Optically Active Transition Metal Compounds. 135.[1] Half-Sandwich Complexes [(η^5-C_5Me_5)M(P-P′)Hal]X with Chiral Metal (Rh, Ir) and Phosphorus Atoms

Henri Brunner,* Ilias Grau, and Manfred Zabel†

Institut für Anorganische Chemie, Universität Regensburg, D-93040 Regensburg, Germany

Received March 8, 2004

Reaction of [(Cp*MHal)$_2$](μ-Hal)$_2$] (Cp* = η^5-C_5Me_5; M = Rh, Ir; Hal = Cl, Br, I) with the unsymmetrical chelate phosphane P-P′ (=*P*,*P*,*P*′-tris[(+)-9-phenyldeltacyclan-8-yl]-1,2-bis-(phosphanyl)benzene) in the presence of the metathesis reagents NH_4PF_6, $NaBF_4$, and $NaBPh_4$ gave [Cp*M(P-P′)Hal]X (X = PF_6, BF_4, BPh_4; **1**−**9**) in high yields. The P-P′ ligand, easily accessible from norbornadiene and phenylacetylene in a highly enantioselective synthesis, contains three (+)-9-phenyldeltacyclan-8-yl substituents with a total of 24 homochiral asymmetric carbon atoms. The stereogenic metal center and the secondary phosphorus atom give rise to four diastereomers, all of which are formed in the synthesis of compounds **1**−**9**. Crystallization of the diastereomer mixtures afforded 11 single crystals of compounds **1**−**9**, which served to determine the absolute configurations at the metal atom and the secondary phosphorus atom. Surprisingly, all the compounds with the same configuration adopted almost identical conformations (types I−III). Moreover, compounds belonging to the same configuration series showed remarkably constant chemical shifts of their $^{31}P\{^1H\}$ NMR signals. The (+)-Norphos complexes [Cp*M(Norphos)Cl]PF_6 (M = Rh, Ir; Norphos = (2*S*,3*S*)-(+)-bis(diphenylphosphanyl)bicyclo[2.2.1]hept-5-ene; **10** and **11**) were synthesized for comparison, which formed two diastereomers. On crystallization both the Rh and the Ir complexes crystallized as 1:1 mixtures of diastereomers, differing in the metal configuration.

Introduction

Deltacyclenes are the products of the [2 + 2 + 2] homo-Diels−Alder reaction of 2,5-norbornadiene and acetylenes in the presence of transition-metal catalysts.[2] In 1978 a procedure was published which afforded deltacyclenes from terminal acetylenes in high yields by using a combination of $Co(acac)_3$, triphenylphosphane, and a reducing agent as the catalyst.[3] Replacement of the achiral triphenylphosphane by optically active phosphanes rendered the reaction enantioselective.[4,5] Thus, the procatalyst $Co(acac)_3$ together with the cocatalyst Norphos and the reducing agent Et_2AlCl in the solvent THF gave nearly enantiopure deltacyclenes.[6] This is a reliable way to prepare (+)-8-phenyldeltacyclene, the starting material in the present study, from 2,5-norbornadiene and phenylacetylene in large quantities with an enantiomeric excess of >97.5%. Subsequently, other catalysts and acetylenic substrates were used.[7−14]

Due to the double bond in (+)-8-phenyldeltacyclene further derivatization reactions can be carried out: e.g., the addition of P−H bonds such as in Ph_2PH leading to chiral phosphanes.[12] The reaction of 1,2-bis(phosphanyl)benzene with a 4-fold excess of (+)-8-phenyldeltacyclene did not give a chelate ligand with four deltacyclanyl substituents at the two phosphorus atoms, because the reaction stopped after three P−H additions.[12] Obviously, steric hindrance prevents the addition of the fourth P−H bond to another (+)-8-phenyldeltacyclene to give a fully substituted diphosphane. The resulting trisubstitution product *P*,*P*,*P*′-tris[(+)-9-phenyldeltacyclan-8-yl]-1,2-bis(phosphanyl)benzene (P-P′) is an unsymmetrical chelate ligand consisting of a tertiary phosphorus atom and a chiral secondary phosphorus atom. Note that in the P−H addition carbon atoms 8 and 9 of the deltacyclane skeleton change priorities. Thus, (+)-8-phenyldeltacyclene becomes the (+)-9-phenyldeltacyclan-8-yl substituent.

(+)-8-Phenyldeltacyclene contains six chiral carbon atoms built up stereospecifically in the deltacyclene formation. After P−H addition to the double bond of (+)-8-phenyldeltacyclene, the number of asymmetric carbon

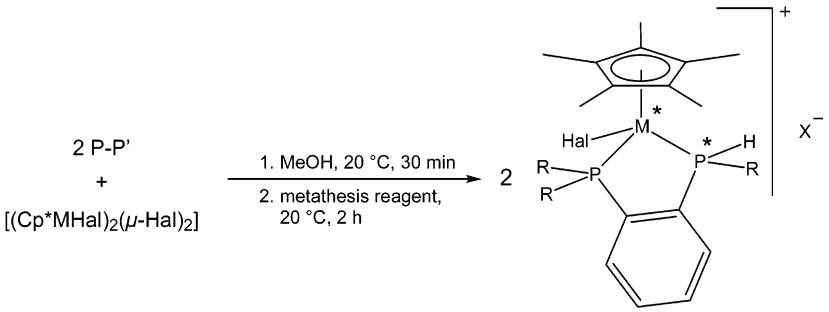
* To whom correspondence should be addressed. Fax: +49-941-9434439. E-mail: henri.brunner@chemie.uni-regensburg.de.

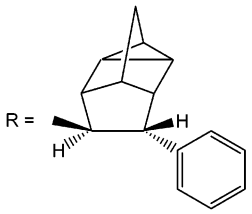
† X-ray structure analyses.

(1) Part 134: Brunner, H.; Weber, M.; Zabel, M.; Zwack, T. *Angew. Chem., Int. Ed.* **2003**, *42*, 1859.
(2) Lautens, M.; Klute, W.; Tam, W. *Chem. Rev.* **1996**, *96*, 49.
(3) Lyons, J. E.; Myers, H. K.; Schneider, A. *J. Chem. Soc., Chem. Commun.* **1978**, 636.
(4) Brunner, H.; Muschiol, M.; Prester, F. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 653.
(5) Lautens, M.; Lautens, J. C.; Smith, A. C. *J. Am. Chem. Soc.* **1990**, *112*, 5627.
(6) Brunner, H.; Prester, F. *J. Organomet. Chem.* **1991**, *414*, 401.
(7) Duan, I. F.; Cheng, C. H.; Shaw, J. S.; Cheng, S. S.; Lion, K. F. *J. Chem. Soc., Chem. Commun.* **1991**, 1347.
(8) Binger, P.; Albus, S. *J. Organomet. Chem.* **1991**, *414*, 401.
(9) Pardigon, O.; Buono, G. *Tetrahedron: Asymmetry* **1993**, *4*, 1977.
(10) Pardigon, O.; Alphonse, T.; Buono, G. *J. Org. Chem.* **1995**, *60*, 1886.
(11) Brunner, H.; Reimer, A. *Bull. Soc. Chim. Fr.* **1997**, *134*, 307.
(12) Brunner, H.; Reimer, A. *Chem. Ber./Recl.* **1997**, *130*, 1495.

10.1021/om0400292 CCC: $27.50
Publication on Web 06/26/2004

Scheme 1. Synthesis of the Half-Sandwich Complexes [Cp*M(P-P′)Hal]X (1−9)





M = Rh, Hal =Cl, X = PF_6	**1**
M = Rh, Hal = Cl, X = BF_4	**2**
M = Rh, Hal = Cl, X = BPh_4	**3**
M = Rh, Hal = Br, X = PF_6	**4**
M = Rh, Hal = Br, X = BF_4	**5**
M = Rh, Hal = Br, X = BPh_4	**6**
M = Rh, Hal = I, X = BPh_4	**7**
M = Ir, Hal = Cl, X = PF_6	**8**
M = Ir, Hal = Cl, X = BPh_4	**9**

atoms increases to 8 in the (+)-9-phenyldeltacyclan-8-yl substituent. Thus, the trisubstituted ligand P-P′ comprises 24 chiral centers (8 × 3) in the three deltacyclanyl substituents. The 25th stereogenic center in P-P′ is the secondary phosphorus atom. Due to the well-known configurational lability of secondary phosphanes fast epimerization takes place in the free ligand.[15−17] The diastereomer ratio of P-P′ at room temperature in $CDCl_3$ is 64:36 (28% de).[18]

Recently the coordination chemistry of the ligand P-P′ and its anion toward Ni(II), Pd(II), and Pt(II) was investigated. Mononuclear, dinuclear, and, surprisingly, trinuclear complexes were formed,[18,19] in which the square-planar M(II) arrangements did not contribute to stereogenicity. This is different for half-sandwich complexes of the type [Cp*M(P-P′)Hal]X (M = Rh, Ir) in which the metal atom is a stereogenic center. The present study deals with the various combinations of the configurations at the metal atoms and the secondary phosphorus atoms in compounds of the type [Cp*M(P-P′)Hal]X (M = Rh, Ir) in addition to the stable chiral carbon centers in the (+)-9-phenyldeltacyclan-8-yl substituents, which only show up in the + sign in front of the name of the substituent.[20] This + sign implies that the P-substituted carbon atom of the (+)-9-phenyldeltacyclanyl group has an *S* configuration, the phenyl-substituted carbon atom an *R* configuration, etc.[18] The compounds [Cp*M(P-P′)Hal]X with P-P′ = *P*,*P*,*P*′-tris-[(+)-9-phenyldeltacyclan-8-yl]-1,2-bis(phosphanyl)benzene are compared with the corresponding compounds [Cp*M(Norphos)Hal]X ((+)-Norphos = (2*S*,3*S*)-(+)-bis-(diphenylphosphanyl)bicyclo[2.2.1]hept-5-ene).[20,21]

Results

Synthesis and $^{31}P\{^1H\}$ NMR Spectra. Reaction of the dinuclear chloro complex $[(Cp^*RhCl)_2(\mu\text{-}Cl)_2]$ with the chelate ligand *P*,*P*,*P*′-tris[(+)-9-phenyldeltacyclan-8-yl]-1,2-bis(phosphanyl)benzene (P-P′) in methanol (molar ratio 1:2) followed by addition of the metathesis reagent NH_4PF_6 in small excess afforded the half-sandwich compound $[Cp^*Rh(P\text{-}P')Cl]PF_6$ (**1**) in 96% yield (Scheme 1).

Compound **1** should consist of four diaststereomers differing in the configuration at the metal center and the secondary phosphorus atom. All four were observed in the $^{31}P\{^1H\}$ NMR spectrum (**1** in Figure 1). Each diastereomer gave rise to an AMX pattern: **A** (δ 41.9 and 81.8 ppm, 19%), **B** (δ 51.5 and 78.5 ppm, 18%), **C** (δ 48.3 and 66.6 ppm, 26%) and **D** (δ 47.3 and 60.5 ppm, 37%) with coupling constants in the ranges $^2J_{PP}$ = 32.0−36.6 Hz and $^1J_{PRh}$ = 125.7−133.9 Hz, as expected for compounds of this type.[22−24] The signals at higher ppm values are due to the phosphorus atoms of the PR_2 groups. The signals at lower ppm values were assigned to the stereogenic phosphorus atoms PRH on the basis of PH coupling ($^1J_{PH}$ = 361−402 Hz) in the ^{31}P NMR spectra.

(13) Brunner, H.; Reimer, A. *Bull. Soc. Chim. Belg.* **1997**, *106*, 267.
(14) Pardigon, O.; Alphonse, T.; Buono, G. *Tetrahedron Lett.* **2000**, *41*, 4089.
(15) Bader, A.; Pabel, M.; Salem, G.; Wild, S. B. *J. Chem. Soc., Chem. Commun.* **1994**, 1405.
(16) Bader, A.; Nullmeyers, T.; Pabel, M.; Salem, G.; Willis, A. C.; Wild, S. B. *Inorg. Chem.* **1995**, *34*, 393.
(17) Albert, J.; Cadena, J. M.; Garnell, J.; Muller, G.; Panyella, D.; Snudo, C. *Eur. J. Inorg. Chem.* **2000**, 1283.
(18) Brunner, H.; Dormeier, S.; Zabel, M. *Eur. J. Inorg. Chem.* **2002**, 2594.
(19) Brunner, H.; Dormeier, S.; Grau, I.; Zabel, M. *Eur. J. Inorg. Chem.* **2002**, 2603.
(20) Grau, I. Ph.D. Thesis, University of Regensburg, 2003.
(21) Brunner, H.; Pieronczyk, W. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 620.
(22) Carmona, D.; Lahoz, F. J.; Oro, L. A.; Lamata, M. P.; Viguri, F.; José, E. S. *Organometallics* **1996**, *15*, 2961.
(23) Valderrama, M.; Contreras, R.; Boys, D. *J. Organomet. Chem.* **2003**, *665*, 7.
(24) Hughes, R. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Ed.; Pergamon Press: Oxford, U.K., 1982; Vol. 5.

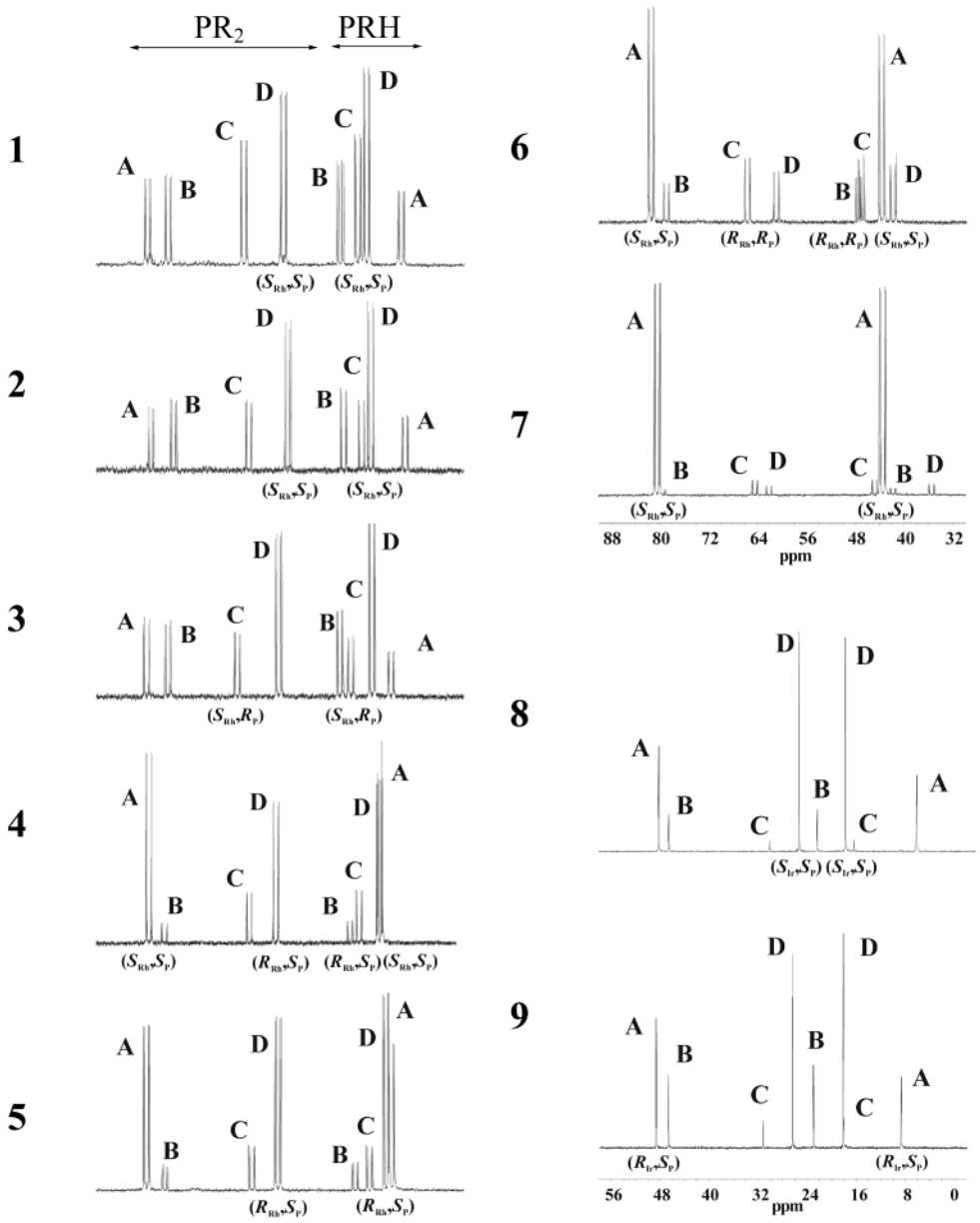
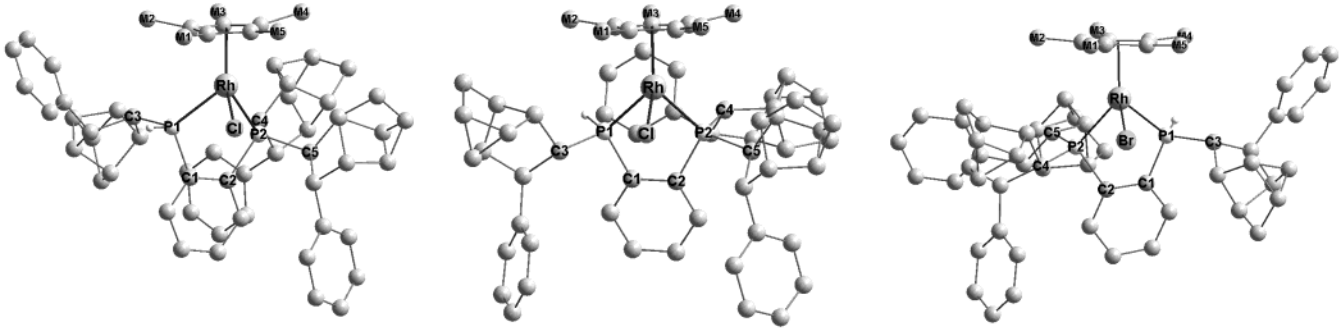


Figure 1. $^{31}P\{^1H\}$ NMR spectra ($CDCl_3$, 162 MHz) for the compounds [Cp*M(P-P′)Hal]X (**1**−**9**). The scales for the Rh complexes **1**−**7** and the Ir complexes **8** and **9** are shifted with respect to each other. The configurations determined by X-ray analysis have been entered.

In the present study nine compounds of the type [Cp*M(P-P′)Hal]X (**1**−**9**; M = Rh, Ir; Hal = Cl, Br, I; X = PF_6, BF_4, BPh_4) were synthesized. The chloro complexes **2** and **3** were prepared using the metathesis reagents $NaBF_4$ and $NaBPh_4$. It was not possible to obtain compounds of the bromo or iodo series [Cp*Rh(P-P′)Hal]X by treating the chloro complexes [Cp*Rh(P-P′)Cl]X with NaBr or NaI in methanol or acetone, which normally is no problem.[25,26] Even in combination with silver salts no exchange took place, indicating the extreme steric hindrance caused by the bulky P-P′ ligand. Thus, the bromo and iodo compounds **4**−**7** had to be synthesized by starting from $[(Cp^*RhHal)_2(\mu\text{-}Hal)_2]$ (Hal = Br, I). For the synthesis of compounds **8** and **9** $[(Cp^*IrCl)_2(\mu\text{-}Cl)_2]$ was used as the starting material. For all compounds **1**−**9** the yields were 90% or better.

The $^{31}P\{^1H\}$ NMR spectra of the rhodium compounds **1**−**7** are very similar (Figure 1). All of them showed the typical AMX signals of the four diastereomers **A**−**D** at nearly the same ppm values. The PH coupling constants are given in the Experimental Section only for those diastereomers for which the signals do not overlap. They were obtained from ^1H-coupled ^{31}P NMR spectra or from PH coupling in ^1H NMR spectra. Throughout the paper the designation **A** is chosen for the diastereomer with the highest ppm value of the PR_2 phosphorus atom, continuing with **B**−**D** to lower ppm values. The amounts of the diastereomers **A**−**D** varied to some extent, although the diastereoselectivity in general was not very high, as indicated in the intensities of the $^{31}P\{^1H\}$ NMR spectra.

(25) Enders, D.; Gielen, H.; Raabe, G.; Runsink, J.; Teles, J. H. *Chem. Ber.* **1997**, *130*, 1253.
(26) Brunner, H.; Köllnberger, A.; Zabel, M. *Polyhedron* **2003**, *22*, 2639.



(S_{Rh},S_P)-[Cp*Rh(P-P')Cl]PF_6 **1** type I

(S_{Rh},R_P)-[Cp*Rh(P-P')Cl]BPh_4 **3** type II

(S_{Rh},S_P)-[Cp*Rh(P-P')Br]BPh_4 **6** type III

Dihedral angles M-P-C_Δ-C(Ph) [°] (order PRH, PR_2(1), PR_2(2))

(S_{Rh},S_P)-**1**: -148.43(14), -172.01(15), 75.29(19)
(S_{Rh},S_P)-**2**: -145.31(14), -172.01(16), 72.3(2)
(R_{Rh},S_P)-**4**: -147.46(12), -171.35(13), 74.86(17)
(R_{Rh},S_P)-**5**: -144.98(0), -171.21(0), 72.78(1)
(S_{Ir},S_P)-**8**: -148.48(0), -171.52(0), 75.47(0)

(S_{Rh},R_P)-**3**: 171.76(29), -109.72(34), 75.02(40)
(R_{Rh},R_P)-**6**: 171.33(49), -107.84(55), 74.87(71)

(S_{Rh},S_P)-**4**: -117.27(43), 170.47(44), -177.14(32)
(S_{Rh},S_P)-**6**: -154.48(1), 157.20(1), 176.37(1)
(S_{Rh},S_P)-**7**: -150.89(45), 157.62(53), 178.34(47)
(R_{Ir},S_P)-**9**: -152.27(85), 155.56(105), 175.91(90)

Figure 2. Structures of the cations of compounds **1**, **3**, and **6** and dihedral angles M−P−C_Δ−C(Ph) (deg) of type I−III conformations.

The Chloro Compounds [Cp*Rh(P-P′)Cl]X (1−3). It was not possible to separate the four diastereomers **A**−**D** of compound **1** by chromatography, but crystallization was successful. Orange prisms suitable for X-ray structure analysis were obtained by slow diffusion of *n*-hexane into a solution of [Cp*Rh(P-P′)Cl]PF_6 (**1**) in acetone. The structure of the cation of the isolated diastereomer of compound **1** is shown in Figure 2 (left). The coordination around the rhodium is octahedral, with the Cp* group occupying three *fac* positions. Applying the priority sequences Cp* > Cl > PR_2 > PRH for the Rh atom[27,28] and Rh > $C_{benzene}$ > C_Δ > H for the stereogenic P atom compound **1** has an S_{Rh},S_P configuration (the subscript Δ is an abbreviation for the (+)-9-phenyldeltacyclanyl substituent).

The cyclopentadienyl ring is roughly planar with slightly different C−C (range 1.396(4)−1.448(4) Å) and Rh−C (range 2.197(3)−2.299(3) Å) bond lengths. The rhodium atom lies 1.881(0) Å apart from the least-squares plane through the five-membered carbocyclic ring. The methyl substituents are bent away from the rhodium. Due to the steric hindrance of the (+)-9-phenyldeltacyclan-8-yl substituents, the largest displacements occur for M2, M3, and M4: 10.68(25), 11.15(24), and 11.42(25)°, respectively (Figure 2). For the methyl groups M1 and M5, oriented to the P−H side and the chloro ligand, smaller displacements 4.23(27) and 6.07(27)° are observed. The two Rh−P bonds are slightly different from each other, 2.260(1) Å for the PRH phosphorus atom P1 and 2.360(1) Å for the PR_2 phosphorus atom P2, carrying two (+)-9-phenyldeltacyclan-8-yl groups. The Rh−Cl distance is 2.400(1) Å. The angles around the rhodium P1−Rh−P2, P2−Rh−Cl, and Cl−Rh−P1 are 82.68(2), 90.54(2), and 81.46(2)° with the chlorine oriented to the less sterically hindered phosphorus atom P1 (see Discussion). Except for (S_{Rh},S_P)-**7** these features are typical for all 11 structures determined for the different diastereomers of compounds **1**−**9** in this study, in line with literature results.[22,29,30]

Interestingly, the 11 structures belong to only three conformation types, designated I (5 cases), II (2 cases), and III (4 cases), depending on the configurations at the Rh and P atoms (Figure 2). It is the rotation about the P−C_Δ bonds that is responsible for the position of the deltacyclanyl groups and, in particular, its phenyl substituent (and to a lesser extent the rotation of the phenyl ring about the C_{ipso}−C_Δ bond), which determines the conformation of the cations [Cp*M(P-P′)Hal]$^+$ irrespective of the anions PF_6^-, BF_4^-, and BPh_4^-. A measure of the rotation of the deltacyclanyl substituents about the P−C_Δ bond is the torsion angle M−P−C_Δ-C(Ph). For **1** (type I) Rh−P1−C3−C(Ph) = −148.43(14)° places the phenyl ring in a kind of equatorial position slightly oriented toward Cp*, whereas Rh−P2−C5−C(Ph) = 75.29(19)° turns the phenyl ring in a hanging position away from Cp*. Rh−P2−C4−C(Ph) = −172.01(15)° allows the phenyl ring to form a π-stack with the phenylene system of the chelate ring (distance of ring centers 4.611(0) Å), present in all type I structures but absent in the type II and III structures (Figure 2).

The $^{31}P\{^1H\}$ NMR spectrum, obtained on dissolution of the isolated crystals of **1**, showed only the AMX pattern of diastereomer **D**. Consequently, from the **A**−**D** diastereomer mixture of compound **1** the most abundant diastereomer **D** had crystallized and, according to the X-ray analysis, its signals can be assigned to (S_{Rh},S_P)-**1** (Figure 1). The $^{31}P\{^1H\}$ NMR spectrum of a solution of (S_{Rh},S_P)-**1** in $CDCl_3$ did not show any change after 1 week. Thus, epimerization leading to diastereomers

(27) Lecomte, C.; Dusausoy, Y.; Protas, J.; Tirouflet, J.; Dormond, A. *J. Organomet. Chem*. **1974**, *73*, 67.
(28) Brunner, H. *Enantiomer* **1997**, *2*, 133.
(29) Kölle, U.; Raabe, E.; Krüger, C.; Rotzinger, F. P. *Chem. Ber*. **1987**, *120*, 979.
(30) Voninon, T.; Ziessel, R. *J. Organomet. Chem*. **1989**, *363*, 179.

A−**C** of **1** did not take place. (S_{Rh},S_P)-**1** is a half-sandwich complex configurationally stable both at the rhodium atom and at the secondary phosphorus atom. This behavior was typical for all the diastereomers isolated in pure form in this study. On standing in solution for 1 week there was no interconversion to other diastereomers, in accord with the results of Carmona et al., who did not observe a change of the metal configuration in the complexes [Cp*Rh(Prophos)Cl]X (X = Cl, BF_4) in $CHCl_3$ up to temperatures of 55 °C.[22]

The diastereomer mixture of [Cp*Rh(P-P′)Cl]BF_4 (**2**), differing from compound **1** in the counterion, has almost the same composition as that of **1**: **A**, 17%; **B**, 25%; **C**, 21%; **D**, 37%. From the yellow acetone solution of the diastereomer mixture of **2** crystals suitable for X-ray structure analysis were obtained after layering with *n*-hexane. The absolute configuration of the cation of the orange prisms **2** turned out to be S_{Rh},S_P. Independent of the change in the anion the cation of **2** had the same configuration as the cation of **1**, and moreover, it adopted the same type I conformation (Figure 2). The molecular parameters found for (S_{Rh},S_P)-**2** compared well with those of (S_{Rh},S_P)-**1**. The $^{31}P\{^1H\}$ NMR spectrum of (S_{Rh},S_P)-**2** showed only the AMX pattern of the main diastereomer **D** at ppm values and with chemical shifts and coupling constants similar to those of (S_{Rh},S_P)-**1** (Figure 1).

For the yellow BPh_4^- salt [Cp*Rh(P-P′)Cl]BPh_4 (**3**), formed in quantitative yield according to Scheme 1, the composition of the diastereomer mixture was as follows: **A**, 18%; **B**, 21%; **C**, 19%; **D**, 42%. By slow diffusion of *n*-hexane into an acetone solution of **3** extremly fine orange needles were obtained. The X-ray structure analysis carried out with a suitable crystal revealed an S_{Rh},R_P configuration. Thus, in contrast to **1** and **2**, in which the phosphorus configuration had been S_P, in **3** the secondary phosphorus atom adopted an R_P configuration, the metal configuration being in all three cases S_{Rh}. The signals in the $^{31}P\{^1H\}$ NMR spectrum obtained with the solution of the fine needles corresponded to diastereomer **A** of the **A**−**D** mixture. This observation led to a discrepancy in that according to the unambiguous system presented in the Discussion the S_{Rh},R_P configuration of the crystal selected for the X-ray analysis must be assigned to diastereomer **C** (see Discussion). Obviously, in the fine needles consisting of diastereomer **A** obtained on crystallization there had been a few crystals of diastereomer **C** which served for the X-ray analysis but did not show up in the $^{31}P\{^1H\}$ NMR spectrum of the bulk solution (Figure 1). (S_{Rh},R_P)-**3** belongs to a type II conformation (Figure 2, middle) with two hanging phenyls and one phenyl opposite to the chloride ligand close to Cp*.

The Bromo Compounds [Cp*Rh(P-P′)Br]X (4−**6).** [Cp*Rh(P-P′)Br]PF_6 (**4**) was obtained as the following diastereomer mixture: **A**, 48%; **B**, 6%; **C**, 12%; **D**, 34%. Surprisingly, crystallization by slow diffusion of *n*-hexane into an acetone solution of **4** gave two different types of crystals: orange plates and red cubes. After the crystals were separated under a microscope, both were submitted to X-ray structure analysis. The absolute configuration of the orange plates was S_{Rh},S_P, and that of the red cubes R_{Rh},S_P. The molecular parameters found for (S_{Rh},S_P)-**4** and (R_{Rh},S_P)-**4** compared well with each other and with those of the chloro complexes **1**−**3**, the Rh−Hal distance in the bromo complexes being longer than in the chloro complexes. The $^{31}P\{^1H\}$ NMR spectrum of the orange plates (S_{Rh},S_P)-**4** showed only the AMX pattern of diastereomer **A**, whereas the red cubes (R_{Rh},S_P)-**4** corresponded to the main diastereomer **D** of the mixture **A**−**D** (Figure 1).

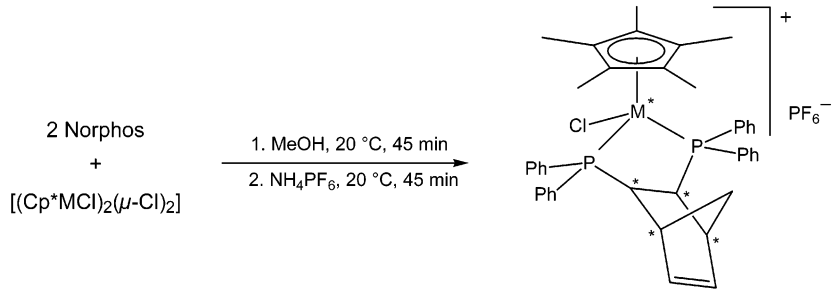
Whereas (R_{Rh},S_P)-**4** has a type I structure, (S_{Rh},S_P)-**4** is of type III (Figure 2). Conformation type III is characterized by the phenyl of the PRH group being close to Cp*. One phenyl of the PR_2 group points in the direction opposite to Cp*, and the other one is arranged horizontally. Note that the ligand priority for the specification of the metal configuration changes on going from the chloro complexes (Cp* > Cl > PR_2 > PRH) to the bromo (and iodo) complexes (Br(I) > Cp* > PR_2 > PRH). This results in opposite configurational symbols for the same configurations in the bromo (iodo) series compared to the chloro series.

When the anion was changed from PF_6^- to BF_4^-, the $^{31}P\{^1H\}$ NMR spectrum of the orange product [Cp*Rh-(P-P′)Br]BF_4 (**5**) showed a diastereomer mixture very similar to that of **4** (Figure 1): **A**, 40%; **B**, 7%; **C**, 11%; **D**, 42%. By slow diffusion of *n*-hexane into an acetone solution of **5** orange rodlike crystals were obtained. The isolated crystals gave rise to the $^{31}P\{^1H\}$ AMX pattern of the most abundant diastereomer **D**, which had the absolute configuration R_{Rh},S_P according to an X-ray structure analysis. (R_{Rh},S_P)-**5** is another type I structure (Figure 2).

In the case of [Cp*Rh(P-P′)Br]BPh_4 (**6**) a slightly different diastereomer mixture was obtained: **A**, 58%; **B**, 11%; **C**, 18%; **D**, 13%. Crystallization by slow diffusion of *n*-hexane into an acetone solution of **6** afforded yellow needles. Surprisingly, the $^{31}P\{^1H\}$ NMR spectrum of solutions of these needles showed two AMX patterns of diastereomers **A** and **C** in a molar ratio of 1.6:1. Separation of the different diastereomers **A** and **C** of **6** under a microscope as for compound **4** was not possible, because the crystals of **A** and **C** were too similar. X-ray structure analysis of a selected crystal gave a unit cell with two independent ion pairs. The cations of both had an S_{Rh},S_P configuration. Checking several other crystals, we also could establish the R_{Rh},R_P configuration for the other diastereomer in the batch of needles obtained on crystallization. (S_{Rh},S_P)-**6** had a type III conformation (Figure 2, right) and (R_{Rh},R_P)-**6** a type II conformation (Figure 2, middle). Unequivocal assignment to **A** and **C** was possible on the basis of the correlation of configuration and chemical shift given in the Discussion.

The Iodo Compound [Cp*Rh(P-P′)I]BPh_4 (7). The formation of [Cp*Rh(P-P′)I]BPh_4 (**7**) was the most stereoselective in the rhodium series **1**−**7**. The composition of the red diastereomer mixture was as follows; **A**, 85%; **B**, 3%; **C**, 7%; **D**, 5%. Slow diffusion of *n*-hexane into an acetone solution of **7** gave red needles, which had the absolute configuration S_{Rh},S_P according to X-ray structure analysis (type III, Figure 2). Interestingly, the displacement of the five methyl groups of the Cp* ligand from the plane of the five-membered ring in (S_{Rh},S_P)-**7** was much smaller (<0.06°) than in the chloro and bromo complexes **1**−**6**. The other molecular parameters found for the iodo compound **7** linked well to those of com-

Scheme 2. Synthesis of the Half-Sandwich Complexes [Cp*M(Norphos)Cl]PF_6 (10 and 11)



M = Rh **10**

M = Ir **11**

pounds **1**−**6**, the Rh−Hal distance in (S_{Rh},S_P)-**7** being longer than in the chloro and bromo series. The $^{31}P\{^1H\}$ NMR spectrum of the isolated crystals showed only the AMX pattern of the most abundant diastereomer **A** of the mixture **A**−**D** (Figure 1).

Iridium Compounds [Cp*Ir(P-P′)Cl]X (8 and 9). Similar to the rhodium compounds **1**−**7** the two iridium complexes [Cp*Ir(P-P′)Cl]PF_6 (**8**) and [Cp*Ir(P-P′)Cl]-BPh_4 (**9**) were prepared using [(Cp*$IrCl)_2(\mu$-$Cl)_2$] as the starting material. The $^{31}P\{^1H\}$ NMR spectra of **8** and **9** consist of four different diastereomers **A**−**D**. In contrast to compounds **1**−**7** (AMX patterns), each diastereomer gave rise to a simple AB pattern due to the missing IrP coupling. The PP coupling constants in the complexes **8** and **9** were much smaller ($^2J_{PP}$ = 6.5−11.4 Hz) than in the corresponding Rh complexes **1**−**7** ($^2J_{PP}$ = 32.0−36.6 Hz).

The yellow compound [Cp*Ir(P-P′)Cl]PF_6 (**8**) was obtained as the following diastereomer mixture: **A**, 37%; **B**, 9%; **C**, 3%; **D**, 51% (Figure 1). Crystallization by slow diffusion of *n*-hexane into an acetone solution of **8** afforded yellow plates having an S_{Ir},S_P configuration according to X-ray structure analysis (type I, Figure 2). The $^{31}P\{^1H\}$ NMR spectrum of the isolated crystals showed only the AB pattern of the most abundant diastereomer **D** of the mixture **A**−**D**. (S_{Ir},S_P)-**8** turned out to be as configurationally stable as the Rh complexes. There was no isomerization after standing in $CDCl_3$ solution for 1 week or heating to 50 °C for 1 day.

For the BPh_4^- salt **9** $^{31}P\{^1H\}$ NMR measurement revealed the following diastereomer mixture: **A**, 31%; **B**, 19%; **C**, 6%; **D**, 44% (Figure 1). X-ray structure analysis of the yellow plates grown by slow diffusion of *n*-hexane into an acetone solution of **9** gave a unit cell with two independent diastereomers, both having an R_{Ir},S_P configuration (type III, Figure 2). The $^{31}P\{^1H\}$ NMR of the isolated crystals of **9** showed only the AB pattern of the second abundant diastereomer **A** of the mixture **A**−**D**.

Compounds [Cp*Rh(Norphos)Cl]PF_6 (10) and [Cp*Ir(Norphos)Cl]PF_6 (11). The (+)-Norphos compounds **10** and **11** (Scheme 2) were prepared in high yields similarly to compounds **1**−**9**. In comparison to P-P′ (*P*,*P*,*P*′-tris[(+)-9-phenyldeltacyclan-8-yl]-1,2-bis-(phosphanyl)benzene), in (+)-Norphos ((2*S*,3*S*)-(+)-bis-(diphenylphosphanyl)bicyclo[2.2.1]hept-5-ene) the stereogenic secondary phosphorus atom is missing. Therefore, in the formation of **10** and **11** the number of possible diastereomers decreases to two, which differ only in the configuration at the metal center. As P_{exo} and P_{endo} in Norphos are different, the same AMX patterns arise in the $^{31}P\{^1H\}$ NMR spectra of each diastereomer of the Norphos complexes as occur in the P-P′ complexes. The assignment of P_{exo} and P_{endo} and the different hydrogen atoms in the norbornene system of the two diastereomers of **10** and **11** was achieved with 2D NMR $^1H-^1H$-COSY, $^1H-^1H$-ROESY, and $^{31}P-^1H$ correlation spectra in analogy to and an extension of experiments with [CpRu(Norphos)I].[20,31]

The $^{31}P\{^1H\}$ NMR spectrum of the orange-yellow compound **10** in $CDCl_3$ showed two AMX patterns of the diastereomers **A** (δ 42.7 and 25.6 ppm, 51%) and **B** (δ 42.1 and 24.6 ppm, 49%) with $^2J_{PP}$ = 48.8 Hz (**A**) and $^2J_{PP}$ = 50.0 Hz (**B**). Thus, in comparison to the P-P′ complex **1** in the Norphos complex **10** there was a high-field shift of the $^{31}P\{^1H\}$ NMR signals and an appreciable increase in the PP coupling constants. The PRh coupling constants for both signals at higher chemical shift were 131.6 Hz (**A** and **B**) and 138.9 Hz for the signals at lower chemical shift (**A** and **B**). By diffusion of *n*-hexane into an acetone solution of **10** orange-yellow needles were obtained. Surprisingly, the X-ray structure analysis showed that the single crystals contained two diastereomers differing in the metal configuration in a 1:1 ratio (see below). Bond lengths and angles around the metal center and the phosphorus atoms compared well with those found for the 11 structures of compounds **1**−**9**.

The $^{31}P\{^1H\}$ NMR spectrum of the yellow iridium compound **11** showed two AB patterns in the diastereomer ratio **A**:**B** = 42:58. The PP coupling constants of [Cp*Ir(Norphos)Cl]PF_6 ($^2J_{PP}$ = 30.5 Hz (**A**) and 30.1 Hz (**B**)) were smaller than in [Cp*Rh(Norphos)Cl]PF_6 ($^2J_{PP}$ = 50.0 Hz (**A**) and 48.8 Hz (**B**)) but distinctly larger than in [Cp*Ir(P-P′)Cl]PF_6 ($^2J_{PP}$ = 6.5−11.4 Hz). By slow diffusion of *n*-hexane into an acetone solution of **11** yellow plates were obtained. As for **10** the X-ray structure analysis gave a unit cell with two diastereomers differing in the metal configuration of the cations.

Discussion

Diastereoselectivity. For all the compounds [Cp*M-(P-P′)Hal]X (**1**−**9**) the four possible diastereomers and for [Cp*M(Norphos)Cl]PF_6 (**10** and **11**) the two possible diastereomers were observed, which differed in the configuration of the metal center (and the secondary phosphorus atom for **1**−**9**). From Figure 1 it is obvious

(31) Brunner, H.; Nishiyama, N. *J. Organomet. Chem.* **1991**, *405*, 247.

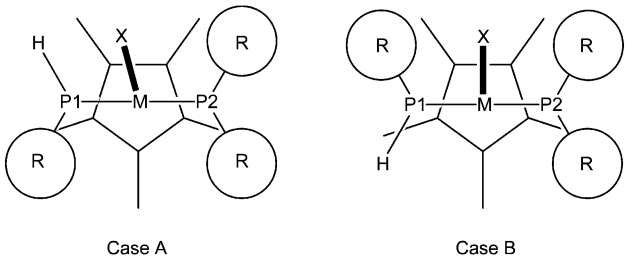


Figure 3. Angles Hal−M−P1 and Hal−M−P2 in compounds **1**−**9**.

that the intensity ratios of the signals changed. However, the diastereoselectivity with respect to the metal configuration in complexes **1**−**11** is not very high, except for the iodo complex **7**. This is different for the configuration of the secondary phosphorus atom in the P-P′ complexes **1**−**9**, which is labile in the free P-P′ ligand (see Introduction). In contrast to the free ligand, in which the H atom of the P−H group could not be located, its configuration could be determined in the 11 X-ray analyses of complexes **1**−**9**. Interestingly, 9 of the 11 structures had the S_P configuration. Moreover, Figure 1 shows that all the diastereomers with the S_P configuration were much more abundant than the R_P isomers. This indicates that the 24 asymmetric carbon atoms in the three (+)-9-phenyldeltacyclanyl substituents of the P-P′ ligand tend to induce an S_P configuration during complex formation. The same observation was made for the complex $Mo(CO)_4$(P-P′).[32] Therefore, in the free P-P′ ligand the dominating diastereomer, for which an assignment is still lacking, should have the same configuration, which would be R_P due to a change in the priority sequence from M > $C_{benzene}$ > C_Δ > H for the complexes to $C_{benzene}$ > C_Δ > H > lone pair in the free P-P′ ligand.

Correlation Configuration/Chemical Shift. Figure 1 shows that the chemical shifts of the diastereomers of the Rh complexes **1**−**7** and the Ir complexes **8** and **9** are remarkably constant, in particular with respect to the PR_2 signals. Whereas for the PRH signals there are some signal inversions, the PR_2 signals are all in the same order and almost equidistant, irrespective of the halide ligand and the anion. In eight cases X-ray structure analyses were obtained for pure diastereomers, the $^{31}P\{^1H\}$ NMR spectra of which could be measured. This unambiguously established the correlation of the configuration of the diastereomers with their chemical shifts, as shown in Figure 1. This system allowed for compound **6**, for which the two diastereomers characterized by X-ray crystallography could not be separated, the assignment of configuration and chemical shift, and it showed for compound **3** that the crystal selected for X-ray analysis was different from the bulk material, which consisted of the diastereomer (R_{Rh},S_P)-**3**.

Hal−M−P Angles. A comparison of the 11 X-ray structure analyses permits a correlation of the bond angles Hal−M−PR_2 and Hal−M−PRH. Two different cases, A and B, can be distinguished (Figure 3). In case A the halogen is between a large (+)-9-phenyldeltacyclanyl group at PR_2 and the small hydrogen atom at

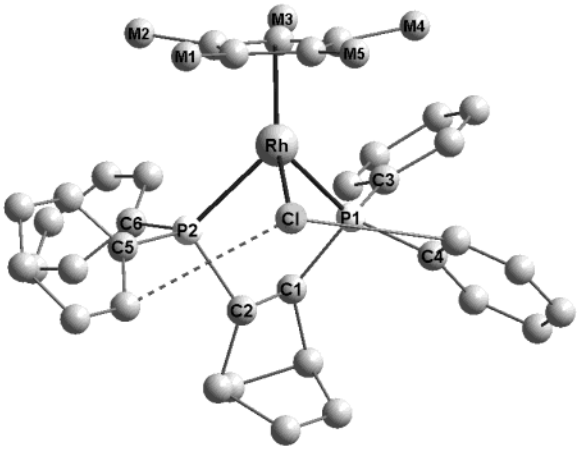


Figure 4. Distances Cl−C_{ortho} in (S_{Rh})-**10**.

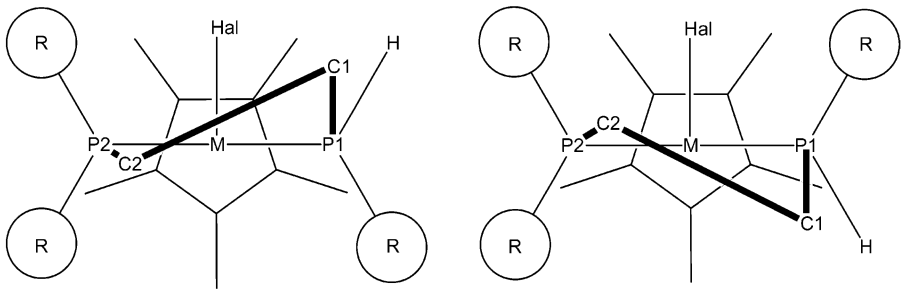
PRH. In this case the halogen orients toward the PRH side and the angle Hal−M−PR_2 is larger than Hal−M−PRH: e.g., in (R_{Rh},S_P)-**4** 91.64(2) and 81.60(2)°. For case B, in which the halogen is between two large (+)-9-phenyldeltacyclanyl groups, the angles Hal−M−PR_2 and Hal−M−PRH are almost identical, as in (S_{Rh},S_P)-**4** at 87.44(4) and 87.23(5)°, lying between those of case A. All isolated diastereomers of compounds **1**−**9** which are either of case A or case B adhere to this correlation. The angle R_2P−M−PRH is defined by the ligand geometry and is in the narrow range of 83.5 ± 1°. For case A it tends to lower values and for case B to higher values within this range.

In the Norphos complexes **10** and **11**, surprisingly, the two angles Cl−M−P are different, although the halide ligands are between two PPh_2 substituents. It is the different orientations of the phenyl rings with respect to the chloro ligands which cause this difference. One of the phenyl rings orients its *o*-CH bond to the chlorine atom, forming a hydrogen bond. For (S_{Rh})-**10** the C_{ortho}···Cl distance (solid line in Figure 4) is 3.38 Å Cl···H = 2.70 Å, and Cl···H−C = 131.3°; for (R_{Rh})-**10** these data are C_{ortho}···Cl = 3.26 Å, Cl···H = 2.77 Å, and Cl···H−C = 114.6°. This hydrogen bond needs space such that the angles Cl−Rh−P are 94.6° in (S_{Rh})-**10** and 90.9° in (R_{Rh})-**10** compared to 81.5 and 82.9° for the other Cl−Rh−P angles. On the small-angle side of the molecule the phenyl ring is rotated to avoid a close contact between Cl and *o*-CH (dashed line in Figure 4).

Helicity of the Chelate Rings.[33] The M(P-P′) chelate ring in compounds **1**−**9** is not planar but slightly puckered. This puckering results in δ or λ helicity, measured as the torsion angle P1−C1−C2−P2 in the chelate ring. For (S_{Rh},S_P)-**1** this torsion angle is −7.30(16)°, defining the δ conformation according to Figure 5. At −6.41(0)° (S_{Rh},S_P)-**2** has a similar P1−C1−C2−P2 torsion angle, implying a δ conformation for the chelate ring. In contrast to (S_{Rh},S_P)-**1** and (S_{Rh},S_P)-**2**, the torsion angle P1−C1−C2−P2 = 7.44(32)° in (S_{Rh},R_P)-**3** is positive, defining the λ conformation of the chelate ring. The reason is the different configurations of the secondary phosphorus atom in **1** and **2** compared to that in **3**. Figure 5 shows that C1 (PRH side) and the adjacent parts of the benzene ring tend to orient toward the less sterically hindred P−H side of the chelate

(32) Brunner, H.; Grau, I.; Zabel, M. Submitted for publication in *Z. Naturforsch.*

(33) *Inorg. Chem.* **1970**, *9*, 1.



Ligand configuration: R_P Ligand configuration: S_P

Chelate ring: **λ conformation** Chelate ring: **δ conformation**

Figure 5. Helical chirality of the chelate rings in the compounds [Cp*M(P-P′)Hal]X (**1**−**9**).

ligand. Thus, independent of the configuration at the metal center, the helicity of the chelate ring is determined by the configuration of the stereogenic phosphorus atom. The S_P configuration enforces a δ conformation and the R_P configuration a λ conformation in the chelate ring. All 11 isolated diastereomers of compounds **1**−**9** adhere to this correlation. Thus, with dihedral angles P−C−C−P between 5.3 and 9.5° this chiral puckering in the P-P′ complexes **1**−**9** is a small but stereospecific distortion.

In the (+)-Norphos complexes **9** and **10** the rigid norbornene skeleton dictates dihedral angles P−C−C−P around 35°, giving rise to δ helicity for the *S*,*S* ligand configuration (Figure 4).[34]

1:1 Cocrystallization of Diastereomers in 10 and 11. The (+)-Norphos compounds **10** and **11** crystallize as single crystals which contain both diastereomers differing in the metal configuration in a 1:1 ratio. 1:1 cocrystallization of different diastereomers in the same single crystal is well understood for half-sandwich complexes.[35,36] However, the molecular recognition motif of the inverted three-legged piano stools does not involve pentamethylcyclopentadienyl complexes. In compounds **10** and **11** intermolecular H···F and H···Cl hydrogen bonds stabilize the unusual arrangement in the same crystal (Figure 6). The H···F distances in **10** between the PF_6^- anions and the cations are in the range of 2.42−2.86 Å, and the H···Cl distances from the chloro ligand of the R_{Rh} cation and the protons of the methyl groups of the S_{Rh} cation are between 2.70 and 3.57 Å. For the iridium compound **11** the same 1:1 diastereomer cocrystallization with very similar H···Cl and H···F distances was found. According to subrule 3 of the Cahn−Ingold−Prelog system (*seqcis* has priority over *seqtrans*) the priority sequence for compounds **10** and **11** is Cp* > Cl > P_{endo} > P_{exo}.[37] Clearly, the 1:1 cocrystallization of the two diastereomers prevented the separation of the diastereomer mixtures of **10** and **11** by fractional crystallization.

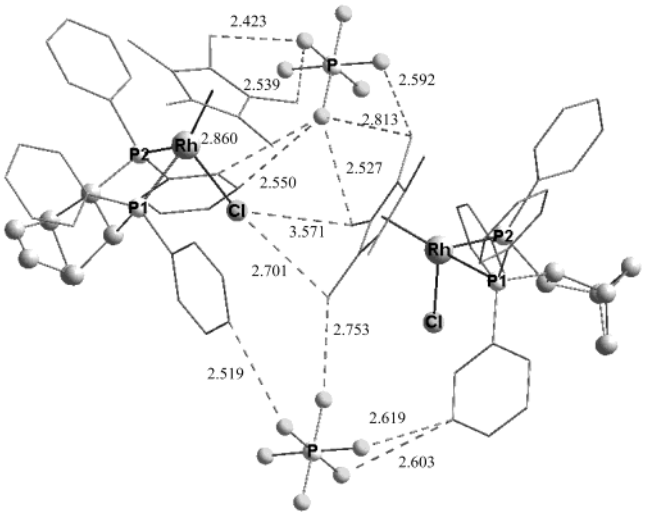


Figure 6. Intermolecular hydrogen bonds (Å) drawn as dashed lines between the adjacent carbon atoms and the halogens in (R_{Rh})-**10** (left side) and (S_{Rh})-**10** (right side).

Experimental Section

General Remarks. All manipulations and reactions were carried out under an inert atmosphere of dry nitrogen using standard Schlenk techniques. Solvents were dried by standard methods and distilled prior to use. Melting points: Büchi SMP 20. Mass spectra: Finnigan MAT 95, Finnigan MAT 311 A, and Thermoquest TSQ 7000. Optical rotations: Perkin-Elmer 241 polarimeter at room temperature. ^{1}H NMR spectra: Bruker ARX-400 (400 MHz). ^{31}P NMR spectra: Bruker ARX-400 (162 MHz). Elemental analyses: Elementar Vario EL III. X-ray structure analyses: STOE-IPDS diffractometer (Mo Kα radiation, 173 K, Oxford Cryosystems Cooler,[38] graphite monochromator), SIR-97[39] and SHELXS-97.[40] For the crystallographic data of compounds **1**−**11** see Tables 1−3. Since in all crystal structures described in this article there is at least one heavy atom, it was possible to determine the absolute structure. In the course of the final structure factor calculation, the program SHELXL97 estimated the absolute structure parameter *x* (Flack, 1983) and its esd. It should be zero within 2 esds if the absolute structure is correct. In all given structures the Flack parameter *x* fulfills this condition. [(Cp*RhCl)$_2$(μ-Cl)$_2$],[41] [(Cp*RhBr)$_2$(μ-Br)$_2$],[42] [(Cp*RhI)$_2$(μ-I)$_2$],[43] [(Cp*IrCl)$_2$(μ-Cl)$_2$],[44] (+)-Norphos,[21] and *P*,*P*,*P*′-tris[(+)-9-phen-

(34) Brunner, H.; Winter, A.; Breu, J. *J. Organomet. Chem.* **1998**, *553*, 285.
(35) Brunner, H.; Weber, M.; Zabel, M.; Zwack, T. *Angew. Chem., Int. Ed.* **2003**, *42*, 1859.
(36) Brunner, H.; Weber, M.; Zabel, M. *Coord. Chem. Rev.* **2003**, *242*, 3.
(37) Cahn, R. S.; Ingold, C.; Prelog, V. *Angew. Chem., Int. Ed. Engl.* **1966**, *5*, 385.
(38) Cosier, J.; Glazer, A. M. *J. Appl. Crystallogr.* **1986**, *19*, 105.
(39) Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A. *J. Appl. Crystallogr.* **1993**, *26*, 343.
(40) Sheldrick, G. M. SHELXL-97: Program for Crystal Structure Refinement; University of Göttingen, Göttingen, Germany, 1997.
(41) Maitlis, P. M.; White, C.; Yates, A. *Inorg. Synth.* **1992**, *29*, 228.
(42) Maitlis, P. M.; Gill, D. S. *J. Organomet. Chem.* **1975**, *87*, 359.
(43) Jones, W. D.; Feher, F. J. *Inorg. Chem.* **1984**, *23*, 2376.
(44) Graham, W. A. G.; Heinekey, D. M. *Inorg. Chem.* **1990**, *29*, 2023.

Table 1. Crystallographic Data for Compounds (S_{Rh},S_P)-1, (S_{Rh},S_P)-2, (S_{Rh},R_P)-3, (S_{Rh},S_P)-4, (R_{Rh},S_P)-4, and (R_{Rh},S_P)-5

	(S_{Rh},S_P)−**1**	(S_{Rh},S_P)−**2**	(S_{Rh},R_P)−**3**	(S_{Rh},S_P)−**4**	(R_{Rh},S_P)−**4**	(R_{Rh},S_P)−**5**
empirical formula	$C_{61}H_{65}ClF_6P_3Rh$	$C_{61}H_{65}BClF_4P_2Rh$	$C_{85}H_{85}BClP_2Rh$	$C_{61}H_{65}BrF_6P_3Rh{\cdot}C_3H_6O$	$C_{61}H_{65}BrF_6P_3Rh$	$C_{61}H_{65}BBrF_4P_2Rh$
fw	1143.40	1085.15	1317.64	1245.93	1187.85	1128.40
cryst syst	orthorhombic	orthorhombic	monoclinic	monoclinic	orthorhombic	orthorhombic
space group	$P2_12_12_1$	$P2_12_12_1$	$I2$	$P2_1$	$P2_12_12_1$	$P2_12_12_1$
Z	4	4	8	2	4	4
a (Å)	11.1641(1)	18.4434(9)	29.5904(11)	11.0680(6)	13.4752(7)	13.1505(8)
b (Å)	11.5681(5)	13.1227(9)	15.5790(6)	14.7164(9)	18.1940(11)	18.4765(11)
c (Å)	34.2577(16)	21.3209(11)	32.5698(13)	17.8126(9)	21.8958(13)	21.3123(18)
α (deg)	90	90	90	90	90	90
β (deg)	90	90	93.458(5)	107.112(6)	90	90
γ (deg)	90	90	90	90	90	90
V (Å^3)	5279.2(4)	5160.2(5)	14987.0(10)	2772.9(3)	5368.1(5)	5178.4(6)
ρ_{calcd} (g cm^{-3})	1.439	1.397	1.168	1.492	1.470	1.447
abs coeff (mm^{-1})	0.527	0.499	0.348	1.179	1.212	1.218
F(000)	2368	2256	5536	1284	2440	2323
θ range (deg)	2.41−25.91	1.90−25.83	1.96−25.31	2.76−25.84	1.86−25.85	1.90−25.84
no. of rflns	50 297	72 679	50 612	21 666	71 932	70 906
R_{int}	0.0310	0.0779	0.0510	0.0596	0.0360	0.0518
no. of data/params	10 249/652	9909/633	27 100/1627	10 622/688	10 320/653	9913/629
goodness of fit on F^2	1.023	1.040	0.817	0.930	1.036	0.961
R1/wR2 ($I > 2\sigma(I)$)	0.0292/0.0720	0.0317/0.0799	0.0460/0.0960	0.0452/0.0921	0.0234/0.0612	0.0298/0.0668
R1/wR2 (all data)	0.0310/0.0726	0.0337/0.0806	0.0710/0.1007	0.0682/0.0974	0.0245/0.0616	0.0364/0.0685
largest diff peak and hole (e Å^{-3})	0.643/−0.267	1.052/−0.552	0.864/−0.301	0.861/−0.447	0.580/−0.343	0.518/−0.580
CCDC no.	232090	232092	232097	232099	232100	232446

Table 2. Crystallographic Data for Compounds (R_{Rh},R_P)-6, (S_{Rh},S_P)-6, (S_{Rh},S_P)-7, (S_{Ir},S_P)-8, and (R_{Ir},S_P)-9

	(R_{Rh},R_P)−**6**	(S_{Rh},S_P)−**6**	(S_{Rh},S_P)−**7**	(S_{Ir},S_P)−**8**	(R_{Ir},S_P)−**9**
empirical formula	$C_{85}H_{85}BBrP_2Rh$	2 × ($C_{85}H_{85}BBrP_2Rh$)	$C_{85}H_{85}BIP_2Rh{\cdot}C_3H_6O$	$C_{61}H_{65}ClF_6IrP_3$	2 × ($C_{85}H_{85}BClIrP_2$)·C_3H_6O
fw	2724.18	1362.09	1467.17	1232.71	2869.97
cryst syst	monoclinic	monoclinic	monoclinic	orthorhombic	monoclinic
space group	$I2$	$P2_1$	$P2_1$	$P2_12_12_1$	$P2_1$
Z	8	2	4	4	2
a (Å)	29.5900(13)	11.7563(9)	11.8220(8)	13.4234(7)	11.6588(11)
b (Å)	15.5978(6)	17.2076(11)	17.1569(9)	18.0518(9)	17.1024(10)
c (Å)	32.7185(14)	36.096(4)	35.950(3)	21.7550(13)	35.471(4)
α (deg)	90	90	90	90	90
β (deg)	93.165(5)	93.718(11)	85.582(9)	90	93.041(12)
γ (deg)	90	90	90	90	90
V (Å^3)	15 077.8(11)	7286.8(11)	7270.0(9)	5271.6(5)	7062.6(11)
ρ_{calcd} (g cm^{-3})	1.199	1.242	1.340	1.553	1.350
abs coeff (mm^{-1})	0.841	0.870	0.751	2.736	2.020
F(000)	5672	2840	3040	2496	2956
θ range (deg)	1.91−20.00	1.74−25.82	1.86−25.81	2.11−25.91	2.10−20.00
no. of rflns	21 248	35 258	54 948	75 137	38 934
R_{int}	0.0714	0.058	0.0952	0.0461	0.0985
no. of data/params	13 788/1581	20 123	23 675/1580	10 215/653	13 010/777
goodness of fit on F^2	0.814	0.808	0.843	1.082	0.738
R1/wR2 ($I > 2\sigma(I)$)	0.0439/0.0818	0.0464/0.0898	0.0524/0.1080	0.0238/0.0608	0.0464/0.0839
R1/wR2 (all data)	0.0642/0.0858	0.0851/0.0981	0.0964/0.1190	0.0247/0.0611	0.1075/0.0940
largest diff peak and hole (e Å^{-3})	0.721/−0.248	1.040/−0.588	1.135/−1.687	1.501/−0.444	3.719/−0.649
CCDC no.	232094	232089	232093	232096	232098

yldeltacyclan-8-yl]-1,2-bis(phosphanyl)benzene[12] (P-P′) were prepared as reported in the literature.

General Procedure for the Preparation of the Complexes [Cp*M(P-P′)Hal]X (1−9) and [Cp*M(Norphos)Cl]-PF_6 (10 and 11). The chelate ligand P-P′ (=*P*,*P*,*P*′-tris[(+)-9-phenyldeltacyclan-8-yl]-1,2-bis(phosphanyl)benzene; 0.26 mmol) and the appropriate dinuclear metal complex [(Cp*MHal)$_2$(μ-Hal)$_2$] (0.13 mmol) were dissolved in absolute MeOH (20 mL) at room temperature. The solution, the color of which changed from red to yellow, was stirred for 30 min. After adding the metathesis reagent (NH_4PF_6, $NaBF_4$, or $NaBPh_4$) in a slight excess (1.2 equiv) the solution was stirred for another 2 h. A precipitate started to form. The solvent was removed under vacuum. The residue was dissolved in absolute CH_2Cl_2 and filtered over a column loaded with Celite. Removing the solvent afforded the compounds [Cp*M(P-P′)Hal]X (**1**−**9**) in high chemical yields. Crystals suitable for X-ray structure analysis were obtained by slow diffusion of *n*-hexane into an acetone solution of compounds **1**−**9**.

The (+)-Norphos complexes **10** and **11** were prepared in high chemical yield as described for compounds **1**−**9** with a total reaction time of 1.5 h. Slow diffusion of *n*-hexane into an acetone solution afforded crystals of **10** and **11** suitable for X-ray structure analysis.

[Cp*Rh(P-P′)Cl]PF_6 (1). Diastereomer mixture **A** (19%), **B** (18%), **C** (26%), and **D** (37%). Yield: 281 mg (96%). Mp: >190 °C dec. Anal. Calcd for $C_{61}H_{65}ClF_6P_3Rh$ (1143.53): C, 64.07; H, 5.74. Found: C, 64.27; H, 5.74. MS (ESI, CH_2Cl_2/CH_3CN; *m*/*z* (relative intensity)): 997.5 (100) [cation]; 1031.5 (35) [cation − H + Cl]. ^{1}H NMR (400 MHz, $CDCl_3$) of diastereomers **A**/**B**/**C**/**D**: δ 0.44−4.25 (m, aliphat H), 1.64 (t, $^4J_{PH}$ = 3.2 Hz, Cp* H **A**), 1.75 (t, $^4J_{PH}$ = 3.2 Hz, Cp* H **D**), 1.84 (t, $^4J_{PH}$ = 3.3 Hz, Cp* H **C**), 1.94 (t, $^4J_{PH}$ = 3.1 Hz, Cp* H **B**), 5.44 (dd, $^1J_{PH}$ = 361 Hz, J = 7.2 Hz, PH **C**), 5.50 (dd, $^1J_{PH}$

Table 3. Crystallographic Data for Compounds (S_{Rh})/(R_{Rh})-10 and (S_{Ir})/(R_{Ir})-11

	(S_{Rh})/(R_{Rh})-**10**	(S_{Ir})/(R_{Ir})-**11**
empirical formula	2 × ($C_{41}H_{43}ClF_6P_3Rh$)·$3C_3H_6O$	2 × ($C_{41}H_{43}ClF_6IrP_3$)·$3C_3H_6O$
fw	1936.28	2114.90
cryst syst	monoclinic	monoclinic
space group	$P2_1$	$P2_1$
Z	2	2
a (Å)	9.2268(5)	9.2428(5)
b (Å)	42.3235(18)	42.294(3)
c (Å)	12.1033(7)	12.0887(6)
α (deg)	90	90
β (deg)	107.408(6)	107.364(6)
γ (deg)	90	90
V (Å^3)	4500.0(4)	4510.3(5)
ρ_{calcd} (g cm^{-3})	1.426	1.557
abs coeff (mm^{-1})	0.604	3.186
F(000)	1992	2120
θ range (deg)	1.83−23.95	1.83−23.92
no. of rflns	46 796	23 838
R_{int}	0.0433	0.0810
no. of data/params	13 796/1045	11 637/515
goodness of fit on F^2	1.073	1.146
R1/wR2 ($I > 2\sigma(I)$)	0.0326/0.0874	0.0647/0.1629
R1/wR2 (all data)	0.0336/0.0886	0.0671/0.1642
largest diff peak and hole (e Å^{-3})	0.512/−0.329	1.710/−2.225
CCDC no.	232095	232097

= 402 Hz, J = 6.6 Hz, PH **D**), 5.62 (m, $^1J_{PH}$ = 391 Hz, PH **B**), 6.22 (d, $^1J_{PH}$ = 373 Hz, PH **A**), 6.16−8.02 (m, aromat H). ^{31}P-{^{1}H} NMR (162 MHz, $CDCl_3$): δ 41.9 (dd, $^2J_{PP}$ = 36.2 Hz, $^1J_{PRh}$ = 133.9 Hz, PRH **A**), 47.3 (dd, $^2J_{PP}$ = 34.7 Hz, $^1J_{PRh}$ = 125.5 Hz, PRH **D**), 48.8 (dd, $^2J_{PP}$ = 32.0 Hz, $^1J_{PRh}$ = 132.4 Hz, PRH **C**), 51.5 (dd, $^2J_{PP}$ = 36.6 Hz, $^1J_{PRh}$ = 127.4 Hz, PRH **B**), 60.5 (dd, $^2J_{PP}$ = 34.7 Hz, $^1J_{PRh}$ = 131.2 Hz, PR_2 **D**), 66.6 (dd, $^2J_{PP}$ = 32.0 Hz, $^1J_{PRh}$ = 131.6 Hz, PR_2 **C**), 78.5 (dd, $^2J_{PP}$ = 36.6 Hz, $^1J_{PRh}$ = 127.4 Hz, PR_2 **B**), 81.8 (dd, $^2J_{PP}$ = 36.2 Hz, $^1J_{PRh}$ = 128.2 Hz, PR_2 **A**), −144.2 (sept, PF_6).

Crystallization from *n*-hexane/acetone gave (S_{Rh},S_P)-**1** (diastereomer **D**). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.82−4.19 (m, 30H, aliphat H), 1.85 (t, $^4J_{PH}$ = 3.2 Hz, 15H, Cp* H), 5.58 (dd, $^1J_{PH}$ = 403 Hz, J = 6.4 Hz, 1H, PH), 6.31−7.84 (m, 19H, aromat H). ^{31}P NMR (162 MHz, $CDCl_3$): δ 46.7 (dd, $^2J_{PP}$ = 34.9 Hz, $^1J_{PRh}$ = 125.7 Hz ($^1J_{PH}$ = 403 Hz), PRH), 59.8 (dd, $^2J_{PP}$ = 34.9 Hz, $^1J_{PRh}$ = 131.2 Hz, PR_2), −144.3 (sept, PF_6). [α]$_D$ (c = 0.108, CH_2Cl_2): 278°.

[Cp*Rh(P-P′)Cl]BF$_4$ (2). Diastereomer mixture **A** (17%), **B** (25%), **C** (21%), and **D** (37%). Yield: 93%. Mp: >190 °C dec. Anal. Calcd for $C_{61}H_{65}BClF_4P_2Rh$ (1085.28): C, 67.51; H, 6.04. Found: C, 67.22; H, 6.16. MS (PI-LSIMS, CH_2Cl_2/NBA; m/z (relative intensity)): 997.2 (100) [cation]. ^{1}H NMR (400 MHz, $CDCl_3$) of diastereomers **A**/**B**/**C**/**D**: δ 0.36−4.33 (m, aliphat H), 1.70 (t, $^4J_{PH}$ = 3.0 Hz, Cp* H **A**), 1.82 (t, $^4J_{PH}$ = 3.2 Hz, Cp* H **D**), 1.90 (t, $^4J_{PH}$ = 3.2 Hz, Cp* H **C**), 2.00 (t, $^4J_{PH}$ = 2.8 Hz, Cp* H **B**), 5.54 (dd, $^1J_{PH}$ = 363 Hz, J = 7.1 Hz, PH **C**), 5.54 (dd, $^1J_{PH}$ = 403 Hz, J = 6.4 Hz, PH **D**), 5.67 (m, $^1J_{PH}$ = 392 Hz, PH **B**), 6.22−8.13 (m, aromat H). The PH **A** signals overlapped. ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ 41.7 (dd, $^2J_{PP}$ = 36.2 Hz, $^1J_{PRh}$ = 133.5 Hz, PRH **A**), 47.1 (dd, $^2J_{PP}$ = 35.1 Hz, $^1J_{PRh}$ = 125.9 Hz, PRH **D**), 48.7 (dd, $^2J_{PP}$ = 32.2 Hz, $^1J_{PRh}$ = 132.2 Hz, PRH **C**), 51.4 (dd, $^2J_{PP}$ = 36.8 Hz, $^1J_{PRh}$ = 127.2 Hz, PRH **B**), 60.3 (dd, $^2J_{PP}$ = 35.1 Hz, $^1J_{PRh}$ = 131.6 Hz, PR_2 **D**), 66.5 (dd, $^2J_{PP}$ = 32.2 Hz, $^1J_{PRh}$ = 131.8 Hz, PR_2 **C**), 78.3 (dd, $^2J_{PP}$ = 36.8 Hz, $^1J_{PRh}$ = 127.2 Hz, PR_2 **B**), 81.9 (dd, $^2J_{PP}$ = 36.2 Hz, $^1J_{PRh}$ = 127.8 Hz, PR_2 **A**).

Crystallization from *n*-hexane/acetone gave (S_{Rh},S_P)-**2** (diastereomer **D**). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.71−4.11 (m, 30H, aliphat H), 1.78 (t, $^4J_{PH}$ = 3.2 Hz, 15H, Cp* H), 5.49 (dd, $^1J_{PH}$ = 402 Hz, J = 6.4 Hz, 1H, PH), 6.19−7.75 (m, 19H, aromat H). ^{31}P NMR (162 MHz, $CDCl_3$): δ 47.1 (dd, $^2J_{PP}$ = 35.1 Hz, $^1J_{PRh}$ = 125.9 Hz ($^1J_{PH}$ = 403 Hz), PRH), 60.1 (dd, $^2J_{PP}$ = 35.1 Hz, $^1J_{PRh}$ = 131.6 Hz, PR_2). [α]$_D$ (c = 0.080, CH_2Cl_2): 252°.

[Cp*Rh(P-P′)Cl]BPh$_4$ (3). Diastereomer mixture **A** (18%), **B** (21%), **C** (19%), and **D** (42%). Yield: 100%. Mp: >160 °C dec. Anal. Calcd for $C_{85}H_{85}BClP_2Rh$ (1317.70): C, 77.48; H, 6.50. Found: C, 75.98; H, 6.98. MS (ESI, CH_3CN; m/z (relative intensity)): 997.5 (100) [cation]. ^{1}H NMR (400 MHz, $CDCl_3$) of diastereomers **A**/**B**/**C**/**D**: δ 0.48−4.26 (m, aliphat H), 1.48 (t, $^4J_{PH}$ = 3.0 Hz, Cp* H **A**), 1.56 (t, $^4J_{PH}$ = 2.9 Hz, Cp* H **B**), 1.59 (t, $^4J_{PH}$ = 3.2 Hz, Cp* H), 1.73 (t, $^4J_{PH}$ = 2.9 Hz, Cp* H), 5.04 (dd, $^1J_{PH}$ = 351 Hz, J = 7.5 Hz, PH **B**), 5.49 (dd, $^1J_{PH}$ = 405 Hz, J = 5.9 Hz, PH **D**), 5.59 (m, $^1J_{PH}$ = 393 Hz, PH **C**), 5.82 (d, $^1J_{PH}$ = 358 Hz, PH **A**), 6.12−7.84 (m, aromat H). The Cp* H **C** and **D** signals overlapped. ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ 43.5 (dd, $^2J_{PP}$ = 36.2 Hz, $^1J_{PRh}$ = 135.0 Hz, PRH **A**), 46.5 (dd, $^2J_{PP}$ = 34.6 Hz, $^1J_{PRh}$ = 125.3 Hz, PRH **D**), 49.9 (dd, $^2J_{PP}$ = 31.9 Hz, $^1J_{PRh}$ = 132.9 Hz, PRH **C**), 51.6 (dd, $^2J_{PP}$ = 36.6 Hz, $^1J_{PRh}$ = 127.0 Hz, PRH **B**), 61.2 (dd, $^2J_{PP}$ = 34.6 Hz, $^1J_{PRh}$ = 130.4 Hz, PR_2 **D**), 67.8 (dd, $^2J_{PP}$ = 31.9 Hz, $^1J_{PRh}$ = 131.4 Hz, PR_2 **C**), 78.7 (dd, $^2J_{PP}$ = 36.6 Hz, $^1J_{PRh}$ = 126.6 Hz, PR_2 **B**), 82.1 (dd, $^2J_{PP}$ = 36.2 Hz, $^1J_{PRh}$ = 127.0 Hz, PR_2 **A**).

Crystallization from *n*-hexane/acetone gave needles from which a crystal was selected for X-ray structure analysis of (S_{Rh},R_P)-**3** (diastereomer **C**). The solution of the bulk showed the signals of diastereomer **A**. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.47−4.21 (m, 30H, aliphat H), 1.43 (t, $^4J_{PH}$ = 3.1 Hz, 15H, Cp* H), 5.76 (d, $^1J_{PH}$ = 358 Hz, 1H, PH), 6.08−7.84 (m, 39H, aromat H). ^{31}P NMR (162 MHz, $CDCl_3$): δ 43.4 (dd, $^2J_{PP}$ = 36.6 Hz, $^1J_{PRh}$ = 135.8 Hz ($^1J_{PH}$ = 358 Hz), PRH), 82.1 (dd, $^2J_{PP}$ = 36.6 Hz, $^1J_{PRh}$ = 127.0 Hz, PR_2). [α]$_D$ (c = 0.148, CH_2Cl_2): 288°.

[Cp*Rh(P-P′)Br]PF$_6$ (4). Diastereomer mixture **A** (48%), **B** (6%), **C** (12%), and **D** (34%). Yield: 97%. Mp: >190 °C dec. Anal. Calcd for $C_{61}H_{65}BrF_6P_3Rh$ (1187.89): C, 61.68; H, 5.52. Found: C, 60.55; H, 5.46. MS (PI-LSIMS, CH_2Cl_2/NBA; m/z (relative intensity)): 1043.5 (100) [cation]. ^{1}H NMR (400 MHz, $CDCl_3$) of diastereomers **A**/**B**/**C**/**D**: δ 0.36−4.24 (m, aliphat H), 1.70 (t, $^4J_{PH}$ = 3.2 Hz, Cp* H **A**), 1.84 (t, $^4J_{PH}$ = 3.1 Hz, Cp* H **D**), 1.93 (t, $^4J_{PH}$ = 3.2 Hz, Cp* H **C**), 2.02 (t, $^4J_{PH}$ = 2.9 Hz, Cp* H **B**), 5.34 (dd, $^1J_{PH}$ = 359 Hz, J = 6.8 Hz, PH **C**), 5.79 (dd, $^1J_{PH}$ = 404 Hz, J = 7.2 Hz, PH **D**), 6.20 (d, $^1J_{PH}$ = 372 Hz, PH **A**), 6.22−8.13 (m, aromat H). The PH **B** signals overlapped. ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ 42.7 (dd, $^2J_{PP}$ = 34.7 Hz, $^1J_{PRh}$ = 134.3 Hz, PRH **A**), 42.9 (dd, $^2J_{PP}$ = 34.3 Hz, $^1J_{PRh}$ = 126.6 Hz, PRH **D**), 46.2 (dd, $^2J_{PP}$ = 30.7 Hz, $^1J_{PRh}$ = 128.6 Hz, PRH **C**), 47.8 (dd, $^2J_{PP}$ = 35.9 Hz, $^1J_{PRh}$ = 128.6 Hz, PRH **B**), 60.1 (dd, $^2J_{PP}$ = 34.3 Hz, $^1J_{PRh}$ = 132.4 Hz, PR_2 **D**), 64.5 (dd, $^2J_{PP}$ = 30.7 Hz, $^1J_{PRh}$ = 132.0 Hz, PR_2 **C**), 78.7 (dd, $^2J_{PP}$ = 35.9 Hz, $^1J_{PRh}$ = 128.2 Hz, PR_2 **B**), 81.2 (dd, $^2J_{PP}$ = 34.7 Hz, $^1J_{PRh}$ = 128.9 Hz, PR_2 **A**), −143.7 (sept, PF_6).

Crystallization from *n*-hexane/acetone gave (S_{Rh},S_P)-**4** (diastereomer **A**) and (R_{Rh},S_P)-**4** (diastereomer **D**), which could be separated under a microscope. ^{1}H NMR (400 MHz, $CDCl_3$) of (S_{Rh},S_P)-**4** (diastereomer **A**): δ 0.52−4.23 (m, 30H, aliphat H), 1.73 (t, $^4J_{PH}$ = 3.2 Hz, 15H, Cp* H), 6.27 (d, $^1J_{PH}$ = 373 Hz, 1H, PH), 7.11−8.12 (m, 19H, aromat H). ^{31}P NMR (162 MHz, $CDCl_3$): δ 42.8 (dd, $^2J_{PP}$ = 34.7 Hz, $^1J_{PRh}$ = 134.3 Hz ($^1J_{PH}$ = 373 Hz), PRH), 81.2 (dd, $^2J_{PP}$ = 34.7 Hz, $^1J_{PRh}$ = 129.1 Hz, PR_2), −143.7 (sept, PF_6). ^{1}H NMR (400 MHz, $CDCl_3$) of (R_{Rh},S_P)-**4** (diastereomer **D**): δ 0.68−4.06 (m, 30H, aliphat H), 1.88 (t, $^4J_{PH}$ = 3.2 Hz, 15H, Cp* H), 5.83 (dd, $^1J_{PH}$ = 403 Hz, J = 7.2 Hz, 1H, PH), 6.29−7.69 (m, 19H, aromat H). ^{31}P NMR (162 MHz, $CDCl_3$): 42.8 (dd, $^2J_{PP}$ = 34.3 Hz, $^1J_{PRh}$ = 126.3 Hz ($^1J_{PH}$ = 403 Hz), PRH), 59.9 (dd, $^2J_{PP}$ = 34.3 Hz, $^1J_{PRh}$ = 132.3 Hz, PR_2), −143.8 (sept, PF_6).

[Cp*Rh(P-P′)Br]BF$_4$ (5). Diastereomer mixture **A** (40%), **B** (7%), **C** (11%), and **D** (42%). Yield: 95%. Mp: >190 °C dec. Anal. Calcd for $C_{61}H_{65}BBrF_4P_2Rh$ (1129.73): C, 64.85; H, 5.80. Found: C, 64.28; H, 5.67. MS (PI-LSIMS, CH_2Cl_2/NBA; m/z (relative intensity)): 1043.4 (100) [cation]; 962.4 (10) [cation

− Br]. ^{1}H NMR (400 MHz, $CDCl_3$) of diastereomers **A**/**B**/**C**/**D**: δ 0.41−4.28 (m, aliphat H), 1.75 (t, $^4J_{PH}$ = 3.1 Hz, Cp* H **A**), 1.91 (t, $^4J_{PH}$ = 3.1 Hz, Cp* H **D**), 2.02 (t, $^4J_{PH}$ = 3.2 Hz, Cp* H **C**), 6.24−8.26 (m, aromat H). The Cp* H **B** and PH **A**, **B**, **C**, and **D** signals overlapped. ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ 41.7 (dd, $^2J_{PP}$ = 34.3 Hz, $^1J_{PRh}$ = 133.1 Hz, PRH **A**), 42.6 (dd, $^2J_{PP}$ = 34.3 Hz, $^1J_{PRh}$ = 126.5 Hz, PRH **D**), 45.3 (dd, $^2J_{PP}$ = 30.5 Hz, $^1J_{PRh}$ = 132.0 Hz, PRH **C**), 47.6 (dd, $^2J_{PP}$ = 36.0 Hz, $^1J_{PRh}$ = 128.4 Hz, PRH **B**), 60.2 (dd, $^2J_{PP}$ = 34.3 Hz, $^1J_{PRh}$ = 132.5 Hz, PR_2 **D**), 64.4 (dd, $^2J_{PP}$ = 30.5 Hz, $^1J_{PRh}$ = 132.4 Hz, PR_2 **C**), 78.5 (dd, $^2J_{PP}$ = 36.0 Hz, $^1J_{PRh}$ = 128.4 Hz, PR_2 **B**), 81.4 (dd, $^2J_{PP}$ = 34.3 Hz, $^1J_{PRh}$ = 129.3 Hz, PR_2 **A**).

Crystallization from *n*-hexane/acetone gave (R_{Rh},S_P)-**5** (diastereomer **D**). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.75−4.15 (m, 30H, aliphat H), 1.91 (t, $^4J_{PH}$ = 3.1 Hz, 15H, Cp* H), 5.83 (dd, $^1J_{PH}$ = 404 Hz, J = 6.4 Hz, 1H, PH), 6.24−8.26 (m, 19H, aromat H). ^{31}P NMR (162 MHz, $CDCl_3$): δ 42.7 (dd, $^2J_{PP}$ = 34.3 Hz, $^1J_{PRh}$ = 126.5 Hz ($^1J_{PH}$ = 404 Hz), PRH), 59.9 (dd, $^2J_{PP}$ = 34.3 Hz, $^1J_{PRh}$ = 132.5 Hz, PR_2). $[\alpha]_D$ (c = 0.165, CH_2Cl_2): 288°.

[Cp*Rh(P-P′)Br]BPh$_4$ (6). Diastereomer mixture **A** (58%), **B** (11%), **C** (18%), and **D** (14%). Yield: 94%. Mp: >170 °C dec. Anal. Calcd for $C_{85}H_{85}BBrP_2Rh$ (1362.15): C, 74.95; H, 6.29. Found: C, 75.07; H, 6.33. MS (PI-LSIMS, CH_2Cl_2/NBA; m/z (relative intensity)): 1043.3 (100) [cation]; 962.4 (15) [cation − Br]. ^{1}H NMR (400 MHz, $CDCl_3$) of diastereomers **A**/**B**/**C**/**D**: δ 0.43−4.20 (m, aliphat H), 1.49 (t, $^4J_{PH}$ = 3.1 Hz, Cp* H **A**), 1.60 (t, $^4J_{PH}$ = 3.0 Hz, Cp* H), 1.63 (t, $^4J_{PH}$ = 3.2 Hz, Cp* H **C**), 1.77 (t, $^4J_{PH}$ = 2.9 Hz, Cp* H), 4.84 (dd, $^1J_{PH}$ = 350 Hz, J = 6.7 Hz, PH **C**), 5.77 (d, $^1J_{PH}$ = 355 Hz, PH **A**), 5.85 (m, $^1J_{PH}$ = 393 Hz, PH **B**), 6.10−7.90 (m, aromat H). The Cp* H **B** and **D** and the PH **D** signals overlapped. ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ 42.1 (dd, $^2J_{PP}$ = 34.0 Hz, $^1J_{PRh}$ = 125.9 Hz, PRH **D**), 43.9 (dd, $^2J_{PP}$ = 35.1 Hz, $^1J_{PRh}$ = 136.2 Hz, PRH **A**), 47.2 (dd, $^2J_{PP}$ = 30.5 Hz, $^1J_{PRh}$ = 132.8 Hz, PRH **C**), 47.6 (dd, $^2J_{PP}$ = 35.5 Hz, $^1J_{PRh}$ = 128.2 Hz, PRH **B**), 61.1 (dd, $^2J_{PP}$ = 34.0 Hz, $^1J_{PRh}$ = 131.6 Hz, PR_2 **D**), 65.7 (dd, $^2J_{PP}$ = 30.5 Hz, $^1J_{PRh}$ = 132.0 Hz, PR_2 **C**), 78.9 (dd, $^2J_{PP}$ = 35.5 Hz, $^1J_{PRh}$ = 127.8 Hz, PR_2 **B**), 81.4 (dd, $^2J_{PP}$ = 35.1 Hz, $^1J_{PRh}$ = 128.6 Hz, PR_2 **A**).

Crystallization from *n*-hexane/acetone gave crystals of (S_{Rh},S_P)-**6** and (R_{Rh},R_P)-**6** (diastereomers **A** and **C**) which could not be separated. ^{1}H NMR (400 MHz, $CDCl_3$) of (S_{Rh},S_P)-**6**/(R_{Rh},R_P)-**6**: δ 0.42−4.18 (m, aliphat H), 1.51 (t, $^4J_{PH}$ = 3.1 Hz, Cp* H **A**), 1.67 (t, $^4J_{PH}$ = 3.2 Hz, Cp* **C**), 5.00 (dd, $^1J_{PH}$ = 352 Hz, J = 6.7 Hz, PH **C**), 5.98 (d, $^1J_{PH}$ = 359 Hz, PH **A**), 6.24−8.26 (m, aromat H). ^{31}P NMR (162 MHz, $CDCl_3$): δ 43.2 (dd, $^2J_{PP}$ = 35.1 Hz, $^1J_{PRh}$ = 136.2 Hz ($^1J_{PH}$ = 359 Hz), PRH **A**), 46.8 (dd, $^2J_{PP}$ = 30.5 Hz, $^1J_{PRh}$ = 132.8 Hz ($^1J_{PH}$ = 352 Hz), PRH **C**), 65.4 (dd, $^2J_{PP}$ = 30.5 Hz, $^1J_{PRh}$ = 132.0 Hz, PR_2 **C**), 81.4 (dd, $^2J_{PP}$ = 35.1 Hz, $^1J_{PRh}$ = 128.6 Hz, PR_2 **B**).

[Cp*Rh(P-P′)I]BPh$_4$ (7). Diastereomer mixture **A** (85%), **B** (3%), **C** (7%), and **D** (5%). Yield: 90%. Mp: >170 °C dec. Anal. Calcd for $C_{85}H_{85}BIP_2Rh$ (1409.15): C, 72.04; H, 6.25. Found: C, 70.77; H, 6.15. MS (PI-LSIMS, CH_2Cl_2/NBA; m/z (relative intensity)): 1089.3 (100) [cation]; 962.3 (20) [cation − I]. ^{1}H NMR (400 MHz, $CDCl_3$) of diastereomers **A**/**B**/**C**/**D**: δ 0.44−4.31 (m, aliphat H), 1.66 (t, $^4J_{PH}$ = 3.2 Hz, Cp* H **A**), 5.84 (d, $^1J_{PH}$ = 349 Hz, PH **A**), 6.14−8.01 (m, aromat H). The Cp* H **B**, **C,** and **D** and the PH **B**, **C,** and **D** signals overlapped. ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ 35.5 (dd, $^2J_{PP}$ = 32.4 Hz, $^1J_{PRh}$ = 127.4 Hz, PRH **D**), 41.8 (dd, $^2J_{PP}$ = 34.0 Hz, $^1J_{PRh}$ = 129.3 Hz, PRH **B**), 43.5 (dd, $^2J_{PP}$ = 32.8 Hz, $^1J_{PRh}$ = 136.6 Hz ($^1J_{PH}$ = 349 Hz), PRH **A**), 44.8 (dd, $^2J_{PP}$ = 28.2 Hz, $^1J_{PRh}$ = 132.4 Hz, PRH **C**), 62.1 (dd, $^2J_{PP}$ = 32.4 Hz, $^1J_{PRh}$ = 133.1 Hz, PR_2 **D**), 64.3 (dd, $^2J_{PP}$ = 28.2 Hz, $^1J_{PRh}$ = 132.8 Hz, PR_2 **C**), 79.1 (dd, $^2J_{PP}$ = 34.0 Hz, $^1J_{PRh}$ overlapped, PR_2 **B**), 80.4 (dd, $^2J_{PP}$ = 32.8 Hz, $^1J_{PRh}$ = 129.7 Hz, PR_2 **A**).

Crystallization from *n*-hexane/acetone gave (S_{Rh},S_P)-**7** (diastereomer **A**). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.43−4.19 (m, 30H, aliphat H), 1.60 (t, $^4J_{PH}$ = 3.2 Hz, 15H, Cp* H), 5.81 (d, $^1J_{PH}$ = 349 Hz, 1H, PH), 6.75−8.00 (m, 39H, aromat H). ^{31}P NMR (162 MHz, $CDCl_3$): δ 43.3 (dd, $^2J_{PP}$ = 32.8 Hz, $^1J_{PRh}$ = 136.6 Hz ($^1J_{PH}$ = 349 Hz), PRH), 80.3 (dd, $^2J_{PP}$ = 32.8 Hz, $^1J_{PRh}$ = 129.7 Hz, PR_2).

[Cp*Ir(P−P′)Cl]PF$_6$ (8). Diastereomer mixture **A** (37%), **B** (9%), **C** (3%), and **D** (51%). Yield: 92%. Mp: >190 °C dec. Anal. Calcd for $C_{61}H_{65}ClF_6IrP_3$ (1232.75): C, 59.43; H, 5.31. Found: C, 59.37; H, 5.62. MS (PI-LSIMS, CH_2Cl_2/NBA; m/z (relative intensity)): 1087.6 (100) [cation]. ^{1}H NMR (400 MHz, $CDCl_3$) of diastereomers **A**/**B**/**C**/**D**: δ 0.45−4.28 (m, aliphat H), 1.68 (t, $^4J_{PH}$ = 2.1 Hz, Cp* H **A**), 1.81 (t, $^4J_{PH}$ = 2.1 Hz, Cp* H **D**), 1.98 (t, $^4J_{PH}$ = 1.8 Hz, Cp* H **B**), 5.17 (dd, $^1J_{PH}$ = 413 Hz, J = 9.1 Hz, PH **D**), 5.34 (m, $^1J_{PH}$ = 398 Hz, PH **B**), 6.22 (d, $^1J_{PH}$ = 395 Hz, PH **A**), 6.23−8.05 (m, aromat H). The Cp* H **C** and PH **C** signals overlapped. ^{31}P NMR (162 MHz, $CDCl_3$): δ 7.4 (d, $^2J_{PP}$ = 11.4 Hz ($^1J_{PH}$ = 395 Hz), PRH **A**), 17.4 (d, $^2J_{PP}$ = 6.5 Hz ($^1J_{PH}$ overlapped), PRH **C**), 18.7 (d, $^2J_{PP}$ = 6.5 Hz ($^1J_{PH}$ = 413 Hz), PRH **D**), 23.2 (d, $^2J_{PP}$ = 9.5 Hz ($^1J_{PH}$ = 398 Hz), PRH **B**), 26.1 (d, $^2J_{PP}$ = 6.5 Hz, PR_2 **D**), 30.7 (d, $^2J_{PP}$ = 6.5 Hz, PR_2 **C**), 46.7 (d, $^2J_{PP}$ = 9.5 Hz, PR_2 **B**), 48.3 (d, $^2J_{PP}$ = 11.4 Hz, PR_2 **A**), −143.7 (sept, PF_6).

Crystallization from *n*-hexane/acetone gave (S_{Ir},S_P)-**8** (diastereomer **D**). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.86−4.12 (m, 30H, aliphat H), 1.84 (t, $^4J_{PH}$ = 2.1 Hz, 15H, Cp* H), 5.18 (dd, $^1J_{PH}$ = 413 Hz, J = 9.1 Hz, 1H, PH), 6.29−7.78 (m, 19H, aromat H). ^{31}P NMR (162 MHz, $CDCl_3$): δ 18.7 (d, $^2J_{PP}$ = 6.5 Hz ($^1J_{PH}$ = 413 Hz), PRH), 26.1 (d, $^2J_{PP}$ = 6.5 Hz, PR_2), −144.3 (sept, PF_6). $[\alpha]_D$ (c = 2.00, $CHCl_3$): 144°.

[Cp*Ir(P−P′)Cl]BPh$_4$ (9). Diastereomer mixture **A** (31%), **B** (19%), **C** (6%), and **D** (44%). Yield: 95%. Mp: >190 °C dec. Anal. Calcd for $C_{85}H_{85}BClIrP_2$ (1407.01): C, 72.35; H, 6.18. Found: C, 71.56; H, 6.35. MS (PI-LSIMS, CH_2Cl_2/NBA; m/z (relative intensity)): 1087.5 (100) [cation]. ^{1}H NMR (400 MHz, $CDCl_3$) of diastereomers **A**/**B**/**C**/**D**: δ 0.35−4.26 (m, aliphat H), 1.52 (bs, Cp* H **A**), 1.61 (bs, Cp* H **D**), 1.77 (bs, Cp* H **B**), 5.13 (dd, $^1J_{PH}$ = 414 Hz, J = 9.0 Hz, PH **D**), 5.29 (m, $^1J_{PH}$ = 407 Hz, PH **B**), 5.92 (d, $^1J_{PH}$ = 382 Hz, PH **A**), 6.07−7.86 (m, aromat H). The Cp* H **C** and PH **C** signals overlapped. ^{31}P NMR (162 MHz, $CDCl_3$): δ 8.7 (d, $^2J_{PP}$ = 11.4 Hz ($^1J_{PH}$ = 382 Hz), PRH **A**), 18.0 (d, $^2J_{PP}$ = 6.1 Hz, PRH **C**), 18.1 (d, $^2J_{PP}$ = 6.5 Hz ($^1J_{PH}$ = 414 Hz), PRH **D**), 22.9 (d, $^2J_{PP}$ = 9.5 Hz ($^1J_{PH}$ = 409 Hz), PRH **B**), 26.3 (d, $^2J_{PP}$ = 6.1 Hz, PR_2 **D**), 31.1 (d, $^2J_{PP}$ = 6.5 Hz, PR_2 **C**), 46.6 (d, $^2J_{PP}$ = 9.5 Hz, PR_2 **B**), 48.6 (d, $^2J_{PP}$ = 11.4 Hz, PR_2 **A**).

Crystallization from *n*-hexane/acetone gave (R_{Ir},S_P)-**9** (diastereomer **A**). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.50−4.26 (m, 30H, aliphat H), 1.50 (t, $^4J_{PH}$ = 2.1 Hz, 15H, Cp* H), 5.80 (d, $^1J_{PH}$ = 379 Hz, 1H, PH), 6.83−7.82 (m, 39H, aromat H). ^{31}P NMR (162 MHz, $CDCl_3$): δ 8.9 (d, $^2J_{PP}$ = 11.4 Hz ($^1J_{PH}$ = 379 Hz), PRH), 48.6 (d, $^2J_{PP}$ = 11.4 Hz, PR_2). $[\alpha]_D$ (c = 2.00, $CHCl_3$): 101°.

[Cp*Rh(Norphos)Cl]PF$_6$ (10). Diastereomer mixture (S_{Rh})-**10** (diastereomer **A**, 51%) and (R_{Rh})-**10** (diastereomer **B**, 49%). Yield: 94%. Mp: >185 °C dec. Anal. Calcd for $C_{41}H_{43}ClF_6P_3Rh$ (881.05): C, 55.89; H, 4.92. Found: C, 55.71; H, 4.75. MS (PI-LSIMS, CH_2Cl_2; m/z (relative intensity)): 735.2 (100) [cation]; 700.2 (25) [cation − Cl].

Crystallization from *n*-hexane/acetone gave (S_{Rh})/(R_{Rh})-**10**. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.33 (d, $^2J_{H7H8}$ = 8.9 Hz, H7 R_{Rh}), 1.44 (t, $^4J_{PH}$ = 3.6 Hz, Cp* H S_{Rh}), 1.45 (t, $^4J_{PH}$ = 3.6 Hz, Cp* H R_{Rh}), 1.59 (bd, $^2J_{H7H8}$ = 8.9 Hz, H8 R_{Rh}), 1.66 (bd, $^2J_{H7H8}$ = 8.8 Hz, H7 S_{Rh}), 1.88 (bd, $^2J_{H7H8}$ = 8.8 Hz, H8 S_{Rh}), 2.71 (bs, H4 R_{Rh}), 2.74 (m, H2 S_{Rh}), 2.97 (bs, H4 S_{Rh}), 3.09 (bs, H3 R_{Rh}), 3.14 (m, H1 R_{Rh}), 3.17 (bs, H3 S_{Rh}), 3.39 (m, H2 R_{Rh}), 3.88 (m, H1 S_{Rh}), 5.05 (dd, $^3J_{H5H6}$ = 5.5 Hz, $^3J_{H5H3}$ = 2.8 Hz, H5 S_{Rh}), 5.77 (dd, $^3J_{H5H6}$ = 5.6 Hz, $^3J_{H5H3}$ = 2.8 Hz, H5 R_{Rh}), 5.89 (dd, $^3J_{H5H6}$ = 5.5 Hz, $^3J_{H6H4}$ = 3.2 Hz, H6 S_{Rh}), 6.48 (dd, $^3J_{H5H6}$ = 5.6 Hz, $^3J_{H6H4}$ = 3.2 Hz, H6 R_{Rh}), 7.05−7.84 (m, aromat H R_{Rh} and S_{Rh}). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ 24.6 (dd, $^2J_{PP}$ = 50.0 Hz, $^1J_{PRh}$ = 138.9 Hz, P_{endo} R_{Rh}), 25.6 (dd, $^2J_{PP}$ = 48.8 Hz, $^1J_{PRh}$ = 138.8 Hz, P_{exo} S_{Rh}), 42.0 (dd, $^2J_{PP}$ = 50.0 Hz, $^1J_{PRh}$ =

131.6 Hz, P_{exo} R_{Rh}), 42.6 (dd, $^2J_{PP}$ = 48.8 Hz, $^1J_{PRh}$ = 131.6 Hz, P_{endo} S_{Rh}), −143.8 (sept, PF_6 R_{Rh} and S_{Rh}).

[Cp*Ir(Norphos)Cl]PF_6 (11). Diastereomer mixture (S_{Ir})-**11** (diastereomer **A**, 42%) and (R_{Ir})-**11** (diastereomer **B**, 58%). Yield: 96%. Mp: >190 °C dec. Anal. Calcd for $C_{41}H_{43}ClF_6IrP_3$ (970.36): C, 50.75; H, 4.47. Found: C, 49.91; H, 4.53. MS (PI-LSIMS, CH_2Cl_2; *m*/*z* (relative intensity)): 825.3 (100) [cation]; 790.3 (7) [cation − Cl].

Crystallization from *n*-hexane/acetone gave (S_{Ir})/(R_{Ir})-**11**. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.33 (d, $^2J_{H7H8}$ = 9.1 Hz, H7 R_{Ir}), 1.47 (t, $^4J_{PH}$ = 2.4 Hz, Cp* H S_{Ir}), 1.48 (t, $^4J_{PH}$ = 2.4 Hz, Cp* H R_{Ir}), 1.74 (d, $^2J_{H7H8}$ = 8.8 Hz, H7 S_{Ir}), 1.81 (bd, $^2J_{H7H8}$ = 9.1 Hz, H8 R_{Ir}), 2.11 (bd, $^2J_{H7H8}$ = 8.8 Hz, H8 S_{Ir}), 2.69 (bs, H4 R_{Ir}), 2.76 (m, H2 S_{Ir}), 2.98 (bs, H4 S_{Ir}), 3.09 (bs, H3 R_{Ir}), 3.17 (m, H1 R_{Ir}), 3.17 (bs, H3 S_{Ir}), 3.39 (m, H2 R_{Ir}), 3.88 (m, H1 S_{Ir}), 5.01 (dd, $^3J_{H5H6}$ = 5.5 Hz, $^3J_{H5H3}$ = 2.8 Hz, H5 S_{Ir}), 5.84 (dd, $^3J_{H5H6}$ = 5.5 Hz, $^3J_{H5H3}$ = 2.8 Hz, H5 R_{Ir}), 5.89 (dd, $^3J_{H5H6}$ = 5.5 Hz, $^3J_{H6H4}$ = 3.3 Hz, H6 S_{Ir}), 6.50 (dd, $^3J_{H5H6}$ = 5.6 Hz, $^3J_{H6H4}$ = 3.3 Hz, H6 R_{Ir}), 7.02−7.84 (m, aromat H R_{Ir} and S_{Ir}). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ −7.9 (d, $^2J_{PP}$ = 30.5 Hz, P_{endo} R_{Ir}), −6.0 (d, $^2J_{PP}$ = 30.1 Hz, P_{exo} S_{Ir}), 6.7 (d, $^2J_{PP}$ = 30.5 Hz, P_{exo} R_{Ir}), 7.5 (d, $^2J_{PP}$ = 30.1 Hz, P_{endo} S_{Ir}), −143.8 (sept, PF_6 S_{Ir} and R_{Ir}).

Supporting Information Available: Figures and tables giving X-ray data for complexes **1**−**11**, including atomic coordinates, displacement parameters, bond lengths and angles, hydrogen coordinates, and hydrogen bonds; these data are also available as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

OM0400292