Preparation And Structure Of Phosphonium Ions With Intramolecular P ← N Coordination; Novel Diphosphonium Salts And Ionomer Containing Backbone Hypervalent Phosphorus

Francis H. Carré,[a] Claude Chuit,[a] Robert J. P. Corriu,*[a] William E. Douglas,[a]
Daniel M. H. Guy,[a] and Catherine Reyé[a]

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Starting from $R'R_2P$ (R′ = 8-dimethylamino-1-naphthyl) containing a donor dimethylamino group, the new phosphonium salts $[R'R_2P(CH_2Ph)]^+Br^-$ [R = Me (**9**) or Ph (**10**)] and $[R'R_2P(p\text{-}CH_2C_6H_4CH_2)PR_2R']^{2+}[2Br]^{2-}$ [R = Ph (**12**)] have been prepared. An interaction between the N and P atoms is evident from the X-ray crystal structure of **10** the N–P distance being less than the sum of the van der Waals radii of the 2 atoms. The geometry of **10** is that of a monocapped tetrahedron whereas the X-ray crystal structure determination shows essentially regular tetrahedral geometry for the analogous compound without the donor amino group, $[(1\text{-}Np)Ph_2P(CH_2Ph)]^+Br^-$ (**11**). Treatment of 1,5-bis(dimethylamino)-2,6-dilithionaphthalene with chlorodiphenylphosphane gave 1,5-bis(dimethylamino)-2,6-bis(diphenylphosphanyl)naphthalene (**8**) which in the presence of methyl iodide afforded the diphosphonium salt [1,5-bis(dimethylamino)-2,6-bis(diphenylmethylphosphonium)naphthalene]$^{2+}$[2I]$^{2-}$ (**13**). Similarly, treatment of **8** with 1 equivalent of benzyl bromide gave the monophosphonium salt [1,5-bis(dimethylamino)-2-diphenylbenzylphosphonium-6-diphenylphosphanyl-naphthalene]$^+$[Br]$^-$ (**14**) whereas in the presence of 2 equivalents of the same reagent [1,5-bis(dimethylamino)-2,6-bis(diphenylbenzylphosphonium)naphthalene]$^{2+}$[2 Br]$^{2-}$ (**15**) was obtained. The ionomer poly([(1,5-bis{dimethylamino}-2,6-bis{diphenylphosphonium}naphthalene)-(P,P-*p*-xylylene)]$^{2+}$[2 Br]$^{2-}$) (**16**), soluble in liquid SO_2, was prepared by treatment of **8** with α,α′-dibromo-*p*-xylene.

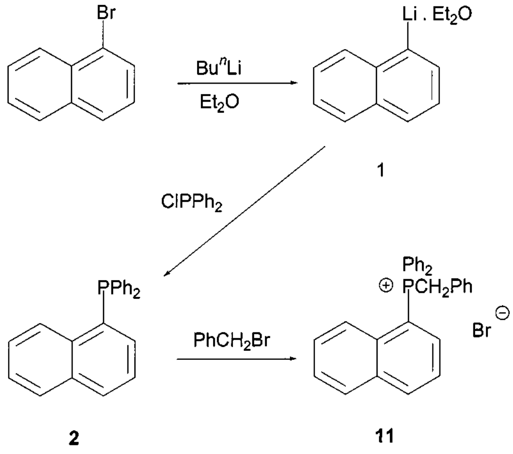
Introduction

Extension of coordination has been widely investigated for phosphoranes[1,2] and silicon compounds[3] but very rarely in the case of phosphanes and phosphonium ions.[4] It has been argued that there is no need to invoke d-orbital participation in the bonding in such hypervalent phosphorus compounds.[5] We have described the preparation, structures and some properties of various phosphanes (and also some phosphonium salts) showing extension of coordination by P←N interactions,[6–8] incorporating in particular the 8-dimethylamino-1-naphthyl ligand first used many years ago for the stabilization of hypercoordinated species[9] and widely applied in silicon chemistry.[3] Here, some new types of such phosphonium salts are reported including those containing two phosphorus atoms, prepared from the 4,8-bis(dimethylamino)-1,5-naphthylidene ligand,[10] in which there are two P←N interactions. The crystal structure of one of the phosphonium salts is compared to that of the corresponding salt without an amine group. We also describe the preparation from this same ligand of a novel ionomer containing hypervalent phosphorus in the backbone.

Results and Discussion

Preparation of Starting Phosphanes

Naphthyllithium (**1**) was prepared by treatment of bromonaphthalene in diethyl ether with *n*-butyllithium[11] (Scheme 1). The presence of one molecule of diethyl ether for each molecule of lithium reagent was shown by the proton NMR spectrum of the hydrolysis product. Naphthyldiphenylphosphane (**2**) was prepared by treatment of **1** with chlorodiphenylphosphane (Scheme 1).



Scheme 1. Preparation of **11**

The hypercoordinate phosphanes were obtained starting from the 8-(dimethylamino)-1-lithionaphthalene (**3**), the latter being prepared quantitatively by treatment of 1-dimethylaminonaphthalene with *n*-butyllithium (Scheme 2).[9] The preparation and the properties of phosphane **4** prepared by treatment of **3** with chlorodiphenylphosphane (Scheme 2) have been previously described;[8,12] a dynamic proton NMR investigation and the X-ray crystal structure determination showed that the geometry of this phosphane

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[a] CNRS UMR 5637, Université Montpellier II,
Place E. Bataillon, 34095 Montpellier Cedex 5, France
E-mail: corriu@crit.univ-montp2.fr

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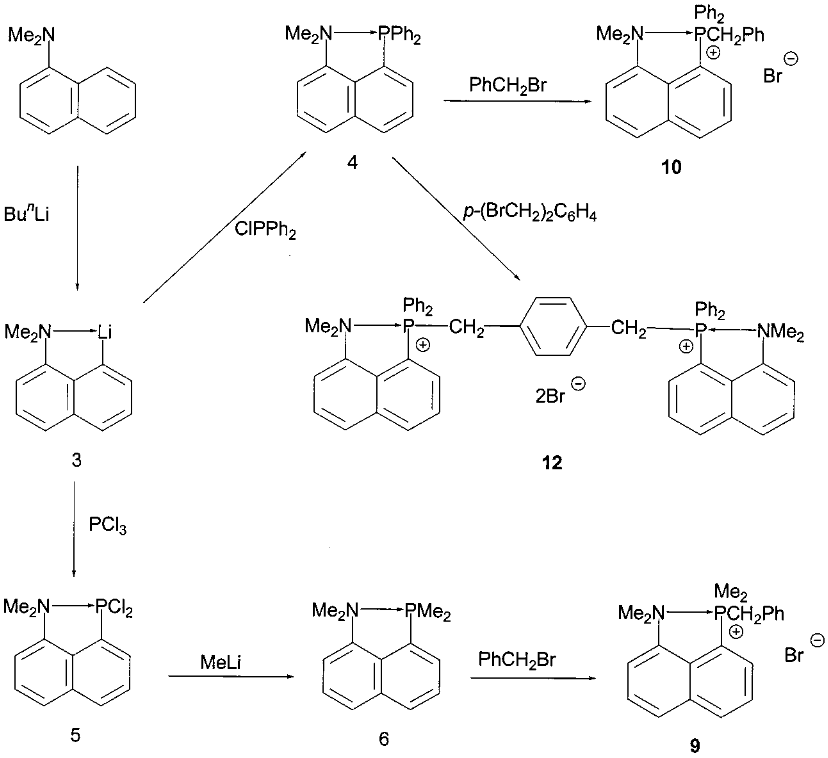


Scheme 2. Preparation of hypervalent phosphorus compounds containing the 8-dimethylamino-1-naphthyl ligand

is not symmetric and that the distance between the nitrogen and the phosphorus atoms (2.7 Å) is smaller than the sum of the van der Waals radii of the two atoms (3.4 Å[13]).[8] The geometry of **4** can be described as a monocapped tetrahedron in which the P atom is pseudo-[4+1]-coordinate (taking into account the electron lone pair).[8]

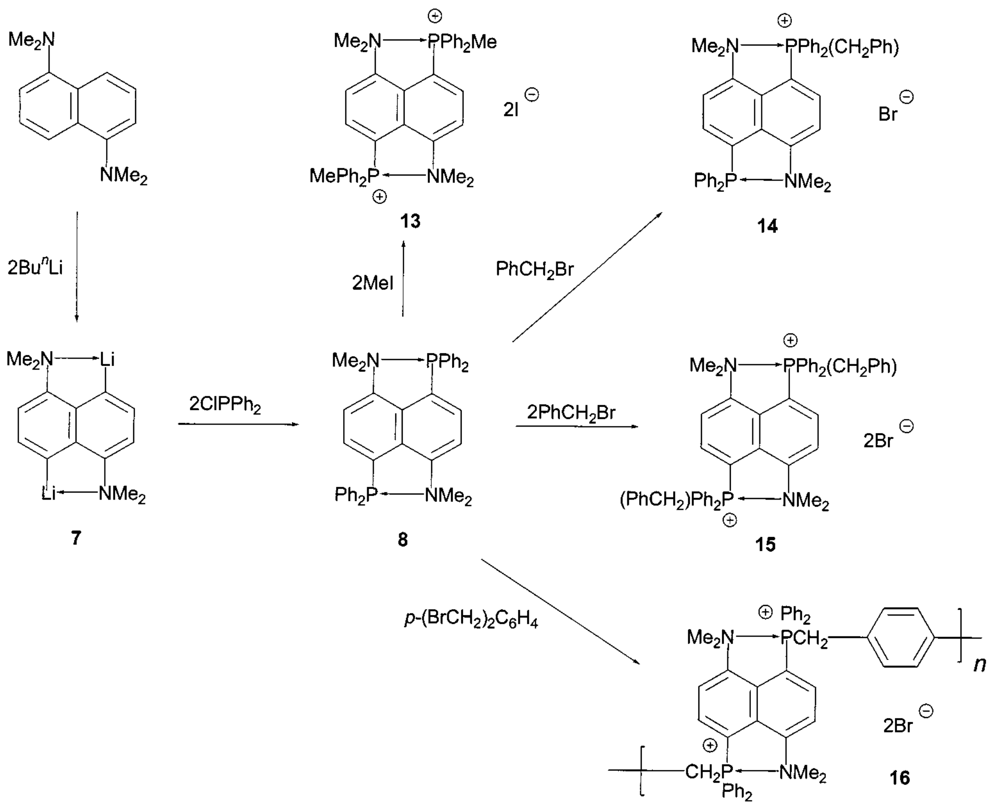
The intermediate dichlorophosphane derivative **5** was obtained by addition of the lithium reagent **3** to a large excess of trichlorophosphane (Scheme 2) at –80 °C. Treatment of **5** with methyllithium gave the dimethylphosphane derivative **6** (Scheme 2). The latter, like **4**, shows a singlet for the amine methyl protons in the proton NMR spectrum at room temperature. However, whereas for **4** this signal is split into two at –95 °C, in the case of **6** at –110 °C (250 MHz) it is merely broadened the permutational isomerization being of lower energy due to the difference in bulk of the phenyl and methyl groups.

Treatment of 1,5-bis(dimethylamino)naphthalene with two equivalents of *n*-butyllithium affords the dilithio reagent **7** (Scheme 3), as we have previously described.[10] Subsequent treatment of **7** with chlorodiphenylphosphane gives the diphosphane **8** containing two hypercoordinate phosphorus atoms (Scheme 3). A dynamic proton NMR study of this compound showed that at –95 °C the singlet corresponding to the amine protons is split into two signals. By use of the Eyring equation the energy of the permutational isomerisation was calculated[14] to be $\Delta G^{\ddagger} = 36.8$ kJ mol^{-1}, a value similar to that previously found for **4**.[8] We have not been able to determine the X-ray crystal structure of **8** but the geometry is most probably similar to that of the corresponding phosphane **4** with a monocapped tetrahedral arrangement of the ligands around each phosphorus.[8]

Preparation of Phosphonium Salts

The very air sensitive hypercoordinate phosphonium salt **9** with methyl groups at P was prepared by treatment of **6** with benzyl bromide (Scheme 2). The analogous stable salt **10** with phenyl groups at P was obtained by reaction of **4** with benzyl bromide. The X-ray crystal structure of **10** (Figure 1) shows a monocapped tetrahedral geometry in which the P atom is [4+1]-coordinate; selected bond lengths and angles are to be found in Table 1 and details of the crystal structure determination in Table 2. The distance between the nitrogen and the phosphorus atoms (2.83 Å) is less than the sum of the van der Waals radii of the 2 atoms (3.4 Å[13]),[8] thus showing that they interact. Indeed, this distance is comparable to the N–N distance (2.79 Å) in 1,8-bis(dimethylamino)naphthalene[15] despite phosphorus being much larger than nitrogen. Moreover, it should be noted that the naphthalene ring in **10** is distorted out of the plane by only *ca.* 17° (dihedral angle between the C9–C1–C2 and C7–C8–C9 planes) whereas for 1,8-bis(dimethylamino)naphthalene[15] the corresponding angle can be evaluated at 28°.

For comparison, the analogous phosphonium salt without the donor nitrogen, $[(1\text{-Np})Ph_2P(CH_2Ph)]^+Br^-$ (**11**), was synthesized by treatment of **2** with benzyl bromide in refluxing toluene (Scheme 1). The X-ray crystal structure analysis of **11** (Figure 2) shows a tetrahedral geometry in



Scheme 3. Preparation of hypervalent phosphorus compounds containing the 4,8-bis(dimethylamino)-1,5-naphthylidene ligand

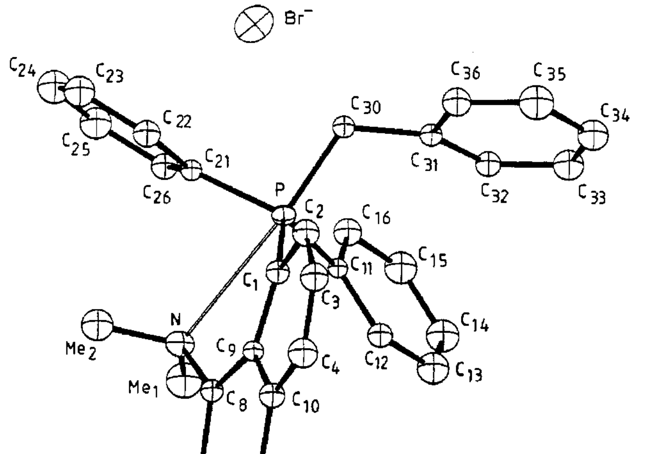


Figure 1. Molecular structure of **10**; hydrogen atoms have been omitted for clarity

which the P atom is 4-coordinate; selected bond lengths and angles are to be found in Table 1 and details of the crystal structure determination in Table 2. Comparison of the angles in **10** and **11** (Table 1) shows that the nitrogen in **10** is opposite to the benzyl group [C(30)] and has little effect on angles C(1)–P–C(30) and C(1)–P–C(11) which remain essentially tetrahedral. However, the presence of the amine group results in a reduction of C(21)–P–C(30) by ca. 9° and C(11)–P–C(30) by ca. 6°, and an enlargement of C(11)–P–C(21) and C(21)–P–C(1) by 5–6°.

Table 1. Selected interatomic distances (Å) and bond angles (°) for **10** and **11**

	10	11
P–C(1)	1.820(12)	1.790(5)
P–C(11)	1.787(11)	1.800(5)
P–C(21)	1.796(11)	1.815(5)
P–C(30)	1.844(11)	1.813(5)
P···N	2.826(10)	
N···P–C(30)	175.7(4)	
N···P–C(1)	72.3(4)	
N···P–C(11)	79.1(4)	
N···P–C(21)	75.8(4)	
C(1)–P–C(30)	109.5(5)	108.2(2)
C(11)–P–C(30)	103.6(5)	109.1(2)
C(21)–P–C(30)	99.9(5)	108.9(2)
C(1)–P–C(11)	110.6(5)	110.4(2)
C(11)–P–C(21)	116.4(5)	111.3(2)
C(21)–P–C(1)	115.3(5)	109.0(2)

The ^1H NMR resonances for the methylene protons in the hypercoordinate salts **9** (δ_H = 4.4) and **10** (δ_H = 4.7) occur at higher field than in the tetracoordinate salt **11** (δ_H = 5.35). This can be explained by the electron-donating effect of the dimethylamino group coordinated to the phosphorus atom. However, the ^{31}P NMR chemical shift remains essentially unchanged with increase in the coordination number from four (**11**) to five (**9** or **10**) as has previously been observed for hypercoordinated silicon compounds containing the 8-dimethylamino-1-naphthyl ligand.[16]

The analogous compound **12** containing two positively-charged phosphorus atoms was prepared by treating two

Table 2. Summary of crystal data, intensity measurements and refinement for **10** and **11**

	10	**11**
Formula	$C_{31}H_{29}BrNP$	$C_{29}H_{24}BrP$
Cryst. system	triclinic	monoclinic
Space group	*P*–1	*P*2$_1$/*c*
a (Å)	9.351(3)	10.123(2)
b (Å)	9.875(3)	20.683(4)
c (Å)	14.664(4)	11.796(3)
α	80.58(2)	
β	74.27(3)	110.29(2)
γ	89.66(3)	
Vol. (Å^3)	1284.8(7)	2316.5(9)
Mol. wt.	526.46	483.4
Z	2	4
$d_{calcd.}$ (gcm^{-3})	1.361	1.386
$d_{measd.}$ (gcm^{-3})	1.32(3)	1.37(2)
Cryst. size (mm)	0.45 × 0.25 × 0.09	0.42 × 0.40 × 0.18
Cryst. colour	colourless	colourless
Recryst. solv.	CH_2Cl_2/heptane, 2:3	ethanol
m.p. (°C)	281.3–282.5	329.5–331.2
Method of data collectn.	ω/φ	ω/φ
Radiation (graphite-monochromated)	Mo-*K*α	Mo-*K*α
μ (cm^{-1})	16.6	18.2
2φ limits (°)	4–50	4–50
No of unique reflectns.	3275	3338
No of obsd reflectns.	1548	2106
Final no of variables.	161	180
R	0.0690	0.0396
Rw	0.0705	0.0409
Residual electron density	0.98	0.41

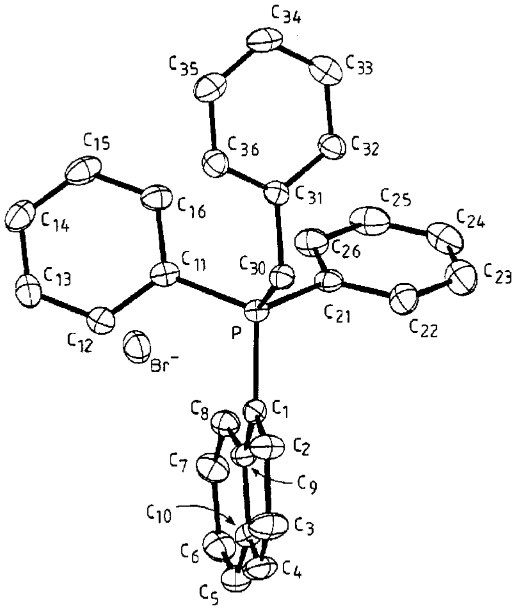


Figure 2. Molecular structure of **11**; hydrogen atoms have been omitted for clarity

equivalents of **4** with one equivalent of α,α'-dibromo-*p*-xylene (Scheme 2). As expected the chemical shifts of the proton and ^{31}P NMR resonances for **12** are very similar to those for **10**, the ^{31}P NMR resonances for these compounds containing phenyl groups occurring at higher field than that for **9** containing methyl groups.

Phosphonium salts containing two hypercoordinate phosphorus atoms were obtained from the diphosphane **8** (Scheme 3). The reactions were followed by ^{31}P NMR, the spectra showing the disappearance of the signal corresponding to the starting phosphane ($\delta_P = 1.9$) and the appearance of the signal corresponding to the phosphonium salt at $\delta \approx 23$. Salt **13** was prepared by treatment of phosphane **8** with a large excess of methyl iodide in toluene under reflux, the reaction being complete after 4.5 h (Scheme 3).

The compound **14** containing both phosphanyl and phosphonium centres was obtained by treatment of **8** with one equivalent of benzyl bromide the reaction being complete after 60 hours under reflux in toluene (Scheme 3). The ^{31}P NMR spectrum shows a signal at δ 22 characteristic of the phosphonium ion and another at $\delta = 5$ corresponding to the phosphanyl atom, the latter being downfield of that for the starting material **8** ($\delta_P = 1.9$). The proton resonances for the dimethylamino group *peri* to the phosphonium centre ($\delta_H = 1.7$) are shifted upfield compared to those for **8** ($\delta_H = 2.3$) whereas the proton resonances for the dimethylamino group *para* to the phosphonium centre are shifted downfield ($\delta_H = 2.5$).

The analogous salt **15** containing two phosphonium centres was prepared by treatment of **8** with two equivalents of benzyl bromide the reaction being complete in this case after 120 hours under reflux in toluene (Scheme 3). As expected only one ^{31}P NMR signal is observed ($\delta_P = 24.8$) characteristic of the phosphonium ion. The proton NMR spectrum shows all the amine protons to be equivalent ($\delta_H = 2.08$) this signal being upfield of that for **8** ($\delta_H = 2.3$).

The ionomer **16** was prepared by heating **8** with one equivalent of α,α'-dibromo-*p*-xylene in toluene under reflux for 10 d (Scheme 3), the product being insoluble except in liquid SO_2. The solid state ^{31}P NMR spectrum shows a signal at $\delta = 16$. The conductivity of a compacted disc of the powdered ionomer was found to be 10^{-5} S cm^{-1} (4-point method), and that of a SO_2 solution at –30 °C was 53 S cm^{-1}.

In conclusion, we have shown that an intramolecular donor-acceptor interaction exists in the phosphonium ion **10** and therefore most probably also in the other new phosphonium ions of this type reported here (**9**, **12**, **13–15** and the ionomer **16**). This confirms that the phosphonium ion is able to undergo an extension of coordination. In particular, it should be noted that, as has been previously observed for the analogous silicon compounds,[16] incorporation of the 8-dimethylamino-1-naphthyl ligand to give pentacoordinate phosphane species does not give rise to any substantial change in NMR chemical shift. This independence of NMR chemical shift on coordination number is due to the specific geometry of the ligand and in no way throws doubt[17] on the existence of an N←P (or N←Si) coordinative interaction. On the contrary, a completely coherent picture is found for the structures and chemical behaviour of the totality of penta- and hexacoordinate derivatives formed by intramolecular coordination of either Si or P.

Experimental Section

All reactions were performed using standard Schlenk-tube techniques under an atmosphere of dry argon. Solvents were distilled from appropriate drying agents and degassed before use. ^{1}H and ^{13}C NMR spectra were obtained using a Bruker DPX-200 spectrometer at 200 MHz and 50.288 MHz, respectively, and ^{31}P NMR spectra on a Bruker 250 AC spectrometer at 101.202 MHz. ^{1}H and ^{13}C NMR chemical shifts are reported relative to Me_4Si, and ^{31}P chemical shifts relative to H_3PO_4. Infrared spectra were obtained in the region 500–4000 cm^{-1} using a Perkin–Elmer 1600 FT spectrophotometer. Elemental analyses were carried out by the Service Central de Microanalyse du CNRS. Phosphane **4** was prepared from **3** as previously described.[8]

Preparation of 1: Diethyl ether (130 mL) was added at 0 °C to 1.9 M *n*-butyllithium solution in hexane (85 mL, 160 mmol) and the resulting solution was cooled to –20 °C. 1-Bromonaphthalene (20 mL, 140 mmol) was added drop by drop and the mixture was stirred at 0 °C for 1 h and then filtered. The precipitate was washed with pentane and dried under vacuum affording 24.65 g of a white pyrophoric solid ($C_{10}H_7Li \cdot Et_2O$) isolated in 85% yield.

Preparation of 2: Chlorodiphenylphosphane (18 mL, 100 mmol) was added drop by drop to a suspension of **1** (16 g, 76.92 mmol) in diethyl ether (100 mL) at –50 °C. The mixture was then allowed to warm to room temp. and was stirred for 16 h. The resulting white suspension was heated under reflux for 5 h, and was then hydrolysed with 10% NaOH solution (50 mL). The precipitate was washed successively with water, acetone and diethyl ether before being dried under vacuum. The crude product was recrystallized from ethanol to give 13.25 g of the desired product, m.p. 122.3–124.0 °C (yield 55%). – ^{1}H NMR ($CDCl_3$): δ_H = 7–8.6 (m, aromatic protons). – ^{13}C-{^{1}H} NMR ($CDCl_3$): δ_C = 126–137 (aromatic carbons). – ^{31}P-{^{1}H} NMR ($CDCl_3$): δ_P = –13.6 (s). – IR (CCl_4): $\tilde{\nu}$ (cm^{-1}) = 3056 s, 1588 w, 1504 m, 1482 m, 1434 vs, 1386 m, 1329 w, 1094 w, 1027 w. – $C_{22}H_{17}P$ (312.34): calcd. C 84.60, H 5.48, P 9.91; found C 85.01, H 5.48, P 9.78.

Preparation of 3: *n*-Butyllithium in hexane (40 mL, 110 mmol) was added drop by drop to a solution of 1-(dimethylamino)naphthalene (16.54 g, 96.7 mmol) in 250 mL of diethyl ether at room temp. After the mixture had been stirred for 3 d the resulting yellow suspension was filtered and the precipitate was washed thrice with diethyl ether before being dried under vacuum to afford 16.8 g of a yellow pyrophoric fine powder (yield 98%).

Preparation of 5: A suspension of **3** (5.67 g, 32.03 mmol) in 150 mL of diethyl ether was added drop by drop to a solution of trichlorophosphane (12 mL, 137 mmol) in 150 mL of diethyl ether at –80 °C. The mixture was stirred at room temp. overnight. The resulting yellow suspension was filtered and the filtrate was concentrated to give 5.43 g of a yellow solid (yield 62%). – ^{1}H NMR ($CDCl_3$): δ_H = 2.87 [s, 6 H, $N(CH_3)_2$], 7.5–8.9 (m, 6 H, aromatic protons). – ^{13}C-{^{1}H} NMR ($CDCl_3$): δ_C = 47.6 (CH_3), 112–148 (aromatic carbons). – ^{31}P-{^{1}H} NMR ($CDCl_3$): δ_P = 130.85 (s).

Preparation of 6: A 1.25 M solution of methyllithium (28.2 mL, 35.22 mmol) in diethyl ether was added to a suspension of **5** (4.79 g, 17.61 mmol) in 100 mL of diethyl ether. The mixture was stirred at room temperature overnight and then heated under reflux for 3 h. The suspension was hydrolysed by addition of degassed 10% NaOH solution (40 mL). The aqueous layer was extracted with diethyl ether. The combined organic phases were washed with degassed water and dried with $MgSO_4$ before removal of the solvent to give a yellow liquid. Vacuum distillation gave 1.63 g of the desired product (40% yield), b.p. 118–120 °C/0.4 Torr. – ^{1}H NMR ($CDCl_3$): δ_H = 1.35 [d, $^{2}J_{1H,31P}$ = 5.7 Hz, 6 H, $P(CH_3)_2$], 2.75 [s, 6 H, $N(CH_3)_2$], 7.3–7.9 (m, 6 H, aromatic protons). – ^{31}P-{^{1}H} NMR ($CDCl_3$): δ_P = –37.8 (s). – IR (CCl_4): $\tilde{\nu}$ (cm^{-1}) = 3054 m, 2945 s, 2902 s, 2864 s, 2828 vs, 2786 s, 1929 w, 1710 w, 1563 vs, 1500 w, 1477 m, 1453 vs, 1366 vs, 1330 s, 1289 m, 1204 m, 1183 s, 1143 s, 1081 s, 1048 m, 1030 m.

Preparation of 7: *n*-Butyllithium in hexane (110 mL, 310 mmol) was added drop by drop to a solution of 1,5-bis(dimethylamino)naphthalene (30.04 g, 140 mmol) in 500 mL of diethyl ether at room temp.. After the mixture had been stirred for 10 d the resulting yellow suspension was filtered and the precipitate was washed thrice with diethyl ether before being dried under vacuum to afford 30.97 g of a white pyrophoric fine powder (yield 98%).

Preparation of 8: Chlorodiphenylphosphane (10.83 mL, 60 mmol) was added drop by drop to a suspension of **7** (8.52 g, 38 mmol) in 100 mL of diethyl ether at –80 °C. The mixture was then allowed to warm to room temp. and was stirred overnight. The resulting white suspension was heated under reflux for 9 h, and it was then hydrolysed with 10% NaOH solution (100 mL). The precipitate was washed successively with water, acetone and diethyl ether before being dried under vacuum. The crude product was recrystallized from benzene to give 9.6 g of the desired product, m.p. 259.4–263.7 °C (yield 55%). – ^{1}H NMR ($CDCl_3$): δ_H = 2.3 [s, 12 H, $N(CH_3)_2$], 6.7–7.4 (m, 24 H, aromatic protons). – ^{13}C-{^{1}H} NMR ($CDCl_3$): δ_C = 46.18 [$N(CH_3)_2$], 118–152 (aromatic carbon atoms). – ^{31}P-{^{1}H} NMR ($CDCl_3$): δ_P = 1.9 (s). – IR (Nujol): $\tilde{\nu}$ (cm^{-1}) = 3059 m, 2853 vs, 2822 s, 2776 m, 1954 w, 1882 w, 1823 w, 1773 w, 1677 w, 1653 w, 1578 m, 1506 m, 1451 s, 1401 w, 1368 s, 1311 m, 1275 w, 1202 m, 1181 s, 1152 m, 1109 m, 1087 m, 1068 w, 1042 s, 976 vs, 836 m, 826 m, 748 s, 738 vs, 717 m, 697 vs, 668 w, 650 m, 613 s. – $C_{38}H_{36}N_2P_2$ (582.66): C 78.32, H 6.23, N 4.81; found C 78.28, H 6.01, N 4.92.

Preparation of 9: A mixture of **6** (0.33 g, 1.43 mmol) and benzyl bromide (0.17 mL, 1.43 mmol) was heated under reflux in toluene (50 mL) for 3 h. The solvent was removed under vacuum to give 0.53 g of a very air-sensitive white powder (yield 93%). – ^{1}H NMR ($CDCl_3$): δ_H = 2.45 [d, $^{2}J_{1H,31P}$ = 10 Hz, 6 H, $P(CH_3)_2$], 2.75 [s, 6 H, $N(CH_3)_2$], 4.4 (d, $^{2}J^{1}{}_{H}{}^{31}{}_{P}$ = 15 Hz, 2 H, CH_2), 6.8–8.2 (m, 11 H, aromatic protons). – ^{31}P-{^{1}H} NMR ($CDCl_3$): δ_P = 24.26 (s).

Preparation of 10: A mixture of **4** (2 g, 5.63 mmol) and benzyl bromide (0.67 mL, 5.63 mmol) was heated under reflux in toluene (100 mL) for 9 d. The solvent was then removed under vacuum to give a white solid. The crude product was recrystallized from a mixture of dichloromethane and heptane to give 2.84 g of the desired product, m.p. 281.3–282.5 °C (yield 96%). – ^{1}H NMR ($CDCl_3$): δ_H = 1.5 [s, 6 H, $N(CH_3)_2$], 4.7 (d, $^{2}J_{1H,31P}$ = 14 Hz, 2 H, CH_2), 6.3–9 (m, 21 H, aromatic protons). – ^{13}C-{^{1}H} NMR ($CDCl_3$): δ_C = 36.14 (d, $^{1}J_{31P,13C}$ = 48.36 Hz, CH_2), 46.44 (CH_3), 111–151 (aromatic carbons). – ^{31}P-{^{1}H} NMR ($CDCl_3$): δ_P = 22.12 (s). – IR (Nujol): ṽ (cm^{-1}) = 3052 w, 2796 w, 1715w, 1694 w, 1570 w, 1497 m, 1438 s, 1412 w, 1376 m, 1338 m, 1286 w, 1209 w, 1195 w, 1152 m, 1114 s, 1105 s, 1081 m, 1036 m, 1023 m, 995 w, 958 w, 929 w, 879 m, 839 s, 831 s, 802 w, 776 vs, 757 s, 727 m, 699 vs, 660.

Preparation of 11: A mixture of naphthyldiphenylphosphane (**2**) (2 g, 6.41 mmol) and benzyl bromide (0.76 g, 6.41 mmol) was heated under reflux in toluene (100 mL) for 6 d. The solvent was removed under vacuum to give a white powder. The crude product was recrystallized from ethanol to give 1.81 g of the desired product, m.p. 329.5–331.2 °C (yield 58%). – ^{1}H NMR ($CDCl_3$): δ_H = 5.35 (d, $^{2}J_{1H,31P}$ = 15 Hz, 2 H, CH_2), 6.8–8.6 (m, 22 H, aromatic protons). – ^{13}C-{^{1}H} NMR ($CDCl_3$): δ_C = 30.53 (d, $^{1}J_{13C,31P}$ = 42.78 Hz, CH_2), 112–138 (aromatic carbon atoms). – ^{31}P-{^{1}H} NMR ($CDCl_3$): δ_P = 22.45 (s). – IR (nujol): ṽ (cm^{-1}) = 2783 m, 2362 w, 1602 w, 1586 w, 1502 m, 1496 m, 1440 vs, 1377 s, 1338 m, 1318 w, 1262 w, 1214 w, 1166 m, 1110 s, 1074 w, 1033 w, 997 w, 986 w, 921 w, 877 w, 832 m, 800 m, 777 s, 751 s, 717 m, 698 s, 690 s, 664 w, 586 s. – $C_{29}H_{24}BrP$ (483.39): C 72.06, H 5.00; found C 72.06, H 5.09.

Preparation of 12: A mixture of α,α'-dibromo-*p*-xylene (0.74 g, 2.81 mmol) and **4** (2 g, 5.63 mmol) was heated under reflux in toluene (100 mL) for 7 d. The solvent was removed under vacuum to give a white powder. The crude product was recrystallized from a mixture of dichloromethane and pentane to give 1.6 g of the desired product, m.p. 309.9–311.4 °C (yield 58%). – ^{1}H NMR ($CDCl_3$): δ_H = 1.5 [s, 12 H, $N(CH_3)_2$], 4.55 (d, $^{2}J_{1H,31P}$ = 16 Hz, 4 H, CH_2), 7–9 (m, 36 H, aromatic protons). – ^{13}C-{^{1}H} NMR ($CDCl_3$): δ_C = 38.25 (d, $^{1}J_{13C,31P}$ = 47.44 Hz, CH_2), 46.4 (CH_3), 110–150 (aromatic carbons). – ^{31}P-{^{1}H} NMR ($CDCl_3$): δ_P = 22.77 (s). – IR (Nujol): ṽ (cm^{-1}) = 3053 w, 2854 vs, 2808 w, 1622 w, 1566 w, 1497 w, 1437 s, 1375 s, 1336 m, 1288 w, 1212 w, 1168 m, 1151 w, 1110 s, 1100 m, 1080 w, 1034 w, 1024 w, 995 w, 954 w, 880 w, 826 m, 773 m, 756 s, 724 m, 697 m, 658 w.

Preparation of 13: A mixture of methyl iodide (1.74 g, 28.0 mmol) and **8** (2 g, 3.44 mmol) was heated under reflux in toluene (20 mL) for 4.5 h. The solvent was removed under vacuum to give a white powder. The crude product was recrystallized in a mixture of ethanol and benzene to give 2.48 g of the desired product, m.p. 323.7–324.9 °C (yield 83%). – ^{1}H NMR ($CDCl_3$): δ_H = 2.1 [s, 12 H, $N(CH_3)_2$], 3.1 (d, $^{2}J_{1H,31P}$ = 13.4 Hz, 6 H, PCH_3), 7.2–7.8 (m, 24 H, aromatic protons). – ^{13}C-{^{1}H} NMR ($CDCl_3$): δ_C = 11.84 (d, $^{1}J_{13C,31P}$ = 65.17 Hz, PCH_3), 46.67 [$N(CH_3)_2$], 111–157 (aromatic carbon atoms). – ^{31}P-{^{1}H} NMR ($CDCl_3$): δ_P = 23.76 (s). – IR (Nujol): ṽ (cm^{-1}) = 1585 w, 1567 m, 1499 s, 1438 vs, 1376 vs, 1318 s, 1211 w, 1155 m, 1121 s, 1101 m, 1038 w, 1012 w, 996 w, 972 m, 914 m, 895 m, 830 w, 785 w, 774 w, 750 s, 715 s, 693 s.

Preparation of 14: A mixture of benzyl bromide (0.61 mL, 5.15 mmol) and **8** (3 g, 5.15 mmol) was heated under reflux in toluene (50 mL) for 60 h. The solvent was removed under vacuum to give a yellow solid, m.p. 275.8–276.5 °C (yield 83%). – ^{1}H NMR ($CDCl_3$): δ_H = 1.7 [s, 6 H, $N(CH_3)_2$ *peri* to P^+], 2.5 [s, 6 H, $N(CH_3)_2$ *para* to P^+], 4.7 (d, $^{2}J_{1H,31P}$ = 14 Hz, CH_2), 6–7.8 (m, 29 H, aromatic protons). – ^{13}C-{^{1}H} NMR ($CDCl_3$): δ_C = 38.6 (d, $^{1}J_{13C,31P}$ = 47.23 Hz, CH_2), 45.72 [$N(CH_3)_2$], 46.16 [$N(CH_3)_2$], 119–150 (aromatic carbon atoms). – ^{31}P-{^{1}H} NMR ($CDCl_3$): δ_P = 4.3 (P), 21.91 (P^+). – IR (Nujol): ṽ (cm^{-1}) = 3045 w, 1584 w, 1558 w, 1498 m, 1376 vs, 1322 m, 1303 m, 1261 w, 1185 m, 1151 m, 1116 s, 1073 m, 1046 w, 1033 m, 998 m, 971 m, 904 m, 860 m, 837 m, 753 s, 723 m, 697 s.

Preparation of 15: A mixture of benzyl bromide (1.22 mL, 10.30 mmol) and **8** (3 g, 5.15 mmol) was heated under reflux in toluene (50 mL) for 120 h. The solvent was removed under vacuum to give a yellow powder. The crude product was recrystallized from a mixture of ethanol and benzene to give 4.52 g of the desired product, m.p. 294.0–294.6 °C (yield 95%). – ^{1}H NMR ($CDCl_3$): δ_H = 2.08 [s, 12 H, $N(CH_3)_2$], 4.87 (d, $^{2}J_{1H,31P}$ = 16 Hz, 4 H, CH_2), 6.5–9 (m, 34 H, aromatic protons). – ^{13}C-{^{1}H} NMR ($CDCl_3$): δ_C = 38.8 (d, $^{1}J_{13C,31P}$ = 47.66 Hz, CH_2), 46.06 (CH_3), 119–150 (aromatic carbons). – ^{31}P-{^{1}H} NMR ($CDCl_3$): δ_P = 24.78 (s). – IR (Nujol): ṽ (cm^{-1}) = 2786 w, 1574 w, 1498 s, 1439 vs, 1376 s, 1315 m, 1260 w, 1175 w, 1112 m, 1074 w, 1037 m, 1010 w, 973 w, 904 w, 851 m, 838 m, 786 w, 761 m, 750 s, 726 m, 696 s.

Preparation of 16: A mixture of α,α'-dibromo-*p*-xylene (0.73 g, 2.78 mmol) and **8** (1.62 g, 2.78 mmol) was heated under reflux in toluene (50 mL) for 10 d. The solvent was removed under vacuum to give an orange powder (d 300 °C) which is soluble in liquid SO_2. Solid-state ^{31}P-NMR HPDEC MAS: δ_P = 16. – IR (Nujol): ṽ (cm^{-1}) = 2722 w, 1614 w, 1568 m, 1498 s, 1438 vs, 1377 vs, 1315 m, 1261 m, 1211 m, 1157 m, 1110 s, 1033 m, 998 m, 968 m, 899 w, 837 s, 749 m, 720 w, 694 s, 634 w.

X-ray Structure Determinations of 10 and 11: The crystal of **10** used was found to produce only moderate diffraction intensities. The direct methods (SHELXS-86[18]) failed to give the solution of the structure with space groups *P*–1. However, an attempt to solve the structure with the non-centrosymmetric space group *P*1 gave the positions of the bromine anion, the phosphorus atom and four carbon atoms from the naphthyl group. The space group *P*–1 was again assumed to be the correct group and two subsequent Fourier syntheses and a difference Fourier map gave the positions of the remaining atoms. Owing to the small number of observed data, only the bromine, phosphorus and nitrogen atoms were refined anisotropically. The calculated hydrogen atoms[19] were included in the last stages of the refinement. Convergence occurred for the *R* value of 0.0690 (*Rw* = 0.0705). – In the case of **11** the systematic absences revealed the space group $P2_1/c$. Direct methods (SHELXS-86[18]) gave the positions of the bromine anion, the phosphorus atom and the phenyl and some of the naphthyl carbons. Two Fourier maps revealed the remaining carbon atoms. The hydrogen atoms were positioned by calculation[19] and taken into account in the next refinements. After ten cycles of least-squares refinement with anisotropic thermal parameters for all non-hydrogen atoms, the final *R* value was 0.0396 (*Rw* = 0.0409). – The crystal structure data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-114826 (**10**) and -114825 (**11**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, G.B. [Fax: int. code + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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