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Intramolecular coordination at phosphorus: donor–acceptor interaction in three- and four-coordinated phosphorus compounds ☆

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Abstract

The phosphorus derivatives $P(X)(O_2C_6H_4\text{-}1,2)_2[C_6H_4(CH_2NMe_2)_2\text{-}2]$ (**9–11**) undergo ready extension of coordination by N → P intramolecular donor–acceptor interaction as shown by ^{31}P NMR and dynamic ^1H NMR spectroscopy. This extension of coordination does not occur with $P(X)(OEt)_2[C_6H_4(CH_2NMe_2)_2\text{-}2]$ (**7** and **8**). The $\Delta G^{\neq}$ of pseudo-rotation was calculated by dynamic ^1H NMR spectroscopy to be 57–58 kJ mol^{-1} for the three compounds $P(X)(O_2C_6H_4\text{-}1,2)_2[C_{10}H_6(NMe_2\text{-}8)]$ (**19–21**).

Keywords: Phosphorus; Hypercoordination; Pseudorotation; Crystal structure

1. Introduction

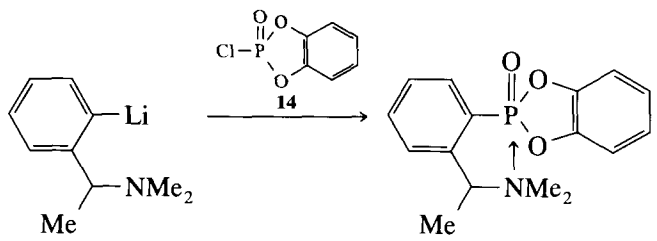
Analogies exist in the chemistries of silicon and phosphorus [1]. Thus the racemization, hydrolysis and alcoholysis of tetracoordinate chlorosilanes [2] on the one hand, and of chlorophosphates and chlorophosphonates [3] and the other, are accelerated by nucleophilic catalysts and involve penta- and hexacoordinate intermediates [4].

In silicon chemistry, many hypercoordinate derivatives have been obtained by intramolecular donor–acceptor interaction [5]. In phosphorus chemistry, with the exception of phosphoranes (e.g., compounds **1** [6], **2** [7], **3** [8], **4** [9] and **5** [10]), only very few examples of intramolecular chelation have been described [10].

In this paper, we describe the intramolecular donor–acceptor N–P interaction on three-and four-coordinated derivatives bearing alkoxy or aryloxy groups. The ligands **A**, **B** and **C** used are those reported by Jastrzebski and Van Koten for tin [11] and by us for silicon [5] derivatives.

2. Results and discussion

The compounds studied were prepared following the synthetic routes shown in Schemes 1 and 2 and in Eq. (1). All these derivatives are air and moisture sensitive.



13 **15** (1)

^{31}P NMR data for compounds **7–11** are collected in Table 1 and are compared with those for reference compounds. The low-temperature (−90°C) spectra show no significant changes in chemical shift and for this reason the data are not given in the table.

^1H NMR data for the NMe_2 groups at 293 and 183 K are collected in Table 2. Free energies of activation for the equivalence of the methyl groups calculated from the Eyring equation [17] are deduced from these data.

☆ Dedicated to Professor Hideki Sakurai in recognition of his outstanding contribution to silicon chemistry.

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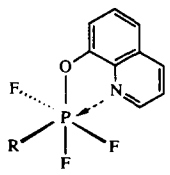

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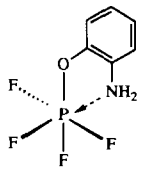

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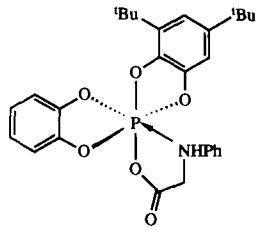

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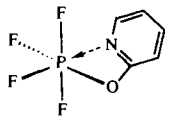

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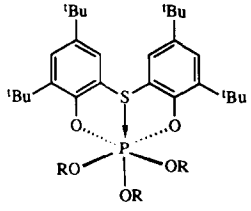

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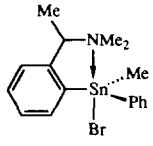

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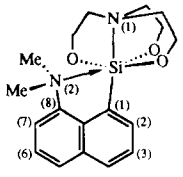

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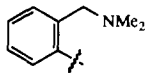
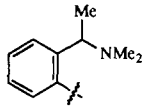


A



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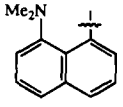

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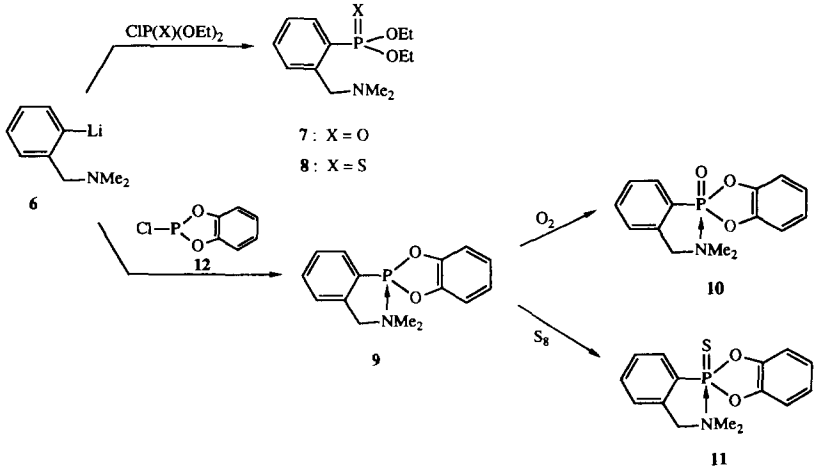


7 : X = O

8 : X = S

6

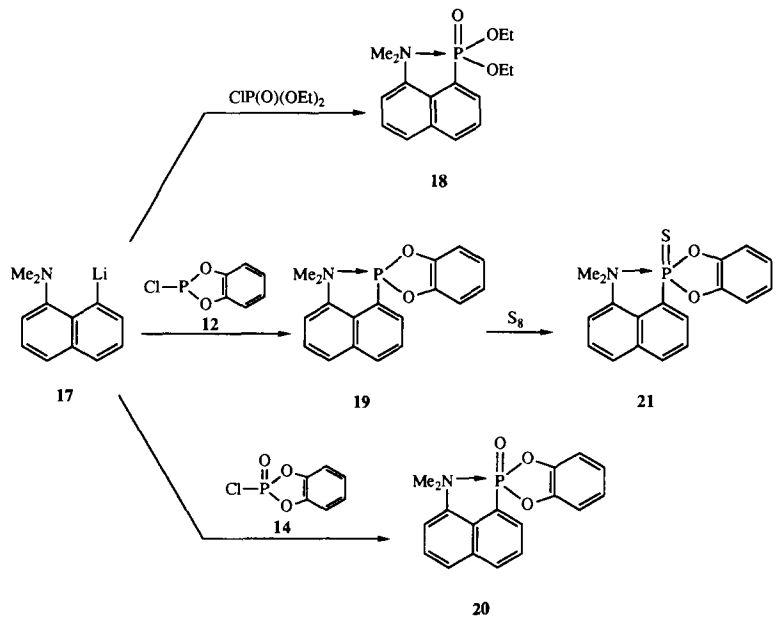
12

9

10

11

Scheme 1.



Scheme 2.

Table 1
^{31}PNMR chemical shifts (at 293 K) of compounds **7–11** versus corresponding derivatives without NMe_2 groups

Compound	δ (^{31}P) (ppm)	Compound	δ (^{31}P) (ppm)	$\Delta\delta$ (ppm)
AP(O)(OEt)$_2$ (**7**)	+19.6	PhP(O)(OEt)$_2$	+16.9 [a]	−2.7
AP(S)(OEt)$_2$ (**8**)	+86.3	PhP(S)(OEt)$_2$	+86.7 [b]	+0.4
AP(o-$O_2C_6H_4$) (**9**)	+130.7	PhP(o-$O_2C_6H_4$)	+177.0 [c]	−46.0
AP(O)(o-$O_2C_6H_4$) (**10**)	+13.3	PhP(O)(o-$O_2C_6H_4$)	+35.7 [d]	−22.4
AP(S)(o-$O_2C_6H_4$) (**11**)	+72.9	PhP(S)(o-$O_2C_6H_4$)	+107.1 [e]	−34.2

[a] Ref. [12]; [b] Ref. [13]; [c] Ref. [14]; [d] Ref. [15]; [e] Ref. [16].

Table 2
^{1}H NMR (250 MHz) data (NMe_2 groups) for compounds **7–11**, **15** and **18–21** (CD_2Cl_2) and free energies of activation ($\Delta G^{\ddagger}$) at the coalescence temperature (T_c) for the equivalence of the NMe_2 groups

Compound	T (K)	δ (NMe_2) (ppm)	T_c (K)	$\Delta G^{\ddagger}$ (kJ mol^{-1})
7	293	2.22 (s)		
	183	2.20 (s)		
8	293	2.31 (s)		
	183	2.20 (s)		
9	293	2.47 (s)	233	48
	183	2.12 (s)–2.69 (s)		
10	293	2.75 (d, $^3J_{PH}$ = 4 Hz)	218	46
	183	2.54 (s)–2.98 (s)		
11	293	2.68 (d, $^3J_{PH}$ = 4.8 Hz)–2.78 (d, $^3J_{PH}$ = 4.8 Hz)		
15 [a] (minor isomer)	293	2.28 (s)	223	47
	183	2.19 (s)–2.28 (s)		
15 [a] (major isomer)	293	2.13 (s)	158	32
	158	2.07 (coalescence)		
18	293	2.68 (s)		
	183	2.68 (s)		
19	293	2.85 (s)	273	57
	183	2.50 (s)–3.00 (s)		
20	293	2.80 (s)	255	57
	183	2.65 (s)–2.75 (s)		
21	293	2.70 (s)	273	58
	183	2.60 (s)–2.90 (s)		

[a] Spectra recorded on a 360 MHz apparatus.

2.1. ^{31}P NMR spectra of 7–11

Ligand **A** [18], which is a potentially chelating ligand, allows N–P donor–acceptor interactions to be studied as a function of the substituents at phosphorus.

The ^{31}P chemical shifts of phosphonate **5** and thiophosphonate **8** are nearly identical with those of diethyl phenylphosphonate and diethyl phenylthiophosphonate, indicating that, in solution, coordination apparently fails to take place. Coordination occurs in solution for **9**, **10** and **11**, which exhibit significant upfield shifts of the ^{31}P resonance.

2.2. Dynamic ^{1}H NMR spectra of 7–11

Non-coordination in **7** and **8** is confirmed by ^{1}H NMR spectroscopy: the two methyls of the NMe_2 groups appear as a singlet at 293 K and also at 183 K. The N–P interaction in **11** is detected by the ^{1}H NMR spectra in which the methyls of the NMe_2 group appear as two doublets resulting from P–H coupling ($^{3}J(P,H) = 4.8$ Hz). Thus the phosphorus atom in **11** is pentacoordinated without intramolecular isomerisation at room temperature.

The ^{1}H NMR spectra of **9** and **10** at 183 K show two singlets for each compound. As the temperature is raised, coalescence of these signals occurs, a singlet being observed for **9** and a doublet for **10** ($^{3}J(P,H) = 4$ Hz). Thus, the phosphorus atom of **9** and **10** is also pentacoordinated in solution, as suggested by ^{31}P NMR. The equivalence of the methyl groups occurs with a $\Delta G^{\neq}$ value of 48 kJ mol^{-1} (at 233 K) for **9** and 46 kJ mol^{-1} (at 218 K) for **10**. This equivalence can be explained by pseudo-rotation around the phosphorus atom or by cleavage of the N–P bond followed by rotation around the CH_2–N bond and pyramidal nitrogen inversion before recoordination. In order to clarify this point, we prepared **15** in which ligand **B** [19] has an asymmetric benzylic carbon. The ^{1}H NMR spectrum of **15** shows two NMR patterns which indicate that in solution at room temperature **15** exists as two diastereoisomers in an 80:20 ratio. This confirms the intramolecular N–P interaction in this derivative. The major diastereoisomer crystallizes from a saturated CH_2Cl_2–pentane solution and slowly epimerizes (3 h at room temperature) in a CH_2Cl_2 solution to give the 80:20 equilibrium mixture. The ^{1}H NMR (360 MHz) spectrum of **15** shows two sharp singlets for the NMe_2 groups at room temperature. On lowering the temperature, the singlet of the minor diastereoisomer splits into two signals (coalescence at 223 K) with $\Delta G^{\neq} = 47$ kJ mol^{-1} whereas the singlet of the major diastereoisomer gives only a broad signal at 158 K with $\Delta G^{\neq}$ estimated to be 32 kJ mol^{-1}. The equivalence of the methyl groups observed above 223 K for the minor diastereoisomer and above 158 K for the major diastereoisomer is explained by a coordination–decoordination process. During this process, equilibration of the two diastereoisomers occurs via slow rotation around the C–P bond. Similar results have been observed and the same explanation was proposed by Jastrzebski et al. [20] for the tin derivative **16**.

2.3. NMR spectra of 18–21

Ligand **C** [21] has a rigid structure which enforces intramolecular coordination to the phosphorus atom. As a result, dynamic ^{1}H NMR spectroscopy of **18–21** allows the study of permutational isomerization in these derivatives, as pointed out in the case of silicon derivatives [22].

The ^{1}H NMR spectra of **18–21** show only one singlet for the methyls of the NMe_2 groups at room temperature. On lowering the temperature, the singlets of **19–21** split into two signals whereas that of **18** remains unchanged.

From the coalescence temperature of the methyl groups (273 K for **19** and **21** and 255 K for **20**), we found the same $\Delta G^{\neq}$ value (57–58 kJ mol^{-1}) for pseudo-rotation around the phosphorus atom for all three derivatives.

The persistence of a singlet at low temperature for **18** can be explained either by a symmetrical arrangement in the molecule or by a facile permutational isomerization around the phosphorus atom. To decide between these two possibilities, the molecular structure of **18** was determined by X-ray crystal structure analysis (see Fig. 1). The striking point with this structure is the dissymmetry of the molecule. The basic pyramidal geometry of the phosphorus atom is only slightly deformed, as indicated by the values of the angles around

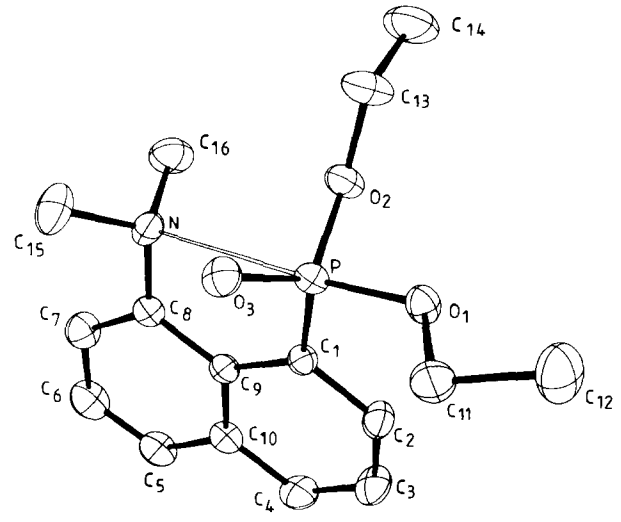


Fig. 1. ORTEP drawing of the molecule of compound **18** with the numbering of the atoms. Thermal ellipsoids are at the 30% probability level.

the phosphorus atom (see Table 5). The lone pair of the nitrogen atom is directed towards the phosphorus atom trans to the P–O(1) bond through the C(1)–O(2)–O(3) face of the tetrahedron with an N–P distance of 2.87 Å. This value is smaller than the sum of van der Waals radii of phosphorus and nitrogen atoms (3.4 Å) [23]. Hence the molecule can be described as a monocapped tetrahedron in which the phosphorus atom is [4 + 1] coordinated. This N–P interaction causes a distortion of naphthalene ring. For instance, the C(2)–C(3) and C(6)–C(7) bonds make a dihedral angle of 4.2°, the dihedral angle of the N–C(8) and P–C(1) bonds being 15.8°. Such a forced intramolecular coordination was observed in the silatrane **22** [24], in which the deformation of the naphthalene ring was more important with dihedral angles of 9.6° for the C(2)–C(3) and C(6)–C(7) bonds and 27° for the N(2)–C(8) and C(1)–Si bonds.

Thus, since **18** is not symmetrical, the non-diastereotopy of the coordinated NMe_2 group is probably due to a very fast permutational isomerization occurring around the phosphorus atom.

3. Conclusion

We have shown that analogies exist between phosphorus and silicon concerning extension of coordination on these atoms induced by intramolecular *N*-chelation. In both cases EtO-substituted derivatives do not easily form hypercoordinated derivatives whereas facile intramolecular *N*-chelation occurs with benzene-1,2 diolato-substituted derivatives. The $\Delta G^{\neq}$ values for pseudo-rotation were determined by using the rigid 8-(dimethylamino)-1-naphthyl ligand. The benzene-1,2 diolato-substituted phosphorus derivatives have values comparable to those of silicon derivatives [22]. Moreover, the very low value for EtO-substituted phosphorus compounds is also comparable with that for the triethoxysilicon derivatives [22].

4. Experimental section

All operations were performed under nitrogen on a vacuum line in Schlenk tubes. ^1H and ^{31}P NMR spectra were obtained using Bruker 200-SY, 250 AC and WM 360 WB spectrometers. ^1H chemical shifts are reported relative to Me_4Si and ^{31}P chemical shifts relative to H_3PO_4. Mass spectra were recorded on a Jeol D 100 instrument. Elemental analyses were carried out by the Service Central de Microanalyse du CNRS.

4.1. Diethyl [(2-dimethylaminomethyl)phenyl]phosphonate (7)

A suspension of 2-dimethylaminophenyllithium (**6**) (6.5 g, 46.1 mmol) in diethyl ether (150 ml) was added at −30°C to a solution of diethylchlorophosphate (7.7 ml, 53.3 mmol) in diethyl ether (30 ml). The reaction mixture was kept for 4 h at this temperature and stirred overnight at room temperature. Water was added and the product was extracted with diethyl ether. Distillation gave 8.1 g (29.9 mmol, 65%) of **7** b.p. 105–110°C/0.1 mmHg. ^1H NMR (250 MHz, $CDCl_3$), $\delta = 1.26$ (t, 6H), 2.21 (s, 6H), 3.68 (s, 2H), 4.05 (q, 4H), 7.1–7.9 (m, 4H); ^{31}P NMR (101 MHz, $CDCl_3$), $\delta = 19.6$ (s); MS (EI), $m/z = 271$ (M^+, 21%), 255 (64%), 227 (100%); Anal. Calc. for $C_{13}H_{22}NO_3P$: C, 57.56; H, 8.17; N, 5.16. Found: C, 57.42; H, 7.83; N, 5.20%.

4.2. Diethyl [(2-dimethylaminomethyl)phenyl]thiophosphonate (8)

A suspension of 2-dimethylaminophenyllithium (**6**) (4.53 g, 32.1 mmol) in diethyl ether (150 ml) was added at −30°C to a solution of diethylchlorothiophosphate (5.1 ml, 32.4 mmol) in diethyl ether (30 ml). The reaction mixture was kept overnight at room temperature. After filtration of the LiCl, about two thirds of the diethyl ether was evaporated and hexanes (30 ml) were added to precipitate more LiCl. After filtration, evaporation of the solvent and distillation, 7.3 g (25 mmol, 78%) of **8** was obtained, b.p. 100–106°C/0.01 mmHg. ^1H NMR (250 MHz, CD_2Cl_2), $\delta = 1.33$ (t, 6H), 2.29 (s, 6H), 3.85 (s, 2H), 4.18 (dq, 4H, $^3J_{PH} = 10$ Hz), 7.3–8.1 (m, 4H); ^{31}P NMR (101 MHz, CD_2Cl_2), $\delta =$ 86.3 (s); MS (EI), $m/z = 287$ (M^+, 10%), 272 (17%), 244 (53%), 134 (100%); Anal. Calc. for $C_{13}H_{22}NO_2PS$: C, 54.34; H, 7.72; N, 4.87; S, 11.16. Found: C, 54.28; H, 7.56; N, 4.72; S, 10.87%.

4.3. (Benzene-1,2-diolato)[(2-dimethylaminomethyl)phenyl]phosphonite (9)

A suspension of **6** (6.5 g, 46.1 mmol) in diethyl ether (200 ml) was added at −35°C to a solution of **12** (8.4 g, 48.1 mmol) in diethyl ether (30 ml). The reaction mixture was kept overnight at room temperature. After filtration of the LiCl, about two thirds of the diethyl ether was evaporated and hexanes (30 ml) were added to precipitate more LiCl. After filtration and evaporation of the solvent, the yellow powder obtained was recrystallized from CH_2Cl_2–hexanes (1 : 1) to give 9.5 g (35 mmol, 76%) of **9**, m.p. 58–60°C. ^1H NMR (250 MHz, CD_2Cl_2), $\delta = 2.47$ (s, 6H), 3.90 (d, 2H, $^4J_{PH} =$ 1.5 Hz), 6.6–7.8 (m, 8H); ^{31}P NMR (81 MHz, CD_2Cl_2), $\delta = 130.7$ (s); MS (EI), $m/z = 273$ (M^+, 100%), 258 (78%); Anal. Calc. for $C_{15}H_{16}NO_2P$: C, 65.93; H, 5.90; N, 5.13. Found: C, 65.67; H, 5.31; N, 5.41%.

4.4. (Benzene-1,2-diolato)[(2-dimethylaminomethyl)phenyl]phosphonate (10)

A stream of dioxygen (dried over $CaCl_2$ and P_2O_5) was bubbled through a solution of **9** (7.0 g, 25.6 mmol)

in toluene (20 ml). After 20 min the product precipitated. Toluene was removed under vacuum and the residue obtained was recrystallized from CH_2Cl_2–hexanes (2:1) to give 3.4 g (11.8 mmol, 46%) of **10**, m.p. 95–96°C. ^{1}H NMR (250 MHz, CD_2Cl_2), $\delta = 2.75$ (d, 6H, $^3J_{PH} = 4.0$ Hz), 4.31 (d, 2H, $^3J_{PH} = 4.5$ Hz), 6.5–8.0 (m, 8H); ^{31}P NMR (81 MHz, CD_2Cl_2), $\delta = 13.3$ (s); MS (EI), $m/z = 289$ (M^+, 12%), 274 (74%); 132 (100%); Anal. Calc. for $C_{15}H_{16}NO_3P$; C, 62.28; H, 5.58; N, 4.84. Found: C, 62.76; H, 5.41; N, 5.13%.

4.5. (Benzene-1,2-diolato)[(2-dimethylaminomethyl)-phenyl]thiophosphonate (11)

Compound **9** (4.0 g, 14.6 mmol) and sulphur (0.5 g, 15.6 mmol) were heated at 60°C in toluene (10 ml). When the sulphur had dissolved, the toluene was removed under vacuum and the residue obtained was recrystallized from toluene to give 3.8 g (12.5 mmol, 86%) of **11**, m.p. 71–72.5°C. ^{1}H NMR (250 MHz, CD_2Cl_2), $\delta = 2.68$ (d, 3H, $^3J_{PH} = 4.8$ Hz), 2.78 (d, 3H, $^3J_{PH} = 4.8$ Hz), 4.33 (d, 1H, $^2J_{HH} = 12.8$ Hz, $^3J_{PH} = 6.0$ Hz), 4.54 (d, 1H, $^2J_{HH} = 12.8$ Hz, $^3J_{PH} = 4.75$ Hz), 6.6–7.7 (m, 8H); ^{31}P NMR (81 MHz, CD_2Cl_2), $\delta = 72.9$ (s) (impurity at 57.2 ppm); MS (EI), $m/z = 305$ (M^+, 13%), 272 (63%); 247 (100%); Anal. Calc. for $C_{15}H_{16}NO_2PS$: C, 59.01; H, 5.28; N, 4.59; S, 10.50. Found: C, 58.60; H, 5.26; N, 4.30; S, 9.87%.

4.6. (Benzene-1,2-diolato)[2-(dimethylamino-1-ethyl)-phenyl]phosphonate (15)

A suspension of **13** (2.0 g, 12.9 mmol) in diethyl ether (150 ml) was added at −35°C to a solution of **14** (2.3 g, 12 mmol) in diethyl ether (20 ml). The reaction mixture was kept overnight at room temperature. After filtration of the LiCl formed, the solvent was evaporated. Crude **15** was recrystallized from CH_2Cl_2–hexanes (1:1) to give 3.0 g (9.9 mmol, 82%) of an 80:20 mixture of diastereoisomers, m.p. 100–102°C. ^{1}H NMR (250 MHz, CD_2Cl_2, minor diastereoisomer), $\delta = 1.36$ (d, 3H), 2.29 (s, 6H), 3.43 (q, 2H), 6.7–7.4 (m, 8H); ^{1}H NMR (250 MHz, CD_2Cl_2, major diastereoisomer), $\delta = 1.31$ (d, 3H), 2.14 (s, 6H), 3.20 (q, 2H), 6.7–7.4 (m, 8H); ^{31}P NMR (81 MHz, CD_2Cl_2), $\delta = 8.8$ (s) (minor diastereoisomer); $\delta = 9.1$ (s) (major diastereoisomer); Anal. Calc. for $C_{16}H_{18}NO_3P$: C, 63.36; H, 5.98; N, 4.62. Found: C, 62.76; H, 5.60; N, 5.03%.

4.7. Diethyl (8-dimethylamino-1-naphthyl)phosphonate (18)

A suspension of 8-dimethylamino-1-naphthyllithium (**17**) (9.0 g, 50.8 mmol) in diethyl ether (180 ml) was added at −30°C to a solution of diethyl chlorophosphate (7.7 ml, 53.3 mmol) in diethyl ether (30 ml). The reaction mixture was stirred overnight at room temperature. Isolation gave, after recrystallization from CH_2Cl_2–hexanes (15:85), 8.1 g (26.4 mmol, 52%) of **18**, m.p. 100–102°C. ^{1}H NMR (250 MHz, CD_2Cl_2), $\delta = 1.32$ (t, 6H), 2.63 (s, 6H), 4.04 (q, 2H), 4.08 (q, 2H), 7.4–8.3 (m, 6H); ^{31}P NMR (101 MHz, $CDCl_3$), $\delta = 19.1$ (s); MS (EI), $m/z = 307$ (M^+, 45%), 292 (8%), 170 (100%); Anal. Calc. for $C_{16}H_{22}NO_3P$: C, 62.53; H, 7.22; N, 4.56; P, 10.08. Found: C, 62.75; H, 7.00; N, 4.39; P, 9.76%.

4.8. X-ray structure determination of 18

4.8.1. Crystal data

$C_{16}H_{22}NO_3P$, $M = 307.33$, monoclinic, space group $P_{21/c}$, $a = 7.716$ (3), $b = 24.060$ (4), $c = 8.659$ (1) Å, $\beta = 94.71$ (2)°, $Z = 4$, $D_c = 1.274$, $D_m = 1.265$ (5) g cm^{-3}, $F(000) = 656$, μ (Mo Kα) = 1.73 cm^{-1}.

4.8.2. Data collection

Data were collected with a Nonius CAD-4 automated diffractometer in the θ range 2–22°. The size of the colourless crystal was approximately 0.40 × 0.40 × 0.15 mm. The method of data collection was w/θ. Three reference reflections were measured at 120 min intervals and showed no significant changes in the intensities. The data were corrected for Lorentz and polarization factors and equivalent reflections were merged to give a total of 1813 unique data, of which 1314 were considered above ground ($F > 3\sigma(F)$).

4.8.3. Structure solution and refinement

The direct methods (MULTAN-80) [25] revealed the positions of the phosphorus and oxygen atoms along with the carbon atom C(1) of the naphthyl. Two difference-Fourier syntheses revealed the positions of the other non-hydrogen atoms. The hydrogen atoms were included in the refinement in idealized positions (C–H 1.08 Å, SHELX-76 [26]). Absorption corrections were neglected. All non-hydrogen atoms were assigned anisotropic thermal parameters. Neutral scattering factors, corrected for the real and imaginary components of anomalous dispersion, were used throughout [27]. Individual weights of $1/(\sigma^2(F_o) + 0.0061F^2)$ were assigned to each reflection and refinement converged at $R = 0.0345$ and $R_w = 0.0353$. Final atomic coordinates are listed in Table 3 and bond lengths and angles are given in Tables 4 and 5, respectively.

4.9. (Benzene-1,2-diolato)(8-dimethylamino-1-naphthyl)phosphonite (19)

A suspension of **17** (4.4 g, 25 mmol) in diethyl ether (200 ml) was added at −35°C to a solution of **12** (3.5 g, 20 mmol) in diethyl ether (30 ml). The reaction mixture

Table 3
Fractional atomic parameters ($\times 10^4$) for compound **18** with e.s.d.s in parentheses

Atom	x/a	y/b	z/c
P	4612.0(12)	1073.7(4)	9417.1(10)
O(1)	2785(3)	799(1)	8884(2)
O(2)	4138(3)	1700(1)	9064(3)
O(3)	5998(3)	809(1)	8628(2)
N	7694(4)	1668(1)	10515(3)
C(1)	4768(4)	1031(1)	11507(4)
C(2)	3353(5)	784(2)	12126(4)
C(3)	3375(5)	650(2)	13697(4)
C(4)	4805(5)	751(2)	14657(4)
C(5)	7752(5)	1102(2)	15126(4)
C(6)	9183(6)	1343(2)	14617(5)
C(7)	9175(5)	1523(2)	13075(4)
C(8)	7756(5)	1451(1)	12056(4)
C(9)	6270(4)	1168(1)	12516(3)
C(10)	6282(5)	1010(1)	14104(4)
C(11)	2674(5)	212(1)	8502(4)
C(12)	921(5)	113(2)	7669(5)
C(13)	3818(6)	1886(2)	7495(4)
C(14)	3101(7)	2455(2)	7422(6)
C(15)	9163(5)	1499(2)	9663(5)
C(16)	7482(6)	2273(2)	10507(5)

was kept overnight at room temperature. After filtration of the LiCl as usual, **19** was recrystallized from CH_2Cl_2–hexanes (1 : 1) to give 4.4 g (14.2 mmol, 71%) of an unstable yellow powder, m.p. 67.5–73.6°C. ^{1}H NMR (250 MHz, CD_2Cl_2), $\delta = 2.82$ (s, 6H), 6.6–7.9 (m, 10H); ^{31}P NMR (81 MHz, CD_2Cl_2), $\delta = 22.4$ (s) (impurities at 18.2 and −20.8 ppm); MS (positive-ion FAB, *m*-nitrobenzyl alcohol), $m/z = 310$ $(M + H)^+$.

4.10. (Benzene-1,2-diolato)(8-dimethylamino-1-naphthyl)phosphonate (20)

Compound **20** was prepared in the same way as **19** starting from **17** (8.2 g, 46.3 mmol) and **14** (7.6 g, 39.9 mmol). After recrystallization from CH_2Cl_2–hexanes (1 : 1), 9.4 g (28.9 mmol, 72%) of **20** were obtained, m.p. 128.5–132.6°C. ^{1}H NMR (250 MHz, CD_2Cl_2), $\delta = 2.78$ (s, 6H), 6.9–8.3 (m, 10H); ^{31}P NMR (81 MHz, CD_2Cl_2), $\delta = 23.2$ (s); MS (positive-ion FAB, *m*-nitrobenzyl alcohol), $m/z = 326$ $(M + H)^+$. Anal. Calc. for $C_{18}H_{16}NO_3P$: C, 66.46; H, 4.96; N, 4.31. Found: C, 66.37; H, 5.02; N, 3.51%.

Table 4
Interatomic distances (Å) for compound **18** with e.s.d.s in parentheses

P–O(1)	1.590(2)	C(6)–C(7)	1.404(5)
P–O(2)	1.576(2)	C(7)–C(8)	1.360(5)
P–O(3)	1.462(2)	C(8)–C(9)	1.418(5)
P–C(1)	1.806(3)	C(9)–C(1)	1.432(4)
P···N	2.869(3)	C(9)–C(10)	1.427(4)
		O(1)–C(11)	1.454(4)
C(1)–C(2)	1.388(5)	C(11)–C(12)	1.499(6)
C(2)–C(3)	1.397(5)	O(2)–C(13)	1.432(4)
C(3)–C(4)	1.348(6)	C(13)–C(14)	1.479(6)
C(4)–C(10)	1.417(5)	N–C(8)	1.430(4)
C(10)–C(5)	1.398(5)	N–C(15)	1.460(5)
C(5)–C(6)	1.353(6)	N–C(16)	1.464(4)

Table 5
Bond angles (°) for compound **18**

O(1)–P–O(2)	98.9(1)	C(1)–C(2)–C(3)	121.9(3)
O(1)–P–O(3)	110.4(1)	C(2)–C(3)–C(4)	120.2(4)
O(1)–P–C(1)	104.6(1)	C(3)–C(4)–C(10)	120.8(3)
O(2)–P–O(3)	119.6(1)	C(4)–C(10)–C(9)	120.1(3)
O(3)–P–C(1)	116.9(1)	C(4)–C(10)–C(5)	119.3(3)
C(1)–P–O(2)	104.1(1)	C(9)–C(10)–C(5)	120.6(3)
N···P–O(2)	76.1(1)	C(10)–C(5)–C(6)	120.2(3)
N···P–O(3)	75.8(1)	C(5)–C(6)–C(7)	120.2(4)
N···P–C(1)	73.2(1)	C(6)–C(7)–C(8)	121.3(4)
N···P–O(1)	173.6(1)	C(7)–C(8)–N	121.5(3)
C(8)–N–C(15)	113.7(3)	N–C(8)–C(9)	118.1(3)
C(8)–N–C(16)	111.2(3)	C(7)–C(8)–C(9)	120.4(3)
C(15)–N–C(16)	111.4(3)	C(8)–C(9)–C(1)	124.9(3)
C(8)–N···P	95.2(2)	C(8)–C(9)–C(10)	117.2(3)
C(15)–N···P	110.5(2)	C(1)–C(9)–C(10)	117.9(3)
C(16)–N···P	113.9(2)		
		P–O(1)–C(11)	120.3(2)
C(9)–C(1)–P	125.6(2)	O(1)–C(11)–C(12)	107.3(3)
C(9)–C(1)–C(2)	119.1(3)	P–O(2)–C(13)	120.1(2)
P–C(1)–C(2)	114.9(2)	O(2)–C(13)–C(14)	108.0(3)

4.11. (Benzene-1,2-diolato)(8-dimethylamino-1-naphthyl)thiophosphonate (21)

Compound **19** (5.9 g, 19.1 mmol) and sulphur (0.7 g, 21.9 mmol) were heated at 60°C in toluene (10 ml). When the sulphur had dissolved, the toluene was removed under vacuum and the residue obtained was recrystallized from CH_2Cl_2–hexanes (1 : 1) to give 4.4 g (13.0 mmol, 72%) of **21**, m.p. 138–139.6°C. ^{1}H NMR (250 MHz, CD_2Cl_2), $\delta = 2.76$ (s, 6H), 6.8–8.5 (m, 10H); ^{13}P NMR (81 MHz, CD_2Cl_2), $\delta = 89.9$ (s) (impurity at 73.8 ppm); MS (positive-ion FAB, *m*-nitrobenzyl alcohol), $m/z = 342$ $(M + H)^+$. Anal. Calc. for $C_{18}H_{16}NO_2PS$: C, 63.33; H, 4.72; N, 4.10; S, 9.40. Found: C, 63.49; H, 4.52; N, 4.27; S, 10.01%.

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