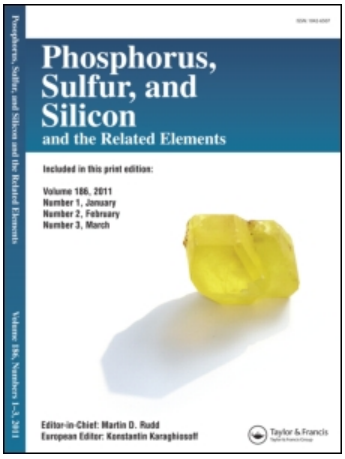

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HEXACOORDINATE PHOSPHONIUM SALTS InCORPORATING TWO (8-DIMETHYLAMINO)-1-NAPHTHYL LIGANDS. STRUCTURE AND REACTIVITY

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HEXACOORDINATE PHOSPHONIUM SALTS INCORPORATING TWO (8-DIMETHYLAMINO)-1-NAPHTHYL LIGANDS. STRUCTURE AND REACTIVITY*

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New hexacoordinate phosphonium salts $Ar_2RZP^+ X^-$[Ar = (8-dimethylamino)-1-naphthyl] with two N→P intramolecular coordinations are described. NMR studies of these salts and the X-ray structure of one of them, **5** (R = Ph, Z = H, X = Br) show that they have a dissymmetric structure with the two Me_2N groups coordinated at the phosphorus centre. Salts **4** (R = Ph or Me, Z = CH_2CO_2Et) react slowly with PhCHO under Wittig conditions probably because of the steric hindrance around the phosphorus atom. This is confirmed by the higher reactivity of the less hindered pentacoordinate phosphonium salts $ArR_2P^+CH_2CO_2Et\ X^-$ **11** (R = Ph or Me) which are also much more reactive than $Ph_3P^+CH_2CO_2Et\ Br^-$. This study points out the increase of reactivity of these salts due to the N→P interaction.

Keywords: Phosphonium salts; hexacoordinate; pentacoordinate; P-H bond; N→P interaction; X-ray structure; Wittig reaction

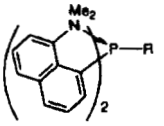
INTRODUCTION

Most of the neutral hexacoordinate phosphorus compounds[1,2] are formed by inter or intramolecular chelation of a donor atom to the phosphorus atom of a phosphorane. The geometries of these derivatives are more or less distorted octahedrons with P-N distances less than 2.0 Å.

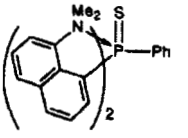
* Cet article est dédié au Docteur Robert Wolf en reconnaissance de son importante contribution dans la chimie des dérivés organophosphorés aussi bien sur le plan scientifique que sur le plan éducatif. Il a su communiquer sa flamme aux plus jeunes, sachant leur faire partager son enthousiasme. Nous le remerçions de nous avoir initié à la chimie du phosphore.

† Corresponding author.

Recently we described the X-ray crystal structure analysis of the pseudohexacoordinate (taking into account the lone pair) phosphane **1a**[3] and that of the hexacoordinate phosphane sulphide **2**[3] in which extra coordination was achieved by chelation of two NMe_2 groups to a P(III) atom in the case **la** and to a P(IV) atom in the case of **2.** The geometries of these derivatives are not octahedral but correspond to slightly distorted bicapped tetrahedrons with long N-P distances (2.8 to 3.0 Å). As these two compounds have unusual geometries, it was of interest to examine the influence of the positive charge of a hexacoordinate phosphonium salt on the geometry of the molecule and on the N-P distances. Moreover, to our knowledge, hexacoordinate phosphonium salts are unknown, and we can expect unusual properties for these derivatives.



1 a : R = Ph
b : R = Me
c : R = H



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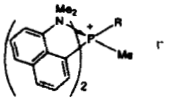
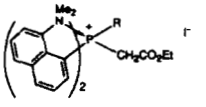
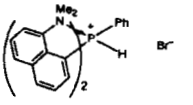
In this paper we describe hexacoordinate phosphonium salts **3-6,** the X-ray structure of **5** and some preliminary results concerning the reactivity of phosphonium salts **4** in the Wittig reaction.



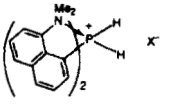
3 a : R = Ph
b : R = Me



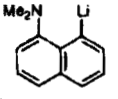
4 a : R = Ph
b : R = Me



5



6 a : X = Br
b : X = TFPB



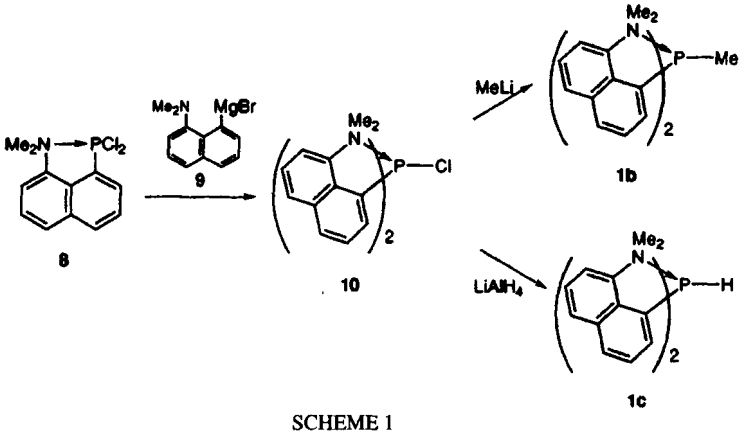
7

RESULTS AND DISCUSSION

1. *Preparation of the phosphonium salts*

While phosphane **1a**[3] was obtained by reaction of lithium derivative **7** with $PhPCl_2$, reaction of **7** with $MePCl_2$ did not give phosphane **1b** in pure form. This

phosphane was better obtained from the reaction described in Scheme 1. Reaction of one molar equivalent of Grignard reagent **9** with dichlorophosphane **8**[4] at -20°C gives the very unstable chlorophosphane **10**. Reaction of **10** with MeLi at -60°C affords **1b** while reaction of **10** with $LiAlH_4$ at -30°C affords **1c**.



SCHEME 1

The phosphonium salts **3** and **4** were prepared by the reaction of the corresponding phosphane with the appropriate alkyl halide in toluene, at 120°C starting from **1a** and at room temperature starting from **1b**. The lower reactivity of phosphane **1a** compared to that of **1b** is probably due to the greater steric hindrance of this phosphane. Phosphanes **1a** and **1c** react with an ethereal solution of HBr to give phosphonium salts **5** and **6a**, respectively. **5** is air-stable but decomposes slowly in solution. **6a** is highly unstable both in solution and in air. Treatment of **6a** with sodium tetrakis[3,5-bis(trifluoromethyl)phenyl borate] (Na TFPB) afforded salt **6b**. Attempts to obtain crystals suitable for X-ray analysis failed probably owing to the solutions of this salt being highly unstable. Salts **6** are the first known examples of isolated phosphonium salts with two P-H bonds. We assume that isolation of **6** was possible because of the steric hindrance of the two (8-dimethylamino)-1-naphthyl ligands.

2. *X-ray structure analysis of* 5

Crystals of **5** were grown from a CH_2Cl_2 solution at room temperature. The compound crystallizes with two molecules of CH_2Cl_2. The ORTEP drawing of **5** is shown in Fig.1. Selected bond distances and angles are given in Tables I and II and other crystallographic details are reported in Tables III and IV. The N(1)Me_2 group is located opposite to the P-C(21) bond and the N(2)Me_2 group is also opposite to the P-C(11) bond, the N(1)···P···N(2) angle value being 94.9°. The

two N···P distances (2.74 and 2.70 Å) are shorter than the N···P distances in thiophosphane **2** (3.011 and 3.009 Å) and significantly shorter than the sum of the P and N van der Walls radii (3.4 Å)[5]. The average C-P-C angle is 107° very close to the expected value for a tetrahedron. The H atom on phosphorus was located through a difference Fourier map. At this stage the P-H bond distance was 1.37 Å and the angle values H-P-C(1), H-P-C(11) and H-P-C(21) were 123, 101, and 110(2)°, respectively. After the last refinement cycles, the P-H distance decreased to 0.89 Å giving less accurate values for the above angles: 133, 93 and 106(8)°. We observed that the four chlorine atoms and the bromide anion have a considerable weight on the refinement and therefore induce a low accuracy on the location of the hydrogen atom.

The two naphthalenic groups are only slightly distorted, the dihedral angle values between the two rings in each case being only 2 and 4°. The C(21)-P, C(28)-N(2), and C(1)-P, C(8)-N(1) bonds are only slightly bent with P-C(1)-C(9) and P-C(21)-C(29) angle values of 125.1 and 122.8° and N(1)-C(8)-C(9) and N(2)-C(28)-C(29) angle values of 116.6 and 117.2°.

Thus the phosphonium salt **5** has the same dissymmetric structure as phosphane **1a** and phosphane sulphide **2** and can be also described as a bicapped tetrahedron. Because of the positive charge on the phosphorus atom, the P-N distances are shorter than the same distances in phosphane sulphide **2** and even in phosphane **1a.**

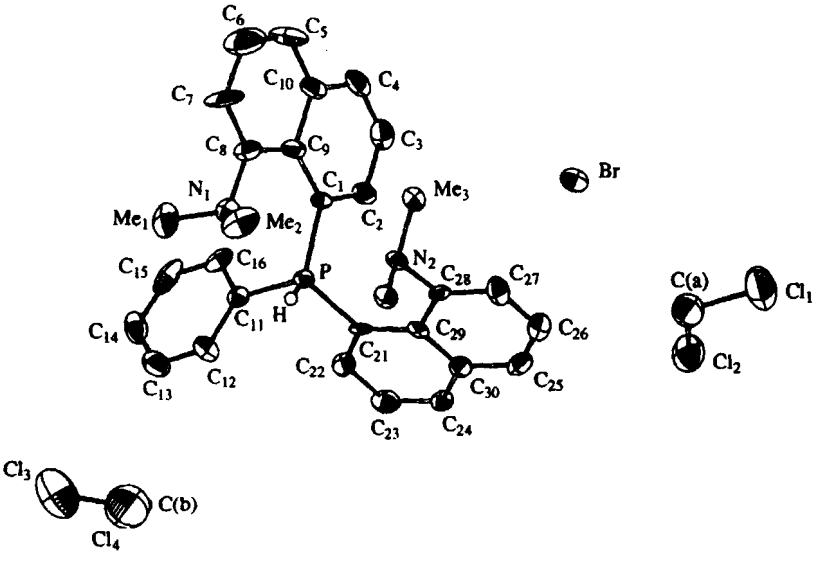


FIGURE 1 ORTEP drawing of the molecular struture of phosphonium salt **5** showing the numbering scheme. The thermal ellipsoids and spheres are at the 30% probability level

TABLE I Interatomic distances (Å) in compound **5**

P - C 1	1.807 (10)	C 13 - C 14	1.38 (2)
P - C 11	1.780 (10)	C 14 - C 15	1.37 (2)
P - C 21	1.828 (10)	C 15 - C 16	1.39 (2)
P - H	0.89 (13)	C 16 - C 11	1.39 (1)
P ... N 1	2.738 (9)	C 21 - C 22	1.37 (1)
P ... N 2	2.700 (8)	C 22 - C 23	1.42 (2)
		C 23 - C 24	1.35 (1)
C 1 - C 2	1.40 (1)	C 24 - C 30	1.37 (1)
C 2 - C 3	1.42 (2)	C 30 - C 25	1.40 (1)
C 3 - C 4	1.37 (2)	C 25 - C 26	1.37 (2)
C 4 - C 10	1.40 (2)	C 26 - C 27	1.42 (2)
C 10 - C 5	1.39 (2)	C 27 - C 28	1.37 (1)
C 5 - C 6	1.34 (2)	C 28 - C 29	1.43 (1)
C 6 - C 7	1.40 (2)	C 29 - C 30	1.45 (1)
C 7 - C 8	1.35 (2)	C 29 - C 21	1.40 (1)
C 8 - C 9	1.39 (1)	C 28 - N 2	1.46(1)
C 9 - C 10	1.46 (2)	N 2 - Me 3	1.45 (1)
C 9 - C 1	1.41 (1)	N 2 - Me 4	1.48 (1)
C 8 - N 1	1.44 (1)		
N 1 - Me 1	1.48 (2)	C(a) - Cl1	1.77 (1)
N 1 - Me 2	1.47 (2)	C(a) - Cl2	1.76 (1)
C 11 - C 12	1.39 (1)	C(b) - Cl3	1.68 (2)
C 12 - C 13	1.39 (2)	C(b) - Cl4	1.72 (2)

TABLE II Selected Bond Angles (deg.) in compound **5**

P-C 1- C 9	125.1 (7)	C 1 - P - C 11	107.1 (5)
P - C 1 - C 2	114.6 (7)	C 1 - P - C 21	108.4 (4)
C 2 - C 1 - C 9	120.2 (9)	C 1 - P...N 2	78.4 (3)
C 1 - C 9 - C 8	125.3 (9)	C 1 - P...N 1	74.8 (4)
C 9 - C 8 - N 1	116.6 (9)	H - P - C 11	93 (8)
C 7 - C 8 - C 9	121.9 (1.0)	H - P - C 21	106 (8)
C 7 - C 8 - N 1	121.4 (1.0)	H - P...N 2	79 (8)
C 8 - N 1...P	98.2 (6)	H - P...N 1	66 (8)
P - C 21 - C 29	122.8 (7)	C 11 - P - C 21	105.2 (4)
P - C 21 - C 22	116.3 (7)	C 21 - P...N 2	77.0 (3)
C 22 - C 21 - C 29	120.9 (9)	N 2...P...N 1	94.9 (3)
C 21 - C 29 - C 28	125.1 (8)	N 1...P - C 11	82.2 (4)
C 29 - C 28 - N 2	116.8(8)	N 1...P - C 21	170.2 (4)
C 27 - C 28 - C 29	121.8 (9)	N 2...P - C 11	173.0 (4)
C 27 - C 28 - N 2	121.4 (9)	C 1 - P - H	133 (9)
C 28 - N 2...P	97.1 (5)		

TABLE III Summary of Crystal data. Intensity measurements and refinement for Compound **5**

Formula	$C_{30}H_{30}BrN_2P$, 2 CH_2Cl_2
Cryst. system	monoclinic
Space group	$P2_1/c$
a, Å	17.504 (4)
b, Å	11.657 (5)
c, Å	18.867 (5)
β deg.	117.58 (2)
Vol,. $Å^3$	3412 (2)
Mol. wt	529.46 (699.3)
Z	4
d_{calcd}, g cm^{-3}	1.36
Cryst. Color	colourless
Recryst. solv	CH_2Cl_2
mp,°C	dec
Method of data collectn	ω / θ
Temp. of data collecta	163 K
Radiatn (graphite monochoromated)	Mo, *K*α
μ, cm^{-1}	15.8
2θ limits, deg.	42
No of unique reflectns	3604
No of obsd reflectns	2310
Final no. of variables	201
R	0.065
R_w	0.070
Residual electron density	1.35

TABLE IV Fractional Atomic Coordinates (x10^4)

Atom	*x/a*	*y/b*	*z/c*
Br	3133.8(7)	2294.2 (9)	5722.3(6)
C(a)	1004 (9)	1261 (12)	5630 (8)
Cl 1	38 (2)	1849 (4)	4876 (3)
Cl 2	1109 (2)	1568 (3)	6584 (2)
C(b)	1963 (13)	336 (18)	4039 (12)
Cl 3	1685 (3)	1366 (4)	3342 (2)
Cl 4	1102 (3)	-400 (4)	4025 (3)
P	7035 (2)	834 (2)	9499 (2)
H	6976(78)	100(113)	9346 (73)
C 1	7186 (6)	2137 (8)	9061 (5)
C 2	6817 (7)	3114 (9)	9207 (6)
C 3	6886 (7)	4204 (9)	8911 (6)

Atom	*x/a*	*y/b*	*z/c*
C 4	7313 (7)	4297 (9)	8463 (6)
C 5	8138 (8)	3460(11)	7851 (7)
C 6	8522 (10)	2549 (13)	7716 (9)
C 7	8500 (9)	1468 (11)	8034 (8)
C 8	8087 (7)	1326 (9)	8479 (6)
C 9	7649 (6)	2223 (9)	8620 (6)
C 10	7707 (7)	3349 (9)	8312 (6)
N 1	8038 (5)	219 (7)	8797 (5)
Me 1	8899 (8)	-254 (13)	9346 (7)
Me2	7552 (8)	-604 (10)	8158 (7)
C 11	8009 (6)	578 (9)	10390 (6)
C 12	8168 (7)	-502 (9)	10739 (6)
C 13	8912 (8)	-698 (10)	11449 (7)
C 14	9514 (7)	164 (10	11803 (7)
C 15	9361 (7)	1220(11)	11446 (7)
C 16	8617 (6)	1447 (10)	10741 (6)
C 21	6222 (6)	1101 (8)	9832 (5)
C 22	6508 (7)	1112 (9)	10639 (6)
C 23	5919 (7)	1357 (9)	10943 (6)
C 24	5090 (6)	1631 (9)	10448 (5)
C 25	3938 (7)	1952 (9)	9122 (7)
C 26	3628 (7)	1991 (9)	8310 (6)
C 27	4169 (6)	1672 (9)	7971 (6)
C 28	5000 (6)	1334 (8)	8450 (6)
C 29	5360 (6)	1323 (8)	9302 (5)
C 30	4790 (6)	1624 (9)	9637 (6)
N 2	5555 (5)	931 (7)	8113 (4)
Me 3	5498 (6)	1613 (9)	7450 (6)
Me 4	5327 (7)	-272 (9)	7851 (7)

3. *NMR studies of phosphonium salts* 3-6

The ^{31}P NMR spectra of phosphonium salts **3** and **4b** in solution show one signal, at 31.3 ppm for **3a**, at 24.8 ppm for **3b** and at 23.7 ppm for **4b**. These values are in the same range as those observed for tetracoordinate phosphonium salts[6]. **4a** displays two signals in ^{31}P NMR (δ = 29.2 and 34.7 ppm in $CDCl_3$) indicating the presence of two isomers as was observed in the case of phosphane sulphide **2**.

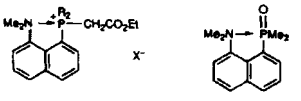
The room temperature ^{1}H and ^{13}C NMR spectra of **3a** and **4b** display four signals for the NMe_2 groups indicating a dissymmetric structure for these compounds. Thus the two nitrogen atoms are coordinated to the phosphorus centre as

was observed in the X-ray structures of **1a**, **2** and **5**. ^{1}H and ^{13}C NMR spectra of **4a** exhibit eight signals for the NMe_2 groups confirming the presence of two isomers in solution. It is to be noted that the chemical shift of the methylene protons for **4a** (δ = 4.35 ppm) is strongly shifted upfield in comparison to that for $Ph_3P^+CH_2CO_2Et\ Cl^-$ (δ = 5.7 ppm)[7]. Furthermore, the chemical shift of the methylene protons for the pseudopentacoordinate (taking into account the lone pair) phosphonium salt **11a** incorporating one (8-dimethylamino)-1-naphthyl ligand (δ = 4.95 ppm)[8] is between that in the case of **4a** and that for $Ph_3P^+CH_2CO_2Et\ Cl^-$. This observation suggests that there is a relation between the upfield shift of the methylene proton resonance and the increase in coordination number of the phosphorus atom due to N→P intramolecular interactions. Phosphonium salt **3a** shows only two signals for the NMe_2 groups at room temperature in the ^{1}H NMR spectrum instead of the four expected for a dissymmetric structure. This can be explained by the existence of a non-dissociative permutational isomerization process in solution. Such a phenomenon which takes place in phosphorus compounds of this type have been studied and will be discussed in a forthcoming paper[9].

^{31}P NMR signals of phosphonium salts **6** are slightly different according to the anion (δ = -6.8 ppm for **6a** and -16.25 ppm for **6b**). This difference may result from an interaction between the anion and the phosphorus atom, an interaction which should be more important in **6a** than in **6b**. The ^{1}H NMR spectrum of **5** displays at room temperature four signals for the NMe_2 groups while those of **6a** and **6b** displays only two broad signals indicating that **6a** and **6b** also undergo a non-dissociative permutational isomerisation process at room temperature.

4. *Reactivity of phosphonium salts 4 and 11 in the Wittig reaction*

In order to study the effect of the coordination of N-dimethylamino groups to the phosphorus atom on the rate and stereoselectivity of the Wittig reaction, we studied first this reaction for pentacoordinate phosphonium salts **11** and then for hexacoordinate phosphonium salts **4.** The results obtained under various experimental conditions are indicated in Table V.



11 a : R = Ph, X = Br
b : R = Me, X = I

12

Phosphonium salt **11b** (with two methyl substituents) is more reactive than phosphonium salt **11a** (with two phenyl substituents) (Table V, compare entries

1,6 and 3,7), but the E selectivity is more important with **11a** (99 %) than with **11b** (88-95 %). The reactivity of **11b** is solvent dependent and is slower in a non polar solvent than in a polar solvent (Table V, compare entries 3 and 4). Under phase transfer conditions, **11a** gives a better yield of ethyl cinnamate (Table V, entry 8) than does **11b** (Table V, entry 5) but this is due to the alkaline hydrolysis of **11b** giving phosphane oxide **12**[6]. Interestingly, the corresponding phosphonium salt derived from Ph_3P shows a very poor reactivity (Table V, entry 9). Thus the N→P interaction in phosphonium **11a** enhances the reactivity of this salt in spite of the steric hindrance of the (8-dimethylamino)-1-naphthyl group.

TABLE V Wittig reaction between phosphonium salts **11** and **4** and benzaldehyde under different experimental conditions

Entry	*Phosphonium salt*	*Reaction conditions*	*yield**	*E/Z ratio of ethyl cinnamate*
(1)	**11 b**	$NaNH_2$ / Et_2O / 1 h	74 %	95/5
(2)		$NaNH_2$ / THF/ 15 mn	75 %	88/12
(3)		NaH / THF/ 5 mn	84 %	92/8
(4)		NaH / CH_2Cl_2 / 24 h	85 %	90/10
(5)		NaOH (5N) / C_6H_6 / H_2O / 5 mn	40 %	86/14
(6)	**11 a**	$NaNH_2$ / Et_2O / 22 h	51 %	99/1
(7)		NaH / THF/ 1 h	35 %	99/1
(8)		NaOH (5N) / C_6H_6 / H_2O / 2 h	79 %	86/14
(9)	$Ph_3P^+CH_2CO_2Et\ Br^-$	$NaNH_2$ / Et_2O / 22 h	8 %	97/3
(10)	**4b**	NaOH (5N) / C_6H_6 / H_2O / 2 d	60 %	92/8
(11)	**4 a**	NaOH (5N) / C_6H_6 / H_2O / 4 d	20 %	97/3

* yields were determined by GC using bibenzyle as internal standard.

The reactivity of phosphonium salts **11** is limited to aldehydes. Indeed no reaction occurs starting from acetone, acetophone, or benzophenone.

Hexacoordinate phosphonium salts are much less reactive than the pentacoordinate ones toward benzaldehyde, giving ethyl cinnamate only under phase transfer conditions, **4b** being slightly more reactive than **4a** (Table V, entries 10 and 11). This low reactivity probably come from the steric hindrance of these phosphonium salts.

In conclusion, investigations of Wittig reaction from phosphonium salts incorporating (8-dimethylamino)-1-naphthyl ligand show that there is an increased reactivity of the salts **11** towards these reactions, the amino group playing an important role in controlling the stereoselectivity of the product. Thus electronic factors dominate over steric factors in compounds **11**. For the phosphonium salts

4 incorporating two ligands steric factors dominate in the outcome of the Wittig reaction resulting in poor reactivity.

EXPERIMENTAL

General. All the reactions were carried out under an argon atmosphere in dry solvents. Chlorophosphanes were distilled from Mg. ^{1}H, ^{13}C, and ^{31}P NMR spectra were obtained using a Bruker WP-200-SY or a Bruker 250 AC spectrometer. ^{1}H and ^{13}C chemical shifts were reported relative to Me_4Si and ^{31}P chemical shifts relative to H_3PO_4. FAB mass spectra (matrix, o-nitrophenyloctyl ether, NPOE, m-nitrobenzyl alcohol, NBA, or thioglycerol, GT) were registered on Jeol JMS-SX102 spectrometer. Elementary analyses were performed by the Centre de Microanalyse du CNRS.

Bis[(8-dimethylamino)-1-naphthyl]chlorophosphane (**10**). To 670 mg (28 mmol) of Mg in 50 ml of Et_2O were added, at O°C, 3.9 mL (25 mmol) of 1.2-dibromoethane in 30 ml of Et_2O. The $MgBr_2$ solution was kept at room temperature for one hour and added at 0°C to 25 mmol of lithium derivative 7[10] in 100 ml of Et_2O. The reaction mixture was then stirred at room temperature for 5 hours. The LiBr formed was filtered through Celite and the Grignard reagent was added slowly dropwise to a solution of 6.1 g (22.4 mmol) of dichlorophosphane **8** in Et_2O (100 mL). The reaction mixture was allowed to return to room temperature and was refluxed overnight. After filtration of the salts through Celite and evaporation of ether, 3.6 g (8.8 mmol, 40 %) of **10** was obtained as a very air-sensitive powder. ^{31}P NMR (101 MHz, $CDCl_3$) δ 33.4 ppm; ^{1}H NMR (250 MHz, $CDCl_3$), δ 3.4 ppm (3H, s), 7.4-8.3 and 9.0-9.1 (12H, m); . This product was used without purification.

Bis[(8-dimethylamino)-1-naphthylmethylphosphane (**1b**). 39 mL (58 mmol) of MeLi in ether was added dropwise at -60°C to 23 g (58 mmol) of raw chlorophosphane **10** in ether (200 mL). The reaction mixture was then stirred overnight at room temperature. After filtration of LiCl through Celite, the solvent was removed under vacuum to give a solid which was washed with pentane (2 x 20 mL) and crystallized from acetone to give 8.9 g (22 mmol, 40 %) of **1b**; mp 170-171°; ^{31}P NMR (101 MHz, $CDCl_3$) δ -13.4 ppm; ^{1}H NMR (250 MHz, toluene d_8) δ 1.7 ppm (d, $^{2}J_{P\text{-}H}$ = 7.7 Hz, 3H, P-CH_3), 2.0 ppm, (coalescence) and 2.7 ppm, (broad signal) (12H, N-CH_3), 7.3-7.6 (m, 12H, Ar) ; ^{1}H NMR (250 MHz, toluene d_8, 233 K) δ 1.65 (s 3H, NCH_3), 1.75 (d, $^{2}J_{P\text{-}H}$ = 8 Hz, 3H, PCH_3), 2.42 (s, 3H, NCH_3), 2.65 (s, 3H, NCH_3), 2.85 (s, 3H, NCH_3), 6.45-7.9 (m, 12H,

Ar); FAB MS (NBA); m/e 387 $(M+1)^+$. Anal. Calcd. for $C_{25}H_{27}N_2P$: C, 77.72; H, 6.99; N, 7.25. Found: C, 77.53; H, 7.12; N, 7.26.

Bis[(8-dimethylamino)-1-naphthyl]phosphane (**1c**). 0.25 g (6.66 mmol) of $LiAlH_4$ in ether (50 mL) was added at -30°C to 2.7 g (6.6 mmol) of raw chlorophosphate **10** in ether (50 mL). The reaction mixture was stirred at room temperature for 15 h and then heated under reflux for 4 h. After removal of ether, pentane (40 mL) was added and the reaction mixture was filtered through Celite. Removal of pentane gave a yellow powder which after recrystallisation in Et_2O-pentane gave 1.48 g (3.97 mmol, 60 %) of yellow crystals; mp 118-119°C; ^{31}P NMR (101 MHz, CD_2Cl_2) δ -22.8 ppm (d, $^1J_{P-H}$ = 208 Hz, P-H); ^1H NMR (250 MHz, CD_2Cl_2) δ 2.6 (s, 12H, NCH_3), 6.0 (d, $^1J_{P-H}$ = 206 Hz, 1H, P-H), 6.85-8.45 (m, 12H, Ar), ^{13}C NMR (50 MHz, CD_2Cl_2,) δ 45.26 (NCH_3), 114.0, 120.0, 122.9, 123.0, 124.2, 125.3, 126.0, 126.4, 128.3, 128.0, 135.0, (Ar); FAB MS: m/e = 372 $(M-H)^+$. Anal. Calcd. for $C_{24}H_{25}NP$: C, 77.14; H, 6.72; N, 7.52. Found: C, 77.86; H, 6.80; N, 7.59.

Bis[(8-dimethylamino)-1-naphthyl]methylphenylphosphonium iodide (**3a**). 0.82 g (1.8 mmol) of phosphane **1a** and 0.95 mL (10 mmol) of methyl iodide was heated under reflux in toluene (15 mL). After 4 hours, the white precipitate was filtered off and recrystallized from CH_2Cl_2-toluene to give **3a** (0.56 g, 1.2 mmol, 67 %); mp 246.5-247.5; ^{31}P NMR (81 MHz, $CDCl_3$) δ 31.3 (s); ^1H NMR (250 MHz, $CDCl_3$) δ 0.92 (s, 3H, NCH_3), 1.30 (s, 3H, NCH_3), 2.24(s, 3H, NCH_3), 2.83 (s, 3H, NCH_3), 3.05(d, $^2J_{P-H}$ = 13 Hz, 3H, PCH_3), 7.05-8.4 (m, 17H, Ar); ^{13}C NMR (63 MHz, $CDCl_3$) δ 18.65 (d, $^1J_{P-C}$ = 76.8 Hz, PCH_3), 46.0 (NCH_3), 47.4 (NCH_3), 49.2 (NCH_3), 50.3 (NCH_3), 121.3, 122.1, 125.0, 125.1, 125.2, 125.7, 127, 128.1, 128.3, 130.4, 133.4, 134.6, 135.4, 136.1, 136.4, 136.7, 136.9, 139.2, 139.4, 150.6, 150.7 (Ar); FAB MS (NBA); m/e 463 $(M-I)^+$. Anal. Calcd. for $C_{31}H_{32}N_2PI$: C, 61.48; H 5.35; N 4.56. Found: C, 61.59; H, 5.13; N, 4.59.

Bis[(8-dimethylamino)-1-naphthyl]dimethylphosphonium iodide (**3b**). 0.31 mL (5 mmol) of methyl iodide was added dropwise at room temperature to a solution of phosphane **1b** (0.39 g, 1 mmol) in toluene (15 mL). After two hours stirring at room temperature, the white precipitate was filtered off and washed with pentane (3 × 20 mL) to give 0.52 g (0.97 mol, 98 %) of **3b**; mp 130°C (decomp.); ^{31}P NMR (101 MHz, $CDCl_3$) δ 24.8; ^1H NMR (250 MHz, $CDCl_3$) δ 1.30 (s, 6H, NCH_3), 2.59 (s, 6H, NCH_3); 2.595 (d, $^2J_{P-H}$ = 10.3 Hz, 6H, PCH_3); 7.4-8.6 (m, 12H, Ar); ^{13}C NMR (63 MHz, $CDCl_3$) δ 18.1 (d, $^1J_{P-C}$ = 63 Hz, PCH_3), 47.7 (NCH_3), 48.7 (NCH_3), 120.2, 121.8, 122.3, 126.1, 126.4, 127.7, 128.1, 129.9, 133.8, 134.0, 134.7, 135.5, 135.6, 150.1 (Ar), FAB MS (NBA); m/e 401 $(M-I)^+$. Anal. Calcd. for $C_{26}H_{30}N_2PI$: C, 59.10; H, 5.68; N, 5.30. Found: C, 58.24; H, 6.14; N 5.44.

Bis[(8-dimethylamino)-1-naphthyl](α-ethoxycarbonyl)methylphenylphosphonium iodide (**4a**). 0.26 mL (2.2 mmol) of ethyl iodoacetate was added dropwise to 0.87 g (2mmol) of phosphane **1a** in toluene (30 mL). The reaction mixture was refluxed for 24 h, and the white precipitate obtained was filtered off, washed with toluene, and dried to give 1.02 g (1.5 mol, 77 %) of **4a**; mp 200-201°C; ^{31}P NMR (101MHz, $CDCl_3$) δ 29.2 (s), 34.7 (s) corresponding to two isomers; ^{1}H NMR (250 MHz, $CDCl_3$) first isomer 0.55 (t, 3H, C-CH_3), 0.73 (s, 3H, NCH_3), 1.24 (s, 3H, NCH_3), 2.27 (s, 3H, NCH_3), 2.66 (s, 3H, NCH_3), 3.13 (q, 2H, CH_2-C), 4.2-4.6 (m, 2H, PCH_2), 7.0-8.3 (m, 17H, Ar); second isomer 0.55 (t, 3H, C-CH_3), 0.96 (s, 3H,NCH_3), 1.48 (s, 3H, NCH_3), 2.12 (s, 3H, NCH_3), 2.53 (s, 3H, NCH_3), 3.13 (q, 2H, CH_2-C), 3.2-3.6 (m, 2H, PCH_2), 6.9-8.7 (m, 17H, Ar); FAB MS (NBA); m/e 535 $(M\text{-}I)^+$. Anal. Calcd. for $C_{34}H_{36}N_2O_2PI$: C, 61.63; H, 5.43; N, 4.22; I, 19.18. Found: C, 61.23; H, 5.20; N, 4.12; I, 19.42.

Bis[(8-dimethylamino)-1-naphthyl](α-ethoxycarbonyl)methylmethylphosphonium iodide (**4b**). 0.16 mL (1.4 mmol) of ethyl iodoacetate was added dropwise to 0.48 g (1.2 mmol) of phosphane **1b** in toluene (20 mL). After 16 h at room temperature the white precipitate obtained was filtered off, washed with toluene, then pentane, and dried to give 0.64 g (1.05 mmol, 90 %) of **4b**; mp 138-139°C; ^{31}P NMR (101 MHz, $CDCl_3$) δ 23.7; ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.55 (t, 3H, C-CH_3), 1.23 (s, 3H, NCH_3), 1.29 (s, 3H, NCH_3), 2.56 (s, 3H, NCH_3), 2.72 (s, 3H, NCH_3), 2.74 (d ,$^{2}J_{P\text{-}H}$ = 9.7 Hz, 3H, PCH_3), 3.2-3.4 (m, 2H, CH_2-C), 3.5-3.7 (m, 1H, CH_2-C), 4.28 (dd $^{2}J_{P\text{-}H}$ = 14.0 Hz, 1H, PCH_2), 4.55 (dd $^{2}J_{P\text{-}H}$ = 14.0 Hz, 1H, PCH_2), 7.15-8.7 (m, 12H, Ar); ^{13}C NMR (50 MHz, $CDCl_3$) δ 13.4 (CH_3), 16.25 (d, $^{1}J_{P\text{-}C}$ = 60 Hz, PCH_3); 36.7 (d,$^{1}J_{P\text{-}C}$ = 55 Hz, PCH_2), 47.6 (NCH_3), 47.9 (NCH_3), 48.4 (NCH_3), 48.9 (NCH_3); 61.9 (OCH_2), 122.1, 122.9, 125.2, 125.5, 126.8, 127.1, 127.5, 127.8, 128.0, 128.2, 129.0, 134.3, 134.5, 134.7, 135.1, 135.5, 135.7, 149.6, 150.4 (Ar), 165.9 (CO); IR ν($CHCl_3$) cm^{-1} (CO) 1715; FAB MS (NBA): m/e 473 $(M\text{-}I)^+$. Anal. Calcd. for $C_{29}H_{34}N_2O_2PI$: C, 58.00; H, 5.67; N, 4.67. Found: C, 56.0; H, 5.44, N, 4.74.

Bis[(8-dimethylamino)-1-naphthyl]phenylphosphonium bromide **5**. 0.2 mL (1 mmol) of a 5.2 M solution of HBr in ether was added dropwise by syringe at 0°C to a stirred solution of phosphane **1a** (0.45 g, 1 mmol) in CH_2Cl_2 (10 mL). After 4 hours stirring at room temperature, the white precipitate was filtered off and washed three times with ether to give 0.46 g (0.87 mmol, 87 %) of **5**; mp 80-81°C (decomp.); ^{31}P NMR (101MHz, $CDCl_3$) δ 5.50 (d $^{1}J_{P\text{-}H}$ = 673 Hz, PH); ^{1}H NMR (250 MHz, $CDCl_3$, 293K) δ 1.6 (broad signal, 3H, NCH_3), 1.8 (broad signal, 3H, NCH_3), 2.9 (broad signal, 3H, NCH_3), 3.15 (broad signal, 3H, NCH_3), 6.5-8.3 (m, 16H, Ar), 9.3 (broad signal, lH, Ar), 10.25 (d $^{1}J_{P\text{-}H}$ = 665 Hz, 1H, PH); ^{13}C NMR (50MHz, $CDCl_3$) δ 45.0(broad signal, NCH_3), 46.4 (broad

signal, NCH_3), 48.8 (broad signal, NCH_3), 51.5 (broad signal, NCH_3), 122.5, 124.4, 124.8, 125.4, 125.7, 125.8, 127.5, 128.0, 129.6, 132.6, 135.2, 150.3 (Ar); FAB MS (GT): m/e = 449 $(M\text{-}Br)^+$ (52%), 447 (43%), 278 (100%), 186 (74%). Anal. Calcd. for $C_{30}H_{30}N_2PBr$: C, 68.05; H, 5.67; N, 5.29; Br, 15.12. Found: C, 68.31; H, 5.68; N, 5.24; Br, 14.89.

Crystal Structure of Phosphonium salt 5

Crystal Preparation. Crystals of **5** were grown by slowly evaporating a dichloromethane solution in under argon. A small block was cut from a plate and stuck with mineral oil on a glass fiber at 163 K.

X-ray Data Collection. Data were collected on a CAD-4 automated diffractometer with graphite-monochromatized MoKα radiation (λ = 0.71069 Å). Lattice constants (Table III) came from a least-squares refinement of 25 reflections obtained in the range $11.3 < 2\theta < 24.2°$. The intensities of three standard reflections were monitored after intervals of 60 min; no significant change of these intensities occurred during data collection. The structure amplitudes were obtained after the usual Lorentz and polarization reduction. Only the reflections having $\sigma(F)/F < 0.33$ were considered to be observed. The aborption corrections on the F's were neglected.

Structure Determination and Refinement. The systematic absences uniquely define the space group $P2_1/c$, with z = 4. The bromide anion, the phosphorus atom, seven atom from the (N1, C1) naphthylamino group and the two chlorine atoms Cl_1 and Cl_2were located by use of direct methods (SHELXS-86 program)[11]. These atomic positions were used to phase a Fourier map which gave the coordinates of part of the naphthyl rings carbon atoms. Two subsequent difference Fourier syntheses revealed the second CH_2Cl_2 molecule and the remaining non-hydrogen atoms. In the first stages of the refinement the site occupation factor was left free to allow adjustment of the atoms of the two dichloromethane molecules. The value of this s.o.f. was found to be 0.934(4) and was subsequently kept fixed. (Loss of dichloromethane occurs readily, at least at room temperature; a previous data collection failed owing to total efflorescence of the sample inside a sealed glass capillary). After four cycles of least-squares refinement with anisotropic thermal parameters for the chlorine, bromine, and phosphorus atoms and isotropic parameters for the others, the hydrogen atoms were positioned by calculation (SHELX-76 program)[12]. Three more cycles gave a R value of 0.081. The nitrogen and carbon atoms were then refined anisotropically. At this stage the hydrogen atom on phosphorus was located on a difference Fourier map (P-H bond distance, 1.353 Å) and the refinement was resumed with

alternatively keeping fixed the anisotropic thermal parameters for one of the dimethylaminonaphthyl group and refining the parameters of the other. During these refinement stages all positional parameters were left free for adjusment. Refinement was difficult to achieve owing to endless changes in the weighting scheme. The best weight $\underline{w} = 0{,}057/(\sigma^2(F) + 0.0073\ F^2)$ was kept fixed, and the refinement converged to the final R value of 0.065. The atomic coordinates (non-hydrogen atoms) are in Table IV. Individual bond lengths are listed in Table I, and important bond angles in Table II. A summary of crystal data, intensity measurements, and refinement is in Table III. A full list of the bond angles (Table VI), a table of the anisotropic thermal parameters (Table VII), and the calculated hydrogen atoms coordinates (Table VIII) have been deposited in Cambridge Crystallographic Data Centre.

Bis[(8-dimethylamino)-1-naphthyil]phosphonium bromide (**6a**). 0.2 mL (1 mmol) of a 5.2 M solution of HBr in ether was added dropwise by syringe at room temperature to a stirred solution of 0.37 g (1 mmol) of phosphane **1c** in CH_2Cl_2 (20 mL). After 2 hours the beige precipitate was filtered off, then washed once with ether and once with pentane to give 0.315 g (0.77 mmol, 70 %) of **6a**; mp 153.6-154.6°C; ^{31}P NMR (101MHz, $CDCl_3$) δ –6.3 (t, $^1J_{P\text{-}H}$ = 590 Hz, PH); ^1H NMR (250 MHz, $CDCl_3$, 293 K) δ 1.55, 3.2 (two broad signals, 12H, NCH_3), 7.1-8.3 (m, broad signals, 12H, Ar), 9.9 (broad signal, 2H, PH); ^1H NMR (250 MHz, CD_2Cl_2, 203K) δ 1.6 (s, 3H, NCH_3), 2.5 (s, 3H, NCH_3), 2.98 (s, 3H, NCH_3), 3.02 (s, 3H, NCH_3), 6.7 (m, 1H, Ar), 7.15-8.6 (m, 11H, Ar), 8.85 (t $^1J_{P\text{-}H}$ = 590 Hz, 2H, PH); ^{13}C NMR (50 MHz, $CDCl_3$) δ 46.2 (broad signal, NCH_3), 48.8 (broad signal, NCH_3), 113.9, 115.8, 121.4, 126.8, 126.8, 127.1, 127.4, 127.7, 130.8, 134.4, 134.63, 137.61, 149.2 (Ar); FAB MS (GT): m/e = 373 $(M\text{-}Br)^+$ (58%), 371 (60%), 186 (100%).

Bis[(8-dimethylamino)-1-naphthyl]phosphonium tetrakis[3,5-bis(trifluoromethyl) phenyl borate (**6b**). A solution of sodium tetrakis[3,5-bis(trifluoromethyl)phenyl] borate (0.12g, 0.132 mmol) in CH_2Cl_2 (15 mL) was added dropwise at 0°C to a solution of **6a** (0.06 g, 0.132 mmol) in CH_2Cl_2 (15 mL). After 8 hours stirring, the reaction mixture was filtered off to eliminate NaBr and the solvent was removed under vacuum. The resulting solid was washed with pentane (3 × 60 mL) to give 0.14 g (0.113 mmol, 87 %) of **6b** as a beige powder; ^{31}P NMR (101 MHz, CD_2Cl_2) δ -16.25 (t, $^1J_{P\text{-}H}$ = 564 Hz); ^1H NMR (200 MHz, CD_2Cl_2) δ 2.26 (broad signal, 6H, NCH_3), 2.73 (broad signal, 6H, NCH_3), 7.4-8.1 (m, 24H, Ar), 8.2 (d $^1J_{P\text{-}H}$ = 565 Hz, 2H, PH). ^{13}C NMR (50 MHz, CD_2Cl_2) δ 48.0 (NCH_3), 117.9, 118.0, 118.1, 122.4, 122.7, 126.2, 126.8, 127.2, 127.8, 128.3 128.9, 129.1, 129.6, 129.7, 129.8, 133.5, 134.8, 134.9, 135.3, 138.3 (Ar, CF_3), 162.34 (q $^1J_{B\text{-}C}$ = 50 Hz, BC). FAB (+) MS (NPOE): m/e = 373 $(M)^+$. FAB (-)

(GT) : m/e = 862 $\{B[Ph(CF_3)_2]_4\}^-$. FAB (+) HRMS Calcd. for $C_{24}H_{26}N_2P$: 373.1834. Found: 373.1833 .

Bis[(8-dimethylamino)-1-naphthyl](α-ethoxycarbonyl)methylphosphonium-iodide (**11b**). 0.24 mL (2 mmol) of ethyl iodoacetate was added to 0.46 g (2 mmol) of (8-dimethylamino-1-naphthyl)methylphosphane[4] in toluene (20 mL). After 3 hours at room temperature, the white precipitate obtained was filtered off and washed with pentane (10 mL) giving 0.8 g (1.8 mmol, 90 %) of **11b**; mp 123.9-124.5°C; ^{31}P NMR (101MHz, $CDCl_3$) δ 21.2; ^1H NMR (250 MHz, $CDCl_3$) δ 1.04 (t, 3H, C-CH_3), 2.58 (d, $^2J_{P-H}$ = 13 Hz, 6H, PCH_3), 2.67 (s, 6H, NCH_3), 3.96 (q, 2H, CH_2-C), 4.44 (d, $^2J_{P-H}$ = 12.8 Hz, 2H, PCH_2), 7.5-7.9 and 8.1-8.3 (m, 6H, Ar); ^{13}C NMR (50 MHz, $CDCl_3$) δ 13.7 (d $^1J_{P-C}$ = 60 Hz, PCH_3), 13.7 (CH_3), 34.8 (d, $^1J_{P-C}$ = 65 Hz, PCH_2), 47.2 (NCH_3), 62.2 (CH_2), 113.2, 115.0, 120.1, 125.4, 125.7, 126.8, 128, 129.6, 129.7, 135.2 137.7, 137.9 149.5 (Ar), 165.3 (CO). FAB MS (GT): m/e = 318 $(M-I)^+$. Anal. Calcd. for $C_{18}H_{25}NO_2PI$: C, 48.54; H, 5.61; N, 3.14. Found: C, 48.80; H, 5.33; N, 3.62.

General procedure for the reaction of phosphonium salts with benzaldehyde. In a typical procedure, $NaNH_2$ (19 mg, 0.49 mmol), bibenzyl (63 mg, 0.35 mmol), and phosphonium salt **11a** (183 mg, 0.35 mmol) were stirred in Et_2O (10 mL) for 30 min. A yellow solution was obtained to which 38 mg (0.36 mmol) of benzaldehyde was added. The progress of the reaction was monitored by GC (column SE 30, 10%). When no further change was observed, water was added and the product was extracted with Et_2O. The yield and the E/Z ratio of ethyl cinnamate determined by GC were confirmed by ^1H NMR of the raw material.

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