Synthesis, Crystal Structure, Dynamic Behavior and Reactivity of Dinaphtho[2,1-*b*:1′,2′-*d*]phospholes and Related Atropisomeric Phosphacyclic Derivatives

Serafino Gladiali,* Antonio Dore, and Davide Fabbri

Dipartimento di Chimica, Università di Sassari, via Vienna 2, I-07100 Sassari, Italy

Ottorino De Lucchi

Dipartimento di Chimica, Università di Venezia, Dorsoduro 2137, I-30123 Venezia, Italy

Giovanni Valle[1]

Centro Studi Biopolimeri del C. N. R., via Marzolo 1, I-35131 Padova, Italy

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7-Phenyldinaphtho[2,1-*b*:1′,2′-*d*]phosphole (**1b**) has been prepared by reaction of dichlorophenylphosphine either with 2,2′-dilithio-1,1′-binaphthalene or with bis-dialin **7**. In the latter case the relevant tetrahydro derivative **8** is formed at the same time. Displacement of the phenyl substituent in **1b** by alkyl groups can be accomplished through a dephenylation–alkylation protocol involving a lithium-promoted phosphole anion formation. By this way the unsubstituted phosphole **1a** and a variety of alkyl-substituted derivatives have been prepared. The X-ray crystal structure of **1b** shows an intracyclic C–P–C angle of 89.3° indicating that phosphole ring is strained. Alkylphospholium iodides **4** undergo ready ring opening by reaction with $LiAlH_4$ or other nucleophiles under mild conditions affording with fair diastereoselectivities (2-(1,1′-binaphthylyl))-substituted phosphines **5** or phosphines oxides **6**, respectively. Dinaphthophospholes **1** are fluxional at ambient temperature because of the rapid interconversion of the atropisomeric conformers. Line shape analysis of the variable temperature NMR spectra lead to estimation of an energy barrier of 55–60 kJ mol^{-1} for this process. Fluxionality is maintained both when the phosphorus center is tetrasubstituted, like in the relevant oxides **2**, and when it is coordinated to a transition metal, like in the Pd-complexes **10**. On the contrary, P-substituted dinaphthophosphepines **9** do not undergo atropisomerization even well above room temperature and can be successfully resolved under ambient conditions. The crystal structures of the *P*-phenyl-substituted derivatives **1b**, **8** and **9a**, as determined by X-ray diffraction, show remarkable differences in the relative disposition of the naphthalene rings.

Introduction

The atropisomeric 1,1′-binaphthalene core is the parent framework of a steadily increasing family of highly efficient chiral auxiliaries which have found several applications in a variety of asymmetric reactions both stoichiometric and catalytic.[2] Among these, phosphorus derivatives play a prominent role because they are among the most efficient chiral inducers in transition metal-catalyzed enantioselective reactions. Asymmetric hydrogenation of olefins and ketones by Rh(I) and Ru(II) catalysts with BINAP[3] and the highly enantioselective hydroformylation of vinylarenes by Rh(I) complexes containing a mixed phosphino–phosphito binaphthalene-core ligand[4] provide outstanding examples of the efficiency of these ligands.

Phospholes and phospholanes are emerging classes of chiral auxiliaries which in the last five years have been introduced in asymmetric catalysis with remarkable success.[5] Good to excellent enantioselectivities have been recorded in the asymmetric hydrogenation and hydroformylation of olefins, respectively, with rhodium[6] and platinum–tin catalysts[7] containing enantiopure phospholes or phospholanes as bidentate ligands. In the latter case, sharp improvements of enantio- and regioselectivities with respect to chelating diphosphines of closely related structure were observed.

These considerations stimulated our interest toward binaphthalene-core phosphacyclic derivatives. These compounds encompass a unique combination of some of the main features which are assumed to be at the basis of the efficiency of the above reported ligands: axial chirality, C_2 symmetry, and an endocyclic phosphorus donor center. A few dinaphthophospholes, the first members of this new family of atropisomeric ligands, have been quite recently synthesized in independent way by us[8] and others,[9] and some aspects of their rich chemistry have been pointed out in a further paper by some of us.[10] The details of these studies and further uncovered topics are described herein.

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(1) Author to whom inquiries concerning X-ray structural determination should be addressed.

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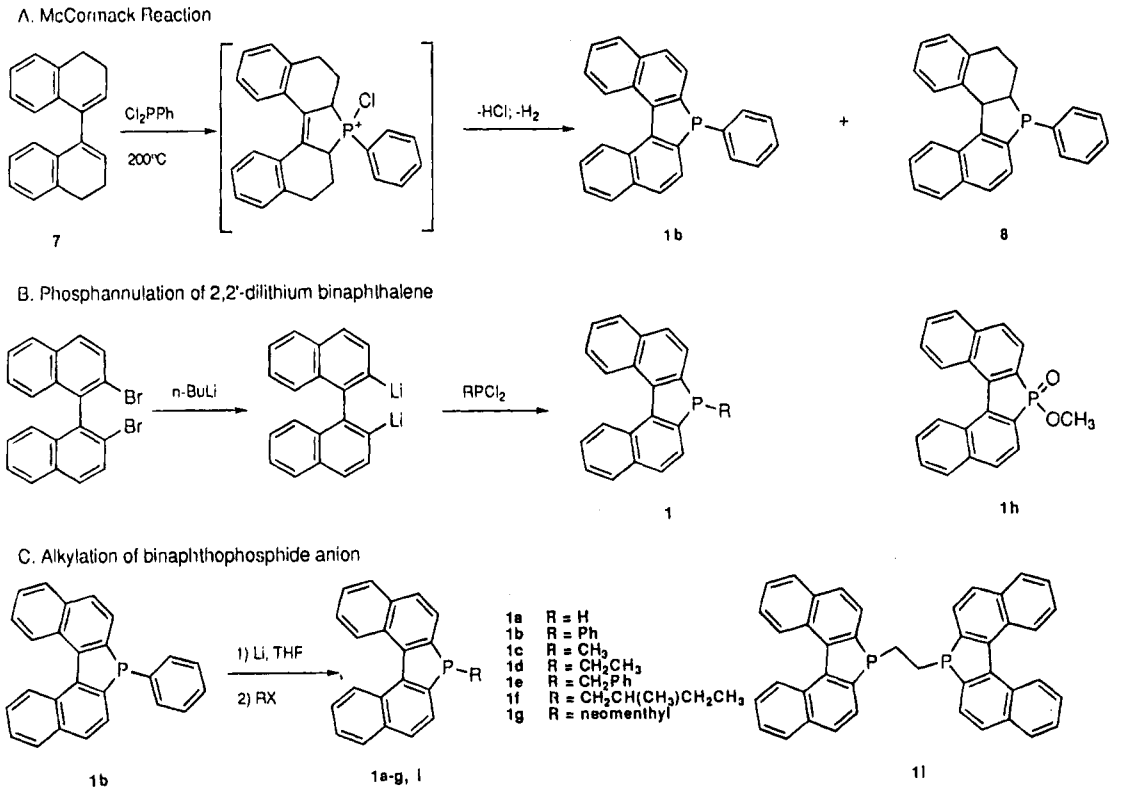
Scheme 1. Synthesis of Dinaphthophospholes



Results and Discussion

For the preparation of dinaphthophosphole derivatives, three different methods were developed (Scheme 1). Methods A and B provide for the building up of the phosphole nucleus by reaction of the suitable dichlorophosphine either with bis-dialin **7** or with 2,2'-dilithio-1,1'-binaphthalene. Method C starts from the preformed phosphacycle derivative **1b** and relies on the easy removal of the phenyl substituent by means of metallic lithium to introduce new susbstituents onto the P-atom.

7-Phenyldinaphtho[2,1-*b*:1',2'-*d*]phosphole (**1b**) was synthesized by both methods A and B. In its original preparation it was obtained in 20–25% yield by cycloaddition of 3,4,3',4'-tetrahydro-1,1'-binaphthalene (bis-dialin **7**) with phenyldichlorophosphine ($PhPCl_2$) at 220 °C (McCormack reaction).[11] In the following, it was prepared more conveniently from 2,2'-dilithium-1,1'-binaphthalene.

Crystallization (MeOH) of the product purified by flash chromatography occurred occasionally with spontaneous resolution, affording light yellow enantiomorphic crystals. Ball & stick representation of the X-ray structure of one of these crystals is reported in Figure 1. The figure points out a modest distortion from planarity of the phosphole ring and a pyramidal geometry at phosphorus. The intracyclic C–P bond lengths (about 1.81 Å) and C–P–C angle (89.3°) are comparable to the ones of other substituted phospholes.[11] The dihedral angle between the average best planes of the naphthyl rings is 29.3° and the contact distance between H(8) and H(17') is 2.049 Å. A chloroform solution ($c = 1$) of these crystals showed no optical activity at the D line at room temperature, suggesting that interconversion of atropisomers may occur in solution (*vide infra*). For the sake of comparison, 1,1'-binaphthalene exists in two distinct crystalline forms having twist angles of 68°[12] and 103°[13a] and contact distances higher than 3.7 Å. The main feature arising from the structural data is the intracyclic C–P–C angle lower than 90°. This value is definitely smaller than in open chain phosphines (about 100°) and suggests that some strain should be present in the phosphole ring. This should be the driving force for the ring opening reactions which will be discussed later.

When prepared from bis-dialin **7**, phosphole **1b** was contamined by several byproducts. One of them, roughly accounting for 10–15% of the crude reaction product, was separated in pure form from the chromatographic column in several instances. Analytical and spectral data indicated for this compound the structure of *P*-phenyltetrahydrodinaphthophosphole **8**. Its formation in the McCormack reaction (Scheme 1, eq 1) is not unexpected on the basis of the commonly accepted reaction path. Interestingly, the ^{13}C-NMR spectrum of this compound showed in the aliphatic chemical shift range only four doublets due to phosphorus–carbon coupling, indicating that the product isolated in several different occasions was always the same single stereoisomer. The stereochemistry of **8** was determined by single-crystal X-ray structure analysis.[13b] A ball & stick view of the crystal structure is reported in Figure 2. This shows the *cis* fusion between the highly distorted phospholene and the cyclohexene rings. The phosphorus atom displays a pyramidal geometry with bond angles and lengths in the normal range. The endocyclic C–P–C angle is 89.4° and

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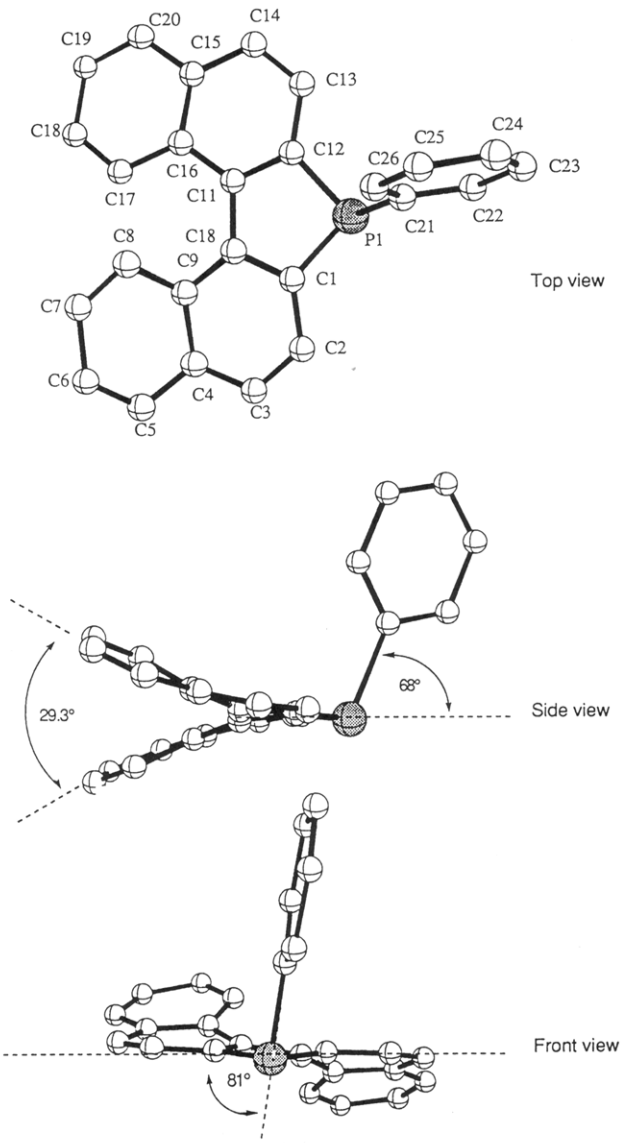

Figure 1. X-ray structure of **1b**.

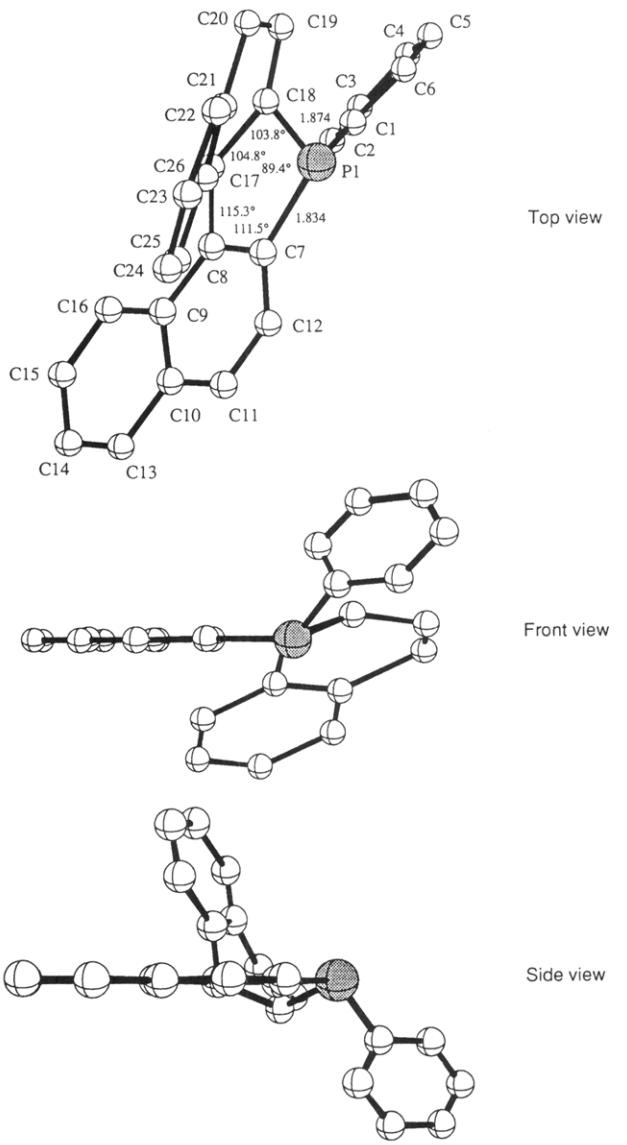

Figure 2. X-ray structure of **8**.

a dihedral angle of about 75° exists between the average planes of the naphthalene and tetrahydronaphthalene rings.

The reaction of $PhPCl_2$ with 2,2′-dilithium-2,2′-binaphthalene is by far more expedient than the McCormack reaction and affords **1b** in more than 80% isolated yield after flash chromatography. In the same way, *P*-methyl- and *P*-ethylphosphole **1c** and **1d**, respectively, could be obtained in 80−85% yield from the appropriate alkyldichlorophosphine (Table 1). This procedure can be therefore recommended as the method of choice for the synthesis of dinaphthophosphole derivatives in those cases where the required dichlorophosphino reagent is available. It is as well useful for the preparation of oxygenated phospholes such as **1h** which could be obtained in high yield by reaction with methyl dichlorophosphinate.

Treatment of **1b** with alkali metal (lithium was routinely used, but sodium and potassium were equally efficient) promotes the heterolytic cleavage of the phenyl carbon−phosphorus bond affording the corresponding phospholyl anion (Scheme 1; eq 3). In light of the ring strain involved, it is remarkable that this reaction leads exclusively to loss of the *P*-phenyl group, with no cleavage of the naphthyl substituents on phosphorus.The high selectivity should be related to the aromatic character of the phosphole ring. Albeit low, this is not negligible as reflected by the different lengths between the intra- and exocyclic P−C bonds (1.81 vs 1.83, respectively).

Table 1. Synthesis of P-Substituted Dinaphthophospholes

entry	compd	method	yield, %	mp °C	^{31}P-NMR[a]
1	**1a**	C	68	102−3	−60.81
2	**1b**	A; B	22; 85	157−8	−4.69
3	**1c**	B; C	80; 50	102−3	−19.66
4	**1d**	B; C	82; 56	122−4	−3.32
5	**1e**	C	73	110−2	−5.42
6	**1f**	C	60	142−3	−11.20
7	**1g**	C	60	117−8	−0.87
8	**1h**	C	57	107−8	−3.78
9	**1i**	B	70	145−6	44.51

[a] In $CDCl_3$ solution at rt.

The phospholyl anion smoothly reacts at room temperature with primary alkyl halides to afford the corresponding *P*-alkyl-substituted phosphole in 50−85% yield (Table 1). The reaction proceeds as well on second-

ary alkyl halides with net inversion at the stereogenic carbon center.

This method is complimentary to the phosphannulation procedures reported above and can be profitably used whenever the alkylphosphine dichloride is hardly accessible. The method has revealed particularly well suited for the preparation of optically active bis-dinaphthophospholyl derivatives such as **1i** to be used as chelating ligands in organotransition metal catalysis. The dinaphthophosphole analogues of the well-known chiral bidentate diphosphine DIOP and SKEWPHOS[14] have been prepared by this way from the corresponding sulfonate esters. Their syntheses and applications in asymmetric catalytic processes will be reported elsewhere.[15]

Quenching the phospholyl anion with protic reagents affords in fair yield the unsubstituted parent dinaphthophosphole **1a** as a moderately air-stable crystalline powder. Unlike simple 1*H*-phospholes, which dimerize rapidly at room temperature,[16] this compound is substantially stable even in solution and could be completely characterized by multinuclear NMR. The main feature of its ^{1}H NMR spectrum is the doublet of the P–H resonance at δ 5.55 ($^1J_{P-H}$ 195 Hz).

Alkylation of phospholyl anion with 1,2-diiodoethane produced 1,2-bis-(dinaphthophospholyl)ethane **1i**. In the NMR at ambient temperature this compound shows the methylene protons as a very broad peak at ca. 1.6 δ, the phosphorus resonance as a sharp singlet at −3.78 ppm, and the aliphatic carbons as a doublet at 21.27 ppm ($^1J_{P-C}$ 28 Hz). At 223 K all these signals are split into two separate sets of peaks. The same occurs to the most deshielded peak of the ^{1}H spectrum which can be confidently attributed to the H(8) and H(17) resonances. The doublet observed at room temperature (8.46 δ, J = 7.5 Hz) splits into two sharply distinct resonances at 8.42 δ (d, J = 7.5 Hz) and 8.50 δ (d, J = 7.5 Hz) at 223 K.

The fluxional behavior of P-substituted dinaphthophospholes is clearly apparent also from the variable temperature ^{31}P NMR spectra of the optically active derivatives **1f** and **1g**. At room temperature both compounds show the phosphorus resonance as a broad singlet that resolves into two sharp peaks in about a 1:1 ratio below 250 K with coalescence temperature (T_c) around 280 K (Figure 3).

A similar pattern, but with slightly different T_c's (ca. 270 K), was observed in the ^{1}H spectra of these compounds. The activation energy of the fluxional process was determined in the case of **1f** by line shape analysis using the coalescence temperature method. Applying the expression reported in ref 9 to the variable temperature ^{31}P and ^{1}H NMR data, leads to approximate $\Delta G^{\ddagger}$ values of 56 and 55 kJ mol^{-1}, respectively. This value equals the energy barrier previously determined by the same method for compounds **1b** and **1c**.[9]

Phospholes **1** may in principle experience two different dynamic processes: pyramidal inversion at phosphorus and flipping of the naphthyl rings. While the first is a chirality-invariant high-energy process for which an energy barrier of about 130 kJ mol^{-1} can be anticipated, the second results in net inversion of configuration. From these results it is estabilished that fluxionality of dinaphthophospholes is determined by the rapid interconversion between the atropisomeric conformations of the dinaphthyl backbone. This seems to configure a common tract in the chemistry of this kind of dinaphthyl derivative, since the same dynamic behavior has been observed in other heteropentahelicenes of closely related structure where the phosphorus center is substituted by a different heteroatom.[17] Fluxionality should be the consequence of the geometrical properties of the five-membered ring, which force the outer phenyl rings of each naphthalene to get more distant than in acyclic derivatives. This renders the H(8)–H(17) hydrogens less sterically demanding and, consequently, they can be more easily forced past one another in the transition state of a *syn*-racemization process. An indirect support to this reasoning comes from the observation that the lactone of 2′-hydroxy-1,1′-binaphthyl-2-carboxylic acid is readily racemized under conditions where the parent acid is otherwise configurationally stable.[18]

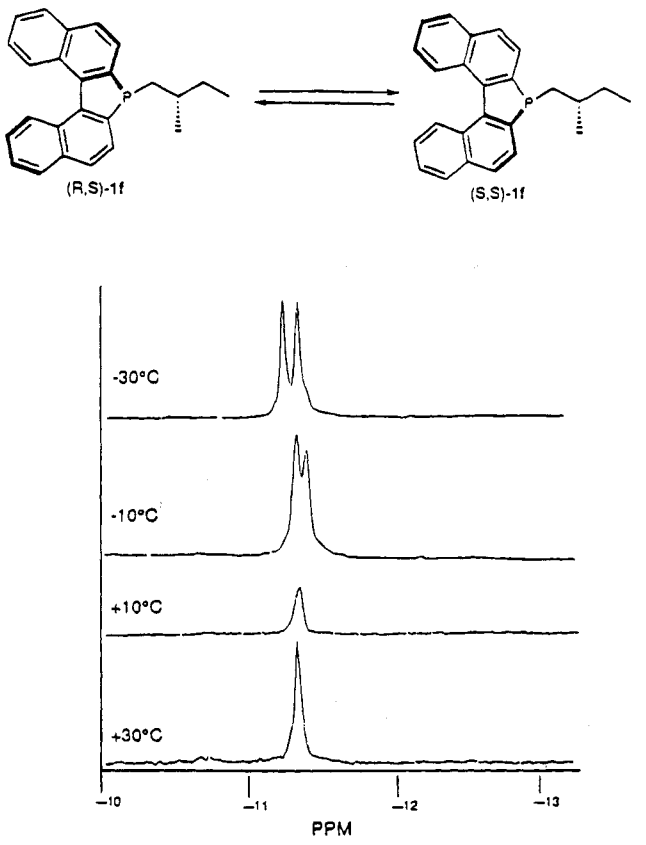

Figure 3. Variable-temperature ^{31}P-NMR of phosphole **1f**.

The fluxional behavior is maintained even when the phosphorus atom is tetrasubstituted like in the case of phosphole oxides **2**, phospholium salts **4**, and phosphole-metal complexes such as **10**. In general, the rate of the dynamic process is only slightly affected upon changing the substitution pattern at the phosphorus center. For instance, in the case of optically active neomenthylphosphole oxide **2g**, application of the coalescence temperature method to the variable temperature ^{1}H NMR data led to calculation of a $\Delta G^{\ddagger}$ of 60 kJ mol^{-1} (T_c = 280 K), very close to the values of the relevant phosphole.

A similar trend is observed when the phosphorus atom of P-substituted dinaphthophospholes is coordinated to

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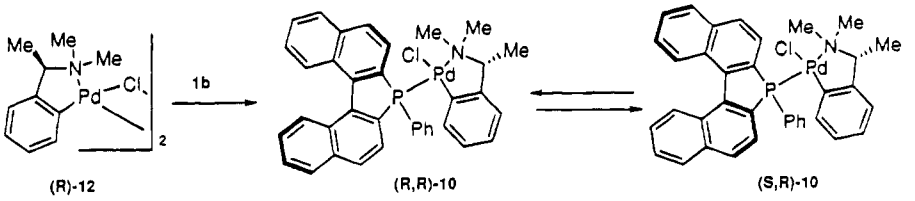
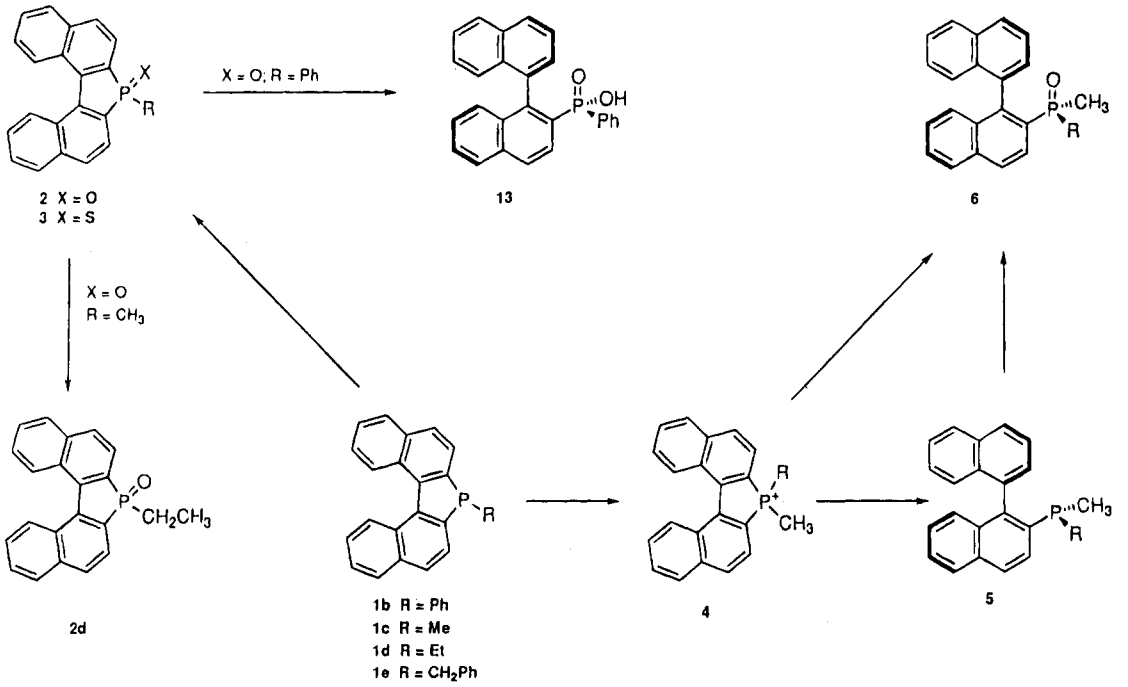
Scheme 2. Interconversion of Pd-Phosphole Complexes



Scheme 3. Transformations of Dinaphthophosphole Derivatives



a metal center. It has been previously reported that at room temperature cyclopentadienyl iron complexes containing **1b** or **1c**[9] are readily equilibrated as a consequence of the atropisomerization of the binaphthyl backbone of the ligand. We have observed that the palladium complex **10**, easily obtained by reaction of **1b** with the enantiopure chloride-bridged complex **12**,[19] is conformationally labile in solution above 270 K as determined from ^1H and ^{31}P NMR (Scheme 2). This suggests that coordination to the metal induces only minor modifications in the geometry of the binaphthyl framework. In fact, the X-ray crystal structure of **10** points out only a modest increase of the dihedral angle between the naphthalene rings (up to 33°) and, consequently, a slightly longer contact distance between H(8)–H(17) (2.20 Å) with respect to the free ligand **1b**.[20] No evidence of dynamic behavior is found in the analogue Pd-derivative **11** of the tetrahydrophosphole **8**. This has been obtained in the form of an equimolar mixture of two diastereoisomers which could not be resolved by fractional crystallization.

Some aspects of the reactivity of phospholes **1** are illustrated in Scheme 3. The reaction with *m*-chloroperbenzoic (mCPBA) acid in chloroform or with sulfur in chloroform affords the corresponding oxides **2** or thioxo derivatives **3**. Elongation of the alkyl chain of oxide **2** can be easily accomplished through a deprotonation–alkylation protocol. By this way, the methyl derivative **2c** has been converted into ethylphosphole oxide **2d**. Heating the oxide **2b** with sodium hydroxide at 260 °C promoted the cleavage of the phosphole ring affording in high yield phenyl(2-(1,1′-binaphthylyl))phosphinic acid (**13**). Although this is not surprising since ring opening of dibenzophosphole oxide under similar conditions was previously observed,[21] this fact confirms that the phosphole ring is strained to some extent even when the heteroatom is tetrasubstituted. Compound **13** is a valuable precursor for the preparation of a variety of chiral phosphorus derivatives containing a binaphthyl substituent. Several synthetic applications can be foreseen for this substrate and some of them are under current investigation and will be reported in due course.

Phospholes **1** are readily alkylated by primary and secondary alkyl halides to afford the relevant phospholium salts **4** which, upon treatment with suitable nucleophiles, undergo ready cleavage of the phosphole ring. For instance, reaction with lithium aluminum hydride in THF at room temperature converts **4b** and **4d** into the corresponding binaphthyl-substituted phosphines **5** (mixture of diastereoisomers). The tendency of phospholium salts to undergo ring opening is quite pronounced and the reduction takes place even below 0 °C with a slight improvement in the diastereoselectivity (4:1 *vs* 3:1). Compounds **5** are the first representatives of a new kind of chiral phosphine ligands characterized by an unprecedented combination of chiral elements, a stereogenic phosphorus center and an axially chiral diaryl group.

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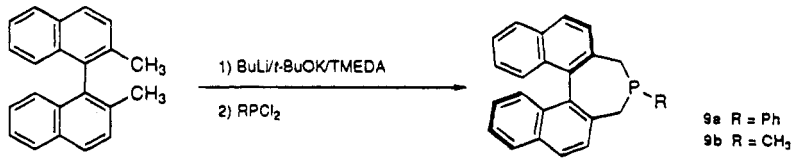
Scheme 4. Synthesis of 4,5-Dihydro-3*H*-dinaphthophosphepines



Stirring phospholium salts **4** with potassium hydroxide in a dichloromethane–water biphasic system at room temperature leads to the acyclic binaphthylylphosphine oxides **6** in high yield as a *ca.* 2:1 mixture of diastereoisomers. The same result is obtained with other nucleophiles (MeONa, MeSNa, EtONa, or AcONa) in alcohol solution. The reaction takes place equally with slightly improved stereoselectivity (*ca.* 3:1) at −10 °C. The same ratio was observed using powdered potassium hydroxide in benzene whereas with sodium acetate no reaction took place. A higher stereoselectivity was attained in the reaction of **4b** with silver acetate in benzene which afforded **6b** in 92:8 diastereomeric ratio. Ring opening is by far the preferred path, accounting for more than 90% of the crude reaction product, even in the case of the benzyl-substituted phospholium derivative **4d** where competition with elimination of benzyl anion is expected. A small amount of the phosphole oxide **2b** is as well formed in this case. The stereochemistry of the ring opening reaction apparently is not affected by the nature of the nucleophilic reagent. Reaction of salt **4b** either with lithium aluminum hydride or with potassium hydroxide led to products of the same relative configuration as shown by oxidation of phosphine **5b** with mCPBA. Strong bases like BuLi converted alkylphospholium salts into the corresponding ylide. This reacts with benzophenone like a normal Wittig olefination reagent.

There is little doubt that the facile cleavage of the phosphole ring is a consequence the inherent strain evidenced in the crystal structure of **1b** by the intracyclic C–P–C angle lower than 90°. We can confidently assume that this amplitude is substantially maintained in the phospholium salts derived from **1b**. A further contribution to the high reactivity observed may come from the relief of the torsional strain originated from the inclusion of the phosphole ring within the diaryl framework. This arises from two contrasting demands: the necessity of the phosphole ring to assume a geometry as planar as possible and the necessity of the binaphthyl group to have the naphthyl rings in twisted planes as orthogonal as possible. The unusually low dihedral angle existing between the naphthyl substituents of **1b** (29.3°) is the result of this compromise.

The phosphorus derivatives **5** and **6** are diastereomorphic compounds which may experience two different fluxional processes: pyramidal inversion at phosphorus and atropisomerization of the diaryl backbone. As the first process is not infrequent in acyclic diarylalkylphosphines,[22] a sample of **5b** was kept at 120 °C for 4 h. No epimerazion was detected by ^{31}P NMR and therefore it can be assumed that these compounds are configurationally stable below this temperature.

The conformational lability displayed by the atropisomeric binaphthyl backbone at room temperature makes dinaphthophospholes unsuitable for optical resolution and hence for application in enantioselective catalysis, as it was our original aim at the beginning of this investigation. We have then addressed our efforts toward different phosphacyclic derivatives presumably endowed with a higher degree of conformational stability. This is the case of 4,5-dihydro-3*H*-dinaphtho[2,1-*c*:1′2′-*e*]phosphepines **9** whose preparation from 2,2′-dimethyl-1,1′-binaphthalene has been quite recently accomplished (Scheme 4).[23] These compounds can be easily resolved by fractional crystallization of the diastereomeric palladium complexes analogue to **10** and are optically stable even after warming several hours at 100 °C in toluene. The twist angle between the naphthalene rings and the intracyclic C–P–C angle are 63.8° and 100.6°, respectively. These values, obtained from the crystal structure of the relevant Pd-complex, are definitely greater than the ones observed in the analogue complex containing **1b**[20] and indicate that, unlike the related phospholes, dinaphthophosphepines are substantially strain-free molecules.

Experimental Section

General. ^{1}H-, ^{13}C-, and ^{31}P-NMR spectra were recorded at 300, 75.5, and 121.42 MHz, respectively, in $CDCl_3$ solution. Chemical shifts of protons and carbons are reported in δ (ppm) referenced to TMS as an internal standard; ^{31}P chemical shifts are reported in ppm with respect to H_3PO_4 as an external standard. Melting points are uncorrected. Infrared spectra were recorded in KBr pellets. Flash column chromatographies were carried out using Merck silica gel 60 (230–400 mesh) according to the literature.[24] Air- and moisture-sensitive reactions were performed under usual inert atmosphere techniques. Commercial chemical reagents were used as received and solvents were dried by standard procedures and stored over molecular sieves under inert atmosphere. 3,4,3′,4′-Tetrahydro-1,1′-binaphthalene,[25] 2,2′-dibromo-1,1′-binaphthalene,[26] and (−)-di-μ-chlorobis[(*R*)-dimethyl(α-methylbenzyl)-aminato-2-C,N]dipalladium(II)[19] were prepared according to the literature.

McCormack Reaction: General Procedure. $PhPCl_2$ (1.11 mL, 8.17 mmol) and bis-dialin **7** (0.4 g, 1.54 mmol) were refluxed at 220 °C for 3 h under N_2. After cooling to room temperature, the solution was poured carefully into a 15% KOH aqueous solution (20 mL). The resulting yellow solid was filtered off, washed with 10 mL of 15% KOH aqueous solution, and dissolved in CH_2Cl_2. The organic phase was washed with water and dried (Na_2SO_4). The solvent was rotoevaporated and the crude product was purified by flash chromatography (*n*-hexane/CH_2Cl_2 8/1 as eluent) and recrystallized from CH_2Cl_2/petroleum ether.

7-Phenyldinaphtho[2,1-*b*:1′,2′-*d*]phosphole (1b): 22% yield; mp 157–8 °C; ^{1}H-NMR δ 7.18–7.35 m, 7.45–7.60 m, 7.75–7.90 m, 7.96 dd (J = 1.5, 7.8 Hz), 8.47 d (J = 8.1 Hz); ^{31}P-NMR δ −4.69 s; MS 360.3 (M^+, 100%), 328.2 (20%), 281.1 (80%), 140.8 (18%). Anal. Calcd for $C_{26}H_{17}P$: C, 86.65; H, 4.75. Found: C, 87.03; H, 4.54.

7-Phenyl-1,2,3,4-tetrahydrodinaphtho[2,1-*b*:1′,2′-*d*]phosphole (8): 10% yield; mp 199–200 °C; ^{1}H-NMR δ 2.18 m, 2.37 m, 2.95 m, 3.36 m, 5.23 dd ($^3J_{HP}$ = 11.7 Hz, J = 8.1 Hz), 6.88

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d (J = 7.8 Hz), 6.96 t (J = 7.5 Hz), 7.17 t (J = 7.5 Hz), 7.25 d (J = 7.5 Hz), 7.34–7.43 m, 7.51–7.63 m, 7.80 dd (J = 2.4, 8.1 Hz), 7.95 d (J = 8.1 Hz), 8.07 d (J = 8.1 Hz); ^{13}C-NMR (aliphatic carbons only) δ 24.10 d (J = 41.77 Hz), 28.70 d (J = 11.55 Hz), 46.53 d (J = 5.55 Hz), 49.95 d (J = 7.5 Hz); ^{31}P-NMR δ 8.39 (s); MS 358.4 (M^+, 81%), 281.4 (75%), 252.3 (100%), 77.0 (70%). Anal. Calcd for $C_{26}H_{21}P$: C, 85.69; H, 5.81. Found: C, 85.90; H, 5.67.

Phosphannulation of 2,2′-Dilithio-1,1′-binaphthalene: General Procedure. *n*-BuLi (3.32 mL, 5.32 mmol of a 1.6 M hexane solution) was added dropwise to a solution of 2,2′-dibromo-1,1′-binaphthyl (1.0 g, 2.42 mmol) in dry THF (12 mL) at −60 °C under N_2. After stirrring at −60 °C for 3 h, a solution of the appropriate dichloroalkylphosphine (5.32 mmol) in dry THF (5 mL) was added. The mixture was allowed to warm to room temperature slowly. After stirring 12 h at rt, saturated NH_4Cl (100 mL) was added, the solution was rotoconcentrated, and the residue was extracted several times with CH_2Cl_2. The organic layer was washed with water and dried (Na_2SO_4). The solvent was rotoevaporated and the crude product was purified by flash chromatography using *n*-hexane/CH_2Cl_2 9/1 as eluent and recrystallized from CH_2Cl_2/petroleum ether.

7-Methyldinaphtho[2,1-*b*:1′,2′-*d*]phosphole (1c): 80% yield; mp 102–3 °C; ^{1}H-NMR δ 1.61 d ($^2J_{HP}$ = 1.5 Hz), 7.52–7.63 m, 7.91–8.02 m, 8.03 dd (J = 1.2, 7.8), 8.53 d (J = 9.0 Hz); ^{13}C-NMR (aliphatic carbons only) δ 12.00 d ($^1J_{CP}$ = 15.3 Hz); ^{31}P-NMR δ −19.66 s; MS 298.3 (M^+, 85%), 281.3 (95%), 252.3 (10%), 140.8 (70%). Anal. Calcd for $C_{21}H_{15}P$: C, 84.55; H, 5.07. Found: C, 84.33; H, 4.90.

7-Ethyldinaphtho[2,1-*b*:1′,2′-*d*]phosphole (1d): 82% yield; mp 122–4 °C; ^{1}H-NMR δ 0.90 dd ($^3J_{HH}$ = 7.5, $^3J_{PH}$ = 12.9 Hz), 2.05 dd ($^3J_{HH}$ = 7.5, $^2J_{PH}$ = 3.0 Hz), 7.49–7.62 m, 7.88–8.03 m, 8.02 dd (J = 1.2, 8.1 Hz), 8.52 d (J = 8.1 Hz); ^{13}C-NMR (aliphatic carbons only) δ 9.45 d ($^2J_{CP}$ = 5 0 Hz), 21.19 d ($^1J_{CP}$ = 19.63 Hz); ^{31}P-NMR δ −3.32 s; MS 312.4 (M^+, 50%), 281.3 (96%), 252.4 (10%), 140.8 (15%). Anal. Calcd for $C_{22}H_{17}P$: C, 84.60; H, 5.49. Found: C, 84.76; H, 5.46.

7-Methoxydinaphtho[2,1-*b*:1′,2′-*d*]phosphole oxide (1i): 70% yield; mp 145–6 °C; ^{1}H-NMR δ 3.66 d ($^3J_{PH}$ = 12.0 Hz), 7.47 t (J = 7.8 Hz), 7.58 t (J = 7.8 Hz, Ar), 7.82–8.07 m; ^{13}C-NMR (aliphatic carbons only) δ 52.80 d (J = 6.0 Hz); ^{31}P-NMR δ 44.51 s; MS 330.2 (M^+, 95%), 315.3 (22%), 297.3 (75%), 252.3 (96%), 149.1 (60%), 125.2 (42%). Anal. Calcd for $C_{21}H_{15}O_2P$: C, 76.36; H, 4.58. Found: C, 76.40; H, 4.47.

Alkylation of Dinaphthophosphide Anion: General Procedure. 7-Phenyldinaphtho[2,1-*b*:1′,2′-*d*]phosphole (**1b**) (0.30 g, 0.83 mmol) was added to a mixture of lithium (0.011 g, 1.66 mmol of a 25% mineral oil dispertion) in dry THF (10 mL) at room temperature under N_2. The solution was refluxed for 3 h and then cooled to room temperature, and a solution of *t*-BuCl (0.09 mL, 0.83 mmol) in dry THF (5 mL) was added (for **1a** AcOH was added and the reaction mixture was then elaborated). After warming at reflux for further 3 h, the dark red solution was cooled to 0 °C, the appropriate alkyl halide (1.0 mmol) in dry THF (5 mL) was added dropwise, and refluxing was continued for 6 h. After cooling to room temperature, saturated NH_4Cl (100 mL) was added, THF was rotoevaporated and the residue was extracted several times with CH_2Cl_2. The organic layer was washed with water and dried (Na_2SO_4). The solvent was rotoevaporated and the crude product was purified by flash chromatography (*n*-hexane/CH_2Cl_2 9/1 as eluent) and recrystallized from CH_2Cl_2/*n*-hexane.

Dinaphtho[2,1-*b*:1′,2′-*d*]phosphole (1a): 68% yield; mp 102–3 °C; ^{1}H-NMR δ 5.50 d (J = 195.0 Hz), 7.45 dt (J = 1.5, 6.8 Hz), 7.55 dt (J = 1.5, 6.8 Hz), 7.90 m, 7.95 d (J = 8.7 Hz), 8.42 d (J = 8.7 Hz); ^{31}P-NMR δ −60.81 d (J = 195.0 Hz); MS 284.3 (M^+, 40%), 251.3 (100%), 91.2 (15%). Anal. Calcd for $C_{20}H_{13}P$: C, 84.50; H, 4.61. Found: C, 84.87; H, 4.75.

7-Benzyldinaphtho[2,1-*b*:1′,2′-*d*]phosphole (1e): 73% yield; mp 110–2 °C; ^{1}H-NMR δ 3.22 bs, 6.85–7.10 m, 7.47 dd (J = 1.2, 6.6 Hz), 7.56 dd (J = 1.2, 8.1 Hz), 7.67 t (J = 6.0 Hz), 7.67 d (J = 6.3 Hz), 7.98 d (J = 7.8 Hz), 8.36 d (J = 8.4 Hz); ^{13}C-NMR (aliphatic carbons only) δ 36.2 d ($^2J_{CP}$ = 24.2 Hz); ^{31}P-NMR δ −5.42 s; MS 374.3 (M^+, 30%), 281.3 (100%), 91.2 (26%). Anal. Calcd for $C_{27}H_{19}P$: C, 86.61; H, 5.11. Found: C, 86.40; H, 5.27.

7-(2-Methylbutyl)dinaphtho[2,1-*b*:1′,2′-*d*]phosphole (1f): 45% yield; mp 142–3 °C; ^{1}H-NMR δ 0.89 t ($^3J_{HH}$ = 9.0 Hz), 1.13 d ($^3J_{HH}$ = 5.4 Hz), 1.20–1.90 m, 7.48 dd (J = 1.5, 6.6 Hz), 7.55 dd (J = 1.5, 8.1 Hz), 7.83–8.02 m, 8.00 d (J = 7.8 Hz), 8.45 d (J = 8.7 Hz); ^{13}C-NMR (aliphatic carbons only) δ 11.2 s, 20.8 d ($^3J_{CP}$ = 9.1 Hz), 30.9 d (J_{CP} = 8.6 Hz), 33.6 d (J_{CP} = 9.6 Hz), 37.2 d (J_{CP} = 20.1 Hz); ^{31}P-NMR δ −11.20 bs; MS 422.5 (M^+, 25%), 284.5 (100%), 212.3 (30%), 140.8 (5%). Anal. Calcd for $C_{25}H_{23}P$: C, 84.72; H, 6.54. Found: C, 84.93; H, 6.32.

7-Neomenthyldinaphtho[2,1-*b*:1′,2′-*d*]phosphole (1g): 60% yield; mp 117–8 °C; ^{1}H-NMR δ 0.37 d ($^3J_{HH}$ = 6.6 Hz), 1.10 d ($^3J_{HH}$ = 6.9 Hz), 1.15 d ($^3J_{HH}$ = 6.9 Hz), 1.40–1.90 m, 2.22 m, 3.10 m, 7.47 dd (J = 1.5, 6.9 Hz, 7.54 dd (J = 1.2, 8.1 Hz), 7.75–8.95 m, 7.99 d (J = 8.5 Hz), 8.46 dd (J = 3.0, 8.7 Hz); ^{13}C-NMR (aliphatic carbons only) δ 15.4 s, 21.5 s, 21.9 s, 25.8 d, ($^2J_{CP}$ = 8.6 Hz), 29.9 d ($^2J_{CP}$ = 20.1 Hz), 33.5 s, 34.8 s, 35.7 s, 41.7 d ($^2J_{CP}$ = 21.6 Hz), 45.8 s; ^{31}P-NMR δ −0.87 bs; MS 422.3 (M^+, 25%), 284.3 (100%), 252.3 (40%), 140.8 (7%). Anal. Calcd for $C_{30}H_{31}P$: C, 85.28; H, 5.11. Found: C, 85.04; H, 5.19.

1,2-Bis(dinaphtho[2,1-*b*:1′,2′-*d*]phospholyl)ethane (1i): 57% yield; mp 107–8 °C; ^{1}H-NMR δ 1.10 d ($^2J_{PH}$ = 9.0 Hz), 7.47 dd (J = 0.6, 7.2 Hz), 7.55 dd (J = 1.2, 6.6 Hz), 7.80–8.20 m, 8.05 d (J = 7.5 Hz), 8.42 d (J = 8.1 Hz); ^{31}P-NMR δ −3.78 bs; MS 594.9 (M^+, 5%), 297.9 (10%), 280.9 (100%), 140.4 (6%). Anal. Calcd for $C_{42}H_{28}P_2$: C, 84.84; H, 4.75. Found: C, 84.52; H, 4.48.

Preparation of Phosphole Oxides 2: General Procedure. A solution of phosphole (0.5 mmol) and mCPBA acid (0.36 g, 5.0 mmol, 75% purity) in CH_2Cl_2 (15 mL) was stirred at rt for 1 h. Water was added, and the organic layer was separated and washed with a saturated solution of $NaHSO_3$ and $NaHCO_3$. The organic phase was dried (Na_2SO_4), and the solvent was rotoevaporated affording a yellow solid which was recrystallized from CH_2Cl_2/*n*-hexane.

7-Phenyldinaphtho[2,1-*b*:1′,2′-*d*]phosphole oxide (2b): 92% yield; mp 254–5 °C; ^{1}H-NMR δ 7.36 m, 7.45 m, 7.50–7.67 m, 7.81 d (J = 6.6 Hz), 7.95 d (J = 7.8 Hz), 8.20 d (J = 8.1 Hz); ^{31}P-NMR δ 35.37 s; MS 376.3 (M^+, 100%), 326.3 (22%), 297.3 (42%), 281.3 (18%), 252.3 (35%), 149.1 (14%). Anal. Calcd for $C_{26}H_{17}OP$: C, 82.97; H, 4.55. Found: C, 82.73; H, 4.38.

7-Methyldinaphtho[2,1-*b*:1′,2′-*d*]phosphole oxide (2c): 92% yield; mp 230–1 °C; ^{1}H-NMR δ 1.87 d ($^2J_{HP}$ = 13.2 Hz), 7.50 t (J = 7.2 Hz), 7.60 d (J = 6.9 Hz), 7.90–8.10 m, 8.13 d (J = 8.7 Hz); ^{13}C-NMR (aliphatic carbons only) δ 15.9 d ($^1J_{CP}$ = 71.0 Hz); ^{31}P-NMR δ 42.75 s; MS 314.3 (M^+, 100%), 299.3 (40%), 252.3 (55%), 156.8 (56%). Anal. Calcd for $C_{21}H_{15}OP$: C, 80.25; H, 4.81. Found: C, 80.11; H, 4.73.

7-Ethyldinaphtho[2,1-*b*:1′,2′-*d*]phosphole oxide (2d): 88% yield; mp 122–4 °C; ^{1}H-NMR δ 1.00 dd ($^3J_{HH}$ = 7.8, $^3J_{PH}$ = 18.9 Hz), 2.19 bs, 7.50 t (J = 6.9 Hz), 7.61 t (J = 6.9 Hz), 7.90–8.10 m, 8.12 d (J = 8.4 Hz); ^{13}C-NMR (aliphatic carbons only) δ 6.22 d ($^2J_{CP}$ = 4.1 Hz), 22.88 d ($^1J_{CP}$ = 70.1 Hz); ^{31}P-NMR δ 47.65 s; MS 328.3 (M^+, 45%), 284.3 (100%), 252.3 (30%), 140.3 (5%). Anal. Calcd for $C_{22}H_{17}OP$: C, 80.48; H, 5.22. Found: C, 80.65; H, 5.11.

7-Benzyldinaphtho[2,1-*b*:1′,2′-*d*]phosphole oxide (2e): 90% yield; mp 120–2 °C; ^{1}H-NMR δ 3.50 bs, 6.80–7.07 m, 7.45 dd (J = 1.2, 6.9 Hz), 7.54 d (J = 6.3 Hz), 7.60 d (J = 9.0 Hz), 7.72 m, 7.90–8.00 m; ^{13}C-NMR (aliphatic carbons only) δ 37.5 d ($^1J_{CP}$ = 64.0 Hz); ^{31}P-NMR δ 42.85 s; MS 390.2 (M^+, 30%), 299.3 (100%), 281.3 (10%), 252.3 (55%), 91.2 (18%). Anal. Calcd for $C_{27}H_{19}OP$: C, 83.06; H, 4.91. Found: C, 82.90; H, 4.75.

7-(2-Methylbutyl)dinaphtho[2,1-*b*:1′,2′-*d*]phosphole oxide (2f): 78% yield; mp 202–4 °C; ^{1}H-NMR δ 0.60–2.20 m, 7.51 t (J = 6.9 Hz), 7.60 t (J = 7.9 Hz), 7.80–8.00 m, 8.13 d (J = 8.7); ^{31}P-NMR δ 51.51 s. Anal. Calcd for $C_{25}H_{23}OP$: C, 81.06; H, 6.26. Found: C, 82.82; H, 6.10.

7-Neomenthyldinaphtho[2,1-*b*:1′,2′-*d*]phosphole oxide (2g): 80% yield; mp 106–8 °C; ^{1}H-NMR δ 0.45–1.80 m, 2.45 bs, 2.96 bs, 7.42–7.55 m, 7.85–8.20 m; ^{31}P-NMR δ 53.31 s;

MS 438.4 (M^+, 85%), 395.2 (15%), 327.2 (80%), 300.3 (60%), 281.3 (90%), 252.3 (100%). Anal. Calcd for $C_{30}H_{31}OP$: C, 82.16; H, 7.13. Found: C, 82.34; H, 7.03.

Alkylation of *P*-Methylphosphole Oxide. *n*-BuLi (0.4 mL, 0.64 mmol of 1.6 M hexane solution) was added dropwise to a solution of **2c** (0.2 g, 0.60 mmol) in dry THF (10 mL) at −60 °C under N_2. The solution was stirred at −60 °C for 3 h and then MeI (0.12 mL, 1.80 mmol) in dry THF (5 mL) was added. The mixture was allowed to warm to room temperature slowly. After stirring 12 h at rt, saturated NH_4Cl (100 mL) was added and THF was rotoevaporated. The reaction crude was extracted several times with CH_2Cl_2, and the organic layer was washed with water and dried (Na_2SO_4). The solvent was rotoevaporated and the crude product was purified by flash chromatography using *n*-hexane/CH_2Cl_2 4/1 as eluent. Recrystallization from CH_2Cl_2/petroleum ether afforded **2d** in 56% yield.

Preparation of Thioxophospholes 3: General Procedure. A solution of phosphole (0.5 mmol) and sulfur (1.6 g, 50.0 mmol) in CH_2Cl_2 (15 mL) was stirred at room temperature for 1 h. Excess sulfur was filtered off, the solvent was rotoevaporated, and the crude product was purified by flash chromatography using CH_2Cl_2 as eluent and recrystallized from CH_2Cl_2/*n*-hexane.

7-Phenyldinaphtho[2,1-*b*:1′,2′-*d*]phosphole sulfide (3b): 90% yield; mp 254−5 °C; ^{1}H-NMR δ 7.26−7.45 m, 7.50−7.77 m, 7.85 d (J = 6.6 Hz), 7.95−8.20 m, 8.28 d (J = 7.8 Hz); ^{31}P-NMR δ 49.31 s. Anal. Calcd for $C_{26}H_{17}PS$: C, 79.57; H, 4.37. Found: C,79.65; H, 4.29.

7-Neomenthyldinaphtho[2,1-*b*:1′,2′-*d*]phosphole sulfide (3g): 89% yield; mp 140−1 °C; ^{1}H-NMR δ 0.25−1.80 m, 7.50 d (J = 6.9 Hz), 7.61 d (J = 6.9 Hz), 7.90−8.08 m, 8.16 d (J = 7.8 Hz); ^{31}P-NMR δ 56.11 s; MS 454.2 (M^+, 6%), 344.1 (12%), 316.1 (100%), 281.1 (43%), 252.3 (15%). Anal. Calcd for $C_{30}H_{31}PS$: C, 79.26; H, 6.87. Found: C, 79.52; H, 6.93.

Alkylation of Phospholes: General Procedure. A solution of phosphole (0.5 mmol) was stirred with MeI (10 mL) for 5 h at room temperature. CH_2Cl_2 was added, the organic solution was washed with water and dried (Na_2SO_4). The solvent was rotoevaporated and the crude product was purified by flash chromatography using AcOEt/MeOH 1/1 as eluent and recrystallized from CH_2Cl_2/AcOEt.

7-Methyl-7-phenyldinaphtho[2,1-*b*:1′,2′-*d*]phospholium iodide (4b): 94% yield; mp 191−3 °C; ^{1}H-NMR δ 3.22 d ($^3J_{PH}$ = 14.7 Hz), 7.50−7.67 m, 7.75 t (J = 6.9 Hz), 8.05 d (J = 8.1 Hz), 8.10−8.16 m, 8.22 d (J = 8.4 Hz), 8.44 bs; ^{13}C-NMR (aliphatic carbons only) δ 10.05 d ($^1J_{CP}$ = 55.1 Hz); ^{31}P-NMR δ 28.04 s; MS 502.3 (M^+, 45%), 360.1 (75%), 281.1 (100%), 142.1 (68%), 78.1 (12%). Anal. Calcd for $C_{27}H_{20}IP$: C, 64.56; H, 4.01. Found: C, 64.89; H, 4.10.

7,7-Dimethyldinaphtho[2,1-*b*:1′,2′-*d*]phospholium iodide (4c): 95% yield; mp 199−200 °C; ^{1}H-NMR δ 3.10 d ($^2J_{PH}$ = 22.2 Hz), 7.61 dd (J = 1.2, 6.9 Hz), 7.74 dd (J = 1.2, 8.4 Hz), 8.05 d (J = 8.1 Hz), 8.20−8.24 m, 8.95 d (J = 8.4 Hz), 9.00 d (J = 8.1 Hz); ^{31}P-NMR δ 31.25 s. Anal. Calcd for $C_{22}H_{18}IP$: C, 60.02; H, 4.12. Found: C, 63.34; H, 4.41.

7-Methyl-7-ethyldinaphtho[2,1-*b*:1′,2′-*d*]phospholium iodide (4d): 92% yield; mp 202−4 °C; ^{1}H-NMR δ 0.82 dd ($^3J_{HH}$ = 7.5 Hz, $^3J_{PH}$ = 22.2 Hz), 3.00 d ($^2J_{PH}$ = 15.3 Hz), 3.80 bs, 7.59 t (J = 8.1 Hz), 7.72 t (J = 6.9 Hz), 8.00 d (J = 8.4 Hz), 8.14−8.25 m, 8.89 t (J = 8.7 Hz); ^{13}C-NMR (aliphatic carbons only) δ 5.57 d ($^2J_{CP}$ = 5.05 Hz), 9.60 d ($^1J_{CP}$ = 48.84 Hz), 17.70 d ($^1J_{CP}$ = 46.35 Hz); ^{31}P-NMR δ 39.37 s. Anal. Calcd for $C_{23}H_{20}IP$: C, 60.81; H, 4.44. Found: C, 60.65; H, 4.36.

7-Methyl-7-benzyldinaphtho[2,1-*b*:1′,2′-*d*]phosphole iodide (4e): 62% yield; mp 103−4 °C; ^{1}H-NMR δ 3.00 d ($^2J_{PH}$ = 20.1 Hz), 3.50 bs, 6.80−8.20 m; ^{31}P-NMR δ 37.32 s. Anal. Calcd for $C_{28}H_{22}IP$: C, 65.13; H, 4.29. Found: C, 65.40; H, 4.18.

7-Methyl-7-(2-methylbutyl)dinaphtho[2,1-*b*:1′,2′-*d*]phospholium iodide (4f): 90% yield; mp 161−3 °C; ^{1}H-NMR δ 0.60−2.80 m, 2.85 d ($^2J_{PH}$ = 12.5 Hz), 7.60 t (J = 8.1 Hz), 7.75 t (J = 8.1 Hz), 8.09 d (J = 7.8 Hz), 8.12−8.30 m, 8.84 d (J = 6.9 Hz), 8.86 d (J = 6.9 Hz); ^{31}P-NMR δ 35.50 s. Anal. Calcd for $C_{26}H_{26}IP$: C, 62.91 H, 5.28.

7-Methyl-7-phenyl-1,2,3,4-tetrahydrodinaphtho[2,1-*b*:1′,2′-*d*]phospholium iodide (4l): 95% yield; mp 205−6 °C; ^{1}H-NMR δ 1.75 m, 2.04 d ($^2J_{PH}$ = 13.5 Hz), 2.67 m, 3.05 m, 4.38 m, 5.58 dd ($^3J_{PH}$ = 23.1 Hz, $^3J_{HH}$ = 5.1 Hz), 6.27 d (J = 7.5 Hz), 6.95 t (J = 7.5 Hz), 7.22 t (J = 7.5 Hz), 7.26 m, 7.50−7.80 m, 7.94 d (J = 7.8 Hz), 7.99−8.15; ^{13}C-NMR (aliphatic carbons only) δ 7.40 d ($^1J_{CP}$ = 49.37 Hz), 20.85 s, 29.40 d (J_{CP} = 8.07 Hz), 38.20 d (J_{CP} = 54.43 Hz), 44.91 d (J_{CP} = 5.05 Hz); ^{31}P-NMR δ 32.5 s. Anal. Calcd for $C_{27}H24IP$: C, 64.04; H, 4.78. Found: C, 63.84; H, 4.39.

Synthesis of Binaphthylylphosphines 5: General Procedure. A large excess of $LiAlH_4$ (0.38 g, 10 mmol) was added to a solution of the phospholium iodide (0.5 mmol) in dry THF (10 mL) at rt under N_2. The heterogeneous solution was stirred at rt for 0.5 h and then water (100 mL) was carefully added. THF was rotoevaporated and the crude product was extracted several times with CH_2Cl_2. The organic layer was washed with water and dried (Na_2SO_4). The solvent was rotoevaporated and the crude product was recrystallized from CH_2Cl_2/*n*-hexane.

(2-(1,1′-Binaphthylyl))methylphenylphosphine (5b): 90% yield; mp 181−2 °C. Anal. Calcd for $C_{27}H_{21}P$: C, 86.15: H 5.62. Found: C, 86.01; H, 5.63. Major diastereoisomer: ^{1}H-NMR δ 1.57 d ($^2J_{PH}$ = 4.8 Hz), 7.10−7.30 m, 7.40−4.69 m 7.80−8.30 m. Minor diastereoisomer: ^{1}H-NMR δ 1.44 d ($^2J_{PH}$ = 4.5 Hz), 7.10−7.20 m, 7.38−4.59 m, 7.81−8.30 m.

(2-(1,1′-Binaphthylyl))methylethylphosphine (5d): 82% yield; mp 140−2 °C. MS 328.1 (M^+, 78%), 232.3 (100%), 221.8 (25%), 188.3 (31%), 67.1 (33%). Major diastereoisomer: ^{1}H-NMR δ 1.20−1.60 m, 7.20−8.00 m. Minor diastereoisomer: ^{1}H-NMR δ 0.85−1.10 m, 7.10−8.10 m. Anal. Calcd for $C_{23}H_{21}P$: C, 84.12; H 6.45. Found: C, 84.32; H, 6.31.

Synthesis of Binaphthylylphosphine Oxides 6: General Procedure. NaOH (0.2 g, 5 mmol) in H_2O (10 mL) was added to a solution of phospholium iodide (0.5 mmol) in CH_2Cl_2 (10 mL). The heterogeneous solution was stirred for 0.5 h. The organic phase was separated and dried (Na_2SO_4) and the solvent was rotoevaporated to obtain a colorless solid that was recrystallized from CH_2Cl_2/*n*-hexane.

(2-(1,1′-Binaphthylyl))methylphenylphosphine oxide (6b): 90% overall yield. Anal. Calcd for $C_{27}H_{21}OP$: C, 82.64; H, 5.39. Found: C, 82.98; H, 5.62. Major diastereoisomer: ^{1}H-NMR δ 1.38 d ($^2J_{PH}$ = 13.5 Hz), 6.8−8.5 m; ^{31}P-NMR δ 31.47 s. Minor diastereoisomer: ^{1}H-NMR δ 1.44 d ($^2J_{PH}$ = 13.5 Hz), 6.8−8.5 m; ^{31}P-NMR δ 32.29 s.

(2-(1,1′-Binaphthylyl))dimethylphosphine oxide (6c): 90% yield; mp 234−5 °C; ^{1}H-NMR δ 0.79 d ($^2J_{PH}$ = 13.2 Hz), 1.26 d ($^2J_{PH}$ = 13.2 Hz), 7.05 d (J = 8.7 Hz), 7.10 d (J = 8.4 Hz), 7.10−7.25 m, 7.40−7.51 m, 7.57 t (J = 7.2 Hz), 7.92 d (J = 8.4 Hz), 7.99 d (J = 8.1 Hz), 8.05 d (J = 8.7 Hz), 8.24 dd (J = 8.4, 8.7 Hz); ^{13}C-NMR (aliphatic carbons only) δ 17.9 d ($^1J_{CP}$ = 70.59 Hz); ^{31}P-NMR δ 36.60 s. Anal. Calcd for $C_{22}H_{19}OP$: C, 79.98; H, 5.80. Found: C, 79.62; H, 5.70.

(2-(1,1′-Binaphthylyl))methylethylphosphine oxide (6d): 91% overall yield. Anal. Calcd for $C_{23}H_{21}OP$: C, 80.01; H, 6.15. Found: C, 80.11; H, 6.37. Major diastereoisomer: ^{1}H-NMR δ 0.67 d ($^2J_{PH}$ = 13.2 Hz), 1.03 dt ($^3J_{PH}$ = 17.7 Hz, $^3J_{HH}$ = 7.5 Hz), 1.65 dq ($^2J_{PH}$ = 11.7 Hz, $^3J_{HH}$ = 7.5 Hz), 7.09 t (J = 8.4 Hz), 7.26 m, 7.41 d (J = 7.2 Hz), 7.45−7.58 m, 7.61 t (J = 7.2 Hz), 7.94 t (J = 8.1 Hz), 8.02 d (J = 7.5 Hz), 8.10 d (J = 8.4 Hz), 8.43 t (J = 6.6 Hz); ^{13}C-NMR (aliphatic carbons only) δ 5.69 d (J = 5.05 Hz), 17.9 d ($^1J_{CP}$ = 5.05 Hz), 15.50 d ($^2J_{CP}$ = 69.00 Hz), 25.80 d ($^1J_{CP}$ = 70.51 Hz); ^{31}P-NMR δ 42.03 s. Minor diastereoisomer: ^{1}H-NMR δ 0.79 d ($^3J_{PH}$ = 17.7 Hz, $^3J_{HH}$ = 7.5 Hz), 1.24 d ($^2J_{PH}$ = 12.9 Hz) 1.98 bs, 7.09 t (J = 8.4 Hz), 7.26 m, 7.41 d (J = 7.2 Hz), 7.45−7.58 m, 7.61 t (J = 7.2 Hz), 7.94 t (J = 8.1 Hz), 8.02 d (J = 7.5 Hz), 8.10 d (J = 8.4 Hz), 8.40 t (J = 6.6 Hz); ^{13}C-NMR (aliphatic carbons only) δ 5.60 d ($^1J_{CP}$ = 5.05 Hz), 17.50 d ($^2J_{CP}$ = 69.08 Hz), 23.80 d (^1JCP = 70.51 Hz); ^{31}P-NMR δ 41.15 s.

(2-(1,1′-Binaphthylyl))methylbenzylphosphine oxide (6e): 90% overall yield. Anal. Calcd for $C_{28}H_{23}OP$: C, 82.74; H, 5.70. Found: C, 82.42; H, 5.65. Major diastereoisomer: ^{1}H-NMR δ 0.90 d ($^2J_{PH}$ = 9.8 Hz), 3.45 bs, 6.80−8.10 m; ^{31}P-NMR δ 40.54 s. Minor diastereoisomer: ^{1}H-NMR δ 0.95 (d ($^2J_{PH}$ = 9.8 Hz), 3.45 bs, 6.80−8.10 m; ^{31}P-NMR δ 41.12 s.

Preparation of (2-(1,1′-binaphthylyl))phenylphosphinic Acid (13). A Pyrex vial fitted with a $CaCl_2$ drying tube, containing 7-phenyldinaphtho[2,1-*b*:1′,2′-*d*]phosphole oxide (**2b**) (0.56 g, 1.48 mmol) and NaOH (0.15 g, 3.72 mmol) was immersed for 3 h into a hot bath containing glycerol at 260 °C. After being cooled to rt, the crude product was recrystallized from CH_2Cl_2/petroleum ether. **13:** 85% yield; mp 180–3 °C; ^{1}H-NMR δ 6.45 d (J = 8.7 Hz), 6.62 m, 6.75–6.90 m, 7.00 d (J = 9.0 Hz), 7.16 m, 7.22 d (J = 8.4 Hz), 7.36 t (J = 8.4 Hz), 7.44 t (J = 8.4 Hz), 7.62 d (J = 8.7 Hz), 7.75 d (J = 9.0 Hz), 7.83 d (J = 8.4 Hz), 8.26 dd (J = 8.4, 9.0 Hz), 10.20 bs; IR ν (cm^{-1}) 3425 (s), 3050 (s), 1160 (s), 1125 (s), 960 (s), 940 (s), 750 (m), 690 (m). Anal. Calcd for $C_{26}H_{19}O_2P$: C, 79.18; H, 4.86. Found: C, 78.93; H, 4.96.

Chloro[(*R*)-dimethyl(α-methylbenzyl)aminato-2-C,N]-[1-phenyldinaphtho[2,1-*b*:1′,2′-*d*]phosphole]palladium-(II) (10). To a suspension of (−)-di-μ-chlorobis[(*R*)-dimethyl(α-methylbenzyl)aminato-2-C,N]dipalladium(II) (0.226 g, 0.391 mmol) in $CHCl_3$ (50 mL) was added a solution of phosphole **1b** (0.280 g, 0.782 mmol) in the same solvent (15 mL). The suspension was stirred for 0.5 h. The solvent was evaporated and the residue washed with Et_2O (100 mL). The solid was filtered off and recrystallized from CH_2Cl_2/petroleum ether.

10: 85% yield; ^{1}H-NMR (rt) δ 1.80 bs, 2.60 bs, 2.80 bs, 3.65 bs, 6.20–8.40 m; ^{31}P-NMR δ 35.6; MS 650 (M$^+$, 78%), 614 (M − Cl − H, 100%); IR (Nujol, cm^{-1}) 3000 (w), 1420 (w), 650 (m), 450 (w), 200 (s). Anal. Calcd for $C_{36}H_{31}PPdClN$: C, 66.47; H, 4.80. Found; C, 66.31; H, 4.75

Chloro[(*R*)-dimethyl(α-methylbenzyl)aminato-2-C,N]-[1-phenyl-1,2,3,4-tetrahydrodinaphtho[2,1-*b*:1′,2′-*d*]phosphole]palladium(II) (11). To a suspension of (−)-di-μ-chlorobis[(*R*)-dimethyl(α-methylbenzyl)aminato-2-C,N]-dipalladium(II) (226 mg, 0.391mmol) in $CHCl_3$ (50 mL) was added a solution of the tetrahydrophosphole **8** (285 g, 0.782 mmol) in the same solvent (15 mL). The suspension was stirred for 0.5 h. The solvent was evaporated and the residue washed with Et_2O (100 mL). The solid was filtered off and recrystallized from CH_2Cl_2/petroleum ether.

11 (two diasteroisomers 1/1 ratio): 82% yield; ^{1}H-NMR (rt) δ 1.20 d (J = 7.5 Hz), 2.25–2.82 m, 3.10–3.20 m, 3.80 m, 5.22 m, 6.10–8.10 m; ^{31}P-NMR (rt) δ 32.8; MS 654 (M$^+$, 67%), 618 (M − Cl − H, 100%); IR (Nujol, cm^{-1}) 3000 (w), 1420 (w), 650 (m), 450 (w), 200 (s). Anal. Calcd for $C_{36}H_{35}PPdClN$: C, 66.06; H, 5.39. Found: C, 66.35; H, 5.45.

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