

Metallation Reactions on 2,2′-Bis(diphenylphosphinoyl)-1,1′-binaphthyl [BINAP(O)$_2$]

Michael Widhalm* **and Kurt Mereiter**†

Institute of Organic Chemistry, University of Vienna, Währinger Straße 38, A-1090 Vienna, Austria

†Institute of Chemical Technology and Analytics, Vienna University of Technology, Getreidemarkt 9, A-1060 Vienna, Austria

(Received October 21, 2002)

The behavior of BINAP(O)$_2$ upon treatment with lithium or magnesium amides under various conditions has been studied. With 2,2,6,6-tetramethylpiperidinomagnesium bromide, the *ortho* positions of opposed phenyl rings were selectively metallated, forming stable intermediates, while the use of lithium amides caused rearrangements with displacement of one diphenylphosphinoyl group and the formation of strained P-heterocycles (**2**, **5**, **6**) with unusual architectures. Monophosphine oxides **2** and **3a** have been reduced to phosphines **13** and **14** in good yield, while substituted BINAP(O)$_2$ derivatives failed to give the desired diphosphines. The stereochemistry of six phosphine oxides (**2**, **3a**, **5**, **8**, **9**, **11a**) and one phosphine (**13**) has been elucidated by crystal structure determinations.

Among the plenitude of chiral ligands already developed, BINAP, a C_2-symmetrical diphosphine, is outstanding due to its broad applicability in numerous asymmetric transformations, frequently yielding products of exceptionally high enantiomeric purity.[1] In the past modifications of the base structure have been undertaken in order to modify electronic and steric properties and to adapt for new reactions and substrates. Ligands with partial hydrogenated biaryl systems,[2] various diarylphosphino[3] and dicyclohexylphosphino substituents,[2] and with additional substituents in remote positions of the binaphthyl skeleton[4] have been prepared. Moreover, 2,2′-unsymmetrically substituted diphosphines[5] and monophosphines[6] have been synthesized, and BINAP has been anchored to polymers.[7] Typically, these modifications are performed before or together with the introduction of a PR_2 group rather than on BINAP itself, since in the latter case often side reactions occur due to oxidation and similar reactivity of aromatic positions. In contrast, 2,2′-bis(diphenylphosphinoyl)-1,1′-binaphthyl [BINAP(O)$_2$] is a stable compound and has been used mainly as a precursor for preparing optically pure BINAP via fractionated crystallization of diastereomeric complexes with tartaric acid.[8]

While phosphines do not stabilize *ortho*-metallated products, phosphine oxides should do so but treatment with R–Li is often accompanied by rearrangement or a rupture of one of the P–C bonds.[9] This has been used recently for the synthesis of unsymmetrical binaphthyl monophosphine ligands.[10] Only a few examples are reported that describe the selective *ortho* lithiation of phosphine oxides using phenyl and *tert*-butyllithium with careful temperature control.[11]

Despite the increasing number of reports on *ortho*-metallation with LDA[12,13] and other lithium or magnesium amides, no attempt seems to have been made to use these reagents for modifying BINAP(O)$_2$. Here we report our findings on metallation reactions of BINAP(O)$_2$ with lithium and magnesium dialkylamides.

Results and Discussion

The metallation of BINAP(O)$_2$ **1** is complicated by the fact that several *ortho* positions are accessible in the molecule. Treatment of **1** with various alkyllithium compounds at −78 °C in THF gave immediately dark brown solutions. Under these conditions unselective rupture of P–C_{ar} bonds takes place rather than *ortho*-metallation; after quenching the reaction with $(CH_3)_3SiCl$ (TMSCl), complex mixtures of products were obtained. In contrast, with LDA at room temperature a rearrangement smoothly occurred, followed by further lithiation and formation of secondary products (Table 1). The reactions were monitored by HPLC to elucidate their relationship and optimize conditions for their formation. For this purpose samples of ∼0.1 mL were removed by syringe and quenched with water or TMSCl. The organic phase was diluted with CH_2Cl_2 (1 mL), filtered through a pad of $MgSO_4$ and analyzed. Above −20 °C the cyclized monophosphine oxide **2** was formed quantitatively (HPLC, entry 1). Its formation can be explained as an intramolecular S_N attack of the *ortho* lithio intermediate **1–Li** at the 2-position of naphthyl with displacement of $Ph_2P(O)Li$ (Scheme 1). The structure was confirmed by X-ray crystallography. With two molar amounts of LDA the reaction was complete within 2 h. Under these conditions, none of the products of subsequent transformations (see below) was detected by HPLC. The solvent dependence is low and isolated yields range from 66 to 70% (entry 2–5). Adding 4 mol amt. of LDA and increasing the reaction time to 4 h gave a lower yield of **2** (50%) and a mixture of **5** and **6** (totally 12%). Quenching the reaction at this state with TMSCl yielded the silylated compound **3a** at the cost of **2**, while the amount of **5** + **6** was nearly unaffected. A prolonged reaction time led to significant decomposition of **2**, possibly via **3a**, and a maximum of 16% of **5** + **6** (entry 6–9). From this we con-

Table 1. Lithiation of BINAP(O)$_2$ Products Isolated after Reaction with Water and TMSCl

Entry[a]	Reagent	Mol amts.	*t*/h	*T*/°C	Electrophile	**7**	**9**	**2**	**3a**	**5**+**6**	**8**
1	LDA	2	2	r.t.	H_2O			66		—[b]	
2[c]	LDA	4	2	r.t.	H_2O			62			
3[c]	LDA	2	2	r.t.	H_2O			70			
4[d]	LDA	4	2	r.t.	H_2O			69			
5[d]	LDA	2	2	r.t.	H_2O			69			
6	LDA	4	4	r.t.	H_2O			50		12	
7	LDA	4	3	r.t.	TMSCl			14	22	13	
8	LDA	4	15	r.t.	TMSCl			—[b]	10	16	
9	Li TMP	4	3	−20	TMSCl				62		
10[e]	LDA	2	f	−78/r.t.	TMSCl	40		—[b]			22
11	LDA	8	f	−78/r.t.	TMSCl	0	—[b]	—[b]			73
12	Li TMP	4	f	−78/r.t.	TMSCl		27				28

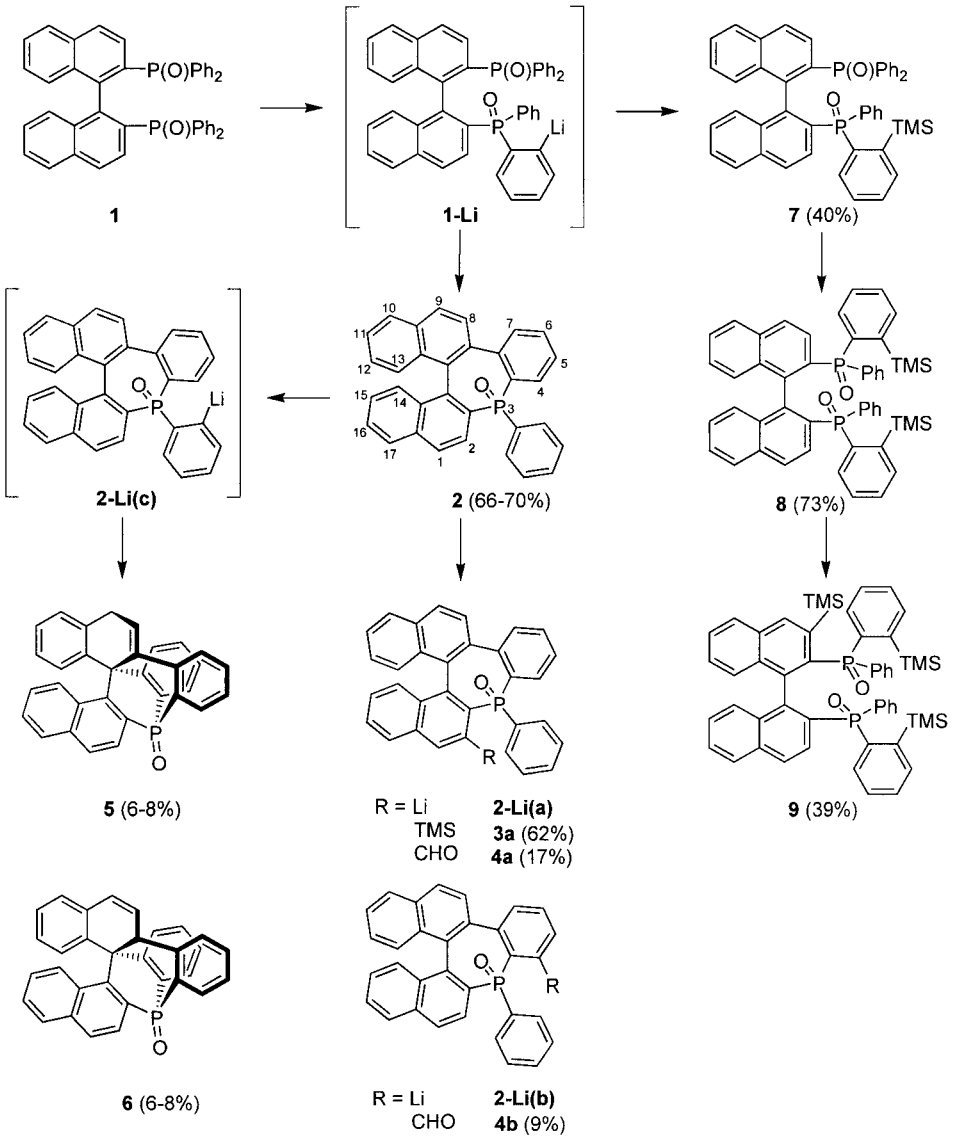
a) All reactions were performed on a 0.5 mmol scale in THF if not otherwise noted; for details see Experimental. In preexperiments the progress of the reaction was monitored by HPLC. In 0.5 h intervals samples were taken and quenched with the electrophile. After extractive work-up and drying ($MgSO_4$) the samples were analyzed (column: Spherisorb S5W, 300 × 4.6 mm, flow: 1 mL min^{-1} at 40 °C, integration wavelength: 280 nm). Retention time (min): **1**: 21.40, **2**: 11.73, **3a**: 3.50, **5**: 8.05, **6**: 8.38, **7**: 10.07, **8**: 3.06, **9**: 2.65. (not in the table: **4a**: 6.68, **4b**: 5.80, **10a**: 8.36, **11a**: 6.30). b) Traces c) In DME d) In dioxane e) 10–20% of unreacted starting material recovered. f) After mixing **1**, LDA, and TMSCl (excess) in THF at −78 °C, the reaction was slowly warmed up to r.t. over night.

cluded that **2** is further metallated but in a less regiospecific manner, as the P=O group has become part of a ring.[13] While the preferential introduction of Li takes place at the naphthyl ring, finally giving rise to **3a**, also the exocyclic phenyl ring is lithiated in position 2 (**2–Li(c)**). Its proximity to C-1 of the naphthyl moiety facilitates a 1,4-addition, ending up with a strained polycyclic structure. After hydrolysis, **6** and its isomer **5** with conjugated double bonds are formed (Scheme 1). Since both are also formed upon reaction with TMSCl we speculate that the primary product is too unstable to be isolated, decomposing under the conditions of work-up to give **5** and **6**. The isomers could be separated by fractionated crystallization. The third site for *ortho* lithiation, attacking the bridging phenylene group, becomes apparent only when quenching the reaction with less encumbered electrophiles like DMF or CH_3I. (HPLC analysis indicated a 2:1 mixture of **4a** and **4b**.) Applying the more powerful and sterically demanding nucleophile *N*-lithio-2,2,6,6-tetramethylpiperidine (Li-TMP) at −20 °C, a better yield of **3a** was obtained. These findings revealed that the ortho position of phenyl rings are preferably attacked, but the high readiness for subsequent cyclization prevented the synthetic use of the primarily formed lithio compounds.

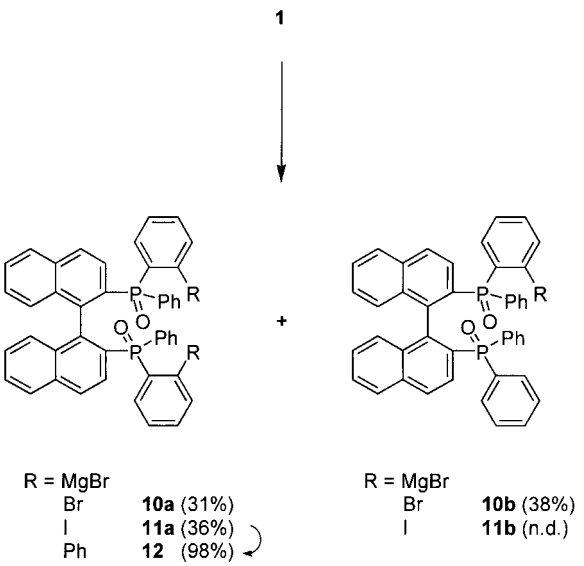
Trapping of lithio intermediates at low temperature has been reported by in situ reaction with electrophiles like $(CH_3O)_3B$ and TMSCl.[14] Under these conditions, the electrophile is not affected by lithio amides but reacts fast with lithiated aromats, thus suppressing subsequent reactions or rearrangements. We made use of this strategy and reacted a mixture of **1** in the presence of TMSCl at −78 °C with varying amounts of LDA or Li-TMP, respectively. As above, the conversion was monitored by HPLC to evaluate optimized conditions for enrichment of three main products (entry 10–12). With two molar amounts of LDA a 40% yield of **7** along with 22% of the C_2-symmetrically disubstituted product **8** could be obtained. At this stage of the reaction, 10–20% of starting material also remained. To make **8** the main product, the amount of LDA was increased to 8 mol amt., giving 73% of **8**. HPLC indicated the complete absence of **7** and that only traces of **2** and **3a** were present. With Li-TMP (4 mol amt.) further lithiation at the position 3 of naphthyl took place, giving a maximum yield of 27% of **9** along with 28% of **8**. Increasing the amount of Li-TMP did not improve the (isolable) yield of **9**, since **9** became a part of an inseparable mixture of polysilylated products.

As the application of lithio amide bases resulted in skeleton rearrangements rather than in clean metallation reactions, we applied the corresponding Grignard reagent, which has been used for diastereoselective *ortho* magnesation.[15] Stirring **1** with 4 molar amounts of 2,2,6,6-tetramethylpiperidinomagnesium bromide (TMP-MgBr) at room temperature for 6–12 h afforded a brown solution, which was quenched with Br_2 or I_2 (Scheme 2). Mixtures of mono- and di-halo products were formed and could be readily separated by column chromatography. Although the yields of **10** and **11** were moderate, no skeleton transformation was observed. The diiodo derivative **11a** served as an excellent precursor for the preparation of **12** via a Suzuki reaction.

For use in asymmetric catalysis, attempts were made to convert phosphineoxides **2**, **3a**, **8**, and **12** to the corresponding phosphines (Scheme 3). Two methods, either the addition of methyl triflate followed by reduction with lithium aluminum hydride,[16] or reduction with aluminum hydride[17] worked well for **2**, affording phosphine **13** in 98% and 85% yield, respectively. Reoxidation of **13** to **2** with hydrogen peroxide proceeded quantitatively. In the same way the trimethylsilyl-substituted substrate **3a** was smoothly reduced, giving **14** (83%). In contrast, all attempts to reduce **8** or **12** to **15** or **16**, respectively failed. With TfOMe/$LiAlH_4$, only the half-reduced compound **15a** was isolated in low yield. This may be attributed to steric hindrance rendering only the formation of the mono triflate. Applying more stringent conditions or excess of alane resulted in the formation of inseparable mixtures of low polar products.



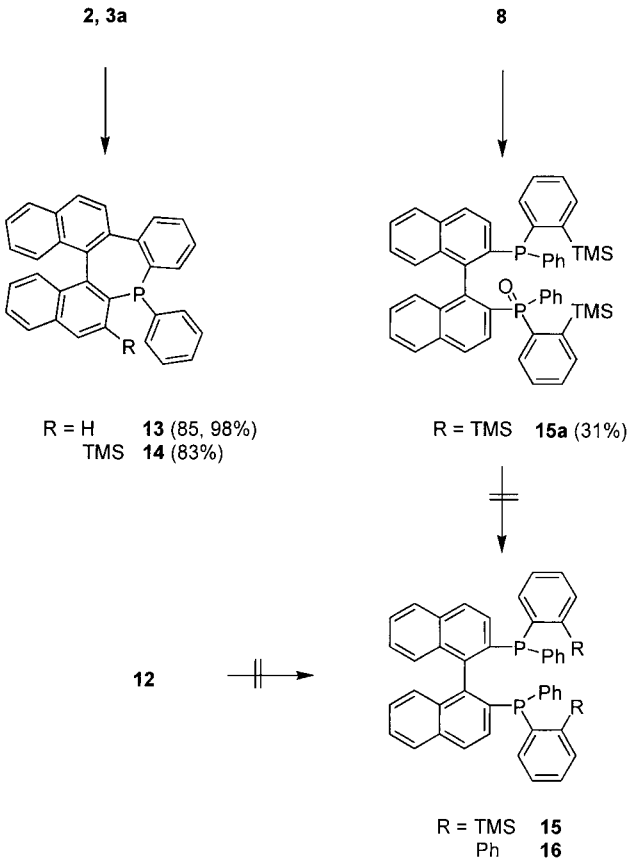
Scheme 1. (Optimized yields in paranthesis).



Scheme 2. (Optimized yields in paranthesis).

Crystal Structure Analyses and Stereochemistry of 2, 3a, 5, 8, 9, 11a, and 13. In order to ascertain molecular structures and to study the stereochemistry of the novel compounds, the crystal structures of seven sufficiently well crystallizing representatives were determined by X-ray single crystal diffraction. Technical details on this work are reported in the experimental section and crystallographic data are compiled in Table 2. According to their carbon-phosphorus backbones, the compounds will be grouped in three classes: (A) binaphthyls with a phosphepine ring comprising the phosphinoyls **2** and **3a** and the phosphine **13**; (B) the phosphinoyl **5** with 1,4-dihydronaphthyl moiety and a cage-like phospha-bicyclo[3.2.2]nonane core; and (C) the substituted 2,2′-bis(diphenylphosphinoyl)-1,1′-binaphthyls **8**, **9**, and **11a**. Two of these compounds crystallized as solvates, namely **3a** as a disordered DMF solvate and **11a** as a well defined and stable bis-chloroform solvate.[18]

The three molecules of class A compounds **2**, **3a**, and **13** are shown in Figs. 1, 2, and 3, with selected geometric data presented in Table 3. One common feature of these three com-



Scheme 3. (Optimized yields in paranthesis).

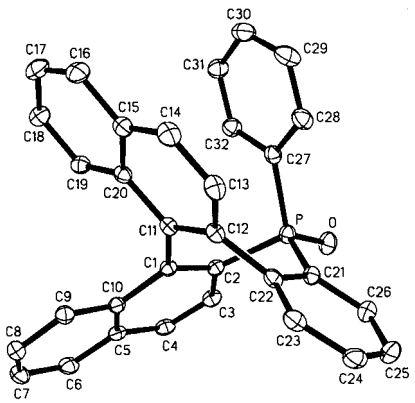


Fig. 1. Solid state structure of **2** (20% ellipsoids, H atoms omitted for clarity). The solid state structure of phosphine **13**, not shown, looks practically identical lacking only the oxygen atom.

pounds is a phosphorus containing seven-membered ring built up from three aromatic C–C, two aliphatic C–C and two P–C bonds. The ring has a relatively regular boat conformation. This boat conformation is a consequence of the geometric restrictions of three essentially planar 4-atom groups P–C2–C1–C11, P–C21–C22–C12, and C2–C1–C12–C22 introduced by the three aromatic ring systems that take part in the formation of the 7-ring. If one omits the outer two phenyl rings of the binaphthyl moiety (see Fig. 1), the saddle-like structure of a tribenzo[*b*,*d*,*f*]phosphepine with potential mirror-symmetry (m = plane defined by C27, P, and midpoint of C11–C12)

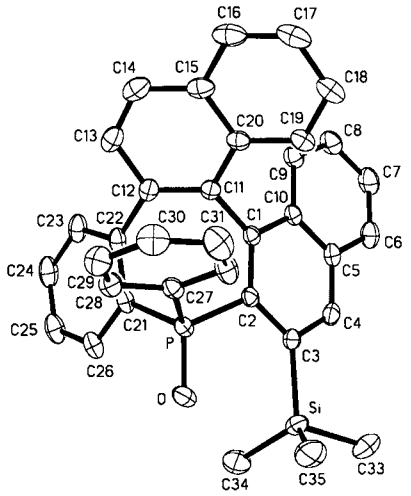


Fig. 2. Solid state structure of **3a** in **3a**·*DMF* (20% ellipsoids. H atoms omitted).

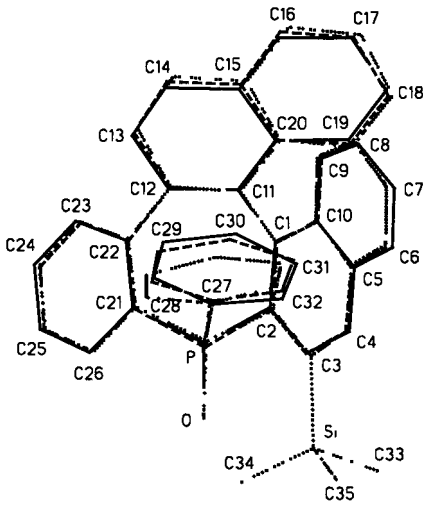


Fig. 3. Superposition plot of the molecular structures of **2** (full lines), **3a** (dotted lines), and **13** (broken lines) in solid state.

would result; it would become desymmetrized in the ring and in the periphery by completing two phenyl residues to a binaphthyl moiety. A distinct stiffness of the system becomes apparent from the torsion angles in the 7-membered ring given in Table 3 and from the superposition plot of **2**, **3a**, and **13** shown in Fig. 3. The only major freedom of the three molecules is the orientation of their phenyl rings C27 through C32 and the phosphinoyl oxygen atom or electron lone-pair of P in **13**. In all cases the respective phenyl ring is in axial orientation relative to the boat, whereas oxygen (**2**, **3a**) or electron lone pair (**13**) are equatorial. One reason for this stereochemistry is that the free phenyl ring gains stabilization by means of an intramolecular π-stacking interaction with the naphthyl residue C11–C20, particularly so for C32–C27–C28 and less for the outer carbon atoms C29–C30–C31. In summary **2**, **3a**, and **13** form compact triaro[*b*,*d*,*f*]phosphepine molecules of boat conformation and of limited flexibility. They show an approximately mirror symmetric aspect when seen from the phosphorus side (except for the $SiMe_3$ group in **3a**)

Table 2. Crystallographic Details for **2**, **3a**·*DMF*, **5**, **8**, **9**, **11a**·2$CHCl_3$, and **13**

Compound	**2**	**3a**·*DMF*	**5**	**8**	**9**	**11a**·2$CHCl_3$	**13**
Formula	$C_{32}H_{21}OP$	$C_{38}H_{36}NO_2PSi$	$C_{32}H_{21}OP$	$C_{50}H_{48}O_2P_2Si_2$	$C_{53}H_{56}O_2P_2Si_3$	$C_{46}H_{32}O_2P_2Cl_6I_2$	$C_{32}H_{21}P$
Formula weight	452.46	597.74	452.46	799.00	871.19	1145.16	436.46
Crystal system	Orthorhombic	Triclinic	Monoclinic	Orthorhombic	Monoclinic	Orthorhombic	Triclinic
Space group	$P2_12_12_1$	$P\bar{1}$	$P2_1/n$	*P*bca	$P2_1/n$	*P*ca2_1	$P\bar{1}$
a/Å	8.458(2)	10.188(2)	9.981(4)	18.101(3)	30.941(17)	21.079(4)	9.830(2)
b/Å	15.560(4)	12.195(3)	11.197(4)	20.908(3)	9.314(5)	12.549(2)	10.939(2)
c/Å	17.427(4)	14.825(3)	20.307(6)	23.039(3)	33.934(19)	17.566(3)	11.822(2)
α/deg		104.86(2)					111.851(3)
β/deg		107.69(2)	103.06(2)		96.48(1)		90.548(3)
γ/deg		91.95(2)					103.535(3)
V/Å^3	2293.5(10)	1683.5(6)	2210.8(14)	8719(2)	9717(9)	4646.6(14)	1140.6(4)
Z	4	2	4	8	8	4	2
T/K	297	297	297	183(2)	297	183(2)	297
D_{calcd}/g cm^{-3}	1.310	1.179	1.359	1.217	1.191	1.637	1.271
μ(Mo Kα)/mm^{-1}	0.144	0.150	0.149	0.194	0.202	1.805	0.139
Θ_{max}/deg	27.0	25.0	25.1	27.0	25.0	30.0	27.5
No. of reflns collected	27729	14623	22402	100459	48233	65055	14290
Transmission ratio min/max	0.90	0.92	0.91	0.91	0.95	0.80	0.89
R_{int}	0.042	0.018	0.048	0.039	0.045	0.025	0.028
No. of unique reflns	5001	5918	3893	9497	17013	13392	5205
No. of observed refl [$I > 2\sigma(I)$]	4208	4760	2901	7432	9887	11740	3866
No. of parameters refined	308	343	307	511	1082	523	298
Goodness of fit	1.024	1.080	1.018	1.080	1.014	1.029	1.018
*R*1 [$I > 2\sigma(I)$]	0.035	0.041	0.035	0.043	0.048	0.028	0.039
*wR*2 (all data)	0.082	0.124	0.088	0.125	0.133	0.067	0.102
$\Delta\rho$ (min/max) (eÅ^{-3})	−0.20/0.18	−0.29/0.18	−0.34/0.18	−0.23/0.43	−0.24/0.23	−0.61/0.78	−0.18/0.28

Table 3. Selected Geometric Data (Å and deg) for **2**, **3a**·*DMF*, **13**, and **5**

	2	**3a**·*DMF*	**13**	**5**
P–O	1.485(1)	1.482(1)		1.478(1)
P–C27	1.803(2)	1.806(2)	1.836(2)	1.769(2)
P–C2	1.806(2)	1.809(2)	1.843(2)	1.787(2)
P–C21	1.805(2)	1.807(2)	1.840(2)	1.807(2)
C2–C1	1.382(2)	1.387(2)	1.390(2)	1.382(2)
C1–C11	1.508(2)	1.490(2)	1.500(2)	1.554(2)
C11–C12	1.387(2)	1.389(2)	1.386(2)	1.547(2)
C12–C22	1.491(2)	1.482(2)	1.495(2)	1.506(3)
C22–C21	1.406(2)	1.399(2)	1.410(2)	1.417(3)
C11–C28				1.564(3)
C12–C13	1.426(3)	1.418(3)	1.429(2)	1.337(3)
C13–C14	1.351(3)	1.354(3)	1.359(2)	1.488(3)
C14–C15	1.402(3)	1.413(3)	1.419(2)	1.500(3)
C3–Si		1.908(2)		
C2–P–C21	100.2(1)	100.8(1)	96.2(1)	100.1(1)
C2–P–C27	106.1(1)	110.9(1)	103.6(1)	103.1(1)
C21–P–C27	110.0(1)	109.3(1)	106.4(1)	104.1(1)
C1–C2–P–C21	56.0(2)	56.5(1)	57.4(1)	56.9(2)
C22–C21–P–C2	−54.6(2)	−59.2(1)	−52.6(1)	−55.8(2)
C2–C1–C11–C12	−62.4(2)	−65.9(2)	−62.1(2)	−90.9(2)
C21–C22–C12–C11	52.5(2)	47.5(2)	52.0(2)	24.3(2)
C1–C11–C12–C22	7.1(3)	10.6(2)	9.3(2)	42.9(2)
C11–C1–C2–P	13.3(2)	14.1(2)	9.4(2)	22.2(2)
C12–C22–C21–P	−12.6(2)	−8.8(2)	−14.0(2)	−9.2(3)
C2–P–C27–C28	136.3(2)	155.1(1)	143.2(1)	22.9(2)

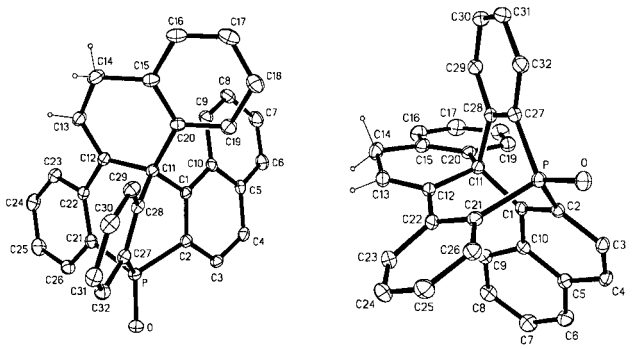


Fig. 4. Solid state structure of **5** in two views (20% ellipsoids). Only the three non-aromatic H atoms are shown.

but are asymmetric on their opposite sides. Only a few other compounds with related phosphepine rings and related stereochemistry but very different synthetic backgrounds have been reported so far. Most of them are based on the dihydro-dibenzo[*b*,*f*]phosphepine skeleton;[19] only one compound has the tribenzo[*b*,*d*,*f*]phosphepine skeleton substituted by five phenyl rings.[20] This last compound is different from **2**, **3a**, and **13** in being very close to mirror symmetry and in having P-phenyl and phosphinoyl oxygen in equatorial and axial positions, respectively.

The only structurally characterized compound of class B is the phosphinoyl **5**, whereas attempts to crystallize **6** for X-ray diffraction were not successful. **5** derives from class A compounds by an additional C–C bond between C11 and C28 (Fig. 4; geometric data are included in Table 3). This additional C–C bond leads to a phospha-bicyclo[3.2.2]nonane core, to the 1,4-dihydro-dearomatization of one phenyl ring (C11–C15, C20) of the second naphthyl moiety, and to a pronounced distortion of the formerly boat-shaped phosphepine ring. As a result of the introduction of two sp^3-hybridized C atoms in 1,4-positions, the second naphthyl unit becomes bent with an angle of 17.1(1)° between the two parts C11–C12–C13–C14 (inner part) and C15 through C20 (outer part). Another consequence of the steric restraints imposed by the phospha-bicyclo[3.2.2]-nonane core is a very significant bend of the naphthyl unit C1 through C10 (to be seen from the interplanar angle between C1–C2–C3–C4 and C5 through C10 of 13.6(1)°) and the very large deviation of phosphorus from the mean plane of the naphthyl group C1 through C10, measuring 0.857 Å. Thus **5** is, despite its straightforward synthesis, a molecule of surprising complexity. Although there is no closely related phosphorus compound, it should be mentioned that some small polycyclic phospha-compounds have been studied so far, such as phosphabicyclo[3.2.1]octanes.[21]

The class C compounds **8**, **9**, and **11** are all heavily substituted BINAP(O$_2$) derivatives, as shown in Figs. 5, 6, and 7. They represent binaphthyls with interplanar angles not far from 90°. Bond lengths and angles show no unusual features, as demonstrated by a selection of geometric data presented in Table 4. Different from class A/B compounds with low molecular symmetries they come close to molecular symmetry C_2. For compounds **8** and **9**, this behaviour is supported by intramolecular π-stacking interactions between the naphthyl moi-

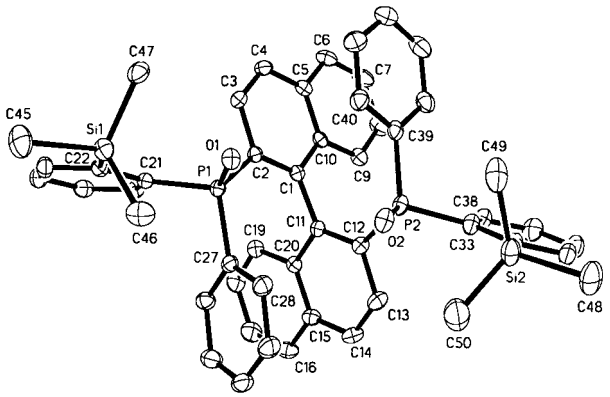


Fig. 5. Solid state structure of **8** (40% ellipsoids, H atoms omitted).

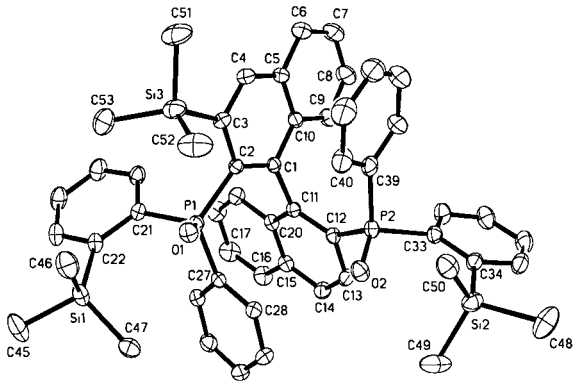


Fig. 6. Solid state structure of **9** (20% ellipsoids, H atoms omitted). Only the first of the two crystallographically independent but geometrically similar molecules is shown.

ety of one half molecule and a phenyl ring of the other half molecule and vice versa, an interaction very common for BINAP's. In both compounds, the oxygen atoms are buried by near $SiMe_3$ groups and other entities, which renders their reduction to the phosphine difficult. **11a** in the form of its solvate **11a**·2$CHCl_3$ shows a different conformation: here the

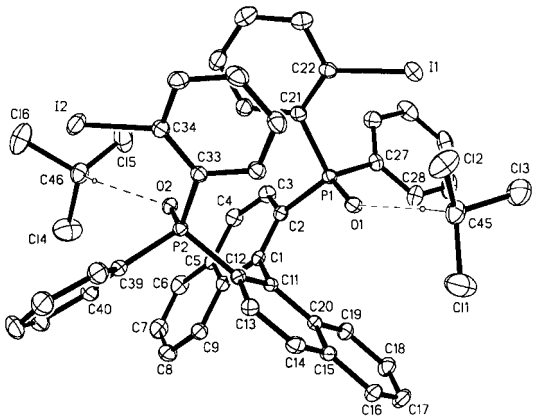


Fig. 7. Solid state structure of **11a**·2$CHCl_3$ (40% ellipsoids) with C–H···O hydrogen bonded $CHCl_3$ solvent molecules, C45···O1 = 3.050(4) Å, C46···O2 = 2.974(4) Å. Aromatic H atoms omitted.

two 2-iodophenyl moieties are mutually π-stacked and orient the P–O bonds nearly parallel to the naphthyl-naphthyl C–C bond. It is typical that the two phosphinoyl oxygen atoms form clear-cut C–H···Cl hydrogen bonds with two $CHCl_3$ molecules (Fig. 7), making the solvate stable at ambient temperature.

Conclusions

Metallation of $BINAP(O)_2$ with lithium or magnesium amides takes place primarily at the *ortho* positions of one of the phenyl rings. Subsequently, a phenyl ring of the opposite phosphino functionality is attacked, resulting in a C_2 symmetrical species. The Grignard-type intermediates are stable at room temperature and react with appropriate electrophiles. The primarily formed lithium intermediates may be trapped in situ at low temperature with TMSCl, giving rise to mono-, di-, and trisubstituted $BINAP(O)_2$ derivatives, while above -40 °C intramolecular ipso-substitution occurs, forming a cyclic phosphine oxide. With excess of lithiating reagent, further lithiation is observed, albeit with moderate site selectivity

Table 4. Selected Geometric Data (Å and deg) for **8**, **9**, and **11a**·2$CHCl_3$

	8	**9** molecule 1	**9** molecule 2*	**11a**·2$CHCl_3$
P1–O1	1.487(2)	1.478(2)	1.480(2)	1.483(2)
P2–O2	1.484(2)	1.478(2)	1.475(2)	1.483(2)
C22–Si1/I1	1.907(2)	1.925(3)	1.920(3)	2.103(3)
<Si1–C_{Me}>	1.876(3)	1.860(3)	1.864(4)	
C34–Si2/I2	1.914(2)	1.910(3)	1.907(3)	2.108(3)
<Si2–C_{Me}>	1.871(3)	1.865(4)	1.855(4)	
C3–Si3		1.925(3)	1.919(3)	
<Si3–C_{Me}>		1.869(4)	1.861(4)	
C2–C1–C11–C12	−91.6(2)	−91.2(3)	−85.8(3)	95.4(3)
O1–P1–C2–C1	109.7(2)	134.9(2)	143.8(2)	11.7(3)
O2–P2–C12–C11	102.0(2)	104.1(3)	92.7(2)	7.2(3)
O1–P1–C21–C22	−21.7(2)	−45.7(3)	−46.3(3)	59.5(2)
O2–P2–C33–C34	−11.2(2)	−22.3(3)	−15.1(3)	61.6(2)
O1–P1–C27–C28	−15.3(2)	−38.3(2)	−38.6(2)	33.9(3)
O2–P2–C39–C40	−22.8(2)	−19.7(3)	−9.7(2)	31.4(2)

* **9** contains two independent molecules of similar conformation.

and in part a second skeleton rearrangement takes place. Structures of all key intermediates have been confirmed by X-ray crystal structure analysis. Monophosphine oxides were readily reduced to the corresponding phosphines, while BINAP(O)$_2$ derivatives afforded only partially reduced products in low yield.

Experimental

Melting points: Kofler melting point apparatus, uncorrected. NMR: Bruker AM 400 spectrometer at 400.13 MHz (^{1}H), and 100.61 MHz (^{13}C), respectively in $CDCl_3$ if not otherwise noted; chemical shifts δ are reported in ppm rel. to $CHCl_3$ (7.24 or 77.00 ppm, respectively). Coupling patterns are designated as s(inglet), d(oublet), t(riplet), p(seudo), and b(road). ^{13}C{^{1}H} NMR spectra are recorded in a *J*-modulated mode; signals are assigned as C for quaternary carbon; undesignated signals refer to CH-resonances. In spectral areas with extensive signal overlapping, multiplets could not be identified; these signals of unclear relationship are underlined, ignoring probable multiplet structures. MS: MAT 900 EI (70 eV). Preparative MPLC was performed on a column (45 × 4 cm) packed with LiChroprep-Si 60 (25–40 μm, MERCK) using an FMI Lab Pump (1–7 bar). HPLC analyses were performed on Spherisorb S5W (300 × 4.6 mm) using an HP 1090 chromatograph equipped with a diode array detector.

Petroleum ether (PE) and ethyl acetate (EA) were distilled; absolute THF, dioxane, and DME were distilled from sodium diphenylketyl and Et_2O from $LiAlH_4$. *n*-BuLi and LDA were used as 1.6 molar (in hexane) and 1.5 molar (as THF complex in cyclohexane) solutions, respectively (Aldrich). All the other chemicals were analytical grade and were used without further purification.

BINAP(O)$_2$ was prepared either according to Ref. 8 or by an analogous procedure, as reported for the preparation of BINAP from 2,2′-dibromo-1,1′-binaphthyl using diphenylphosphinous chloride instead of chlorodiphenylphosphine (66%).[1d]

3-Phenyl-3*H*-benzo[*b*]dinaphtho[2,1-*d*:1′,2′-*f*]phosphepine 3-oxide (2). To a degassed solution of **1** (3.27 g, 5 mmol) in 100 mL of THF was added LDA solution (6.67 mL, 10 mmol) at 0 °C under Ar. The dark brown solution was warmed up to r.t. and stirred for 2 h. After 30 min a precipitate formed. The reaction was quenched by the addition of a small amount of hydrochloric acid (2 M) and the bulk of the solvent was evaporated. More hydrochloric acid (2 M, 50 mL) was added and the mixture was extracted with CH_2Cl_2 (3 × 50 mL). The combined extracts were washed with water (50 mL), dried with $MgSO_4$ and evaporated. The residue was chromatographed on SiO_2 (column 30 × 5 cm) in EA/PE (70:30) to give 1.49 g (66%) of **2**; mp: 329–331 °C. ^{1}H NMR δ 6.68 (m, 2H), 6.87 (m, 1H), 6.89 (bd, 1H, J = 8.1 Hz), 7.06 (m, 2H), 7.17 (m, 3H), 7.36 (m, 1H), 7.44 (d, 1H, J = 8.6 Hz), 7.50 (m, 1H), 7.57 (m, 1H), 7.67 (m, 3H), 7.76 (m, 1H), 7.98 (d, 1H, J = 8.3 Hz), 8.16 (dd, 1H, J = 8.6, 1.8 Hz), 8.30 (ddd, 1H, J = 12.3, 7.7, 1.4 Hz), 8.45 (dd, 1H, J = 10.6, 8.3 Hz). ^{13}C NMR δ 126.03 (d, J = 6.9 Hz), 126.32, 126.62, 126.82, 127.46 (d, J = 13.0 Hz), 126.65, 127.68 (d, J = 10.6 Hz), 128.03, 128.21, 128.24, 128.41, 128.72, 128.88 (d, J = 10.7 Hz), 129.18, 129.33 (d, J = 11.5 Hz), 130.08 (d, J = 9.9 Hz), 130.72 (d, J = 3.1 Hz), 131.23 (d, J = 6.9 Hz), 131.65 (C, d, J = 108 Hz), 132.30 (C), 132.39 (C), 132.49 (d, J = 2.3 Hz), 133.23 (C, d, J = 3.3 Hz), 133.38 (C, d, J = 11.5 Hz), 135.26 (C, d, J = 2.1 Hz), 135.55 (C, d, J = 138 Hz), 136.57 (C, d, J = 137 Hz), 136.66 (C, d, J = 10.3 Hz), 137.73 (C, d, J = 1.5 Hz), 142.33 (C, d, J = 9.7 Hz). ^{31}P NMR δ 21.53 (s). MS (180 °C): m/z 452 (M^+, 66%). Found: C, 84.70; H, 5.07%. Calcd for $C_{32}H_{21}OP$: C, 84.94; H, 4.68%.

3-Phenyl-2-trimethylsilyl-3*H*-benzo[*b*]dinaphtho[2,1-*d*:1′,2′-*f*]phosphepine 3-oxide (3a). To a degassed suspension of **1** (327 mg, 0.5 mmol) in 10 mL of THF was dropwise added a solution of *N*-lithio-2,2,6,6-tetramethylpiperidine (prepared from 372 μL of 2,2,6,6-tetramethylpiperidine and 1.25 mL of *n*-BuLi in 3 mL of THF) during 15 min at −20 °C; stirring was continued for 3 h. The temperature was decreased to −78 °C and the reaction was quenched upon adding excess of TMSCl (4 mmol, 507 μL). After extractive work-up with hydrochloric acid (2 M, 10 mL) and CH_2Cl_2 (2 × 10 mL), the organic extract was dried with $MgSO_4$, evaporated and the residue was chromatographed on SiO_2 in EA/PE (30:70) to afford **3a** as a white foam. ^{1}H NMR δ 0.62 (s, 9H), 6.58 (m, 2H), 6.70 (d, 1H, J = 8.6 Hz), 6.76 (m, 1H), 6.89 (d, 1H, J = 8.6 Hz), 6.96–7.03 (m, 2H), 7.03–7.12 (m, 2H), 7.27 (m, 1H), 7.38 (d, 1H, J = 8.6 Hz), 7.40 (m, 1H), 7.49 (m, 1H), 7.54–7.60 (m, 3H), 7.69 (ddd, 1H, J = 7.8, 4.7, 0.8 Hz), 7.86 (d, 1H, J = 8.1 Hz), 8.33 (ddd, 1H, J = 12.1, 7.6, 1.0 Hz), 8.36 (d, 1H, J = 1.8 Hz). ^{13}C NMR δ 2.89 (CH_3), 122.44, 125.80, 126.20, 126.90, 126.90 (d, J = 13.0 Hz), 127.20, 127.22, 127.29 (d, J ∼11 Hz), 127.58 (2 × CH), 127.98, 128.34, 128.51 (d, J = 12.2 Hz), 128.72, 128.72 (d, J = 9.9 Hz), 129.89 (d, J = 3.1 Hz), 131.70 (d, J = 7.6 Hz), ∼131.37 (C), 131.92 (C, d, J = 105 Hz), 131.97 (d, J = 2.3 Hz), 132.49 (C), 133.38 (C, d, J = 12.1 Hz), 133.38 (C, d, J = 2.1 Hz), 136.74 (C, d, J = 97.7 Hz), 137.09 (C), 137.34 (d, J = 14.5 Hz), 139.36 (C, d, J = 105 Hz), 139.76 (C, d, J = 14.5 Hz), 141.63 (C, d, J = 8.3 Hz), 146.07. ^{31}P NMR δ 26.20 (s). MS (150 °C): 523 ($M^+ - 1$, 1%); m/z 509 ($M^+ - 15$, 100%). Found: C, 79.83; H, 5.27%. Calcd for $C_{35}H_{29}OPSi$: C, 80.12; H, 5.57%.

2-Formyl-3-phenyl-3*H*-benzo[*b*]dinaphtho[2,1-*d*:1′,2′-*f*]-phosphepine 3-oxide (4a) and 4-Formyl-3-phenyl-3*H*-benzo[*b*]dinaphtho[2,1-*d*:1′,2′-*f*]phosphepine 3-oxide (4b). Lithiation of **1** under the same conditions as given for the synthesis of **3a** and reaction with excess of DMF (8 mol. amt.) added at −78 °C afforded a crude mixture of **4a**, **4b**, and **2** which was separated by MPLC. Elution with EA/PE (50:50) eluted **4b** (9%) followed by **4a** (17%). With EA/PE (70:30) **2** (27%) was eluted.

4a: Mp: 305–307 °C. ^{1}H NMR δ 6.60–6.65 (m, 3H), 6.80 (m, 1H), 6.96 (d, 1H, J = 8.6 Hz), 7.03–7.11 (m, 3H), 7.20 (m, 1H), 7.29 (m, 1H), 7.40 (d, 1H, J = 8.6 Hz), 7.46 (m, 1H), 7.51 (m, 1H), 7.60 (m, 2H), 7.62 (d, 1H, J = 8.6 Hz), 7.70 (m, 1H), 7.98 (d, 1H, J = 8.3 Hz), 8.38 (ddd, 1H, J = 12.4, 7.6, 1.0 Hz), 8.61 (d, 1H, J = 2.8 Hz), 11.68 (s, 1H). ^{13}C NMR δ 126.08, 126.56, 127.15 (d, J = 16.1 Hz), 127.20, 127.44, 127.49 (d, J = 10 Hz), 127.76, 127.99, 128.21, 121.56 (d, J = 12.2 Hz), 128.88, 128.98 (d, J = 9.9 Hz), 129.24, 129.91 (d, J = 9.5 Hz), 129.92, 130.38 (C, one branch of a doublet), 130.49 (d, J = 2.3 Hz), 131.70 (C), 131.78 (C, d, J = 63 Hz), 132.17 (d, J = 7.6 Hz), 132.46 (C, d, J = 4.0 Hz), 132.56 (d, J = 2.0 Hz), 133.38 (C), 133.40 (C), 133.76 (C), 134.75 (C), 134.95 (C), 135.06 (C), 135.35 (C), 136.38 (C), 137.08 (C), 137.10 (C), 137.16 (C), 137.24 (C), 138.70 (C, d, J = 11.0 Hz), 141.20 (C, d, J = 9.0 Hz), 193.66 (d, J = 2.3 Hz). ^{31}P NMR δ 28.18(s). MS (140 °C): m/z 480 (M^+, 8%); 452 ($M^+ - 28$, 100%). Found: C, 82.11; H, 4.60%. Calcd for $C_{33}H_{21}O_2P$: C, 82.49; H, 4.41%.

4b: ^{1}H NMR δ 6.62 (m, 2H), 6.84 (m, 1H), 6.97 (d, 1H, J = 8.6 Hz), 7.02 (m, 1H), 7.06 (m, 1H), 7.14–7.23 (m, 4H), 7.35 (m, 1H), 7.48 (ddd, 1H, J = 8.1, 5.8, 2.0 Hz), 7.54 (d, 1H, J = 8.6 Hz), 7.60 (d, 1H, J = 8.2 Hz), 7.64 (m, 1H), 7.76 (m, 1H), 7.92

(d, 1H, $J = 8.3$ Hz), 7.98 (ddd, 1H, $J = 7.6$, 2.8, 1.3 Hz), 8.11 (dd, 1H, $J = 8.6$, 2.3 Hz), 8.53 (dd, 1H, $J = 10.9$, 8.6 Hz), 11.64 (s, 1H). ^{13}C NMR δ 126.34, 126.41 (d, $J = 8.3$ Hz), 126.66, 126.68 (d, $J = 2$ Hz), 127.14 (d, $J = 13.3$ Hz), 127.35 (d, $J = 9.2$ Hz), 127.64, 127.75, 127.82, 128.06, 128.07, 128.43, 128.55 (d, $J = 11.0$ Hz), 128.80 (d, $J = 11.0$ Hz), 129.01, 130.65 (d, $J = 2.8$ Hz), 130.98 (C, d, $J = 109$ Hz), 131.42 (C, d, $J = 1$ Hz), 131.89 (d, $J = 2.3$ Hz), 132.05 (C), 132.54 (C, d, $J = 11$ Hz), 133.05 (C, d, $J = 4.1$ Hz), 134.09 (C, d, $J = 104$ Hz), 134.69 (d, $J = 9.2$ Hz), 135.05 (C, d, $J = 2.3$ Hz), 135.72 (C, d, $J = 10.2$ Hz), 137.10 (C, d, $J = 2.3$ Hz), 137.33 (C, d, $J = 95$ Hz), 142.17 (C, d, $J = 7.0$ Hz), 143.42 (C, d, $J = 9.7$ Hz), 194.13 (d, $J = 2.8$ Hz). ^{31}P NMR δ 28.73(s). Found: C, 81.84; H, 4.62%. Calcd for $C_{33}H_{21}O_2P$: C, 82.49; H, 4.41%.

Cyclization Products 5 and 6. To a degassed solution of **1** (327 mg, 0.5 mmol) in 10 mL of THF was added LDA solution (1.33 mL, 2 mmol) at 0 °C under Ar. The dark brown solution was warmed up to r.t. and stirred for 4 h. The reaction was quenched by the addition of a small amount of saturated ammonium chloride solution. The mixture was extracted with CH_2Cl_2 (3×10 mL) and washed with water and brine and dried with $MgSO_4$. After evaporation of the solvent, the residue was chromatographed on SiO_2 (MPLC) in EA/PE (50:50) to give 28 mg (12%) of a mixture of **5** and **6**. Changing the solvent composition to EA/PE (90:10) the subsequent eluted band contained 114 mg (50%) of **2**. Fractionated crystallization from CH_2Cl_2/acetone afforded a pure crystalline sample of **5**, while **6** remained highly enriched in the mother liquor.

5: mp: ~319 °C (dec.) ^{1}H NMR (600 MHz, CD_2Cl_2) δ 3.98 (dd, 1H, $J = 23.7$, 3.1 Hz), 4.08 (dd, 1H, $J = 23.7$, 5.3 Hz), 6.37 (dd, 1H, $J = 7.9$, 1.2 Hz), 6.53 (dd, 1H, $J = 8.1$, 5.5 Hz), 6.71 (dd, 1H, $J = 5.2$, 3.2 Hz), 6.91 (bpt, 1H, J ~7.6 Hz), 6.99 (ddd, 1H, $J = 9.0$, 6.8, 1.5 Hz), 7.25 (m, 1H), 7.30 (m, 1H), 7.30–7.37 (m, 3H), 7.43 (tdd, 1H, $J = 7.3$, 2.2, 1.0 Hz), 7.44 (bd, 1H, J ~9.0 Hz), 7.51 (bd, 1H, J ~7.8 Hz), 7.59 (ddd, 1H, $J = 8.1$, 5.6, 1.0 Hz), 7.79 (bd, 1H, J ~8.2 Hz), 7.90 (bd, 1H, J ~8.1 Hz), 8.02 (dd, 1H, $J = 13.3$, 8.2 Hz), 8.04 (ddd, 1H, $J = 13.7$, 7.7, 1.7 Hz), 8.15 (dddd, 1H, $J = 12.4$, 7.3, 1.5, 0.5 Hz). ^{13}C NMR (600 MHz, CD_2Cl_2) δ 31.51 (CH_2), 55.00 (C, d, $J = 9.2$ Hz), 122.03 (d, $J = 6.1$ Hz), 124.87, 126.14, 126.57, 127.02, 127.06, 127.10, 127.13 (2d), 127.28, 127.62, 127.77 (d, $J = 6.1$ Hz), 127.93, 128.17, 128.23 (d, $J = 11.2$ Hz), 128.61 (d, $J = 10.2$ Hz), 129.28, 129.33, 129.37, 129.46, 129.54 (2d), 130.10 (C, d, $J = 97.5$ Hz), 131.51, 132.09 (C, d, $J = 98.5$ Hz), 132.20 (d, $J = 2.0$ Hz), 132.32 (d, $J = 3.1$ Hz), 132.52 (C, d, $J = 10.9$ Hz), 133.22 (C), 134.93 (C, d, $J = 99.5$ Hz), 135.20 (C), 136.69 (C, d, $J = 2.2$ Hz), 138.85 (C, d, $J = 8.9$ Hz), 142.21 (C, d, $J = 7.2$ Hz), 142.53 (C), 150.75 (C, d, $J = 10.9$ Hz). ^{31}P NMR (CD_2Cl_2) δ 4.97 (s). MS (210 °C): m/z 452 (M^+, 100%). Found: C, 84.65; H, 4.80%. Calcd for $C_{32}H_{21}OP$: C, 84.94; H, 4.68%.

6: ^{1}H NMR δ 5.49 (bs, 1H), 5.58 (d, 1H $J = 7.3$ Hz), 6.57 (ptd, 1H, $J = 7.5$, 1.3 Hz), 6.91 (d, 1H, $J = 9.6$ Hz), 7.05 (pt, 1H, J ~7.4 Hz), 7.11–7.18 (m, 2H), 7.20–7.28 (m, 2H), 7.30–7.39 (m, 4H), 7.41 (d, 1H, $J = 8.8$ Hz), 7.47 (bpt, 1H, J ~7.7 Hz), 7.78 (d, 1H, $J = 8.1$ Hz), 7.90 (bd, 1H, $J = 8.6$ Hz), 7.95 (ddd, 1H, $J = 12.6$, 7.3, 1.3 Hz), 8.01 (dd, 1H, $J = 7.8$, 5.3 Hz), 8.13 (ddd, 1H, $J = 12.6$, 7.3, 1.3 Hz), 8.44 (dd, 1H, $J = 11.6$, 8.6 Hz). ^{13}C NMR δ 52.17, 52.30 (C, d, $J = 7.5$ Hz), 125.03, 125.20, 125.30 (d, $J = 6.1$ Hz), 126.34, 126.74 (d, $J = 9.4$ Hz), 126.79, 126.93, 127.09, 127.14, 127.17, 127.26, 127.29, 127.45, 127.88 (d, $J = 10.7$ Hz), 128.11 (d, $J = 10.7$ Hz), 128.39, 129.06, 129.12 (d, $J = 6.1$ Hz), 129.38 (C, d, $J = 97$ Hz), 131.07 (d, $J = 3.1$ Hz), 131.48, 131.55 (d, $J = 2.3$ Hz), 132.42 (C, d, $J = 98$ Hz), 133.12 (C, d, $J = 14$ Hz), 133.94 (C), 135.38 (C, d, J ~2 Hz), 135.79 (C, d, $J = 10.5$ Hz), 135.89, 136.54 (C), 136.61 (C, d, $J = 98$ Hz), 140.23 (C, d, $J = 10.0$ Hz), 143.97 (C, d, $J = 8.0$ Hz). ^{31}P NMR δ 17.89 (s). MS (160 °C): m/z 452 (M^+, 100%).

2-Diphenylphosphinoyl-2′-phenyl(2-trimethylsilylphenyl)-phosphinoyl-1,1′-binaphthyl (7). To a degassed solution of **1** (327 mg, 0.5 mmol) in 30 mL of THF was added TMSCl (190 µL, 1.5 mmol) at −78 °C under Ar. At the same temperature was dropwise added LDA (0.67 mL, 1.0 mmol) during 45 min. The yellow solution was stirred at −78 °C for 5 h, and then allowed to come to r.t. overnight. The reaction was quenched by the addition of a small amount of hydrochloric acid (2 M) and the solvent was evaporated. Extractive work-up with hydrochloric acid and CH_2Cl_2 yielded a crude mixture of products which was separated by MPLC in EA to afford pure **8** (86 mg, 22%) followed by **7** (145 mg, 40%; *note: due to excessive tailing the "tail" of the band contained also a small impurity of* ***2***); mp 266–268 °C. ^{1}H NMR δ 0.03 (s, 9H), 6.71 (d, 1H, $J = 8.6$ Hz), 6.81 (t, 1H, $J = 7.6$ Hz), 7.02 (bd, 1H, $J = 6.1$ Hz), 7.04 (d, 1H, $J = 12.0$ Hz), 7.12–7.50 (m, 19H), 7.54 (d, 1H, $J = 8.3$ Hz), 7.59 (t, 1H, $J = 7.5$ Hz), 7.72 (m, 1H), 7.83–7.93 (m, 5H). ^{13}C NMR δ 1.54 (CH_3), 125.67, 126.58, 126.78 (C), 127.01, 127.01 (d, $J = 12.2$ Hz), 127.35, 127.40, 127.47, 127.54, 127.54, 127.57, 127.64, 127.68, 127.71, 127.80, 127.91, 128.04, 129.70 (d, $J = 12.2$ Hz), 129.87 (C, d, $J = 101$ Hz), 130.21 (d, $J = 3.1$ Hz), 130.65, 130.68, 130.75, 131.68, 131.77, 131.81, 131.88, 131.90, 131.98, 132.95 (C), 133.52 (C), 133.54 (C), 133.66 (C), 133.69 (C), 133.71 (C), 133.93 (C), 133.95 (C), 134.56 (C), 135.39 (C), 135.81 (d, $J = 15.3$ Hz), 135.74 (d, $J = 17.6$ Hz), 136.35 (C, d, $J = 94$ Hz), 137.36 (C, d, $J = 99$ Hz), 143.46 (C, m), 144.21 (C, m), 145.18 (C, d, $J = 15.2$ Hz). ^{31}P NMR δ 28.24 (s), 34.25 (s). MS (230 °C): m/z 726 (M^+, 2.5%), 712 ($M^+ - 14$, 65%). Found: C, 77.23; H, 5.86%. Calcd for $C_{47}H_{40}O_2P_2Si$: C, 77.66; H, 5.55%.

2,2′-Bis[phenyl(2-trimethylsilylphenyl)phosphinoyl]-1,1′-binaphthyl (8). To a degassed solution of **1** (327 mg, 0.5 mmol) in 30 mL of THF was added TMSCl (762 µL, 6 mmol) at −78 °C under Ar. This was followed by dropwise addition of LDA (2.66 mL, 4 mmol, 8 mol. amt.) during 45 min at the same temperature. The yellow solution was stirred at −78 °C for 5 h, and then allowed to come to r.t. over night. After the same work-up procedure as given for **7**, the residue was chromatographed on SiO_2 (MPLC) in EA/PE (10:90) to afford a small fraction (76 mg) consisting of polysilylated products and some **9** followed by **8** (292 mg, 73%). Moreover traces of **2** and 17 mg of an unsymmetrically disilylated product (NMR) could be isolated; mp: 285–289 °C. ^{1}H NMR δ 0.11 (s, 9H), 6.85 (m, 4H), 7.02 (m, 4H), 7.14–7.44 (m, 16H), 7.51 (dd, 2H, $J = 8.8$, 1.5 Hz), 7.60–7.65 (m, 4H). ^{13}C NMR δ 1.70 (CH_3), 126.48, 126.89, 126.94, 127.01, 127.07, 127.30, 127.59, 127.92, 127.98 (d, $J = 12$ Hz), 129.69 (d, $J = 3.1$ Hz), 129.95, 129.99, 130.02, 130.05, 131.81 (bd, $J = 9$ Hz), 131.86 (C, bd, $J = 100$ Hz), 133.46 (C, d, $J = 2.4$ Hz), 133.82 (d, $J = 15.3$ Hz), 133.90 (C, d, $J = 12.0$ Hz), ~134.8 (C, b), 136.22 (d, $J = 14.5$ Hz), 138.43 (C, d, $J = 106$ Hz), ~141.0 (C, b), 145.77 (C, d, $J = 15.0$ Hz). ^{31}P NMR δ 33.35 (s). MS (240 °C): m/z 798 (M^+, 1.5%), 784 ($M^+ - 14$, 66%). Found: C, 75.00; H, 6.17%. Calcd for $C_{50}H_{48}O_2P_2Si_2$: C, 75.16; H, 6.05%.

2,2′-Bis[phenyl(2-trimethylsilylphenyl)phosphinoyl]-3-tri-

methylsilyl-1,1′-binaphthyl (9). To a degassed solution of **1** (327 mg, 0.5 mmol) in 30 mL of THF was added TMSCl (762 μL, 6.0 mmol) at −78 °C under Ar. At the same temperature, a solution of *N*-lithio-2,2,6,6-tetramethylpiperidine (2 mmol, prepared from 423 μL of 2,2,6,6-tetramethylpiperidine and 1.25 mL of *n*-BuLi in 10 mL of THF) was dropwise added during 45 min. The yellow solution was slowly warmed up to −25 °C, stirred at this temperature for 5 h, and finally allowed to come to r.t. overnight. The reaction was quenched by addition of a small amount of hydrochloric acid (2 M). After the same work-up procedure as given for **7**, the residue was chromatographed on SiO_2 (MPLC) in EA/PE (10:90) to afford **9** (168 mg, 39%, 1:2 mixture of rotamers) and **8** (113 mg, 28%). From crude **9**, an analytically pure sample was obtained by crystallization from CH_2Cl_2/PE. (Partial assignment of signals to major rotamer (M) and minor rotamer (m) has been performed); mp: 267–270 °C. ^{1}H NMR δ −0.16 (s, 9H, M), −0.05 (s, 9H, m), 0.21 (s, 9H, m), 0.22 (s, 9H, m), 0.32 (s, 9H, M), 0.39 (s, 9H, m), 3.70 (bs, 1H, m), 5.03 (dd, 1H, J = 12.4, 7.6 Hz, M), 6.00 (m, 1H, M), 6.37 (dd, 1H, J = 14.9, 7.6 Hz, m), 6.46 (dd, 1H, J = 13.9, 7.8 Hz, M), 6.49–6.58 (m), 6.61 (d, 1H, J = 8.3 Hz, m), 6.66 (pt, 1H, J = 7.6 Hz, m), 6.75–7.40 (several multiplets), 7.47–7.55 (several multiplets),7.62–7.70 (multiple), 7.72 (dd, 1H, J = 7.3, 3.0 Hz, M), 7.87 (dd, 1H, J = 7.1, 2.5 Hz, m), 7.94 (d, 1H, J = 2.0 Hz, M), 7.97 (d, 1H, J = 8.1 Hz, m), 8.61 (bs, 1H, m), 8.92 (dd, 1H, J = 12.4, 7.8 Hz, M). ^{13}C NMR δ 1.28 (CH_3, M), 1.55 (CH_3, m), 2.12 (CH_3, M), 2.74 (CH_3, m), 3.38 (CH_3, M), 3.98 (CH_3, m), 124.06 (d, J = 13.8 Hz, m), 124.25 (d, J = 13.0 Hz, M), 126.1–131.0 (several multiplets), 131.38 (d, J = 9.2 Hz, ?), 131.40 (C, d, J = 98 Hz), 132.02 (C), 132.05 (C), 132.43 (d, J = 14.5 Hz, m), 132.61 (d, J = 13.8 Hz, M), 132.73 (C), 132.84 (C), 133.16 (d, J = 16.8 Hz, m), 133.28 (C), 133.38 (C), 133.40 (d, J = 13.8 Hz, M), 133.73 (C), 133.92 (C), 133.94 (C), 134.46 (C), 134.63 (d, J = 14.5 Hz, m), 135.44 (C), 136.06 (d, J = 14.5 Hz, M), 136.94 (d, J = 14.5 Hz, M), 137.37 (C), 137.66 (d, J = 15.3 Hz, m), 137.80 (d, J = 9.2 Hz), 138.24 (C), 138.42 (C), 138.85 (C), 138.89 (d, J = 14.5 Hz, m), 138.99 (C), 139.06 (C), 139.12 (C), 139.68 (d, J = 13.8 Hz, M), 140.35 (C, d, J = 105 Hz), 140.54 (C), 140.61 (C), 140.62 (C), 140.67 (C), 141.54 (C, d, J = 14.2 Hz), 142.80 (C, d, J = 13.2 Hz), 142.96 (C, d, J = 103 Hz), 145.39 (C), 145.67 (C, d, J = 16.3 Hz), 146.08 (C, d, J = 16.8 Hz), 146.33 (C, d, J = 15.8 Hz), 146.57 (C, d, J = 15.3 Hz). ^{31}P NMR δ 29.37 (s, M), 31.92 (s, m), 34.76 (s, M), 39.38 (s, m). MS (230 °C): m/z 870 (M^+, 1%), 855 ($M^+ - 15$, 100%). Found: C, 73.08; H, 6.52%. Calcd for $C_{53}H_{56}O_2P_2Si_3$: C, 73.07; H, 6.48%.

2,2′-Bis[(2-bromophenyl)phenylphosphinoyl]-1,1′-binaphthyl (10a) and 2,2′-Bis[(2-iodophenyl)phenylphosphinoyl]-1,1′-binaphthyl (11a). General Procedure: To a degassed suspension of **1** (327 mg, 0.5 mmol) in 6 mL of THF was added TMP-MgBr (4 mL, 2 mmol) at r.t. under Ar. The brown solution was stirred for 6 h, and then cooled to −78 °C. The reaction was quenched by dropwise addition of a concentrated solution of Br_2 (351 mg, 112 μL, 2.2 mmol) or I_2 (558 mg, 2.2 mmol) in THF (5 mL). After warming to r.t., hydrochloric acid (2 M, 10 mL) and a small amount of $NaHSO_3$ was added to destroy excess reagent. Extractive work-up with CH_2Cl_2 (3 × 10 mL) and chromatographic purification with SiO_2 (MPLC in EA/PE, 50:50) afforded **10a** and **11a**, respectively.

10a: 159 mg (39%) white powder; mp: 252–255 °C. ^{1}H NMR δ 6.92 (bpt, 2H, J = 7.6 Hz), 7.05 (bpt, 2H, J = 7.6 Hz), 7.17 (d, 2H, J = 7.6 Hz), 7.20–7.45 (m, 16H), 7.49 (bpt, 2H, J ∼7.5 Hz), 7.71 (ddd, 2H, J = 13.6, 7.8, 1.5 Hz), 7.80 (dd, 2H, J = 8.6, 2.3 Hz), 7.87 (d, 2H, J = 8.1 Hz). ^{13}C NMR δ 125.73 (C, d, J = 106 Hz), 126.26 (d, J = 11.5 Hz), 126.36, 127.18 (d, J = 13.0 Hz), 127.29, 127.60, 127.80 (d, J = 13.0 Hz), 128.26, ∼128.34 (d, J ∼12 Hz), 130.78 (d, J = 9.9 Hz), 131.07 (d, J = 3.1 Hz), ∼131.26 (C, d, J ∼106 Hz), 132.60 (d, J = 2.2 Hz), 133.56 (d, J = 6.9 Hz), 133.79 (C, d, J = 2.2 Hz), 135.20 (C, d, J = 106 Hz), 135.20 (C, d, J = 12 Hz), 138.64 (d, J = 12.2 Hz), 145.46 (C, dd, J ∼5, 3.6 Hz). ^{31}P NMR δ 31.43 (s). MS (FD): m/z 812.3 (M^+, 100%). Found: C, 65.06; H, 3.99%. Calcd for $C_{44}H_{30}Br_2O_2P_2$: C, 65.05; H, 3.72%.

11a: 162 mg (36%) white powder, mp ∼335 °C (dec.). ^{1}H NMR δ 6.74 (bpt, 2H, J = 7.6 Hz), 7.10 (d, 2H, J = 8.6 Hz), 7.18 (bpt, 2H, J = 7.6 Hz), 7.25 (bpt, 2H, J ∼7.8 Hz), 7.29–7.46 (m, 11H), 7.49 (bpt, 2H, J ∼7.5 Hz), 7.55 (dd, 2H, J = 7.8, 3.5 Hz), 7.70 (ddd, 2H, J = 13.4, 7.6, 1.5 Hz), 7.78 (dd, 2H, J = 8.6, 2.3 Hz), 7.85 (d, 2H, J = 8.1 Hz). ^{13}C NMR δ 99.02 (C, d, J = 6.9 Hz), 125.64 (C, d, J = 106 Hz), 126.40, 127.04 (d, J = 12.2 Hz), 127.12 (d, J = 13.0 Hz), 127.28, 127.61, 127.97 (d, J = 13.0 Hz), 128.32, 128.39 (d, J = 13.0 Hz), 131.10 (d, J = 3.1 Hz), 131.29 (d, J = 9.2 Hz), 132.33 (d, J = 2.3 Hz), 133.76 (C, d, J = 106 Hz), 133.82 (C, d, J = 2.0 Hz), 134.74 (C, d, J = 105 Hz), 135.15 (C, d, J = 12.2 Hz), 138.89 (d, J = 13.0 Hz), 140.88 (d, J = 9.2 Hz), 145.43 (C, dd, J = 6.1, 4.6 Hz). ^{31}P NMR δ 34.24(s) . MS (240 °C): m/z 779 ($M^+ - I$, 5%). Found: C, 57.61; H, 3.38%. Calcd for $C_{44}H_{30}I_2O_2P_2$: C; 58.30, H; 3.34%.

2,2′-Bis[(2-biphenylyl)phenylphosphinoyl]-1,1′-binaphthyl (12). Diiodide **11a** (91 mg, 0.1 mmol) was dissolved in toluene and degassed. To this was subsequently added phenylboronic acid (36 mg, 0.3 mmol), dissolved in a minimum quantity of EtOH (∼0.1 mL), $Pd(PPh_3)_4$ (12 mg, 0.01 mmol), and Na_2CO_3 solution (2 M, 0.2 mL, ∼0.4 mmol). The mixture was refluxed under Ar overnight. Work-up with H_2O/CH_2Cl_2 yielded the crude product which was purified by column chromatography (SiO_2, 10 × 2 cm, EA/PE/CH_2Cl_2, 25:25:50) to give 82 mg (∼100%) of **12**; mp: 319–322 °C. ^{1}H NMR δ 6.81–6.94 (m, 12H), 6.97–7.06 (m, 6H), 7.12 (dd, 2H, J = 11.4, 1.0 Hz), 7.15 (d, 2H, J = 11.4 Hz), 7.18–7.26 (m, 4H), 7.37 (bd, 4H, J = 7.1 Hz), 7.44 (m, 2H), 7.48 (dd, 2H, J = 11.1, 8.6 Hz), 7.81 (dd, 2H, J = 8.6, 2.3 Hz), 7.85 (d, 2H, J = 8.1 Hz), 8.60 (dd, 2H, J = 14.9, 7.6 Hz). ^{13}C NMR ($CDCl_3$) δ 126.15, 126.67 (d, J = 13.3 Hz), 126.87, 127.01, 127.19 (br), 127.20 (d, J = 12.4 Hz), 127.45, 127.63, 127.80 (d, J = 12.9 Hz), 128.04 (br), 129. 46 (C, d, J = 104 Hz), 129.94 (d, J = 2.8 Hz), 130.13, 130.85 (d, J = 10.1 Hz), 131.18 (d, J = 2.4 Hz), 131.27 (d, J = 8.7 Hz), 131.40 (C, d, J = 102 Hz), 133.22 (C, d, J = 2.2 Hz), 134.39 (C, d, J = 11.7 Hz), 134.42 (C, d, J = 102 Hz), 138.18 (d, J = 13.3 Hz), 140.95 (C, d, J = 3.9 Hz), 144.56 (C, dd, J = 5.7, 4.1 Hz), 146.22 (C, d, J = 8.9 Hz). ^{31}P NMR ($CDCl_3$) δ 44.72 (s). MS (FD): m/z 806.6 (M^+, 100%). Found: C, 82.94; H, 5.30%. Calcd for $C_{56}H_{40}O_2P_2$: C, 83.36; H, 5.00%.

3-Phenyl-3*H*-benzo[*b*]dinaphtho[2,1-*d*:1′,2′-*f*]phosphepine (13). To a degassed solution of **2** (100 mg, 0.22 mmol) in 4 mL of DME was added TfOMe (82 mg, 0.5 mmol, 2.27 mol. amt., 56 μL) at r.t. under Ar. The reaction was stirred for 5 h and after 10 min precipitation of the triflate started. The mixture was cooled to 0 °C, $LiAlH_4$ (40 mg, 1.1 mmol) was added in one portion, and the reaction was stirred overnight. Quenching with hydrochloric acid (2 M) was followed by extractive work-up with EA. Removal of solvent yielded almost pure **13** (96 mg, 98%) as a white powder; mp 248–251 °C. ^{1}H NMR (CD_2Cl_2) δ 6.40–6.49 (m, 3H), 6.62–

6.68 (m, 2H), 6.92 (d, 1H, $J = 8.6$ Hz), 7.07–7.16 (m, 3H), 7.32 (m, 1H), 7.34–7.43 (m, 2H), 7.45 (d, 1H, $J = 8.6$ Hz), 7.54 (m, 1H), 7.60 (d, 1H, $J = 8.6$ Hz), 7.65 (d, 1H, $J = 8.1$ Hz), 7.76 (dd, 1H, $J = 7.8$, 1.3 Hz), 7.91 (d, 1H, $J = 8.1$ Hz), 7.94–8.01 (m, 2H), 8.16 (dd, 1H, $J = 12.9$, 8.1 Hz). ^{13}C NMR (CD_2Cl_2) δ 125.64, 125.69, 125.95, 126.29, 126.65, 126.88 (d, $J = 4.6$ Hz), 127.25 (d, $J = 17.6$ Hz), 127.75, 128.03 (d, $J = 17.6$ Hz), 128.04, 128.12 (d, $J = 14.5$ Hz), ~128.39 (d, J ~3.8 Hz), 128.41 (2 × CH), 128.86, 130.79, 131.00, 132.08 (C), 132.85 (C), 132.96 (d, $J = 53.5$ Hz), 134.28 (C, d, $J = 1.5$ Hz), 134.49 (C), 134.53 (C), 137.06 (C, d, $J = 10.5$ Hz), 137.16 (d, $J = 53.5$ Hz), 138.80 (C, d, J ~4 Hz), 138.82 (C), 139.86 (C, d, $J = 8.9$ Hz), 141.50 (C, d, $J = 10.3$ Hz), 144.41 (C, d, J ~5 Hz). ^{31}P NMR (CD_2Cl_2) δ −5.42 (s). MS (100 °C): m/z 436 (M^+, 100%). Found: C, 87.30; H, 4.97%. Calcd for $C_{32}H_{21}P$: C, 88.05; H, 4.85%.

2-Trimethylsilyl-3-phenyl-3*H*-benzo[*b*]dinaphtho[2,1-*d*:1′, 2′-*f*]phosphepine (14). To a degassed solution of **3a** (115 mg, 0.22 mmol) in 1 mL of DME was added TfOMe (41 mg, 0.25 mmol, 1.13 mol. amt., 28 μL) at r.t. under Ar. The reaction was stirred for 5 h and then cooled to 0 °C. $LiAlH_4$ (20 mg, 0.55 mmol) was added in one portion and the reaction was stirred overnight. Quenching with hydrochloric acid (2 M) was followed by extractive work-up with EA. After drying ($MgSO_4$) and evaporation of solvent, the crude product was purified by MPLC on SiO_2 in EA/PE (10:90) to yield 96 mg (83%) of **14**. From a second band, 11 mg (10%) of unreacted **3a** have been recovered; mp ~278 °C. ^{1}H NMR δ 0.64 (d, 9H, $J = 2.0$ Hz), 6.34–6.44 (m, 3H), 6.61 (m, 2H), 6.80 (d, 1H, $J = 8.6$ Hz), 6.95 (d, 1H, $J = 8.6$ Hz), 7.00–7.09 (m, 2H), 7.24 (m, 1H), 7.28–7.36 (m, 2H), 7.40 (d, 1H, $J = 8.6$ Hz), 7.47 (m, 1H), 7.52 (d, 1H, $J = 8.6$ Hz), 7.56 (d, 1H, $J = 7.6$ Hz), 7.73 (d, 1H, $J = 7.6$ Hz), 7.82 (d, 1H, $J = 8.6$ Hz), 7.93 (ddd, 1H, $J = 14.1$, 7.6, 1.3 Hz), 8.12 (d, 1H, $J = 2.5$ Hz). ^{13}C NMR δ 1.80 (CH_3, d, $J = 11.0$ Hz), 125.01, 125.17, 125.49, 126.20, 126.34, 126.44 (d, $J = 3.8$ Hz), 126.73 (d, $J = 17.6$ Hz), 127.31, 127.55, 127.61 (d, $J = 16.8$ Hz), 128.01, 128.03, 128.13, 128.23, 130.04, 130.53, 131.54 (C), 132.77 (C), 132.93 (C, d, $J = 1.5$ Hz), 134.49 (C), 134.76 (C), 135.03 (d, $J = 19.1$ Hz), 136.71 (C, d, $J = 12.0$ Hz), 136.94 (d, $J = 53.5$ Hz), 138.31 (C), 139.12 (C, d, $J = 3.1$ Hz), 140.74 (C, d, $J = 11.2$ Hz), 143.59 (C, d, $J = 52.5$ Hz), 144.42 (C), 144.44 (C, d, $J = 12.3$ Hz). ^{31}P NMR δ −15.37 (s). MS (150 °C): m/z 508 (M^+, 100%). Found: C, 82.40; H, 5.97%. Calcd for $C_{35}H_{29}PSi$: C, 82.64; H, 5.75%.

2-[Phenyl(2-trimethylsilylphenyl)phosphino]-2′-[phenyl(2-trimethylsilylphenyl)phosphinoyl]-1,1′-binaphthyl (15a). To a degassed solution of **8** (200 mg, 0.25 mmol) in 7 mL of DME was added TfOMe (98 mg, 0.6 mmol, 1.2 mol. amt., 68 μL) at r.t. under Ar. The reaction was stirred for 6 h; after 10 min, precipitation of the triflate started. The mixture was cooled to −35 °C and $LiAlH_4$ (52 mg, 1.3 mmol) was added. After the precipitate has dissolved during 1 h, the dark red reaction was kept between −10 °C and −20 °C overnight. The reaction was quenched by the addition of a small amount of hydrochloric acid (2 M). Extractive work-up with EA and chromatographic separation of the residue on SiO_2 (MPLC, EA/PE, 10:90) afforded 25–30% (49–59 mg) of **15a**; mp: 288–291 °C. ^{1}H NMR δ −0.39 (d, 9H, $J = 1.3$ Hz), 0.07 (s, 9H), 6.30–6.45 (m, 4H), 6.95–7.40 (m, 19H), 7.52 (dd, 1H, $J = 13.9$, 7.6 Hz), 7.56 (dd, 1H, $J = 11.4$, 8.6 Hz), 7.65–7.75 (m, 4H), 7.83 (dd, 1H, $J = 8.6$, 1.8 Hz). ^{13}C NMR δ 0.44 (CH_3, d, $J = 8.4$ Hz), 1.74 (CH_3), 125.14, 125.87, 126.09, 127.16, 127.23, 127.29, 127.39, 127.45, 127.51, 127.55, 127.62, 127.83, 127.96, 128.10, ~128.22 (C), 128.35, 128.77, ~129.21 (C), 129.81 (d, $J = 12.2$ Hz), 130.30 (d, $J = 3.1$ Hz), 130.80 (d, $J = 2$ Hz), 131.25, 131.76 (d, $J = 9.2$ Hz), 132.91 (d, $J = 17.6$ Hz), 132.95 (C), 133.17 (C), 133.20 (C), 133.28 (C), 133.31 (C), 134.19 (d, $J = 16.1$ Hz), 134.50 (C, d, $J = 2.3$ Hz), 134.69, 134.73 (C), 134.80 (C), ~135.5 (C), 135.98 (d, $J = 14.5$ Hz), ~136.5 (C), 139.78 (C, d, $J = 13.0$ Hz), 141.97 (C, d, $J = 14.0$ Hz), 144.79 (C), 144.85 (C), 146.33 (C, d, $J = 15.5$ Hz), 146.92 (C, d, $J = 47.8$ Hz). ^{31}P NMR ($CDCl_3$) δ 33.43 (brs); −17.42 (s). MS (FAB): m/z 783.4 ($M^+ + 1$, 100%). Found: C, 76.42; H, 6.43%. Calcd for $C_{50}H_{48}OP_2Si_2$: C, 76.69; H, 6.18%.

X-ray Structure Determinations of 2, 3a·DMF, 5, 8, 9, 11a·2CHCl$_3$, and 13. X-ray diffraction measurements were made on a Bruker AXS SMART platform 3-circle diffractometer equipped with a CCD area detector, using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). Complete spheres of diffraction data were collected using ω-scans of 0.3° (0.2° and a hemisphere for **9**). Cell dimensions were obtained by least-squares refinements using the measured positions of about 1000 strong reflections. The frame data were integrated and corrected for Lorentz and polarization effects using the program SAINT.[22] Empirical absorption corrections based on measurements of multiply redundant data were performed using program SADABS.[22] The structures were solved with direct methods, expanded with Fourier techniques, and refined by full matrix least squares on F^2 with all reflections using the SHELXTL programs.[22] Non-hydrogen atoms were refined anisotropically and hydrogen atoms were included in calculated positions and refined with the riding model. A secondary extinction correction was applied if appropriate. For **3a**·*DMF*, the solvent was found to be disordered and was modeled with the SQUEEZE procedure of program PLATON.[23] Crystallographic data are summarized in Table 2.

References

1 a) D. Cai, J. F. Payack, D. R. Bender, D. L. Hughes, T. R. Verhoeven, and P. J. Reider, *J. Org. Chem.*, **59**, 7180 (1994). b) H. Kumobayashi, *Recl. Trav. Chim. Pays-Pas*, **115**, 201 (1996). c) R. Noyori and H. Takaya, *Acc. Chem. Res.*, **23**, 345 (1990). d) A. Miyashita, H. Takaya, T. Souchi, and R. Noyori, *Tetrahedron*, **40**, 1245 (1984). e) A. Miyashita, A. Yasuda, H. Takaya, K. Toriumi, T. Ito, T. Souchi, and R. Noyori, *J. Am. Chem. Soc.*, **102**, 7932 (1980).

2 a) X. Zhang, K. Mashima, K. Koyano, N. Sayo, H. Kumobayashi, S. Akutagawa, and H. Takaya, *J. Chem. Soc., Perkin Trans. 1*, **1994**, 2309. b) X. Zhang, K. Mashima, K. Koyano, N. Sayo, H. Kumobayashi, S. Akutagawa, and H. Takaya, *Tetrahedron Lett.*, **32**, 7283 (1991). c) H. Takaya, K. Mashima, K. Koyano, M. Yagi, H. Kumobayashi, T. Taketomi, S. Akutagawa, and R. Noyori, *J. Org. Chem.*, **51**, 629 (1986).

3 a) N. G. Andersen, R. Mc Donald, and B. A. Keay, *Tetrahedron: Asymmetry*, **12**, 263 (2001). b) T. Senda, M. Ogasawara, and T. Hayashi, *J. Org. Chem.*, **66**, 6852 (2001). c) K. Mashima, K. Kusano, N. Sato, Y. Matsumura, K. Nozaki, H. Kumobayashi, N. Sayo, Y. Hori, T. Ishizaki, S. Akutagawa, and H. Takaya, *J. Org. Chem.*, **59**, 3064 (1994). d) see Ref. 2c.

4 a) P. Guerreiro, V. Ratovelomanana-Vidal, J.-P. Genet, and P. Dellis, *Tetrahedron Lett.*, **42**, 3423 (2001). b) D. J. Birdsall, E. G. Hope, A. M. Stuart, W. Chen, Y. Hu, and J. Xiao, *Tetrahedron Lett.*, **42**, 8551 (2001). c) R. Halle, B. Colasson, E. Schulz, M.

Spagnol, and M. Lemaire, *Tetrahedron Lett.*, **41**, 643 (2000). d) D. Che, N. G. Andersen, S. Y. W. Lau, M. Parvez, and B. A. Keay, *Tetrahedron: Asymmetry*, **11**, 1919 (2000).

5 a) S. Gladiali, A. Dore, D. Fabbri, S. Medici, G. Pirri, and S. Pulacchini, *Eur. J. Org. Chem.*, **2000**, 2861. b) T. Hayashi, T. Senda, Y. Takaya, and M. Ogasawara, *J. Am. Chem. Soc.*, **121**, 11591 (1999).

6 a) T. Hamada and S. L. Buchwald, *Org. Lett.*, **4**, 999 (2002). b) Y. Wang, X. Li, and K. Ding, *Tetrahedron Lett.*, **43**, 159 (2002). c) T. Hayashi, J. W. Han, A. Takeda, J. Tang, K. Nohmi, K. Mukaide, H. Tsuji, and Y. Uozumi, *Adv. Synth. Catal.*, **343**, 279 (2001). d) M. Cavazzini, G. Pozzi, S. Quici, D. Maillard, and D. Sinou, *Chem. Commun.*, **2001**, 1220. e) D. Bonafoux, Z. Hua, B. Wang, and I. Ojima, *J. Fluorine Chem.*, **112**, 101 (2001). f) G. Francio, K. Wittmann, and W. Leitner, *J. Organomet. Chem.*, **621**, 130 (2001). g) Y. Wang, H. Guo, and K. Ding, *Tetrahedron: Asymmetry*, **11**, 4153 (2000). h) M. Kawatsura, Y. Uozumi, M. Ogasawara, and T. Hayashi, *Tetrahedron*, **56**, 2247 (2000). i) H. Kodama, T. Taiji, T. Ohta, and I. Furukawa, *Tetrahedron: Asymmetry*, **11**, 4009 (2000). j) K. Sumi, T. Ikariya, and R. Noyori, *Can. J. Chem.*, **78**, 697 (2000). k) T. Hayashi and M. Ishigedani, *J. Am. Chem. Soc.*, **122**, 976 (2000). l) X. Hu, H. Chen, and X. Zhang, *Angew. Chem.*, **38**, 3518 (1999). m) K. Ding, Y. Wang, H. Yun, J. Liu, Y. Wu, M. Terada, Y. Okubo, and K. Mikami, *Chem. Eur. J.*, **5**, 1734 (1999). n) K. Nozaki, F. Shibahara, Y. Itoi, E. Shirakawa, T. Ohta, H. Takaya, and T. Hiyama, *Bull. Chem. Soc. Jpn.*, **72**, 1911 (1999). o) S. Gladiali, S. Pulacchini, D. Fabbri, M. Manassero, and M. Sansoni, *Tetrahedron: Asymmetry*, **9**, 391 (1998). p) S. Vyskocil, M. Smrcina, V. Hanus, M. Polasek, and P. Kocovsky, *J. Org. Chem.*, **63**, 7738 (1998). q) S. Y. Cho and M. Shibasaki, *Tetrahedron Lett.*, **39**, 1773 (1998). r) A. Ashimori, B. Bachand, M. A. Calter, S. P. Govek, L. E. Overman, and D. J. Poon, *J. Am. Chem. Soc.*, **120**, 6488 (1998). s) M. Ogasawara, K. Yoshida, H. Kamei, K. Kato, Y. Uozumi, and T. Hayashi, *Tetrahedron: Asymmetry*, **9**, 1779 (1998). t) Y. Imai, W. Zhang, T. Kida, Y. Nakatsuji, and I. Ikeda, *Tetrahedron Lett.*, **39**, 4343 (1998). u) K. Nozaki, N. Sakai, T. Nanno, T. Higashijima, S. Mano, T. Horiuchi, and H. Takaya, *J. Am. Chem. Soc.*, **119**, 4413 (1997). v) R. Kadyrov, J. Heinicke, M. K. Kindermann, D. Heller, C. Fischer, R. Selke, A. K. Fischer, and P. G. Jones, *Chem. Ber., Recl.*, **130**, 1663 (1997). w) T. Horiuchi, T. Ohta, E. Shirakawa, K. Nozaki, and H. Takaya, *J. Org. Chem.*, **62**, 4285 (1997). x) K. Inagaki, T. Ohta, K. Nozaki, and H. Takaya, *J. Organomet. Chem.*, **531**, 159 (1997). y) T. Hattori, M. Shijo, J. Sakamoto, S. Kumagai, A. Nakajima, and S. Miyano, *J. Chem. Res. Miniprint*, **1995**, 124. z) S. Gladiali, A. Dore, and D. Fabbri, *Tetrahedron: Asymmetry*, **5**, 1143 (1994). aa) T. Hattori, J. Sakamoto, N. Hayashizaka, and S. Miyano, *Synthesis*, **1994**, 199. bb) Y. Uozumi, N. Suzuki, A. Ogiwara, and T. Hayashi, *Tetrahedron*, **50**, 4293 (1994). cc) N. Sakai, S. Mano, K. Nozaki, and H. Takaya, *J. Am. Chem. Soc.*, **115**, 7033 (1993). dd) Y. Uozumi, A. Tanahashi, S.-Y. Lee, and T. Hayashi, *J. Org. Chem.*, **58**, 1945 (1993). ee) Y. Uozumi and T. Hayashi, *J. Am. Chem. Soc.*, **113**, 9887 (1991). ff) K. J. Brown, M. S. Berry, K. C. Waterman, D. Lingenfelter, and J. R. Murdoch, *J. Am. Chem. Soc.*, **106**, 4717 (1984).

7 a) Q.-H. Fan, R. Wang, and A. S. C. Chan, *Bioorg. & Med. Chem. Lett.*, **12**, 1867 (2002). b) C. Saluzzo, T. Lamouille, F. Le Guyader, and M. Lemaire, *Tetrahedron: Asymmetry*, **13**, 1141 (2002). c) D. J. Baystone, J. L. Fraser, M. R. Ashton, A. D. Baxer, M. E. C. Polywka, and E. Moses, *J. Org. Chem.*, **63**, 3137 (1998).

8 H. Takaya, S. Akutagawa, and R. Noyori, *Org. Synth.*, **67**, 20 (1989).

9 a) O. Desponds and M. Schlosser, *J. Organomet. Chem.*, **507**, 257 (1996). b) S. Ogawa, Y. Tajiri, and N. Furukawa, *Bull. Chem. Soc. Jpn.*, **64**, 3182 (1991). c) B. Schaub, T. Jenny, and M. Schlosser, *Tetrahedron Lett.*, **25**, 4097 (1984). d) D. Seyferth, D. E. Welch, and J. K. Heeren, *J. Am. Chem. Soc.*, **86**, 1100 (1964).

10 T. Shimada, H. Kurushima, Y.-H. Cho, and T. Hayashi, *J. Org. Chem.*, **66**, 8854 (2001).

11 a) see Ref. 9a. b) J. M. Brown and S. Woodward, *J. Org. Chem.*, **56**, 6803 (1991). c) M. Gray, B. J. Chapell, N. J. Taylor, and V. Snieckus, *Synlett*, **1988**, 422.

12 a) S. E. Gibson, H. Ibrahim, C. Pasquier, and J. W. Steed, *Tetrahedron*, **58**, 4617 (2002). b) R. J. Mattson, C. P. Sloan, C. C. Lockhart, J. D. Catt, Q. Gao, and S. Huang, *J. Org. Chem.*, **64**, 8004 (1999). c) I. R. Butler, S. Müssig, and M. Plath, *Inorg. Chem. Commun.*, **2**, 424 (1999). d) F. Mongin, O. Desponds, and M. Schlosser, *Tetrahedron Lett.*, **37**, 2767 (1996). e) O. Desponds, *Chimia*, **50**, 639 (1996). f) F. Mongin and M. Schlosser, *Tetrahedron Lett.*, **37**, 6551 (1996). g) Y.-G. Gu and E. K. Bayburt, *Tetrahedron Lett.*, **37**, 2565 (1996). h) C. Cochennec, P. Rocca, F. Marsais, A. Godard, and G. Quéguiner, *Synthesis*, **1995**, 321. i) Y. Aoyagi, T. Inariyama, Y. Arai, S. Tsuchida, Y. Matuda, H. Kobayashi, A. Ohta, T. Kurihara, and S. Fijihara, *Tetrahedron*, **50**, 13575 (1994). j) P. Rocca, C. Cochennec, F. Marsais, L. Thomas-dit-Dumont, M. Mallet, A. Godard, and G. Quéguiner, *J. Org. Chem.*, **58**, 7832 (1993). k) R. R. Goehring, *Tetrahedron Lett.*, **33**, 6045 (1992). l) F. Marsais, P. Pineau, F. Nivolliers, M. Mallet, A. Turck, A. Godard, and G. Quéguiner, *J. Org. Chem.*, **57**, 565 (1992).

13 S. Ogawa, Y. Tajiri, and N. Furukawa, *Bull. Chem. Soc. Jpn.*, **64**, 3182 (1991).

14 T. D. Krizan and J. C. Martin, *J. Am. Chem. Soc.*, **105**, 6155 (1983).

15 a) U. Nettekoven, M. Widhalm, P. C. J. Kamer, P. W. N. M. van Leeuwen, K. Mereiter. M. Lutz, and A. L. Spek, *Organometallics*, **19**, 2299 (2000). b) M. Sawamura, A. Yamauchi, and Y. Ito, *J. Chem. Soc., Chem. Commun.*, **1991**, 874. c) P. E. Eaton, C. Lee, and Y. Xiong, *J. Am. Chem. Soc.*, **111**, 8016 (1989).

16 T. Imamoto, S. Kikuchi, T. Miura, and Y. Wada, *Org. Lett.*, **3**, 87 (2001).

17 a) A. Bootle-Wilbraham, S. Head, J. Longstaff, and P. Wyatt, *Tetrahedron Lett.*, **40**, 5267 (1999). b) S. Griffin, L. Heath, and P. Wyatt, *Tetrahedron Lett.*, **39**, 4405 (1998).

18 Compound **3a** is prone to form various solvates (e.g. with CH_2Cl_2, *DMF*). In addition to **3a**·*DMF* a second crystalline form **3a**·1/2*DMF* was obtained, studied with X-ray diffraction, and structural data were deposited under CCDC-194684.

19 a) P. Wyatt, S. Warren, M. McPartlin, and T. Woodroffe, *J. Chem. Soc., Perkin Trans. 1*, **2001**, 279. b) D. W. Allen, I. W. Nowell, and P. E. Walker, *Z. Naturforsch.,Teil B*, **35**, 133 (1980).

20 W. Winter, *Chem. Ber.*, **111**, 2942 (1978); For related organometallics see also: E. Luppold and W. Winter, *Chem. Ber.*, **116**, 1923 (1983).

21 B. Krauss, C. Mugge, B. Ziemer, A. Zschunke, and F. Krech, *Z. Anorg. Allg. Chem.*, **627**, 1542 (2001).

22 Bruker, Programs SMART, version 5.054; SAINT, version 6.2.9; SADABS version 2.03; XPREP, version 5.1; SHELXTL, version 5.1./Bruker AXS Inc., Madison, WI, USA, 2001.

23 A. L. Spek (1990): PLATON-A Multipurpose Crystallographic Tool. Utrecht University, Utrecht, The Netherlands.