

## Evidences for intramolecular N → P coordination in (8-dimethylamino-1-naphthyl) diphenylphosphane and derivatives

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### Abstract

An extension of coordination by intramolecular N → P donor–acceptor interaction in (8-dimethylamino-1-naphthyl)diphenylphosphane **1** has been shown by X-ray structure determination. In addition, a very easy intramolecular isomerisation process around the phosphorus atom at room temperature was revealed by dynamic NMR studies. Isomerisation also occurs in the corresponding oxide **2**, sulfide **3**, and phosphonium salts **4** and **5**, but with slightly higher activation energies.

**Keywords:** (8-Dimethylamino-1-naphthyl)diphenylphosphane; N–P coordination; NMR; X-ray structure

### 1. Introduction

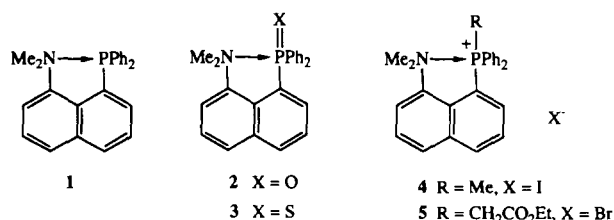
Phosphanes in which an electron-donor atom interacts with the phosphorus atom are interesting compounds, the phosphorus atom being more electron-rich than in normal phosphanes.

Quite a few phosphanes with an amino group well situated to give an intramolecular donor–acceptor N → P interaction are known [1]. They are mainly used as bidentate ligands in transition metal chemistry. The possible existence of intramolecular N → P interactions in these compounds has rarely been considered [2].

There are numerous examples of tin [3] and silicon [4] compounds containing the rigid 8-dimethylaminonaphthyl ligand [5] and it has been shown that this ligand enforces intramolecular coordination around the heteroatom. We were interested by phosphane **1** containing this ligand, and in this paper, we describe the X-ray structure analysis of **1** as well as the results of dynamic NMR studies on **1** and its derivatives **2–5**.

### 2. Results and discussion

At 0°C, <sup>1</sup>H NMR spectrum of **1** displays only one signal at 2.32 ppm (CD<sub>2</sub>Cl<sub>2</sub>–CFC<sub>3</sub>) corresponding to the NMe<sub>2</sub> group. However, on lowering the temperature, this singlet splits into two signals (Table 1). The free energies of activation at 183 K for the equivalence of the methyl groups were calculated from the Eyring equation [6] to be 37.5 kJ mol<sup>-1</sup>. Since the geometry of the ligand imposes an N → P interaction, the NMR data suggest that phosphane **1** is non-symmetrical and undergoes a permutational isomerisation at room temperature. To check this point, an X-ray crystal structure analysis of **1** was performed and its ORTEP drawing is shown in



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Table 1

$^1\text{H}$  NMR (250 MHz) data ( $\text{NMe}_2$  groups) for compounds 1–5 ( $\text{CD}_2\text{Cl}_2$ – $\text{CFCl}_3$ ,  $\delta$  ppm). Free energies of activation ( $\Delta G^\ddagger$ ,  $\text{kJ mol}^{-1}$ ) at the coalescence temperature  $T_c$  for the equivalence of the  $\text{NMe}_2$  groups

Compound	$T$ (K)	$\delta\text{NMe}_2$	$T_c$ (K)	$\Delta G^\ddagger$
1	273	2.32	183	37.5
	163	1.87–2.50		
2	293	2.15	253	53.0
	253	1.60–2.47		
3	273	2.05	243	48.1
	203	1.42–2.50		
4	293	2.05	243	48.1
	238	1.25–2.58		
5	293	1.89	273	55.2
	233	1.32–2.61		

Fig. 1. Phosphane **1** exhibits two different, but very similar, conformations in the solid state. Selected bond distances and bond angles are given in Table 2 and other crystallographic details are given in Tables 3 and 4.

The crystallographic data show that the phosphorus environment in **1** is non-symmetric. The lone pair of the nitrogen atom is directed toward the phosphorus atom trans to the P–C(11) bond of one of the phenyl groups. The pyramidal configuration around the phosphorus atom is retained but slightly flattened (average value of the C–P–C angles,  $100.7^\circ$ ) in comparison with triphenylphosphane [7] (average value of the C–P–C angles,  $103.4^\circ$ ). The N–P distance was found to be 2.71 Å, which is shorter than the sum of the nitrogen and phosphorus van der Waals radii (3.4 Å) [8]. It is worth noting that the N–N distance (2.79 Å) in 1,8-bis dimethylaminonaphthalene **6** [9] and the P–P distance (3.05 Å) in 1,8 bis-diphenylphosponaphthalene **7** [10] are longer than the N–P distance in **1** in spite of the larger ionic radius of phosphorus compared with nitrogen. This may be ascribed to the lone pair repulsion in **6** and **7**. Moreover, the naphthalene rings are undistorted in **1**, whereas in **6** they are twisted out of the plane by  $8^\circ$ . Another measure of the deformation of the naphthalene rings is the value of the dihedral angle N–C(8)–P...C(1) which is no more than  $2^\circ$  in **1**. It should be noted that the value of this angle is much larger in

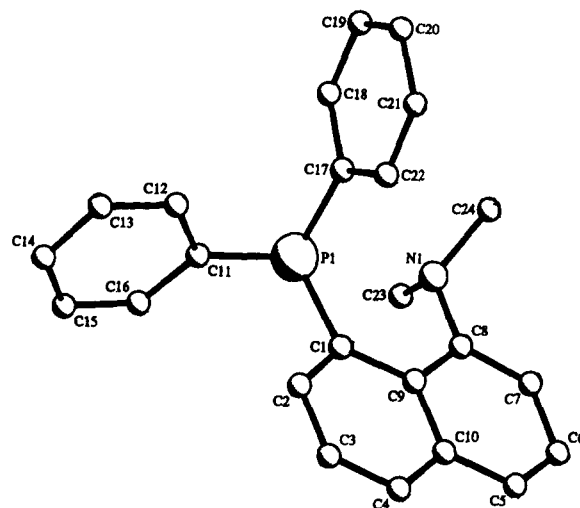


Fig. 1. PLUTO drawing of the molecular structure of **1** showing the atomic numbering scheme. Hydrogen atoms are omitted for clarity.

phosphonate **8** ( $15.8^\circ$ ) [11], silatrane **9** ( $27^\circ$ ) [12] or silane **10** ( $34.3^\circ$ ) [13], thus illustrating the important deformations of the naphthalene rings in these derivatives. This is probably the result of steric hindrance around the phosphorus or silicon atoms in **8**–**10**. That means that an intramolecular donor–acceptor interaction exists in **1** and the molecule of **1** can be described as a monocapped tetrahedron in which the phosphorus atom is pseudo [4 + 1] coordinated (taking into account the lone pair).

Phosphane oxide **2**, phosphane sulphide **3**, as well as phosphonium salts **4** and **5** exhibit the same NMR behaviour as phosphane **1**. One signal is observed at room temperature which splits into two signals on lowering the temperature (Table 1). These compounds also undergo a permutational isomerisation process at room temperature. The  $\Delta G^\ddagger$  for these isomerisations was calculated to be  $53 \text{ kJ mol}^{-1}$  (at 253 K) for **2**,  $48.1 \text{ kJ mol}^{-1}$  (at 243 K) for **3** and **4**, and  $55.2 \text{ kJ mol}^{-1}$  (at 273 K) for **5**.

The chemical shifts of the methyl protons  $\alpha$  to the phosphorus atom of **4** (3.0 ppm) [2] and of the methylene protons  $\alpha$  to the phosphorus atom of **5** (4.95 ppm), are shifted upfield in comparison with the chemical shifts of methyltriphenylphosphonium iodide (3.12 ppm)

Table 2

Selected interatomic distances (Å) and bond angles (deg) for phosphane **1**

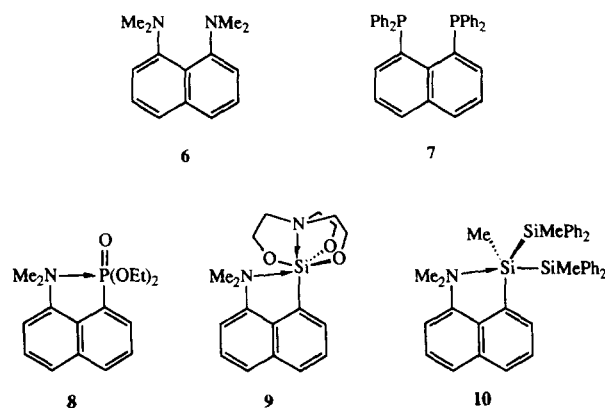
	Molecule A	Molecule B		Molecule A	Molecule B
C(1)–P	1.873(06)	1.855(07)	C(11)–P–C(1)	100.1(03)	101.8(03)
C(11)–P	1.844(06)	1.841(06)	C(17)–P–C(1)	103.0(03)	103.9(03)
C(17)–P	1.840(05)	1.844(05)	C(17)–P–C(11)	99.1(03)	98.9(03)
N...P	2.706(06)	2.729(06)	C(1)–P...N	76.5(03)	76.3(04)
C(8)–N	1.409(09)	1.423(09)	C(11)–P...N	173.9(04)	178.1(04)
			C(17)–P...N	86.6(04)	81.6(04)
			C(8)–P...N	99.1(05)	98.9(06)

Table 3  
Summary of crystallographic data

Molecular formula	C <sub>24</sub> H <sub>22</sub> NP
Molecular weight	355.4
Crystal size (mm)	0.33 × 0.35 × 0.40
Crystal system	Orthorhombic
Space group	<i>Pn</i> 2 <sub>1</sub> <i>a</i>
<i>a</i> (Å)	13.727(3)
<i>b</i> (Å)	16.060(4)
<i>c</i> (Å)	17.601(9)
<i>V</i> (Å <sup>3</sup> )	3880(2)
<i>Z</i>	8 (two independent mol. in asymmetric unit)
<i>D</i> <sub>calc</sub> (g cm <sup>-3</sup> )	1.22
<i>F</i> (000)	1504
Radiation	Mo K α (λ = 0.71069 Å)
μ (cm <sup>-1</sup> )	1.6
No. of unique data ( <i>h</i> = 0/16; <i>k</i> = 0/19; <i>l</i> = 0/21)	3953
No. of used data (with <i>I</i> ≥ 2.5σ( <i>I</i> ))	2286
<i>R</i>	0.048
<i>R</i> <sub>w</sub> ( <i>w</i> = 1/σ <sup>2</sup> ( <i>F</i> ) + 0.0101 <i>F</i> <sup>2</sup> )	0.056
<i>S</i> (goodness of fit)	0.64
Final Δ <i>p</i> (e Å <sup>-3</sup> )	-0.21/+0.31

[14] and of methoxycarbonylmethyltriphenylphosphonium chloride (5.7 ppm) [14]. This reconfirms the existence of N–P intramolecular interactions in these compounds.

In conclusion, we have shown that an intramolecular



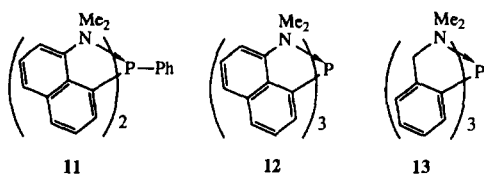
donor–acceptor interaction exists in phosphane **1**, which does not lead to a deformation of the naphthyl group. Intramolecular donor–acceptor interactions are also found in phosphanes **11** [15], **12** [16], and **13** [16], indicating that in these compounds the phosphorus atom is able to undergo an extension of coordination. This is probably due to the weak steric hindrance of the free doublet.

### 3. Experimental section

<sup>1</sup>H and <sup>31</sup>P NMR spectra were obtained using a Bruker spectrometer 250 AC. <sup>1</sup>H chemical shifts are

Table 4  
Fractional atomic coordinates (× 10000) and equivalent isotropic thermal parameters (Å<sup>2</sup>)

	Molecule A				Molecule B			
	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> <sub>eq</sub>	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> <sub>eq</sub>
P	2235(01)	8589(00)	8487(01)	2.8	4893(01)	13638(01)	6532(01)	2.9
N	1018(04)	7263(04)	8494(03)	3.6	6122(04)	12305(04)	6619(03)	3.8
C(1)	3061(04)	7691(04)	8701(03)	2.7	4105(04)	12739(04)	6289(03)	2.8
C(2)	4047(04)	7842(04)	8816(04)	3.3	3143(05)	12881(04)	6084(03)	3.5
C(3)	4679(05)	7203(05)	9022(04)	4.2	2527(05)	12229(05)	5846(04)	4.1
C(4)	4373(05)	6405(05)	9102(04)	4.2	2840(05)	11438(04)	5817(04)	3.7
C(5)	3024(06)	5386(05)	9073(04)	4.4	4144(06)	10418(05)	5981(04)	4.3
C(6)	2068(06)	5186(05)	8988(04)	4.9	5076(06)	10207(05)	6159(04)	4.4
C(7)	1401(06)	5813(04)	8794(04)	4.0	5735(05)	10884(05)	6372(03)	4.0
C(8)	1693(05)	6635(04)	8683(03)	3.4	5454(05)	11664(04)	6420(03)	3.2
C(9)	2704(04)	6860(04)	8785(03)	2.8	4464(05)	11898(04)	6247(03)	2.8
C(10)	3370(05)	6202(04)	8980(03)	3.6	3822(05)	11246(04)	6010(03)	3.1
C(11)	3099(05)	9461(04)	8587(03)	2.9	4031(05)	14513(04)	6465(03)	2.9
C(12)	3589(05)	9876(04)	7992(04)	4.3	3471(05)	14837(04)	7056(04)	4.1
C(13)	4182(05)	10552(05)	8138(04)	4.7	2885(06)	15539(05)	6956(04)	4.7
C(14)	4303(06)	10832(05)	8874(05)	4.7	2828(06)	15919(05)	6252(05)	5.0
C(15)	3805(06)	10446(05)	9464(04)	4.3	3371(06)	15605(04)	5647(04)	4.7
C(16)	3217(05)	9789(04)	9309(04)	3.8	3987(06)	14922(05)	5760(04)	4.4
C(17)	2139(04)	8561(04)	7445(03)	2.8	5004(04)	13582(04)	7575(03)	3.0
C(18)	1446(05)	9085(05)	7123(04)	4.1	5692(05)	14117(04)	7907(03)	3.8
C(19)	1341(06)	9143(05)	6322(04)	4.8	5789(06)	14160(05)	8694(04)	4.5
C(20)	1952(05)	8697(05)	5862(03)	4.1	5226(05)	13675(05)	9158(03)	4.3
C(21)	2631(06)	8162(05)	6187(04)	4.4	4545(05)	13137(04)	8851(04)	3.7
C(22)	2732(04)	8093(05)	6967(04)	3.6	4439(05)	13091(04)	8051(03)	3.5
C(23)	424(05)	7510(05)	9141(04)	5.1	6758(06)	12531(05)	5977(05)	5.6
C(24)	439(06)	7081(06)	7825(04)	5.9	6680(06)	12130(06)	7314(05)	6.2



reported relative to  $\text{Me}_4\text{Si}$ , and  $^{31}\text{P}$  chemical shifts relative to  $\text{H}_3\text{PO}_4$ . Mass spectra were recorded on a Jeol D 100 instrument. Elemental analyses were carried out by the Service Central de Microanalyse du CNRS.

Compounds **1**, **3** and **4** were prepared by the methods previously described. **1**, m.p. 169.5–171°C (Ref. [1d], m.p. 162°C, (Ref. [2], m.p. 163–164°C); **3**, m.p. 194–195.5°C (Ref. [2], m.p. 183–184°C); **4**, m.p. 135–137°C (Ref. [2], m.p. 134–136°C).

### 3.1. X-ray structure determination of **1**

A crystal was mounted on an Huber diffractometer. X-ray diffraction measurements were performed at room temperature with graphite monochromated  $\text{Mo K}\alpha$  radiation. Lattice parameters were refined using 22 reflections in the range  $13 < \theta < 30^\circ$ . No absorption correction was applied to the data. No significant deviation indicated for standard reflection (5,0,3) checked every 50 reflections. The structure was solved by direct-methods of MULTAN-80 [17] and refinements were performed using least squares methods of SHELX-76 [18]. We observe two independent molecules in an asymmetric unit. All hydrogen atoms were located in theoretical position (1.08 Å from carbon). Fractional atomic coordinates are listed in Table 3 and relevant bond lengths and angles in Table 2. The molecular structure is illustrated in Fig. 1 [19].

### 3.2. (8-dimethylamino-1-naphthyl)diphenylphosphane oxide **2**

0.4 ml (4 mmol) of aqueous  $\text{H}_2\text{O}_2$  was added, at room temperature, under stirring, to a solution of **1** (870 mg, 2.45 mmol) in  $\text{CH}_2\text{Cl}_2$  (20 ml). After 30 min, 50 ml of ether was added and the reaction mixture was washed (water and brine) and dried ( $\text{MgSO}_4$ ). After removal of the solvents, the crude product was recrystallized twice in a 50/50 heptane–toluene mixture to give 460 mg (1.24 mmol, 51%), m.p. 131.6–133.5°C;  $^1\text{H}$  NMR (250 MHz,  $\text{CDCl}_3$ ),  $\delta = 2.10$  (s, 6H), 7.10–8.00 (m, 16H);  $^{31}\text{P}$  NMR (101 MHz,  $\text{CDCl}_3$ ),  $\delta = 28.4$  (s); MS (FAB +, *m*-nitrobenzylalcohol),  $m/z = 372$  ( $\text{M} + 1$ )<sup>+</sup>. Anal. Calc.: C, 77.60; H, 5.92; N, 3.77.  $\text{C}_{24}\text{H}_{22}\text{NOP}$ . Found: C, 77.67; H, 6.12; N, 3.70%.

### 3.3. Ethoxycarbonylmethyl(8-dimethylamino-1-naphthyl)diphenylphosphonium bromide **5**

**1** (4 g, 11.3 mmol) and ethylbromoacetate (2 ml, 18 mmol), in solution in toluene, were heated at 65°C for 40 h. The precipitate obtained was filtered, first washed with toluene then with hexane, dried and recrystallized in a 50/50  $\text{Et}_2\text{O}-\text{CH}_2\text{Cl}_2$  mixture to give 2.7 g of **5**, m.p. 145°C (decomp). Another 1.1 g of **5**, m.p. 145°C (decomp) was recrystallized from the mother liquor giving 3.8 g (64%) of **5**;  $^1\text{H}$  NMR (250 MHz,  $\text{CDCl}_3$ ),  $\delta = 0.95$  (t, 3H), 1.94 (broad signal, 6H), 3.84 (q, 2H), 4.95 (d, 2H,  $^2J_{\text{PH}} = 13$  Hz), 7.4–8.3 (m, 16H);  $^{31}\text{P}$  NMR (101 MHz,  $\text{CDCl}_3$ ),  $\delta = 22.6$  (s); MS (FAB +, *m*-nitrobenzylalcohol),  $m/z = 442$  [ $(\text{M}-\text{Br})^+$  62%], 370 (98%), 93 (100%). Anal. Calc. C, 64.36; H, 5.55; N, 2.68; Br, 15.32.  $\text{C}_{28}\text{H}_{29}\text{NO}_2\text{PBr}$ . Found: C, 64.52; H, 6.01; N, 3.03; Br, 15.89%.

## 4. Supplementary materials available

Tables of fractional atomic coordinates of all atoms, thermal parameters, complete sets of bond distances and bond angles of **1** are available from the authors.

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