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Preparative and Structural Chemistry of Diastereomeric Derivatives of 3-Phosphanylpyrrolidine and Their Palladium(II) Complexes – Asymmetric Grignard Cross-Coupling Reaction

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The preparation of both diastereomeric derivatives of 3-(diphenylphosphanyl)pyrrolidine with chiral (tetrahydrofuran-2-yl)methyl and [(*N*-neopentyl)pyrrolidin-2-yl]methyl groups as substituents on the pyrrolidine nitrogen atom and of (2*S*,4*S*)-1-benzyl-4-(diphenylphosphanyl)-2-(methoxymethyl)pyrrolidine is reported. [3*S*,P(*RS*)]-3-(phenylphosphanyl)pyrrolidine, bearing an additional chiral center on phosphorus, is the starting material for the preparation of phosphanes, in which one phenyl group of the PPh_2 moiety is substituted by an 2-methoxyphenyl (= An) or 2,4,6-trimethoxyphenyl (= TMP) group. PdI_2 complexes of these ligands were separated into diastereomers by chromatography on silica gel columns. The structural chemistry of these novel phosphane diastereomers and their PdI_2 complexes is investigated by X-ray crystallography and NMR. At the *P,N*-coordinated palladium center displacement of an iodide anion is found for P,N,N′ ligands only. In the nickel complex catalysed cross-coupling reaction, yielding 3-phenyl-1-butene, we obtain the highest enantioselectivities in the case of simple 1-alkyl-3-(diphenylphosphanyl)pyrrolidine ligands. The enantioselectivity obtained with diastereomeric derivatives, bearing additional ether or amine ligating sites is mainly determined by the chiral center in 3-position of the 3-(phosphanyl)pyrrolidine part of these ligands. Optimisation of enantioselectivity with these ligands can be carried out by a variation of the ligand to nickel ratio and by the choice of the vinyl halide used as starting compound. The catalytic cycle must contain at least one catalytically active species, bearing more than one β-aminoalkylphosphane ligand.

Carbon–carbon bond formation by cross-coupling of main group organometallics with carbon electrophiles catalysed by transition metal complexes is a valuable tool in organic chemistry[1]. The cross-coupling of vinyl halides **1a**, **1b** with Grignard compound **2a** prepared from racemic 1-chloro-1-phenylethane yields 3-phenyl-1-butene (**3**)[2,3] (cf. Scheme 1). The generally accepted catalytic cycle of Grignard cross-coupling catalysis[2] involves oxidative addition of a vinyl halide to a nickel(0) complex, transmetallation from the Grignard compound and reductive elimination of 3-phenyl-1-butene (**3**) regenerating the nickel(0) complex. The cross-coupling reaction using achiral nickel monophosphane (NiL_2) complexes[4] as catalysts has been investigated by Yamamoto[5]. Thermodynamically more stable NiL_2 complexes with *trans*-coordinated phosphane ligands have to be isomerised by associative mechanisms to the *cis* complexes before reductive elimination can occur. This *trans* to *cis* isomerisation can be promoted by the coordination of further phosphane ligands or by transmetallation steps. Reductive elimination from the resulting NiL_2 complex in which alkyl groups are *cis*-oriented may also be induced by coordination of further phosphane ligands[5].

In the asymmetric version of this cross-coupling reaction enantioselection can take place either during reductive elimination or during transmetallation. The highest enantioselectivities in this nickel catalysed reaction are achieved when nickel complexes bearing a P,N monophosphane L* (Ni/L* = 1) are used[2]. The X-ray structures of $PdCl_2$ complexes bearing one P,N phosphane ligand were used as model compounds for mechanistic considerations, because $NiCl_2$ complexes bearing only one P,N monophosphane ligand are not known[6]. We reported on the preparation of both enantiomers of 3-(diphenylphosphanyl)pyrrolidine (**4**) and *N*-alkylated derivatives **5**–**7**[7]. Nickel complexes of this new type of β-aminoalkylphosphanes were shown to be highly enantioselective catalysts; for example the complex bearing (*S*)-**5** is the most enantioselective nickel catalyst ever reported[8].

Contrary to the achiral case all proposed mechanisms of asymmetric Grignard cross-coupling catalysis[10] try to explain enantioselectivity with a nickel center bearing only one P,N monophosphane. Our catalytic results with ligands

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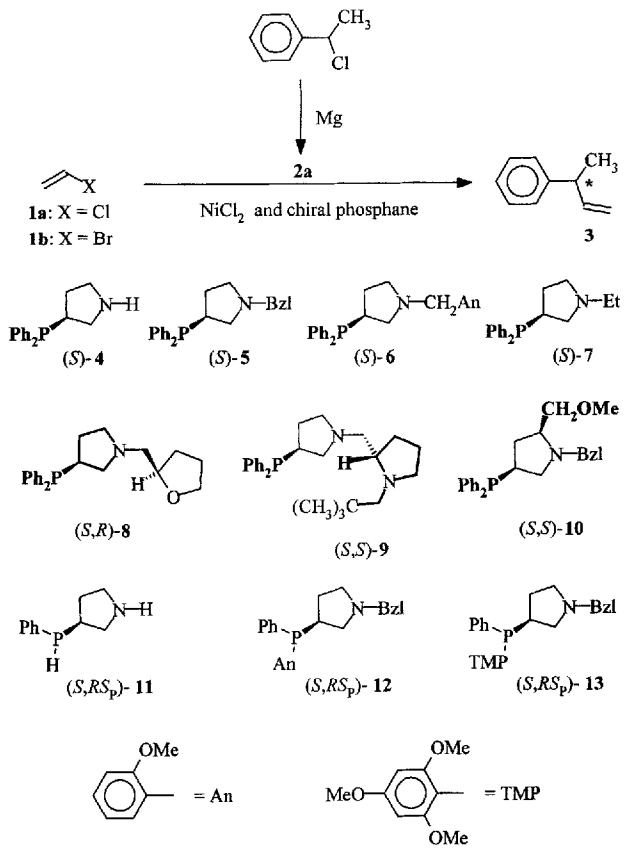
Scheme 1. Catalytic asymmetric cross-coupling of Grignard compound **2a** with vinyl halides **1a** or **1b** yielding chiral 3-phenyl-1-butene (**3**); selected[a] chiral phosphanes, relevant for this paper, are shown below[b,c]



[a] Further phosphane diastereomers [(*R*,*R*)-**8**, (*R*,*S*)-**9** (cf. Scheme 2)] were used in catalysis. – [b] The first stereochemical descriptor of diastereomeric phosphanes always describes the configuration at the secondary alkyl carbon atom bound to the phosphorus atom; the configuration of the phosphorus atom is described with an extended descriptor e.g. (S_P)[9]. – [c] Compounds **12** and **13** were used as diastereomerically pure compounds in catalysis.

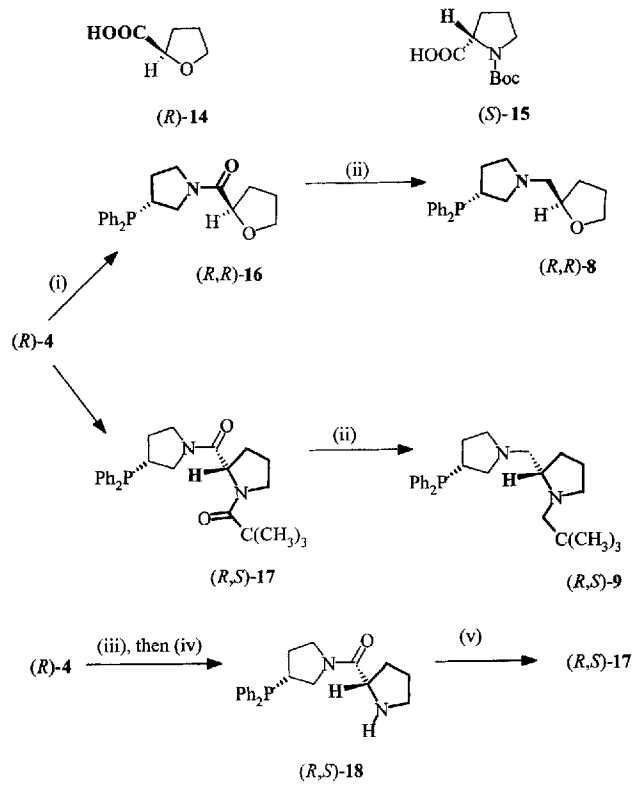
5, **6** of reduced enantiomeric purity showed asymmetric amplification[8], depending on the ligand to nickel ratio. The explanation is the presence of diastereomeric species bearing at least two P,N phosphane ligands. In order to elucidate the influence of additional functional groups on enantioselection (cf. ref.[11]) during the cross-coupling reaction all possible diastereomers of new 3-(phosphanyl)pyrrolidine ligands **8**, **9** and **12**, **13** and additionally the diastereomerically pure ligand (*S*,*S*)-**10** (cf. Scheme 1) were prepared.

Results and Discussion

Synthesis of the Ligands and PdI_2 Complexes

The conversions yielding diastereomerically pure *N*-alkylated derivatives of 3-(diphenylphosphanyl)pyrrolidine [(*R*)-**4**] are outlined in Scheme 2. (*R*)-Tetrahydrofuran-2-carboxylic acid [(*R*)-**14**][12] and (2*S*)-1-*tert*-butoxycarbonylpyrrolidine-2-carboxylic acid [(*S*)-**15**][13] were activated with 1,1′-carbonyl diimidazole (= CDI). Coupling of the resulting acyl imidazolides with (*R*)-**4** afforded amides either (*R*,*R*)-**16** or after further transformations (*R*,*R*)-**17**, which were reduced with $LiAlH_4$ in THF[7] to the *N*-alkylated derivatives (*R*,*R*)-**8** and (*R*,*S*)-**9**. With (*S*)-**4** as starting compounds the diastereomeric phosphanes (*S*,*R*)-**8** and (*S*,*S*)-**9** were obtained. (*R*,*R*)-**8** and (*S*,*R*)-**8** were converted to diastereomeric PdI_2 complexes (*R*,*R*)-**8-Pd** and (*S*,*R*)-**8-Pd** and purified as PdI_2 complexes by chromatography and crystallisation.

Scheme 2. Synthesis of diastereomerically pure *N*-alkylated derivatives (*R*,*R*)-**8**, (*R*,*S*)-**9**, starting with (*R*)-**4**[a]

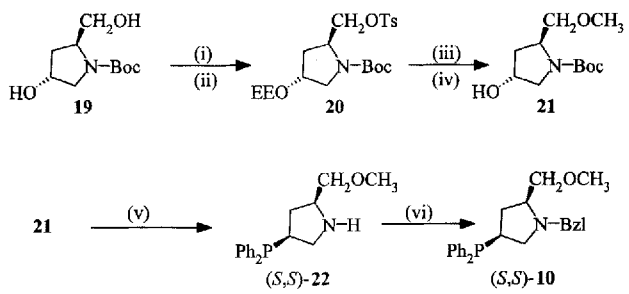


[a] Reactions and conditions used: (i) 1,1′-Carbonyl diimidazole (= CDI), (*R*)-**14** in THF then (*R*)-**4**. – (ii) $LiAlH_4$ in THF. – (iii) CDI, (*S*)-**15** in THF then (*R*)-**4**. – (iv) Trifluoroacetic acid (= TFA) at 0°C yielding (*R*,*S*)-**18**. – (v) Schotten-Baumann acylation with pivaloyl chloride.

CDI-induced coupling is not often used in peptide synthesis, because the carboxylic acids used are often partially racemised during the activation step[14]. (*S*)-**15** is one known exception, because it can not form a (4*H*)-oxazol-5-one (azlactone)[14]. We compared optical rotations of the (*R*)-**14** starting material and of (*R*)-**14**, that was recovered from reaction mixtures. This revealed that there was no racemisation of (*R*)-**14** during the coupling reaction. By inspection of $^{31}P\{^1H\}$-NMR spectra of **8**, **9**, and of **8-Pd** samples no resonances of diastereomeric impurities could be detected. All compounds therefore have an diastereomeric purity de > 98% ee. This result implies that (*S*)-**4** and (*R*)-**4** starting materials both had at least 98% ee[7] and that compounds **8**, **9**, used in catalysis have at least 99% ee.

(2*S*,4*R*)-1-(*tert*-Butoxycarbonyl)-4-(hydroxy)-2-(hydroxymethyl)pyrrolidine (**19**), obtained in three steps (60% yield) from L-hydroxyproline[15] was used as starting material for the synthesis of (2*S*,4*S*)-1-benzyl-4-(diphenylphosphanyl)-2-(methoxymethyl)pyrrolidine [(*S*,*S*)-**10**] (cf. Scheme 3). The

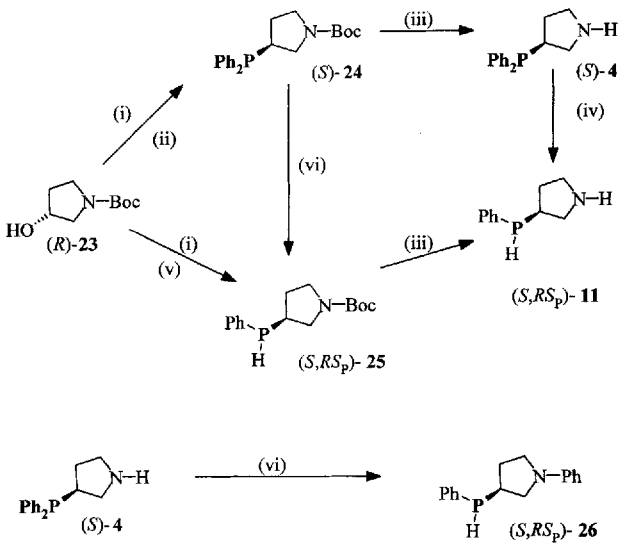
Scheme 3. Synthesis of (*S*,*S*)-**10** from L-hydroxyprolin[a,b]



[a] Reactions and conditions used: (i) *p*-Toluenesulfonyl chloride (= TsCl) in pyridine at −25°C in analogy to ref.[16]. – (ii) Ethyl vinyl ether and traces of trifluoro acetic acid (= TFA), cf. ref.[17]. – (iii) NaOMe in DMSO. – (iv) Cf. ref.[7]. – (v) $KPPh_2$ in THF (cf. ref.[7]). – (vi) Benzoyl chloride, NEt_3, then $LiAlH_4$ in THF. – [b] EE = [1′(*RS*)]-1′-(Ethoxyethyl) acetal group.

synthesis of (2*S*,4*R*)-1-(*tert*-butoxycarbonyl)-4-hydroxy-2-(methoxymethyl)pyrrolidine (**21**) started with a selective tosylation of the primary alcohol group of diol **19**, analogous to a procedure used by Achiwa[16]. The secondary alcohol group was blocked as [1′(*RS*)]-(1′-ethoxyethyl) acetal group (EE)[17], and a solution of product **20** in DMSO was added to a solution of NaOMe in DMSO. The acetal group was cleaved without cleavage of the *tert*-butoxycarbonyl group[7]. An "inverse" ether synthesis in DMSO, with sodium [1-(*tert*-butoxycarbonyl)-4-(1′-ethoxyethyloxy)pyrrolidine-2-methanolate] and MeI as starting compounds did not work, because the sodium alkoxide is not stable and eliminates NaO*t*Bu forming an bicyclic oxazolidinone[18]. (2*S*,4*S*)-1-Benzyl-4-(diphenylphosphanyl)-2-(methoxymethyl)pyrrolidine [(*S*,*S*)-**10**] was prepared from **21** analogous to the synthesis of (*S*)-**4**[7] and was purified as PdI_2 complex [(*S*,*S*)-**10-Pd**] by chromatography and crystallisation.

Scheme 4. Synthesis of (S,RS_P)-**11** from (*R*)-**23**[a] (top), migration of a phenyl group in (*S*)-**4** yielding (S,RS_P)-**26** (bottom)



[a] Reactions and conditions used: (i) First *n*-butyllithium, then methanesulfonyl chloride (MsCl) (cf. ref.[7]). – (ii) $KPPh_2$ in THF (cf. ref.[7]). – (iii) Trifluoro acetic acid (= TFA). – (iv) Lithium in THF, ultrasound irradiation. – (v) KPHPh in THF. – (vi) Potassium and naphthalene in THF.

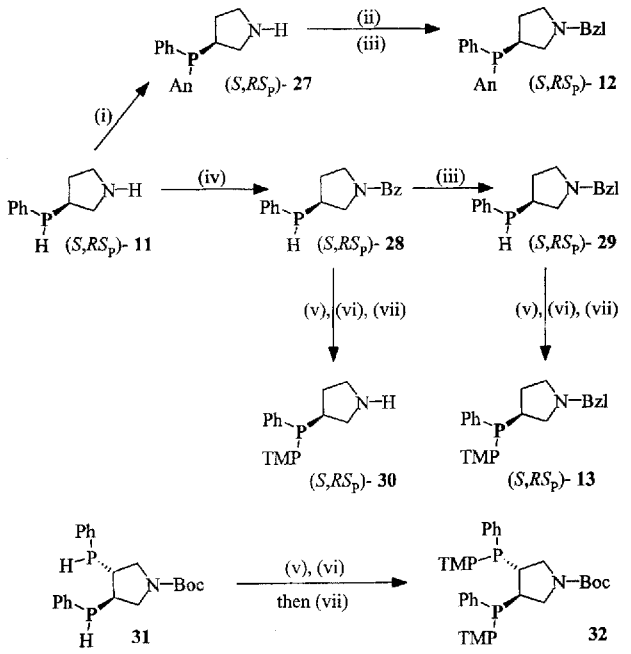
We tried the synthesis of [3*S*,P(*RS*)]-3-(phenylphosphanyl)pyrrolidine [(S,RS_P)-**11**] with the methanesulfonate ester of (3*R*)-1-*tert*-butoxycarbonyl-3-hydroxypyrrolidine [(*R*)-**23**][7] and potassium phenylphosphane as starting compounds[19]. This S_N2 substitution gave a mixture, containing two diastereomers that could not be crystallised. The enantiomeric purity of the phosphanes was about 93% ee. An attempted S_N2 substitution with potassium [(2′-methoxyphenyl)phenylphosphane] gave only a 5% yield of [3*S*,P(*RS*)]-3-[(2′-methoxyphenyl)phenylphosphanyl]pyrrolidine [(S,RS_P)-**27**; vide infra] of unknown enantiomeric purity.

Reductive cleavage of one phenyl group in (3*S*)-3-(diphenylphosphanyl)pyrrolidine [(*S*)-**4**] with lithium metal, accelerated by ultrasonic irradiation[20] gave enantiomerically pure (S,RS_P)-**11** in high yield. This synthesis can, however, be done only with small portions of (*S*)-**4** starting material (safety considerations). We used potassium naphtalene solutions in THF as a safer substitute for lithium metal/ultrasonic irradiation in the reductive cleavage reaction of (*S*)-**4**[21]. Surprisingly [3*S*,P(*RS*)]-1-phenyl-3-(phenylphosphanyl)pyrrolidine [(S,RS_P)-**26**] was obtained in nearly quantitative yield instead of (S,RS_P)-**11**. The elementary analysis and all physical data [MS, IR, NMR] are in accord with the proposed structure of this compound (S,RS_P)-**26**. This unprecedented reaction cannot be extended to the analogous reaction with pyrrolidine and triphenylphosphane as starting materials. Mixtures of cleaved secondary phosphanes and tertiary dihydroarylphosphanes (Birch products) are obtained in reactions of tertiary arylphosphanes with Na/NH_3 solutions[22]. The protic solvent NH_3 is able to trap radical anion intermediates yielding a dihydroarylphoshane instead of the cleaved phosphane[22]. Based on the result that large amounts of 1,4-dihydronaphtalene (product of Birch reduction of potassium naphthalenide) were found in the synthesis of (S,RS_P)-**26** we propose that the proton on the secondary pyrrolidine nitrogen atom of (*S*)-**4** is transferred to the naphthalenide radical anion, accompanying the migration of one phenyl group from the phosphorus to the nitrogen atom.

[3*S*,P(*RS*)]-1-(*tert*-butoxycarbonyl)-3-(phenylphosphanyl)pyrrolidine [(S,RS_P)-**25**] was obtained in an one-pot synthesis by an S_N2 substitution with $KPPh_2$, yielding (3*S*)-1-(*tert*-butoxycarbonyl)-3-(diphenylphosphanyl)pyrrolidine [(*S*)-**24**, cf. ref[7]] and by subsequent reductive cleavage reaction of (*S*)-**24** with an potassium naphthalene solution. Twice the amount of potassium naphthalene compared to the synthesis of (S,RS_P)-**26** yielded an 9:1 mixture of (S,RS_P)-**25** and (*S*)-**24**. This reveals, that the reductive cleavage reaction of (*S*)-**24** is much more difficult compared to the migration reaction yielding (S,RS_P)-**26**. We used a mixture of 90% (S,RS_P)-**11**, and 10% (*S*)-**4** as starting compound for the syntehsis of (S,RS_P)-**13** (cf. Scheme 5). The synthetic transformations converted the impurity (*S*)-**4** to the *N*-alkylated derivative (*S*)-**5** that could be easily separated as a PdI_2 complex [(*S*)-**5-Pd**] from the diastereomeric

(S,S_{MP})-**13-Pd** and (S,R_{MP})-**13-Pd** complexes during the chromatographic separation of these diastereomers.

Scheme 5. Synthesis of tertiary phosphanes (S,RS_P)-**12** and (S,RS_P)-**13** from (S,RS_P)-**11**[a] (top); improved synthesis of 1-(*tert*-butoxycarbonyl)-3,4-bis[(2′,4′,6′-trimethoxyphenyl)phenylphosphanyl]pyrrolidine (**32**)[b] (bottom)



[a] Reactions and conditions used: (i) First potassium in THF then 2-fluoro anisole (cf. ref.[23]). – (ii) Benzoyl chloride, NEt_3. – (iii) $LiAlH_4$ in THF. – (iv) 2 equiv. of benzoyl chloride, NEt_3, then KOH in ethanol. – (v) First potassium in THF then Me_3SiCl. – (vi) C_2Cl_6 in dichloromethane (cf. ref.[24]). – (2,4,6-Trimethoxyphenyl)lithium in diethyl ether. – [b] Same reactions and conditions used as in [a]: cf. ref.[24] for further discussion.

A 1:1 mixture of both diastereomers of [3*S*,P(*RS*)]-3-[(2′-methoxyphenyl)phenylphosphanyl]pyrrolidine [(S,RS_P)-**27**] was obtained, using the reaction[23] of 2-fluoroanisole with a potassium phosphide solution [obtained with (S,RS_P)-**11** and metallic potassium in THF). [3*S*,P(*RS*)]-1-benzyl-3-[(2′-methoxyphenyl)phenylphosphanyl]pyrrolidine [(S,RS_P)-**12**], obtained by benzoylation and $LiAlH_4$ reduction was converted to the mixture of diastereomeric PdI_2 complexes (S,S_{MP})-**12-Pd** and (S,R_{MP})-**12-Pd**, that was separated by chromatography.

The synthetic strategy used for the synthesis of (S,RS_P)-**12** can not be extended to the synthesis of (S,RS_P)-**13** because 1-fluoro-2,4,6-trimethoxybenzene is not available. In a more general procedure, 1-(*tert*-butoxycarbonyl)-3,4-bis-(phenylphosphanyl)pyrrolidine (**31**) was first treated with metallic potassium and with trimethylsilyl chloride and then with hexachloro ethane[24]. The P,P′-chlorinated derivative of compound **31** was subsequently treated with 2,4,6-trimethoxyphenyllithium in THF, yielding 28% of 1-(*tert*-butoxycarbonyl)-3,4-bis[(2′,4′,6′-trimethoxyphenyl)-phenylphosphanyl]pyrrolidine (**32**). This compound can now be prepared with an improved yield. The *P,P′*-chlorinated derivative of compound **31**, dissolved in diethyl ether was added to 2.84 equivalents of solid 2,4,6-trimethoxyphenyllithium, prepared by an improved procedure (cf. Experimental Section). Crude **32** was converted to the mixture of three diastereomeric PdI_2 complexes and was purified and separated into diastereomers[24] by chromatography (54% yield of pure separated PdI_2 complexes).

Possible starting materials for the synthesis of (S,RS_P)-**13** were the amide compound (S,RS_P)-**28** and the tertiary amine compound (S,RS_P)-**29**. We treated (S,RS_P)-**11** with benzoyl chloride and then with KOH/ethanol in order to cleave the P–acyl bond of the *P,N*-benzoylated derivative, thus obtained. From the resulting mixture 20% of the (S,RS_P)-**11** starting material (cleavage at P and N) could be recovered with dilute acid. Pure amide compound (S,RS_P)-**28** was reduced with $LiAlH_4$ to the *N*-benzyl derivative (S,RS_P)-**29**. A shorter one-pot synthesis of $(S$-$RS_P)$-**29** was feasible when the *P,N*-benzoylated derivative of (S,RS_P)-**11** was directly treated with excess $LiAlH_4$. The reductive cleavage reaction of (*S*)-**5** with potassium/naphtalene was, however, shown to yield no (S,RS_P)-**29**.

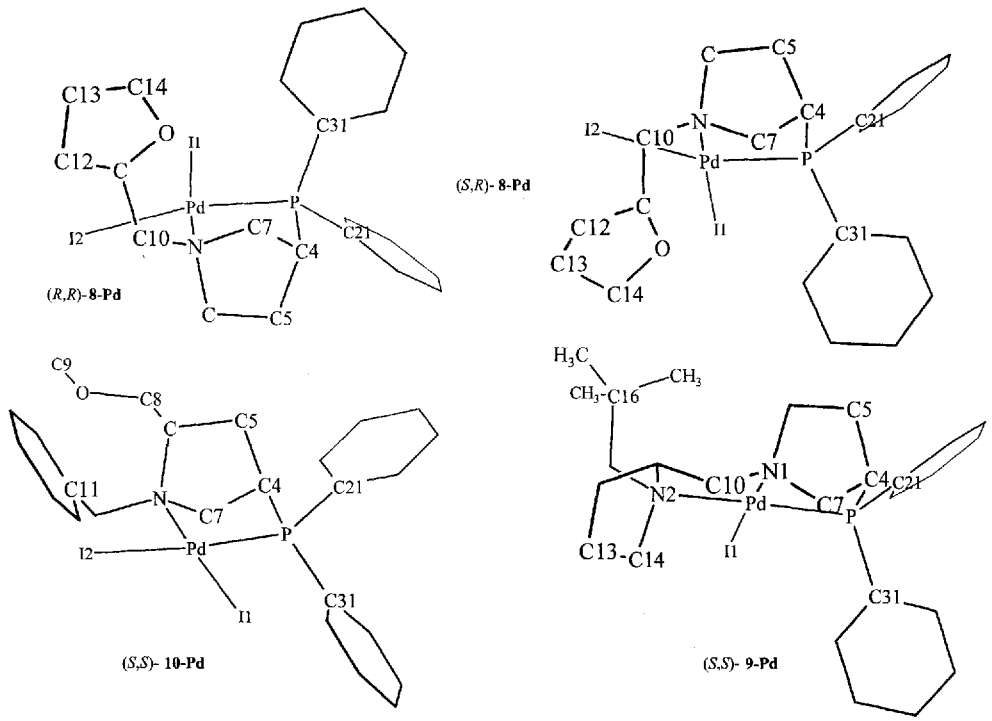
(S,RS_P)-**13** was obtained by the reaction of the chlorophosphane derivative of (S,RS_P)-**29** with 1.35 equivalents of solid 2,4,6-trimethoxyphenyllithium in diethyl ether. The crude phosphane product was converted to (S,RS_{MP})-**13-Pd** and this mixture of PdI_2 complexes was purified and separated into diastereomers by chromatography and crystallisation. The final yield of pure diastereomeric complexes, calculated from (S,RS_P)-**29** starting material was 20% of each diastereomer.

The reaction between the derivative of (S,RS_P)-**28**, obtained by *P*-chlorination of this amide and 2,4,6-trimethoxyphenyllithium gave very small amounts of phosphane products, having no carbonyl vibration in the IR (film) spectrum. The phosphane mixture, containing two phosphanes (S,RS_P)-**30** as major components was converted to a mixture of PdI_2 complexes and one diastereomer could be crystallised and investigated by X-ray crystallography (cf. Scheme 2). This proved that the benzoyl group in the *P*-chlorinated amide was cleaved by 2,4,6-trimethoxyphenyllithium. Phenyl (2′,4′,6′-trimethoxyphenyl) ketone (A) and 1′-chloro-2,4,6-trimethoxybenzene (B) were formed during the reaction, too. (A) is formed by addition of 2,4,6-trimethoxyphenyllithium to the amide bond and subsequent acid catalysed hydrolytic cleavage of this adduct leaving (S,RS_P)-**30** as second product. (B) is formed from 2,4,6-trimethoxyphenyllithium and chlorophosphane by metal halogen exchange. Both reactions have also been found with the *P,P′*-chlorinated derivative of compound **31** and aryl lithiums as starting compounds[25] and are a limit to the general scope of this synthetic strategy.

Structural Chemstriy of Ligands and PdI_2 Complexes

As an extension of our recent[7] study of the structural chemistry of PdI_2 complexes bearing 3-diphenylphosphanylpyrrolidine ligands, the solid state structures of novel derivatives were determined by X-ray structural analysis (cf. Figures 1, 2). The correct absolute structure was assigned by means of the Flack parameter[26]. In the case of PdI_2 complexes bearing ligands with chiral centers at phos-

Figure 1. Molecular structure drawings of (*R*,*R*)-**8-Pd** (second molecule in asymmetric unit not shown)[a], (*S*,*R*)-**8-Pd**[b], (*S*,*S*)-**10-Pd**[c], (*S*,*S*)-**9-Pd**[d]; d_{PdO} (cf. text); α_1, ω_1 given as absolute values were defined in ref.[7], the numbering scheme is consistent with the numbering scheme used in ref.[7]



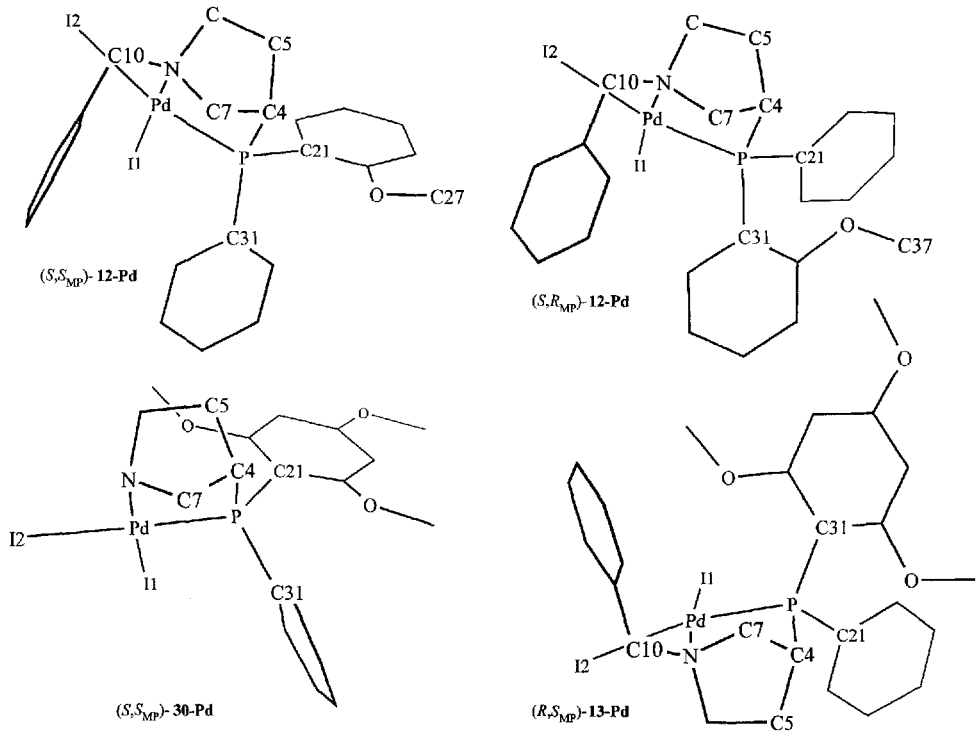
[a] Selected lengths [Å] and angles [°]; mean values of the two molecules in asymmetric unit given: Pd–I(1) 2.589(1), Pd–I(2) 2.682(5), Pd–N 2.171(8), Pd–P 2.248(5), d_{PdO} 3.97(2); I(1)–Pd–I(2) 92.7(5), N–Pd–P 84.1(2), P–Pd–I(1) 91.7(9), N–Pd–I(2) 93.3(2), N–C(7)–C(4) 101.7(6), α_1 13.9(3), ω_1 93.4(10). – [b] Selected lengths [Å] and angles [°]: Pd–I(1) 2.602(2), Pd–I(2) 2.712(2), Pd–(N) 2.181(11), Pd–P 2.243(4), d_{PdO} 3.04; I(1)–Pd–I(2) 91.95(6), N–Pd–P 83.8(3), P–Pd–I(1) 92.50(10), N–Pd–I(2) 94.7(3), N–C(7)–C(4) 102.1(14), α_1 20.1, ω_1 88.0. – [c] Selected lengths [Å] and angles [°]: Pd–I(1) 2.592(2), Pd–I(2) 2.685(2), Pd–N 2.201(4), Pd–P 2.247(2), d_{PdO} 4.08; I(1)–Pd–I(2) 90.44(4), N–Pd–P 84.32(11), P–Pd–I(1) 88.96(5), N–Pd–I(2) 96.92(11), N–C(7)–C(4) 101.4(3), α_1 9.0, ω_1 90.7. – [d] Selected lengths [Å] and angles [°]: Pd–I 2.549(2), Pd–N1 2.056(8), Pd–N2 2.114(8), Pd–P 2.209(3); N(1)–Pd–P 84.7(3), N(1)–Pd–N(2) 83.9(4), P–Pd–I 94.20(8), N(2)–Pd–I 86.7(3), N(2)–Pd–P 167.1(2), N(1)–Pd–I 175.8(2), N–C(7)–C(4) 98.5(38), ω_1 91.4.

phorus (complexes **12-Pd** and **13-Pd**) the absolute configuration of one of both diastereomeric PdI_2 complex was assigned on the basis of an X-ray structural analysis (cf. Figure 2). This necessary information could not be derived from NMR spectroscopy[27]. We always, find that the ligands are bound via P and N forming a hetero-norbornane skeleton with bond lengths and angles that are consistent with our previously reported X-ray structures. Nevertheless we find two different conformations of the five-membered P,Pd,N(1),C(7),C(4) rings in our molecular structures. The first conformation, found in X-ray structures of (*S*,*R*)-**8-Pd**, (*R*,*R*)-**8-Pd**, (*S*,*S*)-**9-Pd**, (*S*,S_{MP})-**30-Pd** [and (*R*)-**9a-I** in ref.[7]] is close to an envelope conformation. The main distortion is due to C(4), which is displaced −0.1 Å away from the expected P,Pd,N,C(4) plane in an undistorted norbornane system. C(7) is displaced further away (0.8 Å) from the P,Pd,N plane. In the second conformation, found in the seven other X-ray structures C(7) is displaced no more than 0.2 Å further away than C(4) from the P,Pd,N plane.

In reported X-ray structures of monocyclic $PdCl_2$ complexes[6], bearing chiral β-alkyl-β-(dimethylamino)ethylphosphane ligands a conformation of the five membered P,Pd,N,C_2 ring with the alkyl substituent in equatorial position is found. An increasing steric bulk of this equatorial substituent stabilises this conformation compared to the conformation with axial substituent[28]. In our molecular structures the carbon substituent on the chiral center [C(4), α-position] is fixed in axial position. Comparing the most stable conformations of both types of palladium complexes, we reach the conclusion, that complexes with a (*S*)-configured carbon center in β-position and our ligands with a (*R*)-configured carbon center in α-position [C(4)] both have the same sense of conformational chirality. Both yield (3*S*)-3-phenyl-1-butene [(*S*)-**3**] as major enantiomer in the cross-coupling reaction[8]. In this reaction Pd complexes give the same predominant product configuration but chemical and optical yields are reduced compared to Ni complexes[29].

For the investigation of structural aspects of PdI_2 complexes in solution $^{13}C\{^1H\}$-NMR spectra were of major importance. They furnish clear evidence that *P*,*N* coordination is retained in solution[7]. The solid state structures of PdI_2 complexes bearing ligands with ether ligating sites either as substituent on the pyrrolidine nitrogen atom (THF in **8-Pd**), as substituent on the phosphorus atom (2-methoxyphenyl in **12-Pd** or 2,4,6-trimethoxyphenyl in **13-Pd**) or as methoxymethyl substituent on a pyrrolidine carbon atom

Figure 2. Molecular structure drawings of (S,S_{MP})-**12-Pd**[a], (S,R_{MP})-**12-Pd**[b], (S,S_{MP})-**30-Pd** (second molecule in asymmetric unit not shown)[c], (R,S_{MP})-**13-Pd** [(S,R_{MP}) enantiomer in asymmetric unit not shown][d]; d_{PdO} (cf. text); α_1, ω_1 given as absolute values were defined in ref.[7], the numbering scheme is consistent with the numbering scheme used in ref.[7]



[a] Selected lengths [Å] and angles [°]: Pd–I(1) 2.6016(13), Pd–I(2) 2.6837(14), Pd–N 2.173(4), Pd–P 2.2578(14), d_{PdO} 5.194; I(1)–Pd–I(2) 90.720(14), N–Pd–P 83.19(10), P–Pd–I(1) 94.5(3), N–Pd–I(2) 93.41(10), N–C(7)–C(4) 100.7(4), α_1 13.7, ω_1 93.5. – [b] Selected lengths [Å] and angles [°]: Pd–I(1) 2.5812(11), Pd–I(2) 2.6657(12), Pd–N 2.201(9), Pd–P 2.249(3), d_{PdO} 5.058; I(1)–Pd–I(2) 90.98(4), N–Pd–P 83.5(2), P–Pd–I(1) 91.96(8), N–Pd–I(2) 93.6(2), N–C(7)–C(4) 100.1(8), α_1 22.2, ω_1 93.9. – [c] Selected lengths [Å] (mean values of the two molecules in asymmetric unit given) and angles [°]: Pd–I(1) 2.603(4), Pd–I(2) 2.660(4), Pd–N 2.08(4), Pd–P 2.246(6), d_{PdO} 2.94(6); I(1)–Pd–I(2) 96.40(7), 94.09(6), N–Pd–P 82.7(5), 83.6(5), P–Pd–I(1) 91.88(14), 93.89(14), N–Pd–I(2) 89.4(5), 88.6(5), N–C(7)–C(4) 101(2), 98(2), α_1 9.0, 3.5, ω_1 83.7, 82.4. – [d] Selected lengths [Å] and angles [°]: Pd–I(1) 2.583(2), Pd–I(2) 2.6827(12), Pd–N 2.184(8), Pd–P 2.244(3), d_{PdO} 3.147; I(1)–Pd–I(2) 91.89(4), N–Pd–P 84.6(2), P–Pd–I(1) 89.65(7), N–Pd–I(2) 93.5(2), N–C(7)–C(4) 102.0(8), α_1 20.7, ω_1 89.9.

(**10-Pd**) all show the common feature, that long PdO distances, designated d_{PdO} in Figures 1 and 2 are found. There is no secondary coordination of these ether ligating sites with palladium. In $^{13}C\{^1H\}$-NMR solution spectra of this compounds the resonances of carbons of ether substituents are not shifted compared to $^{13}C\{^1H\}$-NMR spectra of the corresponding ligands. In the same spectra we find resonances of pyrrolidine carbon atoms shifted downfield upon complexation to PdI_2[7].

The chemistry of the PdI_2 complex bearing ligand (*S,S*)-**9** is more complicated because the second nitrogen ligating site is able to displace an iodide anion forming a cationic P,N,N′ bischelate complex [cf. Scheme 1, X-ray structure of the yellow crystalls of (*S,S*)-**9-Pd**]. The cationic Pd center has slightly shortened bonds to the bound iodine atom and the phosphorus and N(1) atoms but bond lengths and angles of the hetero-norbornane skeleton are not changed significantly. Chiral diamine ligands derived from L-proline (2-pyrrolidinemethylamine part as in **9**) are often applied in enantioselective catalysis[30]. Corey and Hannon[31] have done molecular modelling calculations on a lithium complex bearing a related N,N′,O ligand, and report a conformation of the 2-pyrrolidinemethylamine N,N′ chelate ring that matches the conformation found in the X-ray structure analysis of (*S,S*)-**9-Pd** exactly.

Table 1. Comparison of $^{31}P\{^1H\}$-CP-MAS solid-state and $^{31}P\{^1H\}$-NMR solution data of PdI_2 complexes; study at 298 K with a sample rotation of 10 kHz

Compound		(*S*)-**5-Pd**	(*R,R*)-**8-Pd**	(*S,S*)-**10-Pd**	(*S,S*)-**9-Pd**
CP-MAS	δ =	48.4	54.1	38.9	43.6, 45.7
Solution	δ =	43.2 [a]	42.5 [a]	39.2 [a]	43.9, 48.2[b]
Δδ =		5.2	11.6	-0.3	-0.3, -2.5
Half width	(gauss fit)	3 ppm[c]	3 ppm[c]	1.5 ppm[c]	3 ppm, 2.5 ppm [c]

[a] In CD_2Cl_2. – [b] In [D_6]acetone. – [c] Bruker ASX 300 [7.05 T, 121.49 MHz (^{31}P)][7].

$^{31}P\{^1H\}$-NMR CP-MAS spectra at 298 K with a sample rotation of 10 KHz (cf. Table 1 and ref.[7]) of polycrystalline (*S*)-**5-Pd**, (*R,R*)-**8-Pd**, (*S,S*)-**10-Pd** samples show different half-widths of CP-MAS singlet resonances and very dissimilar chemical shift differences Δδ between solid-state CP-MAS and $^{31}P\{^1H\}$-NMR solution spectra[32]. The CP-MAS spectrum of a (*S,S*)-**9-Pd** sample, crystallised from an acetone solution, showed three singlet resonances. One

resonance at δ = 39.9 was assigned to a PdI_2–*N,N'*-diamine complex with the PPh_2 group oxidised to an $POPh_2$ group. Elementary analysis, MS (FAB) and solution NMR studies [e.g. $^{31}P\{^1H\}$-NMR: δ = 34.7] of a red sample, separated by chromatography were in accord with the proposed structure. Furthermore, this chromatography gave samples containing different ratios of two other Pd complexes with (*S,S*)-**9** as a ligand. A $^{31}P\{^1H\}$-NMR measurement with an ethanol solution, that was saturated with NaI revealed, that this solution contained only complex (A) [δ = 43.9]. A solution containing predominantly the second complex (B) [δ = 48.2] was obtained by chromatography with 80% ethanol/20% water. Solutions of samples containing different ratios of (A) and (B) in acetone and ethanol reached their equilibrium concentrations after several days {acetone: [complex (A)]/[complex (B)] = 2:1 (this ratio found also in the solid state CP-MAS sample); ethanol: [complex (A)]/[complex (B)] = 1:1}. We conclude that complex (B) is the ionic *P,N,N'*-coordinated complex, found in X-ray structural analysis. Depending on the solvent polarity and on iodide ion concentration this complex yields the P,N monochelate complex (A) [molecular structure analogous to. e.g. (*R,R*)-**8-Pd**] and very small amounts of N,N' monochelate complex. This second possibility is found only, because air oxidation of the uncoordinated PPh_2 group of the (*S,S*)-**9** ligand shifts the equilibrium.

The formation of a cationic $(PdIL_2)I$ [L = (*S*)-**5**] chelate complex further revealed that an iodide anion can be displaced from palladium by a nitrogen ligating site. The preparation of this complex with $PdI_2[(S)\text{-}\mathbf{5}]_2$ stoichiometry initially gave a red solution [$^{31}P\{^1H\}$ NMR (acetone): δ = 18.4] of a complex, with both ligands bound (η^1-P). After evaporation of the solvent a yellow powder was obtained, that was sparingly soluble in CD_2Cl_4 only [solution $^{31}P\{^1H\}$ NMR: δ = 44.5, 48.6 (2 s)], A $^{31}P\{^1H\}$ CP-MAS spectrum of this powder gave two strongly shifted resonances [δ = 53, 69; half-width = 3 ppm]. this data and IR, FIR spectra are in accord with a *cis*-$(PdIL_2)I$ structure[33] of the yellow complex with one ligand bound (η^1-P) and the second ligand bound (η^2-P,N). In the case of β-aminoalkylphosphanes [as (*S*)-**5**] as ligands the cleavage of the P,N chelate is known[33] to be a slow process.

Grignard Cross-Coupling Reaction

Catalytic runs (cf. Scheme 1) and quantitative analysis of the thus obtained samples were performed under strictly controlled conditions, described in ref.[8]. Compared to 50–90% yield of 3-phenyl-1-butene (**3**), obtained in catalytic runs employing 1:1 mixtures of $NiCl_2$ and ligands **5**–**7** (cf. ref.[8]) and vinyl chloride (**1a**) the yield of **3** in catalytic runs employing the new nickel complexes, bearing ligands **8** (*R,S*)-**9**, **10**, **12**, **13** were slightly decreased (50–80% range; cf. Table 2). The catalyst with P,N,N' ligand (*S,S*)-**9** (cf. entries 9, 10 in Table 2) gave only a 20–40% yield, indicating some contribution of the second nitrogen ligating site. The quantitative analysis of the phenylethane contents of hydrolysed reaction mixtures revealed, that 4–5.5 mmol of Grignard compound **2a** was consumed by 5 mmol of vinyl chloride (**1a**) in most cases with the only exception of catalytic runs with (*S,S*)-**9**/$NiCl_2$ catalyst (2–3 mmol consumed). 2–5% of Grignard compound **2a** was converted to styrene (β-elimination of coordinated 1-phenylethyl groups[8]) with nickel complexes of (*S,S*)-**10** ligands as only exception (10% of styrene). At a (*S,S*)-**10** to nickel of 4 ratio (cf. entry 15) decreased quantities of 3-phenyl-1-butene (**3**) and styrene were formed. Nevertheless 5 mmol of Grignard compound **2a** was consumed. (We are unable to detect homocoupling products in our enantioselective GLC analysis.)

Table 2. Enantioselectivity of nickel P,N monophosphane catalysts in diethyl ether; conditions: 5 mmol of vinyl chloride (**1a**) and 6 mmol of Grignard compound **2a**

Entry	Ligand (L)	L / Ni ratio[a]	Yield (% [b])	**3** % ee (confign.)	ln (*R/S*)	No of catalytic runs
1	(*R,R*)-**8**	1	50 - 80	29 (*S*)	-0.59	4
2	(*R,R*)-**8**	3/2	50 - 80	37 (*S*)	-0.77	3
3	(*R,R*)-**8**	2	72, 76	16 (*S*)	-0.34	2
4	(*S,R*)-**8**	1	50 - 80	11 (*R*)	0.22	4
5	(*S,R*)-**8**	3/2	62	14 (*R*)	0.29	1
6	(*S,R*)-**8**	2	53, 65	17 (*R*)	0.35	2
7	(*R,S*)-**9**	1	50 - 70	54 (*S*)	-1.2	4[e]
8	(*R,S*)-**9**	2	50 - 70	67 (*S*)	-1.6	4[e]
9	(*S,S*)-**9**	1	20 - 40	67 (*R*)	1.6	3[f]
10	(*S,S*)-**9**	2	20 - 40	72 (*R*)	1.8	3[g]
11	(*S,S*)-**10**	4/5	60	12 (*R*)	0.24	1
12	(*S,S*)-**10**	1	60 - 70	20 (*R*)	0.40	2
13	(*S,S*)-**10**	3/2	56	12 (*S*)	-0.24	1
14	(*S,S*)-**10**	2	62	30 (*S*)	-0.60	3
15	(*S,S*)-**10**	4	30	57 (*S*)	-1.30	2
16	(*S,R*p)-**12**[c]	1	68, 79	63 (*R*)	1.47	2
17	(*S,R*p)-**12**[c]	2	64, 78	66 (*R*)	1.58	2
18	(*S,S*p)-**12**[c]	1	62, 82	55 (*R*)	1.24	2
19	(*S,S*p)-**12**[c]	2	73, 81	58 (*R*)	1.36	2
20	(*S,R*p)-**13**	1	78	57 (*R*)	1.30	1
21	(*S,R*p)-**13**	2	72	58 (*R*)	1.32	1
22	(*S,S*p)-**13**	1	73	60 (*R*)	1.40	1
23	(*S,S*p)-**13**	2	79	61 (*R*)	1.44	1
24	(*S*)-**5**[d]	1	70, 65	88.5 (*R*)	2.80	2
25	(*S*)-**5**[d]	2	50	88.0 (*R*)	2.75	1
26	(*S*)-**7**[d]	1	50, 82	71.5 (*R*)	1.79	2
27	(*S*)-**7**[d]	2	79, 64	62.0 (*R*)	1.45	1

[a] 50 μmol of Ni. – [b] The yield is based on the amount of **1a** used. – [c] Ligand of 93% ee. – [d] Data from ref.[8], (*S*)-**7** of 94% ee. – [e] σ[ln(*R/S*)] = 0.2. – [f] σ[ln(*R/S*)] = 0.1. – [g] σ[ln(*R/S*)] = 0.15.

Catalytic runs (cf. Table 3) in which vinyl chloride (**1a**) is replaced by vinyl bromide (**1b**) always consume more Grignard compound **2a**, give larger amounts of styrene (4–8%) and slightly higher yields of 3-phenyl-1-butene (**3**). There is no reactivity difference between nickel complexes bearing diastereomeric P,N,N' ligands (**9**) for vinyl bromide (**1b**) as

Table 3. Enantioselectivity of nickel P,N monophosphane catalysts in diethyl ether; conditions: 5 mmol of vinyl bromide (**1b**) and 6 mmol of Grignard compound **2a**

Entry	Ligand (L)	L / Ni ratio[a]	Yield (%[b])	**3** % ee (confign.)	ln (*R*/*S*)	No of catalytic runs
1	(*R*,*R*)-**8**	1	70 - 90	8 (*S*)	-0.17	2
2	(*R*,*R*)-**8**	3/2	50, 60	25 (*S*)	-0.52	2
3	(*S*,*R*)-**8**	1	70 - 90	4 (*R*)	0.08	3
4	(*R*,*S*)-**9**	1	50 - 60	15 (*S*)	-0.3	3[e]
5	(*S*,*S*)-**9**	1	40 - 60	24 (*R*)	0.5	3[f]
6	(*S*,*S*)-**10**	1	40, 50	3 (*S*)	0.06	2
7	(*S*,*S*)-**10**	2	30	29 (*S*)	-0.60	1
8	(*S*,*R*p)-**12**[c]	1	68, 79	58 (*R*)	1.33	3
9	(*S*,*S*p)-**12**[c]	1	86, 88	59 (*R*)	1.35	2
10	(*S*,*R*p)-**13**	1	88	52 (*R*)	1.15	1
11	(*S*,*S*p)-**13**	1	89	55 (*R*)	1.25	1
12	(*S*)-**5**[d]	1	98	74.5 (*R*)	1.92	1
13	(*S*)-**7**[d]	1	82, 99	68.0 (*R*)	1.66	2

[a] 50 μmol of Ni. – [b] The yield is based on the amount of **1a** used. – [c] Ligand of 93% ee. – [d] Data from ref.[8], (*S*)-**7** of 94% ee. – [e] σ[ln(*R*/*S*)] = 0.15. – [f] σ[ln(*R*/*S*)] = 0.1.

starting compound. Catalytic runs with a nickel complex of (*S*,*S*)-**10**, however, gave lower yield of 3-phenyl-1-butene (**3**) with vinyl bromide (**1b**) instead of vinyl chloride (**1a**) (again 10% of styrene found).

We conclude that additional functional groups have only a small influence on reactivity. Exceptions found for nickel complexes with P,N,N′ ligands (**9**) and with ligand (*S*,*S*)-**10** are dependant on the choice of vinyl halide.

We use ln(*R*/*S*) values as enantioselectivity scale (cf. ref.[8]). Repeated catalytic runs with a constant set of parameters reproduce with absolute standard deviations σ[ln(*R*/*S*)] < 0.05. Repeated catalytic runs with nickel complexes bearing diastereomeric P,N,N′ ligands (cf. Table 2, 3) have a increased absolute standard deviation {σ[ln(*R*/*S*)] ≈ 0.15}. This might be caused by a greater manifold of coordination modes of this ligand [cf. discussion of the structural chemistry of (*S*,*S*)-**9-Pd**]. Catalytic runs with nickel complexes bearing either PNO ligands **8** or P,N,N′ ligands **9** exhibit a large enantioselectivity difference {Δ[ln(*R*/*S*)] ≈ 1; Table 2} in the case of vinyl chloride (**1a**) as starting compound. This difference is absent when vinyl bromide (**1b**) is used (Table 3). Catalytic runs with ligands **8**, **9**, **12**, and **13** give improved enantioselectivities in the case of vinyl chloride (**1a**) as starting compound (cf. ref.[8]). In the case of (*S*,*S*)-**10** as ligand the predominating product configuration is dependant both on the choice of vinyl halide and on the (*S*,*S*)-**10** to nickel ratio (cf. later discussion). At low (*S*,*S*)-**10** to nickel ratios and with vinyl chloride (**1a**) as a starting compound (3*R*)-3-phenyl-1-butene [(*R*)-**3**] is mainly formed, the other enantiomer (*S*)-**3** is, however, mainly formed with vinyl bromide (**1b**) as a starting compound. At high (*S*,*S*)-**10** to nickel ratios (*S*)-**3** is the predominating enantiomer with both vinyl halides.

The nickel complex bearing (*S*)-**5** [or (*R*)-**5**] is the most enantioselective catalyst of all investigated 3-(phosphanyl)-pyrrolidine ligands (cf. Scheme 1). *All variations of this ligand tried in catalysis invariably depressed the enantioselectivity.* Variations are the substitution of the benzyl group at the pyrrolidine nitrogen atom by ethyl [(*S*)-**7**], (tetrahydrofuran-2-yl)methyl [(*S*,*R*)-**8**, (*R*,*R*)-**8**], or [(*N*-neopentyl)pyrrolidin-2-yl]methyl [(*S*,*S*)-**9**, (*R*,*S*)-**9**] groups, the substitution of one phenyl group of the diphenylphosphanyl moiety by 2-methoxyphenyl [(*S*,*R*p)-**12**, (*S*,*S*p)-**12**] or 2,4,6-trimethoxyphenyl [(*S*,*R*p)-**13**, (*S*,*S*p)-**13**] groups or the introduction of a methoxymethyl substituent at a carbon atom of the pyrrolidine ring [(*S*,*S*)-**10**]. If these variation give diastereomeric ligands, all diastereomers are less enantioselective compared with (*S*)-**5** [or (*R*)-**5**].

Table 4. Chiral cooperativity effects[11] in Grignard cross-coupling catalysis with nickel P,N monophosphane catalysts

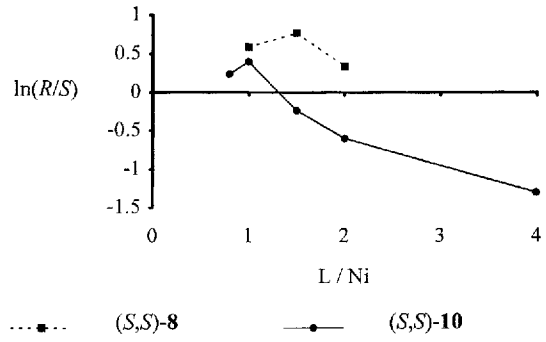
Entry	Ligand (L)	L/Ni ratio	ln (*R*/*S*)	Δ[ln (*R*/*S*)] Change to (*S*,*R*) Diastereomer[a]	Δ[ln (*R*/*S*)] Change to (*R*,S) Diastereomer[b]
1	(*S*,S)-**8**	1	0.59	-0.37	-0.81
2	(*S*,*S*)-**8**	3/2	0.77	-0.48	-1.06
3	(*S*,*S*)-**8**	2	0.34	0.01	-0.69
4	(*S*,*S*)-**9**	1	1.6	-0.4	-2.8
5	(*S*,*S*)-**9**	2	1.8	-0.6	-3.4
6	(*S*,*S*p)-**12**	1	1.24	0.23	-2.71
7	(*S*,*S*p)-**12**	2	1.36	0.22	-2.94
8	(*S*,*S*p)-**13**	1	1.40	-0.10	-2.70
9	(*S*,*S*p)-**13**	2	1.44	-0.12	-2.76

[a] Change to the diastereomer with configuration inside the pyrrolidine ring retained. – [b] Change to the diastereomer with different configuration inside the pyrrolidine ring.

All phosphane ligands, used in this study have a common chiral center in the β-aminoethylphosphane (called P,N) part and a second chiral center, connected with the additional functional group[11]. On the basis of catalytic results with vinyl chloride (**1a**) as starting compound, we find (cf. Table 4), that *enantioselectivity is mainly determined by the P,N part* with minor contributions to enantioselectivity of the second chiral center, connected with the additional functional group. In most cases [ligands **8**, **9**, and **13** but not **12**] increased enantioselectivity is obtained, when both chiral centers have (*S*)- or (*R*)-configuration and decreased in ligands with different configuration [(*S*,*R*) or (*R*,*S*)]. These relative contributions of the two different chiral centers to enantioselectivity depend on the ligand to nickel ratio.

Different ligand to nickel ratios influence enantioselectivity, obtained with nickel complexes of diastereomeric ligands **8**, **9** and **12**, **13**. A dependence of enantioselectivity on ligand to nickel ratios is already known for monophos-

Figure 3. Relationship between enantioselectivity and ligand to nickel ratios[a]



[a] Data for (*S,S*)-**8** [enantiomer of (*R,R*)-**8**] plotted.

phane-catalysed addition of CO to bis[μ-methyl-(1,3-dimethyl-η³-allyl)nickel] yielding 3-methyl-4-hexen-2-one[34]. With **8**, **9** and **12**, **13** as ligands higher enantioselectivities are obtained at a ligand-to-nickel ratio of 2 than for a ligand-to-nickel ratio of 1, with the exception of the nickel complex, bearing (*R,R*)-**8**. This complex is most enantioselective at an (*R,R*)-**8** to nickel ratio of 3:2 (cf. Figure 3). The Ni complexes of (*S,S*)-**10** (cf. Figure 3; enantiomerically pure ligand) even give ln(*R*/*S*) values of different sign, depending on ligand to nickel ratios. This relationship between (*R,R*)-**8** or (*S,S*)-**10** to nickel ratios and enantioselectivity can only be explained with *at least two catalytically active species, bearing different numbers of phosphane ligands.* For example, a Ni complex, bearing one (*S,S*)-**10** ligand, assumed to be the singular catalytically active species, which determines enantioselectivity, can not yield either (*S*)-**3** or (*R*)-**3** as major enantiomer. There must be additionally at least one catalytically active species in the catalytic cycle, bearing more than one (*S,S*)-**10** ligand.

We conclude, that optimisation of enantioselectivity in Grignard cross-coupling reactions with P,N monposphane ligands can be carried out by a variation of the ligand to-nickel ratio and additionally by the proper choice of the vinyl halide used as starting compound. All variations of simple 1-alkyl-3-(diphenylphosphanyl)pyrrolidine ligands by additional functional groups did not improve enantioselectivity.

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Experimental Section

A description of equipment and conditions used for elementary analysis, polarimetry, mass spectra, IR spectra, and NMR spectra (^{1}H-NMR, ^{13}C{^{1}H}-NMR, ^{31}P{^{1}H}-NMR, and ^{31}P(^{1}H} solid-state NMR spectra) has been given in ref.[7]. The numbering schemes of carbon atoms relevant for ^{1}H-NMR, ^{13}C{^{1}H}-NMR spectra are defined in connection with the physical data of PdI_2 complexes (*S,R*)-**8-Pd**, (*R,R*)-**8-Pd**, and (*S,S*)-**10-Pd** (cf. Figures 1 and 2 for the X-ray numbering schemes). Most ^{13}C{^{1}H}-NMR spectra were measured with the DEPT-135 technique[35]. Additional standard ^{13}C{^{1}H}-NMR spectra of amide products were analysed in order to obtain resonances of CO (amide) carbon atoms. – Abbreviations: An = 2′-methoxyphenyl and TMP = 2′,4′,6′-trimethoxyphenyl. The separation of diastereomeric PdI_2 complexes was carried out with preparative column chromatography on a 1-m (3.3 cm diameter) silica-gel column. The silica gel used was a 15–25 μm (diameter) fraction of 60H silica gel (Merck). The column was pretreated with ethanol/5% H_2O/0.5% NaI and acetone/3% H_2O/0.3% NaI. Then the column was washed with the solvent mixture, appropriate for the separation. R_f values given were determined on TLC (60H; Merck) plates without any pretreatment. No detector was necessary, because the fractions containing PdI_2 complexes are red.

All solvents were dried by standard methods, purified by distillation and kept under argon. All manipulations involving phosphanes (standard Schlenk technique) and moisture-sensitive compounds were conducted under dry argon. The starting materials for phosphane synthesis were prepared according to published procedures: Phenylphoshane[36]. – (2*R*)-1-(*tert*-Butoxycarbonyl)-3-hydroxypyrrolidine [(R)-**23**][7]. – Both enantiomers of 3-(diphenylphosphanyl)pyrrolidine (**4**)[7]. – (*R*)-Tetrahydrofuran-2-carboxylic acid [(*R*)-**14**][12]; on the basis of a specific rotation measurement the compound obtained corresponds to (*R*)-**14** of 95% ee[37]. – (2*S*)-1-*tert*-Butoxycarbonylpyrrolidine-2-carboxylic acid [(*S*)-**15**][13]. – (2*S*,4*R*)-1-(*tert*-Butoxycarbonyl)-4-hydroxy-2-(hydroxymethyl)pyrrolidine (**19**)[15]. All procedures and starting materials used in catalysis were the same as in ref.[8].

(3R,2′R)-3-(Diphenylphosphanyl)-1-[(tetrahydrofuran-2′-yl)-carbonyl]pyrrolidine [(*R,R*)-**16**] *and Diastereomeric* (*S,R*)-**16** *with (3S,2′R) Configuration:* To a solution of (*R*)-**14**-imidazolide, prepared from (*R*)-tetrahydrofuran-2-carboxylic acid [(*R*)-**14**] (2.15 g, 18.5 mmol) and 1,1′-carbonyl diimidazole (3 g, 18.5 mmol) at 0°C, a solution of one enantiomer of 3-(diphenylphosphanyl)pyrrolidine (**4**) (4.1 g, 16 mmol) in 50 ml of THF was added. Experimental details and workup for this CDI coupling were given in ref.[7].

(*S,R*)-**16**: Yield 5.2 g [92% calcd. from 16 mmol of (*S*)-**4**]. – MS (FD); *m/z*: 352.9 [M$^+$]. – IR (film): $\tilde{\nu}$ = 3070, 3051, 2971, 2947, 2869 cm^{-1} (C–H), 1652 (CO), 1480 (C=C, C–N), 1434, 1334, 1182, 1093, 1060 (C–P, C–N, C–C, C–O), 744, 698 (Ph). – ^{1}H NMR ($CDCl_3$, 400.13 MHz): δ = 1.76, 1.94, 2.10 (3 m, 6H, 3′-H, 4′-H, 4-H), 2.77, 2.88 (2 m, 1H, 3-H), 3.28, 3.37, 3.57, 3.75, 3.87 (5 m, 6H, 2-H, 5-H, 5′-H), 4.32, 4.39 (2 m, 1H, 2′-H), 7.26, 7.38 [2 m, 10H, CH (Ph)]. – ^{13}C{^{1}H} NMR[38] ($CDCl_3$, 100.62 MHz): δ = 22.7, 25.6 (2 s, C-4′), 28.2, 28.4 (2 d, $^2J_{CP}$ = 18 Hz, C-4), 30.4, 30.6 (2 s, C-3′), 34.4, 36.8 (2 d, $^1J_{CP}$ = 10 Hz, C-3), 46.2, 46.3 (2 d, $^3J_{CP}$ = 8 Hz, C-5), 49.8, 49.9 (2 d, $^2J_{CP}$ = 18 Hz, $^2J_{CP}$ = 19 Hz, C-2), 69.0 (2 s, C-5′), 76.9, 77.0 (2 s, C-2′), 128.8, 129.3 [2 m, CH (Ph)], 133.3 [m, CH (Ph)], 170.5 (s, CO, standard ^{13}C{^{1}H} NMR). – ^{31}P{^{1}H} NMR ($CDCl_3$, 32.34 MHz): δ = –8.9, –9.9. – $[\alpha]_D^{20}$ = –101.5 [*c* = 0.55, diethyl ether; (*S,R*)-**16** with de > 98%, ee > 99%]. – $C_{21}H_{24}NO_2P$ (352.9): calcd. C 71.37, H 6.85, N 3.96; found C 71.13, H 7.10, N 3.92.

(*R,R*)-**16**: Yield 4.7 g [83% calcd. from 16 mmol of (*R*)-**4**]. – MS (FD), IR (film): cf. (*S,R*)-**16**. – ^{1}H NMR ($CDCl_3$, 400.13 MHz): δ = 1.76, 1.92, 2.06 (3 m, 6H, 3′-H, 4′-H, 4-H), 2.75, 2.92 (2 m, 1H, 3-H), 3.28, 3.37, 3.66, 3.75, 3.87 (5 m, 6H, 2-H, 5-H, 5′-H), 4.34, 4.40 (2 m, 1H, 2′-H), 7.26, 7.38 [2 m, 10H, CH (Ph)]. – ^{13}C{^{1}H} NMR[38] ($CDCl_3$, 100.62 MHz): δ = 25.9, 26.0 (2 s, C-4′), 28.6, 28.7 (2 d, $^2J_{CP}$ = 18 Hz, C-4), 30.8, 31.0 (2 s, C-3′), 34.8, 36.9 (2 d, $^1J_{CP}$ = 9 Hz, C-3), 46.4 (d, $^3J_{CP}$ = 8 Hz, C-5), 50.2 (d, $^2J_{CP}$ = 27 Hz, C-2), 69.3 (s, C-5′), 76.9, 77.1 (2 s, C-2′), 128.8, 129.3 [2 m, CH (Ph)], 133.3 [m, CH (Ph)], 170.5 (s, CO, standard ^{13}C{^{1}H} NMR). – ^{31}P{^{1}H} NMR ($CDCl_3$, 32.34 MHz): δ = –9.0,

−9.5. − $[\alpha]_D^{20}$ = −7.23 [*c* = 2.2, diethyl ether; (*R,R*)-**16** with de > 98%, ee > 99%].

*Reduction of (R,R)-**16** to (3R,2'R)-3-(Diphenylphosphanyl)-1-[(tetrahydrofuran-2'-yl)methyl]pyrrolidine [(R,R)-**8**] and of the (S,R)-**16** Diastereomer to (S,R)-**8** with (3S,2'R) Configuration:* The samples of (*R,R*)-**16**, (*S,R*)-**16** previously obtained were reacted with 0.77 g (20 mmol) $LiAlH_4$ in THF. Experimental details and workup were given in ref.[7].

(*S,R*)-**8**: Yield 4.5 g [91% calcd. from 14.7 mmol of (*S,R*)-**16**]. − MS (70 eV); *m/z* (%): 339.1 (5) [M^+], 255.1 (5) [$M^+ - CH_2THF$], 185.0 (100) [Ph_2PH], 153.1 (35) [$M^+ - Ph_2PH$]. − IR (film): $\tilde{\nu}$ = 3071, 3052, 3001, 2961, 2865, 2798 cm^{-1} (C−H), 1480 (C=C, C−N), 1435, 1270, 1250, 1198, 1158, 1118, 1093, 1069, 1027 (C−P, C−N, C−C, C−O), 746, 697 (Ph). − ^1H NMR ($CDCl_3$, 400.13 MHz): δ = 1.38, 1.72, 1.85, 1.96 (4 m, 6H, 3'-H, 4'-H, 4-H), 2.33, 2.52 (2 m, 4H, 2-H, 5-H), 2.87 (m, 3H, 3-H, 1'-H), 3.59, 3.71 (2 m, 2H, 5'-H), 3.86 (m, 1H, 2'-H), 7.16, 7.35 [2 m, 10H, CH (Ph)]. − $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.62 MHz): δ = 29.1 (d, $^2J_{CP}$ = 18 Hz, C-4), 33.8 (d, $^1J_{CP}$ = 8 Hz, C-3), 54.3 (d, $^3J_{CP}$ = 5 Hz, C-5), 59.3 (d, $^3J_{CP}$ = 23 Hz, C-2), 60.8 (s, C-1'), 77.6 (s, C-2'), 30.1 (s, C-3'), 25.5 (s, C-4'), 67.9 (s, C-5'), 128.3 [d, $^3J_{CP}$ = 6 Hz, CH (*meta* Ph)], 128.9 [d, $^4J_{CP}$ = 5 Hz, CH (*para* Ph)], 132.9, 133.1 [2 d, $^2J_{CP}$ = 18 Hz, CH (*ortho* Ph)]. − $^{31}P\{^1H\}$ NMR ($CDCl_3$, 101.26 MHz): δ = −4.57. − $[\alpha]_D^{20}$ = −8.46 (*c* = 0.79, dichloromethane). − $C_{21}H_{26}NOP$ (339.4): calcd. C 74.31, H 7.72, N 4.13; found C 74.01, H 7.62, N 4.09.

(*R,R*)-**8**: Yield 4.15 g [92% calcd from 13.3 mmol of (*R,R*)-**16**]. − MS (70 eV), IR (film): cf. (*S,R*)-**8**. − ^1H NMR ($CDCl_3$, 400.13 MHz): δ = 1.38, 1.71, 1.84, 1.96 (4 m, 6H, 3'-H, 4'-H, 4-H), 2.21, 2.40, 2.47 (3 m, 4H, 2-H, 5-H), 2.88 (m, 3H, 3-H, 1'-H), 3.60, 3.73 (2 m, 2H, 5'-H), 3.84 (m, 1H, 2'-H), 7.16, 7.35 [2 m, 10H, CH (Ph)]. − $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.62 MHz): δ = 29.0 (d, $^2J_{CP}$ = 18 Hz, C-4), 33.9 (d, $^1J_{CP}$ = 8 Hz, C-3), 55.2 (d, $^3J_{CP}$ = 5 Hz, C-5), 58.6 (d, $^3J_{CP}$ = 17 Hz, C-2), 60.8 (s, C-1'), 77.7 (s, C-2'), 30.1 (s, C-3'), 25.4 (s, C-4'), 67.9 (s, C-5'), 128.6 [2 d, $^3J_{CP}$ = 7 Hz, CH (*meta* Ph)], 128.3 [d, $^4J_{CP}$ = 5 Hz, CH (*para* Ph)], 132.9, 133.1 [2 d, $^2J_{CP}$ = 18 Hz, CH (*ortho* Ph)]. − $^{31}P\{^1H\}$ NMR ($CDCl_3$, 101.26 MHz): δ = −4.59. − $[\alpha]_D^{20}$ = 2.84 (*c* = 0.56, dichloromethane). − $C_{21}H_{26}NOP$ (339.4): calcd. C 74.31, H 7.72, N 4.13; found C 74.15, H 7.42, N 4.18.

*(3R,2'S)-3-(Diphenylphosphanyl)-1-[(pyrrolidin-2'-yl)carbonyl]pyrrolidine [(R,S)-**18**] an Diastereomeric [(S,S)-**18**] with (3S,2'S)-Configuration:* To a solution of (2*S*)-1-*tert*-butoxycarbonylpyrrolidine-2-carboxylic acid [(*S*)-**15**] (1.51 g, 7.0 mmol) in 40 ml of THF at 0°C, 1,1'-carbonyl diimidazole (1.45 g, 7.0 mmol) was added in several small portions. The mixture was stirred 1 h and then a solution of one enantiomer of 3-diphenylphosphanylpyrrolidine (**4**) (1.5 g, 5.9 mmol) in 50 ml of THF was added and the mixture was stirred overnight. THF was evaporated and the oily residue was treated with 30 ml of trifluoroacetic acid (TFA) at 0°C until it was dissolved. Then TFA was evaporated immediately in vacuo and 100 ml of 10% aqueous KOH solution was added. The product was extracted with three portions diethyl ether (3 × 50 ml) and the collected diethyl ether phases were stirred overnight with 100 ml of aqueous saturated citric acid solution. The diethyl ether phase was separated and the aqueous phase was extracted twice with further diethyl ether (2 × 50 ml). Then 200 ml of 40% aqueous KOH solution was added to the aqueous phase and the product was extracted with four portions diethyl ether (4 × 50 ml). The collected diethyl ether phases were filtered through Celite covered with $MgSO_4$. The oily product obtained by evaporation of diethyl ether was dried in vacuo.

(*R,S*)-**18**: Yield 1.45 g [70% calcd. from (*R*)-**4**]. − MS (70 eV); *m/z* (%): 352.2 (20) [M^+], 283.1 (60) [$M^+ - C_4H_7NH$], 254.2 (80) [$M^+ - COC_4H_7NH$], 186.8 (100) [Ph_2PH]. − IR (film): $\tilde{\nu}$ = 3300 cm^{-1} (N−H), 3071, 3049, 2961, 2955, 2868 (C−H), 1641 (CO), 1494, 1480 (C=C, C−N), 1444, 1274, 1250, 1148, 1030 (C−P, C−N, C−C), 750, 738, 700, 697 (Ph). − ^1H NMR ($CDCl_3$, 400.13 MHz): δ = 1.68, 1.96 (2 m, 6H, 4-H, 3'-H, 4'-H), 2.59 (s, 1H, NH), 2.74, 3.09, 3.34 (3 m, 5H, 2-H^1, 5-H^1, 5'-H, 3-H), 3.64 (m, 3H, 2-H^2, 5-H^2, 2'-H), 7.26, 7.39 [2 m, 10H, CH (Ph)]. − $^{13}C\{^1H\}$ NMR[38] ($CDCl_3$, 100.62 MHz): δ = 25.9, 26.0 (2 s, C-4'), 27.9 (d, $^2J_{CP}$ = 19 Hz, C-4), 29.8 (2 s, C-3'), 34.2, 36.1 (2 d, $^1J_{CP}$ = 9 Hz, $^1J_{CP}$ = 10 Hz, C-3), 45.5, 45.7 (2 d, $^3J_{CP}$ = 8 Hz, C-5), 47.2 (2 s, C-5'), 49.1, 49.5 (2 d, $^2J_{CP}$ = 20 Hz, $^2J_{CP}$ = 27 Hz, C-2), 59.1 (s, C-2'), 128.8, 129.3 [2 m, CH (Ph)], 133.3 [m, CH (Ph)], 171.2 (s, CO, standard $^{13}C\{^1H\}$ NMR). − $^{31}P\{^1H\}$ NMR ($CDCl_3$, 32.39 MHz): δ = −7.3, −9.2. − $C_{21}H_{25}N_2OP$ (352.4): calcd. C 71.57 H, 7.15 N, 7.95; found C 70.92, H 7.05, N 9.69 (imidazole impurities).

(*S,S*)-**18**: Yield 1.49 g [71% calcd. from (*S*)-**4**]. − $^{31}P\{^1H\}$ NMR ($CDCl_3$, 32.39 MHz): δ = −7.2, −7.8.

*(3R,2'S)-3-(Diphenylphosphanyl)-1-{[(1'-pivaloyl)pyrrolidin-2'-yl]carbonyl}pyrrolidine (R,S)-**17** and Diastereomeric (S,S)-**17** with (3S,2'S) Configuration:* To 80 ml of a diethyl ether solution containing 1.4 g (4 mmol) of (*R,S*)-**18** or (*S,S*)-**18**, 100 ml of 2 N KOH was added. Then 0.12 ml of pivaloyl chloride (6 mmol) was added by syringe at 0°C. The mixture was stirred for 3 d and the diethyl ether phase was separated. The aqueous phase was further extracted twice with diethyl ether and the collected diethyl ether phases were washed with 20 ml of 2 N HCl. They were filtered through Celite covered with $MgSO_4$ and the solvent was evaporated in vacuo. The oily product was dried in vacuo.

(*R,S*)-**17**: Yield 1.6 g [90% calcd. from 4 mmol of (*R,S*)-**18**]. − MS (70 eV); *m/z* (%): 436.2 (2) [M^+], 379.1 (5) [$M^+ - C_4H_9$], 351.2 (5) [$M^+ - COC_4H_9$], 283.1 (20) [$M^+ - C_4H_7NCOC_4H_9$], 254.2 (20) [$M^+ - COC_4H_7NCOC_4H_9$], 186.8 (100) [Ph_2PH], 85.0 (70) [$M^+ - COC_4H_9$]. − IR (film): $\tilde{\nu}$ = 3047, 2961, 2939, 2864, 2848 cm^{-1} (C−H), 1647, 1615 (CO), 1479 (C=C, C−N), 1436, 1412, 1384, 1250, 1148, 1030 (C−P, C−N, C−C), 753, 705 (Ph). − ^1H NMR ($CDCl_3$, 400.13 MHz): δ = 1.15 [s, 9H, $COC(CH_3)_3$], 1.61, 2.02 (2 m, 6H, 4-H, 3'-H, 4'-H), 2.81, 3.18, 3.48, 3.64 (4 m, 7H, 2-H, 5-H, 3-H, 5'-H), 4.49 (m, 1H, 2'-H), 7.23, 7.34 [2 m, 10H, CH (Ph)]. − $^{13}C\{^1H\}$ NMR[38] ($CDCl_3$, 100.62 MHz): δ = 26.3, 26.4 (2 s, C-4'), 26.6 [s, $COC(CH_3)_3$], 28.9 (d, $^2J_{CP}$ = 18 Hz, C-4), 30.9, 31.2 (2 s, C-3'), 35.7, 36.7 (d, $^1J_{CP}$ = 9 Hz, C-3), 38.9 [s, $COC(CH_3)_3$], 46.3, 46.8 (2 d, $^3J_{CP}$ = 7 Hz, $^3J_{CP}$ = 9 Hz, C-5), 48.6 (s, C-5'), 50.2 (d, $^2J_{CP}$ = 27 Hz, C-2), 60.2 (s, C-2'), 128.8, 129.3 [2 m, CH (Ph)], 133.3 [m, CH (Ph)], 171.2, 176.8 (2 s, CO, standard $^{13}C\{^1H\}$ NMR). − $^{31}P\{^1H\}$ NMR ($CDCl_3$, 101.26 MHz): δ = −7.33, −9.34. − $C_{26}H_{23}N_2O_2P$ (436.5): calcd. C 71.54, H 7.05, N 6.42; found C 71.42, H 7.07, N 6.43.

(*S,S*)-**17**: Yield 1.6 g [90% from 4 mmol of (*S,S*)-**18**]. − MS (70 eV); IR (film): cf. (*R,S*)-**17**. − ^1H NMR ($CDCl_3$, 400.13 MHz): δ = 1.17 [s, 9H, $COC(CH_3)_3$], 1.88 (m, 6H, 4-H, 3'-H, 4'-H), 2.72, 2.98, 3.30, 3.69, 3.91 (5 m, 7H, 2-H, 5-H, 3-H, 5'-H), 4.48, 4.46 (2 m, 1H, 2'-H), 7.25, 7.36 [2 m, 10H, CH (Ph)]. − $^{13}C\{^1H\}$ NMR[38] ($CDCl_3$, 100.62 MHz): δ = 26.4, 27.8 (2 s, C-4'), 27.7 [s, $COC(CH_3)_3$], 29.0 (d, $^2J_{CP}$ = 17 Hz, C-4), 31.0, 31.3 (2 s, C-3'), 34.9 (d, $^1J_{CP}$ = 9 Hz, C-3), 38.9 [s, $COC(CH_3)_3$], 46.7 (d, $^3J_{CP}$ = 8 Hz, C-5), 48.8 (s, C-5'), 50.0 (d, $^2J_{CP}$ = 22 Hz, C-2), 60.2 (s, C-2'), 128.8, 129.3 [2 m, CH (Ph)], 133.3 [m, CH (Ph)], 171.2, 176.8 (2 s, CO, standard $^{13}C\{^1H\}$ NMR). − $^{31}P\{^1H\}$ NMR ($CDCl_3$, 101.26 MHz): δ = −7.33, −7.93.

*Reduction of (R,S)-**17** to (3R,2'S)-3-(Diphenylphosphanyl)-1-{[(1'-neopentyl)pyrrolidin-2'-yl]methyl}pyrrolidine [(R,S)-**9**] and*

*of the (S,S)-***17** *Diastereomer to (S,S)-***17** *Diastereomer to (S,S)-***9** *with (3S,2'S) Configuration:* 3.6 mmol of *(R,S)*-**17** or *(S,S)*-**17** were treated with 20 mmol $LiAlH_4$ in THF. Experimental details and workup were given in ref.[7].

(R,S)-**9**: Yield 1.32 g [88% calcd. from 3.6 mmol of *(R,S)*-**17**]. – MS (70 eV); *m/z* (%): 409.4 (2) [M^+], 351.3 (5) [$M^+ - C_4H_9$], 268.2 (20) [$M^+ - C_4H_7NCH_2C_4H_9$], 255.2 (20) [$M^+ - CH_2C_4H_7NCH_2C_4H_9$], 223.3 (15) [$M^+ - Ph_2PH$], 183.1 (30) [$Ph_2PH$], 140.1 (100) [$M^+ - Ph_2PC_4H_7NCH_2$]. – IR (film): $\tilde{\nu}$ = 3065, 3052, 2949, 2864, 2793 cm^{-1} (C–H), 1479 (C=C, C–N), 1460, 1430, 1394, 1359, 1203, 1149, 1069, 1026 (C–P, C–N, C–C), 739, 695 (Ph). – ^1H NMR ($CDCl_3$, 400.13 MHz): δ = 0.78 [s, 9H, $C(CH_3)_3$], 1.41–2.41, 2.69, 2.78, 3.05 (several m, 18H), 7.25, 7.36 [2 m, 10H, CH (Ph)]. – $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.62 MHz): δ = 29.1 (d, $^2J_{CP}$ = 18 Hz, C-4), 34.0 (d, $^1J_{CP}$ = 8 Hz, C-3), 55.3 (d, $^3J_{CP}$ = 4 Hz, C-5), 58.8 (d, $^2J_{CP}$ = 23 Hz, C-2), 23.7 (s, C-4'), 30.3 (s, C-3'), 48.5 (s, C-5'), 57.8 (s, C-1'), 65.4 (s, C-2'), 28.7 [s, $CH_2C(CH_3)_3$], 62.2 [s, $CH_2C(CH_3)_3$], 128.6 [2 d, $^3J_{CP}$ = 5 Hz, CH (Ph)], 128.3 [2 d, $^4J_{CP}$ = 5 Hz, CH (Ph)], 132.9, 133.1 [2 d, $^2J_{CP}$ = 18 Hz, CH (Ph)]. – $^{31}P\{^1H\}$ NMR ($CDCl_3$, 101.26 MHz): δ = −4.2. – $[\alpha]_D^{20}$ = −56.3 [*c* = 0.94, dichloromethane; *(R,S)*-**9** with de > 98%, ee > 99%]. – $C_{26}H_{37}N_2P$ (408.6): calcd. C 76.43, H 9.13, N 6.86; found C 76.70, H 9.21, N 6.84.

(S,S)-**9**: Yield 1.34 g [88% from 3.6 mmol of *(S,S)*-**17**]. – MS (70 eV), IR (film): cf. *(R,S)*-**9**. – ^1H NMR ($CDCl_3$, 400.13 MHz): δ = 0.78 [s, 9H, $C(CH_3)_3$], 1.41–2.41, 2.69, 2.78, 3.05 (several m, 18H), 7.25, 7.36 [2 m, 10H, CH (Ph)]. – $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.62 MHz): δ = 28.8 (d, $^2J_{CP}$ = 16 Hz, C-4), 33.8 (d, $^1J_{CP}$ = 7 Hz, C-3), 54.7 (d, $^3J_{CP}$ = 5 Hz, C-5), 59.3 (d, $^2J_{CP}$ = 24 Hz, C-2), 25.4 (s, C-4'), 30.2 (s, C-3'), 48.6 (s, C-5'), 57.9 (s, C-1'), 65.3 (s, C-2'), 28.7 [s, $CH_2C(CH_3)_3$], 62.1 [s, $CH_2C(CH_3)_3$], 128.6 [2 d, $^3J_{CP}$ = 5 Hz, CH (Ph)], 128.3 [2 d, $^4J_{CP}$ = 5 Hz, CH (Ph)], 132.9, 133.1 [2 d, $^2J_{CP}$ = 18 Hz, CH (Ph)]. – $^{31}P\{^1H\}$ NMR ($CDCl_3$, 101.26 MHz): δ = −4.1. – $[\alpha]_D^{20}$ = −79.3 [*c* = 0.69, dichloromethane; *(S,S)*-**9** with de > 98%, ee > 99%]. – $C_{26}H_{37}N_2P$ (408.6): calcd. C 76.43, H 9.13, N 6.86; found C 76.55, H 9.25, N 7.03.

[1'(RS),2S,4R]-1-(tert-Butoxycarbonyl)-4-(1'-ethoxyethyloxy)-2-(p-toluolsulfonyloxymethyl)pyrrolidine (**20**): A solution of *p*-toluenesulfonyl chloride (12.1 g, 63 mmol) in dry pyridine (30 ml) was added dropwise at −30°C to a stirred solution of (2*S*,4*R*)-1-(*tert*-butoxycarbonyl)-4-(hydroxy)-2-(hydroxymethyl)pyrrolidine (**19**) (13.0 g, 60 mmol) in dry pyridine (100 ml). The mixture was stirred at −25°C for 15 h, at 0°C for 4 h, and at room temperature for 1 h. 6 N hydrochloric acid (260 ml) was added dropwise to the reaction mixture with cooling in an ice bath. The mixture was extracted with ethyl acetate (3 × 200 ml). The combined extracts were washed with 100 ml of saturated K_2CO_3 solution and the solvent was evaporated in vacuo at room temperature. A ^1H-NMR spectrum of the crude oily product revealed that the mono(*p*-toluenesulfonyl) ester of **19** was obtained in a nearly quantitative yield. It was contaminated with less than 15 mmol of pyridine. The crude product was dissolved in 300 ml of ethyl vinyl ether and 2 ml of trifluoroacetic acid (26 mmol) was added by syringe at 0°C. The mixture was stirred at room temperature for 96 h. Then solid K_2CO_3 (6 g) was added and the mixture was further stirred for 30 min. Then ethyl vinyl ether was evaporated in vacuo at room temperature and 100 ml of diethyl ether was added to the residue. The mixture was filtered through Celite and the diethyl ether was evaporated in vacuo at room temperature. **20** was obtained as an viscous oil in nearly quantitative yield which was revealed by ^1H NMR to obtain less than 5 mmol of pyridine as impurity. – IR (film): $\tilde{\nu}$ = 1669 cm^{-1} (Boc), 1367, 1177 (OSO_2Ar). – ^1H NMR ($CDCl_3$, 250.13 MHz): δ = 1.09 (m, 3H, CH_2CH_3), 1.19, 1.21 (2 s, 3H, $CHCH_3$), 1.30, 1.37 [2 s, 9H, CH_3 (Boc)], 1.96, 2.16 (2 m, 2H, 3-H), 2.35 (s, 3H, $ArCH_3$), 3.35, 3.58 (2 m, 6H, 5-H, CH_2CH_3 and CH_2OTs), 4.01, 4.31 (2 m, 2H, 2-H and 4-H), 4.60 (m, 1H, $CHCH_3$), 7.26 (d, 2H, Ar), 7.67 (d, 2H, Ar).

(2S,4R)-1-(tert-Butoxycarbonyl)-4-(hydroxy)-2-(methoxymethyl)pyrrolidine (**21**): Methanol (2.4 ml, 60 mmol) was added slowly by syringe to a suspension of NaH (1.44 g, 60 mmol) in 50 ml of diethyl ether. The mixture was allowed to stir at room temperature overnight. Diethyl ether was evaporated and the residue was dissolved in DMSO (50 ml). To this solution was slowly added a solution containing **20**, obtained before in 20 ml DMSO by syringe maintaining the reaction temperature below 30°C. The solution was stirred for 7 h at room temperature and then at 70°C overnight. The solution was added to 1.5 l of water and 300 ml of ethyl acetate. The aqueous phase was separated and was further extracted with ethyl acetate (3 × 300 ml). Ethyl acetate was evaporated from the combined organic phases and the oily residue was dissolved in methanol (200 ml). To the solution acetic acid (4 ml, 0.07 mol) was added and the solution was heated under reflux for 4 d. The solution was then concentrated in vacuo and the residue again dissolved in methanol/acetic acid and heated under reflux for 4 d. A chromatographic column [prepared with a suspension of 150 ml dry silica gel (230–400 mesh) in ethyl acetate] was charged with the crude product **21** obtained by evaporation of ethanol under reduced pressure. With ethyl acetate as eluent 1 l of eluat was collected. Ethyl acetate was evaporated under reduced pressure to give **21** as an oil; yield 6.5 g (28.2 mmol, 47% calculated from 60 mmol of **19**), contaminated with 3 mmol of 1-(*tert*-butoxycarbonyl)-2-formyl-4-hydroxypyrrolidine (Kornblum oxidation of the tosylate). – MS (70 eV), *m/z* (%): 230.0 (10) [M^+]. – IR (film): $\tilde{\nu}$ = 3465 cm^{-1} (O–H), 1700 [CO (Boc)]. – ^1H NMR ($CDCl_3$, 400.13 MHz): δ = 1.39 [s, 9H, CH_3 (Boc)], 2.16 (m, 2H, 3-H), 3.26 (s, 3H, OCH_3), 3.4, 3.5 (2 m, 4H, 5-H and CH_2OCH_3), 4.01, 4.35 (2 m, 2H, 2-H and 4-H). – $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.62 MHz): δ = 27.6, 28.4 [2 s, CH_3 (Boc)], 34.0, 35.0 (2 s, C-3), 52.2 (s, C-5), 55.2 (s, OCH_3), 59.0 (s, C-2), 72.8, 73.7 (2 s, CH_2OCH_3), 74.8, 75.3 (2 s, C-4).

(2S,4S)-4-(Diphenylphosphanyl)-2-(methoxymethyl)pyrrolidine [*(S,S)*-**22**]: The methanesulfonyl ester of **21** was prepared as THF solution (20 ml) with **21** (6.5 g, 28.2 mmol), *n*-butyllithium (18.0 ml, 28.8 mmol) and methanesulfonyl chloride (2.14 ml, 27.7 mmol) as starting compounds according to ref.[7]. This compound was added at −38°C to a solution of 42 mmol of $KPPh_2$ (9.42 g) in 100 ml of THF. The solution was stirred for 20 h at −20°C and 2 d at room temperature. Then THF was evaporated and the solid residue dried and dissolved in a mixture of 100 ml H_2O and 100 ml of diethyl ether. The diethyl ether phase was separated. The aqueous layer was further extracted twice with 100 ml diethyl ether. The diethyl ether extracts were collected, filtered through Celite and diethyl ether was evaporated. The crude product was dissolved in 70 ml of TFA at 0°C and stirred for 1 h, in order to cleave the *tert*-butoxycarbonyl blocking group[7]. TFA was evaporated and the remaining oil dissolved in a mixture of aqueous KOH (100 ml, 30%) and 100 ml of diethyl ether. The aqueous phase was separated and extracted twice with 50 ml of diethyl ether. The collected diethyl ether extracts were stirred with 100 ml of 2 N HCl and the diethyl ether phase was separated. The aqueous phase was extracted with dichloromethane (3 × 50 ml). The collected dichloromethane solutions were filtered through Celite and evaporated to yield 10 ml of a concentrated solution of *(S,S)*-**22** hydrochloride. This solution was added under vigorous stirring to 200 ml of diethyl ether. The suspension was concentrated to 250 ml and stirred overnight. The white solid was collected by suction filtration,

washed three times with 20 ml of diethyl ether portions and dried under reduced pressure. It was dissolved in a mixture of aqueous KOH (50 ml, 30%) and 50 ml of diethyl ether. The aqueous phase was separated and extracted twice with diethyl ether (50 ml). The collected etheral solutions were dried with solid KOH and concentrated to yield a viscous oil; yield 4.35 g of (*S,S*)-**22** (14.5 mmol, 51% calcd. from **21**). – MS (70 eV); *m/z* (%): 299.6 (5) [M^-] – ^{1}H NMR ($CDCl_3$, 250.13 MHz): δ = 1.75 (m, 3H, 3-H, NH), 2.50, 2.74, 2.85 (3 m, 4H, 2-H, 4-H, 5-H), 3.03 (s, 3H, OCH_3), 3.20 (m, 2H, CH_2OCH_3), 7.19, 7.34 [2 m, 10H, CH (Ph)]. – $^{13}C\{^1H\}$ NMR ($CDCl_3$, 62.90 MHz): δ = 34.4 (d, $^2J_{CP}$ = 19 Hz, C-3), 37.0 (d, $^1J_{CP}$ = 8 Hz, C-4), 51.0 (d, $^2J_{CP}$ = 24 Hz, C-5), 59.3 (s, OCH_3), 59.4 (d, $^3J_{CP}$ = 7 Hz, C-2), 75.7 (s, CH_2OCH_3), 128.6, 133.4 [2 m, CH (PPh)]. – $^{31}P\{^1H\}$ NMR ($CDCl_3$, 101.25 MHz): δ = –4.8. – $C_{18}H_{22}NOP$ (299.4): calcd. C 72.22, H 7.41, N 4.69; found C 72.18, H 7.39, N 4.67.

(2S,4S)-1-Benzyl-4-(diphenylphosphanyl)-2-(methoxymethyl)pyrrolidine [(*S,S*)-**10**]: The acylation of (*S,S*)-**22** (4.35 g, 14.5 mmol) with benzoyl chloride in diethyl ether with added triethylamine as base and the reduction with $LiAlH_4$ to yield **10** was done according to the procedure for the synthesis of 1-benzyl-3-(diphenylphosphanyl)pyrrolidine (**5**)[7]; yield: 4.67 g (12 mmol of (*S,S*)-**10**, 12% yield calcd. from L-hydroxyproline). – MS (70 eV); *m/z* (%): 390.2 (5) [M^+], 183.0 (60) [Ph_2PH], 91.1 (100) [$PhCH_2$]. – ^{1}H NMR ($CDCl_3$, 250.13 MHz): δ = 1.52, 2.04 (2 m, 2H, 3-H), 2.50, 2.74, 2.85 (3 m, 4H, 2-H, 4-H, 5-H), 3.17 (s, 3H, OCH_3), 3.26, 3.41 (2 m, 2H, CH_2OCH_3), 3.34, 4.20 (2 d, 2H, $^2J_{HH}$ = 13 Hz, CH_2Ph), 7.10, 7.16, 7.34 (3 m, 15H, Ph). – $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.62 MHz): δ = 31.8 (d, $^2J_{CP}$ = 17 Hz, C-3), 33.5 (d, $^1J_{CP}$ = 8 Hz, C-4), 56.4 (d, $^2J_{CP}$ = 20 Hz, C-5), 59.2 (s, OCH_3), 62.6 (d, $^3J_{CP}$ = 6 Hz, C-2), 75.4 (s, CH_2Ph), 76.6 (s, CH_2OCH_3), 128.6, 133.4 [2 m, CH (PPh)]. – $^{31}P\{^1H\}$ NMR ($CDCl_3$, 101.25 MHz): δ = –3.9. – $[\alpha]_D^{20}$ = –56.8 (*c* = 0.23, dichloromethane). – $C_{25}H_{28}NOP$ (389.5): calcd. C 77.10, H 7.25, N 3.60; found C 76.85, H 7.29, N 3.69.

[(3S,2'R)-3-(Diphenylphosphanyl)-1-[(tetrahydrofuran-2'-yl)-methyl]pyrrolidine-P,N]diiodopalladium [(*S,R*)-**8-Pd**] *and Diastereomeric* (*R,R*)-**8-Pd** *and [(2S,4S)-1-Benzyl-4-(diphenylphosphanyl)-2-(methoxymethyl)pyrrolidine-P,N]diiodopalladium* (**10-Pd**): These complexes were prepared and purified according to a published procedure[7].

(*S,R*)-**8-Pd**: MS (FAB); *m/z* (%): 572.0 (100) [M^+ – I], 444.0 (35) [M^+ – 2 I], 338.2 (35) [M^+ – PdI_2]. – IR (KBr): $\tilde{\nu}$ = 2971, 2941, 2921, 2867 cm^{-1} (C–H), 1482 (C=C, C–N), 1433, 1189, 1098, 1082, 1021 (C–P, C–N, C–C, C–O), 740, 704, 696 (Ph). – ^{1}H NMR (CD_2Cl_2, 400.13 MHz): δ = 1.76, 2.19, 2.98, 3.61, 3.83, 4.72, 5.24 (several m, 16H), 7.25, 7.36, 7.88, 8.02 [4 m, 10H, CH (Ph)]. – $^{13}\{^1H\}$ NMR ($CDCl_2$ 62.90 MHz): δ = 25.1 [s, C-4; C(5) X-ray], 36.0 [d, $^1J_{CP}$ = 29 Hz, C-3; C(4) X-ray], 57.2 [s, C-5; C(6) X-ray], 61.5 [d, $^3J_{CP}$ = 6 Hz, C-2; C(7) X-ray], 65.5 [s, C-1'; C(10) X-ray], 74.4 [s, C-2'; C(11) X-ray], 29.8 [s, C-3'; C(12) X-ray], 23.8 [s, C-4'; C(13) X-ray], 67.4 [s, C-5'; C(14) X-ray], 127.6, 128.3 [2 d, $^3J_{CP}$ = 12 Hz, $^3J_{CP}$ = 11 Hz, CH (*meta* Ph)], 131.2, 131.6 [2 s, CH (*para* Ph)], 134.1, 134.2 [2 d, $^2J_{CP}$ = 11 Hz, $^2J_{CP}$ = 10 Hz, CH (*ortho* Ph)]. – $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 101.26 MHz): δ = 42.3. – $[\alpha]_D^{26}$ = 106.2 (*c* = 0.098, dichloromethane). – $C_{21}H_{26}I_2NOPPd$ (699.6): calcd. C 36.05, H 3.75, N 2.00; found C 36.01, H 3.91, N 2.03.

(*R,R*)-**8-Pd**: MS (FAB), IR (KBr): cf. (*S,R*)-**23**. – ^{1}H NMR (CD_2Cl_2, 400.13 MHz): δ = 1.71, 2.20, 3.63, 4.62, 5.24 (several m, 16H), 7.25, 7.36, 7.88, 8.02 [4 m, 10H, CH (Ph)]. – $^{13}C\{^1H\}$ NMR (CD_2Cl_2 62.90 MHz): δ = 24.2 [s, C-4; C(5) X-ray], 35.7 [d, $^1J_{CP}$ = 27 Hz, C-3; C(4) X-ray], 58.1 [s, C-5; C(6) X-ray], 63.4 [d, $^3J_{CP}$ = 7 Hz, C-2; C(7) X-ray], 64.5 [s, C-1'; C(10) X-ray], 78.9 [s, C-2'; C(11) X-ray], 28.6 [s, C-3'; C(12) X-ray], 23.4 [s, C-4'; C(13) X-ray], 67.6 [s, C-5'; C(14) X-ray], 127.6, 128.3 [2 d, $^3J_{CP}$ = 12 Hz, $^3J_{CP}$ = 11 Hz, CH (*meta* Ph)], 131.3, 131.5 [2 d, $^4J_{CP}$ = 3 Hz, CH (*para* Ph)], 134.1, 134.2 [2 d, $^2J_{CP}$ = 11 Hz, $^2J_{CP}$ = 8 Hz, CH (*ortho* Ph)]. – $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 101.26 MHz): δ = 42.5. – $[\alpha]_D^{26}$ = –98.2 (*c* = 0.11, dichloromethane). – $C_{21}H_{26}I_2NOPPd$ (699.6): calcd. C 36.05, H 3.75, N 2.00; found C 35.86, H 3.88, N 2.02.

10-Pd: MS (FAB); *m/z* (%): 749.6 (5) [M^+], 621.9 (100) [M^+ – I], 494 (30) [M^+ – 2 I], 388.1 (30) [M^+ – PdI_2]. – IR (KBr): $\tilde{\nu}$ = 2963, 2926, 2853 cm^{-1} (C–H), 1452 (C=C, C–N), 1434, 1262, 1196, 1113, 1084 (C–P, C–N, C–C), 1182 (COC), 748, 697, 691 (Ph). – ^{1}H NMR (CD_2Cl_2, 250.13 MHz): δ = 1.68, 2.37, 2.52, 2.65 (4 m, 5H, 2-H, 4-H, 5-H), 3.49 (s, 3H, OCH_3), 3.93, 3.97 (2 m, 2H, CH_2OCH_3), 4.43 (m, 1H, 3-H), 4.89, 5.03 (2 d, 2H, $^2J_{HH}$ = 14 Hz, CH_2Ph), 7.27, 7.46 (2 m, 12H, Ph), 7.89, 8.03 (2 m, 3H, P-*Ph*). – $^{13}C\{^1H\}$ NMR ($CDCl_3$, 62.90 MHz): δ = 27.5 [d, $^2J_{CP}$ = 3 Hz, C-3; C(5) X-ray], 34.5 [d, $^1J_{CP}$ = 27 Hz, C-4; C(4) X-ray], 58.1 (s, OCH_3), 61.9 [d, $^2J_{CP}$ = 5 Hz, C-5; C(7) X-ray], 64.1 [s, C-2; C(6) X-ray], 65.1 [s, CH_2Ph; C(10) X-ray], 73.6 (s, CH_2OCH_3), 127.8, 128.1 [2 d, $^3J_{CP}$ = 8 Hz, CH (*meta* PPh)], 131.3, 131.4 [2 d, $^4J_{CP}$ = 3 Hz, CH (*para* PPh)], 134.0, 134.6 [2 d, $^2J_{CP}$ = 9 Hz, $^2J_{CP}$ = 10 Hz, CH (*ortho* PPh)], 127.6., 131.2 [2 s, CH (CH_2Ph)]. – $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 101.26 MHz): δ = 39.2. – $[\alpha]_D^{26}$ = 180.1 (*c* = 0.095, dichloromethane). – $C_{25}H_{28}I_2NOPPd$ (749.7): calcd. C 40.05, H 3.76, N 1.87; found C 39.74, H 3.77, N 2.14.

[3S,P(RS)]-3-(Phenylphosphanyl)pyrrolidine [(*S,RS*$_P$)-**11**]

A) (*S,RS*$_P$)-**11** *of 93% ee by S_N2 Substitution with KPHPh:* ***Precaution:*** Phenylphosphane is highly toxic and has a noxious odour even at very low concentrations. All aqueous and organic waste phases should be collected and stored in an efficient hood. They can be combined at the end of synthesis and phenylphosphane can be deleted by addition of excess NaOCl solution. A solution of phenylphosphane (8.25 ml, 75 mmol) in 100 ml of THF was added during 2 h to a suspension of KH (2.85 g, 69 mmol) in 50 ml of THF. The mixture was allowed to stir at room temperature for 2 h. Then the methanesulfonyl ester of (3*R*)-1-*tert*-butoxycarbonyl-3-hydroxypyrrolidine {prepared with (3*R*)-1-*tert*-butoxycarbonyl-3-hydroxypyrrolidine [(*R*)-**23**] (10.0 g, 51 mmol), *n*-butyllithium (32.3 ml, 51 mmol), and methansulfonyl chloride (3.9 ml, 50.4 mmol) as starting compounds according to ref.[7]} in 50 ml of THF was added at –38°C. The solution was stirred for 20 h at –20°C and 2 d at room temperture. THF was evaporated and the solid residue was dried and dissolved in a mixture of 100 ml of H_2O and 100 ml of diethyl ether. The diethyl ether phase was separated. The aqueous layer was further extracted twice with 100 ml of diethyl ether. The diethyl ether extracts, containing [3*S*,P(*RS*)]-1-*tert*-butoxycarbonyl-3-(phenylphosphanyl)pyrrolidine [(*S,RS*$_P$)-**25**] were collected and were added to 70 ml of TFA at 0°C. The mixture was stirred for 2 h and was then concentrated in vacuo. The remaining oil was dissolved in 700 ml of 2 N HCl and 500 ml of the mixture was distilled off. At 0°C aqueous KOH (100 ml, 70%) was added and the aqueous phase was extracted three times with 100 ml diethyl ether. The collected diethyl ether solutions were filtered through Celite and concentrated in vacuo; yield: 5.67 g of (*S,RS*$_P$)-**11** [31.6 mmol, 62% calcd. from (*R*)-**23**]. – MS (70 eV); *m/z* (%): 179.2 (20) [M^+], 109.1 (20) [$PhPH_2$], 69.3 (30) [M^+ – $PhPH_2$]. – IR (film): $\tilde{\nu}$ = 3289 cm^{-1} (N–H), 3052, 2959, 2926, 2867 (C–H), 2300 (P–H), 1482 (C=C, C–N), 1437, 1399, 1187, 1116, 1071 (C–P, C–N, C–C), 745, 697 (Ph). – ^{1}H NMR ($CDCl_3$, 250.13 MHz): δ = 2.14 (s, 1H, NH), 1.49, 1.93 (2 m, 2H, 4-H), 2.33, 3.09 (2 m, 2H, 2-H), 2.63, 2.84 (2

m, 2H, 5-H), 2.81 (m, 1H, 3-H), 4.10 (*q*, 1/2H, $^1J_{HP}$ = 209 Hz, $^3J_{HH}$ = 8 Hz, P–H, 1st diastereomer), 4.13 (*q*, 1/2H, $^1J_{HP}$ = 211 Hz, $^3J_{HH}$ = 6 Hz, P–H, 2nd diastereomer), 7.22, 7.40 (2 m, 5H, Ph). – $^{13}C\{^1H\}$ NMR[39] ($CDCl_3$, 62.9 MHz): δ = 30.2, 30.8 (2 d, $^2J_{CP}$ = 9 Hz, $^2J_{CP}$ = 8 Hz, C-4), 33.9 (2 d, $^1J_{CP}$ = 9 Hz, $^1J_{CP}$ = 8 Hz, C-3), 47.9 (2 d, $^3J_{CP}$ = 5 Hz, $^3J_{CP}$ = 6 Hz, C-5), 50.9, 51.8 (2 d, $^2J_{CP}$ = 21 Hz, $^2J_{CP}$ = 10 Hz, C-2), 128.3 [d, $^3J_{CP}$ = 6 Hz, CH (*meta* Ph)], 128.4 [d, $^4J_{CP}$ = 5 Hz, CH (*para* Ph)], 133.8, 134.1 [2 d, $^2J_{CP}$ = 15 Hz, $^2J_{CP}$ = 16 Hz, CH (*ortho* Ph)]. – $^{31}P\{^1H\}$ NMR ($CDCl_3$, 101.25 MHz): δ = −40.5, −41.0. – $[\alpha]_D^{20}$ = −51.5 (*c* = 1.578, ethanol; with (*S*,*RS*$_P$)-**11** of 93% ee). – $C_{10}H_{14}NP$ (179.2): calcd. for $C_{10}H_{14}NP \cdot 1/2\ H_2O$ C 63.82, H 8.03, N 7.44; found C 64.27, H 8.17, N 7.68.

B) (*S*,*RS*$_P$)-**11** *by Cleavage of 98% ee* (*S*)-**4** *with Lithium Metal Accelerated by Ultrasound Irradiation:* 1.97 g (3*S*)-3-(Diphenylphosphanyl)pyrrolidine [(*S*)-**4**] (7.7 mmol, 98% ee), and 1 g (144 mmol) finely chopped lithium metal were added to 100 ml of THF. The Schlenk tube was put in a ultrasound cleaning bath [120 KW, 35 KHz], containing a mixture of crushed ice and water. The mixture was sonicated with 35 KHz ultrasound during 15 min maintaning 0°C in the bath. Then THF was separated from lithium and 0.7 ml of water (39 mmol) was slowly added by syringe to the red THF solution. The discoloured THF solution was filtered through Celite and THF was evaporated in vacuo. The crude product was dissolved in 20 ml of 6 N HCl and 20 ml of hexane and was stirred overnight. Then the hexane phase was separated and 50 ml of 30% KOH solution was added. (*S*,*RS*$_P$)-**11** was extracted with diethyl ether (3 × 50 ml). The collected diethyl ether solutions were filtered through Celite and concentrated in vacuo; yield 1.22 g (89% calcd. from (*S*)-**4**). – $[\alpha]_D^{20}$ = −49.8 [*c* = 1.655, ethanol; with (*S*,*RS*$_P$)-**11** of 98% ee].

[3S,P(RS)]-1-Phenyl-3-(phenylphosphanyl)pyrrolidine [(*S*,*RS*$_P$)-**26**]: To a solution of 6.79 g (53 mmol) naphthalene in 30 ml of THF was added 2.05 g (52.5 mmol) potassium metal in small pieces. The green solution was stirred for 2 h and 6.69 g (*S*)-**4** (26.6 mmol, 98% ee) dissolved in 50 ml of THF was added by syringe during 5 min. After 10 min of stirring, 4 ml of water (222 mmol) was slowly added at 0°C by syringe to the red THF solution. The discoloured THF solution was filtered through Celite and THF was evaporated in vacuo. The crude product was dissolved in 100 ml of 6 N HCl and 100 ml of hexane and was stirred overnight. Then the hexane phase was separated. The aqueous phase was further extracted twice with 100 ml of hexane and then 100 ml of 50% KOH solution was slowly added. (*S*,*RS*$_P$)-**26** was extracted with diethyl ether (3 × 100 ml). The collected diethyl ether solutions were filtered through Celite and concentrated in vacuo; yield 6.1 g of (*S*,*RS*$_P$)-**26** [91.6% calcd. from (*S*)-**4**]. – MS (70 eV); *m/z* (%): 255.1 (100) [M^+], 145.2 (70) [$M^+ - PhPH_2$], 109.1 (20) [$PhPH_2$], 77.1 (30) [Ph]. – IR (film): $\tilde{\nu}$ = 3054, 3924, 2960, 2922, 2894, 2834 cm^{-1} (C–H), 2280 (P–H), 1597, 1505 (C=C, C–N), 1439, 1366, 1185, 1157 (C–P, C–N, C–C), 744, 691 (Ph). – ^1H NMR ($CDCl_3$, 400.13 MHz): δ = 1.97, 2.26 (2 m, 2H, 4-H), 2.78 (m, 1H, 3-H), 3.24, 3.36, 3.43, 3.56 (4 m, 2H, 5-H), 4.35 (q, 1/2H, $^1J_{HP}$ = 209 Hz, $^3J_{HH}$ = 4 Hz, P–H, 1st diastereomer), 4.34 (q, 1/2H, $^1J_{HP}$ = 212 Hz, $^3J_{HH}$ = 4 Hz, P–H, 2nd diastereomer), 6.61, 6.80, 7.32, 7.42, 7.61 [5 m, 10H, CH (Ph)]. – $^{13}C\{^1H\}$ NMR[39] ($CDCl_3$, 100.62 MHz): δ = 30.9, 31.8 (2 d, $^2J_{CP}$ = 15 Hz, $^2J_{CP}$ = 6 Hz, C-4), 33.5, 33.6 (2 d, $^1J_{CP}$ = 10 Hz, $^1J_{CP}$ = 11 Hz, C-3), 47.9, 48.0 (2 d, $^3J_{CP}$ = 5 Hz, $^3J_{CP}$ = 6 Hz, C-5), 50.5, 51.6 (2 d, $^2J_{CP}$ = 23 Hz, $^2J_{CP}$ = 21 Hz, C-2), 128.8 [d, $^3J_{CP}$ = 5 Hz, CH (*meta* Ph)], 128.8 [d, $^4J_{CP}$ = 5 Hz, CH (*para* Ph)], 134.4, 134.5 [2 d, $^2J_{CP}$ = 10 Hz, $^2J_{CP}$ = 9 Hz, CH (*ortho* Ph)], 111.9, 116.0, 129.3 [3 s, CH (N*Ph*)]. – $^{31}P\{^1H\}$ NMR ($CDCl_3$, 32.39 MHz): δ = −41.4, −41.6. – $C_{16}H_{18}NP$ (255.2): calcd. C 75.27, H 7.11, N 5.49; found C 75.06, H 6.91, N 5.55.

[3S,P(RS)]-1-Benzoyl-3-(phenylphosphanyl)pyrrolidine [(*S*,*RS*$_P$)-**28**]: To a stirred solution of [3*S*,P(*RS*)]-3-(phenylphosphanyl)pyrrolidine [(*S*,*RS*$_P$)-**11**] (7.2 g, 40.2 mmol) in 200 ml of diethyl ether was added triethylamine (13.9 ml, 100 mmol). At 0°C benzoyl chloride (10.45 ml, 90 mmol) was slowly added by syringe. The mixture was allowed to stir for additional 4 h, washed with 100 ml of saturated aqueous citric acid solution and then filtered through Celite. The diethyl ether was concentrated in vacuo to yield 30 ml of a concentrated solution, that was added by syringe to 250 ml of ethanol containing KOH (30 g, 0.54 mol). The mixture was allowed to stir for 3 d and was then filtered through Celite in order to remove precipitated potassium benzoate. The filter cake was washed three times with 80 ml of diethyl ether and the combined ethanol and diethyl ether phases were concentrated in vacuo. Then 100 ml of water and 200 ml of diethyl ether were added and the diethyl ether phase was separated. The diethyl ether phase was stirred with 100 ml of saturated aqueous citric acid solution for 2 d. The separated diethyl ether phase was washed with saturated K_2CO_3 solution and was then filtered through Celite covered with $MgSO_4$. The diethyl ether was evaporated and (*S*,*RS*$_P$)-**28** was dried in vacuo; yield 8.53 g [75% calcd. from (*S*,*RS*$_P$)-**11**]; 8 mmol of (*S*,*RS*$_P$)-**11** can be recovered from the second aqueous citric acid solution. – MS (70 eV); *m/z* (%): 283.2 (20) [M^+], 173.8 (20) [$M^+ - PhPH_2$], 105.0 (100) [COPh]. – IR (film): $\tilde{\nu}$ = 3055, 2966, 2940, 2873 cm^{-1} (C–H), 2285 (P–H), 1631 (CO), 1496, 1478, 1447 (C=C, C–N), 1447, 1340, 1201, 1178 (C–P, C–N, C–C), 792, 747, 717, 699 (Ph). – ^1H NMR ($CDCl_3$, 400.13 MHz): δ = 1.64 (m, 1H, 4-H^1), 1.96, 2.05 (2 m, 1H, 4-H^2), 2.41, 2.53 (2 m, 1H, 3-H), 3.19 3.84 (7 m, 4H, 2-H, 5-H), 3.7, 3.8, 4.3, 4.4 (4 m, 1H, P–H), 7.20, 7.27, 7.40 [3 m, 10H, CH (PH)]. – $^{31}P\{^1H\}$ NMR[40] ($CDCl_3$, 101.25 MHz, 298 K): δ = −42.6, −44.0, −44.2, −46.8. – $C_{17}H_{18}NOP$ (283.2): calcd. C 72.07, H 6.40, N 4.94; found C 71.61, H 6.36, N 5.34.

[3S,P(RS)]-1-Benzyl-3-(phenylphosphanyl)pyrrolidine [(*S*,*RS*$_P$)-**29**]: To a solution of 1.54 g (40 mmol) $LiAlH_4$ in 100 ml of THF a solution of phosphane (*S*,*RS*$_P$)-**28** (8.5 g, 30 mmol) in 50 ml of THF was slowly added at 0°C. After stirring overnight, the mixture was very cautiously added to a vigorously stirred solution of 60 g KOH in 100 ml of water. The clear THF phase was separated and the aqueous phase extracted twice with 50 ml of diethyl ether. The collected organic phases were concentrated in vacuo. The remaining oil was dissolved in 500 ml of 2 N HCl and 300 ml of the mixture were distilled off. At 0°C aqueous KOH (80 ml, 70%) was added and the aqueous phase was extracted three times with 100 ml of diethyl ether. The collected diethyl ether solutions were filtered through Celite and concentrated in vacuo; yield of (*S*,*RS*$_P$P-**29**: 7.7 g [90% calcd. from (*S*,*RS*$_P$)-**28**]. – MS (70 eV); *m/z* (%): 268.1 (30 [M^+], 159.0 (100) [$M^+ - PhPH_2$], 108.9 (15) [$PhPH_2$], 91.1 (75) [Bzl]. – IR (film): $\tilde{\nu}$ = 3054, 3027, 3001, 2955, 2914, 2866, 2791, 2733 cm^{-1} (C–H), 2300 (P–H), 1494, 1480 (C=C, C–N), 1444, 1274, 1250, 1148, 1030 (C–P, C–N, C–C), 750, 738, 700, 697 (Ph). – ^1H NMR ($CDCl_3$, 250.13 MHz): δ = 1.64, 1.99 (2 m, 2H, 4-H), 2.25, 2.39, 2.66, 2.81 (4 m, 5H, 2-H, 5-H, 3-H), 3.55 (m, CH_2Ph), 4.16 (q, 1H, $^1J_{HP}$ = 209 Hz, $^3J_{HH}$ = 6 Hz, P–H), 7.21, 7.37 [2 m, 10H, CH (Ar)]. – $^{13}C\{^1H\}$ NMR[39] ($CDCl_3$, 100.62 MHz): δ = 30.5, 31.3 (2 d, $^2J_{CP}$ = 15 Hz, $^2J_{CP}$ = 9 Hz, C-4), 33.8, 33.9 (2 d, $^1J_{CP}$ = 9 Hz, $^1J_{CP}$ = 10 Hz, C-3), 47.9, 48.1 (2 d, $^3J_{CP}$ = 5 Hz, $^3J_{CP}$ = 6 Hz, C-5), 50.7, 51.3 (2 d, $^2J_{CP}$ = 23 Hz, $^2J_{CP}$ = 13 Hz, C-2), 60.2, 60.9 (2 s, CH_2Ph), 128.7 [d, $^3J_{CP}$ = 5 Hz, CH (*meta* Ph)], 128.8 [d, $^4J_{CP}$ = 5 Hz, CH (*para* Ph)], 134.1, 134.3 [2 d, $^2J_{CP}$ = 10 Hz, $^2J_{CP}$ = 9 Hz, CH (*ortho* Ph)], 127.4, 127.6, 128.5, 128.7,

129.3, 129.4 [6 s, CH (CH_2*Ph*)]. – $^{31}P\{^1H\}$ NMR ($CDCl_3$, 101.25 MHz): δ = −37.4, −38.4. – $C_{17}H_{20}NP$ (269.3): calcd. C 75.81, H 7.49, N 5.20; found C 75.61, H 7.36, N 5.38.

[3S,P(RS)]-3-[(2'-Methoxyphenyl)phenylphosphanyl]-pyrrolidine [(*S*,*RS*$_P$)-**27**]: To a solution of [3*S*,P(*RS*)]-3-(phenylphosphanyl)pyrrolidine [(*S*,*RS*$_P$)-**11**] (3.9 g, 22 mmol) dissolved in 100 ml of THF, 3 g (75.8 mmol) of potassium metal was added in three portions. After 5 h of stirring, the THF solution was separated from remaining potassium metal. To the red phosphide solution at −30°C was added 9 ml of 2-fluoroanisole (80 mmol) by syringe. The reaction mixture was stirred at −18°C overnight. Then THF was evaporated at room temperature in vacuo. The crude product was dissolved in 100 ml of 2 N HCl and 100 ml of diethyl ether and was stirred overnight. Then the diethyl ether phase was separated. The aqueous phase was further extracted twice with 100 ml of diethyl ether and then 100 ml of 40% KOH solution was slowly added. (*S*,*RS*$_P$)-**27** was extracted with diethyl ether (3 × 100 ml). The collected diethyl ether solutions were filtered through Celite and concentrated in vacuo; yield. 2.58 g [90% calcd from (*S*,*RS*$_P$)-**11**]. – MS (70 eV); *m/z* (%): 284.9 (5) [M$^+$], 216.1 (70) [AnPhPH], 69.1 (100) [M$^+$ − AnPhPH]. – IR (film): $\tilde{\nu}$ = 3280 cm^{-1} (N−H), 3067, 3001, 2934, 2862, 2834 (C−H), 1472 (C=C, C−N), 1430, 1399, 1294, 1271, 1243, 1180, 1163, 1130, 1092, 1073, 1042, 1026 (C−P, C−N, C−C), 755, 698 (Ph). – ^1H NMR ($CDCl_3$, 250.13 MHz): δ = 1.78 (s, 1H, NH), 1.56, 1.99 (2 m, 2H, 4-H), 2.80, 2.92 (2 m, 5H, 2-H, 5-H, 3-H), 3.61, 3.62 (2 s, OCH_3), 6.73, 6.89 [2 m, 2H, CH (Ar)], 7.21, 7.37 [2 m, 7H, CH (Ar)]. – $^{13}C\{^1H\}$ NMR[39] ($CDCl_3$, 62.9 MHz): δ = 31.3, 31.3 (2 d, $^2J_{CP}$ = 19 Hz, $^2J_{CP}$ = 20 Hz, C-4), 35.1, 35.3 (2 d, $^1J_{CP}$ = 9 Hz, C-3), 47.7, 47.9 (2 d, $^3J_{CP}$ = 6 Hz, C-5), 51.8, 51.9 (d, $^2J_{CP}$ = 23 Hz, $^2J_{CP}$ = 26 Hz, C-2), 55.4 (s, OCH_3), 127.9 [d, $3J_{CP}$ = 7 Hz, CH (*meta* Ph)], 128.3 [s, CH (*para* Ph)], 132.9, [m, CH (*ortho* Ph)], 110.5, 120.7, 130.2 [3 s, CH (An)], 133.3 [m, CH (An)]. – $^{31}P\{^1H\}$ NMR ($CDCl_3$, 32.39 MHz): δ = −15.7, −16.1. – $C_{17}H_{20}NOP$ (285.1): calcd. C 71.56, H 7.07, N 4.91; found C 71.47, H 7.52, N 4.87.

[3S,P(RS)]-1-Benzyl-3-[(2'-methoxyphenyl)phenylphosphanyl]pyrrolidine [(*S*,*RS*$_P$)-**12**]: To a stirred solution of (*S*,*RS*$_P$)-**27** (3.58 g, 9 mmol) in 100 ml of diethyl ether, triethylamine (3.4 ml, 20 mmol) was added. At 0°C benzoyl chloride (1.0 ml, 8.9 mmol) was slowly added by syringe. The mixture was allowed to stir for additional 4 h and was then hydrolysed by addition of 20 ml of aqueous NaOH solution (0.8 g NaOH, 20 mmol). The diethyl ether phase was separated, washed with 50 ml of saturated aqueous citric acid solution and then 50 ml of 2 N KOH solution. It was filtered through Celite and concentrated in vacuo. The reduction with $LiAlH_4$ to yield (*S*,*RS*$_P$)-**12** was done according to the procedure for the synthesis of 1-benzyl-3-(diphenylphosphanyl)-pyrrolidine (**5**)[7].

[{3S,P(RS)}-1-Benzyl-3-[(2'-methoxyphenyl)-phenylphosphanyl]pyrrolidine-P,N]diiodopalladium [(*S*,*RS*$_{MP}$)-**12-Pd**]: To crude (*S*,*RS*$_P$)-**12** (3.23 g, 8.6 mmol) was added NaI (15 g, 100 mmol) and the mixture was dissolved in 100 ml of acetone. To this mixture was added 1 ml of water and Na_2PdCl_4 (2.67 g, 9 mmol) in one portion. After 2 d, the acetone was concentrated and the dried residue was purified using flash chromatography with ethyl acetate (gradient raised to 50%), dichloromethane on silica gel. The product obtained was separated into both diastereomers with acetone (10%)/toluene with preparative column chromatography. The separated diastereomers were crystallised from dichloromethane/toluene solutions and were displaced with KCN[7] to yield the diastereomerically pure phosphanes (*S*,*S*$_P$)-**12** and (*S*,*R*$_P$)-**12**. We were not able to remove solvent residues, because the phosphanes (*S*,*S*$_P$)-**12** and (*S*,*R*$_P$)-**12** were dried at room temperature in order to prevent epimerisation of the phosphorus center.

[(3S,PR$_{MP}$)-1-Benzyl-3-{(2'-methoxyphenyl)phenylphosphanyl}pyrrolidine-P,N]diiodopalladium [(*S*,*R*$_{MP}$)-**12-Pd**]: Yield 3.06 g (4.16 mmol). – R_f = 0.255 (toluene/10% acetone). – MS (FAB): *m/z* (%): 607.8 (100) [M$^+$ − I], 480.0 (30) [M$^+$ − 2 I], 374.0 (20) [M$^+$ − PdI_2]. – IR (KBr): $\tilde{\nu}$ = 2954, 2926, 2854 cm^{-1} (C−H), 1585, 1576 (Ar), 1474 (C=C, C−N), 1459, 1429, 1277, 1250, 1099, 1077, 1019 (C−P, C−N, C−C), 744, 701 (Ph). – ^1H NMR (CD_2Cl_2, 250.13 MHz): δ = 2.11, 2.64, 3.35 (3 m, 6H, 2-H, 4-H, 5-H), 4.31 (m, 1H, 3-H), 3.47 (s, 3H, OCH_3), 3.55, 5.82 (2 d, 2H, $^2J_{HH}$ = 13 Hz, CH_2Ph), 6.78, 6.89 (2 m, 2H, Ar), 7.21 (m, 5H, Ph), 7.38 (m, 2H, Ph), 7.70 (m, 2H, P-*Ph*), 7.86 (m, 2H, P-*Ph*), 8.34 (m, 1H, P-*Ph*). – $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 62.9 MHz): δ = 26.6 [s, C-4; C(5) X-ray], 35.1 [d, $^1J_{CP}$ = 28 Hz, C-3; C(4) X-ray], 56.0 (s, OCH_3), 59.0 [s, C-5; C(7) X-ray], 61.6 [d, $^2J_{CP}$ = 5 Hz, C-2; C(6) X-ray], 65.0 [s, CH_2Ph; C(10) X-ray], 128.8 [d, $^3J_{CP}$ = 10 Hz, CH (*meta* Ph)], 131.7 [d, $^4J_{CP}$ = 3 Hz, Ch (*para* Ph)], 134.0 [d, $^2J_{CP}$ = 9 Hz, CH (*ortho* Ph)], 111.9, 135.4 [2 s, CH (An)], 121.3 [d, $^3J_{CP}$ = 15 Hz, CH (An)], 143.1 [d, $^2J_{CP}$ = 20 Hz, CH (An)], 128.1, 128.3, 130.7 [3 s, CH (CH_2*Ph*)]. – $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 101.25 MHz): δ = 47.7. – $[\alpha]_D^{26}$ = 259.3 (*c* = 0.12, dichloromethane, sample of 98% ee). – $C_{24}H_{26}I_2NOPPd$ (735.7): calcd. C 39.18, H 3.56, N 1.90; found C 39.58, H 3.59, N 1.79.

[(3S,PS$_{MP}$)-1-Benzyl-3-{(2'-methoxyphenyl)phenylphosphanyl}pyrrolidine-P,N]diiodopalladium [(*S*,*S*$_{MP}$)-**12-Pd**]: Yield 3.06 g (4.16 mmol). – R_f = 0.275 (toluene/10% acetone). – MS (70 eV); IR (KBr): cf. (*S*,*R*$_{MP}$)-**12-Pd**. – ^1H NMR (CD_2Cl_2, 250.13 MHz): δ = 2.11, 2.70, 3.35 (3 m, 6H, 2-H, 4-H, 5-H), 4.26 (m, 1H, 3-H), 3.71 (s, 3H, OCH_3), 4.07, 5.49 (2 d, 2H, $^2J_{HH}$ = 13 Hz, CH_2Ph), 6.88 (m, 2H, Ar), 7.25 (m, 5H, Ph), 7.45 (m, 2H, Ph), 7.72 (m, 2H, P-*Ph*), 7.87 (m, 3H, P-*Ph*). – $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 62.9 MHz): δ = 24.5 [s, C-4; C(5) X-ray], 35.7 [d, $^1J_{CP}$ = 28 Hz, C-3; C(4) X-ray], 55.2 (s, OCH_3), 56.1 [s, C-5; C(6) X-ray], 61.5 [d, $^2J_{CP}$ = 5 Hz, C-2; C(7) X-ray], 65.2 [s, CH_2Ph; C(10) X-ray], 127.7 [d, $^3J_{CP}$ = 4 Hz, CH (*meta* Ph)], 130.9 [d, $^4J_{CP}$ = 3 Hz, CH (*para* Ph)], 133.5 [d, $^2J_{CP}$ = 10 Hz, CH (*ortho* Ph)], 111.3, 119.7, 133.9 [3 s, CH (An)], 138.4 [d, $^2J_{CP}$ = 11 Hz, CH (An)], 127.8, 127.9, 130.2 [3 s, CH (CH_2*Ph*)]. – $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 101.25 MHz): δ = 41.3. – $[\alpha]_D^{26}$ = 160.7 (*c* = 0.134, dichloromethane, sample of 98% ee). – $C_{24}H_{26}I_2NOPPd$ (735.7): calcd. C 39.18, H 3.56, N 1.90; found C 39.32, H 3.68, N 1.91.

(3S,PR)-1-Benzyl-3-[(2'-methoxyphenyl)phenylphosphanyl]pyrrolidine [(*S*,*R*$_P$)-**12**]: Yield 1.56 g (4.16 mmol). – MS (70 eV); *m/z* (%): 375.1 (5) [M$^+$], 284.1 (20) [M$^+$ − CH_2Ph], 216.1 (30) [AnPhPH], 159.1 (100) [M$^+$ − AnPhPH], 91.1 (90) [CH_2Ph]. – IR (film): $\tilde{\nu}$ = 3084, 3063, 3027, 3001, 2956, 2931, 2865, 2833, 2791 cm^{-1} (C−H), 1585, 1576 (Ar), 1484, 1472 (C=C, C−N), 1461, 1431, 1376, 1346, 1295, 1273, 1243, 1179, 1147, 1129, 1093, 1073, 1042, 1027 (C−P, C−N, C−O, C−C), 753, 698 (Ph). – ^1H NMR ($CDCl_3$, 250.13 MHz): δ = 1.73 (m, 1H, 4-H^1), 1.93 (m, 1H, 4-H^2), 2.41 (m, 2H, 2-H^1, 5-H^1), 2.98 (m, 2H, 2-H^2, 5-H^2), 2.75 (m, 1H, 3-H), 3.62 (s, 3H, OCH_3), 3.52, 3.63 (2 d, 2H, $^2J_{HH}$ = 13 Hz, CH_2Ph), 6.72, 6.88 (2 m, 2H, Ar), 7.27, 7.42 (2 m, 13H, Ph, Ar). – $^{13}C\{^1H\}$ NMR ($CDCl_3$, 62.9 MHz): δ = 29.7 (d, $^2J_{CP}$ = 19 Hz, C-4), 33.4 (d, $^1J_{CP}$ = 7 Hz, C-3), 54.6 (d, $^3J_{CP}$ = 4 Hz, C-5), 59.0 (d, $^2J_{CP}$ = 24 Hz, C-2), 55.8 (s, OCH_3), 60.9 (s, CH_2Ph), 128.6 [d, $^3J_{CP}$ = 7 Hz, CH (*meta* Ph)], 128.9 [s, CH (*para* Ph)], 133.4, [d, $^2J_{CP}$ = 17 Hz, CH (*ortho* Ph)], 110.9, 121.3, 130.7 [3 s, CH (An)], 133.7 [d, $^2J_{CP}$ = 20 Hz, CH (An)], 127.4, 128.5, 129.3 [3 s, CH (CH_2*Ph*)]. – $^{31}P\{^1H\}$ NMR ($CDCl_3$, 101.25 MHz): δ = −16.1. – $[\alpha]_D^{20}$ = −30.7, (*c* = 0.33, dichloromethane, sample of 93% ee). – $C_{24}H_{26}NOP$ (375.5): calcd. for $C_{24}H_{26}NOP \cdot 0.5\ CH_2Cl_2$ C 70.41, H 6.51, N 3.35; found C 70.80, H 6.71, N 3.56.

(3S,PS)-1-Benzyl-3-[(2'-methoxyphenyl)phenylphosphanyl]-pyrrolidine [(*S,S*$_P$)-**12**]: Yield 1.56 g (4.16 mmol). – MS (70 eV); IR (KBr): cf. (*S,S*$_P$)-**12**. – ^{1}H NMR ($CDCl_3$, 250.13 MHz): δ = 1.73 (m, 1H, 4-H^1), 2.12 (m, 1H, 4-H^2), 2.37 (m, 2H, 2-H^1, 5-H^1), 2.81 (m, 2H, 2-H^2, 5-H^2), 3.0 (m, 1H, 3-H), 3.61 (s, 3H, OCH_3), 3.48, 3.62 (2 d, 2H, $^2J_{HH}$ = 13 Hz, CH_2Ph), 6.75, 6.92 (2 m, 2H, Ar), 7.23, 7.40 (2 m, 13H, Ph, Ar). – $^{13}C\{^1H\}$ NMR ($CDCl_3$, 62.9 MHz): δ = 29.7 (d, $^2J_{CP}$ = 18 Hz, C-4), 33.2 (d, $^1J_{CP}$ = 7 Hz, C-3), 54.7 (d, $^3J_{CP}$ = 4 Hz, C-5), 59.0 (d, $^2J_{CP}$ = 24 Hz, C-2), 55.9 (s, OCH_3), 60.8 (s, CH_2Ph), 128.6 [d, $^3J_{CP}$ = 7 Hz, CH (*meta* Ph)], 128.9 [s, CH (*para* Ph)], 133.5 [d, $^2J_{CP}$ = 18 Hz, CH (*ortho* Ph)], 111.1, 121.3, 130.7 [3 s, CH (An)], 133.4 [d, $^2J_{CP}$ = 22 Hz, CH (An)], 127.3, 128.5, 129.2 [3 s, CH (CH_2*Ph*)]. – $^{31}P\{^1H\}$ NMR ($CDCl_3$, 101.25 MHz): δ = –15.6. – $[\alpha]_D^{20}$ = 32.1 (*c* = 0.21, dichloromethane, sample of 93% ee). – $C_{24}H_{26}NOP$ (375.5): calcd. for $C_{24}H_{26}NOP \cdot 0.25\ CH_2Cl_2$ C 73.43, H 6.73, N 3.53; found 74.66, H 7.17, N 3.95.

[3S,P(RS)]-1-Benzyl-3-[(2',4',6'-trimethoxyphenyl)phenylphosphanyl]pyrrolidine [(*S,RS*$_P$)-**13**]: a) 2,4,6-Trimethoxyphenyllithium; improved procedure: 2,4,6-Trimethoxyphenyllithium was prepared from a solution of 1,3,5-trimethoxybenzene (12.5 g, 74 mmol) and *N,N'*-tetramethylethylenediamine (5.2 ml, 37.4 mmol) in 70 ml of hexane. To this solution *n*-butyllithium (23.4 ml, 37.4 mmol) in hexane was added and the mixture was stirred overnight. Then precipitated 2,4,6-trimethoxyphenyllithium was separated from the hexane solution and was washed with 100 ml of hexane. – The 2,4,6-trimethoxyphenyllithium content of the reaction mixtures, obtained with varying amounts of 1,3,5-trimethoxybenzene, *n*-butyllithium, and TMEDA was assayed by titrations with 2,5-dimethoxybenzyl alcohol[4]. This revealed that the yield of 2,4,6-trimethoxyphenyllithium (calcd. from *n*-butyllithium used) was increased, when excess 1,3,5-trimethoxybenzene was used. The choice of diethyl ether, instead of THF (cf. ref.[24]) as solvent for phosphane synthesis is necessary because 2,4,6-trimethoxyphenyllithium reacts very fast with THF.

b) (*S,RS*$_P$)–**13**: To a solution of [3*S*,P(*RS*)]-1-benzyl-3-(phenylphosphanyl)pyrrolidine [(*S,RS*$_P$)-**29**] (4.02 g, 15 mmol), dissolved in 100 ml of THF, 3 g (75.8 mmol) of potassium metal was added in three portions. After 5 h of stirring, the THF solution was separated from remaining potassium metal. To the red phosphide solution at –78°C was added 2.5 ml of trimethylsilyl chloride (20 mmol) by syringe. THF was evaporated in vacuo and the solid residue was suspended in 100 ml of dichloromethane. Then hexachloroethane (3.54 g, 15 mmol) was added in three portions and the mixture was stirred for 3 d. Dichloromethane was evaporated in vacuo and the residue was dried 6 h at 50°C in vacuo. To the Schlenk tube containing the solid 2,4,6-trimethoxyphenyllithium [cf. a)] at –78°C a suspension of the solid product of the hexachloroethane reaction in 100 ml of diethyl ether was added. The reaction mixture was stirred overnight. During this time the reaction mixture reached room temperature. Then 10 ml of methanol was added to delete excess 2,4,6-trimethoxyphenyllithium and the reaction mixture was concentrated in vacuo. The crude product was dissolved in 100 ml of 2 N HCl and 100 ml of diethyl ether and was stirred overnight. Then the diethyl ether phase was separated. The aqueous phase was further extracted twice with 100 ml of

Table 5. Crystal data of PdI_2 complexes with 3-(diphenylphosphanyl)pyrrolidine ligands, description of data collection, structural analysis and refinement and CSD numbers, file-IDs and formulae

Compound Empirical formula	(S,R)-**8-Pd** $C_{21}H_{26}I_2NOPPd$	(*R,R*)-**8-Pd** $C_{21}H_{26}I_2NOPPd$ $* 0.5\ CH_2Cl_2 * H_2O$	(*S,S*)-**9-Pd** $C_{26}H_{37}I_2N_2PPd$ $*2\ H_2O$	(*S,S*)-**10-Pd** $C_{25}H_{28}I_2NOPPd$
Mol. mass (g mol^{-1})	699.60	758.06	804.75	749.65
$d_{calcd.}$ (g cm^{-3})	2.009	1.889	1.742	1.871
Crystal dimensions (mm)	0.30, 0.25, 0.10	0.50, 0.40, 0.20	0.25, 0.25, 0.10	0.25, 0.10, 0.05
Space group	$P2_12_12_1$ (No. 19)	*C*2 (No. 5)	*C*2 (No. 5)	$P2_12_12_1$ (No. 19)
a, b, c (Å)	8.283(5), 16.22(1), 17.22(1)	10.937(2), 12.817(3), 38.04(1)	27.15(2), 9.002(8), 13.276(9)	9.164(6), 13.851(8), 20.97(2)
α, β, γ	90°, 90°, 90°	90°, 91.75(2)°, 90°	90°, 109.74(6)°, 90°	90°, 90°, 90°
Volume (nm^3), *Z*	2.313, 4	5.330(2), 8	3.054(4), 4	2.662(3), 4
2Θ-Range (±*h*, ±*k*, ±*l*), scan method	4 - 50 , Wyckoff	4 - 50 , Omega	4 - 50 , Omega	4 - 50, Omega
Reflections (measured, unique, obs. [I>2 σ (I)]	16259, 4076, 2813	17945, 9951, 8832	11091, 5372, 4509	14803, 4672, 4351
μ (mm^{-1})	3.55	3.19	2.71	3.094
Absorption correction: transmission min, max	0.254, 0.426	0.381, 0.530	0.316, 0.411	0.667, 0.730
Parameters, F_0 / parameter[a]	245, 11.48	523, 16.89	299, 15.08	281, 15.48
R, *wR*2	0.0574, 0.1388	0.0413, 0.1093	0.0490, 0.1269	0.0222, 0.0502
GooF, abs. struc.[b]	1.714, -0.06(7)	1.649, 0.00(2)	1.454, -0.02(4)	1.738, -0.02(2)
CSD Nr.,file-ID	406468, S,R-8-Pd	406469, R,R-8-Pd	406470, S,S-9-Pd	406471, S,S-10-Pd
Formula	$C_{21}H_{26}I_2NOPPd$	$C_{21.5}H_{29}ClI_2NO_2PPd$	$C_{26}H_{41}I_2N_2O_2PPd$	$C_{25}H_{28}I_2NOPPd$

[a] All nonhydrogen atoms were refined with anisotropic thermal parameters; hydrogen atoms were included in calculated positions (riding model). – [b] The parameter according to Flack[26] is given.

diethyl ether and then 100 ml of 40% KOH solution was slowly added. (S,RS_P)-**13** was extracted with diethyl ether (3 × 100 ml). The collected diethyl ether solutions were filtered through Celite and concentrated in vacuo. The product was dried 6 h at 50°C in vacuo.

[{3S,P(RS)}-1-Benzyl-3-{(2',4',6'-trimethoxyphenyl)phenylphosphanyl}pyrrolidine-P-N]diiodopalladium [(S,RS_{MP})-**13-Pd**]: Crude (S,RS_P)-**13** (2.82 g, 6.5 mmol), NaI (15 g, 100 mmol), 1 ml of water, and Na_2PdCl_4 (2.02 g, 6.8 mmol) were allowed to react in 100 ml of acetone [cf. synthesis of (S,RS_{MP})-**12**]. Flash chromatography with ethyl acetate (gradient raised to 50%), dichloromethane on silica gel, separation into both diastereomers with ethyl acetate (25%)/toluene by preparative column chromatography and crystallisation from dichloromethane/toluene solutions yielded pure diastereomers that, upon reaction with KCN[7], yielded the diastereomerically pure phosphanes (S,S_P)-**13** and (S,R_P)-**13**. We were not able to remove solvent residues, because the phosphanes (S,S_P)-**13** and (S,R_P)-**13** were dried at room temperature in order to prevent epimerisation of the phosphorus center.

[(3S,PR)-1-Benzyl-3-{(2',4',6'-trimethoxyphenyl)phenylphosphanyl}pyrrolidine-P,N]diiodopalladium [(S,R_{MP})-**13-Pd**]: Yield 2.38 g (3 mmol). – R_f = 0.13 (toluene/25% ethyl acetate). – MS (FAB); *m/z* (%): 796.1 (15) [M^+], 669.2 (100) [M^+ – I], 540.3 (30) [M^+ – 2 I], 434.3 (15) [M^+ – PdI_2]. – IR (KBr): $\tilde{\nu}$ = 2958, 2929, 2871 cm^{-1} (C–H), 1594, 1574 (Ar), 1453, 1434, 1337, 1227, 1206, 1159, 1123, 1092, 1027 (C–P, C–N, C–O, C–C), 741, 693 (Ph). – ^1H NMR (CD_2Cl_2, 250.13 MHz): δ = 2.04, 2.28, 2.44 (3 m, 6H, 2-H, 4-H, 5-H), 4.25 (m, 1H, 3-H), 3.45, 3.74 (2 s, 9H, OCH_3), 3.70, 5.67 (2 d, 2H, $^2J_{HH}$ = 13 Hz, CH_2Ph), 5.93 [d, $^4J_{PH}$ = 3 Hz, CH (TMP)], 7.28 [m, 5H, CH (Ph)], 7.65 [m, 3H, CH (Ph)], 7.85 [m, 2H, CH (P-*Ph*)]. – $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 62.9 MHz): δ = 27.3 [s, C-4; C(5) X-ray], 35.1 [d, $^1J_{CP}$ = 29 Hz, C-3; C(4) X-ray], 59.9 [s, C-5; C(6) X-ray], 61.7 [d, $^2J_{CP}$ = 6 Hz, C-2; C(7) X-ray], 64.5 [s, CH_2Ph; C(10) X-ray], 56.3 (s, OCH_3), 91.8 [d, $^3J_{CP}$ = 4 Hz, CH (TMP)], 127.7 [d, $^3J_{CP}$ = 11 Hz, CH (*meta* Ph)], 131.8 [s, CH (*para* Ph)], 133.5 [d, $^2J_{CP}$ = 8 Hz, CH (*ortho* Ph)], 128.6, 128.8, 130.6 [3 s, CH CH_2*Ph*]. – $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 101.25 MHz): δ = 19.6. – $[\alpha]_D^{26}$ = 79.5 (*c* = 0.095, dichloromethane). – $C_{26}H_{30}I_2NO_3PPd$ (795.7): calcd. for $C_{26}H_{30}I_2NO_3PPd \cdot 0.5$ toluene C 42.09, H 4.07, N 1.66; found C 41.91, H 4.23, N 1.75.

[(3S,PS)-1-Benzyl-3-{(2',4',6'-trimethoxyphenyl)phenylphosphanyl}pyrrolidine-P,N]diiodopalladium [(S,S_{MP})-**13-Pd**]: Yield 2.38 g (3 mmol). – R_f = 0.17 (toluene/25% ethyl acetate). – MS (70 eV); IR (KBr): cf. (S,R_{MP})-**13-Pd**. – ^1H NMR (CD_2Cl_2, 250.13 MHz): δ = 2.04, 2.82 (2 m, 6H, 2-H, 4-H, 5-H), 4.25 (m, 1H, 3-H), 3.45, 3.77 (2 s, 9H, OCH_3), 4.25, 5.25 (2 d, 2H, $^2J_{HH}$ = 13 Hz, CH_2Ph), 5.95 [d, $^4J_{PH}$ = 4 Hz, CH (TMP)], 7.17 [m, 5H, CH (Ph)], 7.60 [m, 3H, CH (Ph)], 7.77 [m, 2H, CH (P-*Ph*)]. – $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 62.9 MHz): δ = 25.8 [s, C-4; C(5) X-ray], 35.7 [d, $^1J_{CP}$ = 29 Hz, C-3; C(4) X-ray], 59.7 [s, C-5; C(6) X-ray], 62.9 [d, $^2J_{CP}$ = 4 Hz, C-2; C(7) X-ray], 66.5 [s, CH_2Ph; C(10) X-ray], 56.1, 56.2 (2 s, OCH_3), 92.0 [d, $^3J_{CP}$ = 5 Hz, CH (TMP)], 128.3 [d, $^3J_{CP}$ = 11 Hz, CH (*meta* Ph)], 131.6 [s, CH (*para* Ph)], 132.2 [d, $^2J_{CP}$ = 8 Hz, CH (*ortho* Ph)], 128.8, 129.4, 130.5 [3 s, CH CH_2*Ph*]. – $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 101.25 MHz): δ = 24.0. – $[\alpha]_D^{26}$ = 131.3 (*c* = 0.055, dichloromethane). – $C_{26}H_{30}I_2NO_3PPd$ (795.7): calcd. C 39.25, H 3.80, N 1.76; found C 39.26, H 4.59, N 1.82.

Table 6. Crystal data of PdI_2 complexes with 3-(phosphanyl)pyrrolidine type ligands with a chiral centre on the phosphorus atom, description of data collection, structural analysis and refinement and CSD numbers, file-IDs and formulae

Compound Empirical formula	(S,R_{MP})-**12-Pd** $C_{24}H_{26}I_2NOPPd$	(S,S_{MP})-**12-Pd** $C_{24}H_{26}I_2NOPPd$	(S,R_{MP})-**13-Pd**, (R,S_{MP})-**13-Pd** $C_{26}H_{28}I_2NO_3PPd$ * 0.5 toluene[c]	(S,S_{MP})-**30-Pd** $C_{19}H_{24}I_2NO_3PPd$
Mol. mass (g mol^{-1})	735.63	735.63	846.74	705.56
$d_{calcd.}$ (g cm^{-3})	1.928	1.970	1.867	1.836
Crystal dimensions (mm)	0.20, 0.15, 0.10	0.50, 0.40, 0.25	0.40, 0.20, 0.10	0.25, 0.25, 0.15
Space group	$P2_12_12_1$ (No. 19)	$P2_12_12_1$ (No. 19)	$P\bar{1}$ (No. 1)	$C2$ (No. 5)
a, *b*, *c* (Å)	8.559(2), 14.731(3), 20.105(5)	11.995(7), 13.906(7), 14.873(7)	8.558(2), 11.916(2), 16.030(3)	21.772(7), 14.376(6), 19.283(6)
α, β, γ	90, 90, 90	90, 90, 90	103.20(3), 103.10(3), 99.92(3)	90, 122.24(2), 90
Volume (nm^3), *Z*	2.535(1), 4	2.481(2), 4	1.5062(5), 2	5.105(3), 8
2Θ-Range ($+h$, $\pm k$, $\pm l$), scan method	4 - 50 Wyckoff	4 - 50 Omega	4 - 50 Omega	4 - 50 Omega
Reflections (measured, unique, obs. [I>2 σ (I)]	14795, 4463, 3649	17439, 4404, 4258	10539, 5294, 3347	9379,4695, 3576
μ (mm^{-1})	3.25	3.32	2.75	3.23
Absorption correction: transmission min, max	0.445, 1.000	0.667, 0.730	0.463, 0.553	0.588, 0.796
Parameters, F_0 / parameter[a]	272, 13.42	272, 15.65	344, 9.73	488, 7.32
R, *wR2*	0.0503, 0.1106	0.0191, 0.0461	0.0526, 0.1503	0.0545, 0.1623
GooF, *abs. struc.*[b]	1.634, -0.02(5),	2.026, -0.04(2)	1.743, -	1.567, 0.04(6)
CSD Nr.,file-ID	406464, S,R-12-Pd	406465, S,S-12-Pd	406466, 13-Pd	406467, S,S-30-Pd
Formula	$C_{24}H_{26}I_2NOPPd$	$C_{24}H_{26}I_2NOPPd$	$C_{26}H_{28}I_2NO_3PPd$ * 0.5Toluol	$C_{19}H_{24}I_2NO_3PPd$

[a] All nonhydrogen atoms were refined with anisotropic thermal parameters; hydrogen atoms were included in calculated positions (riding model). – [b] The parameter according to Flack[26] is given. – [c] Disorder of CH_3 groups of toluene (situated near the inversion center).

(3S,PS)-1-Benzyl-3-[(2',4',6'-trimethoxyphenyl)phenylphosphanyl]pyrrolidine [(*S*,S_P)-**13**]: Yield 1.30 g (3 mmol). – MS (70 eV); *m/z* (%): 435.2 (5) [M^+], 344.2 (20) [$M^+ - CH_2Ph$], 276.2 (30) [TMPPhPH], 159.1 (100) [M^+ – TMPPhPH], 91.1 (90) [CH_2Ph]. – IR (KBr): $\tilde{\nu}$ = 2958, 2929, 2871 cm^{-1} (C–H), 1594, 1577 (Ar), 1495, 1464 (C=C, C–N), 1457, 1436, 1406, 1378, 1330, 1261, 1205, 1158, 1117, 1027 (C–P, C–N, C–C), 743, 697 (Ph). – ^1H NMR ($CDCl_3$, 250.13 MHz): δ = 1.82 (m, 1H, 4-H^1), 2.22 (m, 1H, 4-H^2), 2.35 (m, 2H, 2-H^1, 5-H^1), 2.72 (m, 2H, 2-H^2, 5-H^2), 3.3 (m, 1H, 3-H), 3.72, 3.60 (2 s, 9H, OCH_3), 3.54, 3.64 (2 d, 2H, $^2J_{HH}$ = 13 Hz, CH_2Ph), 5.98 [d, $^4J_{PH}$ = 2 Hz, CH (TMP)], 7.13, 7.24, 7.49, 7.63 [4 m, 10H, CH (Ph)]. – $^{13}C\{^1H\}$ NMR ($CDCl_3$, 62.9 MHz): δ = 28.9 (d, $^2J_{CP}$ = 14 Hz, C-4), 32.0 (d, $^1J_{CP}$ = 5 Hz, C-3), 53.9 (d, $^3J_{CP}$ = 5 Hz, C-5), 60.6 (d, $^2J_{CP}$ = 6 Hz, C-2), 60.9 (s, *C*H_2Ph), 55.6, 56.0 (2 s, OCH_3), 91.3 [s, CH (TMP)], 128.0 [d, $^3J_{CP}$ = 5 Hz, CH (*meta* Ph)], 128.7 [s, CH (*para* Ph)], 131.7 [d, $^2J_{CP}$ = 15 Hz, CH (*ortho* Ph)], 127.4, 128.6, 129.4 [3 s, CH (CH_2*Ph*)]. – $^{31}P\{^1H\}$ NMR ($CDCl_3$, 101.25 MHz): δ = –23.3. – $[\alpha]_D^{20}$ = 31.0 (*c* = 0.45, dichloromethane). – $C_{26}H_{30}NO_3P$ (435.5): calcd. for $C_{26}H_{30}NO_3P$ · 2 diethyl ether C 69.96, H 8.63, N 2.4; found C 69.96, H 7.8, N 2.27.

(3S,PR)-1-Benzyl-3-[(2',4',6'-trimethoxyphenyl)phenylphosphanyl]pyrrolidine [(*S*,R_P)-**13**]: Yield 1.30 g (3 mmol). – MS (70 eV); *m/z* (%); IR (film): cf. (*S*,S_P)-**13**. – ^1H NMR ($CDCl_3$, 250.13 MHz): δ = 1.82 (m, 1H; 4-H^1), 2.05 (m, 1H, 4-H^2), 2.35 (m, 2, 2-H^1, 5-H^1), 2.82 (m, 2H, 2-H^2, 5-H^2), 3.4 (m, 1H, 3-H), 3.71, 3.58 (2 s, 9H, OCH_3), 3.54, 3.64 (2 d, 2H, $^2J_{HH}$ = 13 Hz, CH_2Ph), 5.98 [d, $^4J_{PH}$ = 2 Hz, CH (TMP)], 7.12, 7.30, 7.53, 7.79 [4 m, 10H, CH (Ph)]. – $^{13}C\{^1H\}$ NMR ($CDCl_3$, 62.9 MHz): δ = 31.1 (d, $^2J_{CP}$ = 30 Hz, C-4), 31.7 (d, $^1J_{CP}$ = 8 Hz, C-3), 54.8 (d, $^3J_{CP}$ = 4 Hz, C-5), 59.2 (d, $^2J_{CP}$ = 23 Hz, C-2), 60.2 (s, CH_2Ph), 55.1, 56.1 (2 s, OCH_3), 91.3 [s, CH (TMP)], 128.0 [d, $^3J_{CP}$ = 5 Hz, CH (*meta* Ph)], 128.6 [s, CH (*para* Ph)], 131.6 [d, $^2J_{CP}$ = 16 Hz, CH (*ortho* Ph)], 127.2, 128.5, 129.2 [3 s, *C*H CH_2*Ph*]. – $^{31}P\{^1H\}$ NMR ($CDCl_3$, 101.25 MHz): δ = –24.2. – $[\alpha]_D^{20}$ = –34.9 (*c* = 0.36, dichloromethane). – $C_{26}H_{30}NO_3P$ (435.5): calcd. for $C_{26}H_{30}NO_3P$ · 2 diethyl ether C 69.96, H 8.63, N 2.4; fond C 69.84, H 7.93, N 2.36.

[(3S,PS)-3-{(2',4',6'-Trimethoxyphenyl)phenylphosphanyl}pyrrolidine-P,N]diiodopalladium [(*S*,S_{MP})-**30-Pd**]: the ligand was obtained in a reaction with [3*S*,P(*RS*)]-1-benzoyl-3-(phenylphosphanyl)pyrrolidine [(*S*,RS_P)-**28**] as starting material instead of (*S*,RS_P)-**29** in the synthesis of (*S*,RS_P)-**13**. From crude (*S*,RS_{MP})-**30-Pd** obtained with Na_2PdCl_4, NaI in acetone (cf. synthesis of (*S*,RS_{MP})-**13**) this diastereomerically pure complex could be isolated by preparative column chromatography with acetone (12.5%)/toluene and crystallisation from dichloromethane/toluene solutions; yield 200 mg (0.28 mmol). – MS (FAB); *m/z* (%): 705.2 (15) [M^+], 578.2 (100) [M^+ – I], 450.4 (30) [M^+ – 2 I]. – IR (KBr): $\tilde{\nu}$ = 3200 cm^{-1} (N–H), 2960, 2921, 2849 (C–H), 1591, 1570 (Ar), 1468, 1456, 1409, 1337, 1261, 1228, 1205, 1158, 1126, 1093, 1024 (C–P, C–N, C–O, C–C), 815, 806 (Ph). – ^1H NMR (CD_2Cl_2, 250.13 MHz): δ = 1.91 (s, 1H, NH), 2.25, 2.36 (2 m, 6H, 2-H, 4-H, 5-H), 4.95 (m, 1H, 3-H), 3.48, 3.76 (2 s, 9H, OCH_3), 6.0 [d, $^4J_{PH}$ = 4 Hz, CH (TMP)], 7.07 [m, 1H, CH (Ph)], 7.33 [m, 2H, CH (Ph)], 7.85 [m, 2H, CH (Ph)]. – $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 62.9 MHz): δ = 28.9 [s, C-4; C(5) X-ray], 35.2 [d, $^1J_{CP}$ = 30 Hz, C-3; C(4) X-ray], 54.9, (s, OCH_3), 55.0 [s, C-5; C(6) X-ray], 57.6 [s, C-2; C(7) X-ray], 90.8 [d, $^3J_{CP}$ = 4 Hz, CH (TMP)], 127.2 [d, $^3J_{CP}$ = 11 Hz, CH (*meta* Ph)], 130.6 [s, CH (*para* Ph)], 132.7 [d, $^2J_{CP}$ = 8 Hz, CH (*ortho* Ph)]. – $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 101.25 MHz): δ = 21.3. – $[\alpha]_D^{26}$ = 59.6 (*c* = 0.136, dichloromethane). – $C_{19}H_{24}I_2NO_3PPd$ (705.6): calcd. for $C_{19}H_{24}I_2NO_3PPd$ · 1/2 toluene C 35.95, H 3.75, N 1.86; found C 36.18, H 4.28, N 2.08.

Mixture of [(3S,2'S)]-3-(Diphenylphosphanyl)-1-{[(1'-neopentyl)pyrrolidin-2'yl]methyl}-3-diphenylphosphanyl)pyrrolidine-P,N]diiodopalladium (A) and of {[(3S,2'S)-3-(Diphenylphosphanyl)-1-{[(1'neopentyl)pyrrolidin-2'-yl]methyl}-pyrrolidine-P,N,N']iodopalladium}iodide (B): – $^{31}P\{^1H\}$ NMR ([D_6]acetone, 101.26 MHz): δ = 48.2 (B), 43.9 (A); integration 1:2. – $[\alpha]_D^{26}$ = 41.2 (*c* = 0.059 in acetone). – $C_{26}H_{37}I_2N_2PPd$ (768.8): calcd. C 40.62, H 4.85, N 3.64; found C 40.60, H 5.04, N 3.53.

X-ray Structure Determinations: Data collection: Siemens P4 diffractometer, Mo-K_α (λ = 71.073 pm), graphite monochromator, measuring temp. *T* = 173 K with the exception: *T* = 243 K for (*S*,*S*)-**30-Pd**, absorption correction with Ψ-scan (ellipsoid model). Structure analysis and refinement: program SHELXTL V5.03[42], solution wiht Patterson method, full-matrix least-squares refinement. Details including CSD numbers, file-IDs and formulae are displayed in Tables 8 and 9. Further details of the crystal-structure investigations are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Leopoldshafen-Eggenstein, Germany, on quoting the depository numbers.

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