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o-Hydroxyarylphosphines and diphosphines: metallation–rearrangement versus P–O reduction of o-halogenoaryloxyphosphines by sodium [1]

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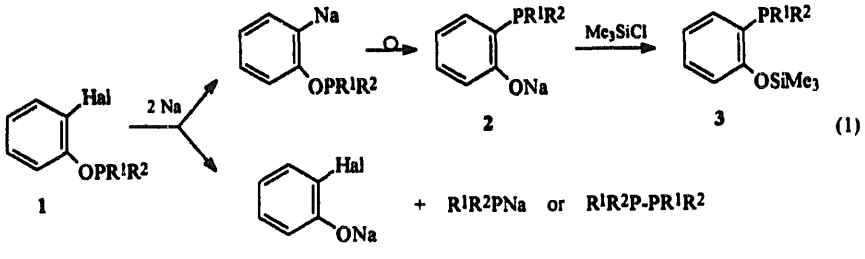
Abstract

o-Bromo- and o-chloroaryloxyphosphines **1** may react with sodium in two competing ways: (i) metal halogen exchange followed by rapid intramolecular 1,3-rearrangement to give sodium o-hydroxylato-arylphosphines **2**, later converted to their $OSiMe_3$ derivatives **3**, and (ii) reductive cleavage of the P–O bond to give diphosphines **4** or phosphides. The o-metallation is preferred with the more reactive bromides and bulky phosphino substituents or screened P–O bonds by substituents at 6-position. The reduction is favoured in the case of the less reactive aryl chlorides, small alkyl and flat phenyl substituents at phosphorus. Mixtures of *meso*- and *rac*-diphosphines are formed from asymmetric derivatives ArOPRR'. The *meso*-isomer of 1,2-di(tert-butyl)-1,2-diphenyldiphosphine is preferred.

Keywords: Hydroxyarylphosphines; Metallation; Rearrangement; Diphosphines; Sodium; Ligand

1. Introduction

PO chelate complexes are of current interest in catalysis [1]. Phosphinophenolate complexes have been obtained by thermolysis of complexes of phosphinoaryl methylethers [2] or from free hydroxy derivatives [3,4]. o-Hydroxyarylphosphines were formed by deprotection of suitable o-phosphinoaryl ethers or trimethylsilyl ethers **3** [3–6], which in turn were synthesized from o-lithiated aryl ethers and Ph_2PCl [3–5] or dilithium reagents and successive reaction with chlorophosphines and chlorotrimethylsilane [6]. We have investigated an alternative access to **3** consisting in the generation of o-metallated aryl-OP derivatives which undergo rapid intramolecular rearrangement to give **2** [7,8]. The direct metallation of o-halogenoaryloxyphosphines with sodium was used because of the slow reaction with lithium and rapid nucleophilic substitution of P(III)–O by butyllithium. Limitations arise, however, from competing reductive cleavage of the P–O bond. Increasing steric screening by P-alkyl or P-dialkylamino groups restrains or prevents the reduction. In contrast, diphenylphosphino derivatives are completely reduced to tetraphenyldiphosphine and sodium-o-halogenophenolate:



Yield of **3** (R^1R^2P): Ph_2P << Me_2P << Et_2P < t-BuMeP ~ i-Pr_2P < $(Me_2N)_2P$

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[1] In memory of Professor Hidemasa Takaya († 4 October 1995).

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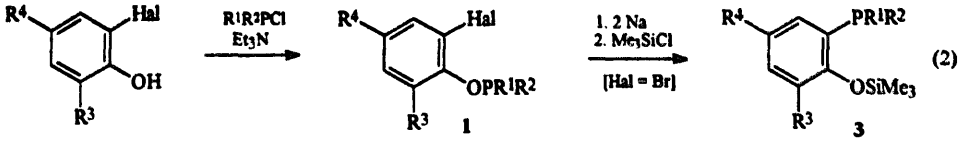
P-asymmetric alkyl-phenyl and dimethylamino-phenyl P–O derivatives, potential precursors of P-asymmetric and P-secondary o-phosphinophenols respectively, bear substituents of both types and have not yet been investigated. The ratio of metallation and reduction can hardly be estimated by previous knowledge. In this work we report on a systematic study of the behaviour of O-*tert*-butylphenylphosphino and O-dimethylaminophenylphosphino derivatives of o-chlorophenol, 2-bromo-4-methyl-phenol, 2-bromo-4,6-di(tert-3-butyl)-phenol and 1-bromo-naphth-2-ol towards sodium. The resulting phosphinoaroxylates **2** are converted into and isolated as trimethylsilyl ethers **3**.

2. Results and discussion

o-Chloro- and o-bromoaryl esters of tert-butylphenylphosphinous acid and of phenylphosphonous acid dimethylamide **1a–i** are obtained in good yields from the o-halogenophenoles or o-bromonaphthol and chlorophosphines in the presence of excess triethylamine:

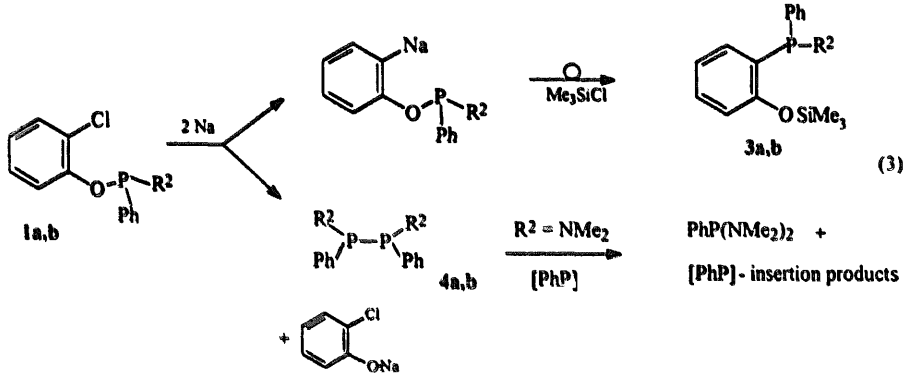


(2)

	a	b	c	d	e	f
R^1	Ph	Ph	Ph	Ph	Ph	NMe_2
R^2	*t*-Bu	NMe_2	*t*-Bu	NMe_2	NMe_2	NMe_2
R^3	H	H	H	H	*t*-Bu	*t*-Bu
R^4	H	H	Me	Me	*t*-Bu	*t*-Bu
Hal	Cl	Cl	Br	Br	Br	Br

The reaction of sodium with o-chlorophenyl esters of tert-butylphenylphosphinous acid and of phenylphosphonous acid dimethylamide, **1a** and **1b** respectively, at 20–40°C leads to a competing attack at the C–Cl and the P–O unit (Eq. (3)). Intensities of ^{31}P NMR signals in the crude mixture indicate similar quantities of diphosphines and of o-metallation–rearrangement products. Yields of isolated **3a** and **3b** are low (20–25%). Working at lower temperatures (0–5°C) usually favours the o-metallation [7] but reduces substantially the rate of reaction. Use of an ultrasound bath, which should accelerate the reaction, was not found to improve the results.

The steric screening by one tert-butyl or one dimethylamino group is not sufficient to retard the reduction so strongly that the metal–halogen exchange becomes dominant. The flat phenyl groups at phosphorus pretend to have a steric screening less than methyl in these reactions and seem to favour the reduction by weak interactions of the π-system with the metal surface. This is also consistent with our earlier observation of complete reduction of o-$HalC_6H_4OPPh_2$ (Hal = Cl, Br), while o-$HalC_6H_4OPMe_2$ gave at least a small yield of o-Me_2P–C_6H_4ONa (15% of O-silylation product) [7].



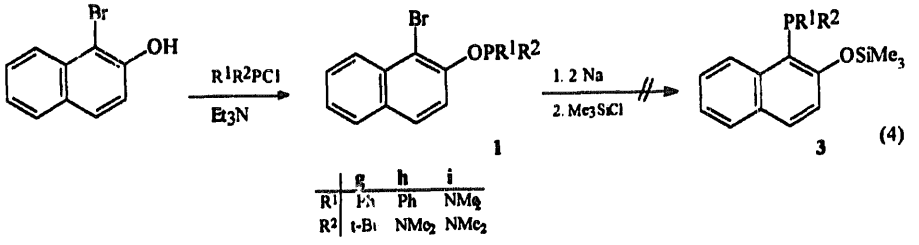
(3)

The main product isolated in the above reaction with **1a** is a diastereoisomeric mixture of 1,2-di(tert-butyl)-1,2-diphenyl-diphosphine **4a** (^{31}P NMR $\delta_{meso} = -3.9$, $\delta_{rac} = +2.8$ ppm, ca. 85:15%). The major *meso* isomer shows the ^{1}H NMR signal of ^{t}Bu at higher field ($\delta =$ 0.83 ppm) than the minor *rac* form ($\delta = 1.21$ ppm). The assignment of the diastereoisomers is based on the $N(PC) = |{}^{1}J_{PC} + {}^{2}J_{PC}|$ values of the α-carbons in ^{13}C NMR, as described in Refs. [9,10]. In the *meso* form both α-carbons have average $N(PC)$ values since both *gauche* rotamers are equivalent. In the *rac* diastereoisomers the *gauche* conformations are different, and according to Ref. [11] the bulky groups are preferrably arranged in *gauche* position to the lone pairs (Fig. 1). The dominance of the *meso* diastereoisomers of **4a** is remarkable since in (^{t}BuAlkP)$_2$ *rac* isomers are strongly preferred [11]. An X-ray structure analysis confirms qualitatively the *trans* conformer of the *meso* form with two molecules per unit cell. One phosphorus atom is disordered so that no sufficient quantitative refinement could be achieved to give detailed data.

The metallation–rearrangement product **3b** (^{31}P NMR $\delta = 56.0$ ppm) and the diastereoisomers of the diphosphine **4b** (^{31}P NMR $\delta = 57.9$, 56.7 ppm) were observed in a ratio of about 105:50:45 in the crude mixture resulting from the reaction of **1b** with sodium. Additionally, some unreacted **1b** and lower amounts of impurities were detected. **4b** is completely decomposed in distillative work-up to give an ill-defined, colourless solid with broad ^{31}P NMR multiplets at −5 to −3 [(PhP)$_5$ range] and ca. 48 ppm ($PhPNMe_2$ units), as well as a strong sharp signal at 100 ppm [$PhP(NMe_2)_2$]. This indicates a heterolytic decay via phenylphosphinidene and formation of insertion products as first described in Ref. [12]. For comparison, pure **4b** (^{31}P NMR $\delta = 58.1$, 56.5 ppm, diastereoisomer ratio 52:48) was synthesized from $PhP(NMe_2)Cl$ and sodium in toluene/ether in good yield. It decomposes slowly at room temperature.

In further investigations, we used o-bromoaryl derivatives to improve the chemoselectivity in the reactions with sodium and to prefer the metal–halogen exchange (Eq. (2)). Indeed, the metallation–rearrangement products were obtained in reasonable to good yield at 20–40°C in dioxane/ether, increasing in the order **3c**(40%) < **3d**(58%) < **3e**(76%) < **3f**(89%). The improved yield of **3d** compared with **3c** may be due to the application of ultrasound and lower temperature. The reduction was not completely suppressed for **3c–e**. **3c** is slightly contamined by **4a** (10%) when worked-up by distillation. **3d** and **3e** can easily be separated from byproducts on distillation. Another side reaction, diminishing the yield especially of **3c**, is the metal–hydrogen exchange of the intermediate o-sodiumarylphosphinite. The latter probably reacts with the solvent dioxane due to a relatively slow rate of rearrangement of the tert-butyl derivative. This is similar to reactions of o-bromophenyl trimethylsilyl ether with Na, in which 50–60% of intermediate arylsodium undergoes metal–hydrogen exchange prior to rearrangement if dioxane is used as solvent [13]. Use of toluene in place of dioxane avoids this problem. The high yields of the 4,6-di-tert-butylphenyl derivatives **3e** and **3f** can be attributed to sterical hindrance of the P–O unit by the tert-butyl substituent in 6-position. This prevents reduction and generally favours the o-metallation–rearrangement-synthesis of o-phosphinophenol derivatives with substituents in 6-position compared with the other methods mentioned above.

Attempts to prepare 1-phosphino-naphth-2-ol trimethylsilyl ethers in an analogous way from 1-bromonaphth-2-oxy phosphorus(III) derivatives **1g–i** (Eq. (4)) have not been successful. Even the reaction of sodium with **1i**, containing an $arylOP(NMe_2)_2$ group which in o-$ClC_6H_4OP(NMe_2)_2$ is not reduced and gives high yields of the corresponding phosphinophenolate, furnished only traces of the expected phosphinonaphthol **3i** (^{31}P NMR $\delta = 106.2$ ppm, intensity ca. 5–10%). Signals for two unsymmetrical diphosphines (^{31}P NMR **A** $\delta = 53.16$, 4.14, $J_{pp} = 263$ Hz, int. 120.80; **B** ($\delta = 50.4$, 7.19, $J_{pp} = 294$ Hz, int. 30:30), a P=P derivative (^{31}P NMR **C** $\delta = 77.0$, 20.97, $J_{pp} = 436$ Hz) and further PN compounds [44.33, 97.08, 100.09 $arylP(NMe_2)_2$, 139.11 $arylOP(NMe_2)_2$] were observed instead of $(Me_2N)_2P$–$P(NMe_2)_2$. These products were not studied in detail. An alternative synthesis of the phosphinonaphthol derivatives **3g–i** is described separately [14].



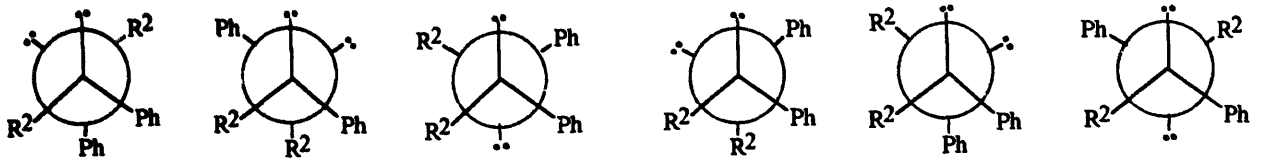


Fig. 1. Conformations of unsymmetrical diphosphines 4 and preferred structure of 4a.

3. Experimental

Solvents were dried over appropiate drying agents and freshly distilled under argon, Me_3SiCl was recondensed prior to use. All reactions were carried out under an argon atmosphere using standard Schlenk techniques. NMR data were recorded on an multi-nuclear FT-NMR instrument ARX300 (Bruker) at 300.1 (^{1}H), 121.5 (^{31}P) and 75.5 MHz (^{13}C). References are TMS or indirectly CH_2Cl_2 for ^{1}H and ^{13}C spectra, H_3PO_4 (85%) for ^{31}P spectra. (Assignment numbers of atoms follow the nomenclature.) Mass spectra (EI, 70 eV) were recorded on a single focussing sector-field mass spectrometer AMD40 (Maurer).

3.1. Chloro-tert-butylphenylphosphine (modification of Ref. [15])

A solution of tert-butylmagnesium chloride, prepared from 50 g (2.1 mol) of Mg and 230 ml (2.1 mol) of tert-butyl chloride in 700 ml of ether, was added dropwise at 0°C to a solution of 253 g (1.4 mol) of dichlorophenylphosphine in 200 ml of petroleum ether. The mixture was then heated under reflux (2 h), filtered and evaporated. The pure product was isolated by rectification at a spinning band column, yielding 168 g (59%) colourless liquid, b.p. 68°C/0.015 Torr. ^{31}P NMR ($CDCl_3$): δ 108.0 ppm. ^{1}H NMR ($CDCl_3$): δ 1.08 (d, J = 13.8 Hz, 9H, ^{t}Bu), δ 7.4–7.7 (m, 5H, aromatic H) ppm.

3.2. General procedure for the preparation of (o-haloaroxy)phosphines 1a–i

A solution of 10 to 200 mmol of chlorophosphine in 20 to 400 ml of petroleum ether was added dropwise to a stirred solution of the equimolar quantity (10 to 200 mmol) of 2-hydroxyaryl halides and a slight excess (1.05 equiv.) of triethylamine in 40 to 500 ml of ether. After overnight stirring the precipitate was filtered off, thoroughly washed and the solvent removed from the filtrate. The residue was distilled at low pressure.

1a: 9.8 g (49 mmol) of ClP(^{t}Bu)Ph and 6.4 g of 2-ClC_6H_4OH (50 mmol) gave 12.6 g (88%), b.p. 116–117°C/0.05 Torr. ^{31}P NMR ($CDCl_3$): δ 130.8 ppm. Anal. Found: C, 65.32; H, 6.37. $C_{16}H_{18}ClOP$ (292.75) Calc.: C, 65.65; H, 6.20%.

1b: 18.7 g of ClP(NMe_2)Ph and 12.9 g of 2-ClC_6H_4OH (100 mmol) yielded 22.9 g (82%), b.p. 117–118°C/0.4 Torr. ^{31}P NMR ($CDCl_3$): δ 136.8 ppm. ^{1}H NMR ($CDCl_3$): δ 2.77 (d, J = 9.6 Hz, 6H, NMe_2), 7.0–7.8 (m, 9H, arylH) ppm. Anal. Found: C, 60.66; H, 5.75. $C_{14}H_{15}ClNOP$ (279.71) Calc.: C, 60.12; H, 5.41%.

1c: 2.0 g of ClP(^{t}Bu)Ph and 1.9 g of 2-Br-4-MeC_6H_3OH (10 mmol) yielded 2.9 g (83%), b.p. 132–134°C/0.05 Torr, solidifying on distillation, m.p. 57–59°C. ^{31}P NMR ($CDCl_3$): δ 130.5 ppm. Anal. Found: C, 58.55; H, 6.03. $C_{17}H_{20}BrOP$ (351.22) Calc.: C, 58.14; H, 5.74%.

1d: From 37.5 g of ClP(NMe_2)Ph and 37.4 g of 2-Br-4-MeC_6H_3OH (200 mmol) was obtained 53.4 g (79%), b.p. 125–126°C/0.001 Torr. ^{31}P NMR ($CDCl_3$): δ 136.4 ppm. ^{1}H NMR ($CDCl_3$): δ 2.28 (s, 3H, 4-Me), 2.74 (d, J = 9.6 Hz, 6H, NMe_2), 6.9–7.1 (m, 2H, arylH), 7.35–7.5 (m, 4H, arylH), 7.7–7.8 (m, 2H, arylH) ppm. MS (70 eV): m/z 339 (40%, M^+), 164 (100%). Anal. Found: C, 53.02; H, 5.13. $C_{15}H_{17}BrNOP$ (338.18) Calc.: C, 53.27; H, 5.07%.

1e: 18.75 g of ClP(NMe_2)Ph and 28.5 g of 2-Br-4,6-(^{t}Bu)$_2C_6H_2OH$ gave 41.5 g (95%) of colourless solid, m.p. 93–95°C, distilling as viscous oil, b.p. 160–166°C/0.001 Torr. ^{31}P NMR ($CDCl_3$): δ 132.6 ppm. ^{1}H NMR ($CDCl_3$): δ 1.29 (s, 9H, CMe_3), 1.44 (s, 9H, CMe_3), 2.66 (d, J = 8.3 Hz, 6H, NMe_2), 7.32 (d, J = 2.5 Hz, 1H, aryl-H), 7.35–7.44 (m, 4H, aryl-H), 7.71 ("tt", 2H, o-arylH) ppm. Anal. Found: C, 60.40; H, 7.02. $C_{22}H_{31}BrNOP$ (436.37) Calc.: C, 60.55; H, 7.16%.

1f: 15.6 g of $ClP(NMe_2)_2$ and 28.8 g of 2-Br-4,6-(^{t}Bu)$_2C_6H_2OH$ (101 mmol) gave 38.7 g (95%) viscous liquid, b.p. 113–115°C/0.001 Torr. ^{31}P NMR ($CDCl_3$): δ 138.8 ppm. ^{1}H NMR ($CDCl_3$): δ 1.27 (s, 9H, CMe_3), 1.38 (s, 9H, CMe_3), 2.67 (d, J = 8.4 Hz, 12H, NMe_2), 7.27 (d, J = 2.5 Hz, 1H, aryl H), 7.38 (d, J = 2.5 Hz, 1H, aryl H) ppm. Anal. Found: C, 53.35; H, 8.34. $C_{18}H_{32}BrN_2OP$ (403.34) Calc.: C, 53.60; H, 8.00%.

1g: 2.0 g of ClP(^{t}Bu)Ph and 2.2 g of 1-bromonaphth-2-ol (10 mmol) yielded 2.1 g (54%), b.p. 163–164°C/0.05 Torr, m.p. 62–63°C. ^{31}P NMR ($CDCl_3$): δ 131.0 ppm. Anal. Found: C, 62.35; H, 5.53. $C_{20}H_{20}BrOP$ (387.26) Calc.: C, 62.03; H, 5.21%.

1h: 1.9 g of $ClP(NMe_2)Ph$ and 2.2 g of 1-bromonaphth-2-ol (10 mmol) furnished 2.4 g (64%) viscous liquid, b.p. 166–174°C/0.05 Torr. ^{31}P NMR ($CDCl_3$): δ 137.0 ppm. Anal. Found: C, 57.35; H, 4.35. $C_{18}H_{17}BrNOP$ (374.22) Calc.: C, 57.77; H, 4.58%.

1i: 16.9 g of $ClP(NMe_2)_2$ and 24.3 g of 1-bromonaphth-2-ol (11 mmol) give in 200 ml Et_2O/16 ml Et_3N 21.4 g (57%) viscous oil, b.p. 154–156°C/0.001 Torr. ^{31}P NMR ($CDCl_3$): δ 136.6 ppm. ^1H NMR ($CDCl_3$): δ 2.71 (d, $J = 9.6$ Hz, 12H, NMe_2), 7.34 (dd, $J = 8.9$, 2.4 Hz, H3), 7.36 (m, J ca. 8.1, 6.9, 1.2 Hz, H6), 7.52 (m, J ca. 6.9, 8.5, 1.4 Hz, H7), 7.69 (d, $J = 8.9$ Hz, H4), 7.73 (dm, $J = 8.1$, ca. 0.6 Hz, H5), 8.21 (dd, $J = 8.5$, 0.9 Hz, H8) ppm. ^{13}C NMR ($CDCl_3$): δ 37.1 (d, $J = 17.8$ Hz, NMe_2), 111.8 (d, $J = 2.3$ Hz, C_q1), 119,8 (d, $J = 17.5$ Hz, C3), 124.4, 126.2, 127.3, 127.9, 128.4, 130.2 (C_q5), 133.2 (C_q10), 150.2 (d, $J = 5.8$ Hz, C_q2) ppm. MS (70 eV, EI): m/z 342/340 (4%, M^+), 298/296 (4%, M^+-NMe_2), 119 (100%, $P(NMe_2)_2^+$), 76 (99.9%, $HP{=}NMe_2^+$), 60 (37%, $P{\equiv}NMe^+$). Anal. Found: C, 50.05; H, 5.63. $C_{14}H_{18}BrN_2OP$ (341.19) Calc.: C, 49.28, H, 5.32%.

3.3. Reactions of (o-haloaroxy)phosphines 1a–f with sodium followed by $ClSiMe_3$

3.3.1. Reaction of o-chlorophenoxy-tert-butylphenylphosphine (1a) with sodium to give 3a and 4a

A sodium dispersion (2.2 g, 96 mmol) was prepared under argon by stirring the molten metal in 100 ml of boiling dioxane and then allowed to cool at about 40°C. A solution of 12.6 g (43 mmol) of **1a** in 50 ml of ether was placed into the funnel and about 10 ml was added to the suspension with vigorous stirring. When the reaction started, the remainder of the solution of **1a** was added dropwise at 30 to 35°C. It was refluxed for 2 h, stirred overnight, cooled in an ice-water bath and 6 ml (48 mmol) of chlorotrimethylsilane was added. After stirring for 0.5 h the mixture was filtered and washed with ether. Colourless crystals of diphosphine **4a** were deposited after removal of the solvent under vacuum. Filtering and washing with pentane/ether gave 2.9 g (41%) *meso/rac*-**4a** m.p. 76–78°C. The evaporation of the mother liquor and the distillation of the residue yielded 3.5 g (25%) **3a**, b.p. 130–137°C/0.02 Torr.

3a: ^{31}P NMR ($CDCl_3$): δ 4.3 ppm. ^1H NMR ($CDCl_3$): δ 0.12 (s, 9H, $SiMe_3$), 1.26 (d, $J = 12.3$ Hz, 9H, CMe_3), 6.8–7.6 (m, 9H, aromatic H) ppm. Anal. Found: C, 69.12; H, 8.17. $C_{19}H_{27}OPSi$ (330.48) Calc.: C, 69.05; H, 8.23%.

meso/rac-**4a**: ^{31}P NMR ($CDCl_3$): δ −3.9, 2.8 ppm (int. 49:9). ^1H NMR ($CDCl_3$): δ 0.83 (t, $N = 12.8$ Hz, ^tBu, int. 85%) 1.21 (t, $N = 13.8$ Hz, ^tBu, int. 15%), 7.2–7.9 (m, aromatic H) ppm. ^{13}C NMR ($CDCl_3$): *major isomer* δ 29.7 (t, $N = 17.5$ Hz, CMe_3), 31.5 (t, $N = 14.0$ Hz, $PCMe_3$), 127.8 (t, $N = 8.2$, m-C), 129.5 (s, p-C), 135.9 (t, $N = 12.9$ Hz, i-C), 137.0 (t, $N = 29.5$ Hz, o-C); *minor isomer* δ ca. 29.7 (CMe_3 superimposed, probably s), 30.7 (s, $N < 2$ Hz, CMe_3), 127.1 (t, $N = 8.2$ Hz, m-C), 128.4 (s, p-C), 135.3 (t, $N = 28.1$ Hz, i-C), 137.3 (t, $N = 24.7$ Hz, o-C) ppm. MS (70 eV): m/z 330 (34%, M^+), 274 (36%, $M-C_4H_8$), 273 (35%, M–Bu), 218 (54%, $Ph_2P_2H_2$), 217 (100%, Ph_2P_2H), 185 (28%, Ph_2P), 139 (74%, PhP_2), 109 (16%, PhPH), 57 (42%). $C_{20}H_{28}P_2$ (330.39).

3.3.2. Reaction of (o-chlorophenyloxy)dimethylaminophenylphosphane (1b) with sodium

14.0 g (50 mmol) of **1b** in 50 ml of ether and 2.5 g (110 mmol) of sodium in 80 ml of dioxane were reacted for 1 h at 35°C, stirred overnight, treated with 6.3 ml (50 mmol) of $ClSiMe_3$, filtered and the solvent removed in vacuum. [^{31}P NMR: δ 56.0 (**3b**), 56.7, 57.9 (**4b**), 136.8 (**1b**), 70.1 ppm (unknown)]. During distillation in vacuum the mixture decomposed. The higher boiling viscous oil (130–140°C/0.02 Torr) formed within two weeks 2.4 g of an impure solid material, m.p. 131–132°C (dec.) after extraction of soluble material with a little ether. ^{31}P NMR: oil δ 29.3, 27.6 (rel. int. 1), 15.8 (rel. int. 1/2), 100 ppm (rel. int. 1/3). $^{31}P\{^1H\}$ NMR ($CDCl_3$): ether treated solid δ −3 to −5 (m), 100.3 (s), impurities at 146.1, 70.0, 29.3, 27.6, 15.8, −47.8 ppm. ^1H NMR ($CDCl_3$): δ 2.75 (d, $J = 9.3$ Hz, NMe_2), 2.62 (d, $J = 9.9$ Hz, NMe_2), 2.47 (t, $N = 12.0$ Hz, $PPNMe_2$), 2.86 (t, $N = 12.0$ Hz, $PPNMe_2$), 7.3–7.5 (m, aromatic H) ppm. {$(PhP)_5$: m.p. 148°C [16], $(PhMe_2NP)_2$: m.p. 85°C, b.p. 150°C/0.5 Torr) [12]}.

3.3.3. 2-(tert-Butylphenylphosphino)-4-methylphenyl trimethylsilylether 3c

About 10 ml of a solution of 5.9 g (16.8 mmol) of **1c** in 50 ml of ether was added to a suspension of sodium (0.8 g, 34.8 mmol) in dioxane (80 ml). When the reaction started (appearance of a blue–violet colour on the sodium surface) the remaining solution of **1c** was added at room temperature and stirred overnight. The reaction mixture was then cooled in an ice-water bath and 3 ml (24 mmol) of chlorotrimethylsilane was added. After stirring for 0.5 h at room temperature the resulting slurry was filtered and washed thoroughly. The solvent was evaporated and the residue fractionally distilled to give 2.3 g of **3c**, b.p. 118–121°C/0.08 Torr, contaminated by ca. 10% ($^tBuPhP)_2$ (**4a**).

3c: ^{31}P NMR ($CDCl_3$): δ 4.5 ppm. ^1H NMR ($CDCl_3$): δ 0.06 (s, 9H, $SiMe_3$), 1.22 (d, $^3J = 12.3$ Hz, 9H, CMe_3), 2.29 (s, 3H, 4-Me), 6.6–7.6 (m, 8H, aromatic H) ppm. The first fraction at b.p. 60–70°C/0.08 Torr was found to be 4-methylphenyl trimethylsilylether (1.5 g, 50%). ^1H NMR ($CDCl_3$): δ 0.27 (s, 9H, $SiMe_3$), 2.30 (s, 3H, 4-CH_3), 6.76 and 7.05 (AA'BB', $J_{AB} \approx 6.6$ Hz, 4H, aromatic H) ppm.

3.3.4. 2-(Dimethylaminophenylphosphino)-4-methylphenyl trimethylsilyl ether (3d)

A dispersion of 1.9 g (83 mmol) of sodium in 80 ml of dioxane was stirred and sonificated (120 W Bandelin ultrasonic bath) while a solution of 12.6 g (37 mmol) of **1d** in 40 ml of ether was added dropwise within 30 min at 10°C (after start). The stirring and sonification were continued for 6 h. Addition of 5 ml (40 mmol) of chlorotrimethylsilane and work-up, as described above, yielded 7.1 g (58%) **3d**, b.p. 128–130°C/0.01 Torr, m.p. 61–65°C. ^{31}P NMR ($CDCl_3$): δ 57.1 ppm. ^{1}H NMR ($CDCl_3$): δ 0.18 (s, 9H, $SiMe_3$), 2.38 (s, 3H, 4-Me), 2.72 (d, J = 9.3 Hz, 6H, NMe_2), 6.67 (dd, J = 8.0, 4.8 Hz, H6), 7.04 (dm, J = 8.0, 2.3, ca. 0.8 Hz, H5), 7.09 (dd, J = 4.3, 2.3 Hz, H3), 7.27–7.37 (m, 5H, phenyl) ppm. Anal. Found: C, 65.61; H, 8.22. $C_{18}H_{26}NOPSi$ (331.46). Calc.: C, 65.22; H, 7.91%.

3.3.5. 4,6-Di-tert-butyl-2-(dimethylaminophenylphosphino)phenyl trimethylsilylether 3e

To a suspension of 2 g (87 mmol) of sodium in 80 ml of dioxane was added 13.7 g (31 mmol) of **1e** in 40 ml of ether and the mixture refluxed for 16 h. On cooling to 10–20°C, 10 ml of Me_3SiCl was dropped into the suspension. The mixture was filtered, the precipitate washed with ether, the solvent evaporated and the remainder fractionated in vacuum. At 130–140°C/0.005 Torr distillation gave 10.3 g (76%) viscous, pale-yellow **3e**. ^{31}P NMR ($CDCl_3$): δ 57.4 ppm. ^{1}H NMR ($CDCl_3$): δ 0.30 (d, $^6J_{PH}$ = 2.0 Hz, 9H, $SiMe_3$), 1.24 and 1.41 (s, 2 × 9H, 4,6-CMe_3), 2.59 (d, $^3J_{PH}$ = 9.2 Hz, 6H, NMe_2), 7.09 (dd, J = 2.6, 3.8 Hz, H3), 7.35 (dd, J = 2.6, 0.4 Hz, H5), 7.3–7.4 (m, 5H, phenyl) ppm. ^{13}C NMR ($CDCl_3$): δ 2.6 (d, $^5J_{PC}$ = 11.5 Hz), 30.6 and 31.5 (2s, 4,6-CMe_3), 34.24 (s, C_qMe_3), 34.98 (d, J = 1.2 Hz, C_qMe_3), 42.1 (d, J = 15.3 Hz, NMe_2), 125.1 (s, C5), 127.3 (s, br, C3), 127.7 (d, J = 4.5 Hz, m-C), 127.7 (s, p-C), 128.9 (d, J = 19.3 Hz, C_q2), 131.2 (d, J = 17.1 Hz, o-C), 139.3 (d, J = 1.2 Hz, C_q6), 139.7 (d, J = 11.1 Hz, i-C), 142.5 (s, C_q4), 153.9 (d, J = 22.9 Hz, C_q1) ppm. Anal. Found: C, 69.95; H, 9.53. $C_{25}H_{40}NOPSi$ (429.66) Calc.: C, 69.89; H, 9.38%.

3.3.6. 4,6-Di-tert-butyl-2-[bis(dimethylamino)phosphino]-phenyl trimethylsilylether 3f

37.9 g (94 mmol) of **1f** in 80 ml of ether was dropped into a suspension of 4.5 g (196 mmol) of Na in 200 ml of dioxane at such a rate that slight refluxing was maintained. After heating for a further 10 h, 15 ml of $ClSiMe_3$ was added dropwise (ca. 10°C) and allowed to react completely at 20°C over 5 h. The precipitate was filtered off and most of the solvent removed in vacuum. Within a few days solid **3f** was formed which recrystallized from a little pentane. Yield 33.5 g (89%), m.p. 35–40°C (pentane). ^{31}P NMR ($CDCl_3$): δ 99.10 ppm. ^{1}H NMR ($CDCl_3$): δ 0.33 (d, $^6J_{PH}$ = 1.3 Hz, 9H, $SiMe_3$), 1.30 and 1.38 (2s, 2 × 9H, 4,6-^{t}Bu), 2.59 (d, J = 8.8 Hz, 12H, NMe_2), 7.22 (dd, J = 2.5, 3.8 Hz, H3), 7.29 (dd, J = 2.5, 1.2 Hz, H5) ppm. ^{13}C NMR ($CDCl_3$): δ 2.4 (d, J = 10.2 Hz, $SiMe_3$), 30.8 and 31.62 (2s, 4,6-CMe_3), 34.2 and 35.0 (2s, 4,6-CMe$_3$), 40.8 (d, J = 15.2 Hz, NMe_2), 124.7 (s, C5), 126.5 (d, J = 6.2 Hz, C2), 130.9 (d, J = 12.8 Hz, C3), 139.4 (s, C6 or 4), 142.23 (s, C4 or 6), 153.0 (d, J = 17.6 Hz, C1) ppm. MS (70 eV): m/z 396 (40%, M^+), 353 (30%), 352 (100%, M^+–NMe_2), 309 (53%, 352-MeNCH_2), 263 (42%, 352-$SiMe_3$), 73 (23%). Anal. Found: C, 63.75; H, 10.22. $C_{21}H_{41}N_2OPSi$ (396.62) Calc.: C, 63.59; H, 10.42%.

3.4. 1,2-Bis(dimethylamino)-1,2-diphenyl-diphosphine 4b from sodium and ClP(Ph)NMe$_2$

To a sodium dispersion (0.7 g, 30 mmol), prepared in 20 ml of boiling toluene and diluted with 50 ml of ether, was added about 1 ml of 4.85 g (25.9 mmol) of $ClP(Ph)NMe_2$ without stirring. After the reaction started, the remainder was added dropwise (bath 20–25°C), the mixture stirred for one day and filtered. To destroy a small content of phosphide (yellow) 1 ml of $ClSiMe_3$ was added. After 1–2 min the solvent and unreacted $ClSiMe_3$ were removed in vacuum. ^{31}P and ^{1}H NMR showed a slightly impure diastereoisomer mixture (48:52%) of **4b**. Within one day the material became solid and was then recrystallized from hexane. Yield 2.25 g (62%), m.p. 72–75°C (85°C [12]). ^{31}P NMR ($CDCl_3$): δ 58.1, 56.5 (54:46) ppm. ^{1}H NMR (C_6D_6): δ 2.57 ("t", N = 13.0 Hz, 48% NMe_2), 2.75 ("t", N = 9.6 Hz, 52% NMe_2), arylH 6.98–7.17 (m, 4H), 7.21–7.29 ("t"m, 2H), 7.58–7.63 ("d"m, 1H), 7.75–7.81 ("d"m, 1H). ^{13}C NMR (C_6D_6): δ 43.2, 43.4 (2t, N = 18.2, 19.3 Hz, NMe_2), 128.5 (t, N = 5.2 Hz, m-C), 131.9, 132.5 (2t, N = 24.7, 25.8 Hz, o-C), 140.0, 141.4 (2t, N = 4.1, 9.7 Hz, i-C); higher-field m-C and p-C are superimposed by C_6D_6 signals, higher-field signals of each pair are slightly more intensive and possess smaller N. **4b** decomposes slowly at room temperature, after a few days signals of $PhP(NMe_2)_2$ and other decomposition products are observed.

3.5. Crystal structure analysis of 4a

The refinement is not sufficient for full publication because of the disorder of one phosphorus atom. The *trans–meso* conformation is, however, confirmed qualitatively. Data were collected with Mo Kα radiation (λ = 71.073 pm) on a Siemens R3 diffractometer at 143(2) K, crystal size 0.40 × 0.40 × 0.25 mm^3, triclinic, space group $P\bar{1}$, unit cell dimensions a = 839.8(4) pm; b = 973.4(4) pm, c = 1249.9(4) pm, α = 101.50(3)°, β = 105.97(3)°, γ = 95.36(3); data/restraints/parame-

ters 3328/160/205, refinement by full-matrix least-squares on F^2, goodness-of-fit at F^2 1.060, final R indices $[I > 2\sigma(I)]$ $R_1 = 0.0879$, $wR_2 = 0.1772$, R indices (all data) $R_1 = 0.1506$, $wR_2 = 0.2299$.

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