Synthesis and Stereochemistry of Chiral Macrocycles Including a 1,2-Bis(phenylphosphanyl)benzene Unit

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The synthesis of the four 1,1'-binaphthyl-based macrocyclic bisphosphane ligands **6b–e** (racemic and optically active) and their square-planar *cis*-P_2-MCl_2 complexes (M = Ni, Pd) is reported. In three cases isomers could be isolated and identified. The absolute and relative stereochemistry of all ligands and complexes was established on the basis of their NMR and CD spectra and finally confirmed by X-ray structural determinations of selected ligands and complexes.

The synthesis of chiral macrocycles has become increasingly attractive to organic chemists for various reasons[1]. One interesting application is their use as chiral auxiliaries in asymmetric catalysis[2]. Although chiral bisphosphanes probably belong to the most frequently used ligands in asymmetric catalysis, so far there seem to be no reports on the use of macrocyclic bisphosphanes in catalytic reactions. Despite the publication of a limited number of papers dealing with the synthesis, geometry, and complexing ability of macrocycles including P atoms[3] and with the application of molecules with concave functionalites in asymmetric synthesis[4], no definite effort has been made to the best of our knowledge to design macrocyclic bisphosphane ligands to be used in asymmetric catalysis. The reasons may be manyfold; beyond their tedious access and difficulty in preparing and purifying air-sensitive compounds, appropriate structures must fulfill two necessary requirements. The chiral cycle generating a chiral sphere embraces the transition metal and has to be rigid enough to keep the metal in the center but sufficiently mobile to follow the necessary conformational changes during the catalytic reaction. It appeared quite clear from our and others previous work that a moderate conformational stability – allowing only tuned changes in geometry – will be a crucial feature and a necessary condition of a chiral macrocycle to work in asymmetric catalysis[5]:

With respect to our intended investigations dealing with a chirality transfer during catalytic reactions, it seemed desirable to get a more detailed understanding how and to what extent the intramolecular distances of complexing sites and asymmetric unit will effect the asymmetric induction. Therefore, a group of macrocyclic ligands were synthesized as model compounds consisting of a chiral biaryl and 1,2-bis(phenylphosphanyl)benzene [Ph–PR–(*o*-C_6H_4)–PR–Ph] as the complexing unit. These two were bound to each other by means of two $(CH_2)_n$ segments of varying length. 2,2'-Disubstituted 1,1'-binaphthyl has been chosen as the chiral moiety due to its easy access in optically pure form and its well-known chiral discrimination in numerous asymmetric stoichiometric[6] and catalytic[7] reactions. Obviously, the size of the ring and the binaphthyl-bisphosphane distance are not only a function of the "length" of the spacer, but probably, more important, a consequence of the conformation of the alkyl chain. The $(CH_2)_n$ segments may adopt a number of energy minima with increasing length. Thus, the conformative mobility of the macrocycle is raised in general. Moreover, conformational changes upon complexation of the ligand with transition metals are expected to be dramatical and should significantly influence the reactivity and stereoselectivity in a transition metal-catalyzed reaction. The present paper deals with the synthesis of model compounds, elucidation of their structure, and investigations of their conformational changes upon complexation.

Results and Discussion

Here we report on the synthesis of four chiral diphosphane macrocycles **6b–e**, prepared under high dilution conditions from Ph–PLi–(*o*-C_6H_4)–PLi–Ph and precursors **5b–e**. Compound **6a** has been prepared recently[8]. Because of three elements of chirality being present in the macrocycles the formation of three diastereomers must be expected (Figure 1). In three cases, **6c–e**, more than one stereoisomer could be isolated (see below).

With respect to their projected application to asymmetric catalysis all ligands and the corresponding Ni(II) and Pd(II) complexes of **6a–e** were also prepared in optically active form by starting from (*S*)-1,1'-binaphthyl-2,2'-diol. A com-

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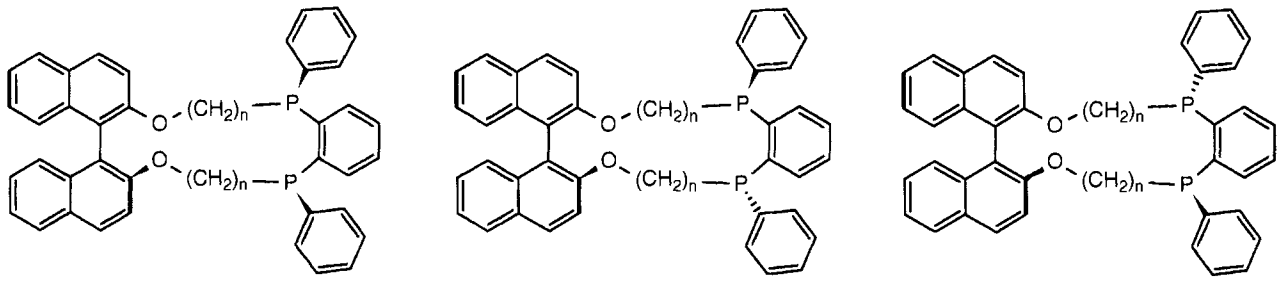


A *B* *C*

$(S)_a(S,R)_P$ $(S)_a(S,S)_P$ $(S)_a(R,R)_P$

Figure 1. Diastereomeric Ligands

parison of the CD spectra of ligands and complexes revealed their absolute and relative configurations and gave a first insight into their structures. These were compared with crystal structures obtained from selected ligands and Ni complexes (see below).

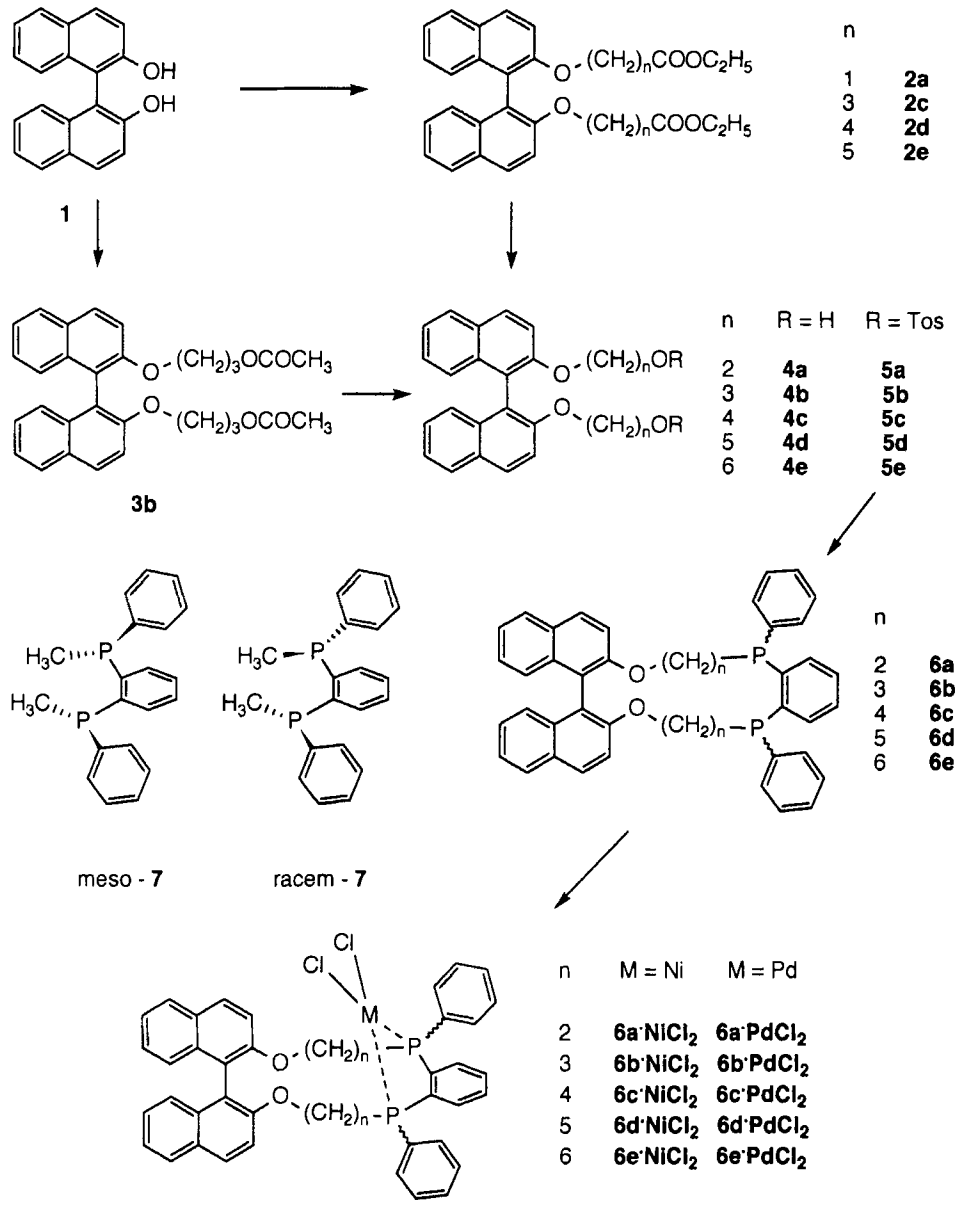
The preparation of the ditosylates **5** started from 1,1'-binaphthyl-2,2'-diol according to a procedure given by Cram's group[9], with the exception of **5b** which was accessible via the diacetate **3b**, because of exclusive formation of ethyl acrylate from ethyl 3-bromopropanoate under basic conditions. Ring closure of the dilithium bisphosphide with the ditosylates **5** under high-dilution conditions afforded the macrocycles **6** in moderate to good yield. In all cases the C_1-symmetrical diastereomer was formed predominantly (**6c–e**) or even exclusively (**6a**, **b**), a behavior which was observed in a similar case and explained by the more pronounced steric repulsions in the transition state leading to the C_2-symmetrical isomers[10]. The yield of *B*- and *C*-configurated cycles rose from zero (**6a**, **b**) to 11 and 6%, resp. (**6e**); this was at the expense of *A*, the yield of which dropped from 71% (**6a**) to 40% (**6e**). The total yield showed only a slight reduction to 57%. In the case of **6e** the distribution of *A*:(*B*+*C*) = 70:(19:11) proved to be unaffected by steric influences during the ring-closing step, as the same ratio, *meso*:*racem* = 70:30, was observed in the alkylation of 1,2-bis(phenylphosphanyl)benzene with *n*-butyl mesylate[10b]. It can be assumed that all diastereoisomers are configurational stable at room temperature as barriers of inversion of 29–31 kcal have been reported for diarylalkylphosphanes[11]. Nevertheless, thermal equilibrium can be reached by heating the mixture or a pure diastereomer, for instance of **6e**, neat in vacuo to 160°C for 30 min. Analysis of the melt by ^{31}P-NMR spectroscopy showed a ratio of *A*:*B*:*C* = 83:13:4 which was close to the product distribution under kinetic control. The separation of the isomers was conveniently achieved by column chromatography with degassed solvents, especially as the C_2-symmetrical compounds proved to be moderately air-sensitive.

The optically active Ni(II) complexes of all ligands and the Pd(II) complexes of C_1-symmetrical ligands were prepared by mixing **6a–e** with $NiCl_2 \cdot 6\ H_2O$ or $Pd(C_6H_5CN)_2Cl_2$, resp. in equimolar proportions in CH_2Cl_2/EtOH. The resulting crystalline precipitates proved to be neutral 1:1 complexes (see below) of poor solubility.

NMR Spectra: ^{1}H-, ^{13}C-, and ^{31}P-NMR spectra of all ligands and complexes were recorded. Especially the latter were helpful for distinguishing between configurations *A* or *B*, *C*. For ligands with configuration *A* only conformations with C_1 symmetry are possible, resulting in a non-equivalence of all atoms. Ligands with configurations *B* or *C* may adopt C_1-symmetrical conformations as well, but two and two of them at times can be combined to an averaged structure of C_2 symmetry. Hence, a fast conversion (on the NMR time scale) of conformers of *B* or *C* will result in a C_2-symmetrical spectrum. Thus, an A_2 system was found for the phosphorus atoms for *B* of **6c–e**, while AB systems were observed for all cycles with configuration *A*. It should be pointed out, however, that the non-equivalence of nuclei (C_1 symmetry) cannot be a proof of configuration *A*, but the appearance of C_2 symmetry in the NMR spectra is indicative of *B* or *C*. Not only the chromatographic behavior on TLC and a characteristic color reaction with $NiCl_2$ was found to be similar within homologs of the same configuration (*A*: yellow-orange, *B*, *C*: red-brown), but also the CD spectra of ligands and complexes showed typical shapes for each configuration (see below). Finally only a differentiation between *B* and *C* was necessary.

With respect to our interest in the conformative stability of the ligands and complexes, their NMR spectra were compared thorougly in order to observe changes due to alterations of their geometry, especially after complexation. The projected investigations were hampered by two serious problems. Especially the ^{13}C-NMR spectra suffered from the poor solubility of the complexes, and the splitting due to PC coupling reduced the sensitivity and made their assignment difficult. Besides, all 34 carbon signals are concentrated in a narrow shift range of about 40 ppm. Only in the case of **6a** a complete assignment of all proton and carbon signals was possible by two-dimensional methods so far[8].

As the ligand structures of configuration *A* are formed from a C_2-symmetrical biaryl and a C_s-symmetrical bisphosphane, the "overall symmetry" has to be C_1 and



may be understood as a mutual disturbance of "higher" symmetries of the subunits. This effect is expected to decrease with the distance, as a rough approximation with the length of the spacer. The expected trend was actually found, but the degree of mutual interference did not vanish completely with progressive length of the alkyl chain. It rather tends to take a limiting value as we observed small but distinct shift differences for all carbon atoms of the binaphthyl skeleton even with C_5 and – very similar – C_6 spacers. The same trend was found with Ni and Pd complexes; the shift differences due to a "persistent" non-equivalence of carbon signals is frequently about 1.5 ppm. This clearly demonstrates the essential possibility of transmitting asymmetric induction to a remote part of a molecule by means of a preferred conformation of the spacer. Although this effect may be small, as in the case of a simple alkyl chain with an only moderately pronounced energy minimum of an "*all-s-trans*" conformation, it obviously will be possible to design suitable spacer groups with enhanced rigidity.

Isomers *B* and *C* of the ligands **6c–e** show C_2 symmetry in all spectra (^1H, ^{13}C, ^{31}P). The corresponding Ni complexes exhibit NMR spectra of C_1 symmetry (**6c**, **d**) or C_2 symmetry (**6e**) at room temperature. Especially the ^1H-NMR spectra suffer from partial broadening of multiplets as a consequence of coalescence.

In the case of **6d***C* the situation was especially troublesome because signals due to a small amount of an unidentified by-product were observed (approx. 20%). While this did not interfere with the signals of the dominant species in the ^{13}C- and ^{31}P-NMR spectra, it unfortunately prevented an interpretation of the ^1H-NMR spectrum.

Generally this result was as expected and reflects the enhanced mobility with progressive chain length and the restriction of mobility by formation of a five-membered che-

late ring. A quantitative investigation of the internal mobility by variable-temperature NMR was found to be impracticable because of the poor solubility and the necessity to record the spectra in CD_2Cl_2.

^{31}P Shift Values: As mentioned above in the case of configuration *A* also the P-P shift differences tend to reach a limiting value of 0.3–1.5 with a center of the AB system near the value for *meso*-1,2-bis(butylphenylphosphanyl)-benzene ($\delta = -26.4$). The same trend was found for the complexes, although less pronounced. Contact shifts of $\Delta\delta = 82.4-86.0$ for Ni complexes and 90.3–93.9 for Pd complexes were observed. Ligands with configuration *B* or *C* showed deshielded P atoms with singlets between $\delta = -19.5$ and -21.9. Also the contact shift of Ni complexes decreased to $\Delta\delta = 71.1-78.9$. As we observed only moderate variations of shift values and coupling constants within homologous complexes, the geometry will be probably the same in all cases. Irrespective of coalescence phenomena all NMR spectra of complexes showed well resolved sharp signals which further supported the formation of neutral, square-planar, low-spin complexes.

Circular Dichroism of Ligands and Complexes: All CD spectra of the major diastereoisomers of ligands $(S)_a$-**6a–e** show a very similar shape with gradually decreasing Cotton effects. The same is true for the Ni and Pd complexes. Generally, the Ni complexes exhibit stronger, the Pd complexes weaker effects than the ligands (Figures 2a, 2b). Calculations of the CD of the binaphthyl unit revealed that a change of the biaryl torsion angle of only 10° would change the shape of the CD significantly[12]. From this we conclude that neither the length of the spacer nor complexation with a transition metal has a significant effect on the binaphthyl angle. As we recorded the spectra in CH_2Cl_2 only the long-wavelength branch of the exciton couplet at ≈230 nm (^1B_b) could be observed. This was positive for ligands **6b–e** and their complexes with configuration *A* (240 nm, $\Delta\varepsilon$ 240–330), indicating a cisoid biaryl conformation[13]. Only **6a** exhibited a weakly negative effect in this region (254 nm, $\Delta\varepsilon = -25$). NMR spectroscopy of the diastereomer under discussion showed C_1 symmetry; the chirality has to be $(S)_a(R,S)_P$ and the Ph–PR–(*o*-C_6H_4)–PR–Ph unit displays a "local" C_s symmetry (Figure 1). A chiral perturbation by the (*S*)-binaphthyl could only give rise to weak bands, partly hidden under the more intensive binaphthyl bands (280–340 nm). In the case of Ni complexes the chiral perturbation of the central band of the corresponding ligand field at about 455 nm manifests itself as a couplet which is most intense for **6a** · $NiCl_2$, very weak for **6b** · $NiCl_2$, and increasingly intense for **6c** · $NiCl_2$ to **6e** · $NiCl_2$ with a change of sign and a blue shift, while the short-wavelength range remains largely unchanged (Figure 2a). From this we conclude that a complexation results only in a more pronounced "out-of-center" torsion of the phosphorus lone pairs without significant change of the biaryl angle. A similar behavior was observed with a 7,7′-bridged 1,1′-binaphthyl and its Ni complex[5].

In the case of the "C_2-symmetrical ligands" *B* of **6c–e** a positive CD at 305 nm is superimposed on the four negative bands at 335, 322, 292, and 282 nm, resulting in generally weakened effects. The long-wavelength band of the ^1B_b transition remains still positive but with significantly lower intensity ($\Delta\varepsilon$ 180 for **6d**, 220 for **6e**). This behavior supports an opening of the biaryl angle toward the critical angle of 100–110° for which the couplet signals should vanish or, more likely, the progressive population of a conformer with a transoid binaphthyl unit[12,13]. From **6c–e**, Ni complexes could be obtained as well which all show a similar strong positive band, dominating the range of 260–310nm ($\Delta\varepsilon$ 40-50!). In the case of **6d,e** small amounts of the third diastereomeric ligand (also with "averaged" C_2 symmetry in ^{31}P-NMR spectroscopy) could be isolated and these both were also converted to the corresponding Ni complexes. Comparison of the CD spectra of the diastereomeric C_2-symmetrical Ni complexes (Figures 3, 4) showed a largely mirror-like shape, with the exception of the couplet at ≈230 nm which was positive for all ligands but negative or significantly diminished for complexes [for example for *B*: λ ($\Delta\varepsilon$) **6c** · $NiCl_2$: 234 (−313), 245 (5); **6d** · $NiCl_2$: 233 (−119), 250 (−99); **6e** · $NiCl_2$: 231 (−165)]. In these cases transoid biaryl conformations with angles >110° seem a reasonable approximation. We assume that these two groups of complexes, *B* and *C*, differ in their chiral environment of the Ni atom, obviously caused by reversed chiralities at P atoms. All Ni complexes of the same configuration effect a similar degree of "expansion" of the macrocycle, which in turn causes an opening of the biaryl angle.

As we were interested in the sole effect of the chiral bisphosphane part on the CD of the ligands we prepared 1,2-bis(methylphenylphosphanyl)benzene (**7**)[14] as a model compound.

1,2-$[Me(Ph)P]_2C_6H_4$ **7**

Compound **7** was accessible by reaction of the dilithio salt of 1,2-bis(phenylphosphanyl)benzene with an excess of methyl iodide[10b]. Purification was achived by bulb-to-bulb distillation and afforded a mixture of *meso*- and *racem*-**7** (NMR). As a stereochemical correlation by optical comparison was intended, only small samples of the optically active ligands and their Ni complexes had to be prepared. Because of this an enantioselective chromatography on microcrystalline cellulose triacetate was found to be the most convenient way to separate diastereoisomers and enantiomers in a single step. Applying a continuous cyclic technique[15] we obtained highly enriched fractions of (*S,S*)-**7** and (*R,R*)-**7** with a 20-mg sample. The first fraction was partly contaminated with *meso*-**7**, which could not be removed completely. Further cycles to improve the chemical and optical purity were unsuccessful, because of a gradual decomposition, which becomes a progressively dominating effect with further cycles. The identity of the fractions was confirmed by ^1H-NMR spectroscopy. Fraction 1 contained *meso*-**7**, fractions 2 and 3 the enantiomers of *dl*-**7** (Figure 5a). Fraction 2 showed a negative, fraction 3 a positive optical rotation (589 nm). This corresponds to (*S,S*)-**7** in fraction 2 and (*R,R*)-**7** in fraction 3[14]. Both fractions were evaporated to dryness. The residues were dissolved in 2ml

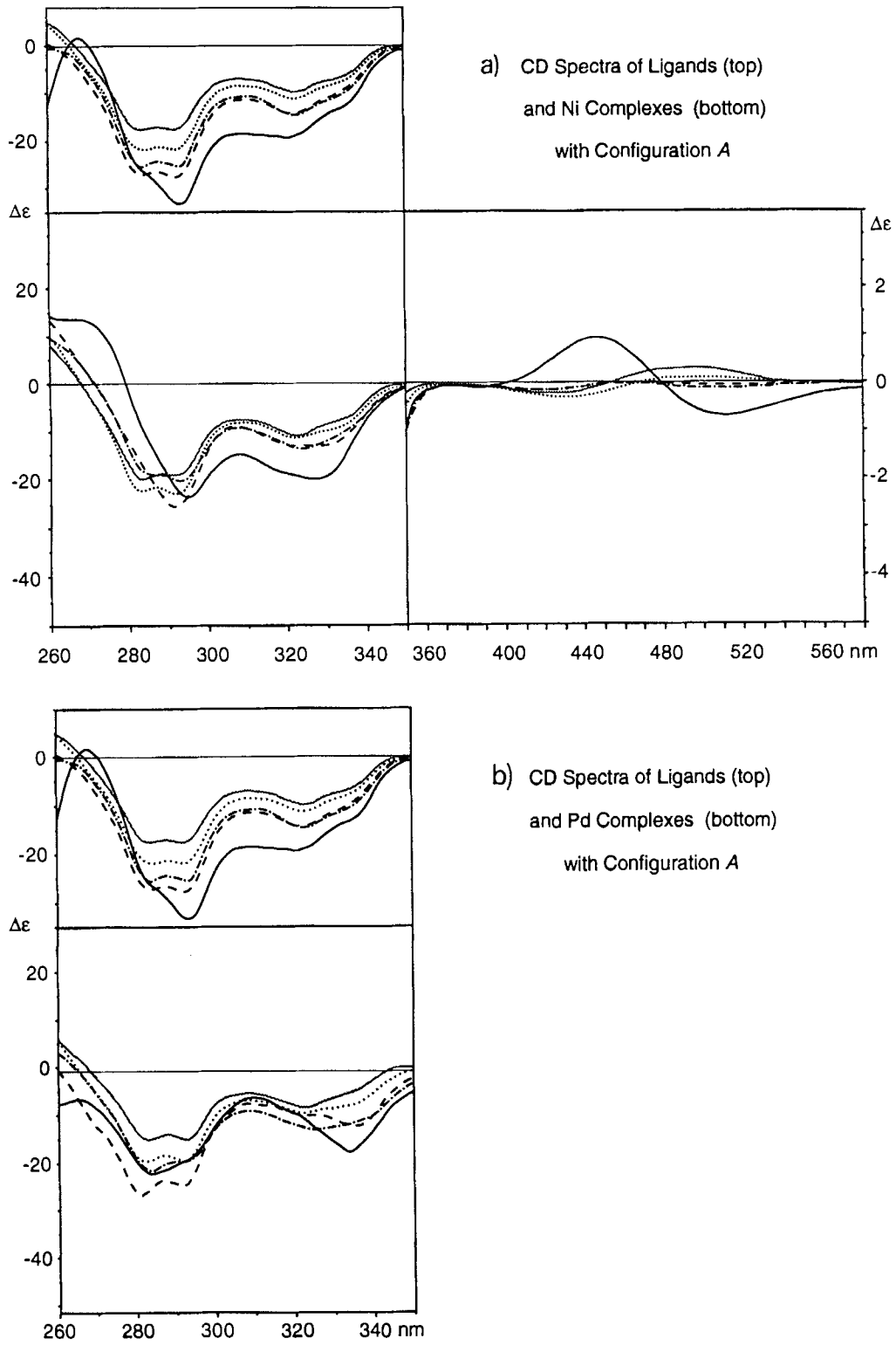


Figure 2. CD spectra of ligands **6** and their metal complexes. **6a** (−), **6b** (---), **6c** (−·−·−), **6d** (·····), **6e** (~~)

of CH_2Cl_2 and a few drops of an ethanolic $NiCl_2$ solution was added, resulting in an immediate color change to orange. CD spectra were taken, evidencing their enantiomeric relationship. The shape of the long-wavelength region of the CD spectrum of the Ni complexes of (*S,S*)-**7** and of one C_2-symmetrical ligand of **6d** are presented in Figure 5b.

Although the spectra are not perfectly congruent, the similarity in shape strongly points to a $(S,S)_P$ configuration of the major C_2-symmetrical isomer of **6d** (configuration *B*) and vice versa $(R,R)_P$ configuration of the minor isomer (configuration *C*). This assignment was finally confirmed by an X-ray structural analysis (see below). Together with

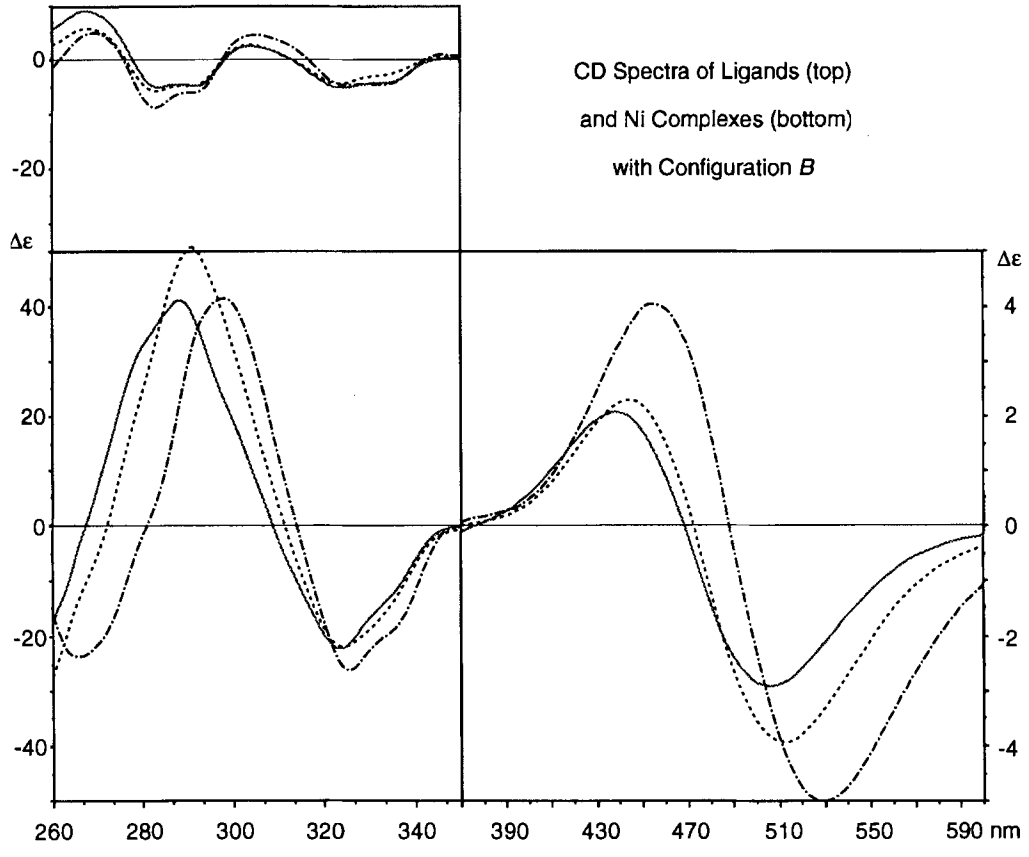


Figure 3. CD spectra of ligands **6** and their metal complexes. **6c** (–·–·–), **6d** (·····), **6e** (~~)

the knowledge of the relative configuration of one of the C_2-symmetrical ligands of **6c**, we could assign all relative (and absolute) chiralities: Assuming the synthesis starts with (*S*)-binaphthol, the predominantly formed diastereomer *A* has the configuration $(S)_a(S,R)_P$, in three cases a smaller amount of the diastereomer *B* with configuration $(S)_a(S,S)_P$, and only traces of the third diastereomer *C* (of **6d**, **e**) with configuration $(S)_a(R,R)_P$ were formed. The absolute chiralities shown in Figure 1 correspond to the CD spectra in Figures 2–4.

Crystal Structure Analyses[16]: As a confirmation of the configurational assignment established above and in order to find out potentional structures suitable for ligands in asymmetric catalysis, crystal structure analyses of two ligands and three Ni complexes were carried out (Figure 6).

As the cycles with a longer alkyl chain $[(CH_2)_{n=4-6}]$ have a considerable degree of conformational freedom and moreover seemed to be the more promising candidates for their use in catalysis, their crystal structures were investigated. Unfortunately, most ligands and some complexes of interest could not be obtained in crystalline form or formed thin needles or feather-like crystals. Especially ligands and complexes of configuration *A* did not afford appropriate single crystals with one exception. Therefore, only in five cases – **6c***B*, **6d** · $NiCl_2$*B*, **6e** · $NiCl_2$*A*, **6e***B*, and **6e** · $NiCl_2$*B* – an X-ray structural determination was successful. A stereoscopic representation of all structures is given in Figure 6. Selected structural data are listed in Table 1, and for experimental details see Table 3

The stereochemistry of all structures was in agreement with the previous configurational assignment on the basis of NMR and CD spectroscopy. Moreover, a definite decision between the two C_2-symmetrical configurations *B* and *C* could be made. The predominantly formed isomer of (*S*)-**6d** has configuration $(S,S)_P$ as was evident from its Ni(II) complex (Figure 6), thus confirming the result of the optical comparison of CD spectra. All Ni complexes showed the expected square-planar array of low-spin complexes with typical Cl–Ni and P–Ni distances. Deviations of bond angles from 90° were as found for similar structures (P–Ni–P 88.4–88.9°, Cl–Ni–Cl 94.1–96.2°).

While **6c***B* showed the desired conformation with (generally) center-directed phosphorus lone pairs, an out-of-center torsion of the lone pairs was observed in **6e***B*, resulting in a roughly perpendicular arrangement of the plane of the *o*-phenylene unit relative to the macrocycle. This effect is still more pronounced in the corresponding Ni complex which shows the $NiCl_2$ portion twisted outside the cycle and the biaryl angle opening from 71.7 to 112.2°. In contrast, the C_1-symmetrical structure of **6e** · $NiCl_2$*A* shows a less strained perimeter with a cisoid binaphthyl conformation and seven from fourteen torsional angles of the alkyl chain near 180°. The square-planar Ni complex unit, although not located inside the cycle, is orientated toward

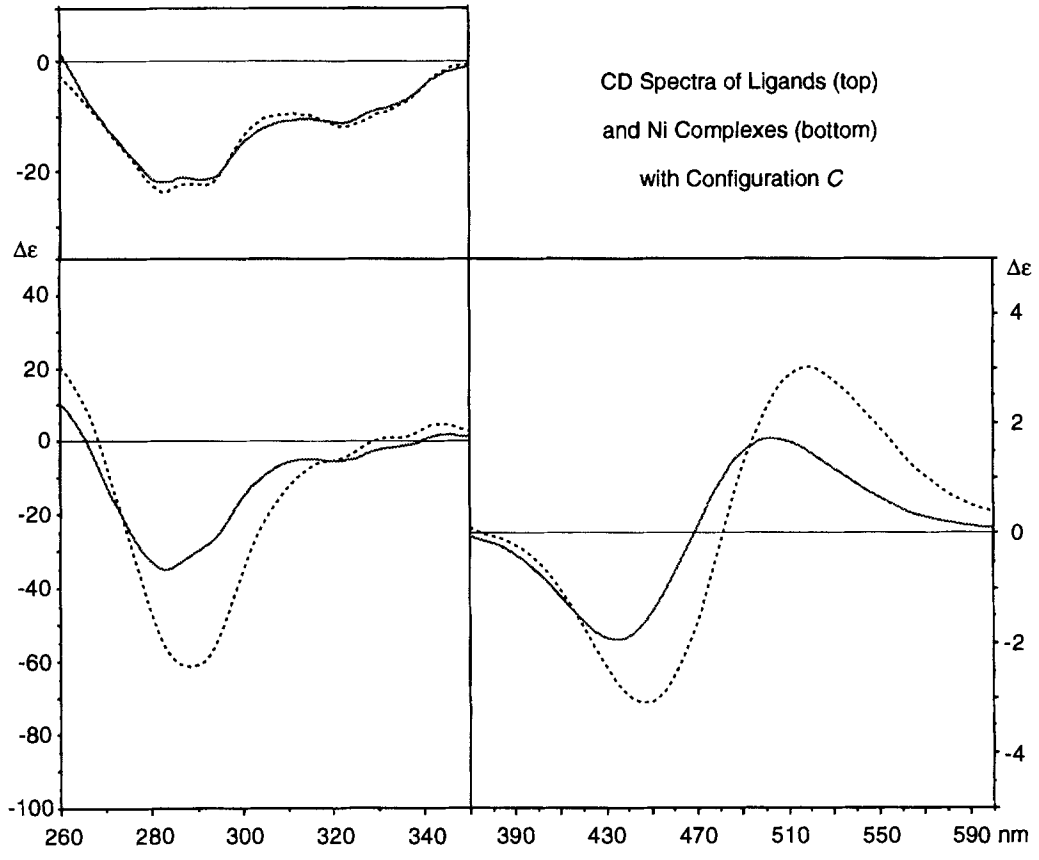


Figure 4. CD spectra of ligands **6** and their metal complexes. **6d** (·····), **6e** (~~)

the binaphthyl moiety. In contrast, the differences found between **6d** · $NiCl_2B$ and **6e** · $NiCl_2B$ are neglegible. In both cases a complete turning away of the transition metal from the chiral binaphthyl is observed, thus making these complexes less suitable for asymmetric catalysis. Additional evidence for ring strain can be found in a bending of the binaphthyl part, expressed as a deviation of C14–C11–C61–C64 from a straight line. The origin may be twofold; besides ring strain steric repulsion of substituents at C19 and C69 ("peri effect") and C12 and C62 will also contribute to a distortion of the binaphthyl moiety. The crystal structure of 2,2′-dimethoxy-1,1′-binaphthyl, a "non-bridged" analog, suitable for comparison, was found in the Cambridge crystallographic data base showing angles C14–C11–C61 and C11–C61–C64 of only −1.7°. Therefore, we assume that the "excess deformation" of up to −7.6° is caused by a pronounced ring strain in Ni complexes of configuration *B*. On the other hand, the number of torsional angles in alkyl spacers which differ from 180° may also be regarded as a qualitative criterion for the inner energy (see Figure 5, **6e** · $NiCl_2A$).

Conclusions

Five chiral macrocyclic bisphosphanes **6a–e** could be synthesized under high dilution conditions. The stereoisomers formed were separated and characterized by spectroscopic methods, revealing the predominance of the isomer *A* (Figure 1) in all cases. All of them formed air-stable crystalline Ni(II) and Pd(II) complexes in good to excellent yield. From two ligands and three Ni complexes crystal structures could be obtained. Although conclusions drawn from this limited number of structures must be considered with care, some features seem to be of generality. C_1-symmetrical compounds show less steric strain than compounds with C_2 symmetry. Enhanced strain causes an opening of the biaryl angle from the cisoid (60–75°) to the transoid form (100–115°) and an out-of-center twist of the phosphorus lone pairs or the Cl_2–Ni–P_2 portion of the molecule. (The latter as a consequence of the reduced conformational mobility after chelation and the repulsion of chlorine atoms.) In turn, this conformation is especially easily adopted, as a flattening of the binanphthyl angle causes an expansion of the macrocycle. This gives enough space for one phenyl ring and the P–Ph–P fragment to be tolerated "inside" the cycle. Presently, we have no proof of a (partially free) rotation of the bisphosphanyl fragment, but an enhanced mobility of the species is evident (see NMR spectra).

Molecular mechanics calculations and a conformational study using two-dimensional NMR methods are planned to gain information about the preferred conformation(s) in solution.

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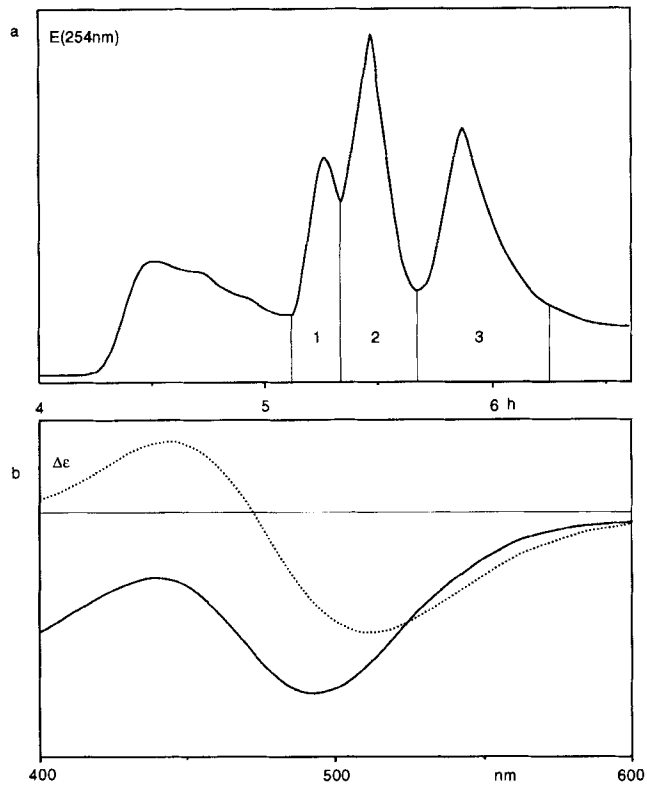


Figure 5a. Chromatogram of a mixture of stereoisomers of **7** on microcrystaline cellulose triacetate (ethanol, 98%, room temp., 15–25 µm, column 29 × 2.5 cm, 3 cycles[15]), fraction 1: *meso*-**7**, fraction 2: (*S,S*)-**7**, fraction 3: (*R,R*)-**7**

Figure 5b. Optical comparison of CD spectra of (−)(*S*)a-**6d** · $NiCl_2$ (configuration *B*) (·····) with (*S,S*)-**7** (−)

Experimental

NMR: Bruker AC-250 F or AM 400 WB. Solvent $CDCl_3$ except for **6b–e** and Ni and Pd complexes where CD_2Cl_2 was used. Internal standards: tetramethylsilane [^1H, ^{13}C (Table 2)] and 85% H_3PO_4 (^{31}P); ^{31}P-NMR spectra were recorded in a proton-decoupled mode. – MS: Varian MAT-CH7. – High-resolution MS (HRMS): "Preselected peak matching method", where the M^+ peak was found to be in agreement with the calculated mol mass for an isotopically pure compound (error ≤2 ppm). – Optical rotation: Perkin-Elmer polarimeter 241 (1-dm cell, thermostated). – CD spectra: Jobin Yvonne dichrographe CD 6 (at 20°C; l = 0.1, 1 cm; CH_2Cl_2, $c = 10^{-4}-10^{-5}$ mol l^{-1}). – Melting points: Kofler melting point apparatus, uncorrected. – Elementary analyses[17]: Mikroanalytisches Laboratorium der Universität Wien (Mag. *J. Theiner*). – EE = Ethyl acetate.

Tosyl chloride was recrystallized from petroleum ether (PE). Pyridine was filtered over alumina (Activity I) and stored over molecular sieves (4 Å). Tetrahydrofuran and diethyl ether were distilled from $LiAlH_4$. All other chemicals were of analytical grade and used without further purification. Thin-layer chromatography (TLC) was performed on TLC aluminum sheets, silica gel 60 F254 precoated (0.2 mm, Merck 5554) and precoated TLC plates, silica gel 60 F254 (0.25 mm, Merck 5715).

1,2-Bis(phenylphosphanyl)benzene was prepared in three steps by starting from 1-bromo-2-chlorobenzene and dichlorophenylphosphane according to literature procedures[18]. The preparation of racemic **6a**, **6a** · $NiCl_2$, and **6a** · $PdCl_2$ has been published recently[8].

Dicarboxylates **2c–e** *and 2,2'-Bis(3-acetoxypropoxy)-1,1'-binaphthyl* (**3b**). – *General Procedure:* 5.72 g (20 mmol) of 1,1'-binaphthyl-2,2'-diol (**1**) was dissolved in 200 ml of dry THF. Then 4.60 g (41 mmol) of potassium *tert*-butylate was added to the solution, and the stirred mixture was heated to reflux under argon for a few min to ensure complete conversion to the dipotassium salt. The slurry containing a cream-colored precipitate was cooled to room temp., and 41 mmol of the correspoding ω-bromoalkanecarboxylate or 1-acetoxy-3-bromopropane, resp., was introduced by a syringe. The reaction mixture was refluxed for 20–24 h. Precipitated KBr was separated and washed with CH_2Cl_2. The filtrate was concentrated, and the residue was dissolved in 200 ml of CH_2Cl_2. The solution was washed with water, brine, and dried with Na_2SO_4. Removal of the solvent in vacuo afforded the crude diester as an oil, which was further purified by column chromatography on SiO_2 [column 40 × 4 cm, ethyl acetate (EE)/PE (15:85 to 30:70)] to give the ester **2** as a viscous colorless or pale yellow oil or a crystalline solid.

2c: 7.20 g (70%), oil. – ^1H NMR: δ = 1.17 (6H, t, J = 7 Hz), 1.71 (4H, m), 1.86 (4H, m), 3.97 (4H, m), 3.99 (4H, q, J = 7 Hz), 7.14 (2H, br. d, J = 8 Hz), ca. 7.20 (2H, ddd, J = 8/7/1.5 Hz), 7.31 (2H, ddd, J = 7/8/1.5 Hz), 7.40 (2H, d, J = 9 Hz), 7.85 (2H, d, J = 8 Hz), 7.93 (2H, d, J = 9 Hz). – MS (150°C), *m/z* (%): 514 (11), 428 (1), 400 (7), 355 (1), 286 (20), 268 (9), 239 (16), 115 (100). – HRMS: $C_{32}H_{34}O_6$: calcd. 514.2355, found 514.2351.

2d: 7.70 g (71%), oil. – ^1H NMR: δ = 1.19 (6H, t, J = 7 Hz), 1.25 (4H, m), 1.42 (4H, m), 1.92 (4H, t, J = 7 Hz), 3.94 (4H, m), 4.03 (4H, q, J = 7 Hz), 7.14 (2H, br. d, J = 8 Hz), 7.19 (2H, ddd, J = 8/7/1.5 Hz), 7.29 (2H, ddd, J = 7/8/1.5 Hz), 7.38 (2H, d, J = 9 Hz), 7.83 (2H, d, J = 8 Hz), 7.91 (2H, d, J = 9 Hz). – MS (200°C), *m/z* (%): 542 (10), 414 (1), 286 (21), 282 (10), 268 (10), 257 (8), 239 (13), 129 (100). – HRMS: $C_{34}H_{38}O_6$: calcd. 542.2668, found 542.2671.

2e: 7.87 g (69%), m.p. 48–53°C. – ^1H NMR: δ = 0.85 (4H, m), 1.23 (6H, t, J = 7 Hz), 1.26 (4H, m), 1.38 (4H, m), 1.94 (4H, m), 3.93 (4H, m), 4.08 (4H, q, J = 7 Hz), 7.15 (2H, dd, J = 8.3/1 Hz), 7.19 (2H, ddd, J = 8/7/1.5 Hz), 7.30 (2H, ddd, J = 7/8/1.5 Hz), 7.39 (2H, d, J = 9 Hz), 7.84 (2H, d, J = 8 Hz), 7.92 (2H, d, J = 9 Hz). – MS (200°C), *m/z* (%): 570 (64), 525 (2), 428 (5), 383 (2), 286 (24), 268 (7), 257 (4), 239 (5), 143 (100). – HRMS: $C_{36}H_{42}O_6$: calcd. 570.2981, found 570.2988.

3b: 7.29 g (75%), m.p. 58–67°C. – ^1H NMR: δ = 1.71 (4H, quintd, J = 6.4/1.7 Hz), 1.89 (6H, s); 3.64 (4H, m), 4.02 (4H, m), 7.13 (2H, br. d, J = 8.2 Hz), ca. 7.19 (2H, m), ca. 7.31 (2H, m), 7.40 (2H, d, J = 9 Hz), 7.85 (2H, d, J = 7.8 Hz), 7.94 (2H, d, J = 9 Hz). – MS (150°C), *m/z* (%): 486 (17), 386 (2), 286 (3), 268 (8), 255 (3), 239 (10), 228 (4), 215 (1), 202 (1), 133 (6), 101 (100). – HRMS: $C_{30}H_{30}O_6$: calcd. 486.2042, found 486.2051.

2,2'-Bis(3-hydroxypropoxy)-1,1'-binaphthyl (**4b**): 7.0 g (14.4 mmol) of **3b** was stirred in a diluted KOH solution (5 g KOH, 50 ml EtOH, 50 ml water) for 45 min at room temp. The bulk of EtOH was removed in water aspirator vacuo, and the residue was treated with 200 ml of water. The mixture was extracted with CH_2Cl_2 (3 × 100 ml), and the organic extracts were washed neutral and dried with Na_2SO_4. Evaporation of the solvent yielded crude **4b** as a yellow oil which was subjected to column chromatography on SiO_2 (column 30 × 4 cm, EE) to give 4.81 g (83%) of **4b**, m.p. 92–96°C. – ^1H NMR: δ = 1.65 (4H, m), 2.05 (2H, br. s), 3.27 (4H, m), 4.18/4.06 (2 × 2H, m), 7.12 (2H, br. d, J = 8 Hz), 7.22 (2H, ddd, J = 8/7/1.5 Hz), 7.33 (2H, ddd, J = 7/8/1.5 Hz), 7.44 (2H, d, J = 9 Hz), 7.87 (2H, d, J = 8 Hz), 7.97 (2H, d, J = 9 Hz). – MS (120°C), *m/z* (%): 402 (100), 344 (44), 327 (2), 299 (3), 286 (94), 268 (30), 239 (30). – HRMS: $C_{26}H_{26}O_4$: calcd. 402.1831, found 402.1826.

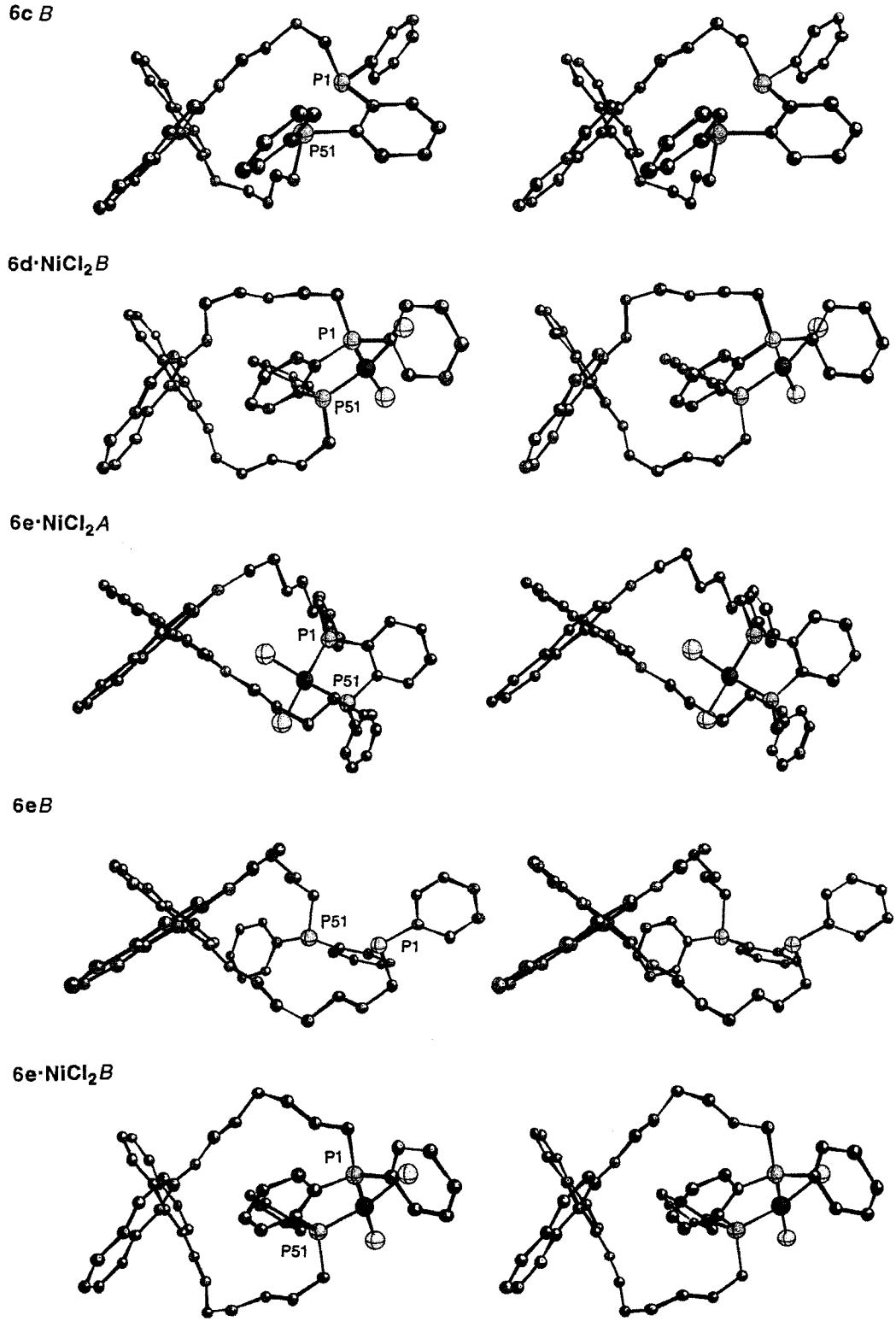
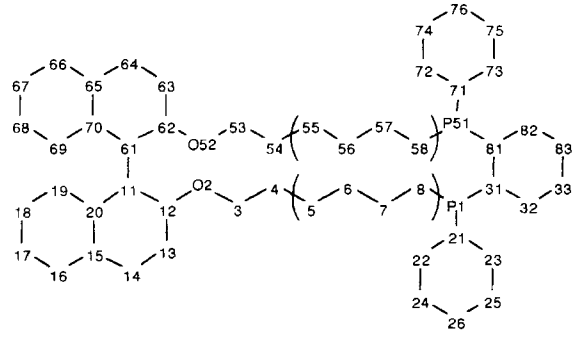


Figure 6. Crystal structures of **6c***B*, **6d** · $NiCl_2$*B*, **6e** · $NiCl_2$*A*, **6e***B*, and **6e** · $NiCl_2$*B*. To facilitate visual comparison, (*S*)a configurations have been drawn in all cases; H atoms are omitted

Diols **4c–e**. – *General Procedure:* 15 mmol of the diester **2** in 50 ml of anhydrous ether was added dropwise to an ice-cooled suspension of 2.0 g (53 mmol) of $LiAlH_4$ in 200 ml of ether with stirring. Stirring was continued for 20 h at room temp., and the reaction was quenched by careful addition of 20 ml of water, followed by 50 ml of 6 N HCl (ice bath). The organic layer was separated, and the aqueous one was extracted with two 50-ml portions of ether. The combined organic extracts were washed successively with a saturated $NaHCO_3$ solution and water, then dried with Na_2SO_4. Removal of the solvent afforded the crude diol, which was chromatographed on SiO_2 (column 30 × 4 cm, EE) to give **4** as a crystalline solid.

Table 1. Selected data from crystal structure analyses. Bond distances in Å



General labeling scheme for crystal structures

	6c*B*	6d·$NiCl_2$*B*	6e·$NiCl_2$*A*	6e*B*	6e·$NiCl_2$*B*
biaryl angle	101.9°	112.6°	73.4°	71.7°	112.2°
14-11-61[a]	-1.6°	-5.7°	-2.7°	-2.8°	-6.8°
11-61-64[a]	-2.0°	-4.2°	-1.9°	-1.4°	-4.2°
P1-31-81-P51	-10.3°	10.2°	-6.1°	-7.5°	6.4°
P1-Ni-P51	-	88.4°	88.9°	-	88.5°
ClA-Ni-ClB	-	94.3°	96.2°	-	94.1°
P1-P51	3.172(3)	2.957(8)	3.004(3)	3.196(4)	2.962(2)
P1-Ni	-	2.111(7)	2.140(2)	-	2.119(2)
P51-Ni	-	2.132(7)	2.149(2)	-	2.127(2)
ClA-Ni	-	2.177(7)	2.204(2)	-	2.185(2)
ClB-Ni	-	2.185(6)	2.188(2)	-	2.182(2)

[a] Deviation from 180°.

4c: 5.29 g (82%), m.p. 99–103°C. – ^{1}H NMR: δ = 1.18 (4H, m), 1.48 (4H, m), 1.87 (2H, br. s), 3.19 (4H, m), 3.92/4.06 (2 × 2H, m), 7.15 (2H, br. d, *J* = 8 Hz), 7.22 (2H, pt, *J* = ca. 7 Hz), 7.32 (2H, pt, *J* = ca. 7 Hz), 7.41 (2H, d, *J* = 9 Hz), 7.87 (2H, d, *J* = 8 Hz), 7.94 (2H, d, *J* = 9 Hz). – MS (150°C), *m/z* (%): 430 (36), 358 (9), 343 (5), 286 (100), 268 (16), 257 (13), 239 (24). – HRMS: $C_{28}H_{30}O_4$: calcd. 430.2144, found 430.2142.

4d: 5.43 g, (79%), m.p. 93–94°C. – ^{1}H NMR: δ = 0.90 (4H, m), 1.17 (4H, m), 1.31 (2H, br. s), 1.41 (4H, m), 3.26 (4H, m), 3.88/4.01 (2 × 2H, m), 7.15 (2H, br. d, *J* = 8 Hz), 7.20 (2H, ddd, *J* = 8/7/1.5 Hz), 7.31 (2H, ddd, *J* = 7/8/1.5 Hz), 7.41 (2H, d, *J* = 9 Hz), 7.86 (2H, d, *J* = 8 Hz), 7.93 (2H, d, *J* = 9 Hz). – MS (170°C), *m/z* (%): 458 (36), 372 (16), 286 (100), 268 (14), 257 (13), 239 (16). – HRMS: $C_{30}H_{34}O_4$: calcd. 458.2457, found 458.2456.

4e: 4.96 g (68%), m.p. 73–74°C. – ^{1}H NMR: δ = 0.96 (8H, m), 1.25 (4H, m), 1.39 (4H, m), 1.77 (2H, br. s), 3.40 (4H, t, *J* = 7 Hz), 3.92 (4H, m), 7.15 (2H, m), 7.19 (2H, m), 7.30 (2H, ddd, *J* = 7/8/1.9 Hz), 7.39 (2H, d, *J* = 9 Hz), 7.84 (2H, d, *J* = 8 Hz), 7.91 (2H, d, *J* = 9 Hz). – MS (230°C), *m/z* (%): 486 (99), 386 (18), 286 (100), 268 (12), 257 (10), 239 (9). – HRMS: $C_{32}H_{38}O_4$: calcd. 486.2770, found 486.2777.

Ditosylates **5b–e**. – *General Procedure:* 9.15 g (4 equiv.) of *p*-tosyl chloride was added to a solution of 12 mmol of **4** in 30 ml of dry pyridine. The mixture was kept in a tightly stoppered flask in a refrigerator (2°C) for 24 h. It was then poured into 200 ml of ice-cold water and extracted with CH_2Cl_2 (3 × 100 ml). The combined extracts were successively washed with 50 ml of 6 N HCl and water (2 × 100 ml) and subsequently dried with Na_2SO_4. Removal of the solvent at room temp. in vacuo gave a crude mixture of mono- and ditosylated product which was separated by column chromatography on SiO_2 (column 40 × 4 cm, $CHCl_3$) to afford the ditosylate **5** and small amounts of the corresponding monotosylate.

5b: 4.35 g (51%), oil. – ^{1}H NMR: δ = 1.73 (4H, m), 2.45 (6H, s), 3.64 (4H, m), 3.98 (4H, m), 7.11 (2H, br. d, *J* = 8.5 Hz), 7.22 (2H, ddd, *J* = 8/7/1.5 Hz), 7.27 (4H, d, *J* = 8.5 Hz), 7.35 (2H, d, *J* = 9 Hz), 7.35 (2H, m), 7.63 (4H, d, *J* = 8.5 Hz), 7.88 (2H, d, *J* = 8 Hz), 7.95 (2H, d, *J* = 9 Hz). – MS (250°C), *m/z* (%): 710 (19), 537 (1), 326 (3), 268 (13), 239 (8), 213 (85). – HRMS: $C_{40}H_{38}O_8S_2$: calcd. 710.2008, found 710.2021.

5c: 2.92 g (33%), oil. – ^{1}H NMR: δ = 1.09 (4H, m), 1.39 (4H, m), 2.43 (6H, s), 3.53 (4H, m), 3.78/3.92 (2 × 2H, m), 7.09 (2H, br. d, *J* = 8.5 Hz), 7.17 (2H, ddd, *J* = 8/7/1.5 Hz), 7.28 (2H, m), 7.29 (4H, d, *J* = 8.5 Hz), 7.31 (2H, d, *J* = 9 Hz), 7.67 (4H, d, *J* = 8.5 Hz), 7.81 (2H, d, *J* = 8 Hz), 7.89 (2H, d, *J* = 9 Hz). – MS (300°C), *m/z* (%): 738 (53), 605 (2), 567 (25), 513 (8), 469 (28), 467 (44), 376 (17), 340 (10), 286 (68). – HRMS: $C_{42}H_{42}O_8S_2$: calcd. 738.2321, found 738.2317.

5d: 4.87 g (53%), oil. – ^{1}H NMR: δ = 0.83 (4H, m), 1.17 (4H, m), 1.32 (4H, m), 2.44 (6H, s), 3.59 (4H, m), 3.83/3.93 (2 × 2H, m), 7.10 (2H, br. d, *J* = 8.5 Hz), 7.15 (2H, ddd, *J* = 8/7/1.5 Hz), 7.26 (2H, m), 7.34 (4H, d, *J* = 8.5 Hz), 7.35 (2H, d, *J* = 9 Hz), 7.74 (4H, d, *J* = 8.5 Hz), 7.80 (2H, d, *J* = 8 Hz), 7.88 (2H, d, *J* = 9 Hz). – MS (290°C), *m/z* (%): 766 (2), 594 (17), 526 (8), 422 (7), 354 (8), 353 (8), 286 (65). – HRMS: $C_{44}H_{46}O_8S_2$: calcd. 766.2634, found 766.2626.

5e: 7.53 g (79%), oil. – ^{1}H NMR: δ = 0.74 (4H, m), 0.89 (4H, m), 1.18–1.38 (8H, m), 2.43 (6H, s), 3.80 (4H, m), 3.81/3.93 (2 × 2H, m), 7.11 (2H, br. d, *J* = 8.5 Hz), 7.16 (2H, ddd, *J* = 8/7/1.5 Hz), 7.27 (2H, ddd, *J* = 7/8/1.9 Hz), 7.36 (2H, d, *J* = 9 Hz), 7.75 (4H, d, *J* = 8.5 Hz), 7.81 (2H, d, *J* = 8 Hz), 7.89 (2H, d, *J* = 9 Hz). – MS (300°C), *m/z* (%): 795 (1), 794 (4), 659 (17), 622 (2), 570 (11), 540 (4), 523 (14), 487 (10), 454 (5), 440 (2), 405 (15), 286 (100), 268 (20), 239 (9). – HRMS: $C_{46}H_{50}O_8S_2$: calcd. 794.2947, found 794.2936.

Preparation of Macrocycles **6b–e**. – *General Procedure:* All operations were carried out under dry argon, and all solvents were degassed prior to use. Solutions of 1.0 mmol of the ditosylate **5** in 10 ml of THF and 1.2 mmol of the dilithium salt of 1,2-bis(phenylphosphanyl)benzene [prepared from 353 mg of 1,2-bis(phenylphosphanyl)benzene and 1.52 ml of a 1.6 molar *n*BuLi solution in hexane] in 8.5 ml of the same solvent were prepared in Schlenk tubes. These solutions were added synchronously under high-dilution conditions to 120 ml of boiling THF during 1 h. The correct drop rate could be easily adjusted as a significant color change to orange occurred when a slight excess of unreacted dilithium salt was present in the reaction vessel. The solvent was distilled off, and the residue was partitioned between 200 ml of CH_2Cl_2 and 100 ml of water. The mixture was filtered over Celite, separated, and the organic layer was dried with Na_2SO_4. Removal of the solvent yielded the crude mixture (of diastereomers) as a pale yellow foam. In all cases, column chromatography on SiO_2 (60 × 2 cm) was necessary to separate the diastereomers. Elution with a degassed mixture of CH_2Cl_2/PE (1:1) afforded diastereomer *B*, followed by *C* and finally *A*, which showed a pronounced tailing. All compounds are white to cream-colored crystalline solids or foams. *B* and probably *C* proved to be moderately air-sensitive in solution, while *A* was found to be completely stable.

12,13,14,15,20,21,22,23-Octahydro-15,20-diphenylbenzo[f]dinaphtho[2,1-m:1',2'-o][1,12,5,8]dioxadiphosphacyclohexadecine (**6b**): 449 mg (68%). – ^{1}H NMR: δ = 1.60–1.93 (4H, m), 2.06 (4H, m), 3.79 (2H, m), 4.14 (1H, m), 4.54 (1H, m), 7.05–7.42 (21H, m), 7.58 (1H, d, *J* = 9.1 Hz), 7.83 (1H, d, *J* = 9.1 Hz), 7.86 (1H, d, *J* = 8.2 Hz), 7.92 (1H, d, *J* = 8.1 Hz), 8.03 (1H, d, *J* = 9 Hz). – ^{31}P NMR: δ = –27.12 (d, *J* = 154 Hz), –30.83 (d, *J* = 154 Hz). – MS (290°C), *m/z* (%): 660 (49), 619 (5), 601 (2), 583 (5), 541 (1), 496 (1), 450 (1), 393 (2), 367 (4), 349 (8), 333 (53), 319 (20), 306 (91). – HRMS: calcd. 660.2347, found 660.2357. –

Table 2. ^{13}C-NMR data of ligands **6b–e** and their Ni(II) and Pd(II) Complexes. Spectra are recorded in a *J*-modulated mode; signals are assigned as C for quaternary carbon; CH signals remain undesigned, *J* refers to PC coupling constants. In spectral areas with extensive signal overlapping multiplets could not be identified; these signals of unclear relationship are underlined, ignoring probable multiplet structures

	δCH_2	δC_{ar}
6b*A*	23.57 (dd, *J* = 16, 4 Hz); 24.00 (dd, *J* = 14, 8 Hz); 26.32 (d, *J* = 14 Hz); 26.46 (d, *J* = 12 Hz); 68.91 (d, *J* = 13 Hz); 70.28 (d, *J* = 9 Hz);	115.38; 116.33; 120.09 (C); 121.10 (C); 123.76; 123.93; 125.47; 125.62; 126.48; 126.54; 127.94; 128.19; 128.35; 128.59; 128.68 (d, *J* = 5 Hz); 128.85 (d, *J* = 6 Hz); 129.38; 129.42; 129.53 (C); 129.66; 129.69; 129.72 (C); 131.77 (d, *J* = 15 Hz); 132.56 (dd, *J* = 6, 1 Hz); 132.78 (d, *J* = 18 Hz); 133.05 (dd, *J* = 6, 2 Hz); 134.56 (C); 138.88 (C, dd, *J* = 16, 7 Hz); 140.51 (C, dd, *J* = 16, 6 Hz); 145.08 (C, dd, *J* = 32, 13 Hz); 146.61 (C, dd, *J* = 34, 12 Hz); 154.35 (C); 154.65 (C).
6c*A*	22.84 (d, *J* = 16 Hz); 23.02 (d, *J* = 15 Hz); 27.86 (dd, *J* = 13, 5 Hz); 28.00 (dd, *J* = 13, 7 Hz); 30.85 (d, *J* = 11 Hz); 31.22 (d, *J* = 10 Hz); 69.28; 70.43;	115.60; 117.01; 120.29 (C); 120.90 (C); 123.72; 123.86; 125.52; 125.54; 126.41; 126.48; 127.92; 128.22; 128.29; 128.58; 128.62 (d, *J* = 5 Hz); 128.80 (d, *J* = 6 Hz); 129.24; 129.44 (C); 129.46; 129.63; 129.66; 129.80 (C); 131.75 (d, *J* = 16 Hz); 132.94 (dd, *J* = 6, 2 Hz); 133.08 (d, *J* = 19 Hz); 134.50 (C); 134.53 (C); 139.17 (C, dd, *J* = 15, 6); 140.87 (C, dd, *J* = 15, 4 Hz); 144.68 (C, dd, *J* = 31, 12 Hz); 147.01 (C, dd, *J* = 33, 13 Hz); 154.82 (C); 155.18 (C).
6c*B*	22.47 (pt, *J* = 10 Hz); 27.17; 29.64 (pt, *J* = 8 Hz); 69.12;	115.18; 120.03 (C); 123.51; 125.48; 126.37; 128.26; 128.78; 128.84; 128.88; 128.91; 129.33 (C); 129.37; 133.37 (pt, *J* = 6 Hz); 133.70 (pt, *J* = 10 Hz); 134.58 (C); 137.15 (C, pt, *J* = 4 Hz); 145.73 (C, pt, *J* = 5 Hz); 154.72 (C).
6d*A*	25.85 (dd, *J* = 11, 5 Hz); 26.28 (dd, *J* = 11, 5 Hz); 26.50 (dd, *J* = 8, 4 Hz); 27.35 (dd, *J* = 8, 4 Hz); 27.77 (d, *J* = 8 Hz); 28.23 (d, *J* = 8 Hz); 29.42; 29.65; 69.53; 69.73;	115.55; 116.22; 120.18 (C); 120.94 (C); 123.70; 123.82; 125.49; 125.60; 126.45; 126.47; 128.02; 128.22; 128.29; 128.35; 128.63; 128.65; 128.67; 128.69; 128.71; 128.73; 128.75; 129.36 (d, *J* = 7 Hz); 129.50 (C); 129.52 (d, *J* = 9 Hz); 129.64 (C); 131.99; 132.04; 132.11; 132.16; 132.19; 132.60; 132.65; 132.72; 132.78; 134.54 (C); 134.58 (C); 139.83 (C, d, *J* = 10 Hz); 140.84 (C, d, *J* = 10 Hz); 145.46 (C, d, *J* = 18 Hz); 146.38 (C, d. *J* = 20 Hz); 154.75 (C); 154.88 (C).
6d*B*	25.83 (pt, *J* = 8 Hz); 26.79 (pt, *J* = 7 Hz); 28.08 (br.s); 29.95; 71.09;	117.11; 121.15 (C); 123.75; 125.53; 126.32; 128.20; 128.72; 128.87 (pt, *J* = 3 Hz); 129.22; 129.37; 129.74 (C); 133.22 (pt, *J* = 10 Hz); 133.59 (m); 134.53 (C); 138.60 (C, pt, *J* = 4 Hz); 146.57 (C, pt, *J* = 6 Hz); 155.37 (C).
6d*C*	25.79 (pt, *J* = 8 Hz); 26.48 (pt, *J* = 6 Hz); 27.96 (pt, *J* = 2 Hz); 29.56; 70.09;	116.83; 120.91 (C); 123.80; 125.56; 126.41; 128.24; 128.36; 128.70 (pt, *J* = 3 Hz); 129.03 (pt, *J* = 1 Hz); 129.45; 129.71 (C); 133.05 (pt, *J* = 10 Hz); 134.53 (C); 134.88 (pt, *J* = 9 Hz); 138.75 (C, pt, *J* = 5 Hz); 145.53 (C, pt, *J* = 3 Hz); 155.36 (C).
6e*A*	25.93; 25.94; 26.40 (dd, *J* = 14, 3 Hz); 26.55 (dd, *J* = 15, 4 Hz); 28.31 (dd, *J* = 10, 3 Hz); 28.43 (dd, *J* = 11, 2 Hz); 29.44; 29.71; 30.74 (dd, *J* = 10, 4 Hz); 30.97 (dd, *J* = 11, 4 Hz); 69.58; 70.19;	115.59; 116.34; 120.42 (C); 120.74 (C); 123.70; 123.78; 125.53 (br.s); 126.43; 126.46; 128.07; 128.23; 128.28; 128.33; 128.60; 128.65 (br.s); 128.71; 129.36; 129.42; 129.48; 129.55; 129.67 (C); 132.10; 132.15; 132.21; 132.24; 132.28; 132.60; 132.65; 132.69; 132.79; 132.83; 134.56 (C); 134.61 (C); 140.15 (C, d, *J* = 12 Hz); 140.75 (C, d, *J* = 12 Hz); 145.57 (C, dd, *J* = 24, 5 Hz); 146.30 (C, dd, *J* = 24, 4 Hz); 154.81 (C); 155.03 (C).
6e*B*	25.53; 26.28 (pt, *J* = 8 Hz); 27.83 (pt, *J* = 2 Hz); 29.76; 29.82 (pt, *J* = 7 Hz); 69.86;	115.83; 120.53 (C); 123.61; 125.52; 126.35; 128.22; 128.71; 128.85 (m); 128.94 (pt, *J* = 3 Hz); 129.39; 129.43; 129.45 (C); 133.49 (pt, *J* = 10 Hz); 134.56 (C); 138.14 (C, m); 146.24 (C, pt, *J* = 7 Hz); 154.78 (C).
6e*C*	25.78; 26.54 (pt, *J* = 8 Hz); 28.31;	115.54; 120.34 (C); 123.67; 125.53; 126.46; 128.26; 128.61;

Table 2. *(Continued)*

	δCH_2	δC_{ar}
	29.58; 29.86 (pt, J = 7 Hz); 69.57;	128.84; 128.89(m); 129.44; 133.40 (pt, J = 10 Hz); 133.56 (m); 134.64 (C); 138.35 (C, m); 145.98 (C, m); 154.74 (C).
6b·NiCl$_2$ *A*	22.57 (d, J = 35 Hz); 23.09 (d, J = 36 Hz); 24.38; 25.32; 68.26 (d, J = 10 Hz); 68.39 (d, J = 16 Hz);	114.43; 114.61; 119.55 (C); 121.38 (C); 123.79; 124.06; 125.16; 125.64; 126.54; 126.63; 128.00; 128.47; 129.20 (d, J = 6 Hz); 129.31 (d, J = 6 Hz); 129.36; 129.50 (C); 129.64 (C); 130.17; 130.48 (C, d, J = 19 Hz); 130.99 (C, d, J = 20 Hz); 131.53; 131.67; 131.76; 131.78; 131.81; 132.19 (d, J = 8 Hz); 132.27 (d, J = 8 Hz); 133.79 (d, J = 4 Hz); 134. 06 (d, J = 6 Hz); 134.46 (C); 134.54 (C); 141.14 (C, dd, J = 50, 37 Hz); 141.73 (C, dd, J = 48, 37 Hz); 152.96 (C); 153.37 (C).
6c·NiCl$_2$ *A*	22.42 (br.s); 22.58 (br.s); 27.07; 27.18; 31.91 (d, J = 5 Hz); 32.13 (d, J = 5 Hz); 68.84; 69.85;	115.08; 118.47; 119.18 (C); 121.48 (C); 123.63; 124.02; 125.24; 125.71; 126.37; 126.47; 128.01; 128.40; 129.17; 129.20; 129.21; 129.23; 129.27; 129.29; 129.48 (C); 129.78 (C); 130.11; 131.56 (br.s); 131.66 (br.s); 132.18 (dd, J = 6, 3 Hz); 132.34 (dd, J = 6, 3 Hz); 133.69 (d, J = 4 Hz); 133.78 (d, J = 4 Hz); 134.11 (C); 134.45 (C); ca. 141 (C, m); 154.88 (C); 155.07 (C).
6c·NiCl$_2$ *B*	22.57; 24.62 (d, J = 11 Hz); 25.86 (d, J = 29 Hz); 26.60 (d, J = 2 Hz); 27.18 (d, J = 28 Hz); 30.32; 68.15; 69.18;	113.40; 115.06; 118.60 (C); 119.05 (C); 123.84; 123.91; 125.42; 126.18; 126.65; 126.82; 128.24; 128.33; 128.68 (d, J = 11 Hz); 128.95 (d, J = 11 Hz); 129.35 (C); 129.78 (C); 129.88; 130.01 (C, d, J = 44 Hz); 130.48; 130.87 (d, J = 3 Hz); 131.57 (d, J = 3 Hz); 131.59 (C, d, J = 57 Hz); 132.35 (d, J = 10 Hz); 132.47 (d, J = 9 Hz); 132.59; 132.88 (d, J = 9 Hz); 133.15 (d, J = 6 Hz); 134.30 (C); 134.56 (C, dd, J = 50, 33 Hz); 136.87 (d, J = 15 Hz); 142.91 (C, dd, J = 47, 39 Hz); 153.49 (C); 154.39 (C).
6d·NiCl$_2$ *A*	25.16 (d, J = 1 Hz); 25.81 (d, J = 2 Hz); 26.73 (d, J = 22 Hz); 26.87 (d, J = 24 Hz); 27.13 (d, J = 35 Hz); 27.48 (d, J = 34 Hz); 29.70; 29.75; 68.27; 68.68;	115.14; 115.55; 119.87 (C); 121.33 (C); 123.65; 123.89; 125.33; 125.68; 126.43; 126.52; 128.13; 128.38; 129.19 (d, J = 3 Hz); 129.22; 129.29 (d, J = 3 Hz); 129.49 (C); 129.54 (C); 129.77; 131.04 (C); 131.07 (C); 131.41; 131.43; 131.52; 131.57; 131.58; 131.63; 131.65; 132.21 (d, J = 2 Hz); 132.29 (d, J = 2 Hz); 133.74 (d, J = 6 Hz); 133.80 (d, J = 6 Hz); 134.48 (C); 134.60 (C); ca.141 (C, m); ca. 142 (C, m); 153.99 (C); 154.12 (C).
6d·NiCl$_2$ *B*	23.20; 24.73; 25.82 (d, J = 7 Hz); 26.84; 27.09 (d, J = 30 Hz); 28.38; 29.50; 30.07; 68.35; 70.62;	118.64, 119.72 (C); 121.57 (C); 124.00; 124.34; 125.32; 125.71; 126.53; 126.75; 128.34; 129.01 (d, J = 10 Hz); 129.30; 129.33 (d, J = 10 Hz); 129.85; 130.07 (C); 130.57 (C); 131.41 (dd, J = 11, 2 Hz); 132.12 (d, J = 8 Hz); 132.71 (d, J = 8 Hz); 132.92 (m); 133.90 (d, J = 5 Hz); 134.25 (C); 134.36 (C); 135.33 (d, J = 13 Hz); 155.22 (C); 155.68 (C).
6d·NiCl$_2$ *C*	22.99; 24.88; 25.12 (d, J = 10 Hz); 27.61 (d, J = 57 Hz); 27.63; 27.79; 29.70; 30.23; 68.66; 70.64;	114.57; 115.07; 119.22 (C); 120.04 (C); 123.82; 123.96; 125.37; 125.56; 126.76; 128.33; 128.47; 128.96 (d, J = 11 Hz); 129.36 (d, J = 10 Hz); 129.66 (C); 130.15; 130.18; 130.57 (C); 131.10 (d, J = 2 Hz); 131.54 (d, J = 2 Hz); 132.62 (d, J = 9 Hz); 132.86 (d, J = 2 Hz); 133.71 (d, J = 15 Hz); 133.85; 134.03 (C); 134.24 (C); 134.82 (d, J = 15 Hz); 136.12 (C, dd, J = 51, 35 Hz); 143.10 (C, dd, J = 48, 39 Hz); 155.44 (C); 155.64 (C).
6e·NiCl$_2$ *A*	25.45 (br.s); 25.71 (br.s); 26.04; 26.21; ca. 25.50 (m); 29.34; 29.41; ca.31.15 (m); 69.27; 69.79;	115.72; 116.52; 119.87 (C); 121.47 (C); 123.58; 123.92; 125.27; 125.73; 126.37; 126.51; 128.05; 128.49; 129.10; 129.21 (br.s); 129.31 (br.s); 129.62 (C); 129.64 (C); 130.16; 131.62 (m); 132.29 (m); 133.66 (m); 134.50 (C); 134.68 (C); 154.89 (C); 154.93 (C).

Table 2. *(Continued)*

	δCH_2	δC_{ar}
6e·NiCl$_2$ *B*	22.48 (br.s); 24.19 (br.s); 26.84 (m); 27.79 (br.s); 69.67 (br.s);	116.26 (br.s); 119.79 (C); 123.97; 125.86; 126.47; 128.24; 129.08 (bm); 129.72; 129.74 (C); 131.65; 132.93 (br.s); 133.22; 133.70 (bm); 134.15 (C); 140.11 (C, pt, J = 43 Hz); 155.09 (C).
6e·NiCl$_2$ *C*	22.42; 23.30; 26.32 (m); 28.09; 28.44 (br.s); 70.58;	116.60; 120.70 (C); 124.02; 125.66; 126.57; 128.29; 129.08 (br.s); 129.79 (C); 129.90; 131.42; 132.42 (m); 133.13; 133.96 (br.s); 134.57 (C); 155.44 (C).
6b·PdCl$_2$ *A*	23.07 (d, J = 36 Hz); 23.77 (d, J = 36 Hz); 24.37; 25.69 (d, J = 3 Hz); 67.96 (d, J = 12 Hz); 68.11 (d, J = 17 Hz);	114.51; 114.53; 119.55 (C); 121.36 (C); 123.87; 124.15; 125.20; 125.70; 126.60; 126.73; 128.07; 128.56; 129.42; 129.43 (d, J = 3 Hz); 129.55 (d, J = 3 Hz); 129.73 (C); 130.29; 130.54 (C); 132.26 (d, J = 10 Hz); 132.33 (m); 132.36 (d, J = 10 Hz); 132.56 (m); 134.26 (m); 134.46 (C); 134.54 (m); 134.60 (C); 152.97 (C); 153.34 (C).
6c·PdCl$_2$ *A*	22.52 (d, J = 2 Hz); 22.60 (d, J = 2 Hz); 27.38 (d, J = 12 Hz); 27.71 (d, J = 12 Hz); 31.51 (d, J = 16 Hz); 31.83 (d, J = 15 Hz); 68.69; 69.88;	115.10; 118.54; 119.07 (C); 121.53 (C); 123.61; 124.06; 125.17; 125.71; 126.38; 126.45; 127.98; 128.41; 129.11; 129.37 (d, J = 10 Hz); 129.47 (C); 129.79 (C); 130.16; 130.58 (C, d, J = 20 Hz); 131.11 (C, d, J = 20 Hz); 132.03; 132.05; 132.09; 132.14; 132.19; 132.21; 132.31; 132.37; 132.44; 132.48; 132.61; 132.65; 134.01; 134.02 (C); 134.08; 134.13; 134.19; 134.43 (C); 140.47 (C, dd, J = 37, 23 Hz); 140.92 (C, dd, J = 37, 23 Hz); 154.86 (C); 155.11 (C).
6d·PdCl$_2$ *A*	25.16 (d, J = 1 Hz); 25.99 (d, J = 3 Hz); 26.34 (d, J = 15 Hz); 26.64 (d, J = 17 Hz); 27.54 (d, J = 34 Hz); 27.93 (d, J = 36 Hz); 29.65 (br.s); 68.21; 68.59;	115.29; 115.50; 119.84 (C); 121.30 (C); 123.66; 123.90; 125.31; 125.69; 126.42; 126.54; 128.12; 128.39; 129.19; 129.33; 129.36; 129.44; 129.47; 129.51 (C); 129.53 (C); 129.81; 130.51 (C, m); 131.04 (C, m); 132.11; 132.14; 132.17; 132.27; 132.41 (m); 132.58 (m); 134.06; 134.15; 134.23; 134.46 (C); 134.60 (C); 141.05 (C, m); 141.20 (C, m); 154.02 (C); 154.14 (C).
6e·PdCl$_2$ *A*	25.48 (br.s); 25.84 (d, J = 2 Hz); 25.98; 26.13; 27.80 (d, J = 22 Hz); 28.14 (d, J = 22 Hz); 29.24; 29.36; 30.77 (d, J = 11 Hz); 30.93 (d, J = 11 Hz); 69.17; 69.80;	115.60; 116.57; 119.78 (C); 121.52 (C); 123.55; 123.93; 125.21; 125.73; 126.35; 126.50; 128.02; 128.52; 129.06; 129.35; 129.45; 129.60 (C); 129.64 (C); 130.20; 130.71 (C, d, J = 7 Hz); 131.23 (C, d, J = 8 Hz); 132.09; 132.15; 132.21; 132.25; 132.31; 132.52; 134.03; 134.46 (C); 134.66 (C); 154.83 (C); 154.90 (C).

$C_{44}H_{38}O_2P_2$ (660.2): calcd. C 79.98, H 5.80, P 9.38; found C 79.01, H 5.67, P 9.35.

13,14,15,16,22,23,24,25-Octahydro-16,21-diphenyl-12H,21H-benzo[g]dinaphtho[2,1-o:1',2'-q][1,14,6,9]dioxadiphosphacyclooctadecine (**6c**): (*A*) 455 mg (66%). – ^{1}H NMR: δ = 1.40–1.85 (8H, m), 2.11 (4H, m), 3.89 (2H, m), 4.04 (1H, m), 4.23 (1H, m), 7.07 (3H, m), 7.18–7.45 (18H, m), 7.57 (1H, d, J = 9 Hz), 7.87 (1H, br. d, J = 8 Hz), 7.87 (1H, d, J = 9.0 Hz), 7.91 (1H, br. d, J = 8 Hz), 8.01 (1H, d, J = 9.0 Hz). – ^{31}P NMR: δ = −24.28 (d, J = 149 Hz), −27.17 (d, J = 149 Hz). – MS (290°C), *m/z* (%): 688 (34), 644 (3), 632 (6), 630 (6), 615 (3), 611 (6), 594 (1), 554 (1), 498 (1), 450 (1), 426 (1), 394 (1), 362 (2), 346 (100), 319 (5), 305 (31). – HRMS: calcd. 688.2660, found 688.2664. – $C_{46}H_{42}O_2P_2$ (688.3): calcd. C 80.21, H 6.15, P 8.99; found C 79.95, H 6.39, P 9.11.

(*B*) 41 mg (6%). – ^{1}H NMR: δ = 1.48 (2H, m), 1.73 (4H, m), 2.00 (2H, m), 2.29 (2H, m), 2.58 (2H, m), 4.02 (2H, m), 4.40 (2H, m), 6.95 (2H, m), 7.05 (2H, br. d, J = 9.0 Hz), 7.09 (2H, dd, J = 5.5/3.5 Hz), 7.19 (2H, ddd, J = 8.5/7.5/1.2 Hz), 7.30 (2H, ddd, J = 8/7.5/1.2 Hz), 7.38 (6H, m), 7.44 (4H, m), 7.50 (2H, d, J = 9.0 Hz), 7.85 (2H, br. d, J = 8 Hz), 7.92 (2H, d, J = 9.0 Hz). – ^{31}P NMR: δ = −20.65 (s). – MS (250°C), *m/z* (%): 688 (24), 630 (3), 615 (3), 570 (2), 498 (3), 347 (57), 305 (25).

12,13,14,15,16,17,22,23,24,25,26,27-Dodecahydro-17,22-diphenylbenzo[m]dinaphtho[2,1-b:1',2'-d][1,6,12,15]dioxadiphosphacycloeicosine (**6d**): (*A*) 321 mg (45%). – ^{1}H NMR: δ = 1.20–1.60 (12H, m), 1.98–2.20 (4H, m), 3.92 (2H, t, J = 7 Hz), 4.09 (2H, m), 7.07 (2H, m), 7.21 (3H, m), 7.26–7.42 (16H, m), 7.55 (1H, d, J = 9 Hz), 7.88 (1H, br. d, J = 8 Hz), 7.90 (1H, d, J = 7.5 Hz), 7.92 (1H, d, J = 9 Hz), 8.00 (1H, d, J = 9 Hz). – ^{31}P NMR: δ = −26.09 (d, J = 150 Hz), −26.45 (d, J = 150 Hz). – MS (250°C), *m/z* (%): 716 (55), 659 (9), 639 (8), 361 (100), 325 (19), 305 (43), 293 (50). – HRMS: calcd. 716.2973, found 716.2976. – $C_{48}H_{46}O_2P_2$ (716.3): calcd. C 80.43, H 6.47, P 8.64; found C 78.73, H 6.47, P 8.78.

(*B*) 51 mg (7%). – ^{1}H NMR: δ = 1.28–1.81 (12H, m), 2.15 (2H, m), 2.35 (2H, m), 4.04 (4H, m), 6.98 (2H, m), 7.11 (4H, m), 7.21 (2H, m), 7.32 (2H, m), 7.39–7.51 (12H, m), 7.78 (2H, d, J = 8.9 Hz), 7.82 (2H, br. d, J = 8.1 Hz). – ^{31}P NMR: δ = −21.89

Table 3. X-ray structure determination

	6c*B*	**6d**·$NiCl_2$ *B*	**6e**·$NiCl_2$ *A*	**6e** *B*	**6e**·$NiCl_2$ *B*
a[Å]	8.469(3)	11.012(4)	11.656(3)	11.420(2)	11.184(7)
b[Å]	10.98(2)	14.595(6)	15.072(7)	12.612(3)	14.932(9)
c[Å]	40.45(10)	25.448(11)	15.728(3)	15.622(3)	25.123(15)
α[°]	90	90	115.00(3)	86.31(3)	90
β[°]	90	90	106.34(2)	86.03(3)	90
γ[°]	90	90	93.11(2)	67.78(3)	90
V[Å^3]	3762.6(14)	4090.0(29)	2354.9(16)	2076.2(12)	4195.5(14)
size [mm]	0.4 x 0.2 x 0.2	0.2 x 0.2 x 0.15	0.5 x 0.4 x 0.2	0.4 x 0.3 x 0.2	0.5 x 0.3 x 0.3
d_{calc}[gcm^{-3}]	1.486	1.375	1.233	1.191	1.384
determ. of cell data: number of reflections	33	25	18	29	18
2Θ range	8.8° - 40.0°	9.3° - 29.2°	8.6° - 55.6°	6.2° - 14.2°	6.4 - 13.2°
crystal system	orthorhombic	orthorhombic	triclinic	triclinic	orthorhombic
space group	$P2_12_12_1$	$P2_12_12_1$	P1	P1	$P2_12_12_1$
Z	4	4	2	2	4
radiation	CuK_α	CuK_α	CuK_α	MoK_α	MoK_α
max. 2Θ for data collection	107.5	103.4	107.5	40.0	60.1
reciprocal lattice segment	$-1 \le h \le 8$ $-1 \le k \le 11$ $-1 \le l \le 42$	$-1 \le h \le 11$ $-1 \le k \le 11$ $-1 \le l \le 25$	$-1 \le h \le 12$ $-14 \le k \le 14$ $-16 \le l \le 16$	$-8 \le h \le 10$ $-11 \le k \le 12$ $-15 \le l \le 10$	$-1 \le h \le 15$ $-1 \le k \le 21$ $-1 \le l \le 35$
number of reflections:					
observed	3274	3361	6349	4456	7448
unique	3016	3130	5367	3853	7294
significant ($F > 4\sigma$)	2363	1729	4110	1967	4349
R1 (against *F*) for data $F > 4\sigma$	0.0742	0.0944	0.0695	0.0881	0.0635
ωR2 (against F^2) for all data	0.2109	0.2845	0.2128	0.2176	0.1680
number of parameters	321	496	538	487	514
temperature [K]	293	293	293	293	93
weighting[a]					
a	0.1000	0.1345	0.1241	0.0975	0.0977
b	0	15.7181	5.8463	0	0
μ[mm^{-1}]	2.22	2.93	2.56	0.14	0.71
highest feature in Δ*F-Fourier* synthesis [eA^{-3}]	0.36	0.57	0.52	0.31	0.57
diffractometer	Siemens P4	Siemens P4	Siemens P4	Stoe	Stoe
monochromator	graphite	graphite	graphite	graphite	graphite

[a] $1/[\sigma^2(F_o^2) + (aP)^2] + bP$ where $P = [\mathrm{Max}(F_o^2,0) + 2F_c^2]/3$.

(s). – MS (250°C), *m/z* (%): 716 (19), 659 (2), 639 (2), 571 (1), 494 (1), 422 (1), 361 (31), 305 (15).

(*C*) 26 mg (4%). – ^{1}H NMR: δ = 1.30–1.70 (12H, m), 2.31 (4H, m), 3.91 (2H, m), 4.00 (2H, m), 7.05 (2H, br. d, *J* = 8.5 Hz), 7.17–7.36 (18H, m), 7.42 (2H, d, *J* = 9 Hz), 7.89 (2H, br. d, *J* = 8 Hz), 7.92 (2H, d, *J* = 8 Hz). – ^{31}P NMR: δ = –19.48 (br. s).

13,14,15,16,17,18,24,25,26,27,28,29-Dodecahydro-18,23-diphenyl-12H,23H-benzo[n]dinaphtho[2,1-b:1',2'-d][1,6,13,16]dioxadiphosphacyclododocosine (**6e**): (*A*) 299 mg (40%). – ^{1}H NMR: δ = 1.18–1.60 (16H, m), 2.13 (4H, m), 3.94 (2H, t, *J* = 6.9 Hz), 4.05 (2H, m), 7.05 (2H, br. d, *J* = 8.5 Hz), 7.20 (2H, m), 7.25–7.39 (17H, m), 7.52 (1H, d, *J* = 9.0 Hz), 7.88 (3H, m), 7.99 (1H, d, *J* = 8.9 Hz). – ^{31}P NMR: δ = –25.83 (d, *J* = 150 Hz), –27.29 (d, *J* = 150 Hz). – MS (290°C), *m/z* (%): 745 (30), 743 (25), 570 (100), 519 (20), 516 (15), 454 (85), 452 (38), 428 (28), 375 (35), 370 (30). – HRMS: calcd. 744.3286, found 744.3281. – $C_{50}H_{50}O_2P_2$ (744.3): calcd. C 80.62, H 6.77, P 8.32; found C 79.66, H 6.87, P 8.30.

(*B*) 83 mg (11%). – ^{1}H NMR: δ = 1.19 (2H, m), 1.33–1.74 (14H, m), 2.26–2.45 (4H, m), 4.00 (2H, m), 4.16 (2H, m), 6.94 (2H, m), 7.06 (2H, d, *J* = 9 Hz), 7.10 (2H, dd, *J* = 6/3.5 Hz), 7.19 (2H, m), 7.31 (2H, m), 7.35 (2H, d, *J* = 9.5 Hz), 7.38–7.57 (12H, m), 7.77 (2H, d, *J* = 9.5 Hz), 7.84 (2H, d, *J* = 8.5 Hz). – ^{31}P NMR: δ = –21.70 (br. s). – MS (290°C), *m/z* (%): 745 (25), 715 (3), 662 (4), 583 (2), 499 (4), 375 (43), 293 (36).

(*C*) 46 mg (6%). – ^{1}H NMR: δ = 1.15–1.75 (16H, m), 2.36 (4H, m), 4.05 (4H, m), 6.97 (2H, m), 7.03 (2H, br. d, *J* = 9 Hz), 7.12 (2H, m), 7.19 (2H, ddd, *J* = 8.1/6.7/1.4 Hz), 7.31 (2H, ddd, *J* = 8.1/6.8/1.3 Hz), 7.38 (4H, m), 7.44 (2H, d, *J* = 9 Hz), 7.46 (6H, m), 7.88 (2H, br. d, *J* = 8 Hz), 7.94 (2H, d, *J* = 9 Hz). – ^{31}P NMR: δ = –20.70 (br. s).

Optically Active Compounds were prepared in the same manner as the racemates with the only exception that (–)(*S*)-1,1'-binaphthyl-2,2'-diol [(–)(*S*)-**1**], $[\alpha]_{546}^{20} = -52.2$ ($[\alpha]_{546}^{25} = -51.3$[9]), was used instead of (±)-**1**. The spectral properties were found to be

identical with those of the racemic compounds. Yields do not differ more than ±2% from the racemic reactions.

(−)(*S*)-**2a**: oil, $[\alpha]_D^{20}$ = −28.9 (EtOH); (−)(*S*)-**3b**: oil, $[\alpha]_D^{20}$ = −37.5 (EtOH); (−)(*S*)-**2c**: oil, $[\alpha]_D^{20}$ = −51.0 (EtOH); (−)(*S*)-**2d**: oil, $[\alpha]_D^{20}$ = −47.4 (EtOH); (−)(*S*)-**2e**: oil, $[\alpha]_D^{20}$ = −43.7 (EtOH).

(−)(*S*)-**4a**: m.p. 124−129°C (133−134°C[9]), $[\alpha]_D^{20}$ = −2.6 (EtOH) ($[\alpha]_{546}^{25}$ = +23.2, THF[9]); (−)(*S*)-**4b**: oil, $[\alpha]_D^{20}$ = −54.8 (EtOH); (−)(*S*)-**4c**: oil, $[\alpha]_D^{20}$ = −48.8 (EtOH); (−)(*S*)-**4d**: oil, $[\alpha]_D^{20}$ = −55.2 (EtOH); (−)(*S*)-**4e**: oil, $[\alpha]_D^{20}$ = −58.4 (EtOH).

(+)(*S*)-**5a**: m.p. 144−146°C, $[\alpha]_D^{20}$ = +80.4 (CH_2Cl_2); (−)(*S*)-**5b**: oil, $[\alpha]_D^{20}$ = −22.3 (CH_2Cl_2); (−)(*S*)-**5c**: oil, $[\alpha]_D^{20}$ = −35.2 (CH_2Cl_2); (−)(*S*)-**5d**: oil, $[\alpha]_D^{20}$ = −33.3 (CH_2Cl_2); (−)(*S*)-**5e**: oil, $[\alpha]_D^{20}$ = −29.0 (CH_2Cl_2).

(−)(*S*)-**6a**: $[\alpha]_D^{20}$ = −538 (CH_2Cl_2); (−)(*S*)-**6b**: $[\alpha]_D^{20}$ = −290 (CH_2Cl_2); (−)(*S*)-**6c** (*A*): $[\alpha]_D^{20}$ = −231 (CH_2Cl_2); (−)(*S*)-**6c** (*B*): $[\alpha]_D^{20}$ = −82.6 (CH_2Cl_2); (−)(*S*)-**6d** (*A*): $[\alpha]_D^{20}$ = −181 (CH_2Cl_2); (−)(*S*)-**6d** (*B*): $[\alpha]_D^{20}$ = −117 (CH_2Cl_2); (−)(*S*)-**6d** (*C*): $[\alpha]_D^{20}$ = −144 (CH_2Cl_2); (−)(*S*)-**6e** (*A*): $[\alpha]_D^{20}$ = −128 (CH_2Cl_2); (−)(*S*)-**6e** (*B*): $[\alpha]_D^{20}$ = −60.9 (CH_2Cl_2); (−)(*S*)-**6e** (*C*): $[\alpha]_D^{20}$ = −79.9 (CH_2Cl_2).

Preparation of Optically Active Ni(II) Complexes of **6a**−**e**. − *General Procedure:* To a solution of 0.10 mmol of (*S*)-**6** in 1 ml of CH_2Cl_2 was added a solution of 23.8 mg (0.10 mmol) of $NiCl_2 \cdot 6\,H_2O$ in 2 ml of EtOH. After a few min crystallization started, and the mixture was allowed to stand for ca. 12 h. The crystalline precipitate was collected and dried in vacuo.

(−)(*S*)-**6a** · **$NiCl_2$**: 63 mg (82%), orange plates, $[\alpha]_D^{20}$ = −266 (CH_2Cl_2).

(−)(*S*)-**6b** · **$NiCl_2$**: 41 mg (55%), yellow powder. − ^{1}H NMR: δ = 1.68 (1H, m), 1.77 (1H, m), 2.01 (1H, m), 2.14 (2H, m), 2.44 (1H, m), 3.01 (2H, m), 3.94 (2H, m), 4.25 (1H, m), 5.44 (1H, m), 6.98 (1H, d, *J* = 9 Hz), 7.08 (1H, d, *J* = 8.5 Hz), 7.19 (1H, m), 7.20 (2H, d, *J* = 9 Hz), 7.30 (1H, ddd, *J* = 8/7/1.5 Hz), 7.33 (1H, ddd, *J* = 8/7/1.5 Hz), 7.42 (5H, m), 7.51 (2H, m), 7.55−7.70 (6H, m), 7.66 (2H, d, *J* = 9 Hz), 7.81 (1H, d, *J* = 8 Hz), 7.83 (1H, d, *J* = 9 Hz), 7.92 (1H, d, *J* = 8 Hz), 8.08 (1H, d, *J* = 9 Hz). − ^{31}P NMR: δ = 55.71 (d, *J* = 72.0 Hz), 58.42 (d, *J* = 72.0 Hz). − $[\alpha]_D^{20}$ = −134 (CH_2Cl_2). − $C_{44}H_{38}Cl_2NiO_2P_2$ (790.3): calcd. C 66.87, H 4.85, P 7.84; found C 66.51, H 4.87, P 7.90.

(−)(*S*)-**6c** · **$NiCl_2$**: (*A*) 80 mg (98%), orange, feather-like crystals. − ^{1}H NMR: δ = 1.42 (1H, m), 1.51 (2H, m), 1.65 (1H, m), 1.74 (1H, m), 1.91 (1H, m), 2.07 (1H, m), 2.17 (2H, m), 2.30 (1H, m), 3.04 (2H, m), 3.66 (2H, m), 4.07 (1H, ddd, *J* = 9.5/4/4 Hz), 4.31 (1H, ddd, *J* = 10/10/3 Hz), 6.84 (1H, d, *J* = 9.5 Hz), 6.97 (1H, br. d, *J* = 8 Hz), 7.05 (1H, br. d, *J* = 8 Hz), 7.18 (2H, m), 7.31 (2H, m), 7.42 (5H, m), 7.51 (2H, m), 7.59−7.68 (5H, m), 7.61 (1H, d, *J* = 9.5 Hz), 7.68 (1H, d, *J* = 9 Hz), 7.72 (1H, m), 7.81 (1H, br. d, *J* = 8 Hz), 7.86 (1H, m), 7.90 (1H, br. d, *J* = 8 Hz), 8.03 (1H, d, *J* = 9 Hz). − ^{31}P NMR: δ = 59.21 (d, *J* = 73.4 Hz), 59.35 (d, *J* = 73.4 Hz). − $[\alpha]_D^{20}$ = −108 (CH_2Cl_2). − $C_{46}H_{42}Cl_2NiO_2P_2$ (818.4): calcd. C 67.51, H 5.17, P 7.57; found C 67.35, H 5.06, P 7.29.

(*B*) 42 mg (53%), red prisms. − ^{1}H NMR: δ = −0.35 (1H, m), 1.20−1.67 (5H, m), 1.94 (1H, m), 2.00 (1H, m), 2.09 (1H, m), 2.79 (1H, m), 3.15 (1H, m), 3.50 (1H, dd, *J* = 14/7 Hz), 3.95 (1H, dd, *J* = 13.5/7 Hz), 4.17 (1H, dd, *J* = 14/7 Hz), 4.43 (1H, dd, *J* = 14/6.5 Hz), 5.92 (1H, m), 6.41 (1H, br. s); 6.66 (1H, d, *J* = 9.1 Hz), 6.73 (1H, d, *J* = 9.2 Hz), 7.04 (1H, br. t, *J* = 8 Hz), 7.09 (1H, d, *J* = 8.6 Hz), 7.18−7.42 (7 H, m), 7.52 (2 H, m), 7.59 (1 H, m), 7.74 (1 H, d, *J* = 9.2 Hz), 7.81 (1H, d, *J* = 7.5 Hz), 7.84 (1H, d, *J* = 7.4 Hz), 7.92 (1H, d, *J* = 8.3 Hz), 7.96 (2H, d, *J* = 9.3 Hz), 8.21 (2H, br. s); 8.55 (1H, m). − ^{31}P NMR: δ = 47.89 (d, *J* = 73.4 Hz), 52.96 (d, *J* = 73.4 Hz). − $[\alpha]_D^{20}$ = −792 (CH_2Cl_2).

(−)(*S*)-**6d** · **$NiCl_2$**: (*A*) 66 mg (77%), orange precipitate. − ^{1}H NMR: δ = 1.22 (2H, m), 1.38−1.62 (7H, m), 1.83 (1H, m), 1.99−2.25 (3H, m), 2.37 (1H, m), 3.01 (1H, m), 3.18 (1H, m), 3.88 (2H, m), 4.13 (2H, m), 7.03 (1H, br. d, *J* = 8 Hz), 7.11 (1H, br. d, *J* = 8.5 Hz), 7.21 (2H, m), 7.32 (2H, m), 7.35 (1H, d, *J* = 9 Hz), 7.42 (4H, m), 7.51 (3H, m), 7.55 (1H, d, *J* = 9 Hz), 7.58−7.71 (7H, m), 7.86 (1H, br. d, *J* = 8 Hz), 7.91 (1H, br. d, *J* = 8 Hz), 7.91 (1H, d, *J* = 8.9 Hz), 8.03 (1H, d, *J* = 9 Hz). − ^{31}P NMR: δ = 58.47 (d, *J* = 73.4 Hz), 59.71 (d, *J* = 73.4 Hz). − $[\alpha]_D^{20}$ = −98 (CH_2Cl_2). − $C_{48}H_{46}Cl_2NiO_2P_2$ (846.4): calcd. C 68.11, H 5.48, P 7.32; found C 67.80, H 5.41, P 7.62. − (*B*) 71 mg (83%), red prisms. − ^{1}H NMR: δ = −0.01 (1H, m), 0.70 (1H, m), 1.05−1.85 (10H, m), 2.35 (1H, m), 3.00−3.30 (2H, m), 3.65 (1H, m), 3.85 (3H, m), 4.05 (1H, m), 6.20 (1H, m), 6.50 (2H, m), 6.95−8.05 (23H, m). − ^{31}P NMR: δ = 55.08 (d, *J* = 75 Hz), 55.94 (d, *J* = 75 Hz). − $[\alpha]_D^{20}$ = −539 (CH_2Cl_2). − (*C*) 77 mg (91%), orange powder. − ^{1}H NMR: (see above). − ^{31}P NMR: δ = 52.57 (d, *J* = 75 Hz), 55.61 (d, *J* = 75 Hz). − $[\alpha]_D^{20}$ = +152 (CH_2Cl_2).

(−)(*S*)-**6e** · **$NiCl_2$**: (*A*) 69 mg (79%), orange prisms. − ^{1}H NMR: δ = 1.05−1.43 (10H, m), 1.48−1.72 (4H, m), 2.05−2.33 (4H, m), 3.11 (2H, m), 3.84 (2H, m), 3.97 (1H, m), 4.13 (1H, m), 7.00 (1H, br. d, *J* = 8.5 Hz), 7.10 (1H, br. d, *J* = 8.5 Hz), 7.19 (2H, m), 7.23 (1H, d, *J* = 8.0 Hz), 7.32 (2H, m), 7.43 (4H, m), 7.57 (1H, d, *J* = 9.1 Hz), 7.49−7.70 (8H, m), 7.77 (2H, m), 7.81 (1H, d, *J* = 9.0 Hz), 7.84 (1H, br. d, *J* = 8.3 Hz), 7.94 (1H, br. d, *J* = 8.2 Hz), 8.13 (1H, d, *J* = 9.1 Hz). − ^{31}P NMR: δ = 55.73 (d, *J* = 73.4 Hz), 56.03 (d, *J* = 73.4 Hz). − $[\alpha]_D^{20}$ = −66.8 (CH_2Cl_2). − $C_{50}H_{50}Cl_2NiO_2P_2$ (874.5): calcd. C 68.67, H 5.76, P 7.08; found C 68.33, H 5.61, P 7.42. − (*B*) 38 mg (44%), red crystals. − ^{1}H NMR: δ = 0.90 (2H, m), 1.00−1.40 (12H, m), 1.68 (2H, m), 2.37 (2H, m), 2.82 (2H, m), 3.30 (2H, m), 3.72 (2H, m), 7.03 (6H, br. m), 7.22 (2H, d, *J* = 9 Hz), ca. 7.25 (2H, br. m), 7.27 (2H, td, *J* = 8.5/1.5 Hz), ca. 7.38 (2H, br. m), 7.39 (2H, ddd, *J* = 8.5/6.5/1.5 Hz), 7.63 (2H, br. m), 7.81 (4H, br. m), 7.97 (2H, br. d, *J* = 8 Hz), 8.06 (2H, d, *J* = 9 Hz). − ^{31}P NMR: δ = 57.19 (br. s). − $[\alpha]_D^{20}$ = −336 (CH_2Cl_2). − (*C*) 69 mg (79%), orange powder. − ^{1}H NMR: δ = 0.59 (2H, m), 0.73 (2H, m), 0.91 (2H, m), 1.00−1.45 (8H, m), 1.62 (2H, m), 2.23 (2H, m), 2.66 (2H, m), 3.70 (4H, m), 6.80 (2H, m), 7.14−7.28 (8H, m), 7.33−7.53 (6H, m), 7.53 (2H, d, *J* = 9 Hz), 7.97 (2H, d, *J* = 8 Hz), 8.03 (4H, m), 8.12 (2H, d, *J* = 9 Hz). − ^{31}P NMR: δ = 56.16 (br. s). − $[\alpha]_D^{20}$ = +43.8 (CH_2Cl_2).

Preparation of Optically Active Pd(II) Complexes of **6a**−**e**. − *General Procedure:* To a solution of 0.10 mmol of (*S*)-**6** in 1 ml of CH_2Cl_2 was added a solution of 38.5 mg (0.10 mmol) of $Pd(C_6H_5CN)_2Cl_2$ in 2 ml of CH_2Cl_2. Then EtOH was added slowly and the precipitated product, cream to pale yellow in color, was collected and dried in vacuo.

(−)(*S*)-**6a** · **$PdCl_2$**: 57 mg (70%). $[\alpha]_D^{20}$ = −219 (CH_2Cl_2).

(−)(*S*)-**6b** · **$PdCl_2$**: 56 mg (68%). − ^{1}H NMR: δ = 1.62 (2H, m), 1.82 (1H, m), 2.19 (1H, m), 2.40 (2H, m), 3.18 (2H, m), 3.85 (1H, m), 3.97 (1H, m), 4.16 (1H, m), 4.92 (1H, m), 6.97 (1H, br. d, *J* = 8.4 Hz), 7.06 (1H, br. d, *J* = 8.5 Hz), 7.17 (1H, d, *J* = 9 Hz), 7.20 (2H, m), 7.32 (2H, m), 7.45 (4H, m), 7.50−7.65 (8H, m), 7.68−7.77 (2H, m), 7.79 (1H, m), 7.81 (1H, d, *J* = 8.1 Hz), 7.94 (1H, d, *J* = 9.0 Hz), 7.92 (1H, d, *J* = 8.2 Hz), 8.08 (1H, d, *J* = 9.0 Hz). − ^{31}P NMR: δ = 63.25 (d, *J* = 16.9 Hz), 66.61 (d, *J* = 16.9 Hz). − $[\alpha]_D^{20}$ = −94.8 (CH_2Cl_2). − $C_{44}H_{38}Cl_2O_2P_2Pd$ (838.1): calcd. C 63.06, H 4.57, P 7.39; found C 62.12, H 4.30, P 7.64.

(−)(*S*)-**6c** · **$PdCl_2$**: 43 mg (50%). − ^{1}H NMR: δ = 1.33 (2H, m), 1.46 (1H, m), 1.61 (2H, m), 1.80 (2H, m), 1.96 (1H, m), 2.38 (2H,

m), 3.21 (2H, m), 3.60 (2H, m), 4.01 (1H, m), 4.22 (1H, m), 6.83 (1H, d, J = 8.9 Hz), 6.95 (1H, d, J = 8.4 Hz), 7.04 (1H, d, J = 8.5 Hz), 7.17 (2H, m), 7.31 (2H, m), 7.39–7.65 (11H, m), 7.69 (1H, d, J = 8.9 Hz), 7.81 (3H, m), 7.89 (1H, d, J = 8.1 Hz), 7.95 (1H, m), 8.03 (1H, d, J = 9.1 Hz). – ^{31}P NMR: δ = 67.31 (d, J = 17.2 Hz), 67.50 (d, J = 17.2 Hz). – $[\alpha]_D^{20}$ = −112 (CH_2Cl_2). – $C_{46}H_{42}Cl_2O_2P_2Pd$ (866.1): calcd. C 63.79, H 4.89, P 7.15; found C 63.14, H 4.64, P 7.35.

(−)(*S*)-**6d** · **$PdCl_2$**: 49 mg (55%). – ^{1}H NMR: δ = 1.20 (2H, m), 1.30–1.68 (8H, m), 1.76 (1H, m), 1.98 (1H, m), 2.41 (2H, m), 3.19 (1H, m), 3.35 (1H, m), 3.76 (1H, m), 3.89 (1H, m), 4.05 (2H, m), 7.01 (1H, br. d, J = 8.5 Hz), 7.08 (1H, br. d, J = 8.5 Hz), 7.20 (2H, m), 7.31 (3H, m), 7.42 (4H, m), 7.48–7.70 (8H, m), 7.52 (1H, d, J = 9.2 Hz), 7.77 (3H, m), 7.85 (1H, br. d, J = 8.2 Hz), 7.90 (2H, d, J = 8.9 Hz), 8.02 (1H, d, J = 9.0 Hz). – ^{31}P NMR: δ = 66.39 (d, J = 17.1 Hz), 67.97 (d, J = 17.1 Hz). – $[\alpha]_D^{20}$ = −87.7 (CH_2Cl_2). – $C_{48}H_{46}Cl_2O_2P_2Pd$ (894.2): calcd. C 64.48, H 5.19, P 6.93; found C 63.92, H 5.05, P 7.20.

(−)(*S*)-**6e** · **$PdCl_2$**: 50 mg (54%). – ^{1}H NMR: δ = 1.00–1.38 (11H, m), 1.42–1.59 (3H, m), 1.90 (2H, m), 2.41 (2H, m), 3.27 (2H, m), 3.80 (2H, m), 3.94 (1H, m), 4.07 (1H, m), 6.97 (1H, br. d, J = 8.5 Hz), 7.09 (1H, br. d, J = 8.5 Hz), 7.18 (2H, m), 7.21 (1H, d, J = 9.0 Hz), 7.31 (2H, m), 7.44 (4H, m), 7.51 (2H, m), 7.53 (1H, d, J = 9.1 Hz), 7.62 (4H, m), 7.71–7.90 (6H, m), 7.95 (1H, br. d, J = 7.8 Hz), 8.13 (1H, d, J = 9.1 Hz). – ^{31}P NMR: δ = 63.70 (d, J = 16.5 Hz), 64.25 (d, J = 16.5 Hz). – $[\alpha]_D^{20}$ = −83.5 (CH_2Cl_2). – $C_{50}H_{50}Cl_2O_2P_2Pd$ (922.2): calcd. C 65.12, H 5.46, P 6.72; found C 63.97, H 5.28, P 6.61.

X-Ray Analyses (see Table 3)[19]: Crystals were grown from CH_2Cl_2/Et_2O mixtures (ligands) or CH_2Cl_2/EtOH mixtures (complexes) by slow evaporation under argon.

6c*B*: Structure solution was carried out by means of direct methods followed by full-matrix least-squares refinement including anisotropic atomic displacement parameters (a.d.p.) for all non-hydrogen atoms against F^2. All data were used for refinement with no σ-cut-off being applied. Positions of hydrogen atoms were calculated according to stereochemical aspects and isotropic a.d.p.'s were fixed at a value of 0.08.

6d · **$NiCl_2$***B*: Procedure as above. Because of the poor data-to-parameters ratio several restraints were applied. Both chemical equal parts of the molecule were assumed to have the same 1,2 and 1,3 distances with σ = 0.03. The same procedure was applied to both halves of both phenyl groups. In addition, a "rigid bond" restraint was imposed on all atoms, forcing the components of the a.d.p.'s in the direction of a bond to be similar with an effective standard deviation 0.01.

6e · **$NiCl_2$***A*: Procedure as for **6c***B*. An ethanol molecule was found to be disordered and some dummy atoms were introduced to account for the residual electron density. For these atoms isotropic a.d.p.'s were refined. An extinction correction was applied.

6e*B*: Procedure as for **6c***B*, and the same restraints as in the case of **6d** · **$NiCl_2$***B* were applied.

6e · **$NiCl_2$***B*: Procedure as for **6c***B*.

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[17] In several cases, **6b**, **6d**, **6e**, **6b** · **$PdCl_2$**, **6c** · **$PdCl_2$**, and **6d** · **$PdCl_2$**, the C elemental analyses failed to give acceptible results (0.5–1.2% too low). Even prolonged drying (1–2 days) at elevated temperature (80–140°C) in vacuo (0.01 Torr) did not improve the results significantly. We suspect that the inclusion of CH_2Cl_2 from the column chromatography (ligands) or from the preparation (Pd complexes) was responsible for this problem. This assumption was further supported as some CH_2Cl_2 was detected in the ^{1}H-NMR spectrum, and disordered solvent molecules were observed in X-ray structure analyses.

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