102. Axially Dissymmetric Bis(triaryl)phosphines in the Biphenyl Series: Synthesis of (6,6'-Dimethylbiphenyl-2,2'-diyl)bis(diphenylphosphine) ('BIPHEMP') and Analogues, and their Use in Rh(I)-Catalyzed Asymmetric Isomerizations of *N,N*-Diethylnerylamine

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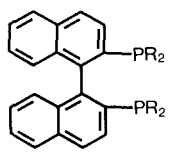
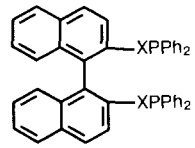
The axially dissymmetric diphosphines (–)-(*R*)- and (+)-(*S*)-(6,6'-dimethylbiphenyl-2,2'-diyl)bis(diphenylphosphine) ((–)-(*R*)-**10** and (+)-(*S*)-**10**; 'BIPHEMP') have been synthesized, starting from (*R*)- and (*S*)-6,6'-dimethylbiphenyl-2,2'-diamine ((*R*)- and (*S*)-**16**), respectively, *via Sandmeyer* reaction, lithiation, and phosphinylation. Moreover, racemic 4,4'-dimethyl- and 4,4'-bis(dimethylamino)-substituted analogues **11** and **12**, respectively, and the 6,6'-bridged analogue 1,11-bis(diphenylphosphino)-5,7-dihydrodibenz[*c,e*]oxepin (**13**) were synthesized and resolved into optically pure (*R*)- and (*S*)-enantiomers *via* complexation with di-μ-chlorobis{(*R*)-2-[1-(dimethylamino)ethyl]phenyl-*C,N*}dipalladium(II) ((*R*)-**18**). The molecular structures of the diphosphines (*S*)-**10** and (*R*)-**13** and of two derived cationic Rh(I) complexes, [Rh((*S*)-**10**)(nbd)]BF_4 and [Rh((*R*)-**13**)(nbd)]BF_4 were determined by X-ray analyses. Absolute configurations were established for (+)-(*S*)-**10** by X-ray analyses of both the free diphosphine and of the derived Rh(I) complex, and for (–)-(*R*)-**13** by X-ray analysis of the derived Rh(I) complex. Configurational assignments for the substituted BIPHEMP analogues **11** and **12** were achieved by means of ^{1}H-NMR comparisons of the Pd(II) complexes derived from the diphosphines and (*R*)-**18**, and by means of CD comparisons. The BIPHEMP ligand **10** and analogues **11**, **12**, and **13** are the first examples of optically active bis(triarylphosphines) containing the axially dissymmetric biphenyl moiety. All these new diphosphines proved to be excellent asymmetry-inducing ligands in Rh(I)-catalyzed isomerizations of *N,N*-diethylnerylamine affording citronellal enamine of 98–99% ee.

1. Introduction. – The axially dissymmetric 1,1'-binaphthyl moiety has proved to be a highly efficient asymmetry-inducing unit which displays generally very marked chiral recognition properties (*cf.* [1] and lit. cit. therein). Several diphosphines containing this chiral moiety have been reported: (*R*)- and (*S*)-**1a–c** [2], (*S*)-**2** [3], (*R*)- and (*S*)-**3** [4], (*R*)-**4** [4], (*S*)-**5a** [5a], and (*S*)-**5b** [5b]. Among them, the diphosphine **1a** ('BINAP') was found to be a particularly effective ligand in Rh(I)-catalyzed asymmetric hydrogenations of α-(acylamino)acrylic acids [2a], Rh(I)-catalyzed enantioselective (1,3)-H-shift reactions of allylamines such as *e.g. N,N*-diethylgeranyl- and *N,N*-diethylnerylamine [6], and, more recently, also in Ru(II)-catalyzed hydrogenations of isoquinoline-alkaloid precursors [7], allylic alcohols [8], unsaturated acids [9], and β-keto esters [10]. Axially dissymmetric biphenyl derivatives, in contrast to the binaphthyl derivatives, have found as yet much less attention (see [11] and lit. therein)[1]). A single optically active diphosphine has been reported so far in this series, *viz.* the aminophosphine **6** [12]. Furthermore, the

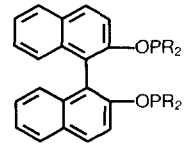
[1]) For example, enantioselective reductions of prochiral ketones with 2,2'-diamino-6,6'-dimethylbiphenyl-derived aluminium hydride complex [11a] or 2,2'-dihydroxy-6,6'-dimethylbiphenyl-derived amine-borane complex [11b].



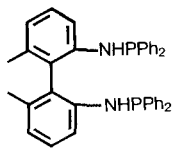
1a R = Ph ('BINAP')
b R = *p*-Me–C_6H_4
c R = *p*-Me_3C–C_6H_4



2 X = CH_2
3 X = NH
4 X = NMe



5a R = Ph
b R = 3,5-$(Me_3Si)_2C_6H_3$



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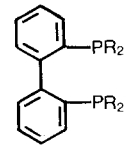
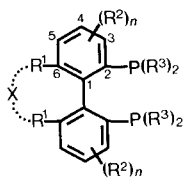


7 R = Ph
8 R = Me
9 R = Et



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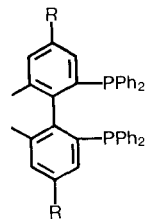
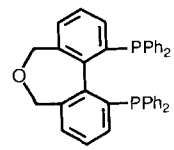


10 R = H ('BIPHEMP')
11 R = Me
12 R = NMe_2



13

diphosphines **7** [13], **8** [14], and **9** [15] have been reported, and cationic Rh(I) complexes of **7** have been resolved *via* diastereoisomeric salts using (+)-3-bromocamphor-10-sulfonate as optically active counterion [13a].

Some time ago, we started a project to synthesize axially dissymmetric biphenylylene diphosphines of type **I**. These chiral compounds, like the structurally related BINAP diphosphines, have a two-fold symmetry axis and, since the biphenyl group, like the binaphthyl group, is not completely rigid, they may form a variety of stable chelate complexes with many transition metals (*cf.* [16]). The biphenyl system has certain unique characteristics which allow one to make subtle alterations in its geometric, steric, and electronic properties. The preliminary substitution of the 6,6′-positions was deemed necessary to warrant sufficient thermal stability to thermal racemization[2]). By varying the steric bulk of the 6,6′-substituents, one might control the minimal dihedral angle of the biphenyl moiety. On the other hand, bridging the 6,6′-positions, *e.g. via* a 7- or 8-membered ring, would hold the dihedral angle within a limited range, thus restricting torsional mobility and introducing additional rigidity. Furthermore, bridging might allow one to prepare diphosphines suitable for polymer attachment, *e.g.* through an N-atom in the

[2]) Optically active, 2,2′-disubstituted biphenyl derivatives bearing no 6,6′-substituents are generally prone to racemization (*cf. e.g.* [17]). On the other hand, an activation energy of 45.1 kcal/mol has been reported, for instance, for the racemization of 2,2′-diamino-6,6′-dimethylbiphenyl [18]. In this context, it obviously would be of interest to learn about the ease of racemization of diphosphine **7** [13].

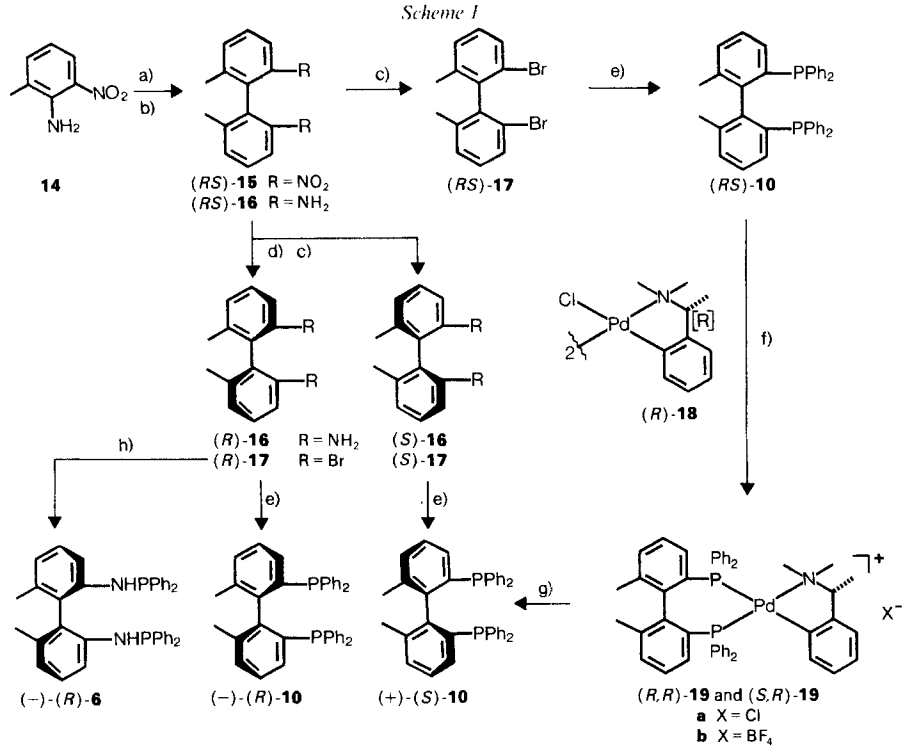
central position of a 7-membered ring. Moreover, the 'fine-tuning' of the basicity of the phosphine groups *via* introduction of electron-donating or electron-withdrawing substituents in the biaryl system appears to be easier to achieve in the biphenyl series as compared to the binaphthyl series. In this regard, we expected to rely on the highly advanced chemistry of atropisomeric biphenyl derivatives which has mainly been developed by *Mislow* and coworkers [19].

We report in this paper the synthesis of the parent diphosphine within this class, the 6,6′-dimethyl-substituted diphosphine **10**, for which the acronym BIPHEMP has been chosen, and the synthesis of the 4,4′-disubstituted analogues **11** and **12**, and the bridged analogue **13** [20]. Moreover, we describe the successful application of these diphosphines in the Rh(I)-catalyzed allylic isomerization of *N*,*N*-diethylnerylamine [6]. After completion of this work [20], *Frejd* and coworkers [21] published the X-ray structure of the cationic Rh(I) complex [Rh((*R*)-**10**)(nbd)]BF_4 (nbd = 8,9,10-trinorborna-2,5-diene). These authors have independently prepared the BIPHEMP ligand **10**, and they used the acronym 'dimep' for this ligand.

2. Diphosphine Syntheses. – The first synthesis of the optically active parent diphosphines **10** (BIPHEMP) relied on the diphosphine-resolution method developed by *Otsuka et al.* [22], and *Roberts* and *Wild* [23] which is based on the use of the chiral Pd(II)-amine complex (*R*)-**18** as resolving agent *(Scheme 1)*. The racemic diphosphine (*RS*)-**10** was synthesized by standard procedures. Starting from 6-methyl-2-nitroaniline (**14**), racemic biphenyldiamine (*RS*)-**16** was prepared in an overall yield of 67% (crude) or 55% (recrystallized) by means of diazotization/iodination, *Ullmann* coupling, and catalytic hydrogenation [24] (*cf.* also [11a] [12]). Diamine (*RS*)-**16** then was converted by *Sandmeyer* reaction [25] (*cf.* [19e]) into dibromide (*RS*)-**17** [25]. This conversion was complicated by side-reactions such as reduction (to afford 6-bromo-2,2′-dimethylbiphenyl and 2,2′-dimethylbiphenyl), hydrolysis (to afford 2-bromo-2′-hydroxy-6,6′-dimethylbiphenyl), and formation of tribromides of unknown structure; yields of dibromide (*RS*)-**17** amount, therefore, to only about 35%. Dilithiation of (*RS*)-**17** followed by reaction with Ph_2PCl (*cf.* [2a]) then afforded 73% of (*RS*)-**10**, m.p. 242–243°. Treatment of a methanolic solution of (*RS*)-**10** with 0.5 mol-equiv. of dimeric Pd(II) complex (*R*)-**18** followed by addition of aq. NH_4BF_4 solution (*cf.* [23]) led to a mixture of diastereoisomers (*R*,*R*)-**19b** and (*S*,*R*)-**19b** in 90% yield, which was separated by fractional crystallization from CH_2Cl_2/Et_2O to afford the less soluble diastereoisomer (*R*,*R*)-**19b** and the more soluble diastereoisomer (*S*,*R*)-**19b** in yields of 53% and 56% of theory, respectively. Finally, reductive degradation of each of the diastereoisomers with $LiAlH_4$ (*cf.* [2a]) produced (*R*)-**10** and (*S*)-**10**. For instance, pure (*R*)-**10**, m.p. 210–212.5°, $[\alpha]_D^{20} = -42.7°$ (c = 1.0, $CHCl_3$), was obtained in 20–46% yield.

While this route led to the optically pure diphosphines **10** for the first time, it clearly suffered from being inexpedient. Therefore, an improved synthesis was developed based on the known resolution [24c,d] (*cf.* [11a] [12]) of (*RS*)-**16**. The resolution was carried out according to *Meisenheimer* and *Höring*'s procedure [24c] using (*R*,*R*)- and (*S*,*S*)-tartaric acid, respectively. To achieve high optical purities, it proved necessary to repeatedly recrystallize the tartrate salts (1:1 salts of **16** and tartaric acid according to ^{1}H-NMR measurements) as well as the free bases after decomposition of the salts. Results of some of these resolutions are summarized in the *Exper. Part (cf. Table 5)*. Optical purities (op) of the resolved diamines **16** were determined by optical rotation and enantiomeric

Scheme 1



a) $NaNO_2$, HCl, KI; then Cu powder, 180–230° [24b]; 67% of (*RS*)-**15**. b) H_2, Pd/C, AcOH (*cf.* [24d]); 100% (crude) or 83% (recryst.) of (*RS*)-**16**; overall yield **14**→(*RS*)-**16** 67% (crude) or 55% (recryst.). c) $NaNO_2$, HBr, CuBr, 70–75° (*cf.* [19e]); 34.5% of (*RS*)-**17** [25] *ex* (*RS*)-**16**; 32% of (*R*)-**17** [19e] *ex* (*R*)-**16**; 30.5% of (*S*)-**17** [25c] *ex* (*S*)-**16**. d) Resolution with (*R*,*R*)-tartaric acid [24c], 21–23% of th. of (*R*)-**16**; resolution with (*S*,*S*)-tartaric acid [24c], 18–23% of th. of (*S*)-**16**. e) 4 mol-equiv. *t*-BuLi, Et_2O, −110° to −95°, then 2 mol-equiv. Ph_2PCl, −100° to r.t. (*cf.* [2a]); 73% of (*RS*)-**10** *ex* (*RS*)-**17**; 52% of (*R*)-**10** *ex* (*R*)-**17**; 51.5% of (*S*)-**10** *ex* (*S*)-**17**. f) 0.5 mol-equiv. (*R*)-**18**, aq. NH_4BF_4 (*cf.* [23]); fract. cryst.; 53% of th. of (*R*,*R*)-**19b** and 56% of th. of (*S*,*R*)-**19b**. g) $LiAlH_4$, Et_2O (*cf.* [2a]); 20–46% of (*R*)-**10** *ex* (*R*,*R*)-**19b**. h) 2 mol-equiv. BuLi, THF, 2 mol-equiv. Ph_2PCl, − 30° to r.t.; 90% of (*R*)-**6** [12].

purities (ee) by ^{1}H-NMR spectroscopy in presence of Eu(hfc)$_3$[3]). A sample of (*R*)-**16** (ee 99% according to ^{1}H-NMR) showed $[\alpha]_D^{20} = -39.16°$ (*c* = 1.0, 1N HCl), and likewise, a sample of (*S*)-**16** (ee 96% according to ^{1}H-NMR) had $[\alpha]_D^{20} = +37.8°$ (*c* = 1.0, 1N HCl). Thus, $[\alpha]_D^{20} = 39.3–39.6°$ (*c* = 1.0, 1N HCl) may be assigned to optically pure **16**. This value is substantially higher than reported specific rotations[4]).

The conversion of (*R*)-**16** (op 98%) and (*S*)-**16** (op 96.5%) by *Sandmeyer* reaction (*cf.* [19e]) into the optically active dibromides afforded 32% of (*R*)-**17** and 31% of (*S*)-**17**.

[3]) 'Tris[3-(heptafluoropropyl-hydroxymethylidene)-*d*-camphorato]europium'.

[4]) In the literature, the following $[\alpha]_D^{20}$ values were quoted for the 'optically pure' diamine (*R*)-**16**: −34.8° (*c* = 1.0, 1N HCl) [24c]; −34.8° (*c* = 1.0, 0.3N HCl) [24d]; −35° (*c* = 3.5, 1N HCl) [19d]; −36° (*c* = 2.0, 2N HCl) [26]; −37.3° (*c* = 1.05, 1N HCl) [11a]. It should be noted that rotations measured in acidic solution refer to protonated forms (*cf.* [19d]), and that the free bases, measured in organic solvents, exhibit opposite signs of rotation, *e.g.* $[\alpha]_D^{20} = +49°$ (*c* = 1.52, EtOH) for (*R*)-**16** [19d]. It should also be emphasized that the notations (+)-(*R*)-**16** and (−)-(*S*)-**16** used by *Mislow* and coworkers [19d] refer to the solvent EtOH.

These dibromides showed $[\alpha]_D^{20}$ of +11.6° and −11.7° (c = 1.0, EtOH), respectively, in agreement with the reported values [19e]. Further conversion into the diphosphines **10** was carried out as described above in the racemic series to afford *ca.* 65% of optically active diphosphines **10**. These materials were clearly not optically pure; but separation of the racemic part, which proved to be largely insoluble in Et_2O or AcOEt, was readily achieved *via* fractional crystallization. In this way, starting from (*R*)-**17** we obtained 51.5% of (*R*)-**10** (m.p. 212–213°, $[\alpha]_D^{20} = -43.1°$ (c = 1.0, $CHCl_3$)) and 15% of (*RS*)-**10** (m.p. 242–243°). Likewise, in the (*S*)-series 56% of (*S*)-**10** (m.p. 212–213°, $[\alpha]_D^{20} = +41.7°$ (c = 1.0, $CHCl_3$)) and 10% of (*RS*)-**10** were obtained.

Obviously, racemization to an extent of at least 10–15% had occurred in the two-step conversion of the diamines into the diphosphines. The double *Sandmeyer* reaction **16**→**17** has been reported to proceed without significant racemization [19e], yet the observation that the specific rotation of **17** may be increased by recrystallization suggests that some racemization in fact occurs. Thus, for instance, twofold recrystallization of (*R*)-**17** of $[\alpha]_D^{20} = +11.7°$ (c = 0.6, EtOH) obtained from (*R*)-**16** of 98% op led to an increase of $[\alpha]_D^{20}$ to +12.4° (c = 0.6, EtOH), indicating that the dibromides **17** obtained in the *Sandmeyer* reaction and carried through the further synthesis were 94% optically pure at most. Hence, at least 4% racemization took place in the *Sandmeyer* reaction. Since this still would account for only about half of the 10–15% racemization observed in the conversion **16**→**17**→**18**, we cannot exclude the possibility of some racemization also in the lithiation/phosphinylation step[5])[6]).

Clearly, the synthesis of the BIPHEMP ligand is hampered by the partial racemization, but, because of the solubility differences, the optically active diphosphines **10** may still be prepared in a quite efficient manner. The ee values of the diphosphines obtained by crystallization were shown to be 96–98% by ^{1}H-NMR of the derived Pd(II) complexes **19a** *(vide infra)*.

The diphosphines **10** are air-stable, white crystalline solids. Solutions of **10** turned out to be slightly sensitive towards oxidation, but chromatography without exclusion of air led to rapid oxidation to mixtures of the corresponding mono- and bis(phosphinoxides) (**10**-monoxide, **10**-bis-oxide). The presence of any oxidized material in the diphosphines **10** is easily recognized by ^{1}H-NMR through the characteristic absorptions of the Me groups at 1.37 ppm for **10**, 1.49 and 1.24 ppm for **10**-monoxide, and 1.43 ppm for **10**-bis-oxide. These rather unusual high-field absorptions of the *Me*-Ph groups are probably due to ring-current shielding by adjacent Ph rings[7]).

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[5]) *Frejd* and *Klingenstedt* [27] have recently shown that optically active 2,2′-dilithio-6,6′-dimethylbiphenyl (prepared by lithiation with BuLi of the corresponding diiodide) is configurationally stable at −10° for at least 20 min. While this renders unlikely the occurrence of racemization in our case, it cannot be excluded entirely, since the actual reaction temperature required for the phosphinylation to take place remains unknown.

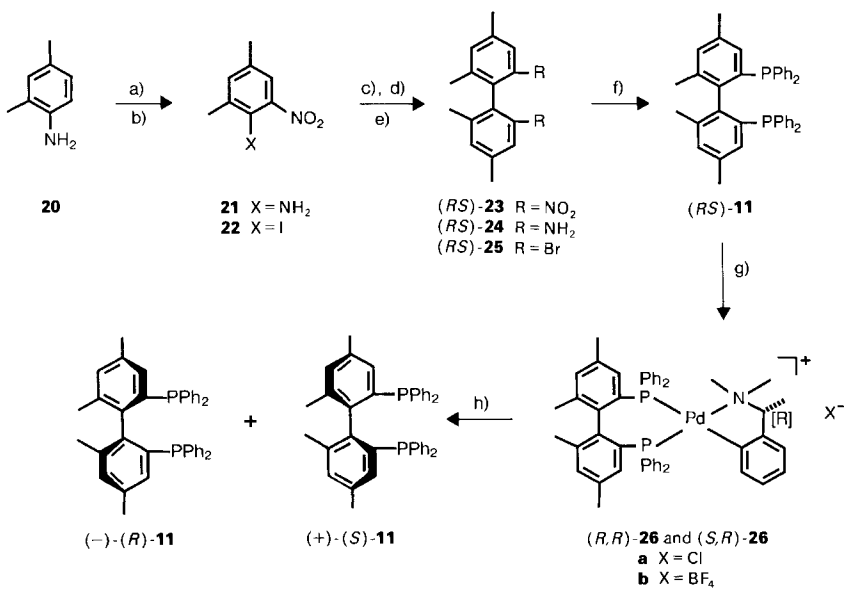
[6]) *Cf.* the investigations of *Brown* and *Murdoch* [28] on the configurational stability of 2,2′-dilithio-1,1′-binaphthyl.

[7]) Ring-current shielding of the Me protons in 2,2′-dimethylbiphenyls is known to be dependent on the interplanar angle, θ, of the biphenyl system. For instance, a chemical shift of 1.87 ppm (*i.e.* a maximal ring-current shift of *ca.* +0.45 ppm) is observed for 2,2′,4,4′,6,6′-hexamethylbiphenyl which is known to have θ close to 90° [29] (*cf.* also [19f]). Since the diphosphine **10**, by its X-ray analysis *(cf. Chapt. 5)*, also has $\theta \approx 90°$, one can expect a similar magnitude for the ring-current shift in **10**. This, however, still is not sufficient to explain the observed chemical shift of 1.37 ppm, and we assume that further shielding of the Me protons in **10** (and the derived mono- and bis-oxides) is exerted by adjacent P–Ph groups (*cf.* the stereographic view of the molecular structure of (*S*)-**10** in *Fig. 3*).

Having in hand the optically active diamines **16**, we have additionally prepared, *via* lithiation/phosphinylation of (*R*)-**16**, the bis(diphenylphosphinamino)biphenyl derivative (*R*)-**6**, m.p. 102–103°; $[\alpha]_D^{20} = -146.2°$ (*c* = 1.1, benzene). This bis(aminophosphine) had previously been synthesized by *Uehara et al.* [12] according to the same synthetic scheme, m.p. 98–100°, $[\alpha]_D^{20} = -140°$ (*c* = 1.0, benzene), but it had been wrongly assigned the (*S*)-configuration[8]).

The 4,4′-dimethyl- and 4,4′-bis(dimethylamino)-substituted BIPHEMP analogues **11** and **12**, respectively, and the bridged analogue **13** were synthesized utilizing again the resolution *via* the Pd-complex-salt method [22] [23] (*Schemes 2*, *3*, and *4*). Racemic diphosphine (*RS*)-**11** was prepared in analogy to (*RS*)-**10** starting from xylidine **20** *via* the sequence given in *Scheme 2*. Resolution of (*RS*)-**11** according to [23b] afforded, *via* sequential precipitation and crystallization, the individual diastereoisomers of Pd complex **26b** (75% of th. of the less soluble (*R*,*R*)-**26b**, 60% of th. of the more soluble (*S*,*R*)-**26b**). Degradation by acidolysis and decomplexation with CN^- ions in a two-phase system (HCl, acetone, 55°; then KCN, CH_2Cl_2/H_2O; *cf.* [23a]) then furnished 81% of (*R*)-**11** (m.p. 217–218°, $[\alpha]_D^{20} = -21.5°$ (*c* = 1.0, $CHCl_3$)) and 48% of (*S*)-**11** (m.p. 217.5–219°, $[\alpha]_D^{20} = +21.4°$ (*c* = 1.0, $CHCl_3$)).

Scheme 2



a) Ac_2O, HNO_3, then HCl; 75% of **21**. b) $NaNO_2$, H_2SO_4; KI; 65% of **22** [30a]. c) Cu powder, 190–230°; 50% of (*RS*)-**23** [30b]. d) H_2, Pd/C, AcOH; 82% of (*RS*)-**24** [31]. e) $NaNO_2$, HBr; CuBr, 70° (*cf.* [19e]); 24% of (*RS*)-**25**. f) 4 mol-equiv. *t*-BuLi, Et_2O, −90°; then 2 mol-equiv. Ph_2PCl, −90° to r.t.; 57% of (*RS*)-**11**. g) 0.5 mol-equiv. (*R*)-**18**, MeOH, aq. NH_4BF_4; 75% of th. of (*R*,*R*)-**26b** and 60% of th. of (*S*,*R*)-**26b**. h) HCl, acetone, then KCN, CH_2Cl_2/H_2O (*cf.* [23a]); 81% of (*R*)-**11** and 48% of (*S*)-**11**.

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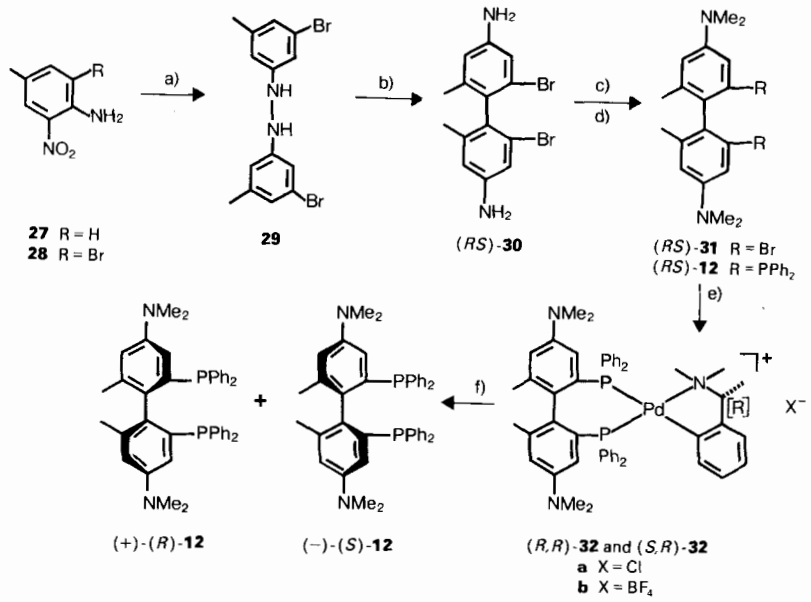
[8]) The erroneous assignment has to be traced back to confusing the relationship between configuration and sense of rotation of optically active diamine **16** (*cf. Footnote 4*). With the corrected absolute configuration of **6** the sense of enantioface differentiation in the Rh(I)-catalyzed asymmetric hydrogenation of α-(acetamido)acrylic acids is actually no longer opposite but the same for the ligand **6** and its binaphthyl analogue **3** (*cf.* [4b]).

Scheme 3



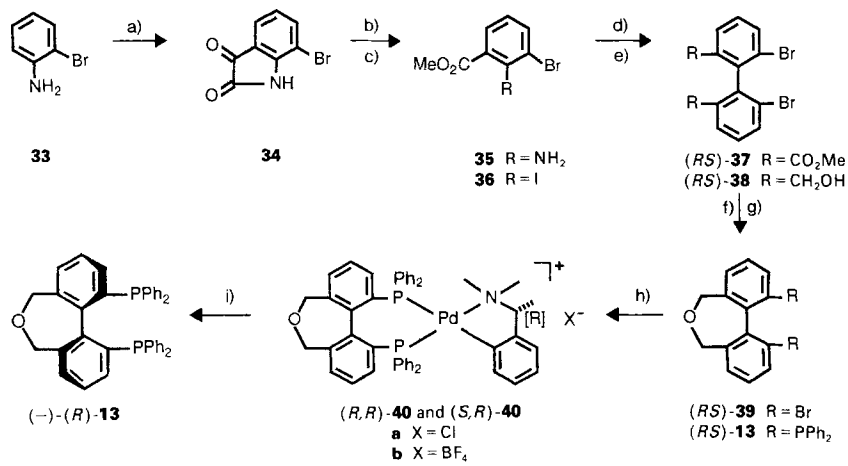
a) **27** → **28**: Br_2, AcOH; **28** → **29**: $NaNO_2$, H_2SO_4, EtOH; then Zn, NaOH, EtOH; 45% of **29** overall (*cf.* [32]). b) 25% HCl, 60° (*cf.* [33]); 88–96% of 2:1 mixture of (*RS*)-**30** and 2,4′-diamino-2′,6-dibromo-4,6′-dimethylbiphenyl (*cf.* [32]). c) CH_2O, CH_3CN, $NaBH_3CN$, AcOH (*cf.* [34]); 48% of (*RS*)-**31**. d) 4 mol-equiv. *t*-BuLi, Et_2O/THF 4:1, −75°; 2 mol-equiv. Ph_2PCl, −75° to r.t.; 72.5% of (*RS*)-**12**. e) 0.5 mol-equiv. (*R*)-**18**, MeOH-THF 5:2, aq. NH_4BF_4; 92% of th. of (*R*,*R*)-**32b** and 9% of th. of (*S*,*R*)-**32b**. f) $LiAlH_4$, THF (*cf.* [2a]); 67.5% of (*R*)-**12** and 58.5% of (*S*)-**12**.

Access into the series of 4,4′-diamino-substituted biphenyl derivatives was realized *via* the known benzidine rearrangement of hydrazobenzene **29** [32] which had been secured in 45% overall yield from 2-nitro-4-methylaniline (**27**) *via* bromination, deamination, and reductive dimerization [32] (*Scheme 3*). The benzidine rearrangement (25% HCl, 60°; cf. [33]) afforded 88–96% of a 2:1 mixture of benzidine (*RS*)-**30** and 2,4′-diamino-2′,6-dibromo-4,6′-dimethylbiphenyl which was difficult to separate (*cf.* [32])[9]). By methylation of the mixture (CH_2O, $NaBH_3CN$, AcOH [34]), pure tetramethylbenzidine (*RS*)-**31** was obtained in 48% yield. The usual lithiation/phosphinylation procedure then furnished (*RS*)-**12** in 72.5% yield which again was resolved *via* the diastereoisomeric Pd complexes **32b** (92% of th. of (*R*,*R*)-**32b**) and subsequent reductive degradation with $LiAlH_4$ (*cf.* [2a]) to afford (*R*)-**12** (67%, m.p. 184–185°, $[\alpha]_D^{20} = +25.4°$ ($c = 1.0$, $CHCl_3$)) and (*S*)-**12** (58%, m.p. 184–185°, $[\alpha]_D^{20} = -26.3°$ ($c = 1.0$, $CHCl_3$)).

The bridged BIPHEMP analogue **13** was synthesized as depicted in *Scheme 4*. An *Ullmann* coupling served again to prepare the biphenyl system. The required coupling substrate **36** was secured, starting from 2-bromoaniline, by standard isatin (= *1*H-*indole*-

[9]) Pure **30** can be obtained from the mixture *via* crystallization of the salt with (*R*,*R*)-tartaric acid. Only very little optical enrichment takes place in this purification as was shown by diazotization/dediazoniation ($NaNO_2$, HCl; H_3PO_2) to yield almost racemic **17**. A resolution at the benzidine stage obviously might constitute an advantageous access into the optically active biphenyl series.

Scheme 4



a) Cl_3CCHO, $NH_2OH \cdot HCl$, H_2O, 37–70°/60 h; then 90% H_2SO_4, 60° (*cf.* [35]); 65–72% of **34** [36]. b) MeOH, NaOMe, H_2O_2; 0° – r.t. (*cf.* [37]); 60% of **35** [38]. c) $NaNO_2$, H_2SO_4; KI; 84% of **36**. d) Cu powder, 160–170°; 81% of (*RS*)-**37**. e) $LiAlH_4$, THF; 84.5% of (*RS*)-**38**. f) TsOH, toluene, reflux; 85% of (*RS*)-**39**. g) 4 mol-equiv. *t*-BuLi, THF/Et_2O 1:1, −110° to −100°; then 2 mol-equiv. Ph_2PCl, −110° to r.t.; 35% of (*RS*)-**13**. h) 0.5 mol-equiv. (*R*)-**18**, MeOH; aq. NH_4BF_4; 86% of (*R*, *R*)-**40b**, 104% of (*S*, *R*)-**40b** of 80% d.e. i) CF_3CO_2H, acetone; then KCN, CH_2Cl_2/H_2O; 87.5% of (*R*)-**13** *ex* (*R*, *R*)-**40b**.

2,3-dione) synthesis (*cf.* [35]; 65–72% of 7-bromo-1*H*-indole-2,3-dione (**34**) [36]) followed by oxidative ring scission (*cf.* [37]; 60% of **35** [38]), and diazotization/iodination (84% of **36**). Coupling, then, afforded 81% of dibromodiphenate (*RS*)-**37**[10]) which in turn was converted by hydride reduction (84.5% of (*RS*)-**38**) and acid-catalyzed cyclic-ether formation into dibromodibenzoxepine (*RS*)-**39** (85% yield, 21% overall yield based on **33**). The lithiation/phosphinylation sequence (*cf.* [2a]) was accompanied by side-reactions and afforded a yield of only 35% of (*RS*)-**13**. Diastereoisomerically pure Pd complex (*R*, *R*)-**40b** (86% of th.) was then obtained in the usual way [23a], while diastereoisomer (*S*, *R*)-**40b** could not be obtained in a diastereoisomeric purity higher than 80%. A modified version for the degradation of **40b** had to be developed, since both the hydride treatment as well as the HCl acidolysis/decomplexation procedure failed to produce the free diphosphine ligand, presumably due to the sensitivity of the dibenzoxepine-ether moiety. Eventually, CF_3COOH treatment proved to be mild enough to convert **40b** into a presumable (diphosphine)bis(trifluoroacetato)Pd(II) complex which then was subjected to KCN treatment to liberate the diphosphine. In this way, optically pure (*R*)-**13** (m.p. 197.5–199°, $[\alpha]_D^{20} = -396.6°$ (*c* = 1.0, $CHCl_3$)) was obtained in 87.5% yield starting from (*R*, *R*)-**40b**.

3. Absolute Configurations and Enantiomeric Purities of the Diphosphines. – Absolute configurations of (−)-(*R*)-**10** and (+)-(*S*)-**10** are defined by the synthetic pathway *via* the optically active diamines (*R*)-**16** and (*S*)-**16** *(Scheme 1)*. The absolute configuration of (+)-(*S*)-**10** was independently determined by X-ray analyses of (+)-(*S*)-**10** itself and of

[10]) *Cf.* the syntheses of the corresponding diiodo [35b], dichloro [39], and difluoro [40] analogues.

Table 1. *Selected ^{1}H-NMR Data*[a]) *of Pd Complexes* **19**, **26**, **32**, *and* **40**

Phosphine	Pd complex	NC*H*-Me	NCH-*Me*	N-Me_a	N-Me_b	6,6′-Me[b])	
(*R*)-**10**	(*R,R*)-**19b**	5.25 (*q*, *J* = 6.5)	1.27 (*d*, *J* = 7)	1.28 (br. *s*)	2.54 (*dd*, *J* = 3.5, 3.5)	1.015	1.56
(*R*)-**11**	(*R,R*)-**26b**	5.3 (*q*, *J* = 7)	1.27 (*d*, *J* = 6.5)	1.29 (br. *s*)	2.53 (*m*)	1.00	1.51
(*R*)-**12**	(*R,R*)-**32b**	5.24 (*q*, *J* = 6.5)	1.29 (*d*, *J* = 6.5)	1.34 (*m*)	2.54 (*m*)	1.03	1.54
(*R*)-**13**	(*R,R*)-**40b**	5.50 (*q*, *J* = 6.5)	1.33 (*d*, *J* = 6.5)	1.58 (*m*)	2.64 (*m*)		
(*S*)-**10**	(*S,R*)-**19b**	3.45 (~ *quint.*, 6)	2.21 (*d*, *J* = 6.5)	1.70 (*d*, *J* = 2)	2.14 (*dd*, *J* = 3.5, 3.5)	1.06	1.65
(*S*)-**11**	(*S,R*)-**26b**	3.46 (*m*)	2.21 (*d*, *J* = 6.5)	1.72 (*m*)	2.11 (*m*)	1.05	1.57
(*S*)-**12**	(*S,R*)-**32b**	3.45 (*m*)	2.21 (*d*, *J* = 6.5)	1.70 (*m*)	2.16 (*m*)	1.045	1.63
(*S*)-**13**	(*S,R*)-**40b**	3.59 (~ *quint.*, 6)	2.30 (*d*, *J* = 6.5)	2.0 (*m*)	2.20 (*m*)		

[a]) In $CDCl_3$, at 270 MHz (**26b**, **32b**, **40b**) or at 400 MHz (**19b**); chemical shifts [ppm] relative to TMS (= 0), *J* in Hz.
[b]) *Singulet* signals.

the derived cationic Rh(I) complex [Rh((*S*)-**10**)(nbd)]BF_4 *(vide infra)*. Assignments of the absolute configurations of the analogues **11**, **12**, and **13** are based on comparisons of the ^{1}H-NMR properties within the series of the Pd complexes **19b**, **26b**, **32b**, and **40b** *(cf. Table 1)*. Thus, the individual, less soluble diastereoisomers in this series display a characteristic low-field quadruplet absorption at 5.2–5.5 ppm for NC*H*–Me of the (*R*)-*N*,*N*-dimethyl-1-phenylethylamine moiety. In the series of the more soluble diastereoisomers, this signal is observed at 3.45–3.6 ppm, *i.e.* in the normal ppm range. In turn, the chemical shift of the NCH-*Me* group is normal within the series of the less soluble diastereoisomers (*ca.* 1.3 ppm) but low-field (2.2–2.3 ppm) within the series of the more soluble diastereoisomers[11]). Similarly, the NMe_2 groups absorb at ppm ranges which are consistent and characteristic within the same series of Pd complexes. Consequently, based on the known configurational relationship between the parent diphosphines **10** and the derived Pd complexes **19b**, we assign the (*R*,*R*)-configuration to the series of the less soluble and the (*S*,*R*)-configuration to the series of the more soluble diastereoisomers. A confirmation of these assignments was obtained by X-ray analysis of [Rh((*R*)-**13**)(nbd)]-BF_4 *(vide infra)*.

Enantiomeric purities of the diphosphines were determined by NMR measurements of the derived Pd complexes **19a**, **26a**, **32a**, or **40a** according to the method developed by *Kyba* and *Rines* [41]. Thus, the diastereoisomeric purity of the Pd complexes formed *in situ* by dissolving in $CDCl_3$ the diphosphine and 0.5 mol-equiv. of Pd reagent (*R*)-**18** *(Scheme 1)* were analyzed by ^{1}H-NMR (270 or 400 MHz) or ^{31}P-NMR measurements. The very sharp ^{1}H-NMR *singulet* absorptions of the 6,6′-Me groups *(cf. Table 1)* served particularly well to quantify the diastereoisomeric ratio allowing one to detect the presence of the minor diastereoisomer in amounts as low as 0.5%. ^{31}P-NMR measurements, on the other hand, proved also suitable but were less sensitive. Using this ^{1}H-NMR analysis, the enantiomeric purities of the diphosphines **10**, obtained *via* resolution at the diamine stage, were determined to be in the range of 96–97.5% after a single crystallization.

4. Chiroptical Properties. – CD Spectra of the diphosphines in ethanolic solutions are represented in *Fig. 1*. Excellent mirror-image curves are observed for the enantiomers of both of the diphosphines **10** and **11**. The shape of the CD curves for **10** and **11** are as

[11]) Presumably, deshielding effects of the aromatic ring belonging to the 'benzpalladazole' system on the CH or the CH_3 group are responsible for the observed low-field displacements.

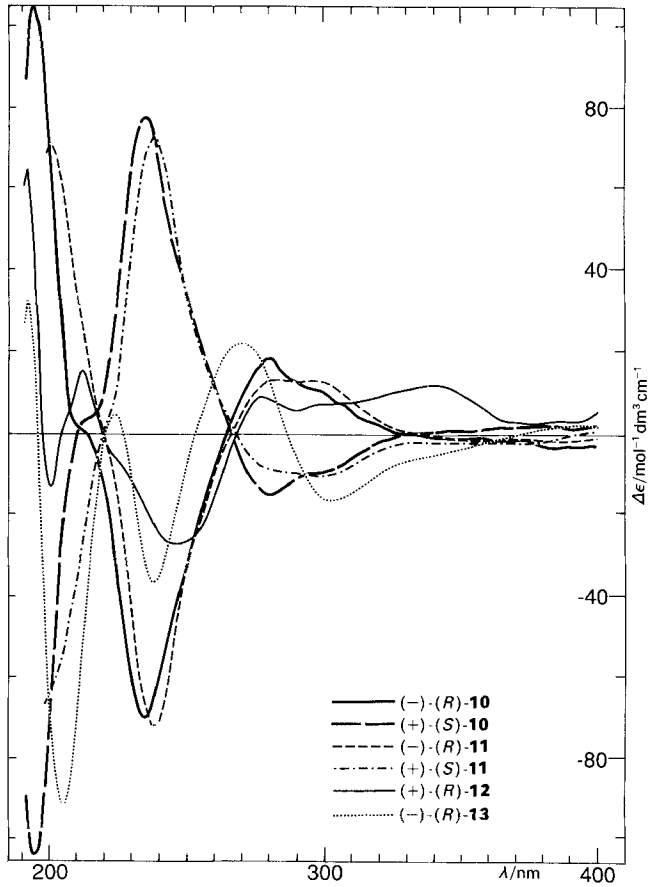


Fig. 1. *CD spectra of diphosphines* **10**–**13** *in EtOH*

expected nearly identical. All the diphosphines **10**–**13** exhibit strong maxima in the regions of 190–200 and 235–250 nm and a weaker long-wavelength maximum in the region of 270–280 nm. Additional maxima at 201, 212, and 341 nm are observed for the bis(dimethylamino) compound **12**, while the bridged diphosphine **13** displays additional maxima at 205, 223, and 303 nm. The signs of the major cotton effects (CE) within the series of (*R*)-configurated diphosphines were found to be positive for the short-wavelength CE (190–200 nm), negative for the 235–250 nm CE, and positive for the long-wavelength CE around 270–280 nm[12]).

Since chiral bis(diphenyl)diphosphines such as DIOP, CHIRAPHOS, NORPHOS, or BPPM show no or only very weak CE's in the 235–250 nm region[13]), the observed strong CE's in BIPHEMP and its analogues in this region can be attributed to the phosphino-substituted twisted biphenyl system. The long-wavelength CE and the CE at 235 nm of

[12]) The BINAP ligand (*R*)-**1a** shows major CE's at *ca.* 216 nm (negative), 231 nm (positive), and 243 nm (negative) (*cf.* [2d]).

[13]) Measurements in EtOH at r.t.

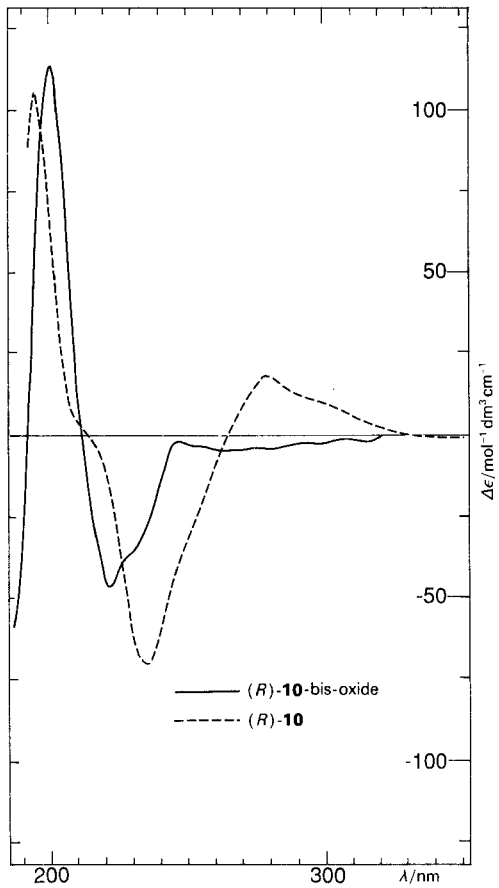


Fig. 2. *CD spectra of* (R)-**10** *and* (R)-**10**-*bis-oxide in EtOH*

BIPHEMP are strongly effected by oxidation of BIPHEMP to the corresponding bis-(phosphinoxide) *(cf. Fig. 2)*.

On the other hand, the X-ray structure analysis of (*S*)-BIPHEMP *(cf. Fig. 3)* shows that the two Ph moieties of the biphenyl part are oriented perpendicularly to each other (interplanar angle θ between least-squares planes 88.7°), and that the lone pair of the pyramidal P-atom lies nearly in the plane of the Ph ring of the biphenyl system to which the P-atom is bonded. This signifies that neither biphenyl conjugation nor conjugation of the P-atom to the Ph ring of the biphenyl systems can play a dominant role. Therefore, we suppose that the long-wavelength CE's of BIPHEMP and its analogues may be attributed to CT transitions of the diphenyl-phosphino moiety with the remote Ph ring of the biphenyl system which is suitably oriented for such interactions *(cf. Fig. 3)*.

5. Synthesis of Rh(I) Complexes of the Diphosphines. – To test the new diphosphines in asymmetric hydrogenations and isomerizations and to compare their efficacy with that of the BINAP ligand **1a** in these reactions (*cf.* [2a] [6]), we have synthesized

several cationic Rh(I) complexes of the type [Rh(P⌒P)(diene)]X[14]). Complexes [Rh(P⌒P)(nbd)]BF_4[14]) (P⌒P = (*R*)-**10**, (*S*)-**10**, (*R*)-**11**, (*S*)-**11**, (*R*)-**13**) were prepared in 67–91% yield according to the method of *Schrock* and *Osborn* [42] (treatment of $[Rh(nbd)Cl]_2$ with the diphosphine in MeOH followed by precipitation with an aqueous solution of $NaBF_4$). The complexes [Rh(P⌒P)(cod)]BF_4[14]) (P⌒P = (*R*)-**10**, (*S*)-**10**, (*R*)-**11**, (*R*)-**12**, (*R*)-**13**) and [Rh(P⌒P)(cod)]ClO_4(P⌒P = (*R*)-**10**, (*S*)-**10**) were prepared using the Ag salt method [42c] ($[Rh(cod)Cl]_2$, $AgBF_4$ or $AgClO_4$, THF; P⌒P) in yields of 70–88%. All these complexes proved to be fairly air-stable, yellow-to-orange microcrystalline solids. The nbd complexes could be readily recrystallized from MeOH to afford dark-red coarse crystals. Most of the complexes tend to retain solvent molecules; the nbd complexes usually contained *ca.* 20 mol-% of MeOH and/or H_2O, while the cod perchlorate complexes contained *ca.* 1 mol-equiv. of H_2O, and the cod tetrafluoroborate complexes up to 1.0 mol-equiv. of THF. Specific rotations of the complexes proved to be rather unreliable; thus, the nbd complexes derived from (*R*)- or (*S*)-**10** of ee $\geq$ 96% displayed $|[\alpha]_D^{20}|$ of 26.2–35.9° (*c* = 0.5, $CHCl_3$), and the cod perchlorate complexes even exhibited time-dependent specific rotations, presumably due to ligand exchange *(cf. Exper. Part)*.

6. X-Ray Analyses. – Single-crystal X-ray analyses[15]) have been carried out for (*S*)-**10**, (*R*)-**13**, and the derived cationic Rh(I) complexes [Rh((*S*)-**10**)(nbd)]BF_4 and [Rh((*R*)-**13**)(nbd)]BF_4. Stereoscopic drawings of the free ligands and of the cationic moieties of the Rh complexes are presented in *Figs. 3–6*, and perspective ORTEP diagrams including the atomic numbering schemes of the cationic moieties of the Rh complexes are provided in *Figs. 7* and *8*[16]). Selected interatomic distances, bond and torsion angles, and interplanar angles (angles between least-squares planes) are compiled in *Tables 2* and *3*.

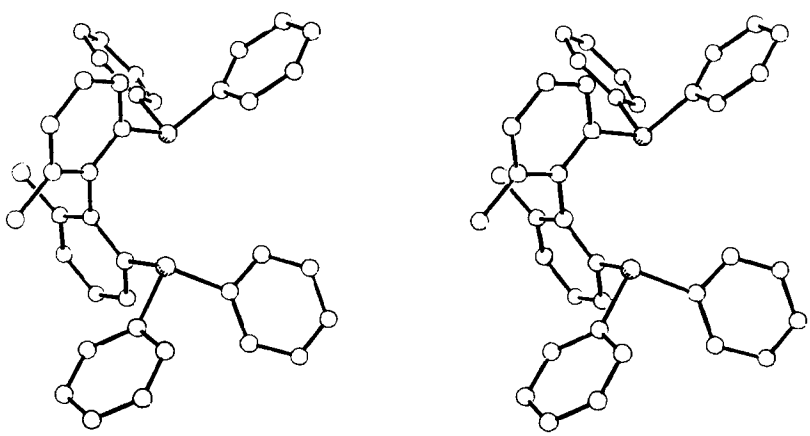


Fig. 3. *Stereoscopic drawing of* (S)-**10**

[14]) The symbol P⌒P denotes the chelating diphosphine, and the abbreviations nbd and cod denote norbornadiene (IUPAC name: 8,9,10-trinorborna-2,5-diene) and (*Z*,*Z*)-1,5-cyclooctadiene, respectively.

[15]) See *Exper. Part* for details.

[16]) H-atoms are omitted for clarity in all representations. Atoms in the ORTEP diagrams are represented by 50% probability thermal ellipsoids. The atomic numbering scheme for the free diphosphines is the same as depicted for the Rh complexes.

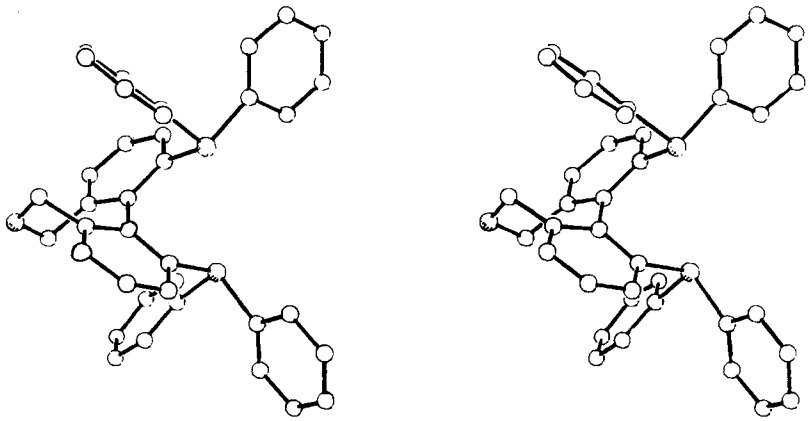


Fig. 4. *Stereoscopic drawing of* (R)-**13**

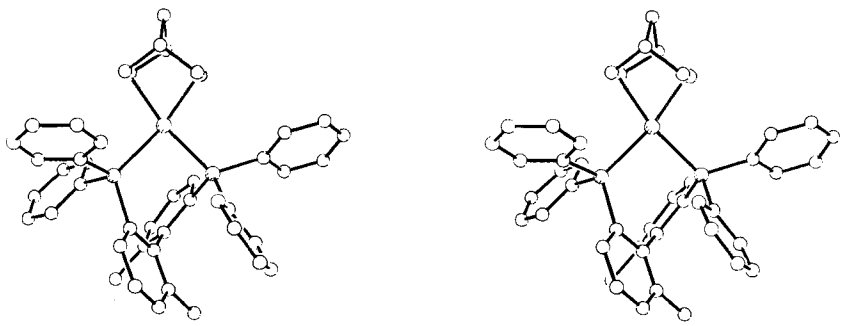


Fig. 5. *Stereoscopic drawing of the [Rh((S)-***10***)(nbd)] cation*

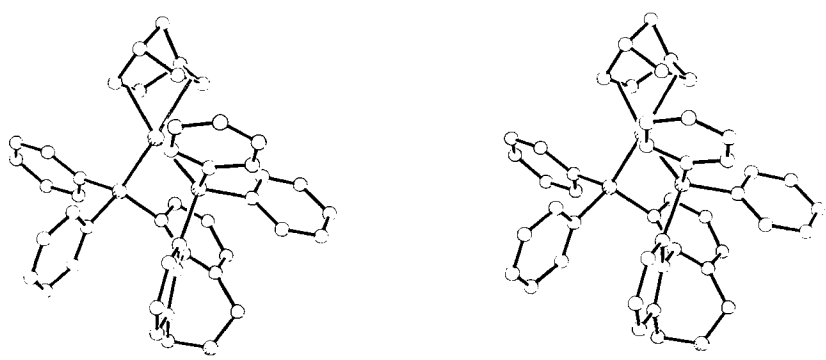


Fig. 6. *Stereoscopic drawing of the [Rh((R)-***13***)(nbd)] cation*

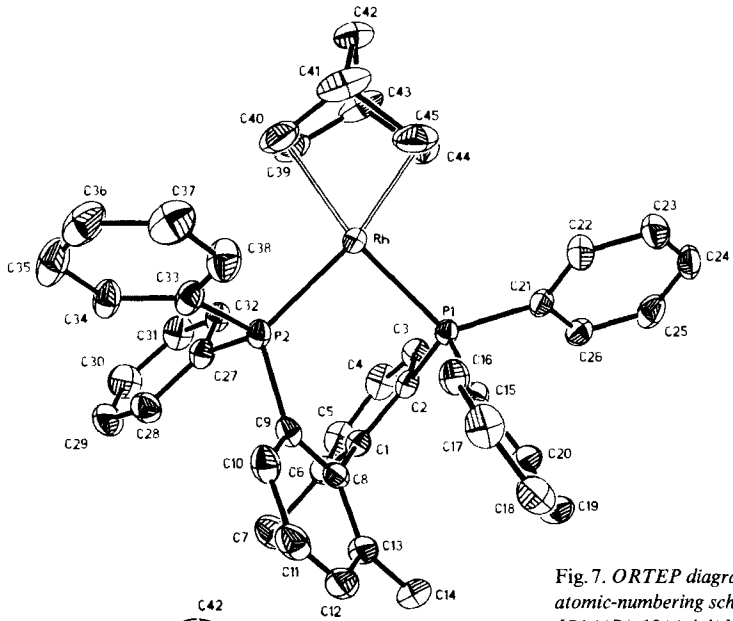


Fig. 7. *ORTEP diagram and atomic-numbering scheme for the [Rh((S)-**10**)(nbd)] cation*

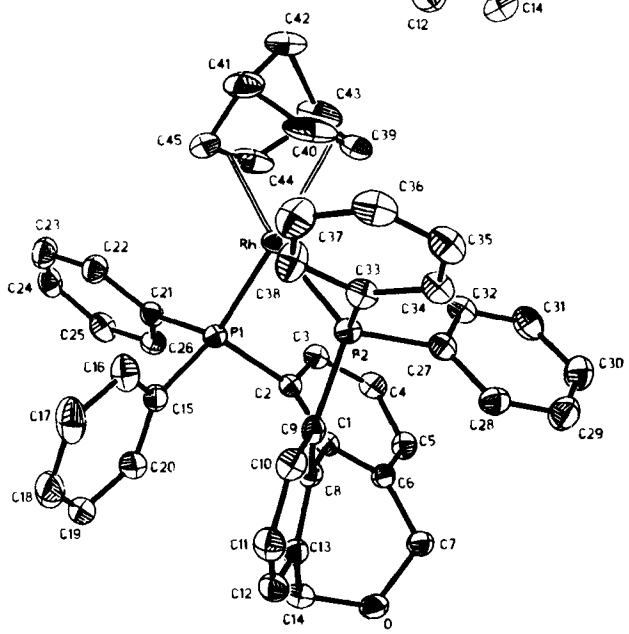


Fig. 8. *ORTEP diagram and atomic-numbering scheme for the [Rh((R)-**13**)(nbd)] cation*

As expected from X-ray structure analyses of other 2,2′,6,6′-substituted biphenyls, (*S*)-**10** exhibits an interplanar angle between the least-squares planes of the two Ph rings of the biphenyl system, θ, of *ca.* 90°[17]), specifically of 88.7°. The spatial arrangement of the

[17]) For instance, the following θ angle have been determined by X-ray analyses: 93° in (*S*)-**16** [43a], 81.7° in 2,2′,6,6′-tetrachlorobiphenyl [43b], 87.3° in 2,2′,4,4′,6,6′-hexachlorobiphenyl [43c], 83.0° in 2,2′,4,4′,6,6′-hexabromobiphenyl [43b], 86.6° in decachlorobiphenyl [43d], and 89.9° in 2,2′,4,4′,6,6′-hexamethylbiphenyl [29c].

Table 2. *Selected Interatomic Distances* [Å] *and Bond Angles* [°] *for* (S)-**10**, (R)-**13**, *[Rh((S)-***10***)(nbd)]BF_4, and [Rh((R)-***13***)(nbd)]BF_4*

	(*S*)-**10**	(*R*)-**13**	[Rh((*S*)-**10**)(nbd)]BF_4	[Rh((*R*)-**13**)(nbd)]BF_4
Distances [Å]				
P(1)–C(2)	1.839(3)	1.839(8)	1.828(3)	1.834(3)
P(2)–C(9)	1.839(3)	1.848(7)	1.839(3)	1.839(3)
P(1)–C(15)	1.831(3)	1.840(8)	1.826(3)	1.823(3)
P(1)–C(21)	1.830(3)	1.834(7)	1.823(3)	1.836(3)
P(2)–C(27)	1.828(3)	1.849(8)	1.819(3)	1.827(3)
P(2)–C(33)	1.837(3)	1.840(7)	1.833(3)	1.833(3)
C(1)–C(8)	1.504(4)	1.509(9)	1.497(4)	1.492(4)
C(6)–C(7)	1.502(5)	1.484(11)	1.509(5)	1.510(4)
C(13)–C(14)	1.510(4)	1.526(10)	1.500(5)	1.504(4)
C(7)–O	–	1.463(9)	–	1.448(4)
C(14)–O	–	1.404(11)	–	1.445(4)
Rh–P(1)	–	–	2.276(1)	2.264(1)
Rh–P(2)	–	–	2.350(1)	2.329(1)
Rh–C(39)	–	–	2.240(4)	2.220(4)
Rh–C(40)	–	–	2.232(4)	2.244(4)
Rh–C(44)	–	–	2.159(4)	2.167(3)
Rh–C(45)	–	–	2.146(4)	2.186(3)
P(1)···P(2)	4.133	3.474	3.283	3.201
Bond angles [°]				
C(1)–C(8)–C(9)	121.1(2)	121.8(5)	120.9(3)	122.7(2)
C(8)–C(1)–C(2)	119.7(2)	121.2(6)	121.0(3)	123.4(2)
C(1)–C(2)–P(1)	118.1(2)	114.6(5)	122.3(2)	123.2(2)
C(8)–C(9)–P(2)	119.5(2)	117.7(5)	120.0(2)	120.0(2)
C(2)–P(1)–C(21)	101.3(1)	103.8(3)	108.3(1)	107.9(1)
C(9)–P(2)–C(27)	101.7(1)	98.4(3)	102.6(1)	100.9(1)
C(15)–P(1)–C(21)	101.3(1)	103.8(3)	97.2(1)	98.6(1)
C(27)–P(2)–C(33)	102.6(1)	104.2(4)	106.3(2)	107.1(1)
C(1)–C(6)–C(7)	121.7(3)	119.7(6)	122.3(3)	119.1(2)
C(8)–C(13)–C(14)	121.7(3)	118.4(6)	122.1(3)	119.7(3)
P(1)–Rh–P(2)	–	–	90.4(1)	88.4(1)
Rh–P(1)–C(2)	–	–	98.8(1)	102.4(1)
Rh–P(2)–C(9)	–	–	118.7(1)	120.7(1)
Rh–P(1)–C(15)	–	–	123.0(1)	118.7(1)
Rh–P(1)–C(21)	–	–	117.8(1)	118.5(1)
Rh–P(2)–C(27)	–	–	117.1(1)	115.5(1)
Rh–P(2)–C(33)	–	–	106.3(1)	106.4(1)

Ph rings around the pyramidal P-atoms is such that the lone pair of each of the P-atoms lies virtually in the plane of the adjacent Ph ring of the biphenyl system and nearly parallel to the plane of the remote Ph ring of the biphenyl system. Thus, the BIPHEMP ligand can be thought of as being composed of two independent Ph_3P moieties[18]). In (*R*)-**13**, θ is reduced to 60.5°. This value is slightly larger than calculated (43–44°, *cf.* [19f] [45]) or observed (37.4° [46]) for similar 6,6′-(C–O–C)-bridged biphenyls that are lacking substituents in the 2,2′-positions. Undoubtedly, steric repulsion of the two bulky Ph_2P substitu-

[18]) Indeed, the UV spectrum of **10** corresponds quite closely to the summation curve of two individual UV spectra of Ph_3P (solvent EtOH, λ_{max} (nm/ε); (*S*)-**10**: 205.5 (88700), 269.5 (20150); Ph_3P (*cf.* [44]): 205 (40150), 259 (10800)).

Table 3. *Selected Torsion Angles* [°] *and Interplanar Angles* [°] *for* (S)-**10**, (R)-**13**, *[Rh((S)-***10***)(nbd)]BF$_4$, [Rh((R)-***13***)(nbd)]BF$_4$, and [Rh((R)-***1a***)(nbd)]ClO$_4$*

	(*S*)-**10**	(*R*)-**13**	[Rh((*S*)-**10**)(nbd)]BF_4	[Rh((*R*)-**13**)(nbd)]BF_4	[Rh((*R*)-**1a**)(nbd)]ClO_4 [2b]
Torsion angles [°]					
Rh–P(1)–C(2)–C(1)	–	–	–90.1(3)	91.0(2)	70.8
P(1)–C(2)–C(1)–C(8)	–4.9(3)	–8.3(8)	–4.5(4)	–0.3(4)	11.1
C(2)–C(1)–C(8)–C(9)	91.0(3)	–64.9(9)	69.5(4)	–56.7(4)	–74.4
C(1)–C(8)–C(9)–P(2)	5.7(4)	–6.6(9)	–3.3(4)	–6.0(4)	10.4
C(8)–C(9)–P(2)–Rh	–	–	–64.6(3)	70.6(2)	67.2
C(9)–P(2)–Rh–P(1)	–	–	18.0(1)	–20.0(1)	–35.0
P(2)–Rh–P(1)–C(2)	–	–	58.4(1)	–57.1(1)	–40.6
Rh–P(1)–C(15)–C(20)	–	–	171.6(2)	–164.2(2)	–169.8
Rh–P(1)–C(21)–C(26)	–	–	–125.8(3)	128.8(2)	54.8
Rh–P(2)–C(27)–C(28)	–	–	179.0(2)	–179.6(2)	–171.1
Rh–P(2)–C(33)–C(38)	–	–	–42.1(3)	44.2(3)	54.1
C(2)–P(1)–C(15)–C(20)	18.5(3)	–34.1(8)	54.6(3)	–46.3(3)	–46.2
C(2)–P(1)–C(21)–C(26)	–126.7(3)	110.8(7)	–14.9(3)	13.3(3)	–71.3
C(9)–P(2)–C(27)–C(28)	171.2(2)	–45.2(6)	47.2(3)	–47.7(3)	–42.2
C(9)–P(2)–C(33)–C(38)	78.5(3)	–70.8(6)	84.2(3)	–84.9(3)	–74.0
Interplanar angles[a])					
[C(1–6)]/[C(8–13)]	88.7	60.5	71.8	55.9	74.4
[C(1–6)]/[C(27–32)]	73.5	17.6	13.2	16.5	18.0
[C(8–13)]/[C(15–20)]	42.4	20.1	17.6	21.5	15.6
[P(1),Rh,P(2)]/[MP(1),Rh,MP(2)]	–	–	14.7	8.8	14.9
[P(1),Rh,P(2)]/[C(39,40,44,45)]	–	–	89.3	81.3	86.9

[a]) Angles between the least-squares planes through the atoms indicated; MP(1) and MP(2) are the midpoints of the nbd double bonds C(39)=C(40) and C(44)=C(45), respectively.

ents in the 2,2′-positions of (*R*)-**13** prevents the biphenyl system from adopting a smaller θ angle. The bridging of the biphenyl moiety, *i.e.* the reduction of θ from *ca.* 90° to 60°, has a remarkable effect on the spatial arrangement of the Ph rings of the Ph_2P moieties. Thus, one P–Ph ring of each of these moieties is brought into a roughly parallel orientation with respect to the more remote Ph ring of the biphenyl system. This results in the formation of two pairs of approximately parallel Ph rings *(cf. Fig. 4)* with distances of 4.262 Å and 4.446 Å between the centres of and interplanar angles of 17.6° and 20.1° between the least-squares planes of the parallel Ph rings *(cf. Table 3)*. This effect can be observed also and in an even more pronounced form, in the Rh(I) complexes of (*S*)-**10** and (*R*)-**13** (see below).

As mentioned in the *Introduction, Frejd* and coworkers [21] recently have reported – and discussed in detail – the X-ray structure of the complex [Rh((*R*)-**10**)(nbd)]BF_4. Our analysis of [Rh((*S*)-**10**)(nbd)]BF_4 (*i.e.* the corresponding complex derived from (*S*)-**10**) is in full accord with the reported one[19]). The complex [Rh((*R*)-**13**)(nbd)]BF_4 derived from (*R*)-**13** shows close resemblance in the molecular structure to the BIPHEMP-derived complex as shown by comparison of the structural parameters *(Table 2)* and by the superposition of the two structures in *Fig. 9a*. In both complexes, the Rh-atom is coordinated in a slightly distorted square-planar geometry by the two P-atoms of the diphosphine and the two double bonds of norbornadiene. The angle between the [P(1)–Rh–P(2)] plane and the least-squares plane through the two norbornadiene double bonds is nearly 90° in both complexes (specifically 89.3° for the (*S*)-**10**-derived complex and 81.3° for the (*R*)-**13**-derived complex, *cf. Table 3*). The angle between the [P(1)–Rh–P(2)] plane and the plane defined by the Rh-atom and the midpoints of the two norbornadiene double bonds is 14.7° in the (*S*)-**10**-derived complex and 8.8° in the

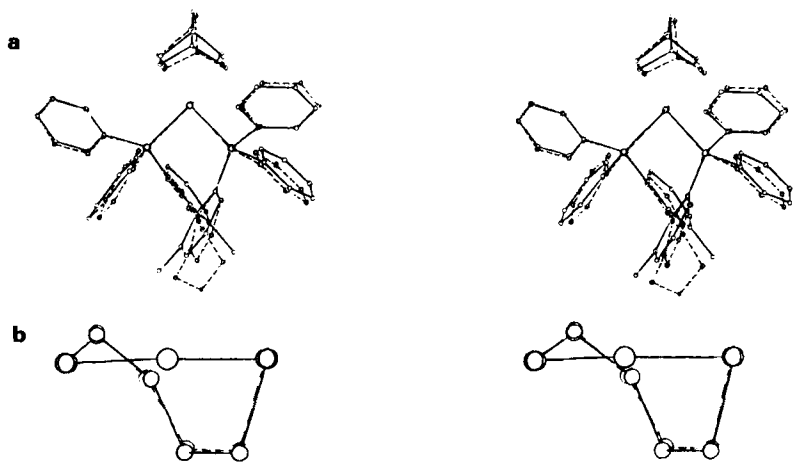


Fig. 9. *Stereoscopic drawing of superpositions of* a) *the cation moieties and* b) *the 7-membered chelate rings of mirror-inverted [Rh((S)-**10**)(nbd)]BF_4* (full lines) *and [Rh((R)-**13**)(nbd)]BF_4* (dotted lines). Matched are the Rh- and the P-atoms (large circles). The perspective view is approximately perpendicular to the [P(1)–Rh–P(2)] plane in *a* and down the [P(2)–Rh–P(1)] bisector in *b*.

[19]) Some minor differences are probably due to the different temperature of analysis (293 K *vs.* 210 K [21]).

(*R*)-**13**-derived complex, indicating a slightly less tilted coordination (*cf.* [2b] [21]) of the diene ligand in the latter complex. The interplanar angles θ of the biphenyl system in the (*S*)-**10**- and the (*R*)-**13**-derived complex are 71.8° and 55.9°, respectively *(cf. Table 3)*. Obviously, coordination of the ligand to the Rh-atom requires only very little conformational adjustment in the case of the 6,6′-bridged diphosphine (*R*)-**13** (θ = 60.5°), while a rotation of *ca.* 20° around the pivotal bond of the biphenyl system is required in the case of (*S*)-**10**. Indeed, (*R*)-**13** can be considered as being ideally predisposed for coordination. This becomes also evident from the P(1)···P(2) interatomic distances of 3.477 Å in the free ligand and of 3.201 Å in the complex. In both complexes derived from (*S*)-**10** and (*R*)-**13**, two pairs of parallel Ph rings are observed as has been discussed before for the free ligand (*R*)-**13**. The interplanar angles between the parallel Ph rings of these pairs amount to 13.2° and 17.6° for the (*S*)-**10**-derived and to 16.5° and 21.5° for the (*R*)-**13**-derived complex.

The topology of the seven-membered chelate ring Rh–P(1)–C(2)–C(1)–C(8)–C(9)–P(2) and the spatial arrangement of the Ph groups of the two Ph_2P moieties are remarkably similar in the (*S*)-**10**-derived and the (*R*)-**13**-derived complex. This is clearly demonstrated by the comparison of the endocyclic torsion angles of these chelate rings and the torsion angles defined by the P–Ph rings relative to the Rh–P bond (see *Table 3*, *cf.* also [21]). It is furthermore illustrated by a superposition of the crystal conformations of the chelate rings *(Fig. 9b)*. The spatial arrangement of the P–Ph rings in both complexes is such, that the rings [C(15)–C(20)] and [C(27)–C(32)] which adopt parallel orientations with regard to the respective remote ring of the biphenyl system orient pseudo-axially on the seven-membered chelate ring and expose their edge towards the Rh-atom (torsion angles with absolute values between 164° and 180°, *cf. Table 3*). On the other hand, the two P–Ph rings of the non-parallel type (*i.e.* rings [C(21)–C(26)] and [C(33)–C(38)]) orient pseudo-equatorially and adopt intermediate expositions between edge and face. All together, the comparison of the two structures indicates that the smaller interplanar angle of the biphenyl moiety in the (*R*)-**13**-derived complex hardly translates into significant differences in the coordination sphere at the Rh-atom.

Comparison of the complexes derived from BIPHEMP and its bridged analogue **13** with the BINAP-derived complex [Rh((*R*)-**1a**)(nbd)]ClO_4 [2b] reveals, as has been mentioned already by *Frejd* and coworkers [21], two distinct differences between the biphenyl and the binaphthyl series. Firstly, the seven-membered chelate rings in the biphenyl series are considerably more distorted from the virtually C_2 symmetrical skew (v) boat conformation [47] of the chelate ring in the BINAP-derived complex [Rh((*R*)-**1a**)(nbd)]ClO_4 [2b]. This is supported by comparison of endocyclic torsion angles *(Table 3)* of the chelate rings and the superposition in *Fig. 10b*. This distortion is reflected also by a more pronounced overall deviation from the C_2 symmetry of the cationic moieties of the complexes in the biphenyl series compared to the binaphthyl series. Secondly, the spatial orientation of the P–Ph groups and in particular of the two pseudo-equatorially oriented rings is distinctly different as evident by comparison of the relevant torsion angles *(cf. Table 3)* and the superposition in *Fig. 10a*. The most notable difference is the orientation of the [C(21)–C(26)] Ph ring, torsion angles Rh–P(1)–C(21)–C(26) being −125.8° and 128.8° in the (*S*)-**10**- and (*R*)-**13**-derived complexes, respectively, but 54.1° in the (*R*)-**1a**-derived complex. Thus, the array of the four P–Ph rings shows some deviation from the pronounced alternating edge/face orientation that is observed in the BINAP complex [2b] [16].

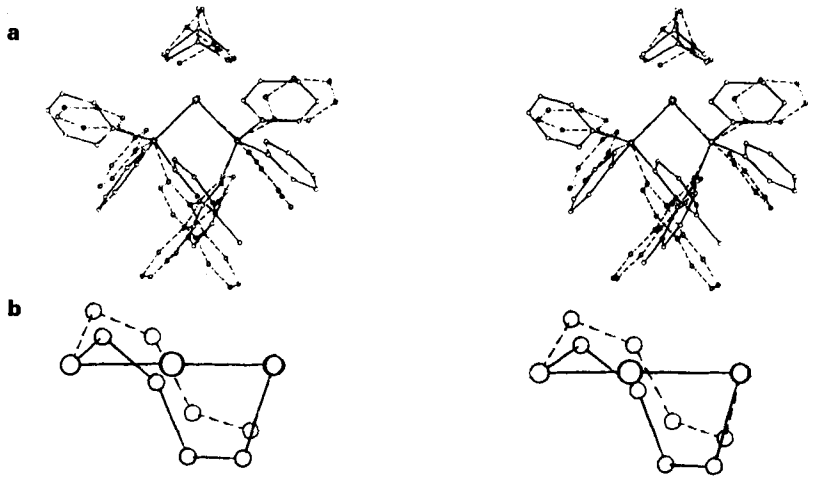
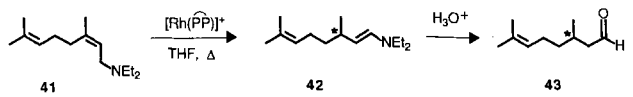


Fig. 10. *Stereoscopic drawing of superpositions of* a) *the cation moieties and* b) *the 7-membered chelate rings of mirror-inverted [Rh((S)-**10**)(nbd)]BF_4* (full lines) *and [Rh((R)-**1a**)(nbd)]ClO_4* [2b] (dotted lines). Matched are the Rh- and the P-atoms (large circles). The perspective view is approximately perpendicular to the [P(1)–Rh–P(2)] plane in *a* and down the [P(2)–Rh–P(1)] bisector in *b*.

7. Asymmetric Isomerization of *N,N*-Diethylnerylamine (41). – The Rh(I)-catalyzed asymmetric isomerization [6] of *N,N*-diethylnerylamine (**41**; *cf. Table 4*) was chosen as model reaction for evaluation of the efficacy of the diphosphines **10–13** as asymmetry-inducing ligand and for comparison with the BINAP diphosphine **1a**. The isomerization reactions were carried out according to *Otsuka's* procedure (0.1–0.5 mol-% [Rh($\widehat{PP}$)(diene)]$^+$ catalyst, THF, 60–85°) [6b]. Asymmetric inductions were determined, after enamine hydrolysis to citronellal (**43**), according to the method of *Valentine et al.* [48], by Ag_2O oxidation to the corresponding acid, amide formation [49] with (*R*)-α-methyl-4-nitrobenzylamine, and GC and HPLC analysis of the formed diastereoisomers. Results of the isomerization experiments are listed in *Table 4*. Remarkably, all of the diphosphines **10–13** gave rise to very high asymmetric inductions in the range of 98–99.5% ee. As a matter of point, these inductions were obtained with Rh(I) complexes which, in part, had been derived from **10** possessing only about 96–98% ee. This suggests that the enantiomeric purity of the ligand is increased to nearly 100% in the process of the preparation of the Rh(I) complexes.

Thus, the BIPHEMP diphosphine **10** and its analogues appear to be equally efficient as asymmetry-inducing ligands to the BINAP diphosphine **1a** which has been reported to afford 96–99% ee in the isomerization of **41** [6]. The correlation between ligand and product configuration was found to be the same for the BIPHEMP ligands and the BINAP ligand (*cf.* [6]). The findings by *Otsuka* and coworkers [6a,b] that rates of isomerization are faster for cod than for nbd complexes and that there is no temperature effect on the optical induction in the range of 40–90° appear to hold true also for our new catalyst systems. In terms of activities, rates were similar for [Rh(BIPHEMP)]$^+$- and [Rh(BINAP)]$^+$-catalyzed isomerizations of **41**. Qualitatively, isomerization rates were observed to be slightly higher with the catalysts derived from diphosphines **11** and **12** but considerably lower with the catalyst derived from bridged diphosphine **13** with respect to

Table 4. *Asymmetric Isomerizations of* N,N-*Diethylnerylamine* (**41**)[a])



41 **42** **43**

Entry	[Rh(PP)]$^+$	S/C[b])	Temp. [°]	Citronellal (**43**)			
				Yield[c]) [%]	$[\alpha]_D^{20}$ (5%, $CHCl_3$)	Config-uration	ee[d]) [%]
1	[Rh((*R*)-**10**)(nbd)]BF_4	250	85	93.5	+19.1	*R*	98
2	[Rh((*S*)-**10**)(nbd)]BF_4	1000	80	96	−19.3	*S*	99
3	[Rh((*R*)-**10**)(cod)]ClO_4	500	60	71[e])	+19.4	*R*	99
4	[Rh((*R*)-**10**)(cod)]BF_4	525	70	95	+19.0	*R*	98
5	[Rh((*S*)-**10**)(cod)]BF_4	590	60	95	−19.5	*S*	99.5
6	[Rh((*R*)-**11**)(nbd)]BF_4	560	80	88	[f])	*R*	98
7	[Rh((*R*)-**11**)(cod)]BF_4	525	80	90	+19.0	*R*	98.5
8	[Rh((*R*)-**12**)(cod)]BF_4	280	75	60	[f])	*R*	98
10	[Rh((*R*)-**13**)(cod)]BF_4	180	70	89	+19.2	*R*	98.5

[a]) All isomerizations were carried out in THF in sealed tubes at the temp. indicated; substrate concentrations 0.6–1.6 mol **41**/l; reaction times 1.5–88 h.

[b]) Molar substrate/catalyst ratio.

[c]) Isolated yields after hydrolysis (20–50% AcOH) and bulb-to-bulb distillation.

[d]) Determined according to the method of *Valentine et al.* [48] (see text). The ee's indicated are mean values of GC and HPLC analyses; the accuracy of the values is estimated to be ±0.5%.

[e]) 73% conversion by GC.

[f]) Not measured.

10. However, differences were rather small, and interpretation is difficult because of different rates of solubilization and/or deactivation of the catalyst complexes. The Rh(I) complexes derived from **13** were found to dissolve particularly slowly in the reaction medium.

8. Concluding Remarks. – The BIPHEMP ligand **10**, and analogues **11**, **12**, and **13** represent the first examples of optically active bis(triarylphosphines) containing the axially dissymmetric biphenyl moiety as chiral element. The synthetic route starting from optically active diamines **16** opens a versatile access to the optically active BIPHEMP ligand **10**. As exemplified by analogues **11**, **12**, and **13**, the central biphenyl moiety may readily be modified. All these biphenylylene diphosphines proved to be highly efficient in the asymmetric isomerization of *N*, *N*-diethylnerylamine (**41**). The similar isomerization results may be rationalized in terms of structural resemblance of the Rh(I) complexes. This resemblance has been clearly revealed by X-ray analyses of the complexes derived from **10** and **13**. Although bridging of the 6,6′-positions in **13** compared to **10** substantially decreased the dihedral angle of the biphenyl unit, this hardly had any effect on the topology of the coordination sphere of the Rh-atom. In particular, it did not effect the spatial orientation of the four Ph groups of the Ph_2P moieties which provides the chiral environment at the olefin coordination site and which, as is generally accepted, is responsible for chiral recognition. Obviously, more profound modifications of the biphenyl unit would be required to substantially alter the structural features in the Rh-coordination sphere. The BIPHEMP diphosphine and its analogues proved to be equally efficient to the BINAP ligand with respect to the enantioselectivity in the asymmetric isomerization

of *N,N*-diethylnerylamine (**41**). The previously discussed differences in the crystal structures of the Rh(I) complexes in the two series, therefore, did not translate noticeably into a difference in enantioselectivities. Work towards a further assessment of the potential of the BIPHEMP ligand and analogues thereof in asymmetric catalysis is in progress.

We wish to thank our colleagues from *Central Research Units, F. Hoffmann-La Roche & Co. AG*, for UV and CD spectra and optical rotation measurements (Mrs. Dr. *M. Grosjean*, Dr. *K. Noack*, Mrs. *J. Kohler*), IR spectra (Mr. *A. Bubendorf*), NMR spectra (Dr. *G. Englert*, Dr. *W. Arnold*, Mr. *Y. Mercadal*), MS (Dr. *W. Vetter*, Mr. *W. Meister*), elemental analyses (Dr. *A. Dirscherl*), and GC and HPLC analyses (Dr. *M. Vecchi*, Dr. *R. Maurer*, Mr. *W. Walther*). We thank also Dr. *J.J. Daly* for carrying out the X-ray analysis of [Rh((*S*)-**10**)(nbd)]BF_4.

Experimental Part

We thank Mr. *A. Grieder* for his excellent experimental assistance.

General. All reactions with air- and moisture-sensitive reactants and solvents were carried out in oven- or flame-dried glassware under a positive pressure of dry Ar. Transfers of air- and moisture-sensitive solns. and solvents were performed using predried syringes or cannulas. Solvents used in the preparations and reactions of all diphosphines and derived Rh(I) complexes were deoxygenated: THF and Et_2O were distilled under Ar from Na/benzophenone prior to use; toluene, AcOEt, acetone, EtOH, MeOH were all distilled under Ar, while H_2O was deoxygenated by heating under reflux for 2 h under Ar. Usual workup refers to extraction with the specified solvent in 2–3 fractions, washing the combined org. layers with H_2O, sat. $NaHCO_3$ soln., and sat. NaCl soln., drying over Na_2SO_4, filtering, and evaporating in a *Büchi Rotavapor-R* at 30–40° H_2O-bath temp. and aspirator pressure. TLC on silica gel plates *Merck* (SiO_2 *60* F_{254}) or *Macherey-Nagel (Polygram Sil G/UV*$_{254}$), detection by UV_{254} light and spraying with $KMnO_4$ (2% aq. $KMnO_4$ in 10% aq. Na_2CO_3) or phosphomolybdic acid or anisaldehyde/H_2SO_4. Column flash chromatography (FC) [50] on silica gel (0.063–0.200 mm, 70–230 mesh ASTM; *Merck*). Solvent mixtures are specified by parts or % volume-by-volume. Anal. GC on 5% *OV-17* (3 m × 2.2 mm), carrier gas N_2, or on capillary columns *SE-54* (18 m or 21 m × 0.3 mm), carrier gas H_2. Bulb-to-bulb distillations were carried out in a *Büchi GKR-50 Kugelrohrofen;* b.p. refer to air-bath temp. M.p. were determined on a *Büchi SMP-20* apparatus and are uncorrected. Optical rotations on a *Perkin-Elmer* polarimeter *241*, specific rotation at 20° at the indicated wave length [nm], concentration [%], and solvent. UV: on a *UVICON 810/820* spectrometer, in EtOH ($c = 1–2 \times 10^{-5}$ M), unless otherwise noted; λ_{max} in nm (ε). CD: on a *Jobin-Yvon 185 Dichograph* at ambient temp., $c = 0.002$ in EtOH, unless otherwise noted; λ in nm ($\Delta\varepsilon$). IR: on a *Nicolet 7199 FT-IR* spectrometer; solids were recorded in KBr pellets, liquids as thin films; indication of characteristic bands in cm^{-1}. ^{1}H-NMR at 60 MHz *(Varian A-60D* or *EM-360)*, 80 MHz *(Bruker WP-80 CW)*, 90 MHz *(Bruker HX-90/15FT)*, 270 MHz *(Bruker HX-270)*, or 400 MHz *(Bruker WM-400);* $CDCl_3$ solns., unless otherwise noted, *TMS* as internal standard; chemical shifts of signals centres or ranges in ppm (δ), *J* in Hz. ^{31}P-NMR: at 162 MHz *(Bruker WM-400)*, $CDCl_3$ solns. with H_3PO_4 as external standard. MS: on a *MS9* (*AEI*, Manchester, GB), indication of characteristic peaks in *m/z* (% rel. to base peak (= 100%)).

1. Synthesis of the Diphosphines 10. – 1.1. *(RS)-(6,6'-Dimethylbiphenyl-2,2'-diyl)diamine* ((*RS*)-**16**). The synthesis of (*RS*)-**16** has been described [24]. Diazotization/iodination of 205 g (1.35 mol) of *6-methyl-2-nitroaniline* (**14**)[20]) afforded 339.4 g (96%) of crude 2-iodo-3-nitrotoluene, m.p. 63–65° ([24b]: 66–68°). *Ullmann* coupling of 333 g of this material according to [24b] afforded, after crystallization from EtOH, 120.8 g (70%) of *2,2'-dimethyl-6,6'-dinitrobiphenyl* ((*RS*)-**15**), m.p. 108–109° ([24d]: 110°). Hydrogenation of (*RS*)-**15** according to [24d] over Pd/C in AcOH furnished 98.2 g (104%) of crude (*RS*)-**16**, m.p. 134–135°, and, after recrystallization from EtOH, 68.55 g (82.6%) of (*RS*)-**16**, m.p. 136–137° ([24d]: 136°); overall yield based on **14**: 67% crude, 55% recrystallized. The crude material was sufficiently pure for the use in the optical resolution.

1.2. *Optical Resolution.* Resolutions of (*RS*)-**16** were carried out according to [24c]. Results are summarized in *Table 5*. (*R*)-**16**: m.p. 160–160.5° ([11a]: 159–160°); $[\alpha]_D^{20} = -39.16°$ ($c = 0.93$, 1N HCl) ([24c]: −34.8° ($c = 1.0$, 0.1N HCl); [24d]: −34.8° ($c = 1.0$, 0.3N HCl); [19d]: −35° ($c = 3.5$, 1N HCl); [26]: −36° ($c = 2.0$, 2N HCl); [11a]: −37.3°

[20]) Commercially available from *Schweizerische Sprengstoff-Fabrik AG*, Dottikon; for the preparation by nitration of *o*-toluidine, see [51].

Table 5. *Resolution of (*RS*)-***16***

Exper.	Diamine **16** (*R*)/(*S*) ratio	Tartaric acid Config.	Tartrate salt Cryst. [b])	Tartrate salt $[\alpha]_D^{20}$ (c = 1.0 0.1N HCl)	Optically active **16** Crude[a]) Yield[c]) [%] of theory	Crude[a]) $[\alpha]_D^{20}$ (c = 1.0 1N HCl)	Crude[a]) op [%] (Config.)	Recryst. Cryst. [b])	Recryst. Yield[c]) [%] of theory	Recryst. $[\alpha]_D^{20}$ (c = 1.0 1N HCl)	Recryst. op[d]) [%] (Config.)
1	50:50	(*R,R*)	4 × [e])	−10.36°	65	−34.0°	86.5 (*R*)	3 ×	23.3	−39.16°	99.5 (*R*)
2	50:50	(*R,R*)	6 ×	−11.61°				1 ×	22.4	−35.9°	91 (*R*)
3	41:59	(*S,S*)	6 ×	+13.17°				2 ×	22.9	+37.8°	96.5 (*S*)
4	50:50	(*R,R*)	6 ×	−10.14°		−32.9°	83.5 (*R*)	2 ×	20.9	−38.3°	97.5 (*R*)
5	38:62	(*S,S*)	1 × [f])	+5.1°	36	+26.8°	68 (*S*)	2 ×	18	+37.2°	94.5 (*S*)
6	50:50	(*R,R*)	1 × [f])	−3.8°		−20.8°	53 (*R*)	3 ×	19.3	−37.9°	96.5 (*R*)

[a]) Crude **16** after decomposition of the tartrate salt. [b]) Number of crystallizations performed. [c]) Isolated yields. [d]) Based on $[\alpha]_D^{20}$ = +39.3 for optically pure **16**. [e]) 1:1 salt. [f]) Poorly soluble tartrate modifications, containing 1.2–1.5 mol-equiv. of tartaric acid.

(c = 1.05, 1N HCl)). ^{1}H-NMR (60 MHz): 7.3–6.5 (*m*, 6 arom. H); 3.4 (br. *s*, 2 NH_2); 1.95 (*s*, 2 CH_3); upon addition of Eu(hfc)$_3$, a single signal is observed for the CH_3 group; 0.5% estimated limit for the detection of the CH_3 signal of (*S*)-**16**; ee ≧ 99%. ^{1}H-NMR of (*S*)-**16** of 40% ee in the presence of Eu(hfc)$_3$: 2.53, 2.28 (2*s*, ratio of intensities 3:7, CH_3 of (*R*)- and (*S*)-**16**). (*S*)-**16**: m.p. 159–160.5°; $[\alpha]_D^{20}$ = +37.8° (c = 1.0, 1N HCl). ^{1}H-NMR (80 MHz) in the presence of Eu(hfc)$_3$: 3.1, 2.65 (2*s*, ratio of intensities 2:98, CH_3 of (*R*)-**16** and (*S*)-**16**, respectively); ee = 96%.

1.3. *(*RS*)-, (*R*)-, and (*S*)-2,2'-Dibromo-6,6'-dimethylbiphenyl* ((*RS*)-, (*R*)-, and (*S*)-**17**). 1.3.1. *(*RS*)-***17*** (*cf.* [25] [19e]). To 80 ml of 48% aq. HBr were added 21.2 g (0.10 mol) of (*RS*)-**16** in several portions. The mixture was cooled to −5°, and to the resulting suspension was added within 40 min a soln. of 13.8 g (0.20 mol) of $NaNO_2$ in 20 ml H_2O. The resulting dark diazonium-salt soln. was filtered through a plug of glasswool into a jacketed dropping funnel which was cooled with ice-water. The cold soln. then was added within 15 min to 150 ml of a *ca.* 2M soln. of CuBr in 48% aq. HBr which was preheated to 70–75°. The mixture was heated under reflux for an additional 15 min. After cooling, the mixture was extracted with Et_2O (3 × 200 ml) and the combined org. layers were washed with 2N HCl and further processed as usual. The resulting brown oil (31.75 g), containing, according to GC, 16.5% of 2-bromo-6,6'-dimethylbiphenyl, 19% of (*RS*)-2-bromo-2'-hydroxy-6,6'-dimethylbiphenyl, and 62.5% of (*RS*)-**17**, was filtered with hexane through a short plug of silica gel to remove the phenolic parts. The semi-crystalline residue from the filtrate was purified by chromatography on silica gel (hexane) and subsequently recrystallized twice from EtOH to afford 11.75 g (34.5%) (*RS*)-**17**; m.p. 112.5–113° ([25b]: 109–110°); 99.5% purity (GC). IR: 1627, 1589, 1557 (Ar.); 1375 (CH_3); 772 (1,2,3-trisubst. benzene). ^{1}H-NMR (60 MHz): 7.65–7.1 (*m*, 6 arom. H); 2.0 (*s*, 2 CH_3). MS: 342/340/338 (17/35/18, M^+), 180 (100, M^+ − 2 Br), 165 (58). Anal. calc. for $C_{14}H_{12}Br_2$ (340.06): C 49.45, H 3.56, Br 46.99; found: C 49.51, H 3.75, Br 47.10.

A sample of the residue from the mother liquor was analyzed by GC/MS: *2-bromo-6,6'-dimethylbiphenyl:* 262/260 (45/45, M^+), 181 (30), 166 (100), 165 (59); *tribromides:* 422/420/418/416 (14/42/45/15, M^+), 260/258 (23/23, M^+ − 2 Br), 179 (100); 422/420/418/416 (3/10/12/4, M^+), 260/258 (45/46, M^+ − 2 Br), 179 (100). In another experiment, *2-bromo-2'-hydroxy-6,6'-dimethylbiphenyl* was isolated in 17% yield by chromatography on silica gel (hexane/AcOEt 10% → 20%). ^{1}H-NMR (60 MHz): 7.65–6.8 (*m*, 6 arom. H); 4.4 (br. *s*, OH); 2.05 (*s*, CH_3); 1.95 (*s*, CH_3). MS: 278/276 (79/78, M^+), 197 (100, M^+ − Br), 182 (89). Anal. calc. for $C_{14}H_{13}BrO$ (277.16): C 60.67, H 4.73, Br 28.83; found: C 60.26, H 4.74, Br 29.69.

1.3.2. (*R*)-**17** (*cf.* [19e]). Conversion of 17.8 g (80.1 mmol) of (*R*)-**16** ($[\alpha]_D^{20}$ = −38.3° (c = 1.0, 1N HCl); op 98%) as described above afforded 25.2 g of a brown oil consisting, according to GC, of 10% monobromide, 22% bromophenol, and 56% dibromide. Chromatography on silica gel (hexane) and subsequent crystallization from EtOH afforded 8.8 g (32%) (*R*)-**17**, m.p. 109–109.5° ([19e]: 108.5–110°); 99.6% purity (GC); $[\alpha]_D^{20}$ = +11.6° (c = 1.0, EtOH) ([19e]: $[\alpha]_D^{20}$ = +11.7° (c = 0.6, EtOH)). A sample was recrystallized twice from EtOH, $[\alpha]_D^{20}$ = +12.4° (c = 0.6, EtOH).

1.3.3. (*S*)-**17** (*cf.* [25c] [19e]). An analogous conversion of 10.6 g (49.9 mmol) of (*S*)-**16** ($[\alpha]_D^{20}$ = +37.8° (c = 1.0, 1N HCl); op 96.5%) afforded, after 3 crystallizations, 4.2 g of (*S*)-**17**, m.p. 108.5–109°; 99.7% purity (GC); $[\alpha]_D^{20}$ = −11.7° (c = 1.0, EtOH), and from the combined mother liquors 1.0 g of (*S*)-**17**, m.p. 108–109°; $[\alpha]_D^{20}$ = −12.4° (c = 1.0, EtOH); combined yield 5.2 g (30.5%).

1.4. *(RS)-, (R)-, and (S)-(6,6'-Dimethylbiphenyl-2,2'-diyl)bis(diphenylphosphine)* ((*RS*)-, (*R*)-, and (*S*)-**10**, 'BIPHEMP'). 1.4.1. (*RS*)-**10**. To a soln. of 10.2 g (30 mmol) of (*RS*)-**17** in 200 ml of Et_2O was added at $-110°$ to $-95°$ within 25 min 84 ml of a 1.4M soln. of *t*-BuLi in pentane (118 mmol). The resulting slightly opaque mixture was stirred for 20 min at $-110°$ to $-90°$, then a soln. of 13.2 g (60 mmol) of freshly distilled Ph_2PCl in 60 ml of Et_2O was added at this temp. Then, the mixture was allowed to attain r.t. within 1 h. At *ca.* $-60°$, the precipitation of a white solid started. After stirring for 2 h at r.t., the mixture was quenched by addition of 40 ml of H_2O, filtered under Ar, and the collected white solid was washed 4 times with each 10 ml of EtOH and 10 ml of H_2O, and dried *in vacuo*. The resulting white powder (14.7 g, m.p. 240–243°) was recrystallized from a mixture of 140 ml of AcOEt and 60 ml of toluene to afford 12.04 g (73%) of (*RS*)-**10** as white crystals, m.p. 242–243°. IR: 1584, 1478 (Ar.); 1448; 1398, 1380 (CH_3); 1092 (P–Ph); 780 (1,2,3-trisubst. benzene); 741, 694 (monosubst. benzene). ^{1}H-NMR (80 MHz): 7.4–7.0 (*m*, 26 arom. H); 1.38 (*s*, 2 CH_3); in addition 1.49, 1.24 (2*s* of very low intensities, CH_3 of trace of (*RS*)-**10**-monoxide. ^{31}P-NMR (162 MHz): −13.9 (*s*). MS: 549 (0.1, M^+ – H), 473 (3, M^+ – Ph), 365 (100, M^+ – PPh_2). Anal. calc. for $C_{38}H_{32}P_2$ (550.62): C 82.89, H 5.86; found: C 82.67, H 6.06.

1.4.2. (*R*)-**10**. The reaction mixture of an analogous conversion of 8.5 g (25.0 mmol) of (*R*)-**17** ($[\alpha]_D^{20} = +11.6°$ (*c* = 1.0, EtOH)) was filtered after quenching with 100 ml of H_2O. The solid residue was washed with 4 × 60 ml of Et_2O and dried *in vacuo* to afford 2.10 g (15%) of (*RS*)-**10**, m.p. 242–243°. The aq. layer of the filtrate was removed *via* cannula, and the org. layer was washed with 3 × 20 ml of H_2O, dried (Na_2SO_4), and evaporated. The resulting white solid (12.4 g) was crystallized from a mixture of 100 ml of EtOH and 35 ml of toluene to afford 6.3 g (*R*)-**10**, m.p. 212–213°; $[\alpha]_D^{20} = -43.1°$ (*c* = 1.0, $CHCl_3$). Another 1.0 g of (*R*)-**10**, m.p. 209–210.5°, $[\alpha]_D^{20} = -36.7°$ (*c* = 1.0, $CHCl_3$), was obtained from the mother liquor; combined yield 7.1 g (52%). UV: 203 (104700); 269.5 (20000). CD: 195 (+104, pos. max.); 212 (+0.7, sh); 213 (0); 235 (−70, neg. max.); 266 (0); 280 (+18, pos. max.). IR: 1584, 1478 (Ar.); 1448; 1433; 1397, 1380 (CH_3); 1091 (P–Ph); 779 (1,2,3-trisubst. benzene); 742, 695 (monosubst. benzene). ^{1}H-NMR, MS: identical with corresponding spectra of (*RS*)-**10**. ^{1}H-NMR (270 MHz) after addition of 0.5 mol-equiv. of (*R*)-**18**: 98:2 mixture (*R*,*R*)-**19a**/(*S*,*R*)-**19a**, ee 96%. Anal. calc. for $C_{38}H_{32}P_2$ (550.62): C 82.89, H 5.86; found: C 82.69, H 5.81.

1.4.3. (*S*)-**10**. The reaction mixture of an analogous conversion of 5.1 g (15.0 mmol) of (*S*)-**17** ($[\alpha]_D^{20} = -11.7°$ (*c* = 1.0, EtOH)) was quenched with 50 ml of H_2O, filtered, and the filter cake was washed with H_2O and dried *in vacuo*. The filtrate, after removal of the aq. phase *via* cannula, was washed with 2 × 50 ml of deoxygenated H_2O, dried (Na_2SO_4), and evaporated. The residue was combined with the solid obtained in the filtration and dissolved in 130 ml of refluxing AcOEt. After standing for 2 days at r.t., filtration and drying *in vacuo* yielded 0.85 g (10%) of (*RS*)-**10**, m.p. 242–243°. The filtrate was evaporated and the residue was crystallized from a mixture of 50 ml of EtOH and 22 ml of toluene to afford 4.25 g (51.5%) of (*S*)-**10**, white needles, m.p. 212–213°; $[\alpha]_D^{20} = +41.7°$ (*c* = 1.0, $CHCl_3$). Another 0.4 g of (*S*)-**10**, m.p. 213–214°; $[\alpha]_D^{20} = +41.4°$ (*c* = 0.7, $CHCl_3$), was obtained from the mother liquor; combined yield 4.65 g (56%). UV: 205.5 (88700); 269.5 (20150). CD: 195 (−103, neg. max.); 208 (0); 215 (+4, sh); 235 (+78, pos. max.); 267 (0); 281 (−15, neg. max.). IR: identical with corresponding spectrum of (*R*)-**10**. ^{1}H-NMR, ^{31}P-NMR, MS: identical with corresponding spectra of (*RS*)-**10**. ^{1}H-NMR (400 MHz) after addition of 0.5 mol-equiv. of (*R*)-**18**: 98.75:1.25 mixture (*S*,*R*)-**19a**/(*R*,*R*)-**19a**; ee 97.5%. Anal. calc. for $C_{38}H_{32}P_2$ (550.62): C 82.89, H 5.86; found: C 82.81, H 5.91.

1.5. *Resolution of (RS)-***10**. 1.5.1. *Di-μ-chlorobis{(R)-2-[1-(dimethylamino)ethyl]phenyl-C,N}dipalladium(II)* ((*R*)-**18**) was synthesized according to the procedure of *Roberts* and *Wild* [23b]; m.p. 184–185.5° (dec.), $[\alpha]_D^{20} = -78.4°$ (*c* = 0.49, benzene) ([22b]: m.p. 186–189°, $[\alpha]_D^{20} = +72.1°$ (*c* = 0.36, benzene), [2c]: $[\alpha]_D^{20} = +78.5°$ (*c* = 0.56, benzene) for the corresponding (*S*)-stereoisomer). ^{1}H-NMR (400 MHz): 7.21, 7.16 (2*d*, *J* = 8, 1 arom. H); 6.97 (*m*, 1 arom. H); 6.87 (*m*, 1 arom. H); 6.77 (~ *dd*, *J* = 8, 1, 1 arom. H); 3.88 (~ *quint.*, *J* = 7, C*H*CH_3); 2.94, 2.91 (2*s*, intensity ratio 4:3, NCH_3); 2.67, 2.64 (2*s*, intensity ratio 4:3, NCH_3); 1.59, 1.58 (2*d*, *J* = 7, intensity ratio 4:3, $CHCH_3$); the doubling of the signals is probably caused by the presence of *cis*- and *trans*-isomers.

1.5.2. *{(R)-2-[1-(Dimethylamino)ethyl]phenyl-C,N}{(R)- or (S)-(6,6'-dimethylbiphenyl-2,2'-diyl)bis(diphenylphosphine)}palladium(II) Tetrafluoroborate* ((*R*,*R*)-**19b** and (*S*,*R*)-**19b**). A suspension of 1.31 g (2.26 mmol) of (*R*)-**18** and 2.44 g (4.52 mmol) of (*RS*)-**10** in 100 ml of MeOH was stirred for 4 h under Ar. To the resulting yellow soln. was added a soln. of 0.95 g (9.04 mmol) of NH_4BF_4 in 63 ml of H_2O, and the precipitated solid was collected by filtration, washed with MeOH/H_2O 1:1, and dried *in vacuo* to afford 1.79 g of yellowish crystals. The filtrate was diluted with 50 ml of H_2O, stirred for 1 h, and the additionally precipitated solid was collected by filtration and dried *in vacuo* to afford another 1.84 g of yellowish crystals; combined yield 3.63 g (90%) of (*R*,*R*)- and (*S*,*R*)-**19b**[21]). The combined solids were dissolved in 150 ml of CH_2Cl_2/Et_2O 1:2, 50 ml of hexane

[21]) It is likely that partial separation of the two diastereoisomers had already occurred in this sequential precipitation procedure (*cf. 3.5* and *4.4*).

were added slowly with stirring, and the precipitated solid was collected by filtration to afford 1.50 g of the less soluble (*R*, *R*)-**19b**. Twofold recrystallization from CH_2Cl_2/Et_2O eventually yielded 1.07 g (53% of th.) of pure (*R*, *R*)-**19b**; m.p. 213–216°. The filtrate from the above crystallization from CH_2Cl_2/Et_2O/hexane was evaporated to dryness, the residue dissolved in 10 ml of CH_2Cl_2 and 50 ml of Et_2O, and the soln. seeded with a few crystals of (*R*, *R*)-**19b**. After standing at −15° overnight, 150 mg of (*R*, *R*)-**19b**, m.p. 214–216°, were removed by filtration. The filtrate was evaporated, and the yellow foam was crystallized from 9 ml of CH_2Cl_2/AcOEt/Et_2O 2:5:2 at −15° to afford 1.47 g of yellow crystals, m.p. 186–190° (dec.). Recrystallization finally yielded 1.12 g (56% of th.) of (*S*, *R*)-**19b** as yellowish crystals, m.p. 187–189° (dec.). This material still contained 4% of (*R*, *R*)-**19b** (^{1}H-NMR).

(*R*, *R*)-**19b**. M.p. 213–216° (dec.); $[\alpha]_D^{20} = +301.4°$ (*c* = 1.0, $CHCl_3$). IR: 1577, 1479 (Ar.); 1057 (br., BF_4^-); 771 (1,2,3-trisubst. benzene); 745, 698 (monosubst. benzene). ^{1}H-NMR (400 MHz): 7.8 (br. *s*, 2 arom. H); 7.65–7.35 (*m*, 16 arom. H); 7.18 (*m*, 4 arom. H); 7.11 (*t*, *J* = 8.5, 1 arom. H); 6.93 (*td*, *J* = 8, 2, 1 arom. H); 6.84 (*d*, *J* = 7.5, 1 arom. H); 6.77 (*d*, *J* = 8, 1 arom. H); 6.67 (*m*, 2 arom. H); 6.41 (*q*, *J* = 7.5, 1 arom. H); 6.25 (*m*, 1 arom. H); 5.25 (*q*, *J* = 6.5, NC*H*CH_3); 2.54 (~ *dd*, *J* = 3.5, 3.5, NCH_3); 1.56 (*s*, 1 arom. CH_3); 1.28 (br. *s*, NCH_3); 1.27 (*d*, *J* = 7, NCHC*H*$_3$); 1.015 (*s*, 1 arom. CH_3). Anal. calc. for $C_{48}H_{46}BF_4NP_2Pd$ (892.05): C 64.63, H 5.20, N 1.57; found: C 63.86, H 5.25, N 1.42, H_2O 0.22.

(*S*, *R*)-**19b**. M.p. 187–189° (dec.); $[\alpha]_D^{20} = -256.2°$ (*c* = 1.0, $CHCl_3$). IR: 1576, 1479 (Ar.); 1055 (br., BF_4^-); 748, 697 (monosubst. benzene). ^{1}H-NMR (400 MHz): 8.0–7.6 (*m*, 6 arom. H); 7.57–7.3 (*m*, 11 arom. H); 7.25 (*m*, 1 arom. H); 7.15 (*m*, 4 arom. H); 7.01 (*t*, *J* = 8.5, 1 arom. H); 6.9 (*m*, 3 arom. H); 6.82 (*d*, *J* = 8, 1 arom. H); 6.7 (*t*, *J* = 7.5, 1 arom. H); 6.3–6.2 (*m*, 2 arom. H); 3.45 (~ *quint.*, *J* = 6, NC*H*CH_3); 2.21 (*d*, *J* = 6.5, NCHC*H*$_3$); 2.14 (~ *t*, *J* = 3.5, NCH_3); 1.70 (~ *d*, *J* = 2, NCH_3); 1.65 (*s*, 1 arom. CH_3); 1.06 (*s*, 1 arom. CH_3); additional low intensity signals of approx. 4% of (*R*, *R*)-**19b**. ^{31}P-NMR: 37.22 (*d*, *J* = 45); 11.23 (*d*, *J* = 45). Anal. calc. for $C_{48}H_{46}BF_4NP_2Pd$ (892.05): C 64.63, H 5.20, N 1.57; found: C 64.18, H 6.00, N 1.69.

1.5.3. *Degradation of Pd Complexes* **19b**. To a suspension of 42.6 mg (1.12 mmol) $LiAlH_4$ in 15 ml of THF was added portionwise at ambient temp. 1.0 g (1.12 mmol) of (*R*, *R*)-**19b**. The resulting black mixture was stirred for 1 h, then quenched by addition of a few drops of sat. NaCl soln., treated with charcoal, and filtered through a short plug of Na_2SO_4 and *Celite*. The residue obtained after evaporation was purified by filtration through silica gel (CH_2Cl_2) and by recrystallization from EtOH/toluene to afford 121 mg (20%) of (*R*)-**10**, white crystals, m.p. 210–212.5°; $[\alpha]_D^{20} = -42.7°$ (*c* = 1.0, $CHCl_3$). An analogous reaction afforded a 46% yield of (*R*)-**10**, m.p. 212–214°.

1.6. *Mono- and Bis-oxides of* **10**. Chromatography of 0.40 g of crude (*RS*)-**10** on silica gel (40 g, CH_2Cl_2/MeOH 1%) without exclusion of air afforded 50 mg of (*RS*)-**10**-monoxide and, from the more polar fractions, 230 mg of (*RS*)-**10**-bis-oxide. Alternatively, a soln. of 550 mg (1.0 mmol) of (*RS*)-**10** in 40 ml of CH_2Cl_2 was treated at 0° with 1 ml of 30% aq. H_2O_2 soln., and the mixture was stirred for 1 h at 0° and 1 h at r.t. The mixture was dried (Na_2SO_4), filtered, and evaporated. Crystallization of the residue from 10 ml of toluene afforded 590 mg (101%) of (*RS*)-**10**-bis-oxide. The bis-oxides of (*R*)- and (*S*)-**10** were obtained by analogous H_2O_2 oxidations.

(RS)-[6,6'-Dimethyl-2'-(diphenylphosphino)biphenyl-2-yl](diphenylphosphine) Oxide ((*RS*)-**10**-monoxide). M.p. 247.5–248° (CH_2Cl_2/AcOEt). IR: 1585, 1569, 1480 (Ar.); 1204 (P=O); 778, 768 (1,2,3-trisubst. benzene); 748, 721, 696 (monosubst. benzene). ^{1}H-NMR (60 MHz): 7.9–6.9 (*m*, 26 arom. H); 1.5 (*s*, CH_3); 1.25 (*s*, CH_3). MS: 566 (0.2, M^+), 565 (0.2, M^+- H), 489 (2, M^+- Ph), 365 (100, M^+- P(O)Ph_2); 283 (4, M^{++}).

(RS)-(6,6'-Dimethylbiphenyl-2,2'-diyl)bis(diphenylphosphine Oxide) ((*RS*)-**10**-bis-oxide). M.p. 283.5° (CH_2Cl_2/acetone). UV: 208 (78100); 266 (3200); 273 (3450); 285 (2450). IR. 1589, 1573, 1483 (Ar.); 1203 (P=O); 774 (1,2,3-trisubst. benzene); 751, 721, 696 (monosubst. benzene). ^{1}H-NMR (80 MHz): 7.9–7.0 (*m*, 26 arom. H); 1.43 (*s*, 2 CH_3). MS: 582 (1, M^+), 581 (1, M^+- H), 505 (4, M^+- Ph), 381 (100, M^+- P(O)Ph_2). Anal. calc. for $C_{38}H_{32}O_2P_2$ (582.62): C 78.34, H 5.54; found: C 78.31, H 5.41.

*(R)-***10***-Bis-oxide*. M.p. > 300° (CH_2Cl_2/AcOEt); $[\alpha]_D^{20} = +2.1°$ (*c* = 1.0, EtOH), $[\alpha]_{365}^{20} = -92°$ (*c* = 1.0, EtOH). CD (*c* = 0.02, EtOH): 192 (0), 200 (+114, pos. max.); 211 (0); 222 (−46, neg. max.); 228 (−37, sh). UV, IR, ^{1}H-NMR, and MS superimposable to those of (*RS*)-**10**-bis-oxide. Anal. calc. for $C_{38}H_{32}O_2P_2$ (582.61): C 78.34, H 5.54; found: C 78.36, H 5.60.

*(S)-***10***-Bis-oxide*. M.p. > 300° (CH_2Cl_2/AcOEt); $[\alpha]_D^{20} = -1.2°$ (*c* = 1.0, EtOH), $[\alpha]_{365}^{20} = +93.2°$ (*c* = 1.0, EtOH). CD (*c* = 0.02, EtOH): 192 (0); 200 (−115, neg. max.); 211 (0); 222 (+40, pos. max.); 223 (40, sh), 231 (30, sh). UV, IR, ^{1}H-NMR, and MS superimposable to those of (*RS*)-**10**-bis-oxide. Anal. calc. for $C_{38}H_{32}O_2P_2$ (582.61): C 78.34, H 5.54; found: C 78.12, H 5.55.

2. (*R*)-*N*,*N*'-(6,6'-Dimethylbiphenyl-2,2'-diyl)bis(*P*,*P*-diphenylphospinous Amide) ((*R*)-6). – To a soln. of 8.48 g (40 mmol) of (*R*)-**16** in 100 ml of THF were added dropwise at −30° 54 ml of 1.5N BuLi soln. in hexane (80 mmol), and the mixture was stirred for 30 min at −30°. Then, a soln. of 19.4 g (88 mmol) of Ph_2PCl in 50 ml of THF was added within 30 min. The mixture was stirred for 30 min at −30° and 1 h at r.t., washed 3 times with each 60 ml

of H_2O (added *via* syringe and removed *via* cannula), and evaporated. Then, 150 ml of EtOH were added to the oily residue to induce crystallization, the crystals were separated by filtration and recrystallized from 150 ml of EtOH to afford 21.0 g (90%) of slightly impure (*R*)-**6**, m.p. 102–103°. Another crystallization from 130 ml of EtOH afforded 6.4 g (28%) of pure (*R*)-**6**, m.p. 102–103°; $[\alpha]_D^{20} = -146.2°$ ($c = 1.1$, benzene), $-161.7°$ ($c = 1.0$, EtOH) ([12]: m.p. 98–110°, $[\alpha]_D^{20} = -140°$ ($c = 1.1$, benzene)). IR: 3357 (NH); 1579, 1479 (Ar.); 1092 (P–Ph); 773 (1,2,3-trisubst. benzene); 736, 696 (monosubst. benzene). ^{1}H-NMR (80 MHz): 7.45–7.05 (*m*, 26 arom. H); 6.85–6.65 (*m*, 2 arom. H); 4.35 (br. *d*, $J = 7$, 2 NH); 1.85 (*s*, 2 CH_3). MS: 580 (4, M^+), 503 (2, $M^+ -$ Ph), 394 (100, $M^+ -$ $HPPh_2$). Anal. calc. for $C_{38}H_{34}N_2P_2$ (580.65): C 78.60, H 5.90, N 4.82; found: C 78.52, H 6.00, N 4.98.

3. (4,4′,6,6′-Tetramethylbiphenyl-2,2′-diyl)bis(diphenylphosphine) (11). – 3.1. *(RS)-2,2′,4,4′-Tetramethyl-6,6′-dinitrobiphenyl* ((*RS*)-**23**). The synthesis of (*RS*)-**23** was carried out as described in [30]: nitration of 248 ml (2.0 mmol) of *2,4-dimethylaniline* (**20**) afforded 250 g of crude *2,4-dimethyl-6-nitroaniline* (**21**) as orange powder, which, upon diazotization/iodination [30a], afforded 269 g (49% based on **20**) of *2-iodo-3,5-dimethyl-1-nitrobenzene* (**22**), m.p. 102° (EtOH/H_2O) ([30a]: 105°). *Ullmann* coupling [30b] of 250 g (0.90 mmol) of **22** furnished 66.8 g (50%) of (*RS*)-**23** as yellow crystals, m.p. 132–133° (i-PrOH) ([30b]: 136–137°).

3.2. *(RS)-4,4′,6,6′-Tetramethylbiphenyl-2,2′-diamine* ((*RS*)-**24**). To a soln. of 10.0 g (0.033 mol) of (*RS*)-**23** in 100 ml of AcOH were added 1.2 g of 5% Pd/C, and the mixture was hydrogenated at 1.1 atm of H_2 pressure. Filtration through a short pad of *Hyflo*, evaporation, and crystallization of the residue from i-PrOH afforded 6.5 g (82%) of (*RS*)-**24** as off-white crystals, m.p. 184–185° ([31]: 180–181.5°). In an analogous hydrogenation of 0.30 mol of (*RS*)-**23**, a yield of 87% of (*RS*)-**24** was achieved. IR: 3447, 3354, 1611 (NH_2). ^{1}H-NMR (80 MHz): 6.5 (br. *s*, 2 arom. H); 6.4 (br. *s*, 2 arom H); 3.3 (br. *s*, 2 NH_2); 2.3 (*s*, 2 CH_3); 1.9 (*s*, 2 CH_3). MS: 240 (100, M^+), 225 (53), 210 (27), 208 (25). Anal. calc. for $C_{16}H_{20}N_2$ (240.35): C 79.96, H 8.39, N 11.66; found: C 79.82, H 8.41, N 11.61.

3.3. *(RS)-2,2′-Dibromo-4,4′,6,6′-tetramethylbiphenyl* ((*RS*)-**25**). Diamine (*RS*)-**24** (50 g, 0.21 mol) was diazotized and brominated as described in *1.3.1* to afford, after filtration with hexane of the crude product through silica gel, 27.7 g of white crystalline material consisting mainly of the desired (*RS*)-**25** and some monobromide (2-bromo-4,4′,6,6′-tetramethylbiphenyl). Crystallization from 100 ml of EtOH furnished 18.7 g (24%) of pure (*RS*)-**25**, white crystals, m.p. 125–126°. IR: 1603, 1549 (Ar). ^{1}H-NMR (60 MHz): 7.3 (br. *s*, 2 arom. H); 7.0 (br. *s*, 2 arom. H); 2.35 (*s*, 2 CH_3); 1.95 (*s*, 2 CH_3). MS: 370/368/366 (36/75/39, M^+), 208 (100, $M^+ -$ 2 Br). Anal. calc. for $C_{16}H_{16}Br_2$ (368.11): C 52.21, H 4.38, Br 43.41; found: C 51.99, H 4.08, Br 44.17.

3.4. *(RS)-(4,4′,6,6′-Tetramethylbiphenyl-2,2′-diyl)bis(diphenylphosphine)* ((*RS*)-**11**). Reaction of 16.56 g (45 mmol) of (*RS*)-**25** with *t*-BuLi and Ph_2PCl as described in *1.4.1* afforded 18.9 g of crude (*RS*)-**11**. Recrystallization from a mixture of 300 ml of AcOEt and 145 ml of toluene yielded 14.8 g (57%) of (*RS*)-**11**, white powder, m.p. 249–251°. IR: 1594, 1584, 1479 (Ar.); 1377 (CH_3); 1092 (P–Ph); 742, 695 (monosubst. benzene). ^{1}H-NMR (60 MHz): 7.25 (*m*, 20 arom. H); 6.9 (br. *s*, 4 arom. H); 2.25 (*s*, 2 CH_3); 1.4 (*s*, 2 CH_3). MS: 501 (2, $M^+ -$ Ph), 393 (100, $M^+ -$ PPh_2). Anal. calc. for $C_{40}H_{36}P_2$ (578.68): C 83.02, H 6.27; found: C 82.98, H 6.16.

3.5. *{(R)-2-[1-(Dimethylamino)ethyl]phenyl-C,N}[(R)- or (S)-(4,4′,6,6′-tetramethylbiphenyl-2,2′-diyl)-bis(diphenylphosphine)]palladium(II) Tetrafluoroborate* ((*R*,*R*)-**26b** and (*S*,*R*)-**26b**). A suspension of 11.0 g (20 mmol) of (*RS*)-**11** and 5.80 g (10 mmol) of (*R*)-**18** in 200 ml of MeOH was stirred overnight at ambient temp. To the resulting yellow soln. was added dropwise a soln. of 1.16 g (11 mmol) NH_4BF_4 in 50 ml of H_2O. After an additional stirring period of 3 h, the precipitated solid was collected by filtration, washed with 20 ml of MeOH/H_2O 4:1, and dried *in vacuo* to afford 6.86 g (75% of th.) of (*R*,*R*)-**26b** which proved to be diasteroisomerically pure (^{1}H-NMR). To the filtrate was added again a soln. of 1.16 g (11 mmol) of NH_4BF_4 in 50 ml of H_2O, and the mixture was stirred for 1 h. The precipitate was collected by filtration, washed with 20 ml of MeOH/H_2O 2:1, and dried *in vacuo* to yield 9.6 g of a yellowish powder consisting, according to ^{1}H-NMR, of a 17:83 mixture (*R*,*R*)-**26b**/(*S*,*R*)-**26b**. Dilution of the second filtrate with 200 ml of H_2O produced a further 0.92 g of a 7:93 mixture (*R*,*S*)-**26b**/(*S*,*R*)-**26b**. Crystallization of the combined materials from a mixture of 40 ml of CH_2Cl_2 and 100 ml of Et_2O furnished 5.54 g (60% of th.) of pure (*S*,*R*)-**26b** as yellowish crystals.

(*R*,*R*)-**26b**. A sample for analysis was recrystallized from CH_2Cl_2/Et_2O at 0°; m.p. 190–193° (dec., darkening from *ca.* 150°); $[\alpha]_D^{20} = +286.0°$ ($c = 1.16$, $CHCl_3$). IR: 1599, 1574, 1479 (Ar.); 1095, 1058 (P–Ph, BF_4^-); 749, 697 (monosubst. benzene). ^{1}H-NMR (270 MHz): 8.0–7.1 (*m*, 21 arom. H); 6.92 (*d*, $J = 10$, 1 arom. H); 6.7–6.6 (*m*, 3 arom. H); 6.2 (*s*, 1 arom. H); 6.4 (*q*, $J = 8$, 1 arom. H); 6.24 (*m*, 1 arom. H); 5.3 (*q*, $J = 7$, $NCHCH_3$); 2.53 (*m*, NCH_3); 2.23 (*s*, CH_3); 2.08 (*s*, CH_3); 1.51 (*s*, CH_3); 1.29 (*m*, NCH_3); 1.27 (*d*, $J = 6.5$, $NCHCH_3$); 1.00 (*s*, CH_3). Anal. calc. for $C_{50}H_{50}BF_4NP_2Pd$ (920.11): C 65.27, H 5.48, N 1.52; found: C 65.11, H 5.79, N 1.66.

(*S*,*R*)-**26b**. A sample for analysis was recrystallized from CH_2Cl_2/Et_2O; m.p. 198–200° (dec., darkening from 150°); $[\alpha]_D^{20} = -298.0°$ ($c = 1.19$, $CHCl_3$). IR: 1601, 1577, 1479 (Ar.); 1084, 1057 (P–Ph, BF_4^-); 748, 695 (monosubst. benzene). ^{1}H-NMR (270 MHz): 7.9–7.1 (*m*, 21 arom. H); 6.92 (*m*, 1 arom. H); 6.81 (*d*, $J = 10$, 1 arom. H); 6.75–6.65 (*m*, 2 arom. H); 6.57 (*s*, 1 arom. H); 6.3–6.17 (*m*, 2 arom. H); 3.46 (*m*, $NCHCH_3$); 2.21 (*d*, $J = 6.5$,

NCHCH_3); 2.20 (*s*, CH_3); 2.11 (*m*, NCH_3); 2.05 (*s*, CH_3); 1.72 (*m*, NCH_3); 1.57 (*s*, CH_3); 1.05 (*s*, CH_3). Anal. calc. for $C_{50}H_{50}BF_4NP_2Pd$ (920.11): C 65.27, H 5.48, N 1.52; found: C 65.22, H 5.60, N 1.49.

3.6. *(R)-(4,4',6,6'-Tetramethylbiphenyl-2,2'-diyl)bis(diphenylphosphine)* ((*R*)-**11**). A soln. of 6.30 g (6.85 mmol) of (*R*, *R*)-**26b** in 85 ml of acetone and 17 ml of 10N HCl was heated under reflux for 1 h. To the warm yellow soln. was added dropwise 300 ml of H_2O, and the resulting yellow suspension was stirred for 30 min at ambient temp. The precipitate was collected by filtration, washed twice with H_2O, and dried *in vacuo* to afford 5.62 g (109% of th.) of crude dichloro[(*R*)-(4,4',6,6'-tetramethylbiphenyl-2,2'-diyl)bis(diphenylphosphine)]palladium(II) as yellow powder. To a soln. of 5.57 g of this material in 100 ml of CH_2Cl_2 were added 40 ml of H_2O and 5.3 g (81 mmol) of KCN. The two-phase system was stirred vigorously for 30 min, the org. layer was then separated, and the aq. layer was extracted with CH_2Cl_2. The combined org. phases were washed with H_2O and sat. NaCl soln., dried (Na_2SO_4), filtered, and evaporated. Crystallization of the yellow residue from toluene/EtOH gave, after charcoal treatment of the hot soln., 2.70 g (68%) of (*R*)-**11**, white crystals, m.p. 217–218°; $[\alpha]_D^{20} = -21.5°$ (*c* = 1.03, $CHCl_3$). An additional 0.50 g of (*R*)-**11** was obtained from the mother liquor, m.p. 215.5–218°; combined yield 81%. UV: 205.5 (94450); 272 (20550). CD: 200 (+71, pos. max.); 218 (0); 220 (−1, sh); 238 (−72, neg. max.); 267 (0); 283 (+13, pos. max.); 290 (+12, pos. min.); 296 (+13, pos. max.). IR: 1585, 1555, 1480 (Ar.); 1374 (CH_3); 1091 (P–Ph); 739, 694 (monosubst. benzene). ^{1}H-NMR (270 MHz): 7.3–7.15 (*m*, 20 arom. H); 6.89, 6.87 (2*s*, 4 arom. H); 2.25 (*s*, 2 CH_3); 1.38 (*s*, 2 CH_3). MS: 501 (3, M^+ − Ph), 393 (110, M^+ − PPh_2). Anal. calc. for $C_{40}H_{36}P_2$ (578.68): C 83.02, H 6.27; found: C 82.70, H 6.60.

3.7. *(S)-(4,4',6,6'-Tetramethylbiphenyl-2,2'-diyl)bis(diphenylphosphine)* ((*S*)-**11**). Decomposition of (*S*, *R*)-**26b** was carried out as described above. Crude (*S*)-**11** was purified by filtration with hexane/CH_2Cl_2 through a short pad of silica gel and crystallization from AcOEt; yield 48% of (*S*)-**11** as white crystals, m.p. 217.5–219°; $[\alpha]_D^{20} = +21.4°$ (*c* = 1.11, $CHCl_3$). UV: 204 (103050); 272 (20800). CD: 219 (0); 221 (+3, sh); 238 (+73, pos. max.); 254 (+22, sh); 268 (0); 286 (−10, neg. max.); 289 (−9.5, neg. min.); 300 (−11, neg. max.). IR, ^{1}H-NMR, and MS: identical with the corresponding data of (*R*)-**11**. Anal. calc. for $C_{40}H_{36}P_2$ (578.68): C 83.02, H 6.72; found: C 83.00, H 6.60.

4. (4,4'-Bis(dimethylamino)-6,6'-dimethylbiphenyl-2,2'-diyl)bis(diphenylphosphine) (12). – 4.1. *(RS)-2,2'-Dibromo-6,6'-dimethylbenzidine* ((*RS*)-**30**). The synthesis of (*RS*)-**30** was carried out according to *Carlin* and *Foltz* [32]: bromination of 304.0 g (2.0 mol) of *4-methyl-2-nitroaniline* (**27**) afforded 467 g (101%) of crude *2-bromo-4-methyl-6-nitroaniline* (**28**), m.p. 63–65° ([32]: 63–64°). Deamination [32] of 450 g (1.95 mol) of this material produced 308.8 g (74%) of 3-bromo-5-nitrotoluene, m.p. 83–84° ([32]: 81–83°). Zn reduction [32] of 411 g (1.90 mol) of 3-bromo-5-nitrotoluene afforded, after crystallization from petroleum ether, 212.0 g (60%) of **29** as off-white crystals, m.p. 133–134° ([32]: 132.5–134.5°). Benzidine rearrangement of 125 g (0.34 mol) of **29** in 25% HCl (*cf.* [33]) afforded 120.8 g (96%) of crystalline material which, according to ^{1}H-NMR, consisted of a 2:1 mixture of (*RS*)-**30** and 2,4'-diamino-2',6-dibromo-4,6'-dimethylbiphenyl (*cf.* [32]). Attempts to separate this mixture by crystallization or by chromatography on silica gel failed. Pure (*RS*)-**30** was obtained, however, by salt formation with (*R*, *R*)-tartaric acid, recrystallizing the salt twice, decomposing the salt, and crystallizing the benzidine from EtOH; m.p. 176–178° ([32]: 179–181°). Only very little enantiomeric enrichment had taken place in this operation, as became evident from optical rotation ($[\alpha]_D^{20} = 0.0°$ (*c* = 3.0, EtOH)) and from conversion *via* diazotization/dediazoniation ($NaNO_2$, HCl; H_3PO_2) into (*RS*)-**17**, m.p. 106–108°; $[\alpha]_D^{20} = +0.3°$ (*c* = 1.0, EtOH).

4.2. *(RS)-2,2'-Dibromo-4,4'-bis(dimethylamino)-6,6'-dimethylbiphenyl* ((*RS*)-**31**). The *N*-methylation of (*RS*)-**30** was carried out according to *Borch* and *Hassid* [34]: to a soln. of 29.7 g (80 mmol) of a 68:32 mixture (*RS*)-**30**/(*RS*)-2,4'-diamino-2',6-dibromo-4,6'-dimethylbiphenyl in 640 ml of MeCN were added 120 ml of 37% aq. HCHO soln. and 31.7 g (0.48 mol) of $NaBH_3CN$. Then, 16 ml of AcOH was added dropwise at a reaction temp. of 20–40°. After 3 h of stirring at ambient temp., an additional 16 ml of AcOH was added, and the mixture was stirred for another 2 h. The mixture was partitioned between Et_2O and 4N NaOH and worked up as usual. The oily residue was crystallized from 600 ml of EtOH, and the material obtained was decolorized with charcoal and recrystallized twice from EtOH to afford 11.2 g (48% based on (*RS*)-**30**) of (*RS*)-**31**; white needles, m.p. 205–206°. IR: 2804 (NCH_3); 1604, 1532, 1498 (Ar.). ^{1}H-NMR (60 MHz): 6.85 (*d*, *J* = 2.5, 2 arom. H); 6.55 (*d*, *J* = 2.5, 2 arom. H); 2.95 (*s*, 2 $N(CH_3)_2$); 2.0 (*s*, 2 CH_3). MS: 428/426/424 (52/100/52, M^+), 332 (6), 330 (6), 214 (9). Anal. calc. for $C_{18}H_{22}Br_2N_2$ (426.20): C 50.73, H 5.20, N 6.57, Br 37.50; found: C 50.73, H 5.28, N 6.63, Br 37.58.

4.3. *(RS)-[4,4'-Bis(dimethylamino)-6,6'-dimethylbiphenyl-2,2'-diyl]bis(diphenylphosphine)* ((*RS*)-**12**). To a soln. of 10.65 g (25 mmol) of (*RS*)-**31** in 120 ml of Et_2O and 30 ml of THF was added dropwise, at −70° to −75°, 71.4 ml of a 1.4M *t*-BuLi soln. in pentane (0.10 mol). The resulting suspension was stirred for 4 h at −75°, and 11.0 g (50 mmol) of freshly distilled Ph_2PCl in 30 ml of Et_2O was added at this temp. The mixture was allowed to attain r.t. while stirring overnight. To the yellow suspension were added 30 ml of H_2O and 2 ml of 4N NaOH, and the solid was collected by filtration, washed 3 times with a mixture of 10 ml of each hexane, Et_2O, and H_2O, and dried *in*

vacuo. The obtained powder (11.0 g) was crystallized from a mixture of 100 ml of EtOH and 55 ml of toluene to yield 9.4 g (59%) of (*RS*)-**12** as white crystals, m.p. 218–219°. Processing of the filtrate from the mixture by washing with H_2O, drying (Na_2SO_4), filtration, evaporation, and trituration of the residue with EtOH afforded another 2.0 g of yellow solid. This material, together with the residue from the mother liquor of the above crystallization, was crystallized from EtOH/toluene to afford an additional 2.15 g of (*RS*)-**12** as slightly yellow crystals, m.p. 217.5–219°; combined yield 72.5%. IR: 2796 (NCH_3); 1592, 1545, 1479 (Ar.); 744, 695 (monosubst. benzene). ^{1}H-NMR (60 MHz): 7.2 (*m*, 20 arom. H); 6.45 (br. *s*, 4 arom. H); 2.75 (*s*, 2 $N(CH_3)_2$); 1.4 (*s*, 2 CH_3). MS: 559 (1, M^+ – Ph), 452 (27), 451 (100, M^+ – PPh_2), 435 (8). Anal. calc. for $C_{42}H_{42}N_2P_2$ (636.76): C 79.22, H 6.65, N 4.40; found: C 79.22, H 7.00, N 4.40.

4.4. *{(R)-2-[1-(Dimethylamino)ethyl]phenyl-C,N}[(R)- or (S)-(4,4'-bis(dimethylamino)-6,6'-dimethylbiphenyl-2,2'-diyl)bis(diphenylphosphine)]palladium(II) Tetrafluoroborate* ((*R*,*R*)-**32b** and (*S*,*R*)-**32b**). To a suspension of 4.35 g (7.5 mmol) of (*R*)-**18** in 100 ml of MeOH was added a soln. of 9.54 g (15 mmol) of (*RS*)-**12** in 40 ml of THF, and the resulting yellow soln. was stirred for 1 h at ambient temp. Then, a soln. of 1.73 g (16.5 mmol) of NH_4BF_4 in 100 ml of H_2O was added dropwise, and the mixture was stirred for 2 h. The precipitated yellow solid was collected by filtration, washed with a few ml of MeOH/H_2O/THF 5:5:2, and dried *in vacuo* to afford 13.0 g (88.5%) of a *ca.* 1:1 mixture (*R*,*R*)-**32b**/(*S*,*R*)-**32b**. Recrystallization of 2.85 g of this material from 20 ml of MeOH/THF afforded 1.31 g of pure (*R*,*R*)-**32b** as yellow crystals, m.p. 189–193° (dec.); $[\alpha]_D^{20} = +380.2°$ (*c* = 1.39, $CHCl_3$). ^{1}H-NMR (270 MHz): 8.2–7.3 (*m*, 17 arom. H); 7.2–7.1 (*m*, 3 arom. H); 6.75–6.6 (*m*, 3 arom. H); 6.5–6.4 (*m*, 2 arom. H); 6.27 (*m*, 1 arom. H); 6.11 (*d*, *J* = 2, 1 arom. H); 6.02 (*d*, *J* = 3, 1 arom. H); 5.24 (*q*, *J* = 6.5, $NCHCH_3$); 2.78, 2.73 (2*s*, 2 arom. $N(CH_3)_2$); 2.54 (*m*, NCH_3); 1.54 (*s*, arom. CH_3); 1.34 (*m*, NCH_3); 1.29 (*d*, *J* = 6.5, $NCHCH_3$); 1.03 (*s*, 1 arom. CH_3).

An additional 1.35 g (9%) of yellow solid was precipitated by further diluting the filtrate from the original mixture with 150 ml of H_2O. This material consisted of a 5:95 mixture (*R*,*R*)-**32b**/(*S*,*R*)-**32b** according to ^{1}H-NMR (270 MHz): 8.2–7.3 (*m*, 17 arom. H); 7.25–7.05 (*m*, 3 arom. H); 6.93 (*m*, 1 arom. H); 6.75–6.6 (*m*, 2 arom. H); 6.35–6.17 (*m*, 3 arom. H); 6.13 (*d*, *J* = 2, 1 arom. H); 6.07 (*d*, *J* = 3, 1 arom. H); 3.45 (*m*, $NCHCH_3$); 2.77, 2.69 (2*s*, 2 arom. $N(CH_3)_2$); 2.21 (*d*, *J* = 6.5, $NCHCH_3$); 2.16 (*m*, NCH_3); 1.70 (*m*, NCH_3); 1.63 (*s*, 1 arom. CH_3); 1.04 (*s*, 1 arom. CH_3); and additional low intensity signals of 5% (*R*,*R*)-**32b**.

4.5. *(R)-[4,4'-Bis(dimethylamino)-6,6'-dimethylbiphenyl-2,2'-diyl]bis(diphenylphosphine)* ((*R*)-**12**). To a suspension of 138 mg (3.62 mmol) of $LiAlH_4$ in 10 ml of THF was added, at ambient temp., 1.18 g (1.21 mmol) of (*R*,*R*)-**32b** portionwise over a period of 10 min. After stirring for 1 h, the mixture was diluted with 50 ml of Et_2O, and the excess of $LiAlH_4$ was decomposed by dropwise addition of the minimum amount of H_2O. The mixture was dried (Na_2SO_4), filtered, decolorized with charcoal, and filtered twice through a short pad of silica gel. Evaporation furnished 730 mg of a beige powder which was crystallized from 25 ml of EtOH and 2 ml of toluene to afford 517 mg (67%) of (*R*)-**12**, white needles, m.p. 184–185°; $[\alpha]_D^{20} = +25.4°$ (*c* = 1.0, $CHCl_3$). UV: 202.5 (99400); 270 (35350); 330 (5250, sh). UV (*c* = 2.12 × 10^{-5} M, dioxane): 272 (33590); 330 (6140, sh). CD: 192 (+61, pos. max.); 198 (0); 201 (–12, neg. max.); 205 (0); 212 (+16, pos. max.); 219 (0); 225 (–7, sh); 246 (–27, neg. max.); 268 (0); 277 (+10, pos. max.); 290 (+7, pos. min.); 341 (+12, pos. max.). CD (*c* = 0.1, dioxane): 207 (0); 216 (+9, pos. max.); 222 (0); 230 (–10, sh); 241 (–17, sh); 251 (–22, sh); 254 (–23, neg. max.); 275 (0); 281 (+3, pos. max.); 290 (+0.1, pos. min.); 309 (+5, pos. max.); 345 (+11, pos. max.). IR: 2797 (NCH_3); 1592, 1546, 1481 (Ar.); 744, 695 (monosubst. benzene). ^{1}H-NMR (270 MHz): 7.35–7.15 (*m*, 20 arom. H); 6.45 (*m*, 4 arom. H); 2.77 (*s*, 2 $N(CH_3)_2$); 1.41 (*s*, 2 arom. CH_3). MS: 635 (1, M^+ – H), 559 (1, M^+ – Ph), 452 (33), 451 (100, M^+ – PPh_2). Anal. calc. for $C_{42}H_{42}N_2P_2$ (636.76): C 79.22, H 6.65, N 4.40; found: C 78.82, H 6.94, N 4.39.

4.6. *(S)-[4,4'-Bis(dimethylamino)-6,6'-dimethylbiphenyl-2,2'-diyl]bis(diphenylphosphine)* ((*S*)-**12**). An analogous degradation of 1.0 g (1.02 mmol) of (*S*,*R*)-**32b** (containing 5% (*R*,*R*)-**32b**) afforded 380 mg (58%) of (*S*)-**12**, white needles, m.p. 184–185°; $[\alpha]_D^{20} = -26.3°$ (*c* = 1.0, $CHCl_3$). UV (*c* = 2.19 × 10^{-5} M, dioxane): 274 (37450); 330 (5750, sh). CD (*c* = 0.1, dioxane): 209 (0); 217 (–7, neg. max.); 222 (0); 228 (+10, sh); 241 (+16, sh); 255 (+21, pos. max.); 275 (0); 281 (–3, neg. max.); 291 (–1, neg. min.); 313 (–3.3, neg. max.); 317 (–3.0, neg. min.); 345 (–10, neg. max.). IR, ^{1}H-NMR, and MS: identical with those of (*R*)-**12**. Anal. calc. for $C_{42}H_{42}N_2P_2$ (636.76): C 79.22, H 6.65, N 4.40; found: C 79.44, H 6.79, N 4.42.

5. (*RS*)- and (*R*)-5,7-Dihydrodibenz[*c*,*e*]oxepin-1,11-bis(diphenylphosphine) ((*RS*)-13 and (*R*)-13). – 5.1. *Methyl 3-Bromoanthranilate* (**35**). *7-Bromo-1*H*-indole-2,3-dione* (**34**) [36], obtained, in 67–72% yield, from *2-bromoaniline* (**33**) by standard isatin synthesis (*cf.* [35]), was converted into *methyl 3-bromoanthranilate* (**35**) according to *Reissenweber* and *Mangold* [37]: to a suspension of 143.4 g (0.634 mol) of **34** in 950 ml of MeOH were added 51.4 g (0.952 mol) of NaOMe in 170 ml of MeOH and, at 0–15°, 51.8 g of 50% aq. H_2O_2 (0.761 mol). The mixture was stirred at ambient temp. overnight. Then, 80 ml of sat. Na_2SO_3 soln. was added to destroy the excess H_2O_2 and, after stirring for 1 h, the mixture was poured into ice-water and worked up with CH_2Cl_2 as usual. Filtration

through 500 g of silica gel (CH_2Cl_2) followed by evaporation afforded 87 g (60%) of **35** as yellow oil which solidified upon standing at 0°; GC purity 96%. An anal. sample was obtained by crystallization from hexane/toluene, m.p. 47–48° ([38]: 46–47°).

5.2. *Methyl 3-Bromo-2-iodobenzoate* (**36**). A mixture of 36.8 g (0.16 mol) of **35** in 160 ml of 50% H_2SO_4 was heated to 60° for a short time, then cooled in an ice-bath, and to the resulting suspension was added dropwise at 0–5° a soln. of 11.2 g (0.162 mol) of $NaNO_2$ in 60 ml of H_2O. After stirring at 0° for 15 min, a soln. of 40 g (0.24 mol) of KI in 160 ml of H_2O was added, and the mixture was stirred at ambient temp. overnight. Then, sodium thiosulfate was added in portions, and the mixture was worked up as usual with Et_2O to give 53.3 g of a yellow oil. Distillation through a 7-cm *Vigreux* column afforded 46.0 g (84%) of **36** as pale yellow oil, b.p. 103–112°/0.02 Torr; GC purity 98%. IR: 1734 (C=O); 1291 (C–O); 798, 756 (1,2,3-trisubst. benzene). ^{1}H-NMR (60 MHz): 7.8–7.1 (*m*, 3 arom. H); 3.9 (*s*, CO_2CH_3). MS: 342/340 (94/98, M^+), 311/309 (95/100, $M^+ - OCH_3$), 283/281 (57/60, $M^+ - CO_2CH_3$). Anal. calc. for $C_8H_6BrIO_2$ (340.94): C 28.18, H 1.77, I 37.22; found: C 28.18, H 1.78, I 37.11.

5.3. *Dimethyl (*RS*)-6,6'-Dibromobiphenyl-2,2'-dicarboxylate* ((*RS*)-**37**). To a flask containing 48.6 g (0.143 mol) of **36** were added at 160–170°, under stirring, in small portions 19.06 g (0.30 mol) of activated Cu powder [52]. The mixture was stirred at 165° for 2 h. After cooling, the resulting solid was crushed, ground, and suspended in 200 ml of warm CH_2Cl_2, and the mixture was filtered. The filtrate was evaporated, and the residue was extracted with 350 ml of hot EtOH and 50 ml of hot toluene. From the cold EtOH extract, 9.40 g (*RS*)-**37** was obtained as yellowish crystals, while the toluene extract, after dilution with 25 ml of hexane and cooling, afforded another 15.21 g of (*RS*)-**37** as white crystals, m.p. 173.5–174.5°; combined yield 24.61 g (81%). IR: 1723 (C=O); 1279, 1261 (C–O); 758 (1,2,3-trisubst. benzene). ^{1}H-NMR (60 MHz): 8.05 (*dd*, J = 8, 1.5, 2 arom. H); 7.75 (*dd*, J = 8, 1.5, 2 arom. H); 7.3 (*t*, J = 8, 2 arom. H); 3.6 (*s*, 2 CO_2CH_3). MS: 399/397/395 (2/5/3, $M^+ - OCH_3$), 349/347 (83/84, $M^+ -$ Br), 253 (100). Anal. calc. for $C_{16}H_{12}Br_2O_4$ (428.08): C 44.89, H 2.83; found: C 44.84, H 2.82.

5.4. *(*RS*)-6,6'-Dibromobiphenyl-2,2'-dimethanol* ((*RS*)-**38**). To a suspension of 760 mg (20 mmol) of $LiAlH_4$ in 20 ml of THF was added at 10° a soln. of 4.28 g (10 mmol) of (*RS*)-**37** in 20 ml of THF. The resulting greenish soln. was stirred at 10° for 75 min, then quenched with 5 ml of AcOEt. To the mixture was added 70 ml of 2N HCl and usual workup with Et_2O gave 3.8 g of crude (*RS*)-**38**, GC purity 91%. Crystallization from 60 ml of heptane/toluene 2:1 afforded 3.15 g (84.5%) of (*RS*)-**38** as yellowish crystals, m.p. 136–140° which, according to GC, contained 5% of (*RS*)-**39**. The anal. sample was recrystallized from toluene: white needles, m.p. 138–140°; GC purity 96%, containing 3% of (*RS*)-**39**. IR: 3260 (br., OH); 1557, 1477 (Ar.); 787 (1,2,3-trisubst. benzene). ^{1}H-NMR (60 MHz): 7.75–7.25 (*m*, 6 arom. H); 4.4, 4.15 (*AB*, J = 12, 2 CH_2OH); 2.75 (*s*, 2 OH). MS: 356/354/352 (5/9/5, $M^+ - H_2O$), 275/273 (98/100, $M^+ - H_2O -$ Br). Anal. calc. for $C_{14}H_{12}Br_2O_2$ (372.06): C 45.20, H 3.25, Br 42.95; found: C 45.48, H 3.20, Br 42.51.

5.5. *(*RS*)-1,11-Dibromo-5,7-dihydrodibenz[*c,e*]oxepin* ((*RS*)-**39**). A soln. of 2.60 g (6.99 mmol) of (*RS*)-**38** and 200 mg of TsOH in 50 ml of toluene was heated under reflux using a *Dean-Stark* trap to collect the H_2O formed. After 16 h, an additional 400 mg of TsOH was added, and the soln. was heated for a further 3 h. The cold soln. was diluted with 20 ml of Et_2O and worked up as usual. Crystallization from 20 ml of heptane and 2 ml of toluene produced 2.10 g (85%) of (*RS*)-**39** as yellowish crystals, m.p. 168.5–170°, GC purity 97%. IR: 1558 (Ar.); 1058 (C–O–C); 792 (1,2,3-trisubst. benzene). ^{1}H-NMR (60 MHz): 7.8–7.55 (*m*, 2 arom. H); 7.45–7.25 (*m*, 4 arom. H); 4.5 and 4.0 (*AB*, J = 11.5, CH_2OCH_2). MS: 356/354/352 (14/28/15, M^+), 275/273 (88/89, $M^+ -$ Br), 166 (75), 165 (100). Anal. calc. for $C_{14}H_{10}Br_2O$ (354.04): C 47.50, H 2.85, Br 45.14; found: C 47.71, H 2.83, Br 45.03.

5.6. *(*RS*)-5,7-Dihydrodibenz[*c,e*]oxepin-1,11-bis(diphenylphosphine)* ((*RS*)-**13**). Reaction of 5.30 g (15.0 mmol) of (*RS*)-**39** in 140 ml of THF/Et_2O 1:1 with *t*-BuLi and Ph_2PCl as described in *1.4.1* afforded 4.8 g of crude (*RS*)-**13**, m.p. 288–290°. Processing of the filtrate of the mixture as described in *1.4.2* gave another 0.6 g of crude (*RS*)-**13**, m.p. 287–289°. The combined material was dissolved in 50 ml of warm CH_2Cl_2, the mixture was filtered to remove some insoluble material, and the filtrate was evaporated to leave 3.6 g of a white powder. Crystallization from toluene/EtOH 80:30 yielded 1.8 g of (*RS*)-**13**, white needles, m.p. 290–291°, and, from the mother liquor, another 1.2 g of (*RS*)-**13**, m.p. 290–291°; combined yield 3.0 g (35%). IR: 1583, 1476 (Ar.); 1044 (C–O–C); 790 (1,2,3-trisubst. benzene); 741, 697 (monosubst. benzene). ^{1}H-NMR (60 MHz): 7.8–6.8 (*m*, 26 arom. H); 4.1, 3.55 (*AB*, J = 11.5, CH_2OCH_2). MS: 487 (5, $M^+ -$ Ph), 380 (39), 379 (100, $M^+ - PPh_2$). Anal. calc. for $C_{38}H_{30}OP_2$ (564.61): C 80.84, H 5.36; found: C 80.65, H 5.34.

5.7. *{(*R*)-2-[1-(Dimethylamino)ethyl]phenyl-C,N}[(*R*)- or (*S*)-(5,7-bis(diphenylphosphino)-1,11-dihydrodibenz[*c,e*]oxepin]palladium(II) Tetrafluoroborate* ((*R,R*)-**40b** and (*S,R*)-**40b**). A mixture of 3.0 g (5.31 mmol) of (*RS*)-**13** and 1.54 g (2.66 mmol) of (*R*)-**18** in 53 ml of MeOH was heated to 30–40° for 6 h. To the resulting yellow soln. was added slowly, at 20°, a soln. of 307 mg (2.92 mmol) of NH_4BF_4 in 13 ml of H_2O, and the mixture was stirred overnight. The precipitate was collected by filtration, washed with MeOH/H_2O 4:1 and dried *in vacuo* to

afford 2.10 g (43%, 86% of th.) of pure (*R*, *R*)-**40b** as yellowish powder. To the filtrate was added slowly a soln. of 307 mg (2.92 mmol) of NH_4BF_4 in 13 ml of H_2O and then 30 ml of H_2O. After stirring for an additional 2 h the precipitate was collected by filtration, washed with MeOH/H_2O 1:1, and dried *in vacuo* to yield 2.50 g (52%) of a 1:10 mixture (*R*, *R*)-**40b**/(*S*, *R*)-**40b**.

(*R*,*R*)-**40b**. The anal. sample was recrystallized from CH_2Cl_2/Et_2O, m.p. 232–233° (dec., darkening from 210°); $[\alpha]_D^{20} = +340.2°$ (*c* = 1.07, $CHCl_3$). IR: 1577, 1478 (Ar.); 1150 (br., BF_4^-); 794, 772 (1,2,3-trisubst. benzene); 746, 736, 698 (monosubst. benzene). ^{1}H-NMR (270 MHz): 7.8–6.85 (*m*, 26 arom. H); 6.75 (*m*, 2 arom. H); 6.51 (*q*, *J* = 8, 1 arom. H); 6.4 (*m*, 1 arom. H); 5.50 (*q*, *J* = 6.5, NC*H*CH_3); 4.10, 3.78, 3.57, 2.92 (4*d*, *J* = 11.5, CH_2OCH_2); 2.64 (*m*, NCH_3); 1.58 (*m*, NCH_3); 1.33 (*d*, *J* = 6.5, NCHCH_3). Anal. calc. for $C_{48}H_{44}BF_4NOP_2Pd$ (906.04): C 63.63, H 4.90, N 1.55; found: C 63.76, H 4.98, N 1.60.

(*S*,*R*)-**40b**. Several attempts to obtain pure (*S*, *R*)-**40b** by recrystallization of the 10:1 diastereoisomer mixture failed. ^{1}H-NMR (270 MHz): 7.75–6.95 (*m*, 27 arom. H); 6.77 (*t*, *J* = 7.5, 1 arom. H); 6.48 (*q*, *J* = 7.5, 1 arom. H); 6.30 (*m*, 1 arom. H); 4.20, 3.81, 3.64, 2.97 (4*d*, *J* = 11.5, CH_2OCH_2); 3.59 (~ *quint.*, *J* = 6, NC*H*CH_3); 2.30 (*d*, *J* = 6.5, NCHCH_3); 2.20 (*m*, NCH_3); 2.00 (*m*, NCH_3); and additional low-intensity signals from 10% of (*R*, *R*)-**40b**.

5.8. *(R)-5,7-Dihydrodibenz[c,e]oxepin-1,11-bis(diphenylphosphine)* ((*R*)-**13**). A suspension of 700 mg (0.772 mmol) of (*R*, *R*)-**40b** in 8 ml of acetone and 2 ml of CF_3COOH was stirred at ambient temp. for 20 h. The resulting yellow soln. was evaporated *in vacuo* by solvent condensation into a cold trap. To the residual yellow foam were added 12 ml of CH_2Cl_2, 6 ml of H_2O, and 3 ml of solid KCN, and the two-phase system was stirred vigorously for 30 min. The org. layer was separated and further processed as usual to yield 460 mg of crude (*R*)-**13** as white foam. Crystallization from 15 ml of EtOH and 1.5 ml of toluene afforded 382 mg (87.5%) of (*R*)-**13**, white needles, m.p. 197.5–199°; $[\alpha]_D^{20} = -396.6°$ (*c* = 1.0, $CHCl_3$). UV: 204.5 (88 350); 243 (26 100, sh); 276 (18 700, sh). CD: 192 (+31, pos. max.); 197 (0); 205 (−91, neg. max.); 220 (0); 223 (+4, pos. max.); 227 (0); 238 (−37, neg. max.); 252 (0); 270 (+22, pos. max.); 287 (0); 303 (−17, neg. max.). IR, NMR, and MS: identical with those of (*RS*)-**13**. Anal. calc. for $C_{38}H_{30}OP_2$ (564.61): C 80.84, H 5.36; found: C 80.61, H 5.44.

6. Synthesis of the Rh(I) Complexes. – *General Procedures.* Cationic Rh(I) complexes were prepared according to the methods developed by *Schrock* and *Osborn* [42] (*cf.* [53]).

Method A. A *Schlenk* tube was charged under Ar with 1.0 mmol of diphosphine, 0.5 mmol of $[Rh(nbd)Cl]_2$ and, *via* syringe, with 8 ml of MeOH. The mixture was stirred for 1–2 h at ambient temp. to form a homogeneous red soln. A soln. of 1.1 mmol of $NaBF_4$ in 2.2 ml of H_2O was added slowly within 0.5–2 h *via* a motor-driven syringe resulting in the precipitation of an orange solid. After stirring for an additional 1 h, the solid was collected by filtration under Ar, washed with 1–2 ml of H_2O, and dried *in vacuo* for 1–2 h.

Method B. A *Schlenk* tube was charged under Ar with 1.0 mmol of $[Rh(cod)Cl]_2$ or 1.0 mmol of $[Rh(nbd)Cl]_2$, and 15–20 ml of THF were added *via* syringe to dissolve the solid. Then, a soln. of 2.0 mmol of $AgClO_4 \cdot H_2O$ or $AgBF_4$, respectively, in 4–6 ml of THF, previously prepared in another *Schlenk* tube, was added *via* syringe within 15–20 min. After stirring for an additional 20 min, the AgCl precipitate was removed by filtration under Ar through a bed of *Celite*, and the solid was washed with 2 ml of THF. Turbid filtrates, which formed occasionally, were allowed to settle at 0° overnight, and the supernatant clear yellow soln. was then transferred *via* syringe to another *Schlenk* tube. To the clear yellow filtrate then was added within 1–2 h, *via* a motor-driven syringe, a soln. of 2.0 mmol of diphosphine in 25–35 ml of THF. After stirring for an additional 1–2 h, the precipitated orange solid was collected by filtration under Ar, washed twice with THF, and dried *in vacuo*. Alternatively, in small-scale reactions, the solid was isolated by concentrating the mixture *in vacuo* to *ca.* ¼ of the original volume, addition of a few ml of Et_2O, removal of the supernatant liquid *via* syringe, washing with Et_2O and with hexane or pentane, and drying *in vacuo*.

[Rh((R)-10)(nbd)]BF$_4$. Reaction of 275 mg (0.50 mmol) of (*R*)-**10** (ee 96%) according to *Method A* afforded 360 mg (79%) of [Rh((*R*)-**10**)(nbd)]BF_4 as an orange microcrystalline powder; $[\alpha]_D^{20} = -35.9°$ (*c* = 0.45, $CHCl_3$). IR: 1061, 1048 (BF_4^-); 779, 772 (1,2,3-trisubst. benzene); 744, 697 (monosubst. benzene). ^{1}H-NMR (90 MHz): 7,8–7.2 (*m*, 22 arom. H); 7.05 (*t*, *J* = 7.5, 2 arom. H); 6.8 (*d*, *J* = 7.5, 2 arom. H); 4.72 (*m*, 4 olefin, H); 4.05 (*m*, 2 methine H); 1.52 (br. *s*, CH_2); 1.33 (*s*, 2 arom. CH_3). Anal. calc. for $C_{45}H_{40}BF_4P_2Rh$ (832.47): C 64.93, H 4.84; found: C 64.84, H 5.03.

[Rh((S)-10)(nbd)]BF$_4$. Reaction of 1.10 g (2.0 mmol) of (*S*)-**10** (ee 97.5%) according to *Method A* afforded 1.523 g (91%) of [Rh((*S*)-**10**)(nbd)]BF_4 as orange powder; $[\alpha]_D^{20} = +31.95°$ (*c* = 0.48, $CHCl_3$). IR: 1060, 1048 (BF_4^-); 778, 771 (1,2,3-trisubst. benzene), 744, 697 (monosubst. benzene). ^{1}H-NMR (400 MHz): 7.67 (*m*, 4 arom. H); 7.6–7.28 (*m*, 18 arom. H); 7.05 (*t*, *J* = 7.5, 2 arom. H); 6.79 (*d*, *J* = 7.5, 2 arom. H); 4.74, 4.69 (2*m*, 2 × 2 olefin. H); 4.02 (*m*, 2 methine H); 1.55 (*m*, CH_2); 1.34 (*s*, 2 arom. CH_3). Anal. calc. for $C_{45}H_{40}BF_4P_2Rh$ (832.47): C 64.93,

H 4.84; found: C 64.91, H 5.13. Recrystallization of 1.394 g of this material from 55 ml of MeOH at 0° afforded 1.114 g of [Rh((*S*)-**10**)(nbd)]BF_4 as dark-red, sturdy crystals; $[\alpha]_D^{20} = +34.0°$ ($c = 0.54$, $CHCl_3$) and, after concentrating of the mother liquor, another 109 mg of dark-red crystals; $[\alpha]_D^{20} = +33.5°$ ($c = 0.53$, $CHCl_3$); 80% combined yield based on (*S*)-**10**. According to the ^{1}H-NMR, the recrystallized material contained *ca.* 10 mol-% of MeOH.

*[Rh((R)-***10***)(cod)]ClO_4.* Yield 73% *(Method B)*, orange powder. Mutarotation was observed in the course of the optical-rotation measurements: $[\alpha]_D^{20} = -53.2°$ (1 min), $-45.6°$ (5 min) ($c = 0.53$, CH_2Cl_2); $[\alpha]_D^{20} = +125.4°$ (1 min), +95.1° (5 min) ($c = 0.41$, CH_3CN). IR: 1092 (br., ClO_4^-); 749, 697 (monosubst. benzene). ^{1}H-NMR (270 MHz): 7.7–7.45 (*m*, 16 arom. H); 7.43–7.27 (*m*, 6 arom. H); 7.07 (*t*, $J = 7.5$, 2 arom. H); 6.79 (*d*, $J = 7.5$, 2 arom. H); 4.7, 4.4 (2*m*, 2 × 2 olefin. H); 2.62, 2.37, 2.26, 2.04 (4*m*, 4 CH_2); 1.37 (*s*, 2 arom. CH_3). Anal. calc. for $C_{46}H_{44}ClO_4P_2Rh$ (861.16): C 64.16, H 5.15, Cl 4.12; found: C 63.74, H 5.24, Cl 4.11, H_2O 1.64.

*[Rh((S)-***10***)(cod)]ClO_4.* Yield 87% *(Method B)*, orange powder. Mutarotation was observed in the course of the optical-rotation measurements: $[\alpha]_D^{20} = +20.5°$ (1 min), $-26.9°$ (5 min) ($c = 0.46$, $CHCl_3$). IR and ^{1}H-NMR: identical with those of [Rh((*R*)-**10**)(cod)]ClO_4. Anal. calc. for $C_{46}H_{44}ClO_4P_2Rh$ (861.16): C 64.16, H 5.15, Cl 4.12; found: C 64.07, H 5.30, Cl 4.10.

*[Rh((R)-***10***)(cod)]BF_4.* Yield 88% *(Method B)*, yellow-orange powder. IR: 1054 (br., BF_4^-); 750, 697 (monosubst. benzene). ^{1}H-NMR (80 MHz): 7.7–6.65 (*m*, 26 arom. H); 4.65, 4.35 (2*m*, 2 × 2 olefin. H); 2.6–1.9 (*m*, 4 CH_2); 1.37 (*s*, 2 arom. CH_3). Anal. calc. for $C_{46}H_{44}BF_4P_2Rh$ (848.52): C 65.11, H 5.23; found: C 64.45, H 5.25, Cl 0.85.

*[Rh((S)-***10***)(cod)]BF_4.* Yield 83% *(Method B)*, yellow-orange powder. IR and ^{1}H-NMR: identical with those of [Rh((*R*)-**10**)(cod)]BF_4. Anal. calc. for $C_{46}H_{44}BF_4P_2Rh$ (848.52): C 65.11, H 5.23; found: C 65.02, H 5.52, Cl 0.44.

*[Rh((R)-***11***)(nbd)]BF_4.* Yield 74% (*Method A*, $NaBF_4$ was replaced by NH_4BF_4), orange powder. IR: 1055 (br., BF_4^-); 749, 697 (monosubst. benzene). ^{1}H-NMR (80 MHz): 7.8–7.1 (*m*, 22 arom. H); 6.55 (*s* with fine structure, 2 arom. H); 4.7 (*m*, 4 olefin. H); 4.0 (*m*, 2 methine H); 2.2 (*s*, 2 arom. CH_3); 1.6 (*m*, CH_2); 1.32 (*s*, 2 arom. CH_3). Anal. calc. for $C_{47}H_{44}BF_4P_2Rh$ (860.52): C 65.60, H 5.15; found: C 65.16, H 5.33.

*[Rh((S)-***11***)(nbd)]BF_4.* Yield 70% *(Method A)*, orange powder. IR: identical with that of [Rh((*R*)-**11**)(nbd)]BF_4. ^{1}H-NMR (270 MHz): 7.8–7.2 (*m*, 22 arom. H); 6.54 (*s*, 2 arom. H); 4.72 (*m*, 4 olefin. H); 4.04 (*m*, 2 methine H); 2.20 (*s*, 2 arom. CH_3); 1.55 (*m*, CH_2); 1.31 (*s*, 2 arom. CH_3). Anal. calc. for $C_{47}H_{44}BF_4P_2Rh$ (860.52): C 65.60, H 5.15; found: C 65.26, H 5.26.

*[Rh((R)-***11***)(cod)]BF_4.* Yield 79% *(Method B)*, yellow-orange powder. IR: 1054 (br., BF_4^-); 747, 697 (monosubst. benzene). ^{1}H-NMR (80 MHz): 7.7–7.1 (*m*, 22 arom. H); 6.53 (*s* with fine structure, 2 arom. H); 4.65, 4.35 (2*m*, 2 × 2 olefin. H); 2.6–1.8 (*m*, 4 CH_2); 2.2 (*s*, 2 arom. CH_3); 1.35 (*s*, 2 arom. CH_3).

*[Rh((R)-***12***)(cod)]BF_4.* Yield 76% *(Method B)*, yellow powder. IR: 1054 (br., BF_4^-); 747, 697 (monosubst. benzene). ^{1}H-NMR (80 MHz): 7.8–7.2 (*m*, 20 arom. H); 6.83 (*m*, 2 arom. H); 6.05 (*d*, $J = 2.5$, 2 arom. H); 4.7, 4.4 (2*m*, 2 × 2 olefin. H); 2.85 (*s*, 2 $(CH_3)_2N$); 2.5–1.9 (*m*, 4 CH_2); 1.4 (*s*, 2 arom. CH_3). Anal. calc. for $C_{50}H_{54}BF_4N_2P_2Rh$ (934.65): C 64.25, H 5.82, N 3.00; found: C 63.57, H 6.29, N 2.85.

*[Rh((R)-***13***)(nbd)]BF_4.* Yield 90% *(Method A)*, orange powder. Recrystallization from $MeOH/CH_2Cl_2$ 3:1 at 0° afforded dark-red crystals. IR: 1054 (br., BF_4^-); 792, 779 (1,2,3-trisubst. benzene); 753, 702 (mono-subst. benzene). ^{1}H-NMR (270 MHz, CD_2Cl_2): 7.65–7.15 (*m*, 24 arom. H); 7.05 (*d*, $J = 7$, 2 arom. H); 5.04 (*m*, 4 olefin. H); 4.13 (*m*, 2 methine H); 4.02, 3.34 (2*d*, $J = 11.5$, CH_2OCH_2); 1.71 (*m*, CH_2). Anal. calc. for $C_{45}H_{38}BF_4OP_2Rh$ (846.45): C 63.85, H 4.53; found: C 63.40, H 4.81.

*[Rh((R)-***13***)(cod)]BF_4.* Yield 86% *(Method B)*, orange powder. IR: 1054 (br., BF_4^-); 751, 697 (monosubst. benzene). ^{1}H-NMR (270 MHz, CD_2Cl_2): 7.71–7.13 (*m*, 24 arom. H); 7.05 (*d*, $J = 7$, 2 arom. H); 4.96, 4.63 (2*m*, 2 × 2 olefin. H); 4.00, 3.31 (2*d*, $J = 11.5$, CH_2OCH_2); 2.72–2.40 (*m*, 2 CH_2); 2.40–2.15 (*m*, 2 CH_2). Anal. calc. for $C_{46}H_{42}BF_4OP_2Rh$ (862.50): C 64.06, H 4.91; found: C 63.59, H 5.40.

7. Isomerization of *N,N*-Diethylnerylamine (41). – The isomerizations were carried out according to the method described by *Otsuka* and coworkers [6b]. A representative example is as follows: a degassed mixture of 11.37 g (50 mmol) of N,N-*diethylnerylamine* (**41**; GC purity 96.5%), 42 mg (0.05 mmol, 0.1 mol-%) of [Rh((*S*)-**10**)(nbd)]BF_4 and 50 ml of THF was heated in a sealed tube at 80° for 3 d. Evaporation and bulb-to-bulb distillation at *ca.* 110°/0.5 Torr afforded 11.0 g (96.5%) of (*S*)-**42** as a colorless oil. This material was added to 50 ml of 50% aq. AcOH, the mixture was stirred for 10 min at 0° and, after addition of 50 ml of hexane, for 25 min at ambient temp. Usual workup with hexane followed by bulb-to-bulb distillation at *ca.* 110°/15 Torr afforded 7.74 g *(S)-citronellal* ((*S*)-**43**), GC purity 95.5%; 96% chemical yield based on **41**; $[\alpha]_D^{20} = -19.3°$ ($c = 5.0$, $CHCl_3$); $\alpha_D^{20} = -13.5°$ ($l = 0.1$, neat). The enantiomeric purity of this material was determined according to the method of *Valentine et al.* [48] and found to be 99%.

8. X-Ray Analyses. – 8.1. (*S*)-**10** ((+)-(S)-BIPHEMP). $C_{38}H_{32}P_2$ (550.62); *F(000)* = 1160. *Space group and cell dimensions:* orthorhombic: $P2_12_12_1$; $a = 9.435(4)$, $b = 16.720(5)$, $c = 18.625(6)$ Å; $D_c = 1.24$ Mgm^{-3}, $Z = 4$; μ(Mo– K_α) = 0.17 mm^{-1}; absorption effects ignored. *Data collection:* crystal size 0.21 × 0.33 × 0.55 mm^3; temp. 170 °K; wavelength: 0.71069 Å; scan mode $\theta/2\theta$; scan speed: 1.3°/min minimum speed; strong reflections measured at up to 10°/min; scan width 0.95° (θ); $\theta_{min}/\theta_{max}$ 0/28°; peak: background ratio 5:1, intensity from profile analysis; total data measured: 4030 excluding standards; total data observed: 3330; rejection criterion $I > 2.5\,\sigma(I)$; number of parameters: 362; weights $w = 1/(\sigma^2(F_0) + 0.001\,|F_0|^2)$. *Structure determination and refinement:* the structure was determined by direct methods using 39 starting phase permutations. Refinement proceeded smoothly to convergence at $R = 0.0434$ with anisotropic refinement of all non-H-atoms. The absolute configuration was determined by refining the coefficient p which multiplies the imaginary components of the atomic scattering factors. The final value of p was 0.90 (23) indicating that this is the correct structure. The enantiomer should give a p value of –1.0.

8.2. (*R*)-**13**. $C_{38}H_{30}OP_2$ (564.61); *F(000)* = 1184. *Space group and cell dimensions:* orthorhombic: $P2_12_12_1$; $a = 9.767(3)$, $b = 13.019(2)$, $c = 23.639(8)$ Å; $D_c = 1.21$ Mgm^{-3}, $Z = 4$; μ(Mo– K_α) = 0.17 mm^{-1}, absorption effects ignored. *Data collection:* crystal size 0.17 × 0.25 × 0.42 mm^3; temp. 170 °K; wavelength 0.71069 Å; scan mode $\theta/2\theta$; scan speed 0.9°/min minimum speed; strong reflections measured at up to 15°/min; scan width 0.9° (θ); $\theta_{min}/\theta_{max}$ 0/28°; peak: background ratio 5:1, intensity from profile analysis; total data measured: 4112 excluding standards; total data observed: 2143; rejection criterion $I > 2.5\,\sigma(I)$; number of parameters: 371; weights $w = 1/(\sigma^2(F_0) + 0.001\,|F_0|^2)$. *Structure determination and refinement:* the structure was determined by direct methods using 100 starting phase permutations. Refinement proceeded smoothly to convergence at $R = 0.0700$ with anisotropic refinement of all non-H-atoms.

8.3. *[(+)-(S)-(6,6'-Dimethylbiphenyl-2,2'-diyl)bis(diphenylphosphine)](η⁴-8,9,10-trinorborna-2,5-diene)-rhodium(I) Tetrafluoroborate* ([Rh(*S*)-**10**)(nbd)]BF_4). $C_{45}H_{40}BF_4P_2Rh$ (832.44); *F(000)* = 1704. *Space group and cell dimensions:* orthorhombic $P2_12_12_1$; $a = 12.237(7)$, $b = 16.675(9)$, $c = 18.134(9)$ Å; $D_c = 1.49$ Mgm^{-3}, $Z = 4$; μ(Mo– K_α) = 0.59 mm^{-1}; numerical absorption correction applied. *Data collection:* crystal size 0.25 × 0.29 × 0.33 mm^3; temp. 293 °K; wavelength 0.71069 Å; scan mode ω; $\theta_{min}/\theta_{max}$ 0/28°; peak: background ratio 5:1, intensity from profile analysis; total data measured: 4977 excluding standards; total data observed: 4408; rejection criterion $I > 2.5\,\sigma(I)$; number of parameters: 497; weights $w = 1/(\sigma^2(F_0) + 0.001\,|F_0|^2)$. *Structure determination and refinement:* the structure was determined by direct methods using 39 starting phase permutations. Refinement proceeded smoothly to convergence at $R = 0.0289$ with anisotropic refinement of all non-H-atoms. The absolute configuration was determined by refining the coefficient p which multiplies the imaginary components of the atomic scattering factors. The final value of p was 1.172(9) indicating that this is the correct structure.

8.4. *[(–)-(R)-(1,11-Bis(diphenylphosphino)-5,7-dihydrodibenz[c,e]oxepin](η⁴-8,9,10-trinorborna-2,5-diene)-rhodium(I) Tetrafluoroborate* ([Rh((*R*)-**13**)(nbd)]BF_4). $C_{45}H_{38}BF_4OP_2Rh$ (846.45); *F(000)* = 1728. *Space group and cell dimensions:* orthorhombic $P2_12_12_1$; $a = 12.406(4)$, $b = 16.668(5)$, $c = 17.741(4)$ Å; $D_c = 1.532$ Mgm^{-3}, $Z = 4$; μ(Mo– K_α) = 0.598 mm^{-1}, empirical absorption correction applied; maximum transmission 0.798, minimum transmission 0.759. *Data collection:* crystal size 0.24 × 0.40 × 0.40 mm^3; temp. 170 °K; wavelength 0.71069 Å; scan mode ω; scan speed 1.78°/min minimum speed; strong reflections measured at up to 29.3°/min; scan width 0.97°; $\theta_{min}/\theta_{max}$ 0/28°; peak: background ratio 5:1, intensity from profile analysis; total data measured: 4942 excluding standards; total data observed: 4460; rejection criterion $I > 2.5\,\sigma(I)$; number of parameters: 488; weights $w = 1/(\sigma^2(F_0) + 0.001\,|F_0|^2)$. *Structure determination and refinement:* the structure was determined by direct methods using 39 starting phase permutations. Refinement proceeded smoothly to convergence at $R = 0.0266$ with anisotropic refinement of all non-H-atoms. The absolute configuration was determined by refining the coefficient p which multiplies the imaginary components of the atomic scattering factors. The final value of p was 0.982 (44) indicating that this is the correct structure.

Data were collected on a *Nicolet P3m* (for (*S*)-**10** and (*R*)-**13**) or a *Nicolet R3m* (for [Rh((*S*)-**10**)(nbd)]BF_4 and [Rh((*R*)-**13**)(nbd)]BF_4) four-circle diffractometer fitted with a graphite monochromator and the *LT1* cooling apparatus. H-Atom coordinates were calculated using known geometries. All calculations were carried out with the SHELXTL [54] package of the *R3m* system, except for the direct methods in the case of structure (*R*)-**13** which were carried out using *Multan* [55].

Coordinates and thermal parameters of the four structures have been deposited with the *Crystallographic Data Center*, Cambridge, University Chemical Lab., Cambridge CB2 1EW, England.

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