Synthesis and X-ray Structure of Binaphthyl-Based Macrocyclic Diphosphanes and their Ni(II) and Pd(II) Complexes

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16- and 18-membered diphospha macrocycles (**8**, **12**, and **15**) have been synthesized from the corresponding 1,1′-binaphthyl precursors (**6**, **11**, and **14**, resp.) and o-phenylenebis(phenylphosphane) by means of high-dilution conditions in 55, 49, and 87% yield. X-ray structure analyses of **8a**, **8b**, **12b**, and **12b** · $NiCl_2$ reveal their distinctly different conformations and conformational changes caused by complexation. These structural features are reflected in the pronounced different tendency of the compounds concerned to form Ni(II) and Pd(II) complexes.

Chiral disphosphanes have been used excessively as chiral auxiliaries[1] for asymmetric catalysis by transition metal complexes[2-5]. For the asymmetric hydrogenation reaction, the relationship between structure and asymmetric induction is rather well understood[6,7]. Thus, to obtain a high e.e.[*], a second metal-coordination functionality of the olefin is required, presumably in order to decrease the flexibility of the reacting catalyst-substrate complex. We set out to design a class of chiral catalysts which should replace the flexibility-limiting second functionality by steric interaction between the (prochiral) olefin and the chiral auxiliary.

To this end, we have adopted the following concept (see Figure 1/I): The chiral biaryl C* should be connected to the metal-coordinated diphosphane A by appropriately designed spacers B in such a way that the biaryl "embraces" the (metal-coordinated) substrate S[8]. For C* we have chosen the (symmetrically substituted) 1,1′-binaphthyl system because of its well-known efficiency in asymmetric catalysis[9] and its C_2 symmetry[10]. Depending on the substitution pattern, macrocycles with a small "groove" (2,2′-substitution) or with a large one (7,7′-substitution) are accessible[11]. Such an arrangement would simultaneously limit the substrate's flexibility and transmit the chiral information.

This concept bears the risk that, for spacers long enough to accommodate metal and substrate, the macrocycle (consisting of biaryl, spacers, and diphosphane with the coordinated metal atom) may adopt a conformation in which metal and substrate point away from the (chiral) biaryl (see Figure 1/II).

In the present communication we report on the synthesis of binaphthyl-based macrocyclic diphosphanes **8**, **12**, and **15** and describe the crystal structures of **8a**, **8b**, and **12b**[12].

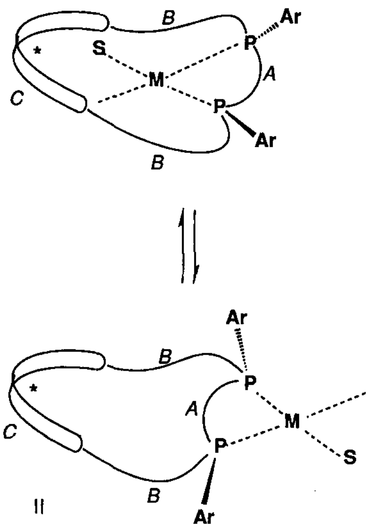

Figure 1. Schematic representation of (interconvertible) arrangements of cyclic diphosphane complexes. A = diphosphane, B = spacer group, C = chiral moiety, M = transition metal, S = substrate

In order to test their behavior upon metal complexation, attempts have been made to prepare Ni(II) and Pd(II) complexes. For one of them, **12b** · $NiCl_2$, the crystal structure has also been determined.

Results and Discussion

In a preceeding communication we have briefly reported on the synthesis of the binaphthyl-based 16-membered macrocycles **8** and **12**[13]. Compounds **2**, **3**, and **9**[14] have been investigated (see Scheme 1) as appropriate precursors for the preparation of 7,7′-disubstituted binaphthyls by *o*-lithiation. **2** and **3** are easily accessible by the reaction of **1**[15] with $NaOCH_3$ or dimethylamine. With **2** all attempts to achieve *o*-lithiation under various conditions have failed, while *o*-lithiation of **3** followed by treatment with oxirane affords monoalcohol and diol **4a** and **4b** in good yields (see Scheme

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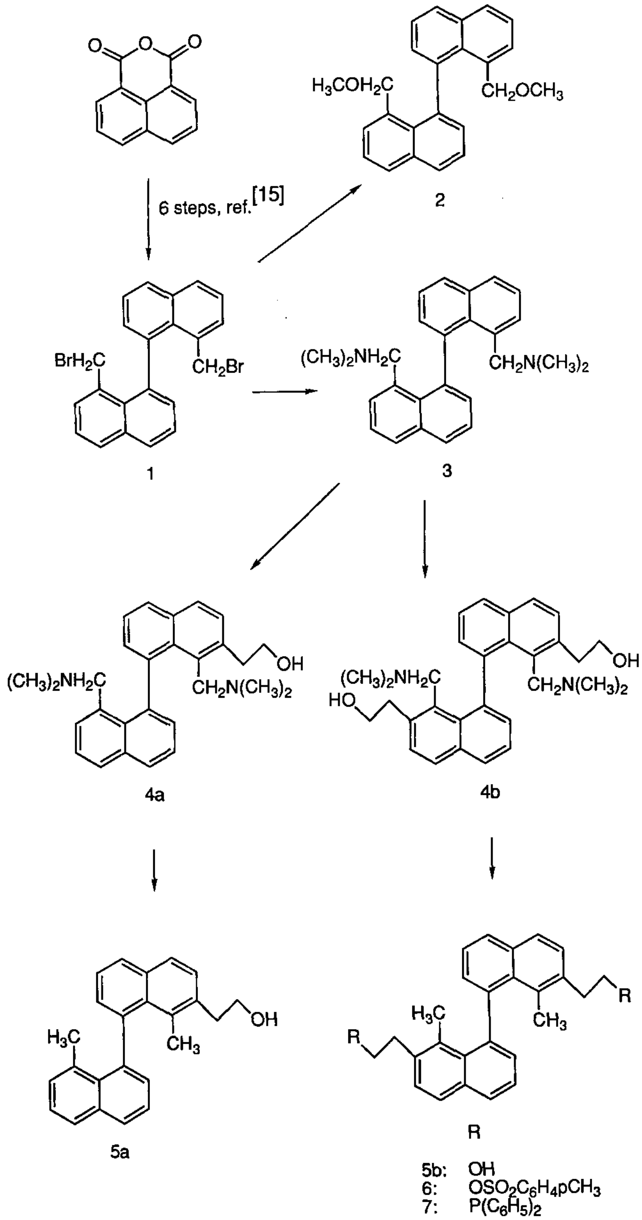
[*] e.e. enantiomeric excess = ([*R*] − [*S*])/([*R*] + [*S*]), for [*R*] > [*S*].

0009–2940/92/0303–0679 $ 3.50+.25/0

Scheme 1

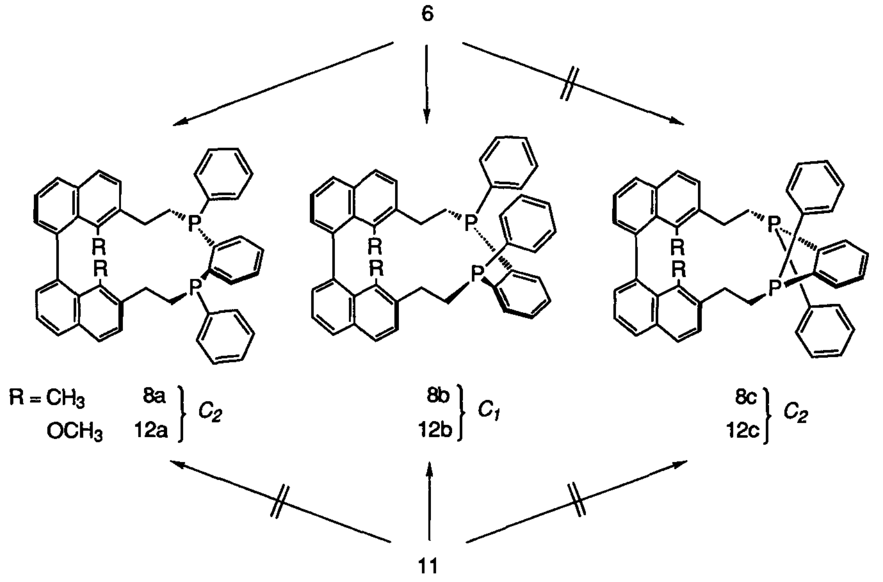


1). No regioisomeric products have been detected. The conversion of the diamino diol **4b** into the diol **5** is achieved by quarternization with methyl iodide and subsequent reductive deamination with sodium amalgam. **5** is converted into the ditosylate **6** which is coupled to the cyclic diphosphanes **8** by means of high dilution conditions[16] (see Scheme 2). From the reaction mixture **8a** and **8b** are isolated by preparative TLC. Their stereochemical assignment is made evident by ^{1}H-NMR spectrometry and finally confirmed by an X-ray analysis (see below). The overall yield is 6.9% (based on **1**, mixture of stereoisomers). In a similar way **12** is prepared from **9** by a three-step sequence (see Schemes 2, 3). In this case only a single stereoisomer, **12b**, with C_1 symmetry can be isolated (overall yield 17%). In addition, **7**, the corresponding open-chain analog of **8**, is prepared for spectroscopic comparison.

X-ray crystal structure analyses have been carried out for **8a, 8b,** and **12b** and the Ni(II) complex **12b · NiCl₂**. These analyses confirm the above constitutional and configurational assignments and permit a first assessment of the potential usability of this class of compounds in view of the above concept.

Figure 2 shows a projection of each structure approximately along the biaryl axis, and in Table 1 are listed selected geometrical parameters. A disorder is observed in the crystal structure of **8a**: one phenyl ring occurs in two equally populated conformations (the projection in Figure 2 shows the more C_2-symmetrical conformation), and a disordered solvent molecule ($CHCl_3$) is observed, which accordingly affects the crystallographic resolution. All structures show biaryl torsion angles in the typical range observed for 1,1′-binaphthyls[17,18], with pronounced "*peri*-effects" (see Table 1). A remarkably different geometry has been found for each cycle[19], especially with respect to the accessibility of the phosphorus atoms, a fact which might explain their distinctly different tendency to form complexes with Ni(II) (see below) and Pd(II). In **8a** the *P*-phenyl groups are found in a "diequatorial" arrangement, obviously forced by steric repulsion overbalancing the electrostatic repulsion of the phosphorus lone pairs. This results in a coplanarity of the *P*-lone pairs (C_2-symmetrical conformation), which should favor complexation. On the other hand, the efficient shielding by phenyl groups appears to prevent oxidation or com-

Scheme 2



Scheme 3

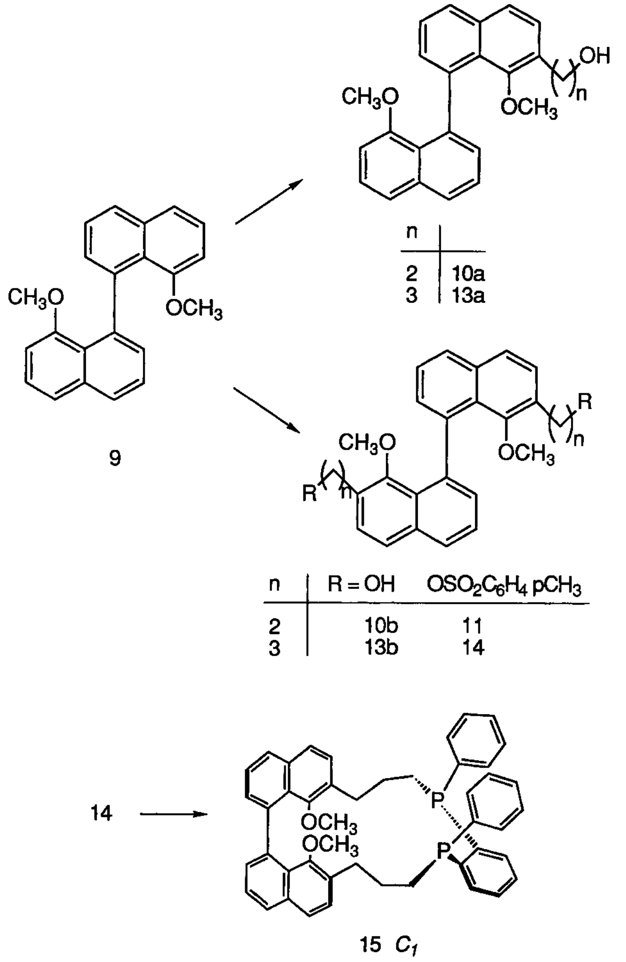
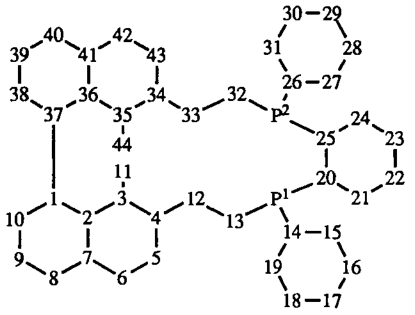


Table 1. Selected data from crystal structure analyses of **8a**, **8b**, **12b**, and **12b** · $NiCl_2$



	8a	**8b**	**12b**	**12b·NiCl$_2$**
2,1,37,38	65.7°	–68.4°	–72.9°	–65.0°
P1,P2	3.05/3.28Å	3.22Å	3.15Å	2.97Å
P1,20,25,P2	0.3°/2.8°	–5.3°	–3.3°	12.1°
21,20,P1,14	-25.4/-7.9°	8.7°	4.6°	45.0°
24,25,P2,26	–6.0°	–77.4°	–99.1°	–67.7°
"peri-effects"				
2,1,37	126.4°	125.3°	124.0°	125.2°
Δ 37[*]	0.07	0.11	0.31	0.09
2,3,11	121.2°	122.6°	118.8°	117.7°
Δ11[*]	–0.18	–0.25	–0.21	–0.13
36,37,11	125.9°	126.0°	122.9°	129.4°
Δ1[*]	–0.25	0.36	–0.09	–0.06
36,35,44	121.9°	120.9°	120.2°	119.3°
Δ44[*]	0.28	–0.32	0.06	0.10

[*] Deviation (in Å) of atom C37 (C11, C1, C44, resp.) from a mean plane through atoms C1 to C10 (C34 to C43, resp.).

plexation, resulting in the inertness of this compound. These findings are paralleled by results from force-field calculations, where the C_2-symmetrical compound **8a** shows exactly center-directed phosphorus lone pairs[20].

Structures **8b** and **12b** with C_1 symmetry show different conformations, which should make them more efficient chelating ligands. In both structures, one of the *P*-phenyl groups adopts a "pseudo-axial", the other one a "pseudo-equatorial" conformation, making the phosphorus atoms more accessible.

Contrary to our expectation, the crystal structure of the $NiCl_2$ complex of **12b** shows the NiP_2Cl_2 plane completely twisted out of the macrocycle, which demonstrates the flexibility of this compound and makes it an unsuitable candidate for efficient chiral catalysis. In this structure, nickel shows a (slightly distorted) square planar coordination with Ni–P distances of 2.13 and 2.14 Å and Ni–Cl distances of 2.20 and 2.21 Å. The P–Ni–P bond angle is 87.9°, and the two chlorine atoms deviate by 0.22 and –0.12 Å from the P–Ni–P plane.

The progressively easier access of the phosphorus lone pairs in the series **8a**–**8b**–**12b** is reflected and paralleled by their reactivity towards the formation of transition metal complexes. This may be followed by UV spectrometry upon addition of a concentrated $NiCl_2$ solution (in EtOH) to a solution of the corresponding diphosphane in CH_2Cl_2: while no UV absorption band corresponding to a Ni chelate can be detected for **8a**, even with a tenfold excess of $NiCl_2$, a yellow solution (λ_{max} 455 nm) is produced with **8b**. Treatment of **12b** with $NiCl_2$ yields an intensively orange solution (λ_{max} 456 nm, ε 1500), from which eventually brown crystals deposit. From **12b** a crystalline 1:1 Pd(II) complex has also been prepared, but it has proved to be of too low solubility for further studies.

These findings support that enlarging the perimeter should further increase the "chelating ability" of the diphosphane. To test this hypothesis **15** has been prepared[21]. It is accessible in analogy to **12** in moderate yield by using trimethylene oxide instead of oxirane (see Scheme 3). Again only the C_1-symmetrical diastereoisomer of **15** is obtained. At the present time, we have no explanation why the C_2-symmetrical cycle cannot be detected at all. In solution **15** is moderately air-sensitive, which prevents a satisfactory purification by TLC (see Experimental). Attempts to prepare

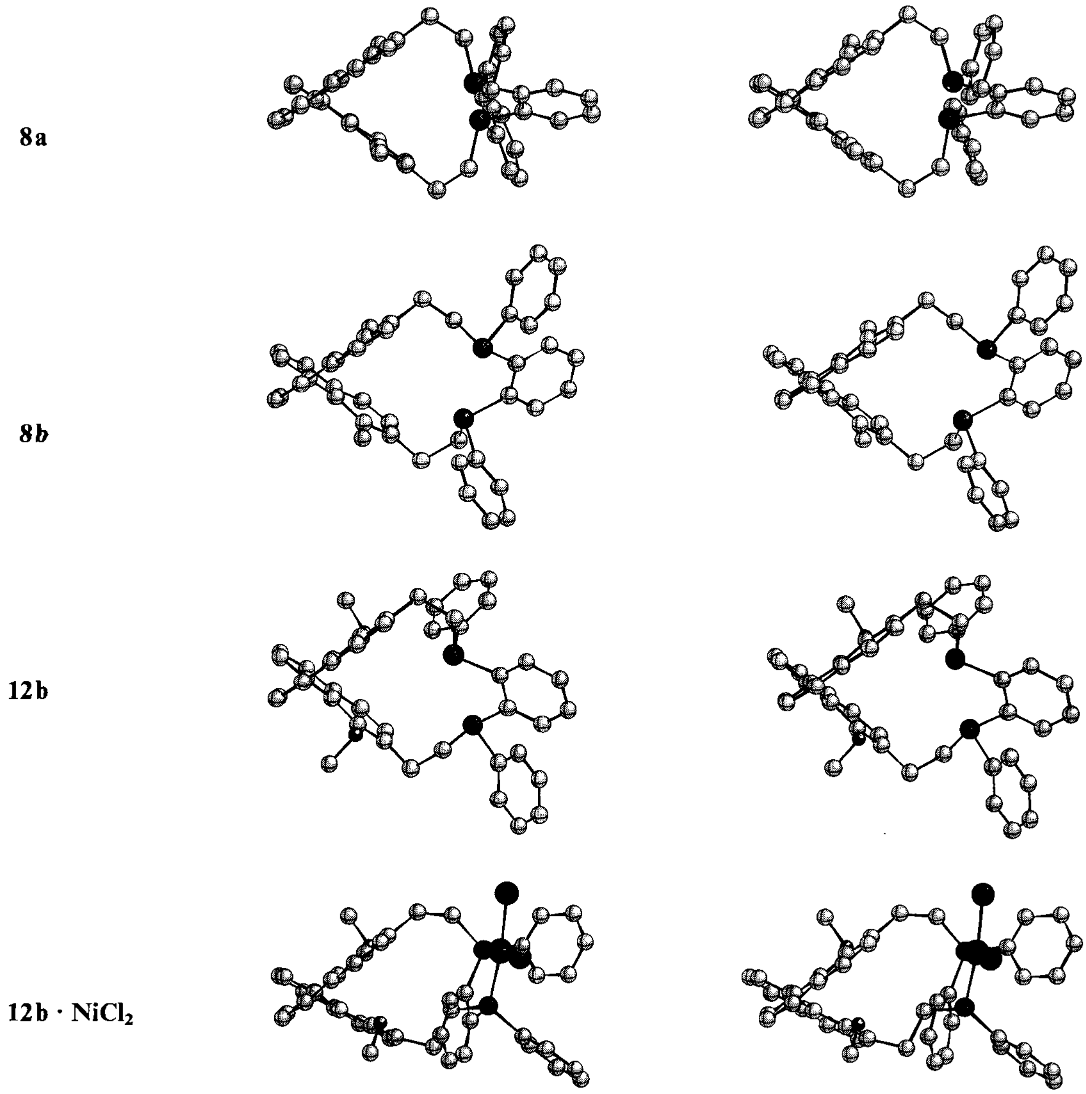


Figure 2. Crystal structures of **8a**, **8b**, **12b**, and **12b** · $NiCl_2$ (H atoms omitted)

suitable crystals for an X-ray structure determination have failed, but stable crystalline complexes with Ni and Pd can be prepared.

All complexes and ligands except **15** exhibit a remarkable stability towards aerial oxidation, a feature which we attribute to the "*endo* reactivity" of phosphorus atoms and/or efficient shielding by aromatic residues. While this fact facilitates workup procedures, it makes them poor candidates for auxiliaries in transition metal catalysts. On the other hand, unfavorable conformational changes may occur during complexation, which may lower the diastereoselective interaction. We expect a significant improvement from a further enlargement of the ring, but with more rigid spacer groups in order to conserve a conformation with "*endo* reactivity" after metal complexation. Appropriate synthetic routes are under investigation.

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Experimental

UV: Perkin-Elmer spectrometer: LAMBDA-7. – NMR: Bruker WP-250 (250 MHz) or AM 400 WB (400 MHz) instrument in $CDCl_3$ if not noted otherwise, and chemical shifts δ are obtained rel. to tetramethylsilane (^1H) or 85% H_3PO_4 (^{31}P); ^{31}P-NMR spectra are recorded in a proton-decoupled mode; abbreviations p and b refer to "pseudo" and "broad". – MS: Varian MAT-CH7. – Melting points: Kofler melting point apparatus, uncorrected. – Elementary analyses: Mikroanalytisches Laboratorium der Universität Wien (Mag. *J. Theiner*).

Note: Crystalline samples of **8a**, **12b**, **12b** · $NiCl_2$, and **12b** · $PdCl_2$ proved to retain tenaciously solvent molecules (see X-ray analyses). Even after prolonged drying in vacuo at elevated temperature[22] the samples contained a few percent of solvent. This was taken into account when calculating the elemental composition.

Tosyl chloride was recrystallized from petroleum ether (PE). Tetramethylethylenediamine (TMEDA) and pyridine were filtered over Al_2O_3 (Akt. I) and stored over molecular sieves (4 Å). Trimethylene oxide was distilled from a small amount of sodium (suspension in mineral oil) and stored over molecular sieves (4 Å). Tetrahydrofuran (THF) and diethyl ether (Et_2O) were distilled from $LiAlH_4$, dioxane from sodium. All the other chemicals were of analytical grade and used without further purification. Analytical and preparative thin-layer chromatography (TLC) were performed on TLC aluminium sheets, silica gel 60 F_{254} precoated (0.2 mm, Merck 5554) and precoated TLC plates, silica gel 60 F_{254} (0.25 mm, Merck 5715), resp. *o*-Phenylenebis(diphenylphosphane) was prepared in three steps by starting from 1-bromo-2-chlorobenzene and dichlorophenylphosphane according to literature procedures[23].

8,8'-Bis(methoxymethyl)-1,1'-binaphthyl (**2**): A solution of 5.0 g (11.4 mmol) of **1** and 3.0 g of NaH (125 mmol) in 60 ml of MeOH/CH_2Cl_2 (1:1) was stirred at room temp. for 3 d. The precipitated NaBr was removed by filtration and the solvent evaporated. The residue was partitioned between water and CH_2Cl_2 (2 × 20 ml). The combined organic extracts were washed with water and dried with Na_2SO_4. Removal of the solvent left 3.9 g ($\approx$100%) of crude **2** as an oil which soon became crystalline. An analytically pure product was obtained by preparative TLC: [CH_2Cl_2/PE (1:1)], R_f = 0.09, m.p. 74–75 °C (ref.[15] 71–73 °C). – ^1H-NMR: δ = 2.62 (6H, s, OCH_3), 3.81 (2H, d, J = 12 Hz, OCH_2), 3.93 (2H, d, J = 12 Hz, OCH_2), 7.27 (1H, dd, J = 7.5, 1.5 Hz, Ar-H^4), 7.41 (1H, pt, J = 8 Hz, Ar-H^6), 7.44 (1H, pt, J = 8 Hz, Ar-H^3), 7.54 (1H, bd, J = 7.5 Hz, Ar-H^5), 7.83 (1H, bd, $J \approx$ 8 Hz, Ar-H^7), 7.86 (1H, dd, J = 8, 1 Hz, Ar-H^2). – MS (140 °C): m/z (%) = 239 (7), 252 (23), 265 (49), 277 (100), 295 (3), 310 (13), 342 (7).

8,8'-Bis[(dimethylamino)methyl]-1,1'-binaphthyl (**3**): 10 g (0.023 mol) of **1**, 30 ml of benzene, and 70 ml (1.06 mol) of dimethylamine were placed in an ice-cooled autoclave. The mixture was heated to 110–120 °C with stirring for 48 h. After cooling to room temp. 200 ml of water and 200 ml of CH_2Cl_2 were added. The organic layer was separated and the aqueous one extracted with 3 × 100 ml of CH_2Cl_2. The combined organic extracts were washed neutral and dried with $MgSO_4$. Evaporation of the solvent left an orange oil which was further purified by kugelrohr distillation (0.2 Torr, 205–225 °C bath temp.). Yield 7.80 g (92%) of **3** as a highly viscous yellow oil. TLC [THF/Et_3N (99:1)]: R_f = 0.74. – ^1H-NMR: δ = 1.66 [12H, s, $(CH_3)_2N$], 2.94 (4H, s, CH_2N), 7.29 (1H, dd, J = 7, 1.5 Hz, Ar-H^4), 7.42 (1H, pt, J = 8 Hz, Ar-H^3), 7.46 (1H, pt, J = 8 Hz, Ar-H^6), 7.64 (1H, bd, J = 8 Hz, Ar-H^5), 7.85 (1H, bd, J = 8 Hz, Ar-H^7), 7.92 (1H, dd, J = 7, 1.5 Hz, Ar-H^2). – MS (130 °C): m/z (%) = 58 (100), 239 (7), 252 (18), 265 (27), 279 (54), 308 (5), 323 (22), 368 (7).

$C_{26}H_{28}N_2$ (368.5)				
	Calcd.	C 84.74	H 7.66	N 7.60
	Found	C 84.78	H 7.74	N 7.33

8,8'-Bis[(dimethylamino)methyl]-7,7'-bis(2-hydroxyethyl)-1,1'-binaphthyl (**4b**): 4.5 g (12.2 mmol) of **3** in 60 ml of absol. Et_2O was cooled to −70 °C and treated with 3 equivalents of *t*BuLi (21.5 ml of a 1.7 M solution in pentane) under argon. The temperature was raised to 20 °C and the orange suspension stirred for 10 h. The reaction mixture was again cooled to −70 °C, and 20.3 g (0.46 mol) of ethylene oxide was introduced through a rubber septum by using a steel cannula. After warming up slowly to room temp., stirring was continued for 1 h. The reaction was quenched by careful addition of 50 ml of water. The organic layer was separated and the aqueous one extracted with three 30-ml portions of Et_2O. The combined extracts were washed with water (2 ×), dried with Na_2SO_4, and evaporated to dryness to give a crude mixture of starting material, mono- and disubstituted products. Preparative column chromatography on SiO_2 (80 × 3 cm, 40–63 µm) in THF/Et_3N (99:1) yielded some starting material (20–30%), followed by 13–24% of poorly characterized monoalcohol **4a**, TLC [THF/Et_3N (99:1)]: R_f = 0.54. From the third band 2.64 g (47%) of **4b** could be isolated as a pale yellow oil; TLC [THF/Et_3N (99:1)]: R_f = 0.33. An analytical sample was purified by preparative TLC yielding **4b** as colorless crystals, m.p. 147–152 °C. The recovered starting material could be recycled without further purification to give an overall yield of 55–60% of **4b**. – ^1H-NMR: δ = 1.41 [6H, s, $(CH_3)_2N$], 1.51 [6H, s, $(CH_3)_2N$], 1.90 (2H, d, J = 14 Hz, CH_2N), 2.42 (2H, d, J = 14 Hz, CH_2N), 2.65–2.77 (2H, m, CH_2CH_2), 3.68–3.84 (4H, m, CH_2CH_2), 3.89–4.00 (2H, m, CH_2CH_2), 7.40 (2H, d, J = 8.5 Hz, Ar-H^5), 7.55 (2H, dd, J = 7.5, 8 Hz, Ar-H^3), 7.68 (2H, dd, J = 7.5, 1.5 Hz, Ar-H^4), 7.82 (2H, d, J = 8.5 Hz, Ar-H^6), 7.90 (2H, dd, J = 8, 1.5 Hz, Ar-H^2). – MS (150 °C): m/z (%) = 205 (100), 220 (26), 265 (4), 277 (21), 291 (5), 303 (4), 322 (8), 367 (8), 411 (5), 456 (0.3). – High-resol. MS: This was performed by using the "preselected peak matching method", where the M^+ peak was found to be in exact agreement with the calculated mol mass of 456.277678 for an isotopically pure compound with the formula $C_{30}H_{36}N_2O_2$.

7,7'-Bis(2-hydroxyethyl)-8,8'-dimethyl-1,1'-binaphthyl (**5b**) *and 7-(2-Hydroxyethyl)-8,8'-dimethyl-1,1'-binaphthyl* (**5a**): A solution of 3.30 g (7.23 mmol) of **4b** in a mixture of 20 ml of acetonitrile and 50 ml of methyl iodide was heated with reflux for 10 h. After cooling to room temp., Et_2O (100 ml) was added with stirring to complete the precipitation. The product was sucked off, washed with some Et_2O and dried to give 5.35 g (quant.) of the bismethiodide of **4b** as a yellow powder which was used without further purification. The latter was dissolved in 100 ml of hot water (80 °C). The solution was vigorously stirred and a total of 135 g of sodium amalgam (5%) was added in portions during 24 h. During that time the crude product separated as a greenish black gum. After cooling this was extracted with Et_2O (2 × 100 ml) and CH_2Cl_2 (2 × 100 ml). The combined extracts were dried with Na_2SO_4 and evaporated to dryness to give 3.24 g of a brown solid. Medium-pressure chromatography on SiO_2 (25–40 µm, 45 × 4.5 cm, flow rate 25–30 ml min^{-1}, 2 bar) with ethyl acetate/CH_2Cl_2 (25:75) as the eluent yielded 1.41 g (53%) of **5b**, m.p. 141–145 °C (PE/CH_2Cl_2). TLC [ethyl acetate/PE (1:1)]: R_f = 0.17. – ^1H-NMR: δ = 1.65 (2H, bs, OH), 1.88 (6H, s, CH_3), 2.98 (4H, t, J = 7 Hz, Ar-CH_2), 3.78 (4H, t, J = 7 Hz, CH_2OH), 7.17 (2H, d, J = 7 Hz, Ar-H^5), 7.36 (2H, d, J = 7 Hz, Ar-H^4), 7.37 (2H, t, J = 7 Hz, Ar-H^3), 7.75 (2H, d, J = 7 Hz, Ar-H^2), 7.83 (2H, d, J = 7 Hz, Ar-H^6). – MS (200 °C): m/z (%) = 252 (8), 265 (16), 276 (26), 279 (25), 293 (20), 307 (24), 321 (15), 325 (21), 340 (11), 355 (4), 370 (100).

$C_{26}H_{26}O_2$ (370.5)	Calcd.	C 84.29	H 7.07
	Found	C 84.02	H 7.20

If a less purified sample of **4b**, containing some mono-substituted product **4a**, was used as the starting material, also a small amount of the monoalcohol **5a** was isolated; m.p. 123–124 °C. TLC [ethyl acetate/PE (1:1)]: R_f = 0.64. – ^1H-NMR: δ = 1.25 (1H, bs, OH), 1.84 (3H, s, CH_3), 1.85 (3H, s, CH_3), 2.98 (2H, t, J = 8 Hz, Ar-CH_2), 3.78 (2H, bt, J = 8 Hz, CH_2OH), 7.14–7.30 (3H, m, ArH), 7.30–7.46 (4H, m, ArH), 7.70–7.95 (4H, m, ArH). – MS (150 °C): m/z (%) = 239 (11), 252 (16), 265 (51), 280 (68), 293 (18), 295 (18), 307 (5), 311 (8), 326 (100).

Ditosylate **6** *of 7,7'-Bis(2-hydroxyethyl)-8,8'-dimethyl-1,1'-binaphthyl:* 0.480 g (1.3 mmol) of **5b** was placed in an Erlenmeyer flask and dissolved in 3 ml of dry pyrdine. To the resulting solution 0.780 g (5.2 mmol) of *p*-tosyl chloride was added, and the tightly stoppered flask was kept in a refrigerator (+2 °C) for 24 h. After pouring the reaction mixture on ice (20 g) it was extracted with three 20-ml portions of CH_2Cl_2. The combined extracts were successively washed with 6 N HCl, water (twice), and brine and finally dried with Na_2SO_4. Removal of the solvent gave crude **6** which was recrystallized from Et_2O; yield: 0.69 g (78%); white crystals of m.p. 165–167 °C. TLC [ethylacetate/PE (3:7)]: $R_f = 0.48$. – ^{1}H-NMR: $\delta = 1.76$ (6H, s, Ar-CH_3), 2.37 (6H, s, $C_6H_4CH_3$), 3.06 (4H, pt, $J =$ 7 Hz, Ar-CH_2), 4.14 (4H, m, CH_2O), 7.04 (2H, dd, $J = 7, 1$ Hz, Ar-H^4), 7.17 (4H, d, $J = 8$ Hz, Ph-$H^{3,5}$), 7.21 (2H, d, $J \approx 8$ Hz, Ar-H^5), 7.35 (2H, pt, $J = 8$ Hz, Ar-H^3), 7.61 (4H, d, $J = 8$ Hz, Ph-$H^{2,6}$), 7.68 (2H, d, $J = 8$ Hz, Ar-H^6), 7.79 (2H, dd, $J = 7, 1$ Hz, Ar-H^2). – MS (210 °C): m/z (%) = 239 (1), 252 (2), 265 (5), 277 (7), 291 (8), 305 (11), 307 (10), 319 (8), 334 (4), 506 (4), 678 (4).

$C_{40}H_{38}O_6S_2$ (678.9)
Calcd. C 70.77 H 5.64 S 9.45
Found C 70.71 H 5.89 S 9.15

7,7'-Bis[2-(diphenylphosphino)ethyl]-8,8'-dimethyl-1,1'-binaphthyl (**7**): To a degassed solution of 264 mg (215 µl, 1.2 mmol) of chlorodiphenylphosphane in 5 ml of dry dioxane 0.114 g (5 mmol) of sodium was added and the mixture refluxed under argon for 7 h. The resulting solution was filtered and dropped with stirring to a degassed solution of 300 mg (0.442 mmol) of the ditosylate **6** in 5 ml of dry THF during 0.5 h. The reaction mixture, now olive-colored and slightly turbid, was kept at room temp. overnight. After evaporation of the solvent, 30 ml of CH_2Cl_2 was added to the residue, and the organic layer was washed with water (3 × 10 ml) and dried with Na_2SO_4. Evaporation of the solvent left an oily residue which could not be crystallized. The purification was therefore carried out via a Ni complex[24]: The crude product was dissolved in Et_2O, the solution filtered over a small pad of SiO_2 and concentrated to approx. 3 ml. Dropwise addition of 100 mg of $NiCl_2 \cdot 6\,H_2O$ in 1 ml of EtOH to the stirred solution produced a red bulky precipitate. After 10 min 100 mg of KSCN dissolved in 2–3 ml of hot EtOH was dropped to the mixture. The resulting yellow precipitate was allowed to stand overnight. The Ni complex was separated, washed (3 ml of EtOH) and dried (vacuo). To liberate the phosphane from the complex it was suspended in 2 ml of CH_2Cl_2 and treated with an aqueous solution of 280 mg of NaCN (1 h). The organic layer, together with some precipitate, was separated and washed with 2 × 2 ml of water. Removal of the solvent left a cream-colored powder. Further attempts to purify a sample by crystallization failed; yield: approx. 150 mg (≈50%). – ^{1}H-NMR (CD_2Cl_2): $\delta = 1.77$ (6H, s, CH_3), 2.18–2.33 (4H, m, Ar-CH_2), 2.68–2.83 (4H, m, CH_2P), 7.06 (2H, dd, $J = 7, 1.8$ Hz, Ar-H), 7.25–7.44 (24H, m, Ar-H), 7.73 (2H, d, $J = 8$ Hz, Ar-H), 7.80 (2H, dd, $J = 7, 1.8$ Hz, Ar-H). – ^{31}P NMR (CD_2Cl_2): $\delta = -14.883$ (2P, s). – MS (200 °C): m/z (%) = 353 (13), 493 (3), 505 (5), 521 (100), 629 (7), 691 (5), 706 (10).

1,4-Diphosphacyclohexadecapentaene Derivatives **8a**, **8b**: Solutions of 500 mg (0.737 mmol) of **6** in 10 ml of dry, degassed THF and 1.2 equiv. of the dilithium salt [prepared from 260 mg (0.884 mmol) of *o*-phenylenebis(phenylphosphane) and 1.77 mmol of *n*BuLi] in 9 ml of the same solvent were prepared. These were added simultaneously by means of high dilution conditions[16] to 120 ml of dry, refluxing THF under argon. The solvent was distilled off, and 20 ml of a saturated NH_4Cl solution and subsequently 50 ml of CH_2Cl_2 were added to the residue with stirring. The organic layer was separated and filtered over silica gel. The adsorbent was washed with 20 ml of CH_2Cl_2 and the solution evaporated to dryness to leave 407 mg of **8** as a white foam. The diastereoisomers could be separated by preparative TLC [CH_2Cl_2/*n*-hexane (1:3)]. After extracting the bands with Et_2O/ethanol two fractions were obtained: a) 52 mg (17%) of **8a** (probably together with a small amount of **8c**), m.p. 172–183 °C (Cyclohexane), $R_f = 0.28$. – ^{1}H NMR (CD_2Cl_2): $\delta = 1.83$ (6H, s, CH_3), 2.42 (2H, m, CH_2P), 2.84 (2H, m, CH_2-Ar), 3.10 (2H, m, CH_2P), 3.35 (2H, m, CH_2-Ar), 6.40 (2H, d, $J = 8.4$ Hz, Ar-H), 6.84 (2H, m, Ar-H), 7.01 (2H, m, Ar-H), 7.35–7.56 (16H, m, Ar-H), 7.84 (2H, dd, $J = 7.9, 1.7$ Hz, Ar-H). – ^{31}P NMR (CD_2Cl_2): $\delta = -39.27$ (2P, s). – MS (350 °C): m/z (%) = 294 (100), 305 (90), 314 (10), 628 (47).

$C_{44}H_{38}P_2 \cdot (CHCl_3)_{0.1}$ (640.7)
Calcd. C 82.67 H 5.99 Cl 1.66 P 9.67
Found C 82.68 H 6.20 Cl 1.49 P 9.63

b) 176 mg (38%) of **8b**, m.p. 207–210 °C, $R_f = 0.22$. – ^{1}H NMR (CD_2Cl_2): $\delta = 1.38$ (3H, s, CH_3), 1.53 (3H, s, CH_3), 2.07 (1H, m, CH_2CH_2), 2.30–2.50 (2H, m, CH_2CH_2), 2.69 (3H, m, CH_2CH_2), 2.88 (1H, m, CH_2CH_2), 3.14 (1H, m, CH_2CH_2), 6.88 (1H, m, Ar-H), 7.10 (2H, m, Ar-H), 7.21 (1H, t, $J \approx 7$ Hz, Ar-H), 7.25–7.48 (12H, m, Ar-H), 7.52 (2H, m, Ar-H), 7.65 (1H, dd, $J = 7, 1.5$ Hz, Ar-H), 7.67 (1H, dd, $J = 7, 1.5$ Hz, Ar-H), 7.74 (2H, t, $J = 8.3$ Hz, Ar-H), 7.88 (1H, dd, $J = 8, 1.5$ Hz, Ar-H), 7.95 (1H, dd, $J = 8.1, 1.4$ Hz, Ar-H). – ^{31}P NMR (CD_2Cl_2): $\delta = -44.07$ (d, $J = 135.4$ Hz, P^1), -45.50 (d, $J = 135.4$ Hz, P^2). – MS (270 °C): m/z (%) = The obtained spectrum was completely superimposable to that of the diastereoisomer **8a**.

7-(2-Hydroxyethyl)-8,8'-dimethoxy-1,1'-binaphthyl (**10a**) *and 7,7'-Bis(2-hydroxyethyl)-8,8'-dimethoxy-1,1'-binaphthyl* (**10b**): To a suspension of 0.587 g (1.87 mmol) of **9** in 30 ml of absol. Et_2O 0.465 g (4 mmol) of TMEDA and 3.25 ml (5.2 mmol) of a 1.6 M *n*BuLi solution were added successively. The mixture became clear and was stirred at room temp. under argon for 10 h. It was cooled to −70 °C, and 2 g (45 mmol) of ethylene oxide was added with stirring. After 1 h the temp. was allowed to raise to room temp., and stirring was continued for 6 h. 50 ml of water and 50 ml of Et_2O were added, and the organic layer was separated. The aqueous layer was extracted with Et_2O (2 × 25 ml), and the combined extracts were washed with water (2 × 30 ml) and dried (Na_2SO_4). Upon concentration of the solution to approx. 30% of its volume the diol **10b** crystallized. It was filtered off and recrystallized from ethyl acetate/acetone. The remaining mother liquors containing more of diol **10b**, monoalcohol **10a**, and some starting material were separated by column chromatography on SiO_2 (20 × 1.5 cm). CH_2Cl_2 eluted 60 mg (10%) of starting material and 100 mg (15%) of **10a**, m.p. 125–128 °C. TLC (ethyl acetate): $R_f = 0.79$. – ^{1}H NMR: $\delta = \approx 1.91$ (1H, bt, OH), 2.64–2.81 (1H, m, Ar-CH_2), 2.78 (3H, s, CH_3O), 2.97 (3H, s, CH_3O), 2.95–3.07 (1H, m, Ar-CH_2), 3.59–3.87 (2H, m, CH_2OH), 6.62 (1H, d, $J \approx 7$ Hz, Ar-H), 7.20–7.50 (6H, m, Ar-H), 7.66 (1H, d, $J = 8.5$ Hz, Ar-H), 7.78 (1H, dd, $J = 7.5, 1.5$ Hz, Ar-H). – MS (100 °C): m/z (%) = 91 (100), 107 (9), 121 (10), 202 (16), 252 (2), 312 (1), 327 (0.5), 358 (2). – Ethyl acetate eluted **10b** to give a total of 360 mg (48%), m.p. 199–201 °C. TLC (ethyl acetate): $R_f = 0.48$. – ^{1}H NMR: $\delta =$ 2.54–2.66 (2H, m, Ar-CH_2), 2.64 (6H, s, OCH_3), 2.93–3.04 (2H, m, Ar-CH_2), ≈3.33 (2H, bt, $J \approx 6$ Hz, OH), 3.60–3.85 (4H, m, CH_2OH), 7.28 (2H, d, $J = 8.5$ Hz, Ar-H^5), 7.42–7.51 (4H, m, Ar-$H^{3,4}$), 7.64 (2H, d, $J = 8.5$ Hz, Ar-H^6), 7.81 (2H, dd, $J = 7.5, 2.5$ Hz, Ar-H^2). – MS (180 °C): m/z (%) = 91 (100), 107 (9), 121 (11), 151 (26), 181 (14), 202 (15), 331 (1), 365 (7), 384 (1), 402 (1).

$C_{26}H_{26}O_4$ (402.5) Calcd. C 77.59 H 6.51
Found C 77.15 H 6.74

Ditosylate **11** *of 7,7'-Bis(2-hydroxyethyl)-8,8'-dimethoxy-1,1'-binaphthyl:* The ditosylate was prepared from 0.371 g (0.923 mmol) of **10b** and 0.703 g (3.692 mmol) of *p*-tosyl chloride in 2 ml of pyridine as described for **6** to give 0.488 g (74%) of **11** as colorless crystals; m.p. 115–119 °C. TLC ($CHCl_3$): $R_f = 0.3–0.5$ (excessive tailing). – ^{1}H NMR: δ = 2.37 (6H, s, $C_6H_4CH_3$), 2.52 (6H, s, OCH_3), 2.84–2.91 (4H, m, Ar-CH_2), 4.06–4.15 (4H, m, CH_2OSO_2), 7.16 (4H, d, *J* = 8.5 Hz, Ph-$H^{3,5}$), 7.18 (2H, d, *J* = 8.5 Hz, Ar-H^5), 7.33 (2H, dd, *J* = 6.8, 1.8 Hz, Ar-H^4), 7.44 (2H, pt, *J* ≈ 7 Hz, Ar-H^3), 7.58 (2H, d, *J* = 8.5 Hz, Ar-H^6), 7.59 (4H, d, *J* = 8 Hz, Ph-$H^{2,6}$), 7.78 (2H, dd, *J* = 7, 1.8 Hz, Ar-H^2). – MS (140°C): no M^+ peak was found, only fragment ions indicative of the presence of a tosylate could be detected; *m/z* (%) = 91 (100), 107 (14), 155 (30), 186 (27), 272 (0.7), 338 (0.7).

$C_{40}H_{38}O_8S_2$ (710.9)
Calcd. C 67.59 H 5.39 S 9.02
Found C 67.59 H 5.59 S 9.05

Diphosphacyclohexadecapentaene Derivative **12** was prepared similarly as described for **8** from 800 mg (1.13 mmol) of **11**, 398 mg (377 µl, 1.36 mmol) of *o*-phenylenebis(phenylphosphane) and 1.70 ml (2.72 mmol) of *n*BuLi. Preparative TLC [PE/CH_2Cl_2 (1:1)] yielded a single diastereomer, **12b**, as the only isolable product, 361 mg (48%), m.p. 210–230°C. TLC (CH_2Cl_2): R_f = 0.77. – ^{1}H NMR (CD_2Cl_2): δ = 2.01–2.12 (1H, m, CH_2), 2.38–2.61 (5H, m, CH_2), 2.58 (3H, s, OCH_3), 2.75 (3H, s, OCH_3), 2.77–2.86 (1H, m, CH_2), 3.12–3.25 (1H, m, CH_2), 6.83–6.88 (1H, m, Ar-H), 7.04 (1H, ptd, *J* = 7.5, 1.5 Hz, Ar-H), 7.08 (1H, d, *J* = 8.5 Hz, Ar-H), 7.12–7.55 (17H, m, Ar-H), 7.63 (1H, d, *J* = 8.5 Hz, Ar-H), 7.65 (1H, d, *J* = 8.5 Hz, Ar-H), 7.82 (1H, dd, *J* = 8, 1.5 Hz, Ar-H), 7.89 (1H, m, Ar-H). – ^{31}P NMR (CD_2Cl_2): δ = –29.791 (2P, bs). – MS (260°C): *m/z* (%) = 294 (100), 305 (62), 366 (27), 583 (6), 628.5 (78), 629 (36), 659 (43), 660 (20).

$C_{44}H_{38}O_2P_2 \cdot (CHCl_3)_{0.05}$ (666.7)
Calcd. C 79.36 H 5.75 Cl 0.80 P 9.29
Found C 79.33 H 5.87 Cl 0.83 P 9.45

7-(3-Hydroxypropyl)-8,8'-dimethoxy-1,1'-binaphthyl (**13a**) *and 7,7'-Bis(3-hydroxypropyl)-8,8'-dimethoxy-1,1'-binaphthyl* (**13b**): To a suspension of 1.174 g (3.74 mmol) of **9** in 50 ml of absol. Et_2O under argon was added 0.930 g (8 mmol) of TMEDA, followed by dropwise addition of 6.5 ml (10.4 mmol) of *n*BuLi (1.6 M solution in hexane). The mixture became clear at this stage and after a few minutes precipitation of the gray lithium salt started. Stirring was continued for 10 h at room temp. to complete the formation of the dilithium compound. The mixture was cooled to –70°C and 3 g (51.6 mmol) of trimethylene oxide added dropwise by means of a syringe. After 30 min the mixture was warmed up to room temp., and stirring was continued for additional 5 h. The reaction was quenched by the addition of 30 ml of water. The organic layer was separated and the aqueous layer, together with some precipitate, was extracted with 2 × 50 ml of CH_2Cl_2. The combined extracts were washed with water (twice) and brine and dried with Na_2SO_4. The solvent was evaporated in vacuo and the residue chromatographed on SiO_2 (50 × 1.5 cm, 40–63 µm) in $CHCl_3$. The following fractions were obtained: a) 89 mg (8%) of starting material, TLC ($CHCl_3$): R_f = 0.83.

b) 89 mg (6%) of **13a**, TLC ($CHCl_3$): R_f = 0.24, m.p. 119–124°C. – ^{1}H NMR: δ = 1.69 (1H, m, $CH_2CH_2CH_2$), 1.85 (1H, m, $CH_2CH_2CH_2$), 1.98 (1H, m, OH), 2.62 (1H, m, Ar-CH_2), ≈2.80 (1H, m, Ar-CH_2), 2.80 (3H, s, OCH_3), 3.03 (3H, s, OCH_3), 3.29 (1H, m, CH_2OH), 3.45 (1H, m, CH_2OH), 6.63 (1H, d, *J* = 8.5 Hz, Ar-H), 7.19–7.49 (7H, m, Ar-H), 7.65 (1H, d, *J* = 8.5 Hz, Ar-H), 7.77 (1H, m, Ar-H). – MS (150°C): *m/z* (%) = 295 (15), 297 (18), 309 (12), 311 (20), 327 (12), 341 (7), 366 (5), 372 (100).

c) 955 mg (59%) of **13b**, TLC ($CHCl_3$): R_f = 0.03, m.p. 155–161°C. – ^{1}H NMR: δ = 1.63 (2H, bs, OH), 1.76 (2H, m, $CH_2CH_2CH_2$), 1.90 (2H, m, $CH_2CH_2CH_2$), 2.52 (2H, m, Ar-CH_2), 2.68 (6H, s, OCH_3), 2.91 (2H, m, Ar-CH_2), ≈3.40 (4H, m, CH_2OH), 7.29 (2H, d, *J* = 8.5 Hz, Ar-H^5), 7.33 (2H, dd, *J* = 7, 1.5 Hz, Ar-H^4), 7.41 (2H, pt, *J* = 7 Hz, Ar-H^3), 7.64 (2H, d, *J* = 8.5 Hz, Ar-H^6), 7.78 (2H, dd, *J* = 7, 1.5 Hz, Ar-H^2). – MS (190°C). – *m/z* (%) = 295 (5), 311 (6), 325 (4), 339 (4), 353 (3), 367 (2), 398 (2), 412 (3), 430 (100).

$C_{28}H_{30}O_4$ (430.5) Calcd. C 78.11 H 7.02
Found C 77.90 H 7.19

Ditosylate **14** *of 7,7'-Bis(3-hydroxypropyl)-8,8'-dimethoxy-1,1'-binaphthyl:* The tosylate was prepared from 0.800 g (1.86 mmol) of **13b** and 1.42 g (7.44 mmol) of *p*-tosyl chloride in 7 ml of pyridine as described for **6**. The crude product was purified by flash chromatography on SiO_2 (1.5 × 25 cm). Some impurities could be eluted with PE/CH_2Cl_2 (1:1) followed by CH_2Cl_2 to give 0.934 g (68%) of **14** as colorless crystals, m.p. 96–100°C. TLC ($CHCl_3$): R_f = 0.63. – ^{1}H NMR: δ = 1.83 (4H, m, $CH_2CH_2CH_2$), 2.40 (6H, s, CH_3), 2.56 (4H, m, Ar-CH_2), 2.60 (6H, s, OCH_3), 3.95 (4H, pt, *J* = 7 Hz, CH_2OSO_2), 7.15 (2H, d, *J* = 8.5 Hz, Ar-H^5), 7.26 (4H, d, *J* = 8 Hz, Ph-$H^{3,5}$), 7.31 (2H, dd, *J* = 7, 1.5 Hz, Ar-H^4), 7.41 (2H, pt, *J* = 7 Hz, Ar-H^3), 7.57 (2H, d, *J* = 8.5 Hz, Ar-H^6), 7.70 (4H, d, *J* = 8 Hz, Ph-$H^{2,6}$), 7.76 (2H, dd, *J* = 7, 1.5 Hz, Ar-H^2). – MS (160°C): no M^+ peak was found, only fragment ions indicative of the presence of a tosylate could be detected; *m/z* (%) = 91 (100), 107 (12), 122 (6), 155 (25), 186 (20), 530 (0.2).

$C_{42}H_{42}O_8S_2$ (738.9)
Calcd. C 68.27 H 5.73 S 8.68
Found C 68.34 H 5.59 S 8.85

Diphosphacyclooctadecapentaene Derivative **15** was prepared as described for **8** from 638 mg (0.86 mmol) of **14**, 381 mg (360 µl, 1.30 mmol) of *o*-phenylenebis(phenylphosphane) and 1.62 ml (2.60 mmol) of *n*BuLi. The resulting glass was dissolved in 5 ml of hot cyclohexane. After standing at room temp. for 2 d the product separated as fine white needles, yield: 520 mg (88%). (An attempted purification by preparative TLC yielded a considerable amount of oxidized product.) M.p. 217–225°C. TLC (CH_2Cl_2): R_f = 0.63. – ^{1}H NMR (CD_2Cl_2): δ = 1.29 (1H, m, $CH_2CH_2CH_2$), 1.72 (1H, m, $CH_2CH_2CH_2$), 1.83 (1H, m, $CH_2CH_2CH_2$), 2.00 (1H, m, $CH_2CH_2CH_2$), ≈2.00–2.40 (6H, m, CH_2), 2.57 (3H, s, OCH_3), 2.67 (3H, s, OCH_3), 2.84 (1H, m, CH_2), 2.96 (1H, m, CH_2), 7.12 (1H, m, Ar-H), 7.16–7.46 (19H, m, Ar-H), 7.56 (1H, d, *J* = 8.5 Hz, Ar-H), 7.66 (1H, d, *J* = 8.5 Hz, Ar-H), 7.77 (1H, dd, *J* = 7, 2 Hz, Ar-H), 7.82 (1H, dd, *J* = 7, 2 Hz, Ar-H). – ^{31}P NMR (CD_2Cl_2): δ = –23.77 (d, *J* = 159.6 Hz, P^1), –27.11 (d, *J* = 159.6 Hz, P^2). – MS (300°C): *m/z* (%) = 91 (21), 107 (36), 152 (16), 183 (100), 293 (27), 398 (12), 688 (40).

$C_{46}H_{42}O_2P_2$ (688.8)
Calcd. C 80.21 H 6.15 P 8.99
Found C 79.94 H 6.12 P 9.05

12b · $NiCl_2$: To a solution of 50 mg ($7.57 \cdot 10^{-5}$ mol) of **12b** in 1 ml of CH_2Cl_2 was added 27 mg (1.5 equiv.) of $NiCl_2 \cdot 6\,H_2O$ in 1 ml of EtOH. From the resulting dark brown solution 49 mg (82%) of **12b · $NiCl_2$** crystallized as orange brown needles; m.p. >350°C (dec.). – ^{1}H NMR (CD_2Cl_2): δ = 2.13 (3H, s, OCH), 2.35 (1H, m, CH_2), 2.50 (3H, s, OCH_3), 2.76 (1H, m, CH_2), 2.99 (2H, m, CH_2), 3.32 (1H, m, CH_2), 3.59–3.79 (2H, m, CH_2), 3.92 (1H, m, CH_2), 7.17–7.29 (2H, m, Ar-H), 7.22 (1H, dd, *J* = 7, 1.5 Hz, Ar-H), 7.28 (1H, dd, *J* = 7, 1.5 Hz, Ar-H), 7.34 (1H, dd, *J* = 7.5, 7 Hz, Ar-H), 7.38–7.53 (10H, m, Ar-H), 7.54–7.63 (6H, m, Ar-H), 7.67 (1H, d, *J* = 8 Hz, Ar-H), 7.69 (1H, dd, *J* = 8.5, 1.5 Hz, Ar-H), 7.88 (1H, dd, *J* = 8.5, 1.5 Hz, Ar-H). – ^{31}P NMR (CD_2Cl_2): δ = 58.54 (d, *J* = 75.4 Hz, P^1), 59.94 (d, *J* = 75.4 Hz, P^2).

$C_{44}H_{38}Cl_2NiO_2P_2 \cdot (CHCl_3)_{0.5}$ (850.0)
Calcd. C 62.88 H 4.57 P 7.29
Found C 62.30 H 4.54 P 7.51

15 · $NiCl_2$ was prepared similarly as described for **12b · $NiCl_2$** from 50 mg ($7.27 \cdot 10^{-5}$ mol) of **15** and 17 mg of $NiCl_2 \cdot 6\,H_2O$ to yield 49 mg (82%) of **15 · $NiCl_2$** as an orange powder which was recrystallized from CH_2Cl_2/EtOH; m.p. >350 °C (dec.). – ^1H NMR (CD_2Cl_2): δ = 0.86 (1 H, m, CH_2), 1.70 (1 H, m, CH_2), 2.23 (4 H, m, CH_2), 2.43 (1 H, dt, J = 12, 3 Hz, CH_2), 2.54 (3 H, s, OCH_3), 2.61 (3 H, s, OCH_3), 2.71 (1 H, m, CH_2), 2.91 (1 H, m, CH_2), 3.01 (1 H, m, CH_2), 3.17 (2 H, m, CH_2), 7.09 (1 H, d, J = 8.5 Hz, Ar-H), 7.36–7.62 (18 H, m, Ar-H), 7.65–7.75 (4 H, m, Ar-H), 7.85 (1 H, dd, J = 8, 1.5 Hz, Ar-H). – ^{31}P NMR (CD_2Cl_2): δ = 59.94 (d, J = 74.0 Hz, P^1), 62.54 (d, J = 74.0 Hz, P^2).

$C_{46}H_{42}Cl_2NiO_2P_2$ (818.4)			
Calcd.	C 67.51	H 5.17	P 7.57
Found	C 67.31	H 5.28	P 7.81

12b · $PdCl_2$: To a solution of 50 mg ($7.57 \cdot 10^{-5}$ mol) of **12b** in 1 ml of CH_2Cl_2 were added 20 mg (1 equiv.) of $Pd(CH_3CN)_2Cl_2$ in 1 ml of CH_2Cl_2 and subsequently 1–2 ml of EtOH. From the resulting pale yellow solution the complex separated as clear colorless crystals, which were recrystallized from $CHCl_3$; m.p. >350 °C (dec.). – ^1H NMR (CD_2Cl_2): δ = 2.15 (1 H, m, CH_2), 2.18 (3 H, s, OCH_3), 2.41 (3 H, s, OCH), 2.75–2.85 (1 H, m, CH_2), 3.04 (1 H, pq, J = 11.5 Hz, CH_2), 3.18–3.37 (2 H, m, CH_2), 3.54–3.75 (2 H, m, CH_2), 3.91 (1 H, m, CH_2), 7.19 (1 H, dd, J = 7, 1.5 Hz, Ar-H), 7.28 (1 H, dd, J = 7, 1.5 Hz, Ar-H), 7.25–7.68 (20 H, m, Ar-H), 7.70 (1 H, dd, J = 8.5, 1.5 Hz, Ar-H), 7.81 (1 H, dd, J = 8.5, 1.5 Hz, Ar-H). – ^{31}P NMR (CD_2Cl_2): δ = 65.03 (d, J = 13.6 Hz, P^1), 67.00 (d, J = 13.6 Hz, P^2).

$C_{44}H_{38}Cl_2O_2P_2Pd \cdot (CHCl_3)_{0.25}$ (867.9)			
Calcd.	C 61.24	H 4.44	P 7.14
Found	C 61.08	H 4.55	P 7.15

15 · $PdCl_2$ was prepared similarly as described for **12b · $PdCl_2$** from 50 mg ($7.27 \cdot 10^{-5}$ mol) of **15** and 28 mg of $Pd(C_6H_5CN)_2Cl_2$ to give 45 mg (71%) of **15 · $PdCl_2$** as a white powder. Crystallization from CH_2Cl_2/EtOH afforded micaceous plates, m.p. >350 °C (dec.). – ^1H NMR (CD_2Cl_2): δ = 0.79 (1 H, m, CH_2), 1.13 (1 H, m, CH_2), 1.28 (1 H, m, CH_2), 1.97 (1 H, m, CH_2), 2.23 (2 H, m, CH_2), 2.44 (2 H, m, CH_2), 2.52 (3 H, s, OCH_3), 2.57 (3 H, s, OCH_3), 2.86 (1 H, m, CH_2), 3.09 (1 H, m, CH_2), 3.17 (1 H, m, CH_2), 3.31 (1 H, m, CH_2), 7.09 (1 H,

Table 2. X-ray structure determination

	8a	**8b**	**12b**	**12b · $NiCl_2$**
unit cell data				
a[Å]	12.540(3)	9.426(4)	9.721(4)	17.564(10)
b[Å]	12.558(3)	22.541(9)	16.307(9)	25.346(18)
c[Å]	22.532(6)	18.241(8)	21.775(17)	21.020(14)
β[°]	102.45(2)	104.63(4)	90.18(4)	90
V[$Å^3$]	3464.7(8)	3749.8(10)	3451.6(11)	9357.6(19)
d_{calc} [gcm^{-3}]	1.43	1.32	1.27	1.46
determination of cell data:				
number of reflections	79	23	44	26
2Θ range	9°≤2Θ≤18°	20°≤2Θ≤22°	9°≤2Θ≤18°	9°≤2Θ≤12°
crystal system	monoclinic	monoclinic	monoclinic	orthorhombic
space group	$P2_1/n$	$P2_1/n$	$P2_1/n$	Pbca
Z	4	4	4	8
formula of asymmetric unit	$C_{44}H_{38}P_2 \cdot CHCl_3$	$C_{44}H_{38}P_2 \cdot CHCl_3$	$C_{44}H_{38}O_2P_2$	$C_{44}H_{38}O_2P_2NiCl_2 . 2\,CHCl_3$
formula weight	748.11	748.11	660.73	1029.08
range of intensity data coll.	5°≤2Θ≤56° –16≤h≤16 0≤k≤16 0≤l ≤29	5.5°≤2Θ≤68° –14≤h≤14 0≤k≤35 0≤l ≤28	5°≤2Θ≤60° –13≤h≤13 0≤k≤22 0≤l ≤30	5.5°≤2Θ≤45° 0≤h≤17 0≤k≤27 0≤l ≤22
3 standard reflections (measured every 100 reflect.)	[–3 –1 9] [3 1 3] [1 –3 –1]	[1 6 7] [4 2 3] [–1 3 9]	[0 4 0] [0 2 –4] [3 –1 –1]	[1 2 6] [1 4 4] [4 2 1]
max. r.m.s. fluctuation	1.6%	3.5%	1.5%	2.6%
number of reflections				
observed	9226	16539	8274	6253
unique	8838	15308	7574	5658
significant [F>5σ(F)]	3555	7692	2189	2489
significance limit n for F>nσ(F)	5	5	5	4
R	0.1006	0.0565	0.0487	0.0799
R_w [$w_i=1/\sigma^2(F_{oi})$]	0.1210	0.0620	0.0448	0.0799
for number of parameters	282	608	242	342
number of observations	3571	7731	2189	2489
temperature	88K	94K	88K	88K
μ [mm^{-1}]	0.39	0.36	0.16	0.98
highest feature in final ΔF-Fourier synthesis [$eÅ^{-3}$]	2.3	1.2	0.4	0.7

Table 3. Fractional atomic coordinates [× 10^4] and isotropic temperature coefficients [$Å^2$ × 10^4] for the crystal structure of **8a**. Estimated standard deviations (in unit of the last significant digit) in parentheses. The isotropic temperature factor has the form $T = \exp\{-[\chi 8\pi^2 U_{iso}(\sin^2\Theta/\lambda^2)]\}$. The equivalent isotropic temperature coefficient was calculated as one third of the trace of the orthogonalized u_{13} matrix

Atom	x/a	y/b	z/c	U_{iso}
P(11)	1365(8)	2853(9)	2447(5)	144(32)
P(12)	1451(8)	2881(10)	2363(5)	146(33)
P(2)	1002(3)	2946(3)	3742(2)	265(18)
C(1)	-2630(8)	4895(8)	1778(5)	98(22)
C(2)	-1903(9)	4291(10)	1505(5)	168(25)
C(3)	-1462(8)	3236(9)	1699(5)	135(24)
C(4)	-722(8)	2760(9)	1412(5)	152(25)
C(5)	-424(9)	3234(9)	911(5)	161(26)
C(6)	-880(9)	4198(10)	698(6)	195(27)
C(7)	-1592(9)	4721(9)	979(5)	157(25)
C(8)	-2058(9)	5712(10)	729(6)	195(27)
C(9)	-2793(9)	6204(10)	966(6)	219(28)
C(10)	-3074(9)	5819(9)	1503(5)	185(26)
C(11)	-1795(9)	2657(10)	2215(5)	180(26)
C(12)	-221(9)	1682(9)	1587(5)	163(25)
C(13)	625(9)	1625(9)	2204(5)	161(25)
C(14)	2168(16)	3174(13)	1871(8)	78(52)
C(15)	2433(17)	2428(15)	1477(8)	112(53)
C(16)	2971(17)	2754(15)	1035(9)	171(60)
C(17)	3242(22)	3811(14)	986(10)	185(69)
C(18)	2996(18)	4560(17)	1384(9)	210(66)
C(19)	2425(16)	4232(13)	1811(9)	92(53)
C(114)	2114(16)	2842(13)	1705(7)	157(52)
C(115)	2279(17)	1956(14)	1373(8)	170(55)
C(116)	2727(18)	2068(16)	868(9)	263(62)
C(117)	3043(20)	3059(14)	703(11)	307(68)
C(118)	2897(22)	3965(17)	1023(10)	292(77)
C(119)	2417(18)	3820(15)	1514(10)	219(61)
C(20)	2488(9)	2364(9)	3028(5)	162(25)
C(21)	3474(9)	1924(10)	2945(6)	230(29)
C(22)	4253(10)	1547(10)	3431(6)	244(29)
C(23)	4081(11)	1596(11)	3988(6)	314(33)
C(24)	3133(9)	2018(10)	4111(6)	244(29)
C(25)	2318(10)	2411(10)	3634(6)	259(29)
C(26)	1098(9)	2649(9)	4554(5)	187(26)
C(27)	579(10)	1739(11)	4690(6)	275(31)
C(28)	574(11)	1469(12)	5281(6)	331(34)
C(29)	1096(10)	2146(11)	5749(6)	287(30)
C(30)	1633(9)	3045(10)	5617(6)	224(28)
C(31)	1637(9)	3294(10)	5034(5)	215(28)
C(32)	1263(11)	4384(11)	3746(6)	298(32)
C(33)	403(11)	5069(12)	3970(7)	368(36)
C(34)	-749(10)	4737(10)	3746(6)	253(30)
C(35)	-1312(9)	4911(10)	3136(6)	191(26)
C(36)	-2424(9)	4553(9)	2941(5)	155(25)
C(37)	-3051(9)	4589(9)	2328(5)	135(24)
C(38)	-4151(10)	4322(10)	2215(6)	214(27)
C(39)	-4672(11)	3944(11)	2673(6)	278(31)
C(40)	-4075(10)	3815(11)	3238(6)	291(31)
C(41)	-2966(10)	4122(10)	3398(6)	234(29)
C(42)	-2375(10)	3977(10)	3990(6)	263(30)
C(43)	-1303(11)	4254(11)	4158(6)	328(33)
C(44)	-733(10)	5520(10)	2716(6)	206(27)
CL(1)	6154(7)	3828(7)	5149(4)	1377(71)
CL(2)	4215(6)	4376(6)	4317(5)	1413(77)
CL(3)	4954(13)	4233(13)	4789(5)	3196(176)

Table 4. Fractional atomic coordinates [× 10^4] and isotropic temperature coefficients [$Å^2$ × 10^4] for the crystal structure of **8b**. See also caption of Table 3

Atom	x/a	y/b	z/c	U_{iso}
C(1)	-3346(3)	-1585(1)	1201(1)	173(11)
C(2)	-1974(3)	-1708(1)	1753(1)	161(11)
C(3)	-526(3)	-1520(1)	1692(1)	158(10)
C(4)	697(3)	-1628(1)	2299(1)	174(11)
C(5)	537(3)	-1928(1)	2956(2)	215(12)
C(6)	-795(3)	-2144(1)	3007(2)	224(13)
C(7)	-2071(3)	-2043(1)	2410(2)	197(12)
C(8)	-3437(3)	-2270(1)	2486(2)	226(13)
C(9)	-4708(3)	-2176(1)	1931(2)	227(13)
C(10)	-4648(3)	-1829(1)	1298(2)	220(13)
C(11)	-275(3)	-1236(1)	982(1)	201(12)
C(12)	2234(3)	-1446(1)	2274(2)	184(11)
C(13)	2525(3)	-773(1)	2337(1)	176(11)
P(1)	2733(1)	-471(0)	3306(0)	149(3)
C(14)	4567(3)	-750(1)	3806(1)	156(10)
C(15)	5650(3)	-962(1)	3454(1)	185(11)
C(16)	7044(3)	-1112(1)	3880(2)	188(11)
C(17)	7406(3)	-1060(1)	4668(2)	214(12)
C(18)	6339(3)	-864(1)	5029(1)	209(12)
C(19)	4934(3)	-715(1)	4602(1)	168(10)
C(20)	3210(3)	303(1)	3109(1)	154(10)
C(21)	4674(3)	496(1)	3242(1)	182(11)
C(22)	5015(3)	1086(1)	3124(2)	206(12)
C(23)	3893(3)	1494(1)	2874(1)	201(12)
C(24)	2420(3)	1306(1)	2734(2)	203(12)
C(25)	2060(3)	716(1)	2844(1)	157(10)
P(2)	127(1)	450(0)	2626(0)	163(3)
C(26)	-494(3)	729(1)	3449(1)	172(11)
C(27)	-579(3)	1332(1)	3618(2)	215(12)
C(28)	-1084(3)	1516(1)	4237(2)	238(13)
C(29)	-1511(3)	1098(1)	4706(2)	257(13)
C(30)	-1431(3)	499(1)	4548(2)	255(13)
C(31)	-933(3)	313(1)	3924(2)	216(12)
C(32)	-765(3)	996(1)	1889(1)	194(11)
C(33)	-2430(3)	868(1)	1563(1)	193(11)
C(34)	-2704(3)	395(1)	953(1)	184(11)
C(35)	-3090(3)	-189(1)	1054(1)	169(11)
C(36)	-3280(3)	-604(1)	429(1)	177(10)
C(37)	-3499(3)	-1235(1)	480(1)	184(11)
C(38)	-3847(3)	-1580(1)	-176(2)	229(12)
C(39)	-3884(3)	-1338(1)	-895(2)	259(14)
C(40)	-3531(3)	-756(1)	-948(2)	256(14)
C(41)	-3220(3)	-382(1)	-299(1)	211(12)
C(42)	-2836(3)	219(1)	-376(2)	253(14)
C(43)	-2556(3)	589(1)	234(2)	237(13)
C(44)	-3376(3)	-376(1)	1803(1)	212(13)
C(100)	-304(3)	2680(1)	364(2)	296(15)
CL(1)	819(1)	2231(0)	1068(1)	395(5)
CL(2)	536(2)	2756(1)	-390(1)	731(9)
CL(3)	-2072(1)	2373(1)	92(1)	881(10)

d, J = 8.5 Hz, Ar-H), 7.34–7.75 (22H, m, Ar-H), 7.83 (1 H, dd, J = 8, 1.5 Hz, Ar-H). – ^{31}P NMR (CD_2Cl_2): δ = 65.34 (d, J = 16.4 Hz, P^1), 68.44 (d, J = 16.4 Hz, P^2).

$C_{46}H_{42}Cl_2O_2P_2Pd$ (866.1)
Calcd. C 63.79 H 4.89 P 7.15
Found C 63.30 H 4.60 P 7.08

X-ray Analysis[25]: X-ray measurements were carried out on a locally modified STOE diffractometer with Mo-K_α radiation (graphite monochromator, λ = 0.71069 Å), equipped with a Nonius cold stream cryostat. Suitable crystals were obtained either by evaporation of chloroform from a solution of **8a** or **8b** in chloroform/ethanol or by gradual condensation of Et_2O into a concentrated solution of **12b** in chloroform. In each case the crystals were colorless, clear prisms of flat shape (**8a**, **12b**) or elongated to rods (**8b**). **12b** · $NiCl_2$ crystallized from a concentrated $CHCl_3$ solution to yield orange elongated prisms. In the case of **8a** and **8b**, a pronounced tendency to lose solvent was observed, resulting in a collapse of crystallinity. To avoid this, all X-ray measurements were conducted at low temperature (see Table 2) in a stream of cold nitrogen gas.

8a: Structure solution by means of direct methods, least-squares refinement of anisotropic atomic displacement parameters (a.d.p.) for P and Cl atoms and of isotropic a.d.p.'s for all other non-hydrogen atoms; one of the phenyl rings (P1, C14 to C19) was

Table 5. Fractional atomic coordinates [× 10^4] and isotropic temperature coefficients [Å^2 × 10^4] for the crystal structure of **12b**. See also caption of Table 3

Atom	x/a	y/b	z/c	U_{iso}
C(1)	-1855(6)	9754(4)	3955(3)	111(14)
C(2)	-2139(6)	9350(4)	3387(3)	121(14)
C(3)	-1976(6)	9714(4)	2791(3)	144(15)
C(4)	-2179(6)	9282(4)	2253(3)	133(15)
C(5)	-2608(6)	8461(4)	2288(3)	170(15)
C(6)	-2859(6)	8097(4)	2843(3)	164(15)
C(7)	-2641(6)	8534(4)	3397(3)	133(14)
C(8)	-2958(6)	8168(4)	3972(3)	234(17)
C(9)	-2790(6)	8584(4)	4509(3)	196(16)
C(10)	-2216(6)	9376(4)	4497(3)	163(15)
O(1)	-1624(4)	10530(3)	2752(2)	175(11)
C(11)	-2819(6)	11043(4)	2788(3)	252(17)
C(12)	-1951(6)	9697(4)	1634(3)	160(15)
C(13)	-431(6)	9730(4)	1448(3)	135(14)
P(1)	252(2)	8694(1)	1298(1)	125(8)
C(14)	-498(6)	8445(4)	540(3)	115(14)
C(15)	-384(6)	7637(4)	350(3)	149(15)
C(16)	-871(6)	7383(4)	-219(3)	159(15)
C(17)	-1537(6)	7934(4)	-598(3)	177(15)
C(18)	-1711(6)	8743(4)	-407(3)	186(15)
C(19)	-1174(6)	8994(4)	157(3)	159(14)
C(20)	2033(6)	8945(4)	1079(3)	118(14)
C(21)	2460(6)	8972(4)	463(3)	139(14)
C(22)	3818(6)	9156(4)	313(3)	156(15)
C(23)	4736(6)	9333(4)	777(3)	166(15)
C(24)	4347(6)	9290(3)	1391(3)	111(14)
C(25)	3007(6)	9088(4)	1553(3)	101(13)
P(2)	2376(2)	9066(1)	2359(1)	114(8)
C(26)	2456(6)	7967(4)	2545(3)	136(14)
C(27)	1293(6)	7627(4)	2816(3)	148(15)
C(28)	1313(6)	6794(4)	3008(3)	205(16)
C(29)	2488(6)	6332(4)	2924(3)	212(15)
C(30)	3627(6)	6680(4)	2643(3)	191(16)
C(31)	3614(6)	7487(4)	2461(3)	163(15)
C(32)	3912(6)	9416(4)	2788(3)	117(14)
C(33)	3628(6)	9426(4)	3487(3)	155(15)
C(34)	2641(6)	10107(4)	3661(3)	116(14)
C(35)	1250(6)	9987(4)	3769(3)	137(15)
C(36)	350(6)	10642(4)	3900(3)	129(14)
C(37)	-1115(6)	10557(4)	4005(3)	118(14)
C(38)	-1854(6)	11224(4)	4183(3)	138(14)
C(39)	-1278(6)	12008(4)	4235(3)	134(14)
C(40)	94(6)	12110(4)	4108(3)	151(14)
C(41)	930(6)	11437(4)	3954(3)	121(14)
C(42)	2342(6)	11555(4)	3840(3)	178(15)
C(43)	3163(6)	10918(4)	3701(3)	148(14)
O(2)	754(4)	9195(2)	3731(2)	142(10)
C(44)	889(6)	8747(4)	4295(3)	190(15)

Table 6. Fractional atomic coordinates [× 10^4] and isotropic temperature coefficients [Å^2 × 10^4] for the crystal structure of **12b** · $NiCl_2$. See also caption of Table 3

Atom	x/a	y/b	z/c	U_{iso}
NI(1)	2273(1)	64(1)	720(1)	189(13)
CL(1)	1390(3)	321(2)	40(2)	254(30)
CL(2)	2998(3)	-313(2)	-12(2)	250(30)
C(1)	4517(12)	2340(8)	1677(9)	246(54)
C(2)	4863(11)	1856(7)	1478(9)	198(49)
C(3)	4693(11)	1352(7)	1695(9)	156(47)
C(4)	5018(12)	908(8)	1447(10)	219(51)
C(5)	5601(13)	932(9)	981(10)	335(59)
C(6)	5790(13)	1419(8)	753(11)	333(55)
C(7)	5437(12)	1906(8)	982(10)	225(51)
C(8)	5647(12)	2393(8)	700(11)	303(54)
C(9)	5296(12)	2847(8)	911(10)	291(55)
C(10)	4734(12)	2819(8)	1389(10)	284(54)
O(1)	4100(7)	1298(5)	2106(6)	183(32)
C(11)	4305(12)	1285(8)	2775(9)	263(54)
C(12)	4646(12)	376(8)	1609(10)	276(54)
C(13)	3948(11)	332(8)	1162(10)	292(55)
P(1)	3160(3)	-98(2)	1389(2)	194(30)
C(14)	3484(11)	-773(7)	1464(9)	138(44)
C(15)	3126(12)	-1118(8)	1862(10)	255(53)
C(16)	3304(13)	-1660(8)	1882(10)	330(58)
C(17)	3923(14)	-1829(10)	1496(12)	468(69)
C(18)	4307(13)	-1486(8)	1106(10)	304(55)
C(19)	4059(12)	-962(8)	1102(9)	253(52)
C(20)	2882(10)	116(7)	2191(9)	156(46)
C(21)	3298(10)	29(7)	2743(8)	126(43)
C(22)	3034(11)	239(7)	3307(9)	209(49)
C(23)	2390(12)	549(8)	3345(10)	280(55)
C(24)	1933(12)	603(8)	2797(9)	221(50)
C(25)	2175(11)	401(7)	2211(9)	148(46)
P(2)	1616(3)	374(2)	1488(3)	208(30)
C(26)	871(11)	-103(7)	1661(8)	162(45)
C(27)	924(11)	-437(7)	2195(9)	154(46)
C(28)	407(11)	-843(7)	2300(9)	148(48)
C(29)	-194(11)	-889(7)	1881(9)	169(48)
C(30)	-300(11)	-574(7)	1362(9)	153(46)
C(31)	247(12)	-167(8)	1267(10)	285(55)
C(32)	1168(12)	1019(7)	1393(10)	235(52)
C(33)	1676(12)	1490(7)	1216(9)	209(48)
C(34)	2049(11)	1767(7)	1751(9)	171(49)
C(35)	2802(12)	1950(8)	1729(10)	240(52)
C(36)	3167(11)	2215(7)	2231(9)	178(47)
C(37)	3945(12)	2393(8)	2205(10)	274(56)
C(38)	4240(14)	2667(9)	2715(10)	354(59)
C(39)	3850(15)	2753(9)	3280(12)	456(69)
C(40)	3072(12)	2572(8)	3344(9)	211(51)
C(41)	2757(13)	2318(9)	2801(11)	380(59)
C(42)	1991(11)	2124(7)	2837(9)	210(50)
C(43)	1651(12)	1884(7)	2349(9)	227(51)
O(2)	3189(8)	1888(5)	1140(6)	243(33)
C(44)	3072(12)	2331(8)	738(10)	292(52)
C(100)	3584(12)	1087(8)	4915(9)	276(130)
CL(11)	3401(3)	1197(2)	5734(3)	348(32)
CL(12)	4582(4)	1040(3)	4812(3)	575(45)
CL(13)	3217(4)	1614(3)	4461(3)	586(46)
C(200)	2901(13)	867(8)	9199(11)	392(146)
CL(21)	3107(4)	1267(3)	9840(3)	584(45)
CL(22)	2289(4)	1170(3)	8646(4)	702(50)
CL(23)	3764(4)	699(3)	8807(3)	609(46)

observed in two conformations; both conformations were included in the refinement, the one with occupation *p* and the other one with occupation 1 − *p*. *p* refined to a value close to 0.5. The C−C distances within the two disordered rings were constrained to a value of 1.38 Å. The $CHCl_3$ solvent molecule was found to be disordered, making it impossible to observe the C and H atoms of this molecule. The three Cl atoms were refined to a stereochemically unreasonable arrangement. H atoms were included and kept at calculated positions with the exception of the atoms on the two disordered half-populated phenyl rings and the six methyl H atoms, which were all omitted. An isotropic a.d.p. was refined for each H atom. Empirical absorption- and extinction correction[26]; computer programs are listed in ref.[27].

8b: Conditions as above: Refinement of anisotropic a.d.p.'s for all non-hydrogen atoms. All aliphatic and aromatic H atoms were included at calculated positions except methyl hydrogens which were included at observed positions; empirical absorption and extinction correction. H atoms were refined with isotropic a.d.p.'s and the corresponding C−H distances were restrained to stereochemically reasonable values.

12b: All H atoms were included at calculated positions, empirical absorption and extinctions were applied and P atoms were refined anisotropically.

12b · $NiCl_2$: Anisotropic refinement of Ni, Cl, P, and the two C atoms of the solvent molecules; all other atoms were refined with isotropic a.d.p.'s. Empirical absorption and extinction corrections were performed. H atoms were included at calculated positions, and only one isotropic a.d.p. was refined for each of them.

CAS Registry Numbers

1: 39092-65-4 / **2**: 39534-10-6 / **3**: 133360-72-2 / **4a**: 138155-63-2 / **4b**: 133360-73-3 / **4b** · 2 CH_3I: 138155-66-5 / **5a**: 138155-64-3 / **5b**:

133360-74-4 / **6**: 133360-75-5 / **7**: 138155-65-4 / **8a**: 133442-72-5 / **8a** · $CHCl_3$: 138284-46-5 / **8b**: 133360-70-0 / **8b** · $CHCl_3$: 138284-47-6 / **9**: 82265-47-2 / **10a**: 138155-67-6 / **10b**: 133360-76-6 / **11**: 133360-77-7 / **12b**: 13360-71-1 / **12b** · $NiCl_2$: 138180-93-5 / **12b** · $NiCl_2$ · 2 $CHCl_3$: 138180-94-6 / **12b** · $PdCl_2$: 138180-95-7 / **13a**: 138155-70-1 / **13b**: 138155-69-8 / **14**: 138155-68-7 / **15**: 138180-96-8 / **15** · $NiCl_2$: 138207-65-5 / **15** · $PdCl_2$: 138207-64-4 / $(CH_3)_2NH$: 124-40-3 / $(C_6H_5)_2PCl$: 1079-66-9 / *o*-phenylenebis(phenylphosphane): 38023-29-9 / ethylene oxide: 75-21-8 / trimethylene oxide: 503-30-0

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