Stereochemical Exploitation of the Chiral (+)-9-Phenyldeltacyclanyl Substituent in Diphosphanes and Their Ni, Pd and Pt Complexes[‡]

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Dedicated to Professor Dr. Gottfried Huttner on the occasion of his 65th birthday

Keywords: Deltacyclenes / Chiral ligands / Phosphanes / Nickel / Palladium / Platinum

The (+)-9-phenyldeltacyclanyl moiety as a chiral phosphorus substituent contains eight configurationally fixed asymmetric carbon atoms. It is easily obtained from the reaction of norbornadiene and phenylacetylene via a Co-catalyzed enantioselective homo-Diels–Alder reaction, to give (+)-8-phenyldeltacyclene. In the reaction of (+)-8-phenyldeltacyclene with 1,2-$(H_2P)_2C_6H_4$ the trisubstitution product *P,P,P′*-tris[(+)-9-phenyldeltacyclan-8-yl)-1,2-bis(phosphanyl)benzene, **(+)$_{\delta}$-LH**, is obtained, in which a single P–H bond at the stereogenic phosphorus atom is left. **(+)$_{\delta}$-LH** crystallizes as a pure diastereomer, which isomerizes in solution with respect to the secondary phosphorus atom at –20 °C resulting in a 64:36 diastereomer mixture. Substitution of the P–H hydrogen atom in **(+)$_{\delta}$-LH** by benzyl, 3-bromobenzyl, 6-bromo-*n*-hexyl and 3-(diphenylphosphanyl)phenyl gave the bis(tertiary) diphosphanes **(+)$_{\delta}$-LR^1–(+)$_{\delta}$-LR^4**. $NiBr_2$, $PdHal_2$ (Hal = Cl, Br, I) and $PtHal_2$ (Hal = Cl, Br) complexes of **(+)$_{\delta}$-LH** and **(+)$_{\delta}$-LR^1–(+)$_{\delta}$-LR^4** have been synthesized. The complexes form two diastereomers differing in the configuration of the chiral P atom. X-ray structure analyses have been carried out with **(+)$_{\delta}$-LH**, **[(+)$_{\delta}$-LR^2]NiBr$_2$**, **[(+)$_{\delta}$-LH]PdI$_2$** and **[(+)$_{\delta}$-LCl]PdI$_2$**. Interestingly, for **[(+)$_{\delta}$-LH]PdI$_2$** both diastereomers are found in the same crystal lattice in a 1:1 ratio. In **[(+)$_{\delta}$-LH]PdI$_2$** and **[(+)$_{\delta}$-LCl]PdI$_2$** the configuration at the secondary phosphorus atom is stable in solution at room temperature, whereas in the free ligand **(+)$_{\delta}$-LH** it is configurationally labile.

Introduction

2,5-Norbornadiene undergoes thermal [2+2+2] homo-Diels−Alder reactions with acetylenes to give deltacyclenes, provided the acetylene carries strongly electron-withdrawing groups such as NO_2.[2] Non-reactive acetylenes form deltacyclenes with 2,5-norbornadiene only in the presence of transition metal catalysts, although other products may also be formed.[3] In 1978, a procedure was published to transform terminal acetylenes into deltacyclenes in high yield using a combination of $Co(acac)_3$, triphenylphosphane and a reducing agent.[4] This reaction was rendered chiral by replacing the achiral triphenylphosphane by optically active phosphanes.[5,6] Further investigations showed that the catalyst $Co(acac)_3$ together with norphos and the reducing agent Et_2AlCl in the solvent THF gave nearly enantiopure deltacyclenes.[7] (+)-8-Phenyldeltacyclene, used in the present work, can be prepared in this way from 2,5-norbornadiene and phenylacetylene in a reliable enantiomeric excess of *ee* > 97.5%. Subsequently, other catalytic systems, allowing the extension to substituted acetylenes, and other enantioselective studies have appeared.[8−15]

The double bond of (+)-8-phenyldeltacyclene enables further derivatization by addition reactions, e.g. of P−H bonds. Ph_2PH has been added to give a monodentate chiral phosphane.[13] The aim of the reaction of 1,2-bis(phosphanyl)benzene with a fourfold excess of (+)-8-phenyldeltacyclene was to synthesize a chelate ligand with four deltacyclanyl substituents at the two phosphorus atoms. However, the tetrasubstituted product, albeit detected in the mass spectrum, could not be obtained.[13] Obviously, the reaction of 1,2-$(H_2P)_2C_6H_4$ with (+)-8-phenyldeltacyclene stops after 3 P−H additions. Due to steric hindrance the fourth P−H bond does not add to another (+)-8-phenyldeltacyclene. The resulting trisubstitution product **(+)$_{\delta}$-LH** is a tertiary/secondary diphosphane open to further derivatization reactions at the chiral phosphorus atom. **(+)$_{\delta}$-LH** is the starting material for the studies described in the present and succeeding paper.[16]

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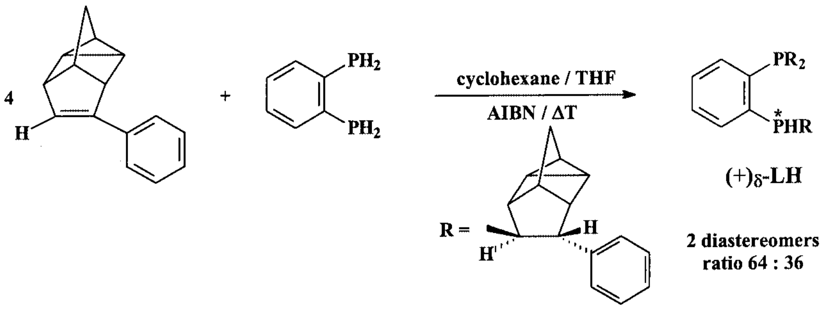


Scheme 1. Reaction of (+)-8-phenyldeltacyclene and 1,2-bis(phosphanyl)benzene to give *P,P,P′*-tris[(+)-9-phenyldeltacyclan-8-yl]-1,2-bis(phosphanyl)benzene, **(+)$_{\delta}$-LH**

Results and Discussion

P,P,P′-Tris[(+)-9-phenyldeltacyclan-8-yl]-1,2-bis(phosphanyl)benzene, (+)$_{\delta}$-LH

The tertiary/secondary diphosphane **(+)$_{\delta}$-LH** was obtained under radical conditions from (+)-8-phenyldeltacyclene and 1,2-bis(phosphanyl)benzene in boiling THF/cyclohexane in the presence of AIBN (Scheme 1).

After recrystallization from ethanol, **(+)$_{\delta}$-LH** was isolated as fine colorless needles in 45% yield. The ^{31}P NMR spectrum, in CDCl$_3$ at room temperature, showed that **(+)$_{\delta}$-LH** consists of two diastereomers with respect to the chiral P atom in a ratio of 64:36 (*de* = 28%). Interestingly, the needles obtained in the crystallization from ethanol contained only one of the two possible diastereomers of **(+)$_{\delta}$-LH**, as shown by low-temperature ^{31}P NMR spectroscopy (Figure 1). The cooled solution (−80 °C) of **(+)$_{\delta}$-LH** in [D$_8$]THF afforded only two doublets at $\delta = -15.0$ and -29.9 ppm, the signals of the major isomer in the equilibrium mixture. The formation of the second diastereomer ($\delta = -10.8$ and -31.7 ppm) was observed by warming up to temperatures around −20 °C. At room temperature the diastereomer ratio of 64:36 was obtained. The fast epimerization is in agreement with the known configurational lability of secondary phosphanes.[17−20]

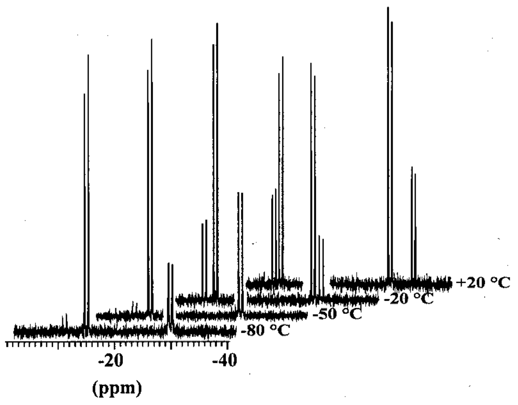


Figure 1. ^{31}P NMR spectrum of crystallized **(+)$_{\delta}$-LH** at −80 °C in [D$_8$]THF and equilibration of the diastereomers of **(+)$_{\delta}$-LH** on warming

A structural study performed with the needles of **(+)$_{\delta}$-LH** confirmed the presence of only one diastereomer (Figure 2). The phosphorus atom is *exo*-bonded to the 9-phenyldeltacyclan-8-yl substituent, pointing away from the deltacyclane cage, whereas the 9-phenyl group is *endo*-arranged beneath the deltacyclane cage. In principle, there are six alternatives to the addition of a P−H bond to (+)-8-phenyldeltacyclene.[13] However, in the structure of **(+)$_{\delta}$-LH** and the structures reported subsequently only one of them, 9-*exo*-P and 8-*endo*-Ph, is found, confirming former ^{1}H NMR assignments and calculations.[13] Note that in the P−H addition carbon atoms 8 and 9 of the deltacyclene skeleton change priorities. Thus, (+)-8-phenyldeltacyclene becomes the 9-phenyldeltacyclan-8-yl substituent. The symbol **(+)$_{\delta}$** in the ligand **(+)$_{\delta}$-LH** (and in its complexes) indicates that the 9-phenyldeltacyclan-8-yl substituents derived from (+)-8-phenyldeltacyclane are formed in a highly enantioselective homo-Diels−Alder reaction. The configuration of the chiral phosphorus atom could not be determined since the hydrogen atom at the secondary phosphorus atom was not localized in the X-ray structure analysis. As it is also labile in solution at room temperature, no configura-

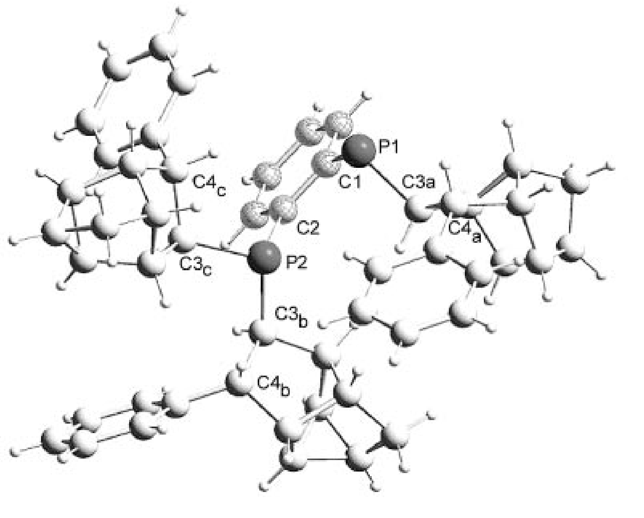


Figure 2. Molecular structure of **(+)$_{\delta}$-LH**, crystallized from ethanol; selected bond lengths [Å] and angles [°]: P1···P2 3.197(6), P1−C1 1.827(5), P2−C2 1.847(4), P1−C3$_a$ 1.853(5), P2−C3$_b$ 1.858(4), P2−C3$_c$ 1.842(3); C1−P1−C3$_a$ 102.01(16), C2−P2−C3$_b$ 100.14(19), C2−P2−C3$_c$ 98.85(18), C3$_b$−P2−C3$_c$ 102.80(14)

tional symbol for the secondary phosphorus atom in the ligand **(+)$_{\delta}$-LH** is used. However, in the complexes of **(+)$_{\delta}$-LH** the configuration of the secondary phosphorus atom is stabilized. Therefore, it is added for all the compounds that could be characterized by X-ray crystallography. The torsion angle P2−C2−C1−P1 of 2.41(44)° shows that the chelate ligand **(+)$_{\delta}$-LH** is nearly planar.

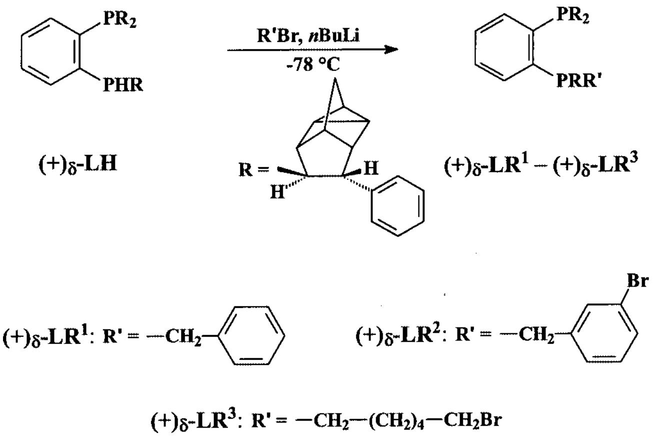
The synthesis of chiral building blocks frequently starts from amino acids and carbohydrates of the natural pool. Due to its easy accessibility from norbornadiene and phenylacetylene, (+)-8-phenyldeltacyclene is a promising artificial chiral building block. It contains six chiral carbon atoms, which are stereospecifically built up in the deltacyclene formation. After P−H addition to the double bond of (+)-8-phenyldeltacyclene, the number of asymmetric carbon atoms increases to eight in the (+)-9-phenyldeltacyclan-8-yl substituent. The trisubstitution product **(+)$_{\delta}$-LH** comprises 24 chiral centers (8 × 3) in the three deltacyclanyl substituents. The 25th stereogenic center in **(+)$_{\delta}$-LH** is the secondary phosphorus atom. In the present paper, **(+)$_{\delta}$-LH** is exploited for the synthesis of unsymmetrical bis(tertiary) phosphanes and mononuclear complexes with transition metal halides.[16] Di- and trinuclear complexes of **(+)$_{\delta}$-LH** will be described in the succeeding paper.

The Unsymmetrical Bis(tertiary) Diphosphanes (+)$_{\delta}$-LR^1 to (+)$_{\delta}$-LR^4

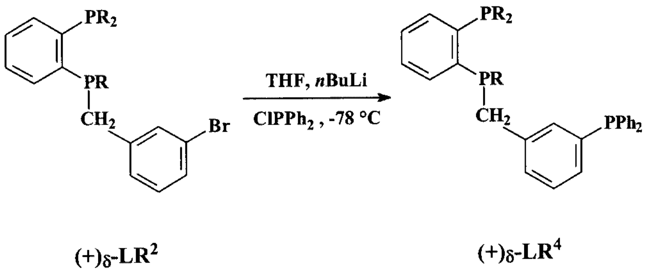
As the P−H bond of the trisubstitution product **(+)$_{\delta}$-LH** did not add to another (+)-8-phenyldeltacyclene due to steric reasons, sterically less demanding groups, to be used as the fourth substituent, were taken into consideration. Deprotonation of the P−H bond and reaction with the bromo derivative of the desired substituent seemed to be a suitable methodology.[12−14] Deprotonation of **(+)$_{\delta}$-LH** with *n*BuLi provides an achiral phosphide anion. Therefore, the diastereomeric excess obtained in consecutive reactions is independent of the diastereomer ratio of the secondary phosphane **(+)$_{\delta}$-LH**. However, the new phosphorus configuration will be influenced by the chirality of the 24 asymmetric centers of the three deltacyclane substituents.

Benzyl bromide is a reactive bromo derivative having only one coupling site. Treatment of a THF solution of **(+)$_{\delta}$-LH** with *n*BuLi at −78 °C followed by addition of benzyl bromide afforded the bis(tertiary) diphosphane **(+)$_{\delta}$-LR^1** in nearly 40% yield (Scheme 2). The ^{31}P NMR spectrum of **(+)$_{\delta}$-LR^1** in $CDCl_3$ displayed an AB system for each of the two diastereomers, the diastereomer ratio being 93:7 (*de* = 86%). Ligand **(+)$_{\delta}$-LR^2** is formed in 42% yield with a diastereomeric excess of *de* = 72% by using 1-bromo-3-(bromomethyl)benzene, which has an extra less reactive bromo substituent in the *meta* position of the benzyl group (Scheme 2). The best diastereomeric excess (*de* = 90%) was achieved with 1,6-dibromohexane. Ligand **(+)$_{\delta}$-LR^3** was isolated in 45% yield (Scheme 2). Formation of the disubstituted product was not observed.[16]

Halogen/metal exchange in **(+)$_{\delta}$-LR^2** with *n*BuLi, followed by reaction with chlorodiphenylphosphane, provided **(+)$_{\delta}$-LR^4** as a diastereomeric mixture with *de* = 56% (Scheme 3). In addition to the signals of the AB system of the chelating unit, the ^{31}P NMR spectrum of **(+)$_{\delta}$-LR^4** showed singlets at δ = −4.73 and −5.09 ppm belonging to the phosphorus atoms of the PPh_2 group of the two diastereomers.



Scheme 2. Formation of the unsymmetrical bis(tertiary) diphosphanes **(+)$_{\delta}$-LR^1** to **(+)$_{\delta}$-LR^3**

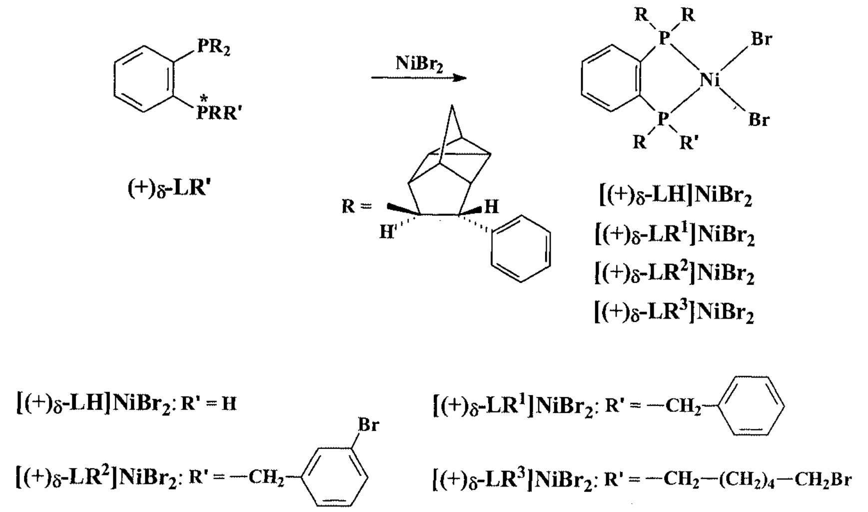


Scheme 3. Synthesis of **(+)$_{\delta}$-LR^4**

The NiBr$_2$ Complexes of the Diphosphanes (+)$_{\delta}$-LH and (+)$_{\delta}$-LR^1 to (+)$_{\delta}$-LR^3

Reaction of anhydrous $NiBr_2$ with **(+)$_{\delta}$-LH** in boiling ethanol provided the expected square-planar mononuclear dibromo(diphosphane)nickel(II) complex **[(+)$_{\delta}$-LH]NiBr$_2$** (Scheme 4). Crystallization of **[(+)$_{\delta}$-LH]NiBr$_2$** from a mixture of acetone, CH_2Cl_2, toluene and pentane gave fine red needles, which were amorphous in the X-ray structure analysis. The ^{31}P NMR spectrum showed two AB systems (δ = 72.34/43.27 and 74.70/49.76 ppm) resulting from the two diastereomers differing in the configuration of the secondary phosphorus atom in a ratio of 84:16. The splitting of the PHR signals at δ = 43.27 ppm (400.5 Hz) and δ = 49.76 ppm (408.2 Hz) in the proton-coupled ^{31}P NMR spectrum clearly proves that the hydrogen atom is still bonded to the secondary phosphorus atom. The tendency of **[(+)$_{\delta}$-LH]NiBr$_2$** to HBr elimination and the formation of dinuclear complexes will be discussed in the succeeding paper.

In the reaction of anhydrous $NiBr_2$ with the bis(tertiary) diphosphanes **(+)$_{\delta}$-LR^1** to **(+)$_{\delta}$-LR^3** mononuclear complexes are expected and found (Scheme 4). The ^{31}P NMR spectrum of **[(+)$_{\delta}$-LR^1]NiBr$_2$** showed two AB systems (δ =



Scheme 4. Synthesis of the dibromonickel(II)-diphosphane complexes **[(+)$_\delta$-LH]NiBr$_2$**, **[(+)$_\delta$-LR^1]NiBr$_2$**, **[(+)$_\delta$-LR^2]NiBr$_2$** and **[(+)$_\delta$-LR^3]NiBr$_2$**

82.37/66.39 and 74.99/72.13 ppm, ratio 8:92) caused by the two possible diastereomers in a ratio which is similar to that of the free ligand **(+)$_\delta$-LR^1**. Compared to the ^{31}P NMR spectrum of **(+)$_\delta$-LR^1** the signals of the diamagnetic square-planar complex **[(+)$_\delta$-LR^1]NiBr$_2$** are shifted to higher ppm (coordination shift).

Using ligand **(+)$_\delta$-LR^2**, the corresponding mononuclear dibromonickel(II) complex **[(+)$_\delta$-LR^2]NiBr$_2$** could also be isolated as a mixture of two diastereomers. Evaluation of the ^{31}P NMR spectrum of **[(+)$_\delta$-LR^2]NiBr$_2$** provided two AB systems (δ = 82.79/67.02 and 74.77/72.57 ppm) with a 16:84 ratio of the two diastereomeric forms. From a mixture of CH$_2$Cl$_2$ and ethanol, fine orange plates of **[(+)$_\delta$-LR^2]NiBr$_2$**, suitable for X-ray structure analysis, were obtained.

The structural study confirmed the mononuclear character of the complex (Figure 3) and proved the presence of only one of the two possible diastereomeric forms. The configuration of the chiral phosphorus atom was determined as (*R*). The ^{31}P NMR spectrum of a solution of these crystals showed that only one diastereomer was present, indicating configurational stability of the chiral phosphorus atom in the complex, whereas the free ligand **(+)$_\delta$-LH** already isomerized at −20 °C. The diastereomer in the isolated crystals corresponded to the major diastereomer formed in the synthesis described above. The dihedral angles P1−C1−C2−P2 [2.66(60)°] and P1−P2−Br2−Br1 [2.82(4)°] showed that in **[(+)$_\delta$-LR^2]NiBr$_2$** the chelate ring and the nickel square were only slightly deformed. In the crystal of **[(+)$_\delta$-LR^2]NiBr$_2$** the bromobenzyl substituent was disordered. The conformation shown in Figure 3 had 92.3% probability. In the conformation with 7.7% probability, the benzyl substituent was rotated by 180° with respect to the C5−C$_{ipso}$ bond.

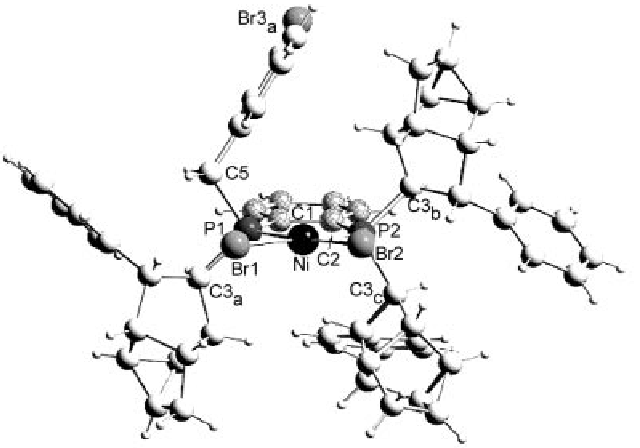


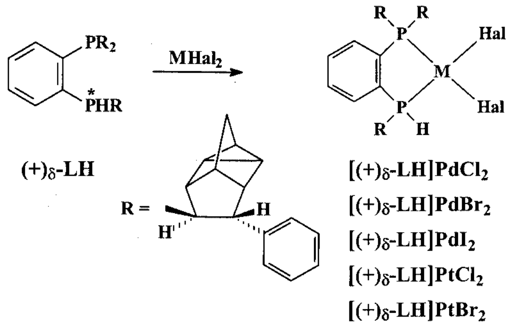
Figure 3. Molecular structure of **[(+)$_\delta$-LR^2]NiBr$_2$**, crystallized from CH$_2$Cl$_2$/ethanol; selected bond lengths [Å] and angles [°]: Ni−Br1 2.342(1), Ni−Br2 2.334(2), Ni−P1 2.151(2), Ni−P2 2.172(2), P1−C1 1.817(6), P2−C2 1.841(6), P1−C3$_a$ 1.858(7), P1−C5 1.839(7), P2−C3$_b$ 1.844(7), P2−C3$_c$ 1.842(7); C1−P1−C3$_a$ 103.20(23), C1−P1−C5 102.24(29), C5−P1−C3$_a$ 101.66(29), C3$_b$−P2−C3$_c$ 104.95(28), C2−P2−C3$_b$ 100.52(22), C2−P2−C3$_c$ 100.61(26), P1−Ni−Br1 86.13(5), P1−Ni−P2 89.24(6), P2−Ni−Br2 92.21(4), Br2−Ni−Br1 92.44(3)

In the complex **[(+)$_\delta$-LR^3]NiBr$_2$**, the ligand of which carried an aliphatic chain as the fourth substituent, there were two diastereomers (^{31}P NMR: δ = 78.14/68.92 (minor) and 73.82/71.85 ppm (major), ratio 4:96).

Palladium and Platinum Complexes of the Secondary Diphosphane (+)$_\delta$-LH

The first products of the reaction of **(+)$_\delta$-LH** with palladium and platinum dihalides were the corresponding mononuclear square-planar complexes (Scheme 5). Their

HHal elimination to afford di- and trinuclear complexes will be discussed in the succeeding paper.



Scheme 5. Preparation of palladium and platinum dihalide complexes of **(+)$_\delta$-LH**

The diastereomeric excess in the preparation of **[(+)$_\delta$-LH]PdCl$_2$** depended on the reactants and the reaction conditions. Heating of **(+)$_\delta$-LH** and PdCl$_2$ in toluene in the presence of a small amount of concentrated HCl provided **[(+)$_\delta$-LH]PdCl$_2$**, the ^{31}P NMR spectrum of which showed two diastereomers in a ratio of 55:45. Using Na$_2$PdCl$_4$ in boiling ethanol, the diastereomer present in excess (δ = 76.75/41.10 ppm) was enriched to *de* = 84% (minor diastereomer: δ = 74.83/38.82 ppm). If the reaction was started in THF at −78 °C with (PhCN)$_2$PdCl$_2$ and diastereomerically pure **(+)$_\delta$-LH** as the starting material, the ^{31}P NMR spectrum of the product also showed the signals of the two diastereomers. However, in this case the diastereomer, which was the minor before, dominated with a ratio of 91:9. In **[(+)$_\delta$-LH]PdCl$_2$** the P−P couplings were typical for (diphosphane)palladium chelate complexes ($^2J_{PP}$ = 9.0 and 11.8 Hz), the P−H couplings were 405 and 410 Hz.

The syntheses of **[(+)$_\delta$-LH]PdBr$_2$** was succeeded by stirring a suspension of PdBr$_2$ and **(+)$_\delta$-LH** in CH$_2$Cl$_2$ for 4 d. The ^{31}P NMR spectrum of **[(+)$_\delta$-LH]PdBr$_2$** showed two isomers (major: δ = 79.10/43.96; minor: δ = 76.52/39.45 ppm; ratio 55:45). For **[(+)$_\delta$-LH]PdBr$_2$** the P−P couplings (14.5 and 17.6 Hz) and the P−H couplings (409 and 414 Hz) were larger than for **[(+)$_\delta$-LH]PdCl$_2$**.

A suspension of **(+)$_\delta$-LH** and PdI$_2$ was refluxed in benzene. After 4 h, all the PdI$_2$ had reacted and a dark red powder was isolated in nearly quantitative yield. The ^{31}P NMR spectrum of **[(+)$_\delta$-LH]PdI$_2$** showed two diastereomers, δ = 80.09/45.29 and 75.77/38.02 ppm in a ratio of 58:42 with P−P couplings (13.5 and 16.5 Hz) and P−H couplings (407 and 405 Hz). After putting a layer of methanol over a solution of **[(+)$_\delta$-LH]PdI$_2$** in CH$_2$Cl$_2$, red crystals of X-ray quality were obtained (Figure 4).

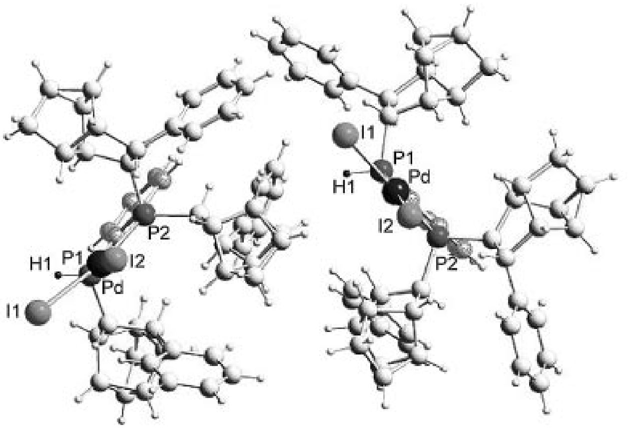


Figure 4. Molecular structures of the two diastereomers of **[(+)$_\delta$-LH]PdI$_2$**, crystallized from CH$_2$Cl$_2$/methanol; (R_P) diastereomer on the right, (S_P) diastereomer on the left; selected bond lengths [Å] and angles [°] of the (S_P) diastereomer of **[(+)$_\delta$-LH]PdI$_2$**: Pd−I1 2.659(1), Pd−I2 2.646(1), Pd−P1 2.244(1), Pd−P2 2.269(2), P1−C1 1.818(5), P2−C2 1.835(5), P1−C3$_a$ 1.842(3), P1−H1 1.219(47), P2−C3$_b$ 1.842(6), P2−C3$_c$ 1.844(3); H1−P1−C3$_a$ 99.87(202), C1−P1−C3$_a$ 112.15(15), C1−P1−H1 105.52(234), C3$_c$−P2−C3$_b$ 104.89(15), C2−P2−C3$_c$ 99.57(15), C2−P2−C3$_b$ 101.26(16), P1−Pd−P2 86.15(3), P2−Pd−I2 95.73(3), I2−Pd−I1 90.66(1), I1−Pd−P1 87.47(2)

In the structural study the hydrogen atoms of the secondary phosphorus atoms could be localized. To our surprise from a solution of the two diastereomers of **[(+)$_\delta$-LH]PdI$_2$**, differing in the configuration at the secondary phosphorus atom in the ratio 58:42, single crystals could be obtained which contained both diastereomers exactly in a 1:1 ratio. This is extremely unusual, because normally each diastereomer crystallizes in its own lattice. In the case of **[(+)$_\delta$-LH]PdI$_2$** the (S_P) diastereomer and the (R_P) diastereomer formed a pair that was repeated in the lattice (Figure 4), a rare case of molecular recognition and supramolecular chemistry.[21] The ^{31}P NMR spectrum of the solution of the crystals showed the two diastereomers in a 50:50 ratio. Thus, the configuration at the secondary P atoms in the diastereomeric complexes was stable. In this specific case diastereomer enrichment on crystallization did not occur in the crystals but in the supernatant mother liquor. Whereas in **[(+)$_\delta$-LH]PdCl$_2$** the palladium square was only slightly deformed [dihedral angle P1−P2−I2−I1 1.28(2)°], the chelate ring was appreciably puckered [dihedral angle P1−C1−C2−P2 11.11(41)°].

In addition to the signals of **[(+)$_\delta$-LH]PdI$_2$** the ^{31}P NMR spectrum of the reaction mixture of PdI$_2$ and **(+)$_\delta$-LH** in CH$_2$Cl$_2$ exhibited many signals of other compounds. Within 12 h dark red crystals of **[(+)$_\delta$-LCl]PdI$_2$** of X-ray quality crystallized from a CH$_2$Cl$_2$/Et$_2$O solution. The X-ray structure analysis of **[(+)$_\delta$-LCl]PdI$_2$** (Figure 5) showed that the hydrogen atom, bonded to the secondary phosphorus atom in the ligand **(+)$_\delta$-LH**, had been replaced by a chlorine atom which must have come from the solvent CH$_2$Cl$_2$. The configuration of the chiral phosphorus atom was determined as (*S*). The ^{31}P NMR spectrum of the dissolved crystals exhibited only signals of one diastereomer at δ = 123.29 and 68.87 ppm. With the torsion angle P1−C1−C2−P2 [4.15(89)°] there was a slight puckering of the chelate ring. On the other hand the square-planar arrangement of the four atoms bonded to the palladium atom in **[(+)$_\delta$-LCl]PdI$_2$** was heavily distorted [dihedral angle P1−P2−I2−I1 13.78(5)°].

To synthesize the mononuclear platinum complex **[(+)$_\delta$-LH]PtCl$_2$**, K$_2$PtCl$_4$ was dissolved in a small amount of concentrated HCl. The dark brown solution was diluted with ethanol and heated to reflux. After dropwise addition of a

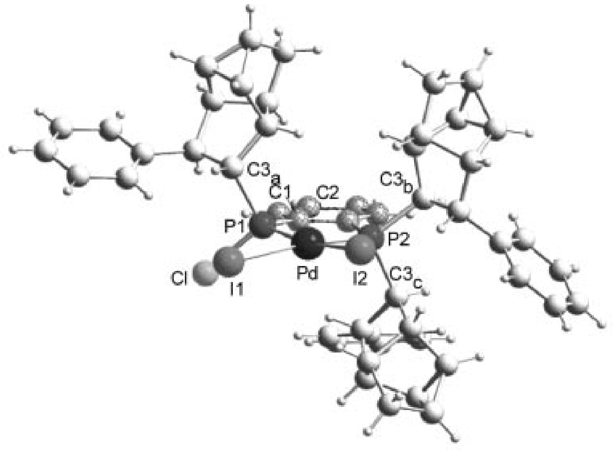


Figure 5. Molecular structure of **[(+)$_\delta$-LCl]PdI$_2$**, crystallized from CH$_2$Cl$_2$/methanol; selected bond lengths [Å] and angles [°]: Pd−I1 2.647(2), Pd−I2 2.653(2), Pd−P1 2.228(2), Pd−P2 2.275(3), I1···Cl 3.901(4), P1−C1 1.818(10), P2−C2 1.836(9), P1−C3$_a$ 1.815(8), P1−Cl 2.231(14), P2−C3$_b$ 1.838(13), P2−C3$_c$ 1.828(8); Cl−P1−C3$_a$ 103.70(29), C1−P1−C3$_a$ 110.10(38), C1−P1−Cl 100.16(28), C3$_c$−P2−C3$_b$ 103.79(37), C2−P2−C3$_c$ 102.67(37), C2−P2−C3$_b$ 101.46(38), P1−Pd−P2 85.84(8), P2−Pd−I2 97.66(6), I2−Pd−I1 90.07(2), I1−Pd−P1 88.19(6)

toluene solution of **(+)$_\delta$-LH**, the complex **[(+)$_\delta$-LH]PtCl$_2$** could be isolated. The ^{31}P NMR spectrum of **[(+)$_\delta$-LH]PtCl$_2$** showed the signals of two different isomers. The diastereomer present in excess (δ = 48.67/15.90 ppm) was enriched to 80% (minor diastereomer: δ = 47.20/15.23 ppm). The P−P couplings (2.5 and 3.1 Hz) were much smaller for **[(+)$_\delta$-LH]PtCl$_2$** than for **[(+)$_\delta$-LH]PdCl$_2$**. In addition to P−H couplings (414 and 416 Hz) Pt−P couplings were observed (3508 and 3531 Hz), typical for mononuclear (diphosphane)platinum complexes.

The corresponding platinum bromide complex **[(+)$_\delta$-LH]PtBr$_2$** was obtained from Pt(cod)Br$_2$ and **(+)$_\delta$-LH** in benzene at room temperature. The ^{31}P NMR spectrum showed two diastereomers, the major diastereomer (δ = 49.77/18.19 ppm) being enriched to nearly 70% (minor diastereomer: δ = 51.81/21.49 ppm). The P−P couplings were smaller (2.2/2.4) and the P−H couplings larger (417/419) than those of the platinum chloride complex **[(+)$_\delta$-LH]PtCl$_2$** with the Pt−P couplings (3322/3504) in the expected range.

Experimental Section

General Remarks: All reactions were performed under dry nitrogen using standard Schlenk techniques. Solvents were purified and dried by standard procedures. (+)-8-Phenyldeltacyclene[7] and 1,2-bis(phosphanyl)benzene[22−24] were prepared as described in the literature. Mass spectra: Finnigan Mat 95 for field desorption (FD) and fast atom bombardment (FAB), Thermo Quest TSQ 7000 for electron spray injection (ESI), M$^+$ = the most intense peak of the isotope cluster of M. ^{1}H NMR spectra: Bruker ARX 400 spectrometer (400 MHz). ^{31}P NMR spectra: Bruker ARX 400 spectrometer (162 MHz). Melting points: Büchi SMP 20. Elemental analyses: Heraeus Elementar Vario EL III.

***P,P,P′*-Tris[(+)-9-phenyldeltacyclan-8-yl]-1,2-bis(phosphanyl)benzene, (+)$_\delta$-LH:** To the boiling solution of (+)-8-phenyldeltacyclene (4.90 g, 25.0 mmol) in 20 mL of cyclohexane, 1,2-bis(phosphanyl)benzene (1.00 g, 7.0 mmol), AIBN (0.16 g, 1.0 mmol) in 20 mL of cyclohexane and 20 mL of THF was added dropwise. After heating for 16 h, the solvents were evaporated and the residue was suspended in 50 mL of pentane. The mixture was cooled to −20 °C for 1 h. Filtration gave the crude product. Recrystallization from hot ethanol provided **(+)$_\delta$-LH** (3.05 g) as thin colorless needles in 45% yield, m.p. 105−110 °C. Crystals of **(+)$_\delta$-LH**·0.75C$_2$H$_5$OH (colorless needles) were obtained from ethanol at −40 °C. $[\alpha]_D^{20}$ = +85 (*c* = 1; CH$_2$Cl$_2$). ^{1}H NMR (CDCl$_3$): δ = 3.76−0.39 (m, 30 H, aliph. H), 4.27 (m, $^1J_{PH}$ = 213.8 Hz, 1 H, PH), 7.63−6.43 (m, 19 H, arom. H) ppm. ^{31}P NMR (CDCl$_3$): δ = −11.3 (d, $^3J_{PP}$ = 116.8 Hz, 36% PR$_2$), −12.3 (d, $^3J_{PP}$ = 105.9 Hz, 64% PR$_2$), −32.3 (d, $^3J_{PP}$ = 105.9, $^1J_{PH}$ = 213.8 Hz, 64% PHR), −38.8 (d, $^3J_{PP}$ = 116.8, $^1J_{PH}$ = 213.8 Hz, 36% PHR) ppm. MS-FD (CH$_2$Cl$_2$): *m*/*z* = 724.3 [M$^+$]. C$_{51}$H$_{50}$P$_2$ (724.9): calcd. C 84.50, H 6.95; found C 84.19, H 7.25.

Preparation of the Tertiary Diphosphanes (+)$_\delta$-LR^1 to (+)$_\delta$-LR^3: A solution of **(+)$_\delta$-LH** in abs. THF (20 mL) was treated with a small excess of a 1.6 M solution of *n*BuLi in *n*-hexane. After stirring at room temperature for 1 h, the deep red solution was cooled to −78 °C. The appropriate bromo compound [1 equiv. relative to **(+)$_\delta$-LH**] was then dissolved in THF (5 mL) and added dropwise to the solution of the deprotonated phosphane. The solution was allowed to warm up to room temperature and stirred for 16 h. Removal of the solvent and purification by crystallization or chromatography provided the pure product.

***P′*-Benzyl-*P,P,P′*-tris[(+)-9-phenyldeltacyclan-8-yl]-1,2-bis(phosphanyl)benzene, (+)$_\delta$-LR^1: (+)$_\delta$-LH** (1.30 g, 1.7 mmol) was treated with *n*BuLi (1.26 mL, 1.8 mmol, 1.6 M solution in hexane) and (bromomethyl)benzene (0.30 g, 1.7 mmol) as described above. Recrystallization from petroleum ether/toluene provided **(+)$_\delta$-LR^1** (0.53 g) as a colorless powder in 38% yield, m.p. 129−132 °C. ^{1}H NMR (CDCl$_3$): δ = 4.07−0.34 (m, 32 H, aliph. H), 7.54−5.95 (m, 24 H, arom. H) ppm. ^{31}P NMR (CDCl$_3$): δ = −12.65 (d, $^3J_{PP}$ = 178.1 Hz, 7% PR$_2$), −13.37 (d, $^3J_{PP}$ = 170.0 Hz, 93% PR$_2$), −16.56 (d, $^3J_{PP}$ = 170.0 Hz, 93% PRR′), −19.93 (d, $^3J_{PP}$ = 178.1 Hz, 7% PRR′) ppm. MS-FD (CH$_2$Cl$_2$): *m*/*z* = 814.1 [M$^+$]. C$_{58}$H$_{56}$P$_2$ (815.0): calcd. C 85.47, H 6.93; found C 84.73, H 7.67.

***P′*-(3-Bromobenzyl)-*P,P,P′*-tris[(+)-9-phenyldeltacyclan-8-yl]-1,2-bis(phosphanyl)benzene, (+)$_\delta$-LR^2: (+)$_\delta$-LH** (3.30 g, 4.6 mmol) was treated with *n*BuLi (3.55 mL, 5.1 mmol, 1.6 M solution in hexane) and 1-bromo-3-(bromomethyl)benzene (1.17 g, 4.6 mmol). Recrystallization from petroleum ether/toluene provided **(+)$_\delta$-LR^2** (1.63 g) as a colorless powder in 42% yield, m.p. 121−127 °C. ^{1}H NMR (CDCl$_3$): δ = 3.67−0.43 (m, 32 H, aliph. H), 7.54−5.95 (m, 23 H, arom. H) ppm. ^{31}P NMR (CDCl$_3$): δ = −12.59 (d, $^3J_{PP}$ = 179.8 Hz, 14% PR$_2$), −12.89 (d, $^3J_{PP}$ = 167.5 Hz, 86% PR$_2$), −16.21 (d, $^3J_{PP}$ = 167.5 Hz, 86% PRR′), −19.48 (d, $^3J_{PP}$ = 179.8 Hz, 14% PRR′) ppm. MS-FD (CH$_2$Cl$_2$): *m*/*z* = 892.3 [M$^+$]. C$_{58}$H$_{55}$BrP$_2$ (893.9): calcd. C 77.93, H 6.20; found C 77.88, H 6.80.

***P′*-(6-Bromohexyl)-*P,P,P′*-tris[(+)-9-phenyldeltacyclan-8-yl]-1,2-bis(phosphanyl)benzene, (+)$_\delta$-LR^3: (+)$_\delta$-LH** (1.70 g, 2.3 mmol) was treated with *n*BuLi (1.7 mL, 2.4 mmol, 1.6 M solution in hexane) and 1,6-dibromohexane (0.53 g, 2.3 mmol). Chromatography with petroleum ether/toluene provided **(+)$_\delta$-LR^3** (0.90 g) as a colorless powder in 45% yield, m.p. 205−210 °C. ^{1}H NMR (CDCl$_3$): δ = 3.72−0.38 (m, 42 H, aliphat. H), 7.46−6.47 (m, 19 H, arom. H) ppm. ^{31}P NMR (CDCl$_3$): δ = −12.90 (d, $^3J_{PP}$ = 164.5 Hz, 5%

PR$_2$), −15.00 (d, $^3J_{PP}$ = 158.6 Hz, 95% PR$_2$), −22.57 (d, $^3J_{PP}$ = 158.6 Hz, 95% PRR′), −25.80 (d, $^3J_{PP}$ = 164.5 Hz, 5% PRR′) ppm. MS-FD (CH$_2$Cl$_2$): *m*/*z* = 887.3 [M$^+$]. $C_{57}H_{61}BrP_2$ (888.0): calcd. C 77.10, H 6.92; found C 77.15, H 6.91.

***P*′-[3-(Diphenylphosphanyl)benzyl]-*P*,*P*,*P*′-tris[(+)-9-phenyldeltacyclan-8-yl]-1,2-bis(phosphanyl)benzene, $(+)_\delta$-LR^4: $(+)_\delta$-LR^2** (0.22 g, 0.25 mmol) was treated with *n*BuLi (1.8 mL, 2.6 mmol, 1.6 M solution in hexane) and chlorodiphenylphosphane (0.06 g, 0.25 mmol). Recrystallization from ethanol provided **$(+)_\delta$-LR^4** (0.15 g) as a fine colorless powder in 42% yield, m.p. 110−113 °C. ^{1}H NMR (CDCl$_3$): δ = 4.63−0.37 (m, 32 H, aliph. H), 7.85−5.59 (m, 33 H, arom. H) ppm. ^{31}P NMR (CDCl$_3$): δ = −4.73 (s, 22% PPh$_2$), −5.09 (s, 78% PPh$_2$), −12.65 (d, $^3J_{PP}$ = 171.8 Hz, 22% PR$_2$), −12.90 (d, $^3J_{PP}$ = 168.5 Hz, 78% PR$_2$), −16.56 (d, $^3J_{PP}$ = 168.5 Hz, 78% PRR′), −19.48 (d, $^3J_{PP}$ = 171.8 Hz, 22% PRR′) ppm. MS-FD (CH$_2$Cl$_2$): *m*/*z* = 998.6 [M$^+$]. $C_{70}H_{65}P_3$ (999.2): calcd. C 84.14, H 6.56; found C 83.31, H 6.95.

Dibromo{*P*,*P*,*P*′-tris[(+)-9-phenyldeltacyclan-8-yl]-1,2-bisphosphanylbenzene}nickel(II), [$(+)_\delta$-LH]NiBr$_2$: A suspension of **$(+)_\delta$-LH** (0.15 g, 0.21 mmol) and anhydrous NiBr$_2$ (0.05 g, 0.21 mmol) was heated in ethanol (20 mL). After cooling to room temperature, the red solution was filtered through silica gel and the solvents were evaporated to provide **[$(+)_\delta$-LH]NiBr$_2$** (0.16 g) as a dark red powder in 83% yield, m.p. 153−155 °C. ^{1}H NMR (CDCl$_3$): δ = 3.54−0.64 (m, 30 H, aliph. H), 7.72−6.34 (m, 19 H, arom. H) ppm. ^{31}P NMR (CDCl$_3$): δ = 43.27 (d, $^2J_{PP}$ = 50.9, $^1J_{PH}$ = 400.5 Hz, 84% PHR), 49.76 (d, $^2J_{PP}$ = 51.5, $^1J_{PH}$ = 408.2 Hz, 16% PHR), 72.34 (d, $^2J_{PP}$ = 50.9 Hz, 84% PR$_2$), 74.70 (d, $^2J_{PP}$ = 51.5 Hz, 16% PR$_2$) ppm. MS-FAB (CH$_2$Cl$_2$): *m*/*z* = 942.3 [M$^+$]. $C_{51}H_{50}Br_2NiP_2$ (943.4): calcd. C 64.93, H 5.34; found C 64.72, H 5.61.

{*P*′-Benzyl-*P*,*P*,*P*′-tris[(+)-9-phenyldeltacyclan-8-yl]-1,2-bisphosphanylbenzene}dibromonickel(II), [$(+)_\delta$-LR^1]NiBr$_2$: A suspension of **$(+)_\delta$-LR^1** (0.17 g, 0.21 mmol) and anhydrous NiBr$_2$ (0.05 g, 0.21 mmol) was heated in ethanol (20 mL). After cooling to room temperature, the red solution was filtered through silica gel and the solvents were evaporated to provide **[$(+)_\delta$-LR^1]NiBr$_2$** (0.21 g) as a red powder in 97% yield, m.p. 170−172 °C. ^{1}H NMR (CDCl$_3$): δ = 3.34−0.12 (m, 32 H, aliph.-H), 7.84−6.23 (m, 24 H, arom.-H) ppm. ^{31}P NMR (CDCl$_3$): δ = 66.39 (d, $^2J_{PP}$ = 50.2 Hz, 8% PRR′), 72.13 (d, $^2J_{PP}$ = 48.3 Hz, 92% PRR′), 74.99 (d, $^2J_{PP}$ = 48.3 Hz, 92% PR$_2$), 82.37 (d, $^2J_{PP}$ = 50.2 Hz, 8% PR$_2$) ppm. MS-FD (CH$_2$Cl$_2$): *m*/*z* = 1032.3 [M$^+$]. $C_{58}H_{56}Br_2NiP_2$ (1033.5): calcd. C 67.40, H 5.46; found C 67.96, H 6.98.

Dibromo{*P*′-(3-bromobenzyl)-*P*,*P*,*P*′-tris[(+)-9-phenyldeltacyclan-8-yl]-1,2-bis(phosphanyl)benzene}nickel(II), [$(+)_\delta$-LR^2]NiBr$_2$: $(+)_\delta$-LR^2 (0.39 g, 0.44 mmol) and anhydrous NiBr$_2$ (0.1 g, 0.44 mmol) were stirred in dichloromethane (10 mL). After 2 h, the red solution was filtered through silica gel and the solvents were evaporated to provide **[$(+)_\delta$-LR^2]NiBr$_2$** (0.46 g) as a red powder in 93% yield, m.p. 162−165 °C. Crystals of **[$(+)_\delta$-LR^2]NiBr$_2$** (orange plates) were obtained from a mixture of CH$_2$Cl$_2$ and ethanol at room temperature. ^{1}H NMR (CDCl$_3$): δ = 3.91−0.28 (m, 32 H, aliph. H), 8.18−5.57 (m, 23 H, arom. H) ppm. ^{31}P NMR (CDCl$_3$): δ = 67.02 (d, $^2J_{PP}$ = 49.6 Hz, 16% PRR′), 72.57 (d, $^2J_{PP}$ = 47.9 Hz, 84% PRR′), 74.77 (d, $^2J_{PP}$ = 47.9 Hz, 84% PR$_2$), 82.79 (d, $^2J_{PP}$ = 49.6 Hz, 16% PR$_2$) ppm. MS-FD (CH$_2$Cl$_2$): *m*/*z* = 1112.3 [M$^+$]. $C_{58}H_{55}Br_3NiP_2$ (1112.4): calcd. C 62.62, H 4.98; found C 62.27, H 4.91.

Dibromo{*P*′-(6-bromohexyl)-*P*,*P*,*P*′-tris[(+)-9-phenyldeltacyclan-8-yl]-1,2-bisphosphanylbenzene}nickel(II), [$(+)_\delta$-LR^3]NiBr$_2$: A suspension of **$(+)_\delta$-LR^3** (0.18 g, 0.20 mmol) and anhydrous NiBr$_2$ (0.044 g, 0.2 mmol) was heated in ethanol (20 mL) for 1 h. After cooling to room temperature and evaporating the solvent, the red residue was dissolved in CH$_2$Cl$_2$ and filtered through silica gel. Concentration provided **[$(+)_\delta$-LR^3]NiBr$_2$** (0.19 g) as a dark red powder in 84% yield, m.p. 160−163 °C. ^{1}H NMR (CDCl$_3$): δ = 3.21−0.60 (m, 40 H, aliph. H), 3.14 (t, ^1J = 6.7 Hz, 2 H, CH$_2$Br), 7.51−6.53 (m, 19 H, arom. H) ppm. ^{31}P NMR (CDCl$_3$): δ = 68.92 (d, $^2J_{PP}$ = 50.1 Hz, 4% PRR′), 71.85 (d, $^2J_{PP}$ = 48.5 Hz, 96% PRR′), 73.82 (d, $^2J_{PP}$ = 48.5 Hz, 96% PR$_2$), 78.14 (d, $^2J_{PP}$ = 50.1 Hz, 4% PR$_2$) ppm. MS-FD (CH$_2$Cl$_2$): *m*/*z* = 1106.3 [M$^+$]. $C_{57}H_{61}Br_3NiP_2$ (1106.5): calcd. C 61.87, H 5.56; found C 61.76, H 5.66.

Dichloro{*P*,*P*,*P*′-tris[(+)-9-phenyldeltacyclan-8-yl]-1,2-bis(phosphanyl)benzene}palladium(II), [$(+)_\delta$-LH]PdCl$_2$: $(+)_\delta$-LH (0.50 g, 0.70 mmol) was dissolved in THF at −78 °C. Pd(NCPh)$_2$Cl$_2$ (0.27 g, 0.70 mmol), dissolved in THF and cooled down to −78 °C, was added dropwise to the solution of the phosphane. The pale yellow solution was stirred while warming to room temperature. Washing several times with *n*-hexane and subsequent drying gave **[$(+)_\delta$-LH]PdCl$_2$** (0.62 g) as a yellow powder in 98% yield, m.p. 169 °C. ^{1}H NMR (CDCl$_3$): δ = 3.62−0.05 (m, 30 H, aliph. H), 7.67−5.33 (m, 19 H, arom. H) ppm. ^{31}P NMR (CDCl$_3$): δ = 38.82 (d, $^2J_{PP}$ = 11.8, $^1J_{PH}$ = 406.5 Hz, 91% PHR), 41.10 (d, $^2J_{PP}$ = 9.0, $^1J_{PH}$ = 410.6 Hz, 9% PHR), 74.83 (d, $^2J_{PP}$ = 11.8 Hz, 91% PR$_2$), 76.75 (d, $^2J_{PP}$ = 9.0 Hz, 9% PR$_2$) ppm. MS-FAB (CH$_2$Cl$_2$): *m*/*z* = 900.8 [M$^+$]. $C_{51}H_{50}Cl_2P_2Pd$ (902.2): calcd. C 67.89, H 5.59; found C 68.11, H 5.62.

Dibromo{*P*,*P*,*P*′-tris[(+)-9-phenyldeltacyclan-8-yl]-1,2-bis(phosphanyl)benzene}palladium(II), [$(+)_\delta$-LH]PdBr$_2$: $(+)_\delta$-LH (0.37 g, 0.51 mmol) and PdBr$_2$ (0.14 g, 0.51 mmol) were stirred in CH$_2$Cl$_2$ for 4 d at room temperature. Filtration and concentration provided **[$(+)_\delta$-LH]PdBr$_2$** (0.49 g) as an orange powder in 97% yield, m.p. 175 °C. ^{1}H NMR (CDCl$_3$): δ = 3.70−0.19 (m, 30 H, aliph. H), 7.53−5.19 (m, 19 H, arom. H) ppm. ^{31}P NMR (CDCl$_3$): δ = 39.45 (d, $^2J_{PP}$ = 17.6, $^1J_{PH}$ = 410.6 Hz, 45% PHR), 43.96 (d, $^2J_{PP}$ = 14.5, $^1J_{PH}$ = 419.0 Hz, 55% PHR), 76.52 (d, $^2J_{PP}$ = 17.6 Hz, 45% PR$_2$), 79.10 (d, $^2J_{PP}$ = 14.5 Hz, 55% PR$_2$) ppm. MS-FAB (CH$_2$Cl$_2$): *m*/*z* = 990.4 [M$^+$]. $C_{51}H_{50}Br_2P_2Pd$ (991.1): calcd. C 61.80, H 5.08; found C 61.16, H 5.72.

Diiodo{*P*,*P*,*P*′-tris[(+)-9-phenyldeltacyclan-8-yl]-1,2-bis(phosphanyl)benzene}palladium(II), [$(+)_\delta$-LH]PdI$_2$: $(+)_\delta$-LH (0.50 g, 0.70 mmol) and PdI$_2$ (0.25 g, 0.70 mmol) were suspended in benzene and refluxed for 4 h. After cooling to room temperature the solution was filtered and the solvent evaporated. **[$(+)_\delta$-LH]PdI$_2$** (0.49 g) remained as a red powder in 99% yield, m.p. 183 °C. Crystals of **[$(+)_\delta$-LH]PdI$_2$·**CH$_2$Cl$_2$ (orange plates) were obtained from a mixture of CH$_2$Cl$_2$ and methanol at room temperature. ^{1}H NMR (CDCl$_3$): δ = 3.35−0.08 (m, 30 H, aliph. H), 4.45 (m, 1 H, $^1J_{PH}$ = 404.9 Hz, 1 H, PH, 42%), 7.63−6.29 (m, 19 H, arom. H) ppm. ^{31}P NMR (CDCl$_3$): δ = 38.02 (d, $^2J_{PP}$ = 16.5, $^1J_{PH}$ = 404.9 Hz, 42% PHR), 45.29 (d, $^2J_{PP}$ = 13.5, $^1J_{PH}$ = 413.8 Hz, 58% PHR), 75.77 (d, $^2J_{PP}$ = 16.5 Hz, 42% PR$_2$), 80.09 (d, $^2J_{PP}$ = 13.5 Hz, 58% PR$_2$) ppm. MS-FAB (CH$_2$Cl$_2$): *m*/*z* = 1084.5 [M$^+$]. $C_{51}H_{50}I_2P_2Pd$ (1085.1): calcd. C 56.45, H 4.64; found C 56.43, H 4.86.

{*P*′-Chloro-*P*,*P*,*P*′-tris[(+)-9-phenyldeltacyclan-8-yl)-1,2-bis(phosphanyl)benzene}diiodopalladium(II), [$(+)_\delta$-LCl]PdI$_2$: $(+)_\delta$-LH (0.59 g, 0.81 mmol) and PdI$_2$ (0.29 g, 0.81 mmol) were suspended in CH$_2$Cl$_2$ and stirred for 3 d followed by filtration and evaporation of the solvent. Crystallization from a 1:2 mixture of CH$_2$Cl$_2$/diethyl ether gave **[$(+)_\delta$-LCl]PdI$_2$** (0.08 g) as dark red-brown crystals in nearly 10% yield, m.p. 188 °C. ^{1}H NMR (CDCl$_3$): δ = 3.50−0.08 (m, 30 H, aliph. H), 7.65−6.38 (m, 19 H, arom. H) ppm. ^{31}P NMR

Table 1. Crystal data, data collection, structure refinement and CCDC numbers

	$(+)_{\delta}$-LH	**$[(+)_{\delta}$-LR$^2]$NiBr$_2$**	**$[(+)_{\delta}$-LH$]$PdI$_2$**	**$[(+)_{\delta}$-LCl$]$PdI$_2$**
Empirical formula	$C_{51}H_{49}P_2 \cdot 0.75C_2H_5OH$	$C_{58}H_{55}Br_3NiP_2$	$C_{51}H_{50}I_2P_2Pd \cdot CH_2Cl_2$	$C_{51}H_{49}ClI_2P_2Pd$
M_r	758.40	1112.32	1170.00	1119.52
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_1$	$P2_1$	$P2_1$	$P2_1$
Z	4	2	4	4
Unit cell dimensions	a = 14.032(5) Å	a = 10.2507(5) Å	a = 17.4832(10) Å	a = 11.1979(8) Å
	b = 10.574(5) Å	b = 21.4953(14) Å	b = 25.0485(16) Å	b = 26.5169(13) Å
	c = 28.351(5) Å	c = 11.2945(5) Å	c = 10.8323(6) Å	c = 17.2105(13) Å
	β = 91.79(0)°	β = 92.277(6)°	β = 81.189(6)°	β = 107.596(9)°
Volume	4205(3) Å^3	2486.7(2) Å^3	4687.8(5) Å^3	4871.3(6) Å^3
$D_{calcd.}$	1.198 g/cm^3	1.486 g/cm^3	1.658 g/cm^3	1.526 g/cm^3
Absorption coefficient	0.14 mm^{-1}	2.902 mm^{-1}	1.931 mm^{-1}	1.80 mm^{-1}
F(000)	1618	1132	2320	2216
Crystal size	0.24 × 0.10 × 0.06 mm	0.18 × 0.08 × 0.03 mm	0.70 × 0.68 × 0.09 mm	0.30 × 0.26 × 0.04 mm
Crystal description	prism	plates	plates	plates
Crystal color	colorless	orange	orange	red-brown
θ range for data collection	2.01−25.25°	1.89−25.81°	1.90−25.75°	1.94−25.23°
Limiting indices	$-16 \le h \le 16$	$-12 \le h \le 12$	$-21 \le h \le 21$	$-13 \le h \le 13$
	$-12 \le k \le 12$	$-26 \le k \le 26$	$-30 \le k \le 30$	$-31 \le k \le 31$
	$-33 \le l \le 33$	$-13 \le l \le 13$	$-13 \le l \le 13$	$-20 \le l \le 20$
Reflections collected	52421	23851	65722	42020
Independent reflections (R_{int})	15114 (0.0947)	9505 (0.0691)	16715 (0.0361)	16817 (0.0711)
Reflections $I > 2\sigma(I)$	7489	6391	16267	13587
Data/restraints/parameters	15114/1/955	9505/1/587	16715/1/1069	16817/1/1027
Absorption correction	none	numerical	numerical	numerical
Transmission (min/max)	−/−	0.8790/0.6667	0.8231/0.2928	0.8978/0.6379
Goodness-of-fit on F^2	0.686	0.848	1.067	0.902
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0436	R_1 = 0.0452	R_1 = 0.0259	R_1 = 0.0420
	wR_2 = 0.0611	wR_2 = 0.0763	wR_2 = 0.0680	wR_2 = 0.0914
R indices (all data)	R_1 = 0.0984	R_1 = 0.0783	R_1 = 0.0269	R_1 = 0.0534
	wR_2 = 0.0719	wR_2 = 0.0833	wR_2 = 0.0716	wR_2 = 0.0949
Absolute structure parameter	−0.03(6)	0.00(1)	−0.02(1)	−0.02(2)
Largest diff. peak/hole	0.318/−0.167 e Å^{-3}	0.749/−0.282 e Å^{-3}	0.949/−0.839 e Å^{-3}	1.489/−0.476 e Å^{-3}
CCDC-	178668	178669	178670	178667

(CDCl$_3$): δ = 62.68 (d, $^2J_{PP}$ = 13.2 Hz, 15% PR$_2$), 68.87 (d, $^2J_{PP}$ = 8.8 Hz, 85% PR$_2$), 123.29 (d, $^2J_{PP}$ = 8.8 Hz, 85% PClR), 126.46 (d, $^2J_{PP}$ = 13.2 Hz, 15% PClR). MS-ESI (CH$_3$OH): m/z = 1151.3 [M + MeOH]$^+$. $C_{51}H_{49}ClI_2P_2Pd$ (1119.6): calcd. C 54.71, H 4.41; found C 55.46, H 4.99.

Dichloro{*P,P,P'*-tris[(+)-9-phenyldeltacyclan-8-yl]-1,2-bis(phosphanyl)benzene]platinum(II), $[(+)_{\delta}$-LH$]$PtCl$_2$: K$_2$PtCl$_4$ (0.16 g, 0.37 mmol) was dissolved in a small amount of concd. HCl, diluted with 40 mL of ethanol and heated to reflux. **$(+)_{\delta}$-LH** (0.27 g, 0.37 mmol), dissolved in 10 mL of toluene, was added dropwise to the dark brown solution and stirred for 3 h. After cooling to room temperature, the solution was filtered and the solvents were evaporated. **$[(+)_{\delta}$-LH$]$PtCl$_2$** (0.30 g) remained as a cream-colored powder in 83% yield, m.p. 225 °C. ^{1}H NMR (CDCl$_3$): δ = 5.03−0.15 (m, 30 H, aliph. H), 7.87−6.39 (m, 19 H, arom. H) ppm. ^{31}P NMR (CDCl$_3$): δ = 15.23 (d, $^2J_{PP}$ = 2.5, $^1J_{PH}$ = 416, $^1J_{PtP}$ = 3531 Hz, 20% PHR), 15.90 (d, $^2J_{PP}$ = 3.1, $^1J_{PH}$ = 414, $^1J_{PtP}$ = 3508 Hz, 80% PHR), 47.20 (d, $^2J_{PP}$ = 2.5, $^1J_{PtP}$ = 3531 Hz, 20% PR$_2$), 48.67 (d, $^2J_{PP}$ = 3.1, $^1J_{PtP}$ = 3508 Hz, 80% PR$_2$) ppm. MS-ESI (CH$_2$Cl$_2$): m/z = 987.5 [M$^+$]. $C_{51}H_{50}Cl_2P_2Pt$ (990.9): calcd. C 61.82, H 5.09; found C 62.24, H 5.02.

Dibromo{*P,P,P'*-tris[(+)-9-phenyldeltacyclan-8-yl]-1,2-bis(phosphanyl)benzene}platinum(II), $[(+)_{\delta}$-LH$]$PtBr$_2$: A solution of Pt(cod)Br$_2$ (0.11 g, 0.24 mmol) and **$(+)_{\delta}$-LH** (0.18 g, 0.24 mmol) in 20 mL of benzene was stirred for 20 h at room temperature. After filtration, the solvent was removed. The residue was washed with pentane to afford **$[(+)_{\delta}$-LH$]$PtBr$_2$** (0.19 g) as a pale yellow powder in 75% yield, m.p. > 250 °C. ^{1}H NMR (CDCl$_3$): δ = 3.75 (m, 30 H, aliph. H), 7.61−6.33 (m, 19 H, arom. H) ppm. ^{31}P NMR (CDCl$_3$): δ = 51.81 (s, $^2J_{PP}$ = 2.2, $^1J_{PtP}$ = 3484 Hz, 31% PR$_2$), 49.77 (s, $^2J_{PP}$ = 2.2, $^1J_{PtP}$ = 3504 Hz, 69% PR$_2$), 21.49 (s, $^2J_{PP}$ = 2.4, $^1J_{PH}$ = 419, $^1J_{PtP}$ = 3305 Hz, 31% PHR), 18.19 (s, $^2J_{PP}$ = 2.2, $^1J_{PH}$ = 417, $^1J_{PtP}$ = 3322 Hz, 69% PHR) ppm. MS-ESI (CH$_2$Cl$_2$/MeOH): m/z = 1079.2 [M − H]$^+$. $C_{51}H_{50}Br_2P_2Pt$ (1079.8): calcd. C 56.73, H 4.67; found C 56.63, H 4.85.

X-ray Crystallographic Studies: The data were collected with a STOE-IPDS diffractometer with Mo-K_{α} radiation and graphite monochromator at a temperature of 173(1) K. Crystal data, data collection, structure refinement and CCDC numbers for **$(+)_{\delta}$-LH**, **$[(+)_{\delta}$-LR$^2]$NiBr$_2$**, **$[(+)_{\delta}$-LH$]$PdI$_2$** and **$[(+)_{\delta}$-LCl$]$PdI$_2$** are given in Table 1. The structures were solved by direct methods (SIR-97) and refined by full-matrix least squares on F^2 (SHELXL-97). The H atoms were calculated geometrically and a riding model was applied during the refinement process. Absorption corrections, when necessary, were carried out numerically from the crystal shape (x-RED).[25] CCDC numbers given in Table 1 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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