Diastereoselective Routes to [Amino{$\sigma(P)$:η^6-(*ansa*-phosphinite)benzene} chlororuthenium(II)] PF_6 Salts: Kinetic versus Thermodynamic Preferences

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A novel chiral phosphinite derivative was designed as a ligand for Ru^{2+} ions to give access to new enantiomerically pure or diastereomerically enriched [{$\sigma(P)$:η^6-(*ansa*-phosphinite)benzene}Ru(II) complexes. We are interested in this class of compounds as potential catalysts for enantioselective transfer hydrogenation of organic carbonyl compounds. The preparation of enantiopure (*R*)-[{$\sigma(P)$:η^6-(*ansa*-phosphinite)benzene}Ru(II)Cl_2] (**6**) was achieved in good yeld on the basis of (*S*)-mandelic acid. Four diastereomeric [{$\sigma(P)$:η^6-(*ansa*-phosphinite)benzene}Ru(II)Cl(NH_2R)]$^+$ complex PF_6^- salts were obtained from neutral **6** by nucleophilic substitution of a chloride ligand with primary amines. For aniline and *p*-fluoroaniline salts **7** and **8** a significant excess of the (S_{Ru},R_C)-diastereomers **7***S* and **8***S* was observed in the reaction mixtures as the kinetically preferred species, and **7***S* could be isolated as a pure diastereomer. No diastereoselectivity was observed in the reaction mixtures of (*R*)- and (*S*)-1-phenylethylamine salts **9** and **10** right after preparation. **7**, **8**, and **9** epimerize at the metal center. This leads to a loss of diastereoselectivity of **7***S* and **8***S* but enrichment of (R_{Ru},R_C)-diastereomer **9***R*. Pure diastereomers **7***S,* **9***R*, and **10***S* as well as a 1:1 diastereomeric mixture **8***S*/**8***R* have been characterized structurally. The experimental setup allowed detailed insight into the specific X-ray crystallographic, CD, and NMR spectroscopic properties of defined stereoisomers of chiral Ru(II) complexes. The kinetic diastereoselectivities of **7***S* and **8***S* are explained by a H-bond delivery effect, while pure diastereomer salt **9***R* is configuratively stable.

Introduction

Configurationally stable *hapto*-arene complexes with pseudotetrahedral chiral metal centers[1] and especially chiral Ru(II) η^6-arene complexes have gained increasing interest after their discovery by Noyori as enantioselective catalysts for transfer hydrogenations.[2] In the scope of potential enantioselective catalysts an *ansa* linkage from the η^6-arene ligand of such complexes via an alkyl chain with a terminal σ-donor functionality complexed to the pseudotetrahedral Ru(II) center bears unique structural features: (i) An *ansa* chain with two to three atoms as covalent links besides the σ-donor functionality stabilizes the η^6-arene moiety toward substitution. (ii) A chiral *ansa* chain can serve as a provider of "chiral information" in the sense that it closes up one diastereotopic side of the Ru(II) center and creates a "chiral pocket" around it.

Thus, not only could ligand substitution proceed diastereoselectively, but also the resulting chiral Ru(II) center should be

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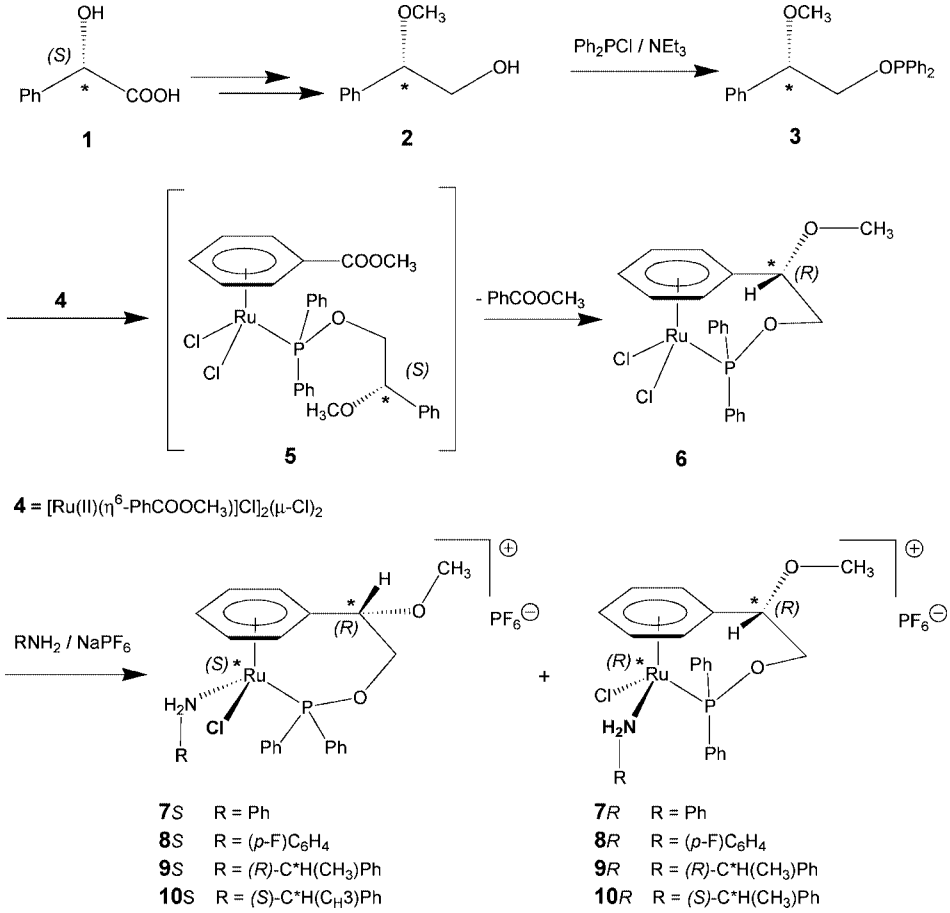
Scheme 1. Syntheses of Diastereomeric Complex Salts {[η^6:σ(*P*)-(arene-*ansa*-phosphinite)]Ru(II)(amino)(chloro)}$^+PF_6^-$ 7−10 Starting from Natural (*S*)-Mandelic Acid (1)



influenced in its configurational stability via diastereomeric interaction with the chiral *ansa* chain. Within this scope Ru(II) η^6-arene complexes containing nitrogen and oxygen[3a,b] as well as phosphorus and carbene[4] donor groups at the terminus of the *ansa* chain attracted attention. In previous studies we also investigated a series of Ru(0) η^6-arene complexes containing unlinked chiral chains with N- and O-donors.[3c,d] Ward succeeded in the full configurational stabilization of a chiral Ru(II) center by anchoring the metal in a rigid bicyclic *ansa* framework connected with a η^6-arene ligand.[5a] Pregosin achieved an unprecedented stabilization of a notorious labile η^6-naphthalene ligand in a Ru(II) complex just by *ansa* linkage.[5b] Wills reported a major breakthrough with this concept by stabilizing Noyori's (*S,S*)-TsDPEN Ru(II) catalyst via an *ansa* linkage to its η^6-arene ligand, thus achieving unchanged high enantioselectivity in the transfer hydrogenation of ketones with a higher TON.[5c] This proved *ansa* linking and stabilized the catalyst in the sense of a "three-point-attachment". Previously we reported on [σ(*P*):η^6-(*ansa*-phosphine)benzene] and [σ(*P*):η^6-(*ansa*-phosphetane)benzene] Ru(II)Cl_2 complexes[5d,e] and studied diastereoselective nucleophilic substitutions of one chloride ligand by various amines resulting in cationic complexes with chiral Ru(II) centers. This simple two-step synthetic strategy enabled us to screen a large variety of *ansa*-linked Ru(II) η^6-arene complexes as potentially enantioselective transfer hydrogenation catalysts

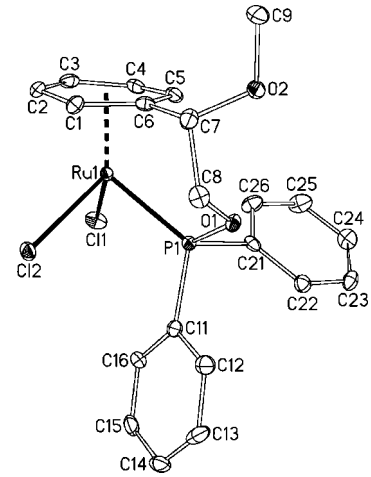


Figure 1. Thermal ellipsoid plot (50% probability) of the molecular structure of chiral complex **6**: (*R*), methoxy group *"out of plane"*; hydrogen atoms omitted for clarity; selected bond distances and angles, see Table 1.

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Table 1. Selected Bond Distances and Angles of Chiral Complex 6

distance	[Å]	angle	[deg]
Ru(1)−Cl(1)	2.4080(8)	Cl(1)−Ru(1)−Cl(2)	86.51(3)
Ru(1)−Cl(2)	2.4089(7)	P(1)−Ru(1)−Cl(1)	89.20(3)
Ru(1)−P(1)	2.2927(8)	P(1)−Ru(1)−Cl(2)	90.90(3)
Ru(1)−C(1)	2.185(3)	P(1)−Ru(1)−C(1)	117.43(11)
Ru(1)−C(2)	2.288(3)	P(1)−Ru(1)−C(2)	154.87(8)
Ru(1)−C(3)	2.287(3)	P(1)−Ru(1)−C(3)	152.14(8)
Ru(1)−C(4)	2.184(3)	P(1)−Ru(1)−C(4)	114.51(9)
Ru(1)−C(5)	2.186(2)	P(1)−Ru(1)−C(5)	88.22(11)
Ru(1)−C(6)	2.214(3)	P(1)−Ru(1)−C(6)	89.72(8)
P(1)−O(1)	1.633(2)	C(9)−O(2)−C(7)	113.0(2)
C(8)−O(1)	1.446(4)	C(6)−C(7)−O(2)	111.5(3)
C(7)−C(8)	1.510(4)	C(6)−C(7)−C(8)	112.5(3)
C(6)−C(7)	1.518(4)	C(7)−C(8)−O(1)	110.4(2)
C(7)−O(2)	1.419(4)	C(8)−O(1)−P(1)	118.8(2)
C(9)−O(2)	1.427(4)	O(1)−P(1)−Ru(1)	111.03(8)

in a combinatorial-divergent approach. However, enantioselectivities achieved in the transfer hydrogenation of ketones with this class of diastereomeric complexes were surprisingly low despite their high configurational stability.[5d] Therefore we searched for novel {σ(Do):η^6-(*ansa*-benzene}Ru(II) complexes (Do = benzene side chain donor functionality), which influence the electronic situation of a transition metal center. Here we report on the approach to replace the *ansa*-phosphine by an *ansa*-phosphinite arene ligand based on cheap natural (*S*)-mandelic acid, **1**. Phosphinite Ru(II) complexes already proved to be successful in enantioselecive hydrogenation and transfer

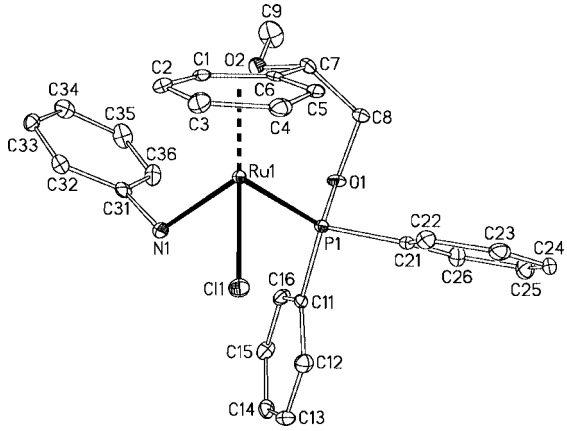

Figure 2. Thermal ellipsoid plot (50% probability) of the molecular structure of diastereomeric complex cation of PF_6^- salt **7***S*: (S_{Ru},*R*), methoxy group *"in plane"*; hydrogen atoms omitted for clarity; selected bond distances and angles, see Table 3.

Table 2. Selected Bond Distances and Angles of the Complex Cation of PF_6^- Salt 7*S*

distance	[Å]	angle	[deg]
Ru(1)−Cl(1)	2.3958(6)	Cl(1)−Ru(1)−P(1)	87.00(2)
Ru(1)−P(1)	2.2944(6)	Cl(1)−Ru(1)−N(1)	82.60(5)
Ru(1)−N(1)	2.182(2)	P(1)−Ru(1)−N(1)	90.72(5)
Ru(1)−C(1)	2.196(2)	P(1)−Ru(1)−C(2)	154.36(6)
Ru(1)−C(2)	2.286(2)	P(1)−Ru(1)−C(3)	152.77(6)
Ru(1)−C(3)	2.278(2)	N(1)−Ru(1)−C(4)	153.50(8)
Ru(1)−C(4)	2.192(2)	N(1)−Ru(1)−C(5)	157.46(7)
Ru(1)−C(5)	2.194(2)	Cl(1)−Ru(1)−C(1)	155.48(6)
Ru(1)−C(6)	2.195(2)	Cl(1)−Ru(1)−C(6)	157.73(6)
P(1)−O(1)	1.621(2)	C(9)−O(2)−C(7)	115.0(2)
C(8)−O(1)	1.447(3)	C(6)−C(7)−O(2)	106.8(2)
C(7)−C(8)	1.525(3)	C(6)−C(7)−C(8)	114.1(2)
C(6)−C(7)	1.524(3)	C(7)−C(8)−O(1)	113.2(2)
C(7)−O(2)	1.417(3)	C(8)−O(1)−P(1)	119.3(2)
C(9)−O(2)	1.419(3)	O(1)−P(1)−Ru(1)	111.97(6)
N(1)−C(31)	1.457(3)	Ru(1)−N(1)−C(31)	117.2(2)

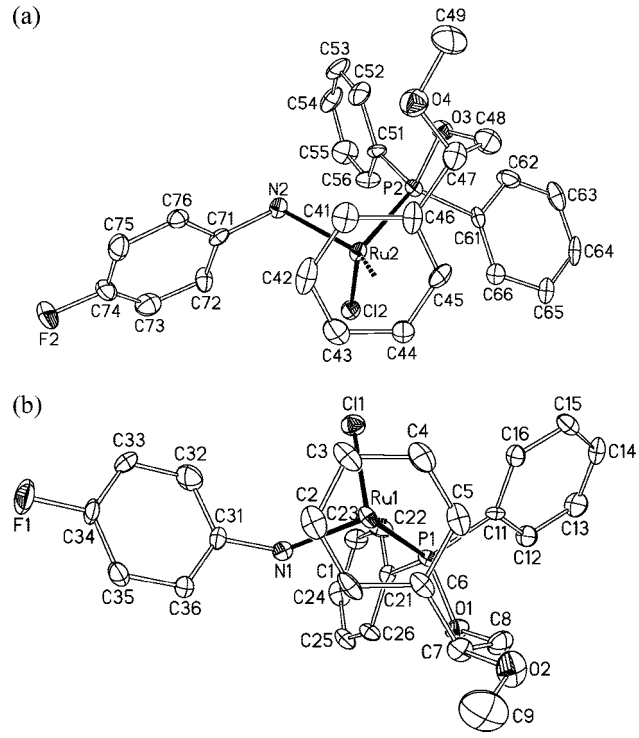

Figure 3. Thermal ellipsoid plot (50% probability) of the molecular structure of the diastereomeric complex cations of PF_6^- salt **8** taken out of a common unit cell (top views on the η^6-arene moieties, hydrogen atoms omitted for clarity): (a) **8***S* (S_{Ru},*R*), methoxy group *"in plane"*; (b) **8***R* (R_{Ru},*R*), methoxy group *"out of plane"*; selected bond distances and angles, see Table 3 for **8***S* and Table 4 for **8***R*. Note the pseudomirror positions of the equatorial phosphinite phenyl groups and the *p*-fluoroaniline ligands in both diastereomers.

Table 3. Selected Bond Distances and Angles of the Complex Cation of PF_6^- Salt 8*S*

distance	[Å]	angle	[deg]
Ru(2)−Cl(2)	2.396(2)	Cl(2)−Ru(2)−P(2)	86.37(5)
Ru(2)−P(2)	2.287(2)	Cl(2)−Ru(2)−N(2)	83.2(2)
Ru(2)−N(2)	2.181(4)	P(2)−Ru(2)−N(2)	87.6(2)
Ru(2)−C(41)	2.219(6)	P(2)−Ru(2)−C(42)	149.7(2)
Ru(2)−C(42)	2.262(5)	P(2)−Ru(2)−C(43)	158.4(2)
Ru(2)−C(43)	2.235(6)	N(2)−Ru(2)−C(44)	150.4(2)
Ru(2)−C(44)	2.197(6)	N(2)−Ru(2)−C(45)	161.4(2)
Ru(2)−C(45)	2.212(5)	Cl(2)−Ru(2)−C(41)	160.8(2)
Ru(2)−C(46)	2.222(5)	Cl(2)−Ru(2)−C(46)	151.5(2)
P(2)−O(3)	1.624(4)	C(49)−O(4)−C(47)	114.8(4)
C(48)−O(3)	1.446(6)	C(46)−C(47)−O(4)	108.1(4)
C(47)−C(48)	1.534(6)	C(46)−C(47)−C(48)	113.5(4)
C(46)−C(47)	1.525(8)	C(47)−C(48)−O(3)	111.4(4)
C(47)−O(4)	1.415(5)	C(48)−O(3)−P(2)	117.2(3)
C(49)−O(4)	1.437(6)	O(3)−P(2)−Ru(2)	112.2(2)
N(2)−C(71)	1.468(7)	Ru(2)−N(2)−C(71)	117.9(3)
F(2)−C(74)	1.366(6)		

hydrogenation reactions of ketones,[6] also, but to the best of our

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Table 4. Selected Bond Distances and Angles of the Complex Cation of PF_6^- Salt 8*R*

distance	[Å]	angle	[deg]
Ru(1)−Cl(1)	2.387(2)	Cl(1)−Ru(1)−P(1)	86.76(5)
Ru(1)−P(1)	2.294(2)	Cl(1)−Ru(1)−N(1)	82.9(2)
Ru(1)−N(1)	2.154(4)	P(1)−Ru(1)−N(1)	88.3(2)
Ru(1)−C(1)	2.176(5)	P(1)−Ru(1)−C(2)	153.5(2)
Ru(1)−C(2)	2.275(5)	P(1)−Ru(1)−C(3)	155.9(2)
Ru(1)−C(3)	2.302(5)	N(1)−Ru(1)−C(4)	152.9(2)
Ru(1)−C(4)	2.200(6)	N(1)−Ru(1)−C(5)	158.8(2)
Ru(1)−C(5)	2.201(6)	Cl(1)−Ru(1)−C(1)	156.5(2)
Ru(1)−C(6)	2.176(5)	Cl(1)−Ru(1)−C(6)	156.3(2)
P(1)−O(1)	1.622(4)	C(9)−O(2)−C(7)	114.2(4)
C(8)−O(1)	1.449(6)	C(6)−C(7)−O(2)	108.7(4)
C(7)−C(8)	1.528(6)	C(6)−C(7)−C(8)	115.9(4)
C(6)−C(7)	1.502(7)	C(7)−C(8)−O(1)	111.6(4)
C(7)−O(2)	1.409(5)	C(8)−O(1)−P(1)	119.7(3)
C(9)−O(2)	1.423(6)	O(1)−P(1)−Ru(1)	112.6(2)
N(1)−C(31)	1.455(7)	Ru(1)−N(1)−C(31)	116.2(3)
F(1)−C(34)	1.377(5)		

knowledge only Kurosawa reported [σ(*P*):η⁶-(*ansa*-phosphinite)benzene]Ru(II)Cl_2 complexes he obtained by coordination of chlorophosphines on a 3-hydroxyropyl Ru(II) η⁶-arene dimer followed by intramolecular alcoholysis.[3a] We wish to present a chiral version of such Ru(II) η⁶-arene complexes with a chiral *ansa*-phosphinite chain that we complementary obtained by an η⁶-arene exchange reaction, previously attempted by Ward.[5a]

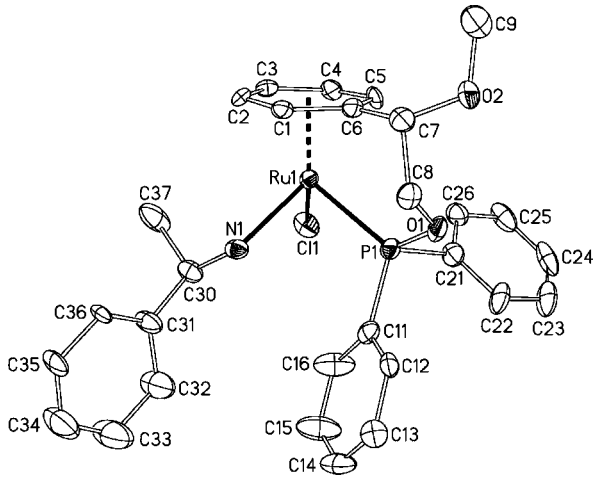


Figure 4. Thermal ellipsoid plot (50% probability) of the molecular structure of the diastereomeric complex cation of PF_6^- salt **9*R***: (R_{Ru},*R*,*R*), methoxy group *"out of plane"*; hydrogen atoms omitted for clarity; selected bond distances and angles, see Table 5.

Table 5. Selected Bond Distances and Angles of the Complex Cation of PF_6^- Salt 9*R*

distance	[Å]	angle	[deg]
Ru(1)−Cl(1)	2.413(2)	Cl(1)−Ru(1)−P(1)	86.55(5)
Ru(1)−P(1)	2.293(2)	Cl(1)−Ru(1)−N(1)	87.5(2)
Ru(1)−N(1)	2.183(4)	P(1)−Ru(1)−N(1)	91.2(2)
Ru(1)−C(1)	2.213(5)	P(1)−Ru(1)−C(2)	151.5(2)
Ru(1)−C(2)	2.281(5)	P(1)−Ru(1)−C(3)	155.7(2)
Ru(1)−C(3)	2.286(5)	N(1)−Ru(1)−C(4)	149.3(2)
Ru(1)−C(4)	2.207(5)	N(1)−Ru(1)−C(5)	158.5(2)
Ru(1)−C(5)	2.211(5)	Cl(1)−Ru(1)−C(1)	158.6(2)
Ru(1)−C(6)	2.222(5)	Cl(1)−Ru(1)−C(6)	151.1(2)
P(1)−O(1)	1.625(4)	C(9)−O(2)−C(7)	114.9(5)
C(8)−O(1)	1.433(7)	C(6)−C(7)−O(2)	111.7(5)
C(7)−C(8)	1.507(8)	C(6)−C(7)−C(8)	111.6(5)
C(6)−C(7)	1.524(7)	C(7)−C(8)−O(1)	111.4(5)
C(7)−O(2)	1.419(7)	C(8)−O(1)−P(1)	120.3(3)
C(9)−O(2)	1.418(8)	O(1)−P(1)−Ru(1)	112.7(2)
N(1)−C(30)	1.506(7)	Ru(1)−N(1)−C(30)	121.6(3)

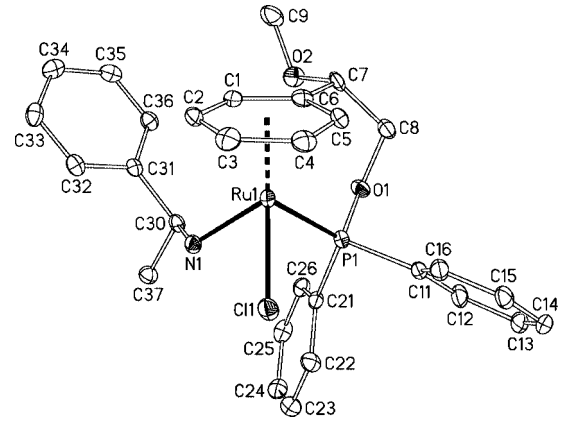


Figure 5. Thermal ellipsoid plot (50% probability) of the molecular structure of the diastereomeric complex cation of PF_6^- salt **10*S***: (S_{Ru},*S*,*R*), methoxy group *"in plane"*; hydrogen atoms omitted for clarity; selected bond distances and angles, see Table 6.

Table 6. Selected Bond Distances and Angles of the Complex Cation of PF_6^- Salt 10*S*

distance	[Å]	angle	[deg]
Ru(1)−Cl(1)	2.4038(7)	Cl(1)−Ru(1)−P(1)	87.61(3)
Ru(1)−P(1)	2.2928(7)	Cl(1)−Ru(1)−N(1)	81.83(7)
Ru(1)−N(1)	2.150(2)	P(1)−Ru(1)−N(1)	89.08(7)
Ru(1)−C(1)	2.184(3)	P(1)−Ru(1)−C(2)	153.65(8)
Ru(1)−C(2)	2.261(3)	P(1)−Ru(1)−C(3)	156.38(8)
Ru(1)−C(3)	2.266(3)	N(1)−Ru(1)−C(4)	150.82(10)
Ru(1)−C(4)	2.211(3)	N(1)−Ru(1)−C(5)	159.89(9)
Ru(1)−C(5)	2.218(3)	Cl(1)−Ru(1)−C(1)	156.07(8)
Ru(1)−C(6)	2.202(3)	Cl(1)−Ru(1)−C(6)	156.06(7)
P(1)−O(1)	1.621(2)	C(9)−O(2)−C(7)	113.1(2)
C(8)−O(1)	1.445(4)	C(6)−C(7)−O(2)	110.2(2)
C(7)−C(8)	1.527(4)	C(6)−C(7)−C(8)	114.2(2)
C(6)−C(7)	1.527(4)	C(7)−C(8)−O(1)	113.2(2)
C(7)−O(2)	1.428(3)	C(8)−O(1)−P(1)	119.3(2)
C(9)−O(2)	1.432(4)	O(1)−P(1)−Ru(1)	112.74(9)
N(1)−C(30)	1.504(3)	Ru(1)−N(1)−C(30)	124.8(2)

Results and Discussion

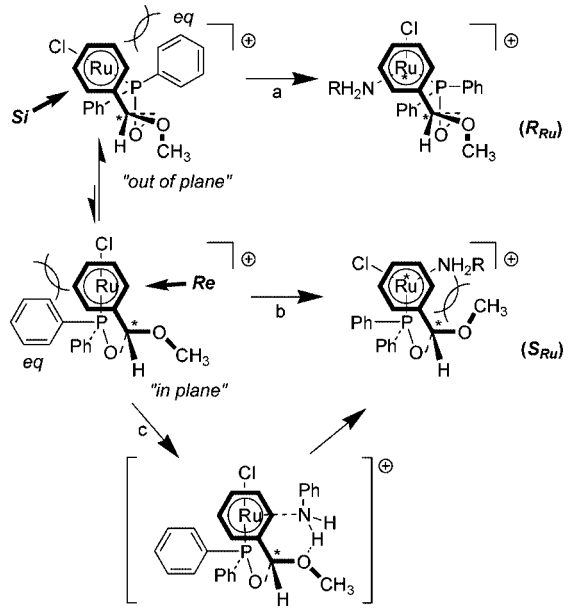
Synthesis of Complex 6. Preparation of chiral complex **6** is based on (*S*)-mandelic acid (**1**), which was converted into (2*S*)-2-methoxy-2-phenylethanol (**2**) according to published procedures[7a–d] (Scheme 1). Base-promoted alcoholysis of **2** afforded the target *ansa*-phosphinite arene ligand **3**. Its σ-complexation to ruthenium was achieved with η⁶-methylbenzoate ruthenium dichloride dimer **4**[5d,e] followed by an arene exchange reaction. Formation of stable σ(*P*)-complex **5** was monitored by ^{31}P NMR. After completion of this step, the solution was heated at 120 °C in a pressure Schlenk tube until the C-phenyl group of **3** substituted the η⁶-methylbenzoate ligand of **5** to form neutral (*R*)-[{σ(*P*):η⁶-(*ansa*-phosphinite)benzene}Ru(II)Cl_2] (**6**) in 62% isolated yield (Figure 1).

The methoxy group of **6** adopts rather an *"out-of-plane"* conformation with respect to the η⁶-arene Ru(II) fragment, whereas the methyl group in the analog *ansa*-phosphine complex occupies a clear *exo* position.[5d,8a] The Ru(1)−Cl bond lengths of 2.41 Å are elongated, but the Ru(1)−P(1) bond, at 2.29 Å, is slightly shortened (Table 1). Therefore it can be concluded that for **6** the Ru(1)−Cl bonds are weakened, while the Ru(1)−P(1) bond is strengthened. Also the *trans* influence of the phosphinite ligand on C(2) and C(3) of the η⁶-arene ligand seems to be retarded. These differences point to a phosphinite moiety, which is a slightly weaker π-acceptor but a little better σ-donor than related tethered phosphine ligand functions.

Table 7. Crystallographic Data, Data Collection, and Refinement Details of Neutral Complex 6 and PF_6^- Salts 7*S*, 8·(MeOH)$_{0.5}$, 9*R*·MeOH, and 10*S* Measured at 100 K

	6	**7S**	**8**·(MeOH)$_{0.5}$	**9***R* (MeOH)	**10***S*
empirical formula	$C_{21}H_{21}Cl_2O_2PRu$	$C_{27}H_{28}ClF_6NO_2P_2Ru$	$C_{27.5}H_{29}ClF_7NO_{2.5}P_2Ru$	$C_{30}H_{36}ClF_6NO_3P_2Ru$	$C_{29}H_{32}ClF_6NO_2P_2Ru$
mol weight	508.35	710.99	745.00	771.06	739.04
cryst syst	monoclinic	monoclinic	triclinic	orthorhombic	monoclinic
space group	$P2_1$ (no. 4)	$P2_1$ (no. 4)	$P1$ (no. 1)	$P2_12_12_1$ (no. 19)	$P2_1$ (no. 4)
a (Å)	9.7487(3)	9.364(1)	10.9667(9)	10.554(2)	9.4734(4)
b (Å)	9.9464(7)	15.414(2)	10.9759(7)	13.150(1)	16.2505(8)
c (Å)	10.4269(6)	9.544(2)	14.2777(7)	23.409(4)	9.7948(7)
α (deg)	90	90	76.588(5)	90	90
β (deg)	91.709(3)	93.54(1)	89.832(5)	90	91.773(6)
γ (deg)	90	90	60.962(5)	90	90
V (Å^3)		1374.9(4)	1449.4(2)	3248.8(9)	1507.2(2)
Z	2	2	2	4	2
ρ (g/cm^3) (calcd)	1.670	1.717	1.707	1.576	1.628
μ (mm^{-1})	1.133	0.852	0.819	0.730	0.781
F(000)	512	716	750	1568	748
abs corr	SADABS	SADABS	numerical	numerical	SADABS
T_{min}; T_{max}	0.871; 0.923	0.801; 0.960	0.790; 0.894	0.773; 0.930	0.759; 0.860
2*θ* interval (deg)	$6.0 \le 2\theta \le 57.4$	$6.8 \le 2\theta \le 55.8$	$6.3 \le 2\theta \le 55.8$	$6.4 \le 2\theta \le 54.2$	$6.5 \le 2\theta \le 57.1$
no. of coll reflns	30 994	38 631	43 503	32 057	39 743
no. of indep reflns	5214	6543	12743	7093	7577
no. of obsd reflns $F_0 \ge 4\sigma(F)$	4541	6135	10553	6386	6701
no. of ref params	246	362	761	456	379
wR2 (all data)	0.0614	0.0451	0.0792	0.1114	0.0623
R1 ($F_0 \ge 4$s(F))	0.0302	0.0219	0.0359	0.0527	0.0306
GooF on F^2	0.826	1.001	1.022	1.173	1.075
abs struct param	−0.03(3)	0.01(2)	−0.01(2)	0.01(4)	−0.01(2)
max.; min. electr dens	0.567; −0.785	0.293; −0.432	0.834; −0.535	0.980; −1.153	0.509; −0.501

Scheme 2. Permutations of Nucleophilic Ligand Attack on Proposed Cationic 16 VE Ru(II) Intermediates (top view on η^6-arene moieties): (a) Sterically Preferred Attack of Incoming Aniline on Cationic 16 VE Intermediate in "*Out-of-Plane*" Conformation, (b) Sterically Preferred Attack of Incoming Aniline on Cationic 16 VE Intermediate in "*in Plane*" Conformation, (c) Proposed Delivery Effect via H-Bond Formation Leading to the Preferred Formation of 7*S* and 8*S* under the Reaction Conditions



Diastereoselective Substitution Reactions. . Complex **6** was subjected to nucleophilic substitution reactions of one chloride ligand at the diastereotopic Ru(II) center with primary anilines and aliphatic chiral amines, to generate complex salts with an additional chiral center at the metal (Scheme 1).[8b] The reactions were performed with $NaPF_6$ as chloride-trapping reagent. Only for aniline and *p*-fluoroaniline PF_6 salts **7** and **8** could a significant excess of the diastereomers **7***S* and **8***S* be determined in the reaction mixtures by NMR spectroscopy, but not for **9** and **10**, with (*R*)- and (*S*)-1-phenylethylamine ligands. A configurational lability of the chiral Ru(II) center of the complex salts was indicated when working up the compounds. **7***S* and

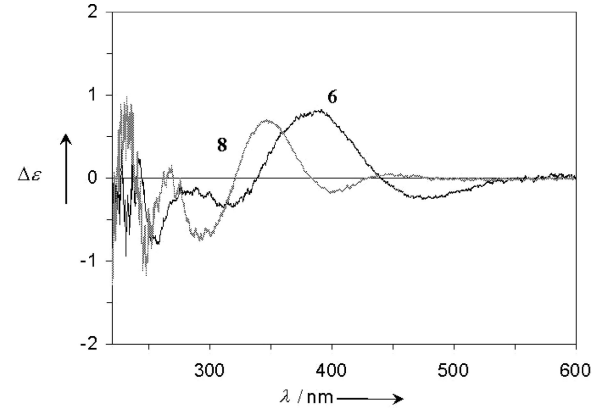


Figure 6. CD spectra of complex **6** (bold line) and salt **8** (nonbold line) in MeOH.

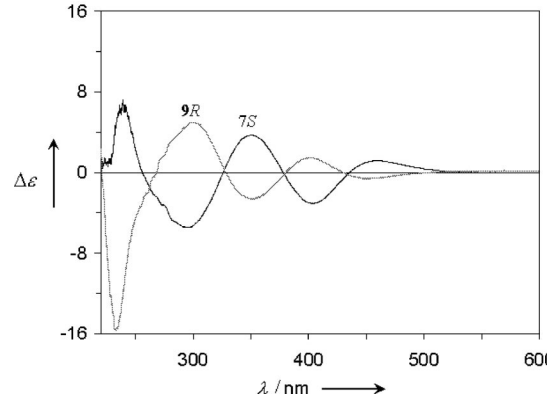


Figure 7. CD spectra of complex salts **7***S* (bold line) and **9***R* (nonbold line) in MeOH.

Table 8. Main UV and CD Spectral Features in Methanol of Compounds 6, 7*S*, 8, 9*R*, and 10

compound	UV $\lambda(\varepsilon \times 10^{-3})$	CD $\lambda(\Delta\varepsilon)$
6	473(0.24), 353(1.5), 228sh(21.4)	475(−0.25), 389(0.81), 316(−0.32), 258(−0.79)
7*S*	349(1.5), 276sh(5.9), 245sh(16.0)	461(1.18), 404(−3.05), 350(3.72), 295(−5.45), 240(6.55)
8	350(1.5), 275sh(6.2), 246sh(15.2)	444(0.04), 403(−0.17), 345(0.69), 294(−0.75), 267(0.11), 248(−1.2)
9*R*	340sh(1.27), 323(1.38), 228(22.81)	452(−0.66), 403(1.43), 352(−2.68), 301(4.91), 233(−15.62)
10	327(1.38), 228(20.67)	419(−0.41), 346(0.44), 301sh(−0.44), 230(−4.07)

8*S* epimerize at the metal center, and longer handling of diastereomeric mixture **9** resulted in an enrichment of diastereomer **9*R***. The ^{31}P NMR signal assignments to particular diastereomers of **7**−**9** were concluded from correlations with the ^{1}H NMR spectra of the reaction samples, of the crude, and of the purified products. This was confirmed with NOE measurements and X-ray crystal structure analysis (*vide infra*), but the approach failed for **10**, because no de was observed in that case. Salts **7**−**9** formed well-defined crystalline materials suitable for X-ray structure analysis: **7** as **7*S*** exclusively (Figure 2, Table 2), **8** in a 1:1 ratio of **8*S*** and **8*R*** (Figure 3, Tables 3, 4), and **9** as **9*R*** only again (Figure 4, Table 5). **10** precipitated regularly as a 1:1 mixture of diastereomers as indicated by NMR and CD, but some single crystals of **10*S*** could be sorted out manually (Figure 5, Table 6). The preservation of the original *R* configuration of the chiral benzylic center of the *ansa* chain was confirmed in all cases, so the benzyl stereogenic center of the ligand is stable with respect to all chemical manipulations applied. A complete set of crystallographic data are summarized in Table 7.

Unlike **7** and **8**, diastereomer **9*R*** did not epimerize over periods of weeks in a number of solvents tested. The configurative stability of **9*R*** resembles that of the analogue (R_{Ru},R_C)-enantiomers of the [{σ(*P*):η⁶-(*ansa*-phosphine)benzene}Ru(II)Cl-(NH_2R)]$^+$ complexes described earlier.[5d] As for neutral **6**, the molecular structure of the cation of **9*R*** in the solid state (Figure 4) is characterized by an *"out-of-plane"* orientatiton of the methoxy group. This stabilizes a chairlike conformation of the *ansa* chain, which in turn geometrically fixes the phosphinite coordination mode in a way that one phenyl group adopts an *axial* (*ax*) and the other an *equatoria*l (*eq*) position. Coordinating from the *si* face, the amine ligand adopts the position with the longest distance to the equatorial phenyl ring with a minimum of steric repulsion. In contrast to that, aniline salt **7*S*** epimerized within hours at ambient temperature in acetone-d_6 to yield mixtures of **7*R*** and **7*S***. The molecular structure of the cation of **7*S*** with its *S* configuration of the Ru(II) center (Figure 2) differs clearly fom **9*R*** and **6** by a sterically unfavored *"in-plane"* conformation of the methoxy group. Again, a chairlike conformation of the *ansa* chain is observed, but with an enhanced strain if compared to the complex cations with *R* configurations of the metal atom. The phosphinite coordination geometry is also fixed in an *"ax-eq"* mode, but with opposite diastereotopic orientation causing the amine to coordinate from the Re side here, to reduce steric repulsion. These stereochemical results are completed by the crystal structure of **8** (Figure 3, Table 4, Table 5), where both diastereomers **8*S*** and **8*R*** are present as independent complex cations in the unit cell. As one would assume, diastereomer **8*S*** adopts the same conformation as **7*S*** and **10*S***, whereas **8*R*** is a close relative of **9*R***. In all investigated cases of (S_{Ru},R_C) diastereomers, the methyl group of the methoxy moiety "turns away" from the η⁶-arene ring, leaving the main steric interactions to the oxygen atom alone. The higher volume of a methyl group with respect to an oxygen atom thus generates the driving force for the highly preferred formation of (S_{Ru},R_C) over (R_{Ru},R_C) diastereomers of the analogue [{σ(*P*):η⁶-(*ansa*-phosphine)benzene}Ru(II)Cl(NH_2R)]$^+$ complex cations.[5d] Complementarily it can be understood why the configurationally labile diastereomer **7*S*** can be isolated at all.

Contrary and unexpected to the analogue phosphine systems the sterically less favored diastereomers **7*S*** and **8*S*** are formed in excess in the reaction mixture; in no case was the formation of the (R_{Ru},R_C) diastereomers preferred under kinetic conditions. Only 1:1 diastereomer mixtures for **9** and **10** resulted; thus the direction of the kinetic diastereoselectivity points to a clear dependence on starting material **6**, while its magnitude is determined by the nature of the amine ligand. For the amine substitution an S_N1-type reaction mode via cationic 16 VE [{σ(*P*):η⁶-(*ansa*-phosphinite)benzene}Ru(II)Cl]$^+$ intermediates by loss of one chloride ligand can be considered,[5d,9] which are closely related to the molecular structures of the tethered species found in this study. This suggests *"out-of-plane"* and *"in-plane"* conformations of the methoxy groups again, and the sterically preferred *"out-of-plane"* conformation is believed to dominate for the 16 VE intermediates in the reaction solution. Due to the orientation of the phenyl substituents of the phosphorus atom, this conformer promotes a sterically favored *si* face attack of the incoming amine ligand, which in turn should lead to the formation of the more stable (S_{Ru},R_C) amine complex (Scheme 2, pathway a). The energetically discriminated *"in-plane"* conformation of the intermediate, however, would lead to a preferred *re* attack of the incoming amine ligand and thus to the less stable (S_{Ru},R_C) complex cation (pathway b). These considerations would account for the S_{Ru} diastereomers only as the minor component; thus another interaction is required to explain their dominance for **7** and **8**. A delivery effect as observed for chromium(0) tricarbonyl η⁶-arene complexes[10] serves as the model. The oxygen atom of the methoxy group has the potential to form a hydrogen bridge with the approaching amine, which can only be delivered to the Ru(II) center in the case of an *"in-plane"* conformation (pathway c). The effect should be controlled by the strength of the resulting O−H−N hydrogen bond, which is a function of the amino protons' acidity. The acidities of aniline (p$K_a \approx 25$) and *p*-fluoroaniline

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(8) (a) Note the denotation of the absolute configuration of the chiral center in the *ansa* chain of **6** formally changes to (*R*). (b) The stereochemical descriptors for the (π-arene)RuL_3 units of this paper follow the recommendations of: Bünzli-Trepp, U. *Handbuch für die systematische Nomenklatur der Organischen Chemie, Metallorganischen Chemie und Koordinationschemie*; Logos Verlag: Berlin, 2001; Part A 6.4(d).

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allow the delivery effect to proceed, but vanishes in the case of 1-phenylethylamine ($pK_a \approx 34$). Due to a missing partner for the formation of hydrogen bridges with incoming amines, the chloride substitution results on tethered arene phosphine and phophetane ruthenium complexes are not influenced that way.[5d,e]

NMR Study. The assignments of the ^{1}H NMR and ^{13}C NMR signals belonging to the particular diastereomers of mixtures **8***S*/**8***R* and **10***S*/**10***R* were accomplished by similarity correlation of NOE measurements of diastereomerically pure **7***S* and is worked out in detail in the Supporting Information. The distinct assignable NOE effects to particular diastereomers give clear evidence that the conformational flexibility of the particular *ansa* chains is highly restricted.

Circular Dichroism Study. UV and CD spectra (210−600 nm range, MeOH) of compounds **6**, **7***S*, **8**, **9***R*, and **10** were recorded (Figures 6 and 7, Table 8), in order to get further information about absolute and relative configurations of these complexes in solution and deeper insight into the epimerization process of **7***S*. The UV spectrum of **6** (Table 8) shows two absorption bands at 473 and 353 nm, which can be ascribed to either d−d or MLCT transitions,[11] followed by a more intense band at 228 nm. The CD spectrum of **6** (Figure 6) shows four Cotton effects, at 475 nm ($\Delta\epsilon$ −0.25), 389 nm ($\Delta\epsilon$ 0.81), 316 nm ($\Delta\epsilon$ −0.32), and 258 nm ($\Delta\epsilon$ −0.79), which are at different wavelength than the UV absorptions, except for the lower energy band. All CD signals can be related to the chiral metal η^6-arene chromophore, because the free aromatic ligand exhibits only very weak CD signals in that range.[12a]

Interestingly, the same sequence of CD bands with nearly the same intensities and wavelengths is displayed by structurally related Ru(II) η^6-arene complexes[1f,3b] with a benzylic chiral center. An empirical correspondence between the sign of the CD bands and the absolute configuration of the benzylic carbon atom is observed in all these compounds. The CD spectrum of diastereomerically pure salt **7***S* (>99% de) displays Cotton effects (Figure 7) at 461 nm ($\Delta\varepsilon$ 1.18), 404 nm ($\Delta\varepsilon$ −3.05), 350 nm ($\Delta\varepsilon$ 3.72), 295 nm ($\Delta\varepsilon$ −5.45), and 240 nm ($\Delta\varepsilon$ 6.55), which are about 5 times more intense than those in the spectrum of **6**. We relate them to a chiroptical dominance of the *S*-configured chiral metal center, which overlaps the signals of the chiral arene chromophore, confirming a high diastereomeric purity of **7***S* in freshly prepared methanol solution. The spectrum rerecorded after some days resembles that of a 1:1 diastereomeric mixture of **8** or neutral **6** (Figure 6), with disappearance of the dominating influence of the metal. This proves the configurational instability of the metal center of **7***S* in several solvents again and a complete retention of the absolute configuration at the benzylic carbon atom by an independent method. The CD spectrum of **8** is characterized by the same band sequence of **6**, with the same sign and signal intensity, although with a 30 nm hypsochromic shift, due to the presence of an amine ligand at the metal, thus confirming complete epimerization at the metal center and retention of the absolute configuration at the benzylic carbon. The CD spectrum of **9***R* (>99% de, Figure 7) is in an almost mirror image relationship with the one of **7***S*, revealing a spectral dominance of the chiral metal atoms and their opposite absolute configurations. Probably, only the strong negative Cotton effect at 233 nm can result from a partial contribution of the chiral amine chromophore, being in correspondence to the absorption band at 228 nm in the UV spectrum, which could be ascribed to a bathochromic shifted aromatic ^1L_a transition of the amine.[12b] Differently from **7***S*, the CD spectrum of **9***R* appeared unchanged even after one month of standing, revealing the high configurational stability of this complex in methanol solution. Finally, the CD spectrum of **10** (1:1 diastereomeric mixture, Table 8) appeared quite similar in intensity, position, and sign of the CD bands to the one of **8**, leading to the same interpretations.

In conclusion, this CD analysis shows that (i) as expected, in all the complexes examined the absolute configuration at the benzylic chiral center is retained; (ii) the complex salts **7***S* and **9***R* have opposite absolute configuration at the chiral Ru(II) centers; (iii) the samples of **8** and **10** show complete epimerization at the chiral metal center; (iv) complex **7***S* epimerizes at the metal center in methanol solution, while under the same conditions **9***R* is configurationally stable.

Catalytic Transfer Hydrogenation of Acetophenone. Compounds **7***S* and **9***R* were tested as precatalysts in the transfer hydrogenation reaction of acetophenone with 2-propanol to yield asymmetric 1-phenylethanol in the presence of strong bases. A limited solubility of the salts in the reaction mixtures required an adjustment of the molar *i*-PrOH/acetophenone ratio, as observed earlier for the analogous (*ansa*-phosphine) and (*ansa*-phosphetane) ruthenium complex salts.[5d,e] The reactivity of both catalysts was fair, but the poor (**7***S*, 9% ee (*R*)-1-phenylethanol) or even completely absent enantioselectivity in the case of **9***R* points to a general lack of suitability of the investigated tethered complex salts as catalysts for enantioselective transfer hydrogenation.

Conclusions

The presented studies on diastereomeric *ansa* complex salts **7**−**10** revealed the following facts that determine the configurational stability of the complex cations: (i) The configurational stabilization of the chiral Ru(II) centers is based on the fixed diastereotopic "*ax-eq*" coordination mode of the diphenyl phosphinite moiety via steric interaction of the *eq* phenyl rings with the amine ligands, for both, the (S_{Ru},R_C) and (R_{Ru},R_C) diastereomers. (ii) The chairlike conformation of the *ansa* chain is not flexible for both diastereomers. Its diastereotopic orientation is determined by the absolute configuration of the chiral Ru(II) center. (iii) The configurational metastability of the (S_{Ru},R_C) diastereomers is evoked by the unfavored "*in-plane*" conformation of the methoxy group. The (R_{Ru},R_C) diastereomers of the [amino{σ(*P*):η^6-[(2′-(*P*,*P*-diphenylphosphinoxy)-1′-methoxyethyl)benzene]}chloroRu(II)]$^+$ complex cations are therefore thermodynamically favored and configurationally stable. In contrast to that, Faller interprets the reason for his slowly epimerizing [{σ(*P*):η^6-(*ansa*-P)benzene}Ru(II)(P∩S)] complex family as the hemilability of the sulfide ligand function of the P∩S chelate.[4g] On the other hand, for Brunner's Mn(I),[13] Gladysz' Re(I),[14] and Davies' Fe(II) η^5-Cp complexes[15] configurational stabilization could be achieved exclusively by electronic control. We demonstrated that chiral Ru(II) η^6-arene complexes require for that purpose additional steric stabilization.

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Right in line with observing a significant configurational lability of aniline salt **7**, isolated diastereomer **7***S* failed to produce useful ee values when being used as an enantioselective transfer hydrogenation catalyst. Not yet fully understood is the complete failure of the configurationally more stable diastereomer **9***R* to produce any observable enantioselectivity in that catalytic reaction, but different conditions for an epimerization of the chiral metal center of the cationic 18 VE precatalysts and their catalytically active 16 VE counterparts are obvious. In both cases, the chosen tether between arene and phosphinite donor functions of the ligand seems not to be rigid enough to stabilize the decisive intermediates of the catalytic transfer hydrogenation. Therefore, the design of potentially highly enantioselective, chiral *ansa*-linked Ru(II) η^6-arene transfer hydrogenation catalysts has to be changed principally. Such work is in progress.[16]

Experimental Section

General Procedures. All reactions were carried out under an atmosphere of dry nitrogen using conventional Schlenk techniques. All workups were performed in air, and all substances prepared are stable in air, including the Ru(II) η^6-arene complexes, which are only slightly airsensitive in solution. Solvents and chemicals were purchased from Acros, Aldrich, Merck, and Strem. The following solvents and reagents were dried and distilled in an atmosphere of nitrogen prior to use: chlorodiphenylphosphine, NEt_3, aniline, *p*-fluoroaniline. Drying agents: CH_2Cl_2 and $CDCl_3$−calcium hydride; THF−sodium/benzophenone; MeOH−magnesium. All other solvents and reagents were employed as received. Silica gel F 60 for flash chromatography (FC) was purchased from Fluka or Merck. Thin-layer chromatography (TLC) was performed on Merck F 60 silica plates with a 364 nm fluorescence indicator and used for the determination of the R_f values. NMR spectra were recorded on Jeol FT-JNM-EX 270 (270 MHz), Bruker AMX 300 (300 MHz), Jeol FT-JNM-LA 400 (400 MHz), and Jeol A 500 (500 MHz) spectrometers in deuterated solvents and referenced to the residual ^1H or $^{13}C\{^1H\}$ signals of the particular solvent. 2D spectra were not symmetrized. $^{31}P\{^1H\}$ NMR spectra were referenced to external 85% H_3PO_4 or to the anion PF_6^- of salts **7**−**10**. Mass spectra were recorded on a Varian MAT 212 spectrometer. Elemental analyses were performed using a Carlo Erba elemental analyzer model 1108. Absorption and circular dichroism spectra were recorded on a JASCO J-600 spectropolarimeter at RT in MeOH, using concentrations of about 1×10^{-3} M. During the measurement, the instrument was thoroughly purged with nitrogen. Polarimetric measurements were performed on a Perkin-Elmer 341 polarimeter. Melting points were determined on a Büchi 530 melting point apparatus and are not corrected. Compounds **2**[7a–d] and **4**[5d,e] were prepared as reported.

(+)-(2*S*)-*P*-(2-Methoxy-2-phenylethyloxy)-*P*,*P*-diphenylphosphine (3). To 5.72 g (37.6 mmol) of **2** and 6.50 mL (4.72 g, 46.6 mmol) of NEt_3 in 200 mL of THF was added dropwise 7.50 mL (9.22 g, 41.8 mmol) of chlorodiphenylphosphine within 5 min at RT, and triethylammonium hydrochloride started to precipitate out immediately. The mixture was then stirred for 12 h at 60 °C. Workup: To the reaction mixture were added 15 mL of NEt_3 and then ca. 10 g of hydrated silica gel to absorb most of excess chlorodiphenylphosphine. The suspension was stirred for 10 min and filtered. Removal of all volatiles by RV and under HV furnished 13.05 g of crude **2** as an oil, which was purified by FC (hexanes: EtOAc = 3:1 + 5% NEt_3, R_f (**2**) = 0.28, R_f (**3**) = 0.59). HV drying yielded 10.79 g of pure **3** (32.1 mmol, 85%) as a clear, colorless oil. $[\alpha]^{23}_D$ +39.8 ($CHCl_3$, *c* 0.18). ^1H NMR (270 MHz, $CDCl_3$): δ 7.49−7.20 (series of m, 15H, *Ph*−CH−, −PPh_2); 4.36 (dd, $^3J_{H,H}$ = 7.8, $^3J_{H,H}$ = 3.8, 2H, −CH−); 4.09−3.87 (2 not res. ddd, 2H, −CH_2−); 3.13 (s, 3H, −OCH_3). $^{13}C\{^1H\}$ NMR (68 MHz, $CDCl_3$): δ 142.19 (d, $^1J_{C,P}$ = 12.1, 1-C of −PPh_2); 141.93 (d, $^1J_{C,P}$ = 12.1, 1-C of −PPh_2); 138.38 (1-C of *Ph*−CH−); 130.42 (d, $^2J_{C,P}$ = 4.7, 2- or 6-C of −PPh_2); 130.10 (d, $^2J_{C,P}$ = 4.7, 6- or 2-C of −PPh_2); 129.06 (4-C of *Ph*−CH−); 128.35 (3,5-C of *Ph*−CH−); 128.17 (d, $^3J_{C,P}$ = 1.4, 3- or 5-C of −PPh_2); 128.07 (d, $^3J_{C,P}$ = 1.4, 5- or 3-C of −PPh_2); 127.94 (4-C of −PPh_2); 126.98 (4-C of *Ph*−CH−); 83.90 (d, $^3J_{C,P}$ = 5.9, −CH−); 74.39 (d, $^2J_{C,P}$ = 17.8, −CH_2−); 56.83 (−CH_3). $^{31}P\{^1H\}$ NMR (109 MHz, $CDCl_3$): δ 116.47 (s, 1P). FD^+-MS (CH_2Cl_2); *m*/*z* (%) 336 (100) [M^+]. $C_{21}H_{21}O_2P$ (336.37): calcd C 74.99, H 6.29; found C 74.78, H 6.27.

(1*R*)-Dichloro{σ(*P*):η⁶-[(2-(*P*,*P*-diphenylphosphinoxy)-1-methoxyethyl)benzene]}ruthenium(II) (6). *Caution! Autoclave burst protection equipment mandatory, the pressure Schlenk tube must be capable of withstanding a pressure of 120 bar*. A 1.773 g (2.88 mmol) portion of methylbenzoate ruthenium dichloride complex dimer **4** and 2.251 g (6.69 mmol) of **3** were stirred in a pressure Schlenk tube in 30 mL of CH_2Cl_2 and 1.5 mL of THF at RT. Within 20 min the reaction mixture turned to a clear, deep red solution and the state of formation of σ-complex **5** can be monitored by $^{31}P\{^1H\}$ NMR (109 MHz, $CDCl_3$): δ 109.95 (s, 1P). Full conversion of **5** into target complex **6** requires 11 h stirring at 120 °C and can be controlled by $^{31}P\{^1H\}$ NMR again. *Caution! Before opening, the pressure Schlenk tube must cool down to RT slowly.* Workup: The reddish-brown reaction mixture was filtered through cellulose, and the solvents were removed by RV. The slimy crude product was washed with Et_2O and redissolved in THF, and the solvent was removed by RV, giving a microcrystalline product, which was recrystallized from a minimum of hot THF down to −30 °C. After filtration from the mother liquor the product was washed consecutively with small amounts of cold THF, MeOH, and Et_2O and dried on air to yield 1.826 g (3.59 mmol, 62%) of **6**, including additional material from the mother liquors. Crystals suitable for X-ray crystal structure analysis were grown by slow solvent evaporation from CH_2Cl_2 solution. Mp: 188−190 °C (dec). $[\alpha]^{23}_D$ +7.4 (CH_2Cl_2, *c* 0.0034). ^1H NMR (270 MHz, $CDCl_3$,): δ 7.88−7.74 (m, 4H, 2,6-H of −PPh_2); 7.41−7.27 (m, 6H, 3,4,5-H of −PPh_2); 6.47 (pseudo t, 1H, 3- or 5-H of η^6-Ph); 6.06 (pseudo t, 1H, 5- or 3-H of η^6-Ph); 5.64−5.56 (m and not res. d, 2H, 2- or 6-H and 4-H of η^6-Ph); 5.25 (d, $^3J_{H,H}$ = 5.1, 1H, 6- or 2-H-C of η^6-Ph); 4.37−4.18 (2 not res. ddd, 2H, −CH_2−); 4.12 (dd, $^3J_{H,H}$ = 5.3, $^3J_{H,H}$ = 3.1, 1H, −CH−); 3.41 (s, 3H, −CH_3). $^{13}C\{^1H\}$ NMR (68 MHz, $CDCl_3$): δ 136.46 (d, $^1J_{C,P}$ = 57.1, 1-C of −PPh_2); 134.51 (d, $^1J_{C,P}$ = 56.4, 1-C of −PPh_2); 131.43 (d, $^2J_{C,P}$ = 9.6, 2,6-C of −PPh_2); 131.27 (d, $^2J_{C,P}$ = 9.6, 6- or 2-C of −PPh_2); 130.97 (d, $^4J_{C,P}$ = 2.7, 4-C of −PPh_2); 130.82 (d, $^4J_{C,P}$ = 2.6, 4-C of −PPh_2); 128.04 (d, $^3J_{C,P}$ = 11.0, 3,5-C of −PPh_2); 127.78 (d, $^3J_{C,P}$ = 11.0, 3,5-C of −PPh_2); 104.05 (d, $^2J_{C,P}$ = 9.6, 3- or 5-C of η^6-Ph); 93.60 (d, $^2J_{C,P}$ = 8.0, 5- or 3-C of η^6-Ph); 90.56 (1-C of η^6-Ph); 86.97 (4-C of η^6-Ph); 86.91 (6- or 2-C of η^6-Ph); 85.05 (2- or 6-C of η^6-Ph); 75.64 (d, $^3J_{C,P}$ = 1.1, −CH−); 70.3 (−CH_2−);

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57.56 ($-CH_3$). $^{31}P\{^1H\}$ NMR (109 MHz, $CDCl_3$): δ 125.08 (*s*, 1P). FD^+-MS (CH_2Cl_2); *m/z* (%) 509 (100) $[M]^+$ with respect to ^{102}Ru. $C_{21}H_{21}Cl_2O_2PRu$ (508.35): calcd C 49.62, H 4.16; found C 49.57, H 4.46.

(S_{Ru},1*R*)-[σ-Chloro{σ(*P*):η^6-[(2-(*P*,*P*-diphenylphosphinoxy)-1-methoxyethyl)benzene]}-σ(*N*)-phenylaminoruthenium(II)]Hexafluorophosphate (7*S*). Representative Procedure. A 300 mg (0.590 mmol) amount of **6** was dissolved in 4 mL of CH_2Cl_2, followed by addition of 0.10 mL (102 mg, 1.097 mmol) of aniline and 4 mL of MeOH. Then 326 mg (1.941 mmol) of solid $NaPF_6$ was added in one portion, and the mixture was stirred for 16 h at RT. Before workup >99% de (**7***S*) was determined by NMR [$^{31}P\{^1H\}$ NMR (121 MHz, acetone-d_6; **7***R*): 131.05 (s, 1P); ^1H NMR (270 MHz, acetone-d_6; **7***R*): 3.40 (s, 3H, $-CH_3$)]. Workup: After removal of solvents by RV the crude product was dissolved in CH_2Cl_2 and excess NaCl and $NaPF_6$ were filtrated off over a disposable pipet filled with cellulose filter flakes. The resulting clear yellow to orange solution was evaporated to dryness by RV, and the residue washed free of excess amine with Et_2O inside the round-bottom flask and dried thoroughly under HV to give 504 mg of crude **7** as an orange solid, but with 74% de **7***S* by NMR. One-time recrystallization from CH_2Cl_2 at RT down to -30 °C afforded 302 mg (0.425 mmol, 72%) of pure **7***S* with >99% de by NMR. The crystals were suitable for X-ray structure analysis. After recrystallization the compound is only sparingly soluble in CH_2Cl_2 and $CHCl_3$, but slightly in MeOH and moderately in acetone, in which it epimerizes at RT within hours. Acetonitrile causes epimerization of **7***S* within minutes, which is followed by η^6-arene ligand decomplexation.

General Procedure for the Preparation of NMR Samples for de Determination. To prevent erroneous de determination, sample preparation and measurement were performed as quickly as possible. Aliquots of 0.1−0.2 mL taken from reaction mixtures were evaporated to dryness by quick vacuum suction, dissolved in the NMR solvent, and pressed with nitrogen through a pipet filled with filter flakes into the NMR tube. To ensure representative samples, all of the material must dissolve completely in the NMR solvent; any residual product was flushed into the NMR tube in the same way. The relative de was determined by the integrals of the particular ^{31}P and ^1H NMR signals.

Mp: 199 °C (dec). $[\alpha]^{23}_D$ −111.5 (CH_2Cl_2, *c* 0.0029). ^1H NMR (500 MHz, acetone-d_6; **7***S*): 7.86−7.80 (m, 4H, 2,6-H of $-PPh_2$); 7.64−7.50 (m, 6H, 3,4,5-H of $-PPh_2$); 7.37−7.33 (m, 4H, 2,3,5,6-H of *Ph*NH_2); 7.24−7.20 (m, 1H, 4-H of *Ph*NH_2); 6.56 (pseudo t, 1H, 4-H of η^6-Ph); 6.09 (pseudo t, 1H, 5-H of η^6-Ph); 5.75 (m, 1H, 2-H of η^6-Ph); 5.60 (not res. d, 1H, $-NH_2$); 5.51 (m, 1H, 6-H of η^6-Ph); 5.48 (m, 1H, 3-H of η^6-Ph); 4.91 (not res. d, 1H, $-NH_2$); 4.62 (not res. ddd, 1H, $-CH_2-$), 4.57 (not res. ddd, 1H, $-CH-$); 4.44 (ddd, $^2J_{H,H}$ = 17.0, $^3J_{H,H}$ = 12.5, $^3J_{H,P}$ = 2.5, 1H, $-CH_2-$); 3.56 (s, 3H, $-CH_3$). $^{13}C\{^1H\}$ NMR (126 MHz, acetone-d_6; **7***S*): δ 148.54 (1-C of $PhNH_2$); 134.45 (d, $^2J_{C,P}$ = 13.4, 2,6-C of $-PPh_2$); 133.21 (d, $^4J_{C,P}$ = 62.1, 4-C of $-PPh_2$); 131.65 (d, $^2J_{C,P}$ = 10.3, 2,6-C of $-PPh_2$); 130.24 (d, $^3J_{C,P}$ = 11.4, 3,5-C of $-PPh_2$); 130.16 (3,5-C of $PhNH_2$); 129.52 (d, $^3J_{C,P}$ = 11.3, 3,5-C of $-PPh_2$); 126.84 (4-C of $PhNH_2$); 121.75 (2,6-C of $PhNH_2$); 107.56 (6-C of η^6-Ph); 103.10 (d, $^2J_{C,P}$ = 10.3, 4-C of η^6-Ph); 95.85 (1-C of η^6-Ph); 86.97 (5-C of η^6-Ph); 82.54 (3-C of η^6-Ph); 81.71 (2-C of η^6-Ph); 73.23 ($-CH-$); 68.19 ($-CH_2-$); 58.24 ($-CH_3$). $^{31}P\{^1H\}$ NMR (121 MHz, acetone-d_6; **7***S*): δ 131.75 (s, 1P). FAB^+-MS; *m/z* (%): 436 (59) $[M - Cl - C_6H_7N - PF_6^-]^+$ with respect to ^{102}Ru, 472 (100) $[M - C_6H_7N - PF_6^-]^+$ with respect to ^{102}Ru, 565 (43) $[M - PF_6^-]^+$ with respect to ^{102}Ru. $C_{27}H_{28}ClF_6NO_2P_2Ru$ (710.99): calcd C 45.61, H 3.97, N 1.97; found C 45.35, H 4.03, N 1.83.

(1′*R*)-[σ-Chloro-σ(*N*)-(4-fluorophenylamino)-{σ(*P*):η^6-[(2′-(*P*,*P*-diphenylphosphinoxy)-1′-methoxyethyl)benzene]}ruthenium(II)] Hexafluorophosphate (8). 8 was prepared according to the procedure above from 392 mg (0.771 mmol) of **6**, 035 mL (405 mg, 3.644 mmol) of *p*-fluoroaniline, and 406 mg (2.417 mmol) of $NaPF_6$ in 4.5 mL of CH_2Cl_2 and 9 mL of MeOH. Before workup 66% de (**8***S*) was determined by NMR. After workup 686 mg of crude **8** were obtained as a brownish microcrystalline powder. The crude product was recrystallized from MeOH (reflux/−30 °C) to give finally 293 mg (0.393 mmol, 51%) of pure **8** with **8***S*:**8***R* = 1:1 (NMR, X-ray crystal structure analysis). **8** is also soluble in CH_2Cl_2, $CHCl_3$, and acetone. Mp: 188−190 °C (dec). $[\alpha]^{23}_D$ −34.9 (CH_2Cl_2, *c* 0.0038).

Properties of epimeric mixtures **8***S*/**8***R* = 1:1: ^1H NMR (500 MHz, acetone-d_6; signals that are assigned to a specific diastereomer are characterized by *R* or *S*): δ 7.90−7.75 and 7.63−7.50 (m, 20H, $-PPh_2$); 7.40 (m, 4H, 2,6-H of (*p*-F)$C_6H_4NH_2$); 7.10 (pseudo t, 4H, 3,5-H of (*p*-F)$C_6H_4NH_2$); 6.59 (pseudo t, 1H, 4-H of η^6-Ph, *S*); 6.56 (pseudo t, 1H, 4-H of η^6-Ph, *R*); 6.11 (pseudo t, 1H, 3-H of η^6-Ph, *S*); 6.08 (pseudo t, 1H, 3- or 5-H of η^6-Ph, *R*); 6.01 (br s, 2H, -NH_2); 5.87 (pseudo t, 1H, 2- or 6-H of η^6-Ph, *R*); 6.77 (pseudo d, 1H, 6- or 2-H of η^6-Ph, *R*); 5.75 (pseudo t, 1H, 2-H of η^6-Ph, *S*); 5.65 (m, 1H, 5-H of η^6-Ph, *S*); 5.63 (pseudo t, 1H, 6-H of η^6-Ph, *S*); 5.38 (m, 1H, 5- or 3-H of η^6-Ph, *R*); 4.95 (not res. br d, 2H, $-NH_2$); 4.69 (m, 2H, $-CH_2-$, *S* and *R*); 4.56 (m, 1H, $-CH-$, *S*); 4.54 (m, 1H, $-CH-$, *R*); 4.52−4.42 (m, 2H, $-CH_2-$, *S* and *R*); 3.56 (s, 3H, $-CH_3$, *S*); 3.42 (s, 3H, $-CH_3$, *R*). $^{13}C\{^1H\}$ NMR (126 MHz, acetone-d_6): δ 161.13 (d, $^1J_{C,F}$ = 127.2, 4-C of (*p*-F)$C_6H_4NH_2$, *S* and *R*); 145.03 (d, $^1J_{C,F}$ = 100.3, 1-C of (*p*-F)$C_6H_4NH_2$, *S* and *R*); 136.42 (d, $^1J_{C,P}$ = 63.1, 1-C of $-PPh_2$); 135.67 (d, $^1J_{C,P}$ = 63.1, 1-C of $-PPh_2$); 134.50−129.36 (series of d, $-PPh_2$); 123.79 (d, $^3J_{C,F}$ = 8.3, 2,6-C of (*p*-F)$C_6H_4NH_2$, *S* or *R*); 123.39 (d, $^3J_{C,F}$ = 8.3, 2,6-C of (*p*-F)$C_6H_4NH_2$, *R* or *S*); 116.86 (d, $^2J_{C,F}$ = 19.6, 3,5-C of (*p*-F)$C_6H_4NH_2$, *S* or *R*); 116.68 (d, $^3J_{C,F}$ = 18.6, 3,5-C of (*p*-F)$C_6H_4NH_2$, *R* or *S*); 108.32 (5- or 3-C of η^6-Ph, *R*); 107.41 (5-C of η^6-Ph, *S*); 102.98 (4-C of η^6-Ph, *S* and *R*); 96.05 (1-C of η^6-Ph, *S*); 94.73 (1-C of η^6-Ph, *R*); 87.63 (3- or 5-C of η^6-Ph, *R*); 87.17 (3-C of η^6-Ph, *S*); 83.68 (d, $^2J_{C,P}$ = 7.3, 6- or 2-C of η^6-Ph, *R*); 82.44 (2- or 6-C of η^6-Ph, *R*; 6-C of η^6-Ph, *S*); 81.78 (2-C of η^6-Ph, *S*); 75.18 ($-CH-$, *R*); 73.25 ($-CH-$, *S*); 70.31 ($-CH_2-$, *S* and *R*); 58.19 (d, $^5J_{C,P}$ = 6.2, $-CH_3$, *S*); 57.75 ($-CH_3$, *R*). $^{31}P\{^1H\}$ NMR (109 MHz, $CDCl_3$): δ 133.29 (s, 1P, *S*); 129.83 (s, 1P, *R*). FAB^+-MS; *m/z* (%) 438 (94) $[M - Cl - C_6H_6FN - PF_6^-]^+$ with respect to ^{102}Ru, 472 (100) $[M - C_6H_6FN - PF_6^-]^+$ with respect to ^{102}Ru, 585 (28) $[M - PF_6^-]^+$ with respect to ^{102}Ru. $C_{27}H_{27}ClF_7NO_2P_2Ru(MeOH)_{0.5}$ (745.00): calcd C 44.34, H 3.92, N 1.88; found C 44.31, H 3.65, N 1.91.

(R_{Ru},1*R*,1′*R*)-[σ-Chloro-{σ(*P*):η^6-[(2-(*P*,*P*-diphenylphosphinoxy)-1-methoxyethyl)benzene]}-σ(*N*)-(1′-phenylethylamino)ruthenium(II)] Hexafluorophosphate (9*R*). 9 was prepared according to the procedure above from 389 mg (0.765 mmol) of **6**, 0.27 mL (257 mg, 2.117 mmol) of (*R*)-1-phenylethylamine, and 440 mg (2.620 mmol) of $NaPF_6$ in 3 mL of CH_2Cl_2 and 9 mL of MeOH. No de was detectable by NMR before workup. After workup 699 mg of crude **9** was obtained as a yellow solid foam with 7% de (**9***R*) [$^{31}P\{^1H\}$ NMR (109 MHz, acetone-d_6; **9***S*): δ 135.29 (s, 1P); ^1H NMR (270 MHz, acetone-d_6; **9***S*): δ 3.49 (s, 3H, $-CH_3$)]. The crude product was recrystallized from a small amount of MeOH at −30 °C to yield 151 mg (0.204 mmol, 27%) of pure **9***R* with >99% de by NMR. The crystals were suitable for X-ray structure determination. The compound is also soluble in CH_2Cl_2, $CHCl_3$, and acetone. Mp: 169 °C. $[\alpha]^{23}_D$ +38.4 (CH_2Cl_2, *c* 0.0037). ^1H NMR (400 MHz, acetone-d_6; **9***R*): δ 7.88−7.82 and 7.75−7.70 and 7.61−7.47 (3 m, 10H, $-PPh_2$); 7.34−7.27 (m, 3H, 3,4,5-H of *Ph*$CH(CH_3)NH_2$); 7.10−7.06 (m, 2H, 2,6-H of *Ph*$CH(CH_3)NH_2$); 6.79 (pseudo t, 1H, 4-H of η^6-Ph); 6.68 (pseudo t, 1H, 3- or 5-H of η^6-Ph); 6.22 (pseudo t, 1H, 2- or 6-H of η^6-Ph); 6.01 (pseudo t, 1H, 6- or 2-H of η^6-Ph); 5.20 (pseudo d, 1H, 5- or 3-H of η^6-Ph); 4.40 (m, 1H, $-CH(OCH_3)-$); 4.35 (2 m, 2H, $-CH_2-$); 3.80 (q, $^3J_{H,H}$ = 6.5; 1H, $-CH(CH_3)NH_2$); 3.65 (br s, 2H, $-NH_2$); 3.36 (s, 3H, $-OCH_3$); 1.23 (d, $^3J_{H,H}$ = 6.5, 3H, $-CH(CH_3)NH_2$). $^{13}C\{^1H\}$ NMR (68 MHz, acetone-d_6; **9***R*): δ 143.90 (1-C of

*Ph*CH(CH$_3$)NH$_2$); 135.82 (d, $^1J_{C,P}$ = 59.9, 1-C of −PPh$_2$); 134.28 (d, $^2J_{C,P}$ = 12.3, 2,6-C of −PPh$_2$); 133.20 (d, $^4J_{C,P}$ = 2.5, 4-C of −PPh$_2$); 132.86 (d, $^4J_{C,P}$ = 2.8, 4-C of −PPh$_2$); 132.09 (d, $^1J_{C,P}$ = 52.1, 1-C of −PPh$_2$); 131.23 (d, $^2J_{C,P}$ = 10.3, 2,6-C of −PPh$_2$); 130.26 (d, $^3J_{C,P}$ = 10.6, 3,5-C of −PPh$_2$); 129.69 (3,5-C of *Ph*CH(CH$_3$)NH$_2$); 129.28 (d, $^3J_{C,P}$ = 11.4, 3,5-C of −PPh$_2$); 129.00 (4-C of *Ph*CH(CH$_3$)NH$_2$); 126.99 (2,6-C of *Ph*CH(CH$_3$)NH$_2$); 103.25 (d,$^2J_{C,P}$ = 7.5, 4-C of η⁶-Ph); 101.89 (d, $^2J_{C,P}$ = 10.6, 3- or 5-C of η⁶-Ph); 93.82 (1-C of η⁶-Ph); 90.97 (2- or 6-C of η⁶-Ph); 82.94 (6- or 2-C of η⁶-Ph); 82.19 (5- or 3-C of η⁶-Ph); 75.28 (−CH$_2$−); 68.87 (−*C*H(OCH$_3$)−); 58.13 (−*C*H(CH$_3$)NH$_2$); 57.66 (−OCH$_3$); 23.81 (−CH(*C*H$_3$) NH$_2$). ^{31}P{^{1}H} NMR (109 MHz, acetone-d_6; **9***R*): δ 133.19 (s, 1P). FAB$^+$-MS: *m*/*z* (%) 436 (76) [M − Cl − C$_8$H$_{13}$N − PF$_6^-$]$^+$ with respect to ^{102}Ru, 472 (100) [M − C$_8$H$_{13}$N − PF$_6^-$]$^+$ with respect to ^{102}Ru, 593 (43) [M − PF$_6^-$]$^+$ with respect to ^{102}Ru. C$_{29}$H$_{32}$ClF$_6$NO$_2$P$_2$Ru (739.04): calcd C 47.13, H 4.36, N 1.90; found C 47.06, H 4.39, N 1.93.

(1*R*,1′*S*)-[σ-Chloro-{σ(*P*):η⁶-[(2-(*P*,*P*-diphenylphosphinoxy)-1-methoxyethyl)benzene]}-σ(*N*)-(1′-phenylethylamino)ruthenium(II)] hexafluorophosphate (10). 10 was prepared according to the procedure above from 392 mg (0.771 mmol) of **6**, 0.23 mL (219 mg, 1.803 mmol) of (*S*)-1-phenylethylamine, and 432 mg (2.572 mmol) of NaPF$_6$ in 3 mL of CH$_2$Cl$_2$ and 9 mL of MeOH. No de was detectable by NMR before and after workup. After workup 665 mg of crude **10** was obtained as a brownish solid foam. The crude product was precipitated from MeOH at −30 °C to give 84 mg (0.204 mmol, 27%) of **10** as a brown powder with (**10***S*):(**10***R*) = 1:1 by NMR. In one batch eventually one crystal could be found in the product (which was not crystalline otherwise) suitable for X-ray crystal structure analysis, which contained **10***S* only. The compound is also soluble in CH$_2$Cl$_2$, CHCl$_3$, and acetone. Mp: 156−157 °C. [α]$^{23}_D$ −49.1 (CH$_2$Cl$_2$, *c* 0.0018).

Properties of epimeric mixtures **10***S*/**10***R* = 1:1: ^{1}H NMR (400 MHz, acetone-d_6): δ 7.89−7.80 and 7.67−7.49 (2 m, 20H, −PPh$_2$); 7.36−7.21 (m, 6H, 3,4,5-H of *Ph*CH(CH$_3$)NH$_2$); 7.09−7.05 (m, 4H, 2,6-H of *Ph*CH(CH$_3$)NH$_2$); 6.74 (pseudo t, 1H, 5-H of η⁶-Ph, *S*); 6.61 (pseudo q, 2H, 4-H of η⁶-Ph, *S* and *R*); 6.21 (pseudo t, 1H, 3-H of η⁶-Ph, *S*); 6.17 (pseudo t, 1H, 3- or 5-H of η⁶-Ph, *R*); 6.03 (pseudo t, 1H, 2- or 6-H of η⁶-Ph, *R*); 6.00 (pseudo t, 1H, 5- or 3-H of η⁶-Ph, *R*); 5.87 (m, 1H, 2-H of η⁶-Ph, *S*); 5.64 (pseudo d, 1H, 6- or 2-H of η⁶-Ph, *R*); 5.33 (pseudo d, 1H, 6-H of η⁶-Ph, *S*); 4.77 (ddd, $^2J_{H,H}$ = 23.3, $^3J_{H,H}$ =13.0, $^3J_{H,P}$ = 4.0, 1H, −CH$_2$−, *S*); 4.54 (m, 1H, −C*H*(OCH$_3$)−, *S*); 4.46 (not res. ddd, 1H, −CH$_2$−, *R*); 4.32 (m, 1H, −C*H*(OCH$_3$)−, *R*); 4.30 (not res. q, 1H, −C*H*(CH$_3$)NH$_2$, *R*); 4.26 (m, 1H, −CH$_2$−, *R*); 4.20 (not res. ddd, 1H, −CH$_2$−, *S*); 3.82 (q, $^3J_{H,H}$ = 6.5, 1H, −C*H*(CH$_3$)NH$_2$, *S*); 3.59 (*s*, 3H, −OCH$_3$, *S*); 3.36 (*s*, 3H, −OCH$_3$, *R*); 1.30 (d, $^3J_{H,H}$ = 6.5, 3H, −CH(C*H*$_3$)NH$_2$, *R*); 1.05 (d, $^3J_{H,H}$ = 6.5, 3H, −CH(C*H*$_3$)NH$_2$, *S*). ^{13}C{^{1}H} NMR (126 MHz, acetone-d_6): δ 144.19 (1-C of *Ph*CH(CH$_3$) NH$_2$, *R*); 143.96 (1-C of *Ph*CH(CH$_3$)NH$_2$, *S*); 135.83−129.12 (series of d, −PPh$_2$); 133.06 (4-C of *Ph*CH(CH$_3$)NH$_2$, *S* and *R*); 129.86 (3,5-C of *Ph*CH(CH$_3$)NH$_2$, *S* or *R*); 129.73 (3,5-C of *Ph*CH(CH$_3$)NH$_2$, *R* or *S*); 127.12 (2,6-C of *Ph*CH(CH$_3$)NH$_2$, *S* or *R*); 127.07 (2,6-C of *Ph*CH(CH$_3$)NH$_2$, *R* or *S*); 103.58 (5-C of η⁶-Ph, *S*; or 5- or 3-C of η⁶-Ph, *R*); 103.53 (5- or 3-C of η⁶-Ph, *R*; or 5-C of η⁶-Ph, *S*); 102.11 (d, $^2J_{C,P}$ = 10.3, 4-C of η⁶-Ph, *R*); 101.70 (d, $^2J_{C,P}$ = 10.3, 4-C of η⁶-Ph, *S*); 95.00 (1-C of η⁶-Ph, *S*); 93.97 (1-C of η⁶-Ph, *R*); 89.97 (3-C of η⁶-Ph, *S*); 89.72 (3- or 5-C of η⁶-Ph, *R*); 83.23 (2- or 6-C of η⁶-Ph, *R*); 82.35 (6- or 2-C of η⁶-Ph, *R*); 81.62 (2-C of η⁶-Ph, *S*); 79.85 (6-C of η⁶-Ph, *S*); 75.15 (−*C*H(OCH$_3$)−, *R*); 72.58 (−*C*H(OCH$_3$)−, *S*); 69.63 (−CH$_2$−, *R*); 66.65 (−CH$_2$−, *S*); 59.22 (−*C*H(CH$_3$)NH$_2$, *S*); 58.83 (−*C*H(CH$_3$)NH$_2$, *R*); 58.20 (−OCH$_3$, *S*); 57.69 (−OCH$_3$, *R*); 24.68 (−CH(*C*H$_3$)NH$_2$, *R*); 24.26 (−CH(*C*H$_3$)NH$_2$, *S*). ^{31}P{^{1}H} NMR (109 MHz, acetone-d_6): δ 133.77 (s, 1P); 129.16 (s, 1P). FAB$^+$-MS: *m*/*z* (%) 438 (88) [M − Cl − C$_8$H$_{13}$N − PF$_6^-$]$^+$ with respect to ^{102}Ru, 474 (100) [M − C$_8$H$_{13}$N − PF$_6^-$]$^+$ with respect to ^{102}Ru, 595 (39) [M − PF$_6^-$]$^+$ with respect to ^{102}Ru. C$_{29}$H$_{32}$ClF$_6$NO$_2$P$_2$Ru (739.04): calcd C 47.13, H 4.36, N 1.90; found C 47.48, H 4.29, N 2.01.

Crystal Structure Determination. Details of crystal parameters, data collection, and structure refinement are summarized in Table 8. X-ray diffraction data were collected at 100 K on a Bruker-Nonius KappaCCD diffractometer (Mo Kα radiation, λ = 0.71073 Å, graphite monochromator). Data were corrected for Lorentz and polarization effects. Absorption correction was performed by numerical Gauss integration[17a] or on the basis of multiple scans with SADABS.[17b] All structures were solved by direct methods and refined by full-matrix least-squares procedures on F^2 in the anisotropic approximation for all atoms except hydrogen.[17c] The absolute configurations were confirmed respectively by anomalous dispersion effects (*f*′ and *f*″)[18a] and the calculation of Flack's absolute structure parameter.[18b] All hydrogen atoms are in positions calculated for optimized geometry and are assigned an isotropic displacement parameter equivalent to the 1.2-fold and 1.5-fold value of the equivalent isotropic displacement parameter of their carrier atoms. In the crystal structure of **9***R*·(MeOH) phenyl ring C31−C36 is disordered; two alternative orientations have been refined that are occupied by 69.9(7)% for C31−C36 and 30.1(7)% for C31A−C36A, respectively. CCDC-665181 (for **6**), CCDC-665182 (for **7***R*), CCDC-665183 (for **8**·(MeOH)$_{0.5}$), CCDC-665184 (for **9***R*·(MeOH)), and CCDC-665185 (for **10***S*) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/data_ request/cif (or from Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: ++44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Supporting Information Available: Crystallographic information files (CIF) of all X-ray structure investigations of this paper. NMR and catalytic transfer hydrogenation study (3 figures, 1 table). The assignments of the ^{1}H NMR and ^{13}C NMR signals belonging to the particular diastereomers of mixtures **8***S*/**8***R* and **10***S*/**10***R* on the basis of diastereomerically pure **7***S* by detailed NOE measurements. This material is available free of charge via the Internet at http://pubs.acs.org or from the authors.

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