CH_2), 48.2(s, CH_2) 106.2(s, C-2 and C-4), 124.4, 129.6, 131.6, 131.8 (C arom)161.7 (s, C-3), 161.8(s, C-1 and C-5).

Cyanine Ib

Yield: 80 %. mp 209°C UV: $\lambda = 455$ nm, $\varepsilon = 65670$ $mol^{-1}dm^3cm^{-1}$ Mass Spectrometry (DCI/NH_3) m/z = 545 (M^+)

^1H NMR ($CDCl_3$, 200.133MHz)

δ 3.3 (m, 4H, NCH_2), 3.6 (m, 4H, NCH_2), 3.9 (m, 8H, O-CH_2), 6.1 (t, 1H, J=12.9, H-3), 6.6 (d, 2H, J=12.9, H-2 and H-4), 6.9 – 7.5 (m, 8H, H arom).

^{13}C NMR ($CDCl_3$, 62.896MHz)

δ 45.0(s, N-CH_2), 66.7 (s, O-CH_2), 108.5(s, C-2 and C-4)125.1, 130.1, 131.0, 132.1(s, C arom), 162.9 (s, C-3), 167.9(s, C-1 and C-5).

Cyanine Ic

Yield: 80%. mp 170°C UV: $\lambda = 445$nm, $\varepsilon = 110346$ $mol^{-1}dm^3cm^{-1}$ Mass Spectrometry (ES, MeOH) m/z = 403.3 (M^+)

^{1}HNMR ($CDCl_3$, 250.133MHz)

δ 0.9 (t, 3H, J=7.5, $CH_2\underline{CH_3}$), 1.3 (t, 3H, J=7.5, $CH_2\underline{CH_3}$), 2.2 (s, 6H, CH_3 arom), 3.1 (q, 4H, J=7.5, N-CH_2 morpholino), 3.5 (m, 2H, N-$\underline{CH_2}CH_3$), 3.6 (q, 2H, J=7.5, N-$\underline{CH_2}CH_3$), 3.7 (m, 4H, O-$\underline{CH_2}$ morpholino), 6.0 (dd, 1H, J=12.5, J=12.5, H-3), 6.2 (dd, 2H, J=12.5, J=5, H-2, H-4), 6.75 – 7.00 (m, 8H, H arom).

^{13}CNMR ($CDCl_3$, 62.896MHz)

δ 12.5(s, CH_3), 14.1(s, CH_3), 21.2(s, CH_3arom), 45.3(s, N-CH_2), 48.3(s, N-CH_2), 48.4(s, N-CH_2 morpholino), 51.0(s, N-CH_2 morpholino), 66.3(s, O-CH_2 morpholino), 66.9(s, O-CH_2 morpholino), 105.9(s, C-2 or C-4), 107.7(s, C-4 or C-2), 127.7, 128.6, 129.0, 129.3(s, C arom), 163.0(s,C-3), 166.6(s, C-1 or C-5), 170.3(s, C-5 or C-1).

Phosphines 2a and 2b

Ph_2PLi synthesis

To 0.94 ml ($1.51\ 10^{-5}$ mol) of n-butyllithium under an inert atmosphere (1.6 M in hexane) were added dropwise 0.26 ml ($1.51\ 10^{-5}$mol) of diphenylphosphine in 3 ml tetrahydrofuran at –76°C

The solution becomes orange. The reaction mixture is kept at –76°C during 45 mn, then allowed to rise to room temperature and left under agitation during 30 mn (δ $^{31}P = -15$).

Phosphine 2a synthesis

To a yellow suspension of 1 g ($1.51\ 10^{-5}$ mol) of cyanine **la** in 10 ml of tetrahydrofuran at – 40°C were added with a transfer needle the freshly prepared solution of Ph_2PLi. The mixture becomes clear green then turns very quickly yellow. After 3 h, the crude reaction mixture is filtrated over Celite to eliminate lithium triflate (the complete elimination of lithium salt is achieved only after two times dissolution in benzene/filtration) The solvent is evaporated under vacuum and the product is obtained as a yellow powder. The process is the same for the phosphine **2b**.

Characterization of **2a**: Yield: 60 % mp 92°C.

UV: $\lambda = 464$ nm, $\varepsilon = 16929\ mol^{-1}dm^3cm^{-1}$

Mass Spectrometry (ES) m/z =705.2 (M^+)

Anal. calcd. for $C_{37}H_{37}Br_2N_2P$: C, 62.27; H, 5.79; N, 3.77 Found: C, 63.08; H, 5.87; N, 3.98. ^{31}P ($CDCl_3$, 81.015 MHz) $\delta = 4.2$(s).

^1H NMR($CDCl_3$, 250.133 MHz)

δ 0.8 (t, 12H, J=7, CH_2CH_3), 2.6 (q, 8H, J=7, CH_2CH_3), 4.0 (td, 1H, J=3, J=9.6, H3), 4.7 (d, 2H, J=9.6, H2 and H4), 6.6 – 7.4 (m, 18H, H arom).

^{13}C NMR ($CDCl_3$, 62.869 MHz)

δ 11.6 (s, CH_3), 43.6 (s, CH_2), 107.3 (s, C_4), 107.7 (s, C_2), 121.2, 128.3, 131.0 (s, C arom), 131.5–136.3 (s, C arom), 137.2 (m, C_3), 143.9 (s, C_5), 144.1(s, C_1).

Phosphine 2b: Yield: 65%. mp 144 °C.

UV: $\lambda = 464$ nm, $\varepsilon = 16500\ mol^{-1}dm^3cm^{-1}$

Mass Spectrometry (DCI, NH_3) m/z = 731 (MH^+).

Anal. calcd. for $C_{37}H_{37}Br_2N_2O_2P$: C, 58.67; H, 4.92; N, 3.21. Found: C, 60.77; H, 5.09; N, 3.82. ^{31}P NMR ($CDCl_3$, 81.015 MHz) $\delta = 2.2$ (s).

^1H NMR ($CDCl_3$, 250.133 MHz)

δ 1.4 (m, 8H, N-CH_2), 3.4 (m, 4H, O-CH_2), 3.6 (m, 4H, O-CH_2), 4.0 (td, 1H, J=3.6, J=6.9, H3), 4.7 (d, 2H, J=6.9, H2 and H4), 6.6–7.1 (m, 18H, H arom).

^{13}C NMR ($CDCl_3$, 62.869 MHz)

δ 38.7 (d, 3=0.4, C_3), 50.3 (s, NCH_2), 66.9 (s, OCH_2), 107.6 (s, C_4), 107.8 (s, C_2), 122.3–136.4 (m, C arom.), 147.8 (s, C_5), 148.0 (s, C_1).

Phosphonates 4

$(EtO)_2POLi$ synthesis

To 0.94 ml ($1.5\ 10^{-5}$ mol) of n-butyllithium under an inert argon atmosphere (1.6 M in hexane) were added dropwise 0.19 ml ($1.5\ 10^{-5}$mol) of diethylphosphite in 5 ml tetrahydrofuran at – 76°C. The solution becomes turbid. The reaction mixture is kept two hours at 0 °C. ^{31}P NMR control of the mixture indicates the formation of $(EtO)_2POLi$ ($\delta\ ^{31}P = 144$).

Phosphonate 4b

1 g ($1.5\ 10^{-5}$ mol) of cyanine **1b** is dissolved in 20 ml acetonitrile at – 76°C. The solution of $(EtO)_2POLi$ is then added dropwise. The solution, initially red, becomes yellow. After 10 mn the solution is allowed to rise to – 10°C, then left at room temperature for 3 h. The ^{31}P NMR spectrum of the crude product indicates the presence of one signal at $^{31}P = 28$ ppm corresponding to the phosphonate **4b**. The mixture is left overnight at –20°C and a fine precipitate is eliminated. The crude filtrate is then dissolved in toluene and filtrated under Celite to eliminate the lithium salt (two times). After evaporation of the solvent, the phosphonate is obtained as a brown solid. Yield: 50%.

Mass Spectrometry: (DCI / CH_4): m/z = 657 (MH^+).

UV: λ = 446 nm, ε = 32874 $mol^{-1}dm^3cm^{-1}$

^{31}P NMR (C_6D_6, 81.026MHz): δ = 28.4 (s)

^1H NMR (C_6D_6, 400.13MHz)

δ 0.9 (t, 6H, J=6, CH_2CH_3), 1.2 (t, 6H, J=6, CH_2CH_3), 2.8 (q, 8H, J=6, CH_2CH_3), 3.5 (dt, 1H, ^3J=10.9, ^2J=21.9, H3), 4.1 (q, 4H,J=6, OCH_2), 4.7 (dd, 2H, ^3J=10.9, ^3J=6.3, H2 and H4)7.0 (d, 4H, J=7, H arom), 7.2 (d, 4H, J=7, H arom).

^{13}C NMR(C_6D_6, 62.896 MHz)

δ 11.8 (s, NCH_2CH_3), 16.6 (s, OCH_2CH_3), 39.1 (d,J=146, C_3), 43.5 (s, N-CH_2), 62.8, (d,J=7.7, OCH_2), 101.1 (d, J=9, C_2 and C_4), 122.1, 131.3, 131.5 (s, C arom), 137.2 (s, C arom), 146.9 (s, C_5), 147.2 (s, C_1)

Phosphonate 4c

The synthesis is the same than for **4b**

Mass Spectrometry: (DCI / NH_3): m/z = 541 (MH^+).

^{31}P NMR (C_6D_6, 81.026MHz): δ = 28.8 (s)

^{1}H NMR ($CDCl_3$, 400.13MHz)

δ 1.0 (t, 6H, J=7, NCH_2CH_3), 1.23 (t, 3H, OCH_2CH_3), 1.24 (t, 3H, OCH_2CH_3), 2.2 (s, 6H, CH_3), 2.8 (m, 4H, NCH_2-morpholino), 2.9 (q, 4H, J=7, NCH_2CH_3),

3.6 (m, 4H, OCH_2-morpholino), 3.85 (dt, 1H, ^{3}J=10.8, ^{3}J=24.2, H3), 4.2 (q, 4H, OCH_2CH_3), 4.9 (dd, 1H, ^{3}J=10.8, ^{3}J=6.2, H4 or H2), 5.0 (dd, 1H, ^{3}J=10.8, ^{3}J=6.2, H_2 or H_4), 6.8 (d, 4H, J=7, H arom), 7.2 (d, 4H, J=7, H arom).

^{13}C NMR ($CDCl_3$, 100.61MHz)

δ 12 (s, NCH_2CH_3), 13.8 (s, OCH_2CH_3), 16.6 (s, CH_3), 39 (d, J=143.6, C_3), 43.3 (s, NCH_2-morpholino), 50.3 (s, NCH_2CH_3), 62.7 (s, P-OCH_2), 62.9 (s, P-OCH_2), 66.7 (s, OCH_2-morpholino), 100.7 (d, J=133, C_4 or C_2), 108.6 (s, J=150, C_2 or C_4), 129, 130, 134.7, 135.7, 136.7, 136.9, (s, CH and C arom), 148.5 (s, C1), 150.8 (s, C_5).

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