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Preparation and structures of 1-dimethylamino-2-bis(dimethylamino)- and 1-chloro-2-bis(diethylamino)-1-phospha-2-phosphonium acenaphthene: the first examples of the 1,2-dihydro-1,2-diphospha-acenaphthene ring system

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Dedicated to Professor François Mathey on the occasion of his 60th birthday

Abstract

This paper describes the preparation of 1,8-bis[bis(dimethylamino)phosphino]naphthalene (**2a**) and the attempted preparation of its isopropyl analogue **2c**, which led to the formation of 1-naphthyl-bis(diisopropylamino)phosphine (**4**), and to other unidentified products. The X-ray structures of **2a** and **4** are discussed in comparison to those of 1,8-bis[bis(diethylamino)phosphino]naphthalene (**2b**) and 1-naphthyl-di-*tert*-butylphosphine (**5**), respectively. In the structures of **2a**, **2b** and **4** the $(R_2N)_2P$ groups (R = alkyl) are eclipsed with respect to the naphthalene plane, whereas the R_2P groups (R = alkyl or aryl) in **5**, as in 1,8-bis(diorganophosphino)naphthalenes in general, adopt a conformation between bisecting and eclipsed. Furthermore, the reactions of **2a** and **2b** with BX_3 ether adducts (X = F, Cl) are described, which furnished the heterocyclic [$\sigma^3P-\sigma^4P^+$]-diphosphorus compounds, 1-dimethylamino-2-bis(dimethylamino)-, 1-diethylamino-2-bis(diethylamino)- and 1-chloro-2-bis(diethylamino)-1-phospha-2-phosphonium-acenaphthene (**6a**, **6b** and **7b**); the first examples of the 1,2-dihydro-1,2-diphospha-acenaphthene ring system. The X-ray structures of **6a** and **7b** display a relief of strain compared to the parent bis-aminophosphines **2a** and **2b**, quantified by negative splay angles [−7.89° (**6a**) and −9.40° (**7b**); cf. +12.16° (**2a**) and +12.0° (**2b**)] and the bonded [225.38 (**6a**) and 223.16 (**7b**) pm] compared to the non-bonded phosphorus–phosphorus distances [311.9 (**2a**) and 311.7 (**2b**) pm]. A mechanism is discussed for the formation of **6b** and **7b** from **2b** and gaseous hydrogen chloride.

Keywords: Phosphorus heterocycles; Naphthalene derivatives; Mixed-valent compounds; Bulky phosphines; Strained molecules; Neighbouring-group effects

1. Introduction

Steric strain associated with 1,8-disubstituted naphthalenes (*peri*-substitution) has received much attention [1]. Relief of such strain may be achieved by distortion of the molecular framework (in-plane and out-of-plane displacement of the substituents and buckling of the aromatic nucleus) or by cyclisation, the latter either by introduction of a bridging group or by bond formation between the *peri*-atoms (Fig. 1) [2].

The structures of a large number of 1-P,8-P disubstituted naphthalene compounds have been studied, demonstrating the whole range of steric strain or relief of such strain by the modes mentioned above, except for the formation of a P–P single bond ($d_{PP} \approx 225$ pm) [3,4]. Fig. 2 shows diphosphorus structures with a

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naphthalene bridge that can be derived from the strained σ^3P, σ^3P structure **A** by formal reduction or oxidation of the phosphorus atoms (**B**, $\sigma^4P^- - \sigma^4P^+$ and **C**, $\sigma^4P^+ - \sigma^4P^+$) or by removal of one (**D**, $\sigma^3P - \sigma^4P^+$) or two (**E**, $\sigma^3P - \sigma^3P$) substituents [5]. On the other hand, we found that addition of a substituent, such as a chalcogen atom or an alkyl group to an arylphosphine of type **A**, results in σ^3P, σ^4P^+ structures (**F**) with increased strain rather than in $\sigma^4P^+ - \sigma^5P$ structures (**F′**). For example, there are no signs of strain relief by dative $P \rightarrow P^+$ interactions in the X-ray structures of the monoselenide and a representative series of phosphonium salts of 1,8-bis(diphenylphosphino)-naphthalene (type **F**) [3f,3j].

The naphthalene systems **A**–**F** are of great interest, especially in comparison to the structurally related mono- and bicyclic urea-bridged diphosphorus compounds, whose diverse chemistry is well documented in the literature [6]. Whereas the latter represent examples of CN_2P_2 or $C_2N_4P_2$ five-membered rings, the naphthalene system is based on a C_3P_2 heterocycle.

Some time ago we described the preparation of 1,8-bis[bis(diethylamino)phosphino]naphthalene (**2b**) and showed that it can serve as a precursor for the synthesis of 1,8-bis(dichlorophosphino)naphthalene, 1,8-$(Cl_2P)_2$-$C_{10}H_6$ (**3**), which was not accessible directly from 1,8-dilithionaphthalene (**1**) and phosphorus trichloride (Scheme 1, I–III) [3d]. Interestingly, the reaction of **2b** with gaseous hydrogen chloride proceeded via a considerable number of stable intermediates that were identified by $^{31}P\{^1H\}$-NMR spectroscopy as ionic, P,P′-bonded, $[\sigma^3P - \sigma^4P^+]$-diphosphorus compounds (type **D** in Fig. 2). As a consequence, the spectra of the reaction mixtures showed several AX patterns with coupling constants between 150 and 350 Hz, typical of $^1J_{PP}$ coupling [7,8]. Due to their ionic nature, the lifetime of these intermediates depended strongly on the polarity of the solvent in which the reaction was performed (*n*-hexane, diethyl ether or dichloromethane). Only a small fraction of the desired product **3** (ca. 9%) could be recovered from the final reaction mixture.

We indicated that the characterisation of the ionic intermediates of type **D** and the elucidation of the reaction mechanism would be studied further in our laboratory. Herein we describe the synthesis of 1,8-bis-[bis(dimethylamino)phosphino]naphthalene (**2a**), which we expected to be easier to handle than the ethyl analogue **2b** because of better crystallisation properties. We also describe our attempts to prepare the corresponding isopropyl derivative **2c**, which led to the formation of the bulky 1-naphthyl-bis(diisopropylamino)phosphine (**4**). Its X-ray structure is compared with that of 1-naphthyl-di-*tert*-butylphosphine (**5**). We also show that two of the ionic reaction intermediates mentioned above can easily be prepared from the bisaminophosphines **2a** or **2b** by treatment with BX_3 ether adducts (X = F, Cl) and we describe their X-ray structures.

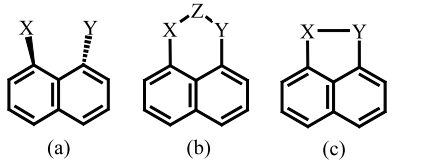


Fig. 1. Steric strain (a) and modes of strain relief (a), (b) and (c) in 1,8-disubstituted naphthalenes.

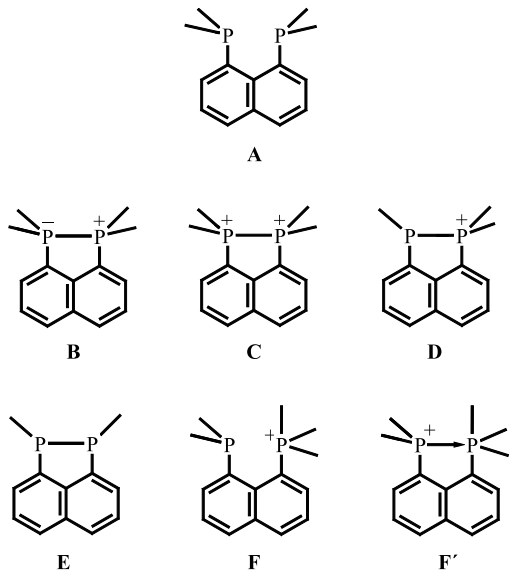
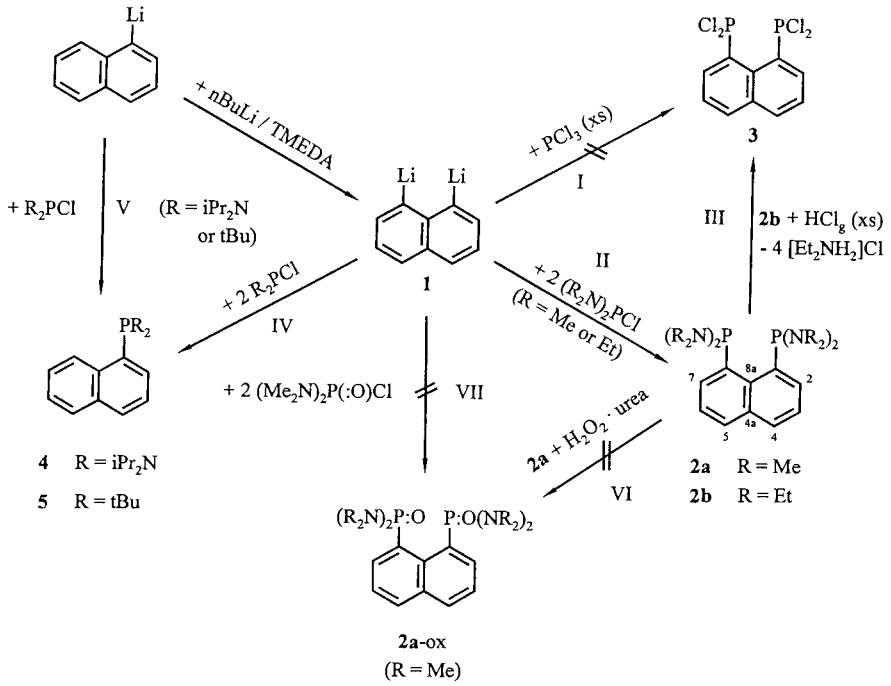


Fig. 2. Diphosphorus structures with a naphthalene bridge that can be derived from the strained σ^3P, σ^3P structure **A** by formal reduction/oxidation of the phosphorus atoms (**B**, $\sigma^4P^- - \sigma^4P^+$ and **C**, $\sigma^4P^+ - \sigma^4P^+$) or by removal of one (**D**, $\sigma^3P - \sigma^4P^+$) or two (**E**, $\sigma^3P - \sigma^3P$) substituents.

2. Results and discussion

In our first report on the chemistry of 1,8-bis[bis(dialkylamino)phosphino]naphthalenes [3d], where we described the synthesis of **2b** (Scheme 1, II), we pointed out that the latter could be crystallised from *n*-hexane at −20 °C, but that the isolated crystals melted when warmed to room temperature to give a viscous product that we found to be an inconvenient starting material for further reactions. We therefore looked for aminophosphine substituents with alkyl groups less flexible than the ethyl groups in **2b** and decided to use $(Me_2N)_2PCl$ and $(^iPr_2N)_2PCl$ instead of $(Et_2N)_2PCl$. It should be noted that $(Me_2N)_2PCl$ and $(Et_2N)_2PCl$ are liquids whereas $(^iPr_2N)_2PCl$ is a solid that can easily be handled in air. These advantageous properties were expected to be retained in the desired product, 1,8-bis-[bis(diisopropylamino)phosphino]naphthalene (**2c**).



Scheme 1.

2.1. Preparation and structure of **2a**

The reaction of **1** [9] with $(Me_2N)_2PCl$ in THF at -70 °C, carried out analogously to the preparation of **2b**, furnished **2a** as a colourless solid in 44% yield after crystallisation from *n*-hexane at -20 °C (Scheme 1, II). Some of the crystals were suitable for an X-ray crystal structure determination (vide infra) but the unsatisfactory elemental analysis showed that the product still contained traces of impurities. Compound **2a** was further characterised by ^{1}H-, ^{13}C{^{1}H}- and ^{31}P{^{1}H}-NMR spectroscopy, including DEPT, HH COSY, CH COSY and COLOC NMR experiments.

In the ^{1}H- and in the ^{13}C{^{1}H}-NMR spectrum of **2a**, virtual triplets were observed for the $N(CH_3)_2$ protons and carbon atoms, indicating that there is coupling to both ^{31}P nuclei, one of which must have a considerable through-space component ($^3J_{PH} + {}^7J_{PH} \approx 4.4$ Hz and $^2J_{CP} + {}^6J_{CP} \approx 10.7$ Hz). In order to confirm that the through-space coupling in **2a** is a consequence of interactions between C or H at P and the non-bonding electron pair at P′ (and vice versa) we tried to prepare the corresponding dioxide, bis-phosphonic acid diamide (**2a**-ox). However, **2a**-ox could neither be obtained from the oxidation of **2a** with H_2O_2·urea, nor from the reaction of **1** with $(Me_2N)_2P(:O)Cl$ (Scheme 1, VI and VII).

Another feature of the ^{13}C-NMR spectra of **2a** and **2b** is noteworthy. Compared to the J_{CP} values [in square brackets] that were observed in the spectra of 1,8-bis(diorganophosphino)naphthalenes [3e], $^2J_{P,C\text{-}8a}$ and $^3J_{P,C\text{-}4a}$ (**2a**: 16.3 and 2.3 Hz, **2b**: 17.3 and 2.2 Hz) were reduced [cf. 20.9–24.4 and 6.0–6.5 Hz, mean values 22.8 and 6.2 Hz] whereas $^2J_{P,C\text{-}2}$ ($= {}^2J_{P,C\text{-}7}$) (**2a**: 3.9 Hz, **2b**: 3.4 Hz) was larger [J_{CP} is unresolved in most cases; only 1,8-bis(dimethylphosphino)naphthalene (dmpn) has a measurable $^2J_{P,C\text{-}2}$ of 1.7 Hz]. (For the numbering of the carbon atoms see Scheme 1.) The magnitude of $^2J_{CP}$ and $^3J_{CP}$ values in the ^{13}C-NMR spectra of arylphosphines strongly depends on the orientation of the lone pair at phosphorus and thereby on the conformation of the PR_2 group [10]. In general, $^2J_{CP}$ and $^3J_{CP}$ are large if the lone pair at phosphorus and the carbon atom are coplanar; a deviation from this plane reduces $^2J_{CP}$ and $^3J_{CP}$. As a consequence, the bis-aminophosphines **2a** and **2b** must adopt different conformations in solution than the 1,8-bis-(diorganophosphino)naphthalenes, characterised by an orientation of the lone pair towards C-2/C-7 and away from C-8a (Fig. 3(c) and (d)). In fact, the X-ray structures of **2a** (vide infra) and **2b** [3d] showed that in the solid state the 1,8-bis{bis(dialkylamino)phosphino}-naphthalenes also adopt a conformation different from that of 1,8-bis(diorganophosphino)naphthalenes [3b, 3c,3e].

The δ_P-value of **2a** ($\delta_P = 100.9$) is very similar to that of $PhP(NMe_2)_2$ ($\delta_P = 100.3$ [11]), shifted by 4.5 ppm downfield, compared to the δ_P-value of **2b** (cf. $\delta_P = 96.4$ [3d]).

Single crystals of **2a**, suitable for an X-ray structure determination, were obtained from *n*-hexane at -20 °C. The compound crystallises in the space group $C2/c$

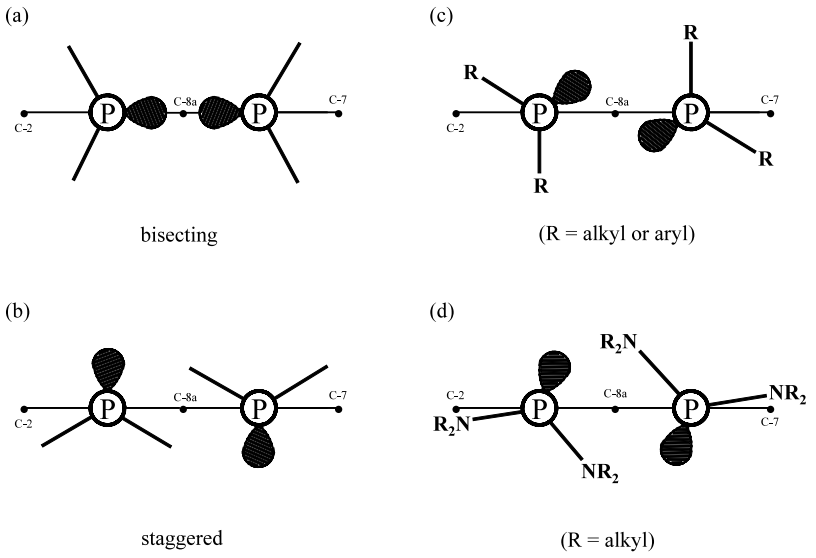


Fig. 3. Idealised bisecting (a) and staggered (b) conformations, situation in 1,8-bis(diorganophosphino)naphthalenes (c) and the eclipsed conformation in 1,8-bis{bis(dialkylamino)phosphino}naphthalenes (d) viewed along the C8a–C4a bond (labelled as C2–C3 in **2a** (Figs. 4 and 5) and as C9–C10 in **2** [3d] because of crystallographic symmetry).

with $Z = 4$ and has a two-fold symmetry axis through C2 and C3 (Fig. 4). For comparison, important bond lengths and angles of **2a** and **2b** [3d] are listed in Table 1.

As in the structure of **2b**, the $P(NR_2)_2$ groups in **2a** (R = Me) adopt an almost eclipsed conformation relative to the C_{10}-plane (Fig. 3(d) and Fig. 5). The corresponding torsion angle N1–P–C1–C6 is $-10.5°$ [**2b**: 9° (N1–P1–C1–C2) and 4° (N4–P2–C8–C7)]. The almost eclipsed conformation seems to be a general feature of the structures of 1,8-bis[bis(dialkylaminophosphino)]-naphthalenes. It should be noted that in the alkyl- and aryl-substituted 1,8-bis(diorganophosphino)naphthalenes [3b,3c,3e] the PR_2 groups adopt a conformation between bisecting and eclipsed (Fig. 3(c)).

Furthermore, the structures of **2a** and **2b** display similar distortions. The $P(NMe_2)_2$ groups in **2a** are bent in-plane and out-of-plane, leading to a non-bonding P···P′ distance of 311.9 pm, almost identical with the value found for **2b** (311.7 pm). The in-plane distortion takes the form of a widening of the bay angles P–C1–C2 [123.23(13)°] and C1–C2–C1′ [125.7(2)°], again similar to the in-plane distortion in **2b** [cf. C1–C9–C8 126.1°]. Moreover, the out-of-plane distortion, quantified by the pseudo torsion angle P–C1···C1′–P′ (25.7°) and the displacement of P and P′ (by -58.0 and $+58$ pm) out of the best plane of the naphthalene ring are very similar (cf. P1–C1···C8–P2 $-24.8°$; displacement of P1 and P2: 42.7 and -76.5 pm). The naphthalene ring in **2a** is strongly distorted, the mean deviation from planarity (least-squares) being 6.6 pm (cf. 7.5 pm in **2b**). The phosphorus atoms display pyramidal geometry, with P–N bond lengths typical of aminophosphines [12], whereas the environment of the nitrogen atoms is almost planar.

In summary, the ethyl groups in **2b** do not seem to make much difference structurally, compared to the methyl groups in **2a**. As far as steric strain is concerned, the situation proved to be different when we tried to introduce ($^i Pr_2N$)P groups.

2.2. Preparation and structures of *4* and *5*

Our attempts to prepare **2c** from **1** and $(^iPr_2N)_2PCl$ according to Scheme 1 (II) failed. Instead, a mixture of phosphorus-containing products was obtained. The main components gave rise to singlets at $\delta_P = 134.0$, 84.1, 76.2 and 51.5 in an intensity ratio of $\approx$ 3:4:14:5 (solvent: THF/*n*-hexane). The reactions of **1** with $(R_2N)_2PCl$ (R = Me or Et), on the other hand, afforded **2a** and **2b** ($\delta_P \approx 100$) without significant amounts of

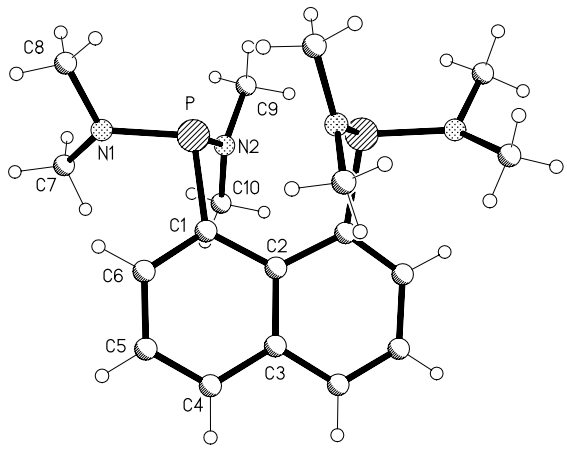


Fig. 4. Structure of **2a** in the crystal; for selected bond lengths and angles see Table 1.

Table 1
Comparison of selected bond distances (pm) and bond angles (°) for **2a** (left column) and **2b** (right column) [a]

Bond lengths [b]			
P–C1	185.1(2)	P1–C1	185.9(5)
		P2–C8	186.3(5)
P–N1	170.0(2)	P1–N1	170.6(4)
		P2–N4	170.8(4)
P–N2	168.6(2)	P1–N2	168.9(4)
		P2–N3	169.1(4)
N1–C7	144.7(3)	N1–C11	145.5(6)
		N4–C23	147.1(6)
N1–C8	144.6(3)	N1–C13	147.5(6)
		N4–C25	147.4(6)
N2–C9	144.6(2)	N2–C17	146.2(6)
		N3–C21	146.3(6)
N2–C10	144.2(3)	N2–C15	146.6(6)
		N3–C19	145.5(6)
P···P′	311.9(1)	P1···P2	311.7(2)
Bond angles [b]			
C1–C2–C1′	125.7(2)	C1–C9–C8	126.1(4)
P–C1–C2	123.23(13)	P1–C1–C9	123.4(3)
		P2–C8–C9	122.5(3)
P–C1–C6	118.05(14)	P1–C1–C2	118.0(4)
		P2–C8–C7	117.9(4)
N1–P–N2	107.49(9)	N1–P1–N2	108.9(2)
		N3–P2–N4	109.5(2)
N1–P–C1	101.69(8)	N1–P1–C1	101.7(2)
		N4–P2–C8	101.1(2)
N2–P–C1	98.10(8)	N2–P1–C1	99.1(2)
		N3–P2–C8	97.5(2)
C8–N1–P	116.6(2)	C11–N1–P1	115.2(3)
		C15–N2–P1	116.4(3)
P–C1···C1′–P′	25.7(1)	P1–C1–C8–P2	−24.8(2)
P–C1–C2–C1′	15.3(1)	P1–C1–C9–C8	−9.0(7)
		P2–C8–C9–C1	−20.5(6)
N1–P–C1–C6	−10.5(2)	N1–P1–C1–C2	9.3(4)
		N4–P2–C8–C7	4.5(4)
Splay angle	12.16	Splay angle	12.0

[a] **2b** crystallised with two independent molecules in the asymmetric unit. Here the values of one of the molecules are listed as in Ref. [3d].
[b] Numbers in parentheses indicate standard deviations in the least significant digits.

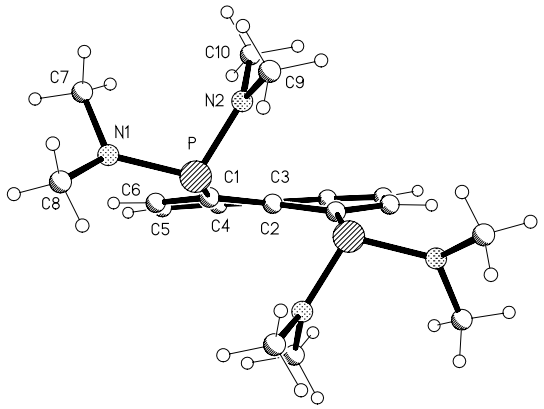


Fig. 5. Structure of **2a** viewed along the C2–C3 bond to emphasise the conformation of the $(Me_2N)_2P$ groups.

by-products. By crystallisation from CH_2Cl_2/n-hexane the component with $\delta_P = 51.5$ could be isolated from the mixture and identified by X-ray analysis as 1-naphthyl-bis(diisopropylamino)phosphine (**4**). Attempts to isolate any of the other components by fractional crystallisation were unsuccessful. Because compound **4** could be independently prepared from 1-naphthyllithium and $(^iPr_2N)_2PCl$ (Scheme 1, V), we do not regard the use of organolithium reagents as generally unsuitable for the preparation of **2c**. Instead, severe steric repulsion seems to prevent two-fold substitution at the *peri*-positions of the C_{10}-unit. We noted similar effects when we tried to prepare 1,8-bis(di-*tert*-butylphosphino)naphthalene from **1** and $^tBu_2PCl$ and obtained only 1-naphthyl-di-*tert*-butylphosphine (**5**) [3e] (Scheme 1, IV). Compounds **4** and **5** were prepared on a preparative scale according to Scheme 1 (V) and fully characterised. Their $^{31}P\{^1H\}$-NMR spectra (in $CDCl_3$) showed sharp singlets at $\delta_P = 52.4$ (**4**) and $\delta_P = 11.4$ (**5**). As is illustrated in Fig. 6, the methyl groups in **4** are diastereotopic, and therefore gave rise to two doublets at $\delta_H = 1.08$ and $\delta_H = 1.33$ ($\Delta\delta_H = 0.25$, $^4J_{HH} = 6.6$ Hz) in the ^{1}H-NMR spectrum and to a virtual triplet at $\delta_C = 23.45$ ($^3J_{CP} = 6.5$ and 5.7 Hz) in the $^{13}C\{^1H\}$-NMR spectrum.

Figs. 7 and 8 show the molecular structures of **4** and **5**. Selected bond lengths and angles are summarised in Table 2.

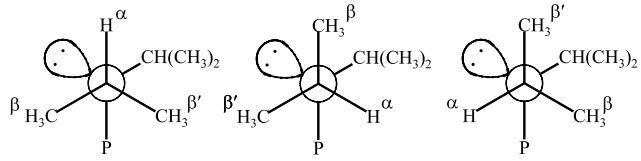


Fig. 6. Newman projection of one $^iPr_2N$ group in **4** viewed along the C–N bond (C in front, N back) to illustrate the diastereotopy of the methyl protons and carbon atoms.

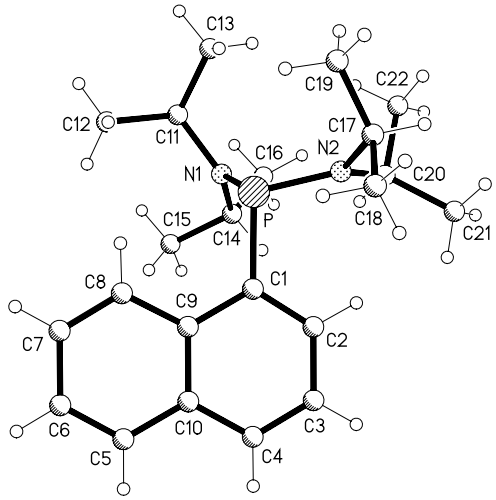


Fig. 7. Structure of **4** in the crystal; for selected bond lengths and angles see Table 2.

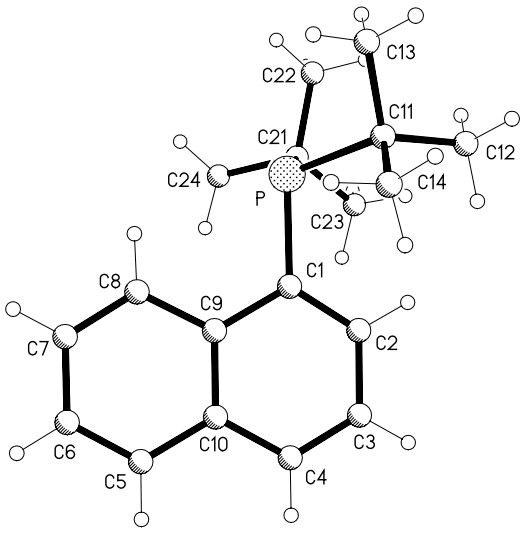


Fig. 8. Structure of **5** in the crystal; for selected bond lengths and angles see Table 2.

Table 2
Comparison of selected bond distances (pm) and bond angles (°) for **4** (left column) and **5** (right column)

Bond distances [a]			
P–C1	185.74(14)	P–C1	185.41(12)
P–N1	169.71(11)	P–C11	189.14(13)
P–N2	170.57(11)	P–C21	188.83(13)
N1–C14	148.1(2)	–	–
N1–C11	148.6(2)	–	–
N2–C17	148.6(2)	–	–
N2–C20	147.6(2)	–	–
C1–C2	137.4(2)	C1–C2	137.7(2)
C7–C8	136.7(2)	C7–C8	137.4(2)
C1–C9	144.2(2)	C1–C9	144.3(2)
C8–C9	141.6(2)	C8–C9	142.3(2)
C4–C10	141.5(2)	C4–C10	141.7(2)
C5–C10	142.0(2)	C5–C10	142.3(2)
Bond angles [a]			
C1–P–N2	103.74(6)	C1–P–C11	106.34(6)
C1–P–N1	100.47(6)	C1–P–C21	101.27(6)
N1–P–N2	109.67(6)	C21–P–C11	111.13(6)
P–C1–C2	121.95(10)	P–C1–C2	123.52(9)
P–C1–C9	119.86(10)	P–C1–C9	118.83(9)
C1–C9–C8	122.87(12)	C1–C9–C8	123.13(11)
C4–C10–C5	121.30(13)	C4–C10–C5	120.16(12)
P–N2–C17	117.22(9)	P–C11–C12	120.05(9)
P–N2–C20	126.18(9)	P–C11–C13	105.10(9)
		P–C11–C14	106.44(9)
P–N1–C11	118.98(9)	P–C21–C23	116.74(10)
P–N1–C14	125.48(9)	P–C21–C24	103.65(9)
N2–P–C1–C2	−2.7(1)	C11–P–C1–C2	−40.4(1)

[a] Numbers in parentheses indicate standard deviations in the least significant digits.

The structure determinations reveal bulky monophosphines in which the geometry at the phosphorus atoms is only moderately distorted [**4**: C1–P–N1 100.47(6)°, C1–P–N2 103.74(6)° and N1–P–N2 109.67(6)°; **5**: C1–P–C11 106.34(6)°, C1–P–C21 101.27(6)°, C11–P–C21 111.13(6)°]. Because of intramolecular repulsion of the ^{t}Bu groups in **5** with each other or, more probably, with the naphthyl substituent (vide infra), P–C11–C12 [120.05(9)°] and P–C21–C23 [116.74(10)°] are significantly larger than 109.4°, whereas P–C11–C13 [105.10(9)°] and P–C11–C14 [106.44(9)°] are slightly reduced. The other angles at C11 and C21 are close to the tetrahedral value. A similar but smaller widening of the trigonal angle due to intramolecular repulsion was observed for the isopropyl groups in **4** [P–N2–C20 126.18(9)° and P–N1–C14 125.48(9)°]. The conformation of the $(^i Pr_2N)_2P$ group in **4** is eclipsed [N2–P1–C1–C2 −2.7°] whereas the $^t Bu_2P$ group in **5** adopts a conformation between bisecting and eclipsed [C11–P–C1–C2 −40.4°] (Fig. 3). This again demonstrates the conformational difference of a bis(dialkylamino)arylphosphine relative to a diorgano-arylphosphine. In both molecules the naphthalene geometry is only slightly distorted, the mean deviation from the C_{10}-plane being 2.8 pm (**4**) and 1.1 pm (**5**). The phosphorus atoms deviate only slightly from this plane by 4.1 pm (**4**) and −1.6 pm (**5**). In order to minimise steric repulsion with the hydrogen atom at C2 (**4**: H2···H21C 199 pm, **5**: H2···H12B 205 pm), the phosphino groups are slightly inclined towards C9 [**4**: P–C1–C2 121.95(10)°, P–C1–C9 119.86(10)° and **5**: P–C1–C2 123.52(9)°, P–C1–C9 118.83(9)°].

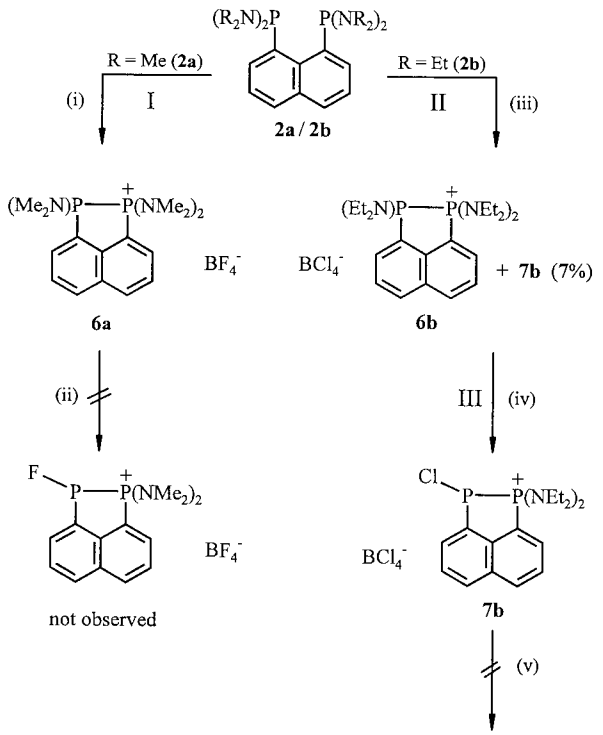
2.3. Preparation and structures of *6a* and *7b*

As mentioned above, compound **3** is not directly accessible from **1** and phosphorus trichloride and was obtained only in poor yield from the reaction of **2b** with gaseous HCl because various ionic, P,P′-bonded [σ^3P–σ^4P$^+$]-diphosphorus compounds of type **D** (Fig. 1) were formed as intermediates. We therefore tried to replace the amino groups in **2a** and **2b** by halogen atoms using BX_3 ether adducts (X = F, Cl) as halogenating agents.

Treatment of **2a** with $BF_3{\cdot}Et_2O$ in THF at −80 °C and warming to room temperature resulted in the formation of 1-dimethylamino-2-bis(dimethylamino)-1-phospha-2-phosphonium acenaphthene as the tetrafluoroborate salt **6a** (Scheme 2, I). Its $^{31}P\{^1H\}$-NMR spectrum, recorded in CD_2Cl_2, showed an AX-pattern at $\delta_P = 28.9$ and $\delta_P = 66.6$ with a $^1J_{PP}$ coupling of 347 Hz, consistent with the cationic, P,P′-bonded, σ^3P–σ^4P$^+$-structure shown in Scheme 2. Heating at reflux in CH_2Cl_2 with an excess of $BF_3{\cdot}Et_2O$ did not lead to further P–N bond cleavage or formation of P–F bonds.

The reaction of **2b** with $BCl_3{\cdot}Et_2O$, carried out in *n*-hexane at −80 °C, took a somewhat different course (Scheme 2, II). In the first step a colourless solid was obtained, which, according to $^{31}P\{^1H\}$-NMR spectroscopic analysis (CH_2Cl_2), was a mixture of **6b**, an

analogue of **6a** [$\delta_P = 28.6$ and 62.6, $^1J_{PP} = 349$ Hz], and the new compound 1-chloro-2-bis(diethylamino)-1-phospha-2-phosphonium acenaphthene tetrachloroborate (**7b**) [$\delta_P = 29.3$ and 76.1, $^1J_{PP} = 253$ Hz] (ca. 7%). Single crystals were obtained by crystallisation from a CH_2Cl_2/*n*-hexane mixture. The X-ray structure analysis and the $^{31}P\{^1H\}$-NMR spectrum of the mother liquor showed that during crystallisation as the second step, **6b** was transformed to **7b** (Scheme 2, III). However, treatment of **7b** with an excess of $BCl_3 \cdot Et_2O$ in refluxing



Scheme 2. (i) $+BF_3 \cdot Et_2O$, THF, -80 °C, 2. room temperature; (ii) $+BF_3 \cdot Et_2O$ (xs), CH_2Cl_2, reflux; (iii) $+BCl_3 \cdot Et_2O$, *n*-hexane, -80 °C; (iv) crystallisation; (v) $+BCl_3 \cdot Et_2O$, CH_2Cl_2, reflux.

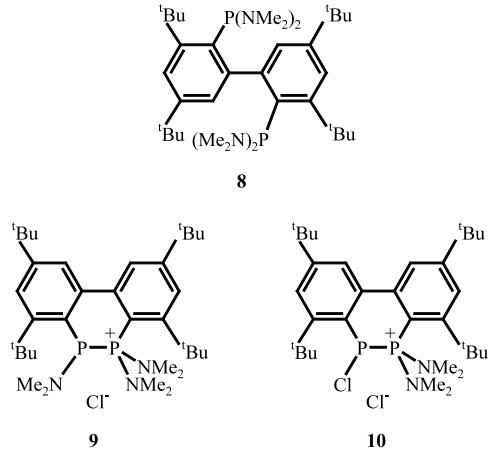


Fig. 9.

Table 3
^{31}P-NMR data of **2a**, **6a**, **6b**, **7b**, **X**, **Y**, and **Z**, and literature values

No.	^{31}P-NMR data [a] (in ppm and Hz)				Ref.
	$\delta(\sigma^3P)$ [b]	$\delta(\sigma^4P^+)$ [b]	$^1J_{PP}$	Solvent	
2a	100.9	–	–	C_6D_6	[c]
2b	96.4	–	–	C_6D_6	[3d]
8	114.1	–	–	C_6D_6	[13]
6a	66.6	28.9	347	CD_2Cl_2	[c]
6b	62.6	28.6	349	CH_2Cl_2/C_6D_6 [d]	[c]
9	57.3	25.9	340	$CDCl_3$	[13]
7b	76.1	29.3	253	CD_2Cl_2	[c]
10	66.9	37.6	268	$CDCl_3$	[13]
X [e]	78.0	25	263	Et_2O/C_6D_6 [d]	[7]
Y [e]	66.0	18	271	CH_2Cl_2/C_6D_6 [d]	[7]
Z [e]	80.0	−61	158	CH_2Cl_2/C_6D_6 [d]	[7]

[a] Recorded at 81.0 (**2b**, **6b**, **X**, **Y**, **Z**) or 162.0 MHz (**2a**, **6a**, **7b**) with 85% H_3PO_4 as external standard at $\delta_P = 0$.
[b] A- and X-part of an AX-spin system; multiplicity ≈ doublet.
[c] This work.
[d] C_6D_6-capillary as 'internal' lock.
[e] See Section 2.4.

CH_2Cl_2 did not lead to further replacement of the remaining amino groups by chlorine atoms.

Compounds **6a** and **7b** are colourless, moisture-sensitive solids that are reasonably stable towards oxidation in air. They were fully characterised, including X-ray crystal structure analysis (vide infra). Their $^{31}P\{^1H\}$-NMR data find some analogy in the phosphonium salts **9** and **10** that were observed by Bickelhaupt et al. in the reaction of **8** with hydrogen chloride (Fig. 9 and Table 3) [13]. Due to the presence of by-products, **9** and **10** could not be obtained in pure form and their structures were assigned, though with confidence, only on the basis of their characteristic NMR data. Our results now confirm these assignments. The replacement of an electron-donating substituent at σ^3P (R_2N in **6a** and **6b**) by an electron-withdrawing substituent (Cl in **7b**) causes deshielding of both phosphorus nuclei and reduces $^1J_{PP}$ (Table 3). This observation is in line with the results that were obtained for the analogous urea-bridged systems [14]. The counterion (BF_4^-, BCl_4^- or Cl^-), however, has no pronounced effect on the NMR data of **6a**, **6b**, and **7b**, which indicates that the [$\sigma^3P-\sigma^4P^+$]-structure predominates also in solution (vide infra).

Compounds **6a** and **7b**, to the best of our knowledge, represent the first examples of 1-P,8-P′-disubstituted naphthalene compounds with a P–P single bond and thus the first examples of the 1,2-dihydro-1,2-diphospha-acenaphthene ring system.

Their structures (Figs. 10 and 11 and Table 4) display phosphorus-containing heterocycles in which the phosphorus and the three carbon atoms of the naphthalene framework form five-membered ring systems. These five-membered rings exhibit an envelope conformation, in which the atoms C8, C9, C1 and P1 form a plane

with a mean deviation of 0.7 (**6a**) and 1.7 (**7b**) pm. P2 lies outside this plane by −18.6 (**6a**) and −39.7 pm (7**b**). The naphthalene rings (mean deviation from planarity 0.6 pm, **6a** and 2.6 pm, **7b**) are less distorted than in the bis-aminophosphines **2a** and **2b**. The phosphorus atoms (P1 and P2) lie −3.2 and −22.3 (**6a**) and 17.6 and −31.4 pm (**7b**) outside the least squares planes of the naphthalene ring systems. The torsion angles P1–C1···C8–P2 are 5.8° (**6a**) and 13.5° (**7b**). There is in-plane distortion in the opposite direction, compared to the structures of **2a** and **2b** as is demonstrated by the bay angles P1–C1–C9 [119.97(10)°, **6a**; 118.1(2)°, **7b**], C1–C9–C8 [120.56(13)°, **6a**; 120.9(2)°, **7b**], both of which are normal sp^2 values, and P2–C8–C9 [111.58(10)°, **6a**; 111.6(2)°, **7b**], the latter being considerably smaller than 120°. As a consequence, the splay

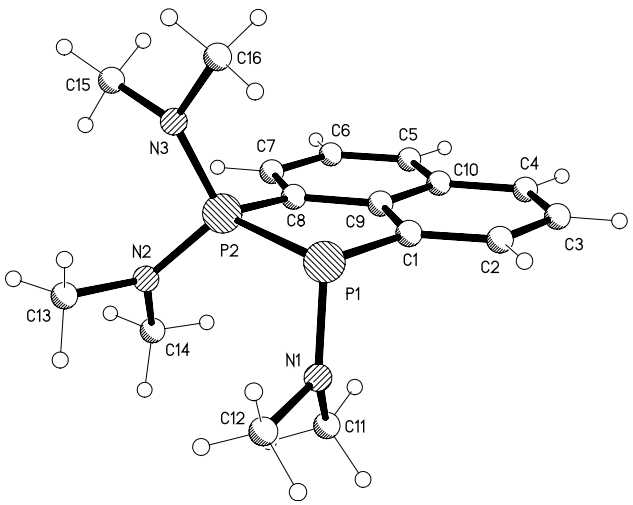


Fig. 10. Structure of **6a** in the crystal. The counterion (BF_4^-) has been omitted for clarity. For selected bond lengths and angles see Table 4.

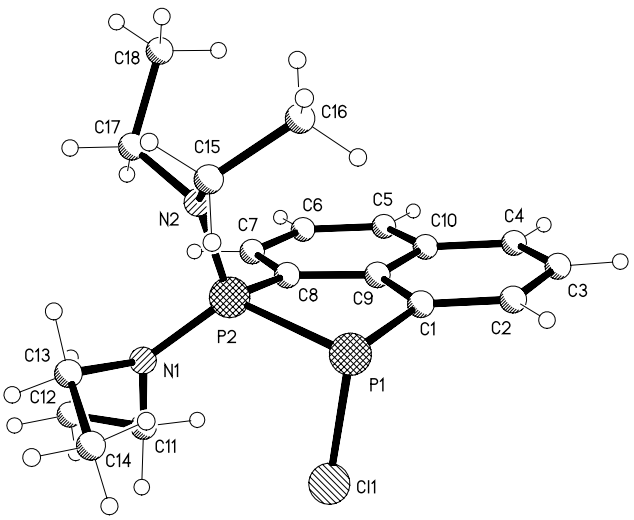


Fig. 11. Structure of **7b** in the crystal. The counterion (BCl_4^-) has been omitted for clarity. For selected bond lengths and angles see Table 4.

Table 4
Comparison of selected bond distances (pm) and bond angles (°) for **6a** (left column) and **7b** (right column)

Bond distances [a]			
P1–P2	225.38(5)	P1–P2	223.16(12)
P1–C1	183.10(15)	P1–C1	182.1(3)
P2–C8	179.41(15)	P2–C8	179.1(3)
P1–N1	167.76(15)	P1–Cl1	207.77(11)
P2–N2	162.41(13)	P2–N1	162.5(2)
P2–N3	163.57(13)	P2–N2	162.5(2)
N1–C11	146.1(2)	–	–
N1–C12	146.3(2)	–	–
N2–C13	147.4(2)	N1–C11	148.3(3)
N2–C14	146.8(2)	N1–C13	148.7(3)
N3–C15	146.4(2)	N2–C15	148.1(3)
N3–C16	146.3(2)	N2–C17	148.8(4)
C1–C2	138.0(2)	C1–C2	136.9(4)
C7–C8	138.3(2)	C7–C8	137.7(4)
C1–C9	143.4(2)	C1–C9	142.7(4)
C8–C9	142.6(2)	C8–C9	141.4(3)
C4–C10	142.1(2)	C4–C10	142.1(4)
C5–C10	142.1(2)	C5–C10	141.3(4)
Bond angles [a]			
C1–P1–P2	88.03(5)	C1–P1–P2	88.77(9)
C1–P1–N1	103.52(7)	C1–P1–Cl1	100.27(9)
N1–P1–P2	104.57(5)	Cl1–P1–P2	92.21(5)
C8–P2–P1	99.09(5)	C8–P2–P1	97.50(9)
C8–P2–N2	109.68(7)	C8–P2–N1	110.89(12)
C8–P2–N3	113.72(7)	C8–P2–N2	111.60(12)
N2–P2–P1	118.56(5)	N1–P2–P1	119.85(9)
N3–P2–P1	108.62(5)	N2–P2–P1	106.05(9)
N2–P2–N3	107.27(7)	N1–P2–N2	110.31(12)
P1–C1–C2	120.93(12)	P1–C1–C2	121.6(2)
P1–C1–C9	119.97(10)	P1–C1–C9	118.1(2)
P2–C8–C9	111.58(10)	P2–C8–C9	111.6(2)
P2–C8–C7	127.00(11)	P2–C8–C7	127.0(2)
C1–C9–C8	120.56(13)	C1–C9–C8	120.9(2)
C4–C10–C5	122.79(15)	C4–C10–C5	123.6(2)
P1–N1–C11	126.27(12)	P2–N1–C11	123.9(2)
P1–N1–C12	116.48(12)	P2–N1–C13	117.8(2)
C11–N1–C12	113.14(15)	C11–N1–C13	115.1(2)

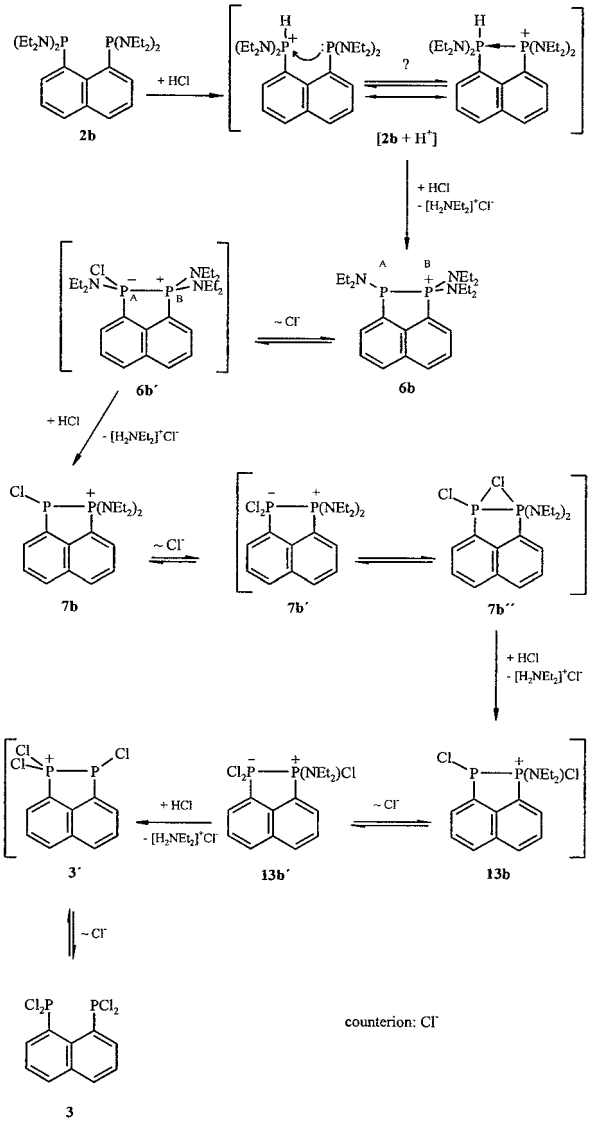
[a] Numbers in parentheses indicate standard deviations in the least significant digits.

angles of the *peri*-bonds (P1–C1–C9 + C1–C9–C8 + C9–C8–P2 −360°) [15] are negative [−7.89 (**6a**) and −9.40° (**7b**)]; a strong indication for attractive interactions in the *peri*-region. Since the latter has an intrinsic C1···C8 separation of about 250 pm, the mutual approach of the substituent groups is a prerequisite for the formation of a P–P bond, which has a typical length of 225 pm [225.38 pm (**6a**) and 223.16 pm (**7b**)]. Because the positive charge of the cation is located at P2, the P2–C8 bond lengths [179.41(15) pm, **5a**; 179.1(3) pm, **7b**] are shorter than the P1–C1 bond lengths [183.10(10) pm, **6a**; 182.1(3) pm, **7b**]. For the same reason, in **6a** the P–N bonds at P2 [162.41(13) and 163.57(13) pm] are shorter than P1–N1 [167.76(15) pm]. The P1–Cl1 bond length [207.77(11) pm] in **7b** is in the usual range [3]. The geometry at the phosphorus atoms may be described as distorted tetrahedral. In the

crystal structure of **7b** there is a short Cl···Cl contact between the cation and BCl_4^- of 338.6 pm.

2.4. Mechanism for the reaction of *2b* with hydrogen chloride

Having isolated and unambiguously identified two of the intermediates that we had observed earlier in the reaction of **2b** with hydrogen chloride [3d,7], we now wish to propose a mechanism, outlined in Scheme 3, that can explain their formation.



Scheme 3.

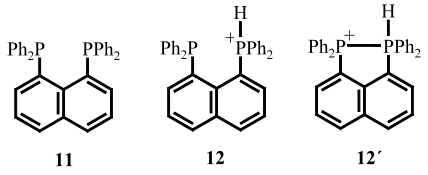


Fig. 12.

In the first step of this mechanism, **2b** is protonated to furnish the phosphonium cation [**2b** + H^+]. Such a protonation is essential and has been observed before in the replacement of amino groups by chlorine [16]. The normal subsequent step would be addition of chlorine to phosphorus. However, in the case of [**2b** + H^+], this would further increase the steric strain in the molecule by additional crowding. Instead, the strain is reduced by concomitant attack of the tertiary, basic phosphorus on the cationic phosphorus and elimination of diethylamine to give the phosphonium cation **6b** with a P–P bond. We conclude that for the formation of a P–P bond from a monophosphonium salt of type **F** (Fig. 2), it is essential that two substituents can be removed from σ^4P^+ during bond formation. The structure of the protonated 1,8-bis(diphenylphosphino)naphthalene, dppnH$^+$ (**12**) (counterion: $CF_3SO_3^-$), for example, was found to be of type **F** (σ^3P, σ^4P^+, **12**) rather than of type **F′** (σ^4P^+–σ^5P, **12′**), according to ^{31}P-NMR spectroscopy and X-ray analysis [3j] (Fig. 12). In this case, cleavage of a P–C bond would have to occur which, under acidic conditions, is unlikely, compared to the cleavage of a P–N bond.

Compound **6b** reacts further by conventional substitution of the diethylamino group at the tertiary phosphorus by chlorine to furnish **7b**. The two remaining amino substituents at the phosphonium group are protected against protonation and chloro substitution by the positive charge. This may also explain why **7b** does not react further with $BCl_3 \cdot Et_2O$. However, the reaction of **2b** with excess HCl in an inert, polar solvent such as dichloromethane with extended reaction times finally furnished **3**. We believe that under these conditions even the two remaining amino substituents can be substituted by chlorine, whereby the intermediates **7b′**/**7b″**, **13b**/**13b′** and **3′** could be formed. In fact, in urea-bridged diphosphorus compounds there is precedence for the existence of zwitterionic structures such as **6b′**, **7b′**, **13b′** and **3′**, for PPCl three-membered ring structures such as **7b″**, and also for equilibria between them and monocationic structures such as **6b** and **7b** [14]. Furthermore, there is evidence for the existence of an equilibrium in solution between ionic phosphonium structures such as **3′** and the covalent form **3** [14b]. In fact, the ^{31}P-NMR-spectra of the reaction mixtures [7] indicated that there are three more products, giving spectra with AX-patterns (**X**–**Z** in Table 3), that are as yet unaccounted for. Their preparation and characterisation is part of on-going work in our laboratory.

3. Experimental

All experiments were carried out in standard Schlenk glassware with exclusion of air and moisture. Solvents were dried, purified, and stored according to common procedures [17]. 1,8-Dilithionaphthalene [9] and the chlorobis(dialkylamino)phosphines [18] were prepared as described in the literature. All other reagents were obtained commercially. NMR: Bruker AC 200 (^{1}H: 200.1 MHz, ^{13}C: 50.3 MHz, ^{31}P: 81.0 MHz, ^{19}F: 188.3 MHz), Bruker AMX 400 and DRX 400 (^{1}H: 400.13 MHz, ^{13}C: 100.61 MHz), reference substances were $SiMe_4$ or $CHCl_3$ (int.) at $\delta_H = 7.25$ and $\delta_C = 77.05$, CD_2Cl_2 (int.) at $\delta_H = 5.32$ and $\delta_C = 53.5$ and C_6D_6 (int.) at $\delta_H = 7.15$ and $\delta_C = 128.00$ (^{1}H, ^{13}C), 85% H_3PO_4 (ext.) and $CFCl_3$ (ext.) at $\delta_P = 0$ (^{31}P) and $\delta_F = 0$ (^{19}F); high-field shifts are given negative, low-field shifts positive signs; m_c denotes a complex multiplet. For compounds **2a** and **6a** assignments were supported by DEPT, HH COSY, CH COSY and COLOC NMR experiments (AMX 400); for compounds **4** and **5** by HH COSY, HC HMBC and HC HSQC NMR experiments (DRX 400). The atom numbering (C, H) is as in Scheme 1. MS: Finnigan MAT 8430; EI at 70 eV; FAB, NBA matrix. IR: recorded in KBr disks on a Nicolet 320 FTIR spectrometer. Elemental analyses: Analytisches Laboratorium des Instituts für Anorganische und Analytische Chemie der Technischen Universität, Braunschweig. Melting points were determined on a Büchi 530 melting point apparatus using sealed 0.1 mm capillary tubes and are uncorrected.

3.1. Preparation of 1,8-bis[bis(dimethylamino)phosphino]naphthalene (2a)

A suspension of 1,8-dilithionaphthalene (**1**) in 20 ml of THF, prepared from 4.11 g (19.8 mmol) of 1-bromonaphthalene, was cooled to −70 °C and a solution of 7.82 g (51.0 mmol) of chlorobis(dimethylamino)phosphine in 5 ml of THF was added. The reaction mixture was allowed to warm to 20 °C and stirred for 12 h. After removal of the solvent in vacuo, the residue was extracted with 20 ml of *n*-hexane and the insoluble lithium salts were separated by filtration. The filtrate was concentrated in vacuo and stored at −20 °C overnight, whereby colourless blocks were formed that were suitable for X-ray analysis. Yield: 3.24 g (9 mmol, 44%). From the mother liquor an additional 3 g (8.2 mmol, 41%) of a wine-red, viscous product, suitable for further reactions, was recovered. ^{1}H-NMR (C_6D_6, 400.1 MHz): δ 2.51 ($m_c \approx$ (t), $J = 4.4$ Hz, 24H, NCH_3), 7.35 (m_c ($\approx$ t), ^3J(HH) ≈ 7.5 Hz, 2H, 3-H), 7.67 (m_c ($\approx$ dd), $^3J(^3H^4H) \approx 8.0$ Hz, $^4J(^2H^4H) \approx 1.4$ Hz, 2H, 4-H), 7.96 (m_c ($\approx$ dq), $^3J(^2H^3H) \approx 7.0$, $^4J(^2H^4H) \approx 1.8$ Hz, 2H, 2-H); ^{13}C{^{1}H}-NMR (C_6D_6, 100.6 MHz): δ 41.22 (m_c ($\approx$ t), $J \approx 10.7$ Hz, NCH_3), 124.22 (s, C-3,6), 130.21 (s, C-4,5), 130.88 (m_c ($\approx$ t), $J \approx 3.9$ Hz, C-2,7), 135.49 (t, $J = 2.3$ Hz, C-4a), 135.66 (t, $J = 16.3$ Hz, C-8a), 141.10 (m_c ($\approx$ t), $J = 18.0$ Hz, C-1,8); on the basis of these assignments the ^{13}C{^{1}H}-NMR data of **2b** in Ref. [3d] read correctly: δ 135.55 (m_c ($\approx$ t), $J \approx 2.2$ Hz, *C-4a*), 143.09 (t, $J = 19.3$ Hz, *C-1,8*); ^{31}P{^{1}H}-NMR (C_6D_6, 162.0 MHz): δ 100.9 (s). Anal. Found: C, 57.66; H, 8.25; N, 14.32. Calc. for $C_{18}H_{30}N_4P_2$ (364.41): C, 59.33; H, 8.30; N, 15.37%.

3.2. Preparation of 1-naphthyl-bis(diisopropylamino)phosphine (4)

A suspension of 1-naphthyl-lithium, prepared from 1 g (4.8 mmol) of 1-bromonaphthalene and 3.8 ml (6.1 mmol) of *n*-BuLi (1.6 M in *n*-hexane) according to the method of Brandsma [9], was cooled at −5 °C and 10 ml of THF were added. At −80 °C a solution of 1.33 g (5 mmol) of chloro-bis(diisopropylamino)phosphine in 10 ml of THF was added dropwise and the mixture was allowed to warm to room temperature (r.t.). After removal of the solvent in vacuo the residue was extracted with *n*-hexane and the insoluble lithium salts were separated by filtration. The filtrate was concentrated and stored at −20 °C, whereby colourless blocks were formed. Yield: 1.3 g (3.64 mmol, 76%), m.p. 151 °C. ^{1}H-NMR ($CDCl_3$, 400.1 MHz): δ 1.08 (d, $^3J_{HH} = 6.6$ Hz, 12H, NCH(CH_3^A)CH_3), 1.33 (d, $^3J_{HH} = 6.6$ Hz, 12H, NCH(CH_3)CH_3^B), 3.50 (m_c ($\approx$ dsept), $^3J_{PH} = 11.3$, $^3J_{HH} = 6.6$ Hz, 4H, NCH(CH_3)$_2$), 7.45 (m_c, 3H, H-3, H-6 and H-7), 7.74 (d, $^3J_{HH} = 8.1$ Hz, 1H, H-4), 7.80 (m_c ($\approx$ dd), $J \approx 6.5$ and 3.1 Hz, 1H, H-5), 7.93 (m_c ($\approx$ ddd), $J = 7.1$, 3.5 and 1.2 Hz, 1H, H-2), 8.71 (m_c ($\approx$ ddm), $J \approx 6.5$ and 3.9 Hz, 1H, H-8); ^{1}H{^{31}P}-NMR ($CDCl_3$, 400.1 MHz): δ 1.08 (d, $^3J_{HH} = 6.6$ Hz, 12H, NCH(CH_3^A)CH_3), 1.32 (d, $^3J_{HH} = 6.7$ Hz, 12H, NCH(CH_3)CH_3^B), 3.50 (sept, $^3J_{HH} = 6.6$ Hz, 4H, NCH(CH_3)$_2$), 7.45 (m_c, 3H, H-3, H-6 and H-7), 7.74 (d, $J = 8.1$ Hz, 1H, H-4), 7.80 (m_c ($\approx$ dd), $J = 6.2$ and 3.3 Hz, 1H, H-5), 7.94 (d, $J = 7.0$ Hz, 1H, H-2), 8.71 (m_c ($\approx$ dd), $J \approx 6.2$ and 3.5 Hz, 1H, H-8); ^{13}C{^{1}H}-NMR ($CDCl_3$, 100.6 MHz): δ 23.45 (m_c ($\approx$ t), $J_{CP} = 6.5$ and 5.7 Hz, NCH(CH$_3$)$_2$), 47.09 (d, $^2J_{CP} = 11.7$ Hz, NCH(CH_3)$_2$), 123.79 (d, $^4J_{CP} = 2.7$ Hz, C-7), 124.14 (s, C-3), 124.57 (s, C-6), 126.19 (d, $^3J_{CP} = 26.7$ Hz, C-8), 127.13 (s, C-4), 127.59 (d, $^4J_{CP} = 2.2$ Hz, C-5), 128.85 (d, $^2J_{CP} = 4.1$ Hz, C-2), 132.77 (d, $^3J_{CP} = 3.4$ Hz, C-4a), 132.95 (d, $^2J_{CP} = 26.1$ Hz, C-8a), 140.86 (d, $^1J_{CP} = 16.5$ Hz, C-1); ^{31}P{^{1}H}-NMR ($CDCl_3$, 162.0 MHz): δ 52.4 (s). IR (KBr, cm^{-1}): 3051 w, 3035 w, 2966 s, 2931 m, 2868 w, 1619 w, 1516 w, 1502 w, 1405 w, 1358 m, 1174 s, 1156 m, 1116 m, 1084 w, 1016 m, 964 w, 948 s, 864 w, 794 m, 775 s, 507 m. EIMS (70 eV): m/z (%) = 358 (28) [M^+], 315 (4) [$M^+ - C_3H_7$], 258 (100) [$M^+ - N(C_3H_7)_2$], 244 (3), 216 (12), 172 (13), 159 (56) [$MH^+ - 2N(C_3H_7)_2$]. Anal. Found: C, 73.48; H, 9.81; N, 7.77.

Calc. for $C_{22}H_{34}N_2P$ (357.50): C, 73.91; H, 9.59; N, 7.84%.

3.3. Preparation of 1-naphthyl-di-tert-butylphosphine (5)

A suspension of 1-naphthyl-lithium, prepared from 1 g (4.8 mmol) of 1-bromonaphthalene and 3.8 ml (6.1 mmol) of *n*-BuLi (1.6 M in *n*-hexane) (see Section 3.2) was cooled to −30 °C and 5 ml of Et_2O were added. At −60 °C a solution of 1.10 g (6.1 mmol, 1.2 eq) of chloro-di-*tert*-butylphosphine in 3 ml of Et_2O was added dropwise and the mixture was stirred at r.t. for 3 days. After aqueous work-up and crystallisation from CH_2Cl_2–EtOH at −60 °C, 1.017 g (3.73 mmol, 75%) of a white, air-stable powder (m.p. 99 °C) was obtained. ^{1}H-NMR ($CDCl_3$, 400.1 MHz): δ 1.25 (d, $^3J_{PH} = 12.0$ Hz, 18H, $CH(CH_3)_3$), 7.49 (m_c, 3H, H-3, H-6 and H-7), 7.83 (d, $^3J_{HH} = 7.9$ Hz, 1H, H-5), 7.87 (d, $^3J_{HH} = 8.2$ Hz, 1H, H-4), 7.99 (dm, $J \approx 7.1$ Hz, 1H, H-2), 9.19 (m_c ($\approx$ t), $J = 7.7$ Hz, 1H, H-8); ^{13}C{^{1}H}-NMR ($CDCl_3$, 100.6 MHz): δ 30.65 (d, $^2J_{CP} = 15$ Hz, $C(CH_3)_3$), 32.66 (d, $^1J_{CP} = 22$ Hz, $C(CH_3)_3$), 124.22 (s, C-3), 125.47 (m_c ($\approx$ t), $J_{CP} = 4.1$ and 2.5 Hz, C-6 and C-7), 127.73 (d, $^3J_{CP} = 36.8$ Hz, C-8), 128.40 (m_c ($\approx$ d), unresolved, C-5), 129.49 (s, C-4), 133.45 (d, $^2J_{CP} = 4.2$ Hz, C-2), 133.64 (d, $^3J_{CP} = 5.4$ Hz, C-4a), 134.56 (d, $^1J_{CP} = 25.9$ Hz, C-1), 139.24 (d, $^2J_{CP} = 25.8$ Hz, C-8a); ^{31}P{^{1}H}-NMR ($CDCl_3$, 162 MHz): δ 11.4 (s). IR (KBr, cm^{-1}): 3054 w, 2978 m, 2933 m, 2894 m, 2860 m, 2362 w, 2327 w, 1649 w, 1500 w, 1471 m, 1384 w, 1360 m, 1318 w, 1256 w, 1172 m, 1134 w, 1017 m, 961 w, 799 s, 780 s, 741 w, 660 w, 636 w, 600 w, 569 w, 535 w, 460 w, 434 w. EIMS (70 eV): m/z (%) = 272 (35) [M^+], 216 (8) [$M^+ - C_4H_8$], 171 (2), 160 (100) [$M^+ - 2C_4H_8$], 133 (15), 128 (18), 115 (9), 57 (34) [C_4H_9]. Anal. Found: C, 79.42; H, 9.17. Calc. for $C_{18}H_{25}P$ (272.37): C, 79.38; H, 9.25%.

3.4. Preparation of 1-dimethylamino-2-bis(dimethylamino)-1-phospha-2-phosphonium-acenaphthene tetrafluoroborate (6a)

A solution of **2a** (1.73 g, 4.75 mmol) in 20 ml of THF was cooled at −80 °C and 3 ml (3.4 g, 23.4 mmol, 5 eq) of $BF_3{\cdot}Et_2O$ were added dropwise. Upon slow warming to 20 °C the deep red colour of the mixture changed to pale yellow. The colourless solid that precipitated from the solution on standing at r.t. was separated by filtration, washed twice with 5 ml portions of THF and dried in vacuo. Yield: 0.370 g (0.9 mmol, 20%), m.p. 124 °C (decomp.). ^{31}P-NMR spectroscopic analysis showed the mother liquor to contain the remainder of the product. After removal of the solvent and of all volatile components in vacuo at 50 °C, 5.57 g of a brown oil was obtained. Attempts to increase the yield by isolating additional quantities of the product from this oil were unsuccessful. ^{1}H-NMR ($CDCl_3$, 200 MHz): δ 2.60 (m_c ($\approx$ dd), $J_{PH} = 10.2$ and 4.9 Hz, 6H, σ^3-PNCH_3), 2.90 (d, $J = 11.0$ Hz, 6H, σ^4-PNCH_3^A), 2.91 (d, $J = 9.9$ Hz, 6H, σ^4-PNCH_3^B), 7.76–7.93 (m_c, 2H, H-3 and H-6), 8.01 (m_c ($\approx$ t), $J_{HH} \approx 7.0$ Hz, 1H, H-2), 8.15 (d, $^3J_{HH} \approx 8.1$ Hz, $^4J_{HH}$ unresolved, 1H, H-7), 8.29 (m_c ($\approx$ dd), $^3J_{HH} \approx 8.8$ Hz, $^4J_{HH}$ unresolved, 1H, H-4), 8.32 (m_c ($\approx$ dd), $^3J_{HH} \approx 8.7$ Hz, $^4J_{HH}$ unresolved, 1H, H-5); ^{1}H-NMR (CD_2Cl_2, 200 MHz): δ 2.62 (m_c, poorly resolved, 6H, σ^3-PNCH_3), 2.91 (d, $J = 10.4$ Hz, 6H, σ^4-PNCH_3^A), 2.91 (d, $J = 9.8$ Hz, 6H, σ^4-PNCH_3^A), 7.83–7.96 (m_c, 2H, H-3 and H-6), 8.09 (m_c ($\approx$ t), $J_{HH} \approx 7.0$ Hz, 1H, H-2), 8.21 (m_c ($\approx$ t), $^3J_{HH} \approx$ 8.4 Hz, $^4J_{HH}$ unresolved, 2H, H-7 and H-4), 8.39 (m_c ($\approx$ dt), $^3J_{HH} \approx 8.8$, $^4J_{HH} = 1.3$ Hz, 1H, H-5); ^{1}H{^{31}P}-NMR (CD_2Cl_2, 200 MHz, σ^3-P): δ 2.62 (m_c ($\approx$ d), poorly resolved, 6H, σ^3-PNCH_3), 2.91 (d, $J = 9.5$ Hz, 6H, σ^4-PNCH_3^A), 2.92 (d, $J = 8.6$ Hz, 6H, σ^4-PNCH_3^B), 7.89 (m_c ($\approx$ q), $J \approx 7.5$ Hz, 2H, H-3 and H-6), 8.09 (m_c ($\approx$ d), $J_{HH} \approx 6$ Hz, 1H, H-2), 8.20 (m_c ($\approx$ dt), $^3J_{HH} \approx$ 8.3 Hz, $^4J_{HH} \approx 1.1$ Hz, 2H, H-7 and H-4), 8.39 (m_c ($\approx$ dt), $^3J_{HH} \approx 8.2$, $^4J_{HH} = 1.2$ Hz, 1H, H-5); ^{1}H{^{31}P}-NMR (CD_2Cl_2, 200 MHz, σ^4-P): δ 2.61 (s, 6H, σ^3-PNCH_3), 2.910 (s, 6H, σ^4-PNCH_3^A), 2.914 (s, 6H, σ^4-PNCH_3^B), 7.83–7.95 (m_c, 2H, H-3 and H-6), 8.09 (m_c ($\approx$ t), $J_{HH} \approx 7$ Hz, 1H, H-2), 8.21 (m_c ($\approx$ dd), $J \approx 7.1$ and 5.3 Hz, 2H, H-7 and H-4), 8.39 (m_c ($\approx$ dd), $^3J_{HH} \approx 8.2$, $^4J_{HH} = 1.0$ Hz, 1H, H-5); ^{13}C{^{1}H}-NMR (CD_2Cl_2, 100.6 MHz): δ 35.70 (s, σ^3-PNCH_3), 37.58 (d, $^2J_{CP} = 9.2$ Hz, σ^4-PNC^AH_3), 38.01 (d, $^2J_{CP} = 5.5$ Hz, σ^4-PNC^BH_3), 121.29 (m_c ($\approx$ dd), $J_{CP} = 74.8$ and 6.1 Hz, C-1), 127.91 (d, $J_{CP} = 9.2$ Hz, C-6), 128.64 (m_c ($\approx$ dd), $J_{CP} = 8.7$ and 4.0 Hz, C-3), 130.96 (m_c ($\approx$ dd), $J_{CP} = 26.6$ and 14.5 Hz, C-8), 131.60 (s, C-4), 132.34 (d, $J_{CP} = 1.2$ Hz, C-7), 133.51 (d, $J_{CP} = 12.7$ Hz, C-4a), 134.38 (m_c ($\approx$ dd), $J_{CP} = 30.1$ and 18.1 Hz, C-2), 135.24 (d, $J_{CP} = 2.5$ Hz, C-5), 138.08 (d, $J_{CP} = 34.7$ Hz, C-8a); ^{31}P{^{1}H}-NMR (CD_2Cl_2): δ 28.9 (m_c ($\approx$ d), $^1J_{PP} = 347$ Hz, σ^3-P), 66.6 (m_c ($\approx$ d), $^1J_{PP} = 347$ Hz, σ^4-P); ^{19}F-NMR (CD_2Cl_2): δ −152.5 (s, BF_4^-). IR (KBr, cm^{-1}): 3054 w, 2919 w, 2814 w, 1484 w, 1181 m, 1166 m, 1097 s (sh), 1058 vs, 1004 s, 988 m, 973 s, 889 w, 832 m. FABMS (NBA): m/z (%) = 320 (100) [M^+]. Anal. Found: C, 46.62; H, 6.06; N, 10.08. Calc. for $C_{16}H_{24}BF_4N_3P_2$ (407.14): C, 47.20; H, 5.94; N, 10.32%.

3.5. Preparation of 1-chloro-2-bis(diethylamino)-1-phospha-2-phosphonium-acenaphthene tetrachloroborate (7b)

Upon dropwise addition of 10 ml (10 mmol, 1.17 g, 2.4 eq) of $BCl_3{\cdot}Et_2O$ (1 M in *n*-hexane) to a solution of **2b** (2 g, 4.2 mmol) in a minimum amount of *n*-hexane (ca. 2 ml) at −80 °C a yellow solid immediately formed. The supernatant solution, which was expected

Table 5
Crystallographic data for **2a**, **4**, **5**, **6a** and **7b**

Compound	**2a**	**4**	**5**	**6a**	**7b**
Empirical formula	$C_{18}H_{30}N_4P_2$	$C_{22}H_{35}N_2P$	$C_{18}H_{25}P$	$C_{16}H_{24}BF_4N_3P_2$	$C_{18}H_{26}BCl_5N_2P_2$
M_r	364.40	358.49	272.35	407.13	520.41
Crystal habit	Colourless prism	Colourless prism	Colourless column	Colourless prism	Colourless tablet
Crystal size (mm)	$0.60\times0.50\times0.30$	$0.60\times0.60\times0.25$	$0.42\times0.18\times0.17$	$0.33\times0.27\times0.19$	$0.50\times0.40\times0.20$
Temperature (°C)	−100	−100	−130	−130	−130
Crystal system	Monoclinic	Triclinic	Monoclinic	Monoclinic	Triclinic
Space group	$C2/c$	$P\bar{1}$	$P2_1/c$	$P2_1/n$	$P\bar{1}$
Unit cell dimensions					
a (pm)	1702.4(3)	814.45(10)	1183.88(12)	1525.96(10)	908.4(2)
b (pm)	901.7(2)	990.38(10)	1074.00(10)	806.23(6)	1156.3(2)
c (pm)	1396.7(3)	1422.2(2)	1307.19(12)	1578.12(10)	1175.1(2)
α (°)	90	71.320(10)	90	90	93.95(3)
β (°)	106.35(3)	75.161(10)	106.029(3)	94.477(3)	102.20(3)
γ (°)	90	78.578(10)	90	90	95.70(3)
U (nm^3)	2.0573(7)	1.0421(2)	1.5975(3)	1.9356(2)	1.1953(4)
Z	4	2	4	4	2
D_{calc} (Mg m^{-3})	1.176	1.143	1.132	1.397	1.446
μ (mm^{-1})	0.219	0.139	0.158	0.267	0.749
$F(000)$	784	392	592	848	536
$2\theta_{max}$ (°)	50	50	57	60	50
Reflections measured	3669	3811	21 348	33 642	4853
Independent reflections	1822	3647	4039	5655	4210
Transmissions	–	–	0.72–0.86	–	0.843–1.00
R_{int}	0.0348	0.0136	0.0338	0.0568	0.0180
wR (F^2, all refl.)	0.1037	0.0824	0.1170	0.1347	0.0880
$R(F>4\sigma(F))$	0.0360	0.0314	0.0418	0.0460	0.0370
Number of parameters	114	234	178	241	257
S	1.080	1.053	1.05	1.041	1.048
Max. $\Delta\rho$ (e nm^{-3})	296	256	602	866	428

to contain unreacted BCl_3, was removed with a syringe and carefully subjected to hydrolysis with melting ice. From the crude product all volatile components were removed in vacuo to afford 1.64 g of an orange solid. $^{31}P\{^1H\}$-NMR spectroscopic analysis (in CH_2Cl_2) showed this to be a mixture of **6b** and **7b** in a ratio of about 15:1 (yield: 3 mmol, 70% based on **6b**). $^{31}P\{^1H\}$-NMR (CH_2Cl_2, C_6D_6-Lock): δ 28.6 (m_c ($\approx$ d), $^1J_{PP}$ = 349 Hz, σ^3-P in **6b**), 29.3 (m_c ($\approx$ d), $^1J_{PP}$ = 253 Hz, σ^3-P in **7b**), 62.6 (m_c ($\approx$ d), $^1J_{PP}$ = 349 Hz, σ^4-P in **5b**), 76.1 (m_c ($\approx$ d), $^1J_{PP}$ = 253 Hz, σ^4-P in **7b**) (signal ratio **6b**:**7b** $\approx$ 15:1). By slow crystallisation from CH_2Cl_2/*n*-hexane (ca. 5:1) at r.t., yellow plates were obtained. The X-ray structure analysis of the latter and the $^{31}P\{^1H\}$-NMR spectrum of the mother liquor showed that **6b** was transformed to **7b** during crystallisation. The crystalline material was washed three times with 5 ml portions of *n*-hexane and dried in vacuo. Yield: 0.380 g (0.73 mmol, 17%), m.p. 161 °C. ^1H-NMR (CD_2Cl_2, 200 MHz): δ 1.18 (t, J_{HH} = 7.1 Hz, 12H, σ^4-PNCH$_2$CH_3), 3.40 (m_c ($\approx$ sextet), $J\approx$ 6.8 Hz, 8H, σ^4-PNCH_2CH$_3$), 7.86–8.07 (m_c, 2H, arom. H), 8.23–8.50 (m_c, 4H, arom. H); the spectrum showed further signals at δ 1.40 (t, J_{HH} = 7.3 Hz, integration to 8H, "NCH$_2$CH_3"), 2.98 (m_c, $J\approx$ 6.8 Hz, integration to 6H, "NCH_2CH$_3$") and 9.44 (br m (unresolved), integration to 2H) that cannot be accounted for; ^{13}C-NMR (CD_2Cl_2, 100.6 MHz): δ 11.09 (s, NCH$_2$*C*H$_3$), 42.27 (s, N*C*H$_2$CH$_3$), 124.0–140.0 (arom. C) (additional singlets at δ_C 14.32 ("N*C*H$_2$CH$_3$") and 42.88 ("NCH$_2$*C*H$_3$"), see above); $^{31}P\{^1H\}$-NMR (CD_2Cl_2, 81.0 MHz): δ 29.2 (m_c ($\approx$ d), $^1J_{PP}$ = 254 Hz, σ^3-P), 76.3 (m_c ($\approx$ d), $^1J_{PP}$ = 254 Hz, σ^4-P). IR (KBr, cm^{-1}): 3397 w, 2972 m, 2824 m, 2777 m, 2481 w, 2363 w, 2342 w, 1559 w, 1484 m, 1459 m, 1385 m, 1204 m, 1151 m, 1094 w, 1060 w, 1021 s, 955 w, 920 w, 890 w, 831 m, 793 w, 770 m, 699 s, 667 s, 595 w, 526 w, 486 w, 460 m. Anal. Found: C, 41.93; H, 5.69; N, 5.76. Calc. for $C_{18}H_{26}BCl_5N_2P_2$ (520.44): C, 41.54; H, 5.04; N, 5.38%.

3.6. Crystal structure analyses

Crystal data are summarised in Table 5.

3.6.1. Data collection and reduction

Crystals were mounted on glass fibres in inert oil and transferred to the cold gas stream of the diffractometer (Stoe STADI-4 with LT-2 low temperature attachment for **2a** and **7b**, Siemens P4 with LT-2 low temperature attachment for **4**, Bruker SMART 1000 CCD with

LT-3 low temperature attachment for **5** and **6a**). The cell constants for **2a** and **7b** were refined from 54 or 60 reflections in the θ range 10–11.5°, for **4** from 42 reflections in the θ range 2.5–12.5. The cell constants for **5** and **6a** were refined from 4210 or 7023 reflections in the θ range 2–28° or 2–30° (monochromated Mo–K_α radiation). Absorption corrections for **5** were performed on the basis of multiple scans (SADABS), for **7b** on the basis of psi-scans.

3.6.2. Structure solution and refinement

The structures were solved by direct methods and refined anisotropically on F^2 (program system: SHELXL-93 for **2a**, **4** and **7b**, SHELXL-97 for **5** and **6a**, G.M. Sheldrick, University of Göttingen). H atoms were included using a riding model or rigid methyl groups. Weighting schemes of the form $w^{-1} = [\sigma^2(F_o^2) + (aP)^2 + bP]$, with $P = (F_o^2 + 2F_c^2)/3$.

4. Supplementary material

Crystallographic data for the structural analysis (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 163675 (**2a**), 163676 (**4**), 163677 (**5**), 163678 (**6a**), and 163679 (**7b**). Copies of this information may be obtained free of charge from The Director, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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References

[1] For a review of early work see: V. Balasubramaniyan, Chem. Rev. 66 (1966) 567.
[2] For more recent examples see: (a) M.A.G.M. Tinga, G.J.H. Buisman, G. Schat, O.S. Akkerman, F. Bickelhaupt, W.J.J. Smeets, A.L. Spek, J. Organomet. Chem. 484 (1994) 137;
(b) R. Schröck, K.-H. Dreihäupl, A. Sladek, K. Angermaier, H. Schmidbaur, Chem. Ber. 129 (1996) 495;
(c) G.S. Hair, S.L. Battle, A. Decken, A.H. Cowley, R.A. Jones, Inorg. Chem. 39 (2000) 27;
(d) G.P. Schiemenz, S. Pörksen, C. Näther, Z. Naturforsch. Teil b 55 (2000) 841.
[3] (a) R.D. Jackson, S. James, A.G. Orpen, P.G. Pringle, J. Organomet. Chem. 458 (1993) C3;
(b) S.L. James, A.G. Orpen, P.G. Pringle, J. Organomet. Chem. 525 (1996) 299;
(c) P.G. Jones, H. Thönnessen, A. Karaçar, R. Schmutzler, Acta Crystallogr. Sect. C 53 (1997) 1119;
(d) A. Karaçar, H. Thönnessen, P.G. Jones, R. Bartsch, R. Schmutzler, Chem. Ber./Recueil 130 (1997) 1485;
(e) A. Karaçar, H. Thönnessen, P.G. Jones, R. Bartsch, R. Schmutzler, Heteroatom Chem. 8 (1997) 539;
(f) A. Karaçar, M. Freytag, H. Thönnessen, J. Omelanczuk, P.G. Jones, R. Bartsch, R. Schmutzler, Z. Anorg. Allg. Chem. 626 (2000) 2361;
(g) M.St.J. Foreman, J.D. Woollins, J. Chem. Soc. Dalton Trans. (2000) 1533 and references therein;
(h) A. Karaçar, M. Freytag, H. Thönnessen, J. Omelanczuk, P.G. Jones, R. Bartsch, R. Schmutzler, Heteroatom Chem. 12 (2001) 102;
(i) A. Karaçar, M. Freytag, P.G. Jones, R. Bartsch, R. Schmutzler, Z. Anorg. Allg. Chem. 627 (2001) 1571;
(j) A. Karaçar, V. Klaukien, M. Freytag, H. Thönnessen, J. Omelanczuk, P.G. Jones, R. Bartsch, R. Schmutzler, Z. Anorg. Allg. Chem. 627 (2001) 2589.
[4] F.H. Allen, O. Kennard, Chem. Des. Autom. News 8 (1993) 31.
[5] L. Lamandé, K. Dillon, R. Wolf, Phosphorus Sulfur Silicon 103 (1995) 1.
[6] For an overview see: V. Pintchouk, PhD thesis, Technische Universität Braunschweig, 1996.
[7] A. Karaçar, Diplomarbeit, Technische Universität Braunschweig, 1996.
[8] J.C. Tebby, Handbook of Phosphorus-31 Nuclear Magnetic Resonance Data, CRC Press, Boca Raton, 1991, p. 93.
[9] L. Brandsma, H.D. Verkruijsse, Preparative Polar Organometallic Chemistry, vol. 1, Springer-Verlag, Berlin, Heidelberg, New York, London, Paris, Tokyo, 1987, p. 195.
[10] For a detailed discussion of the lone pair effect see: (a) V.M.S. Gil, W. von Philipsborn, Magn. Reson. Chem. 27 (1989) 409; (b) T. Schaefer, R. Sebastian, R.W. Schurko, F.E. Hruska, Can. J. Chem. 71 (1993) 1384.
[11] L. Maier, Helv. Chim. Acta 46 (1963) 2667.
[12] F.H. Allen, O. Kennard, D.G. Watson, L. Brammer, A.G. Orpen, R. Taylor, J. Chem. Soc. Perkin Trans. 2 (1987) S1.
[13] Y. van den Winkel, J. van der Laarse, F.J.J. de Kanter, T. van der Does, F. Bickelhaupt, W.J.J. Smeets, A.L. Spek, Heteroatom Chem. 2 (1991) 17.
[14] (a) L. Ernst, P.G. Jones, P. Look-Herber, R. Schmutzler, Chem. Ber. 123 (1990) 35;
(b) R. Vogt, PhD thesis, Technische Universität Braunschweig, 1992;
(c) R. Vogt, R. Schmutzler, Chem. Ber. 126 (1993) 1271.
[15] T. Katoh, K. Ogawa, Y. Inagaki, R. Okazaki, Tetrahedron 53 (1997) 3557.
[16] (a) Th.A. van der Knaap, F. Bickelhaupt, Phosphorus Sulfur 21 (1984) 227 and references cited therein;
(b) E.E. Nifantyev, M.K. Gratchev, S.Yu. Burmistrov, M.Yu. Antipin, Yu.T. Struchkov, Phosphorus Sulfur Silicon 70 (1992) 159.
[17] D.D. Perrin, W.L.F. Armarego, Purification of Laboratory Chemicals, 3rd ed., Pergamon Press, Oxford, New York, Beijing, Frankfurt, Sao Paulo, Sydney, Tokyo, Toronto, 1988.
[18] (a) A.B. Burg, P.J. Slota, J. Am. Chem. Soc. 80 (1958) 1107;
(b) O.J. Scherer, W. Glabel, Chem.-Ztg. 99 (1975) 246.