Synthesis and Properties of Chiral Ruthenium Complexes Containing *O*-, *S*- and *P*-Functionalized Cp-Ligands

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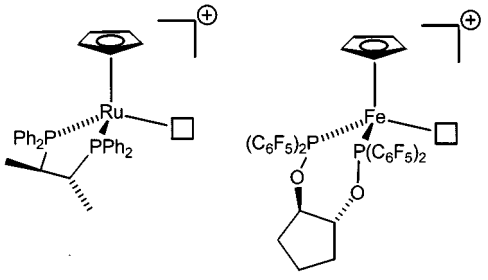
Novel, functionalized, chiral Cp-ligands with S- and P-donor atoms were designed. Together with known analogues containing ether side-chains they were complexed to ruthenium for use as chiral Lewis-acid catalysts. In the ether complexes [RuCl(η^5-$C_5H_4CH_2CH_2OR$)(PPh_3)$_2$] {R = Me, (1*S*)-isobornyl, (1*R*)-menthyl, (1*R*)-fenchyl} the Cp-ligand is only η^5-coordinated; all attempts to provoke a bidentate, Cp/O coordination were unsuccessful. The sulfide complex [Ru{η^5:η^1-$C_5H_4CH_2CH_2S$[(1*R*)-neomenthyl]}(PPh_3)$_2$][OTf] contains a bidentate Cp/S-coordinated ligand, but it is unstable. The stable phosphane complex [RuCl(η^5:η^1-$C_5H_4CH_2CH$(Me)-PPh_2)(PPh_3)] exists as a 77:23 mixture of diastereomers containing a strongly bidentate Cp/P ligand. The diastereomers interchange, with Ru–Cl bond cleavage as the rate-determining step.

Introduction

The use of chiral Lewis acids in organic transformations is mainly confined to derivatives of the elements aluminium, boron, and titanium.[1] The use of other transition metals is very limited mainly because of their reduced Lewis acidity.[2] However, with a proper choice of ligands (notably π-acceptor ligands like NO and CO) and a positive charge, complexes can be obtained with quite high Lewis-acidities {e.g. $Cp(CO)_2Fe^+$}.[3] Moreover, the use of transition metals offers a greater choice of ligands, and therefore more possibilities for (chiral) modifications, than the classical main group and d^0-metal complexes. Last but not least, transition metal Lewis acids are generally much less sensitive to water. The 16-electron half-sandwich complexes of type $CpM(L)_2^+$ (M = Fe, Ru; L = CO, phosphane) have been thoroughly studied as Lewis-acid catalysts especially for the Diels–Alder reaction.[3c,f] Chiral modifications have been synthesized using bidentate diphosphane ligands.[4]

We pursue another strategy, in that we connect a Cp-ring with a chiral functional group capable of intramolecular coordination.[5] Examples of group 8 metal complexes containing Cp-ligands with phosphorous (**1b**), sulfur (**1a**) and amine side-chains are known.[6]



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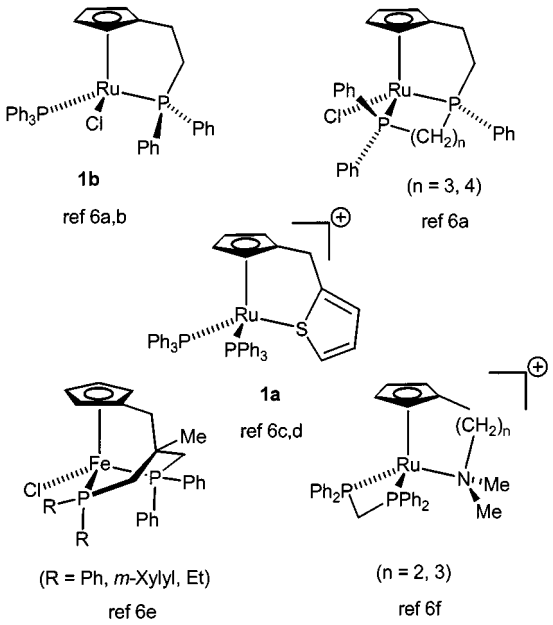

Until recently, only two examples of enantiopure systems were known.[7a,b]

A very recent paper by Trost describes the design of a whole range of chiral, functionalized Cp-ligands as well as the synthesis of their ruthenium derivatives.[7c] In an extension of this work we present our efforts on the synthesis and use of chiral ruthenium complexes using the known ether ligands $C_5H_5CH_2CH_2OR$ {R = Me (**2a**), isobornyl (**2b**), menthyl (**2c**), fenchyl (**2d**)},[5c,d] the newly developed

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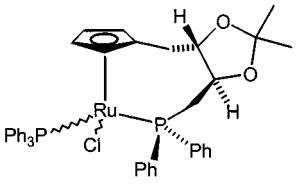

(2 diastereomers in 59:41 ratio)
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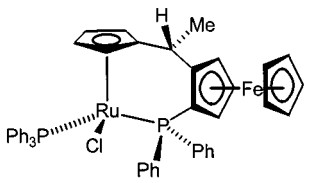

(1 diastereomer)
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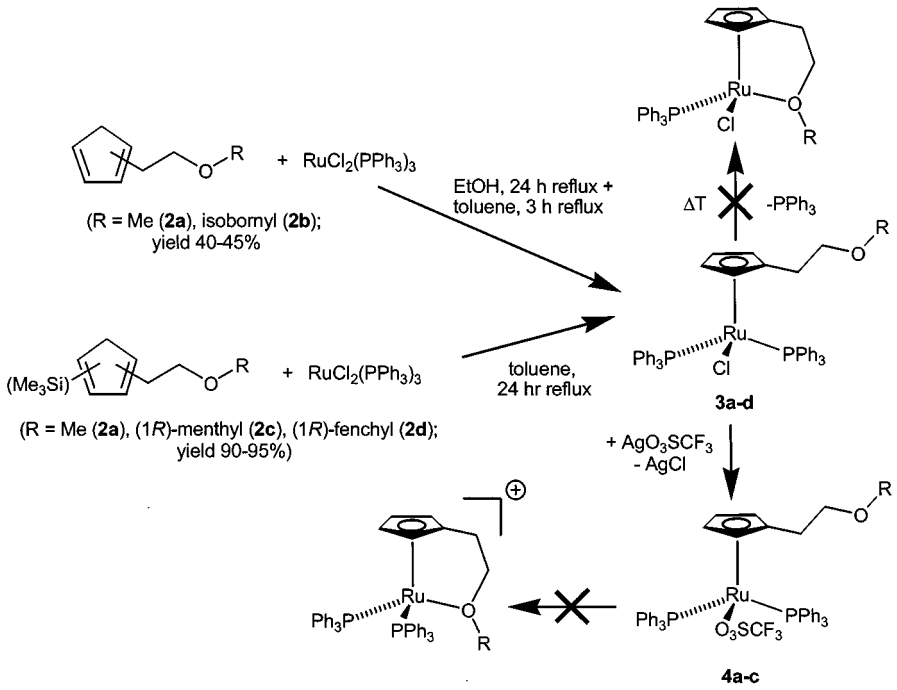
chiral sulfur ligand $C_5H_5CH_2CH_2S$[(*1R*)-neomenthyl] and the phosphorous ligand *(S)*-$C_5H_5CH_2CH(Me)PPh_2$. Special interest is also focused on the stereochemical rigidity of the ruthenium center.

Results and Discussion

According to the procedure of Kauffmann the ether ligands $C_5H_5CH_2CH_2OR$ {R = Me (**2a**), (1*S*)-isobornyl (**2b**)} were reacted with $RuCl_2(PPh_3)_3$ (Scheme 1),[6a] affording $[RuCl(\eta^5\text{-}C_5H_4CH_2CH_2OR)(PPh_3)_2]$ (**3a**, **3b**) in moderate yield. Much better yields were obtained when using the Me_3Si-derivative of the Cp-ligand affording **3a** (R = Me), **3c** {R = (1*R*)-menthyl} and **3d** {R = (1*R*)-fenchyl}. The complexes were characterized by their elementary analyses and their ^1H, ^{31}P and ^{13}C NMR spectra (see supplementary material).

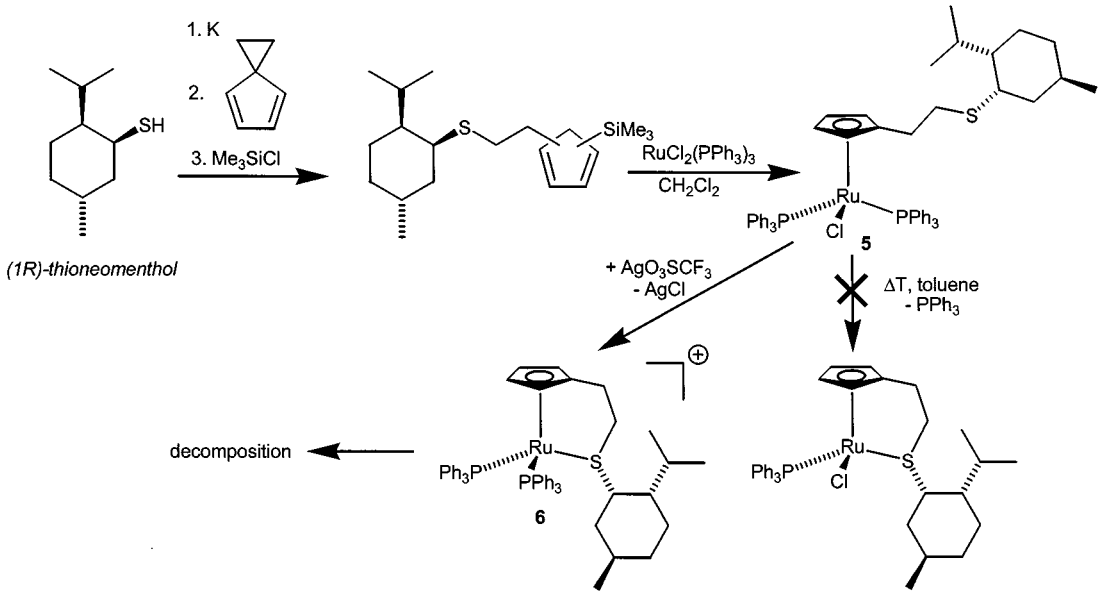
Coordination of the ether-moiety should be revealed by low-field shifts in the ^1H and ^{13}C NMR spectra of the CH_2OCH moieties,[5d] and this is not the case.[9] Moreover, *O*-coordination in the isobornyl derivative **3b** is expected to result in ether cleavage with formation of camphene, and this is also not observed.[5d] The problem is not steric in nature, since the small, achiral methyl ether ligand in **3a** and **4a** doesn't coordinate either. There is obviously a reluctance of the "hard" ether moieties to coordinate to the 'soft' ruthenium center. We therefore concentrated further efforts on the design of Cp-ligands with the "soft" donor atoms sulfur and phosphorous.

A new Cp-ligand with a chiral sulfide side-chain was prepared as outlined in Scheme 2. Its synthesis is based on a method developed by Kauffmann involving a nucleophilic ring-opening reaction of spiro[2.4]hepta-4,6-diene.[10a,b] The potassium salt of (1*R*)-neomenthanethiol[10c,d] was used as the nucleophile. The resulting potassium cyclopentadienide was directly converted into the trimethylsilyl derivative and reacted with $RuCl_2(PPh_3)_3$ affording $[RuCl\{\eta^5\text{-}C_5H_4CH_2CH_2S[(1R)\text{-neomenthyl}]\}\{PPh_3)_2]$ (**5**) in good yield. The chiral ruthenium complex was characterized by its elemental analysis and ^1H, ^{13}C and ^{31}P NMR spectra. As for the ether analogues **3**, the side-chain is not coordinated to the ruthenium center. In this case also prolonged heating in toluene does not result in substitution of one of



Scheme 1. Ruthenium chemistry of the ether-derived Cp ligands

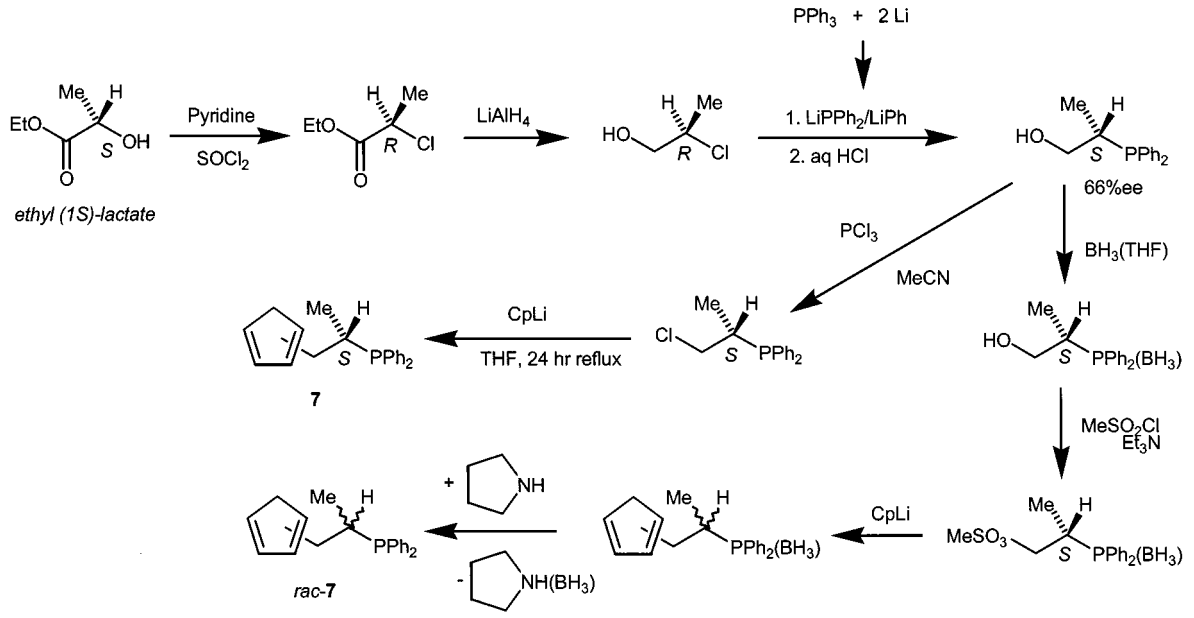
The analytical data indicate that the ether handle in **3** is not coordinated. Prolonged heating of **3** in toluene does not result in expulsion of one of the coordinated PPh_3 ligands (Scheme 1) and subsequent coordination of the ether handle. In another attempt to coordinate the ether handles, and in view of the existence of $[CpRu(PPh_3)_2(THF)][PF_6]$[8], the triflate complexes **4a–c** were synthesized (Scheme 2). the phosphane ligands by the sulfide moiety. Reaction of **5** with AgOTf yields the triflate complex $[Ru\{\eta^5\text{:}\eta^1\text{-}C_5H_4CH_2CH_2S[(1R)\text{-neomenthyl}]\}\{PPh_3)_2][OTf]$ **6**. In contrast to the ether homologues **4**, there is clear evidence for intramolecular coordination of the sulfide side-chain in **6**, and a cationic structure similar to **1a** is proposed.[6c] In comparison to the signals of **5**, low-field shifts are observed



Scheme 2. Synthesis of a chiral sulfur-based Cp ligand and its ruthenium complexes

for the nuclei of the SCH_2-moiety in **6** (^{1}H NMR: from 2.5−2.7 to 3.6−3.9 ppm. ^{13}C NMR: from 31.8 to 53.9 ppm). There is also a smaller low-field shift in the ^{13}C NMR spectrum for the adjacent SCH moiety from 46.5 to 49.9 ppm, whereas the signal shifts to *high*-field in the ^{1}H NMR spectrum (from 3.14 to 2.53 ppm). This contrasting observation may be due to the proximity of the phenyl rings of the PPh_3 ligands causing ring-current shielding. Further evidence for intramolecular coordination of the sulfide moiety comes from the ^{31}P NMR spectrum of **6**, in which the proximity of the chiral neomenthyl moiety causes a clear diastereotopic splitting of the signals of the two PPh_3 ligands ($^2J_{PP}$ = 36 Hz). Unfortunately, complex **6** is unstable and decomposes within a few hours at room temperature, possibly by S−C bond scission. We were therefore unable to use **5** or **6** as an asymmetric Lewis acid catalyst, and therefore concentrated our further efforts on the design of chiral phosphorous ligands.

A novel chiral Cp/phosphane ligand *(S)*-$C_5H_5CH_2CH(Me)PPh_2$ (**7**) was synthesized by the pathway outlined in Scheme 3. The starting material, (*S*)-ethyl lactate, was first converted into (*R*)-$HOCH_2CH(Me)Cl$ according to the literature.[11] The reaction with a mixture of Ph_2PLi and PhLi (prepared in situ from PPh_3 and lithium), after the method developed by Pringle,[12] afforded (*S*)-$HOCH_2CH(Me)PPh_2$ in excellent yield.[13][14] The crude material had an *ee* of 60% by optical rotation {the actual *ee* was 66% (*S*/R = 83:17), vide supra}. As the reaction



Scheme 3. Synthesis of a chiral lactic acid based Cp/phosphane ligand

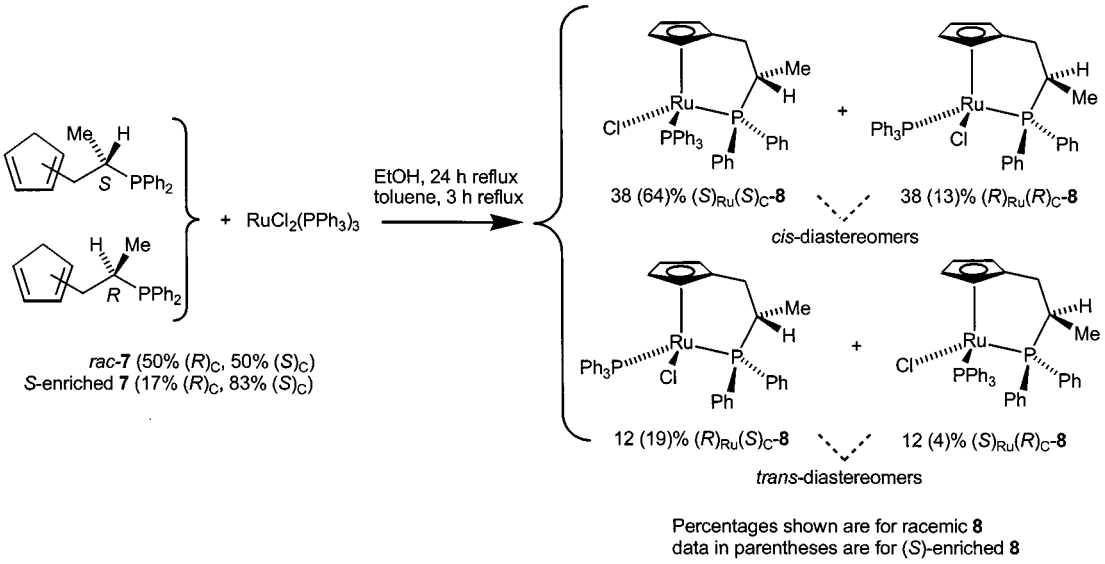
pathway involves two S_N2 reactions (Scheme 3), at least one of them apparently did not proceed with complete inversion at the stereogenic carbon center.

The conversion of the hydroxy functionality into a leaving group (in order to react it with CpLi) without oxidation of the phosphane is quite difficult.[15] Therefore, the phosphane moiety was protected through coordination with borane.[15] The alcohol could then be converted into the mesylate ester. Subsequent reaction with CpLi {curiously, CpNa mainly results in elimination and formation of $H_3BP(allyl)Ph_2$} and decomplexation of borane with pyrrolidine affords $C_5H_5CH_2CH(Me)PPh_2$ (**7**). However, this substance is a racemate, which we discovered after its complexation with ruthenium (vide infra). Racemization probably occurred during the reaction with CpLi by (reversible) deprotonation of the stereogenic carbon which is activated by complexation of BH_3.[16]

Fortunately, we found a method to chlorinate (*S*)-$HOCH_2CH(Me)PPh_2$ without oxidation of the phosphane. The reagent of choice was PCl_3 and, in the presence of excess Et_3NHCl and using acetonitrile as a solvent, (*S*)-$ClCH_2CH(Me)PPh_2$ is obtained in 60−70% yield. The reaction with CpLi afforded **7** in moderate yield, but with 66% *ee*. Reaction of *rac*-**7** or *S*-enriched **7** with $RuCl_2(PPh_3)_3$ according to Kauffmann's method,[6a] afforded $[RuCl\{\eta^5:\eta^1\text{-}C_5H_4CH_2CH(Me)PPh_2\}(PPh_3)]$ (**8**) in low yield {8% based on (*S*)-$HOCH_2CH(Me)PPh_2$, Scheme 4} after isolation by chromatography.

whereas the minor set contains the $(S)_{Ru}(R)_C/(R)_{Ru}(S)_C$ enantiomers (*trans*-diastereomer). Discrimination and assignment was based on an X-ray crystal structure determination of the latter (vide infra). The $(S)_C$ enantiomerically-enriched material contains a total of 83% (64 + 19) $(S)_C$ diastereomers (see Scheme 4). The minor *trans*-diastereomer is much more soluble than the major *cis*-diastereomer, and therefore the former can be selectively extracted and crystallized out of a saturated diethyl ether solution within a few days (interconversion of diastereomers is slow in this solvent, vide infra). Curiously, *rac, trans*-**8** crystallizes in both a monoclinic and a triclinic space group. The X-ray structure determinations show that both unit cells contain enantiomeric pairs of the *trans*-diastereomer (Figure 1). The geometrical data (Tables 3−4) are very similar and also closely resemble those of **1b**.[6b] Minor differences between the three crystal structures are found in the puckering of the chelate ring and in the orientation of some of the phenyl groups, especially those of C(31)−C(36) and C(41)−C(46) of the PPh_3 ligand.

The conformation of the chelate ring of solid **8** is largely maintained in solution (Figure 2). The methyl group in the ring is fixed in an *anti* position with respect to the Cp-ring. Consequently, in the CH_2-moiety one of the hydrogens is in an *anti*-position with respect to the PPh_2-group and the other is *gauche*. This is clearly seen from the $^3J_{HP}$ coupling constants of 48.9 and 8.7 Hz, respectively, for the major *cis*-diastereomer of **8**. The minor *trans*-diastereomer has a simi-



Scheme 4. Ruthenium complexes with ligand **7**

The orange compound was characterized by elementary analysis, mass spectrometry, and ^1H, ^{13}C and ^{31}P NMR spectroscopy (Table 1 and 2). The NMR spectroscopic data are very similar to those of the achiral analogue **1b**, and are in agreement with a bidentate coordination of the Cp/phosphorous ligand. The ruthenium center is chiral, and therefore **8** is composed of two sets of diastereomers in about 77:23 ratio. The major set contains the $(R)_{Ru}(R)_C/(S)_{Ru}(S)_C$ pair of enantiomers (*cis*-diastereomer),[21] lar *anti*-coupling of 45.8 Hz and a *gauche*-coupling of 2.8 Hz.

Another spectroscopic feature of **8** is the extreme upfield chemical shift in the ^1H NMR spectrum of one of the Cp hydrogens (2.35 ppm for the *cis*-diastereomer and 2.98 ppm for the *trans*-diastereomer in $CDCl_3$). This phenomenon has also been observed for **1b** (2.45 ppm) and was ascribed to shielding by one of the phenyl rings of the PPh_3 ligand.[6b] The chemical shifts of the nuclei of the Cp-ring of

Table 1. Selected ^1H and ^{31}P NMR Data of $[RuX\{\eta^5:\eta^1\text{-}C_5H_4CH_2CH(Me)PPh_2\}(PPh_3)]$;[a] (*J*, Hz)

X	Nr	Isomer	C*H*$_3$	C*H*$_2$	PC*H*	C$_5$*H*$_4$	C*P*Ph$_2$	*P*Ph$_3$
Cl	**8**	*cis*-diastereomer (77%) $[(R)_{Ru}(R)_C$ and $(S)_{Ru}(S)_C]$	0.92 (dd, 6.9 and *11.7*)	1.75 (td, 13.0 and *8.7*) 2.08 (ddd, 5.3, 13.0 and *48.9*)	3.12 (m)	2.35, 4.42 5.05, 5.13	67.1 (d, *35*)	42.3 (d, *35*)
		trans-diastereomer (23%) $[(S)_{Ru}(R)_C$ and $(R)_{Ru}(S)_C]$	1.01 (dd, 7.0 and *11.8*)	1.97 (td, 13.5 and *2.8*) 2.42 (ddd, 7.6, 13.8 and *45.8*)	3.68 (m)	2.98, 4.54 5.01 (2 H)	65.3 (d, *37*)	46.2 (d, *37*)
Br	**11**	*cis*-diastereomer (76%) $[(R)_{Ru}(R)_C$ and $(S)_{Ru}(S)_C]$	0.90 (dd, 7.3 and *9.9*)	1.75 (m)* 2.10 (ddd, 5.5, 13.8 and *49.5*)	3.16 (m)	2.42, 4.40 5.08, 5.12	65.7 (d, *34*)	41.1 (d, *34*)
		trans-diastereomer (24%) $[(S)_{Ru}(R)_C$ and $(R)_{Ru}(S)_C]$	0.93*	1.75 (m)* 2.36 (ddd, 6.9, 13.8 and *48.1*)	3.72 (m)	3.40, 4.58 4.95, 5.03	66.5 (d, *37*)	45.0 (d, *37*)
I	**12**	*cis*-diastereomer (74%) $[(R)_{Ru}(R)_C$ and $(S)_{Ru}(S)_C]$	0.86 (dd, 6.7 and *10.8*)	1.71 (td,13.3 and *6.2*) 2.10 (ddd, 5.4, 13.8 and *51.5*)	3.23 (m)	2.60, 4.33 5.10, 5.16	63.3 (d, *33*)	40.3 (d, *33*)
		trans-diastereomer (26%) $[(S)_{Ru}(R)_C$ and $(R)_{Ru}(S)_C]$	0.86*	1.56 (td, 13.7 and *4.7*) 2.27 (m)*	3.65 (m)	3.99, 4.60 4.90, 5.09	67.2 (d, *37*)	44.5 (d, *37*)

[a] In $CDCl_3$; J_{HP} in italics; PPh signals 6.7−8.0 ppm (m, 25 H); signals marked with an asterisk were poorly resolved due to overlap with other signals.

Table 2. Selected ^{13}C NMR Data of $RuX[\eta^5:\eta^1\text{-}C_5H_4CH_2CH(Me)PPh_2](PPh_3)$[a]

X	Nr	Isomer	C*H*$_3$	C*H*$_2$	PC*H*	C$_5$*H*$_4$				
Cl	**8**	*cis*-diastereomer	16.2 (d, 5)	29.6 (d, 6)	52.8 (d, 30)	61.5 (s)	77(d, 12?)*	83.0 (d, 9)	86.1 (d, 4)	110.0 (s, br)
		trans-diastereomer	15.3 (d, 8)	30.8 (d, 6)	60.6 (dd, 27 and 5)	64.9 (s)	75.7 (d, 13)	82.6 (d, 6)	85.1 (d, 9)	112.4 (s, br)
Br	**11**	*cis*-diastereomer	16.1 (d, 5)	29.4 (d, 6)	52.7 (d, 29)	63.3 (s)	76.5 (d?)*	82.7 (d, 9)	85.6 (d, 5)	109.7 (s, br)
		trans-diastereomer	15.5 (d, 7)	29.8 (d, 6)	58.5 (dd, 27 and 5)	66.5 (s)	75.9 (d, 11)	82.6 (d?)*	84.1 (d, 8)	111.5 (s, br)
I	**12**	*cis*-diastereomer	16.4 (d, 5)	29.3 (d, 7)	52.8 (d, 29)	67.9 (s)	75.6 (d, 11)	82.0 (d, 9)	85.2 (d, 4)	109.6 (s, br)
		trans-diastereomer	15.9 (d, 7)	29.2 (d, 7)	56.3 (dd, 28 and 5)	70.4 (s)	75.4 (d, 11)	82.5*	82.6*	110.3 (s, br)

[a] In $CDCl_3$; J_{CP} (Hz) in parentheses; PPh signals 125−137 ppm; signals marked with an asterisk were poorly resolved due to overlap with other signals.

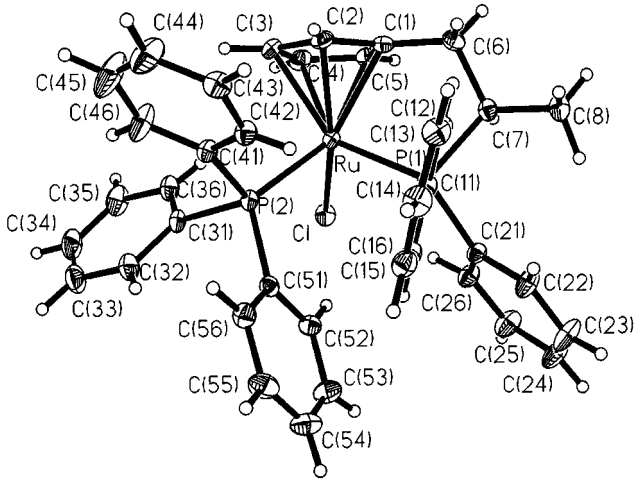


Figure 1. X-ray structure of *racemic, trans*-**8** (monoclinic modification)

cis- and *trans*-**8** could be assigned with help of COSY and $^1H,^{13}C$-HETCOR experiments (see *supplementary material*).

Reaction of **1b** (as a pair of enantiomers) with $AgBF_4$ in the presence of (*R*)-$H_2NCH(Me)Ph$ yields the cationic complex $[Ru(\eta^5:\eta^1\text{-}C_5H_4CH_2CH_2PPh_2)(PPh_3)\{(R)\text{-}H_2NCH(Me)Ph)\}][BF_4]$ as a 50:50 mixture of diastereomers.[6b] A similar reaction conducted with *rac*-**8** (using AgO_3SCF_3 and (*S*)-$H_2NCH(Me)Ph$) affords the salt $\{RuCl[\eta^5:\eta^1\text{-}C_5H_4CH_2CH(Me)PPh_2](PPh_3)[(S)\text{-}H_2NCH(Me)Ph)]\}(O_3SCF_3)$ (**9**) as a mixture of four diastereomers in the ratio of 38:38:12:12 (Scheme 5). The reaction is assumed to proceed with retention of configuration at the metal, as is usual for substitutions on $CpML_2X$ systems.[17] If the same reaction is conducted with $(S)_C$-enriched **8**, the four diastereomers of **9** are obtained in a 64:13:19:4 ratio. Identification of the diastereomers by NMR spectroscopy (Table 5) was possible due to differences in the intensity of the signals. It was assumed that the starting compound (*S*)-$HOCH_2CH(Me)PPh_2$ {having an estimated (*S*)-enrichment of 60% by optical rotation}, did not change its configuration during the synthesis of **7**−**9**. Therefore, from the pair of diastereomers with $(S)_{Ru}(S)_C$ and $(R)_{Ru}(R)_C$ configuration (64 + 13%), the major diastereomer (64%) has configuration $(S)_{Ru}(S)_C$ and the minor one (13%) has $(R)_{Ru}(R)_C$. Consequently, the diastereomer with 19% abundance has configuration $(R)_{Ru}(S)_C$, and that with 4% abundance has $(S)_{Ru}(R)_C$. Finally, the enantiopurity of $(S)_C$-enriched **8** and of the starting compound (*S*)-$HOCH_2CH(Me)PPh_2$ is now more accurately determined as being 66% (64 + 19−13−4). The product mixture of **9** is unstable. Some of the $(S)_{Ru}$ isomers are converted into the $(R)_{Ru}$ isomers within a few days in solution, thereby maintaining the ratio of the $(S)_C$ and $(R)_C$ isomers (83:17). Longer standing times lead to decomposition of the reaction mixture.

Table 3. Crystal data and structure refinement for *rac, trans*-**8**

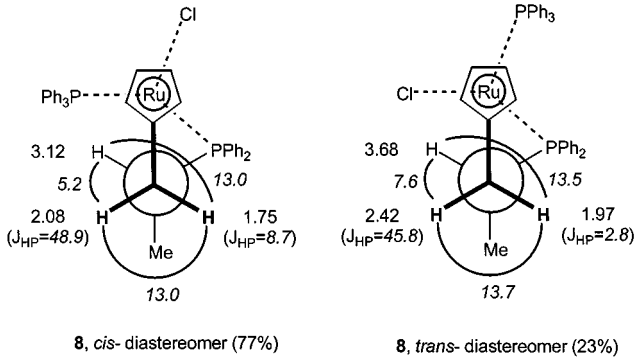
Empirical formula		$C_{38}H_{35}ClP_2Ru$	
Formula weight		690.12	
Measurement device		STOE-STADI IV	STOE-IPDS
Temperature [K]		293	220
Wavelength [Å]		0.71073	
Crystal size [mm]		0.20 × 0.25 × 0.30	0.30 × 0.25 × 0.15
Crystal system		triclinic	monoclinic
Space group		$P\bar{1}$	$P2_1/c$
Unit cell dimensions	a [Å]	10.565(2)	9.269(2)
	b	12.317(6)	36.712(6)
	c	14.632(4)	10.051(2)
	α [°]	67.79(3)	90
	β	89.16(4)	109.68(3)
	γ	68.07(3)	90
Volume [Å^3], Z		1617.3(9), 2	3220.6(12), 4
Calculated density [Mg/m^3]		1.417	1.423
Absorption coefficient [mm^{-1}]		0.692	0.695
F(000)		708	1416
2Θ range [°]		1.04−51.96	4.44−52.14
Limiting indices		$-12 \le h \le 13$, $-15 \le k \le 15$, $-18 \le l \le 18$	$-11 \le h \le 11$, $-44 \le k \le 43$, $-12 \le l \le 12$
Reflections, measured		12811	19977
Reflections, unique		6325 [R(int) = 0.0596]	6236 [R(int) = 0.1525]
No. of refined parameters		516	483
Goodness-of-fit on F^2		1.146	0.822
Final R indices [$I>2\sigma(I)$]		$R1$ = 0.0433, $wR2$ = 0.0730	$R1$ = 0.0573, $wR2$ = 0.1043
R indices (all data)		$R1$ = 0.0768, $wR2$ = 0.0896	$R1$ = 0.1688, $wR2$ = 0.1331
Largest diff. peak and hole [eÅ^{-3}]		0.614 and −0.365	0.711 and −0.522

Table 4. Selected bond lengths [Å] and angles (°) for *rac, trans*-**8** (triclinic/monoclinic)

Ru−Cl	2.4653(12)	2.462(2)	Ru−P(1)	2.3274(18)	2.319(2)
Ru−P(2)	2.3107(13)	2.308(2)	Ru−C(1)	2.177(4)	2.168(9)
Ru−C(2)	2.164(4)	2.177(9)	Ru−C(3)	2.213(4)	2.208(8)
Ru−C(4)	2.231(5)	2.216(8)	Ru−C(5)	2.212(5)	2.193(11)
P(1)−C(7)	1.879(4)	1.868(9)	P(1)−C(11)	1.843(4)	1.826(7)
P(1)−C(21)	1.847(4)	1.833(8)	P(2)−C(31)	1.840(4)	1.856(8)
P(2)−C(41)	1.838(4)	1.833(7)	P(2)−C(51)	1.831(4)	1.843(7)
C(1)−C(2)	1.434(6)	1.399(13)	C(1)−C(5)	1.408(6)	1.423(14)
C(1)−C(6)	1.500(6)	1.496(14)	C(2)−C(3)	1.429(6)	1.446(13)
C(3)−C(4)	1.399(7)	1.388(12)	C(4)−C(5)	1.425(7)	1.396(16)
C(6)−C(7)	1.532(6)	1.545(12)	C(7)−C(8)	1.520(6)	1.553(13)
Cl−Ru−P(1)	100.89(5)	102.42(7)	Cl−Ru−P(2)	89.98(5)	89.77(8)
P(1)−Ru−P(2)	99.59(6)	99.73(7)	Ru−P(1)−C(7)	100.90(15)	102.8(3)
Ru−P(1)−C(11)	117.95(13)	118.8(2)	Ru−P(1)−C(21)	128.34(13)	126.0(3)
C(7)−P(1)−C(11)	106.60(19)	105.0(4)	C(7)−P(1)−C(21)	99.31(19)	101.2(4)
C(11)−P(1)−C(21)	100.57(19)	100.2(3)	Ru−P(2)−C(31)	116.80(16)	116.3(3)
Ru−P(2)−C(41)	111.92(14)	111.9(2)	Ru−P(2)−C(51)	119.19(15)	120.2(3)
C(31)−P(2)−C(41)	100.73(19)	100.4(3)	C(31)−P(2)−C(51)	100.45(19)	100.9(3)
C(41)−P(2)−C(51)	105.5(2)	104.6(3)	C(2)−C(1)−C(5)	108.2(4)	107.1(10)
C(2)−C(1)−C(6)	127.1(4)	126.7(10)	C(5)−C(1)−C(6)	124.5(4)	126.2(11)
C(1)−C(2)−C(3)	106.5(4)	108.6(9)	C(2)−C(3)−C(4)	109.1(4)	106.2(10)
C(3)−C(4)−C(5)	107.8(4)	110.0(10)	C(1)−C(5)−C(4)	108.3(5)	108.0(11)
C(1)−C(6)−C(7)	112.6(3)	111.6(8)	P(1)−C(7)−C(6)	109.7(3)	108.6(7)
P(1)−C(7)−C(8)	119.1(4)	118.3(6)	C(6)−C(7)−C(8)	112.0(4)	113.7(8)

The presumable reaction product of $(S)_C$-enriched **8** with AgOTf, $[Ru(\eta^5{:}\eta^1\text{-}C_5H_4CH_2CH(Me)PPh_2)(PPh_3)][OTf]$ (**10**), is a poor Lewis acid, since for instance it does not catalyse the Diels−Alder reaction between cyclopentadiene and methacrolein. In agreement with this is the fact that the related complex $[RuCp(S,S\text{-chiraphos})(C_2H_4)]^+$ doesn't catalyse this reaction either.[2b] NMR spectra of **10** only show broad signals that are not very diagnostic. Without adding a Lewis base, **10** is unstable and fully decomposes within a few hours at room temperature, presumably by reaction with the solvent. The immediate reaction with Lewis bases like (S)-$H_2NCH(Me)Ph$ (vide supra) appears to be stereoselective, with retention of configuration at ruthenium. The reaction of a freshly prepared solution of **10** with Cl^- (as Et_3NHCl) after 10 min affords **8** with the original diastereomer ratio of 77:23.

It was found that the diastereomers of **8** exchange in solution. When crystals of the *trans*-diastereomer are dissolved, one observes the gradual formation of the *cis*-diastereomer until an equilibrium is reached having the original 77:23 ratio (Figure 3). The ruthenium diphosphane complex $[RuCl(\eta^5\text{-}Cp)\{(R)\text{-}Ph_2PCH(Me)CH_2PPh_2\}]$ shows similar

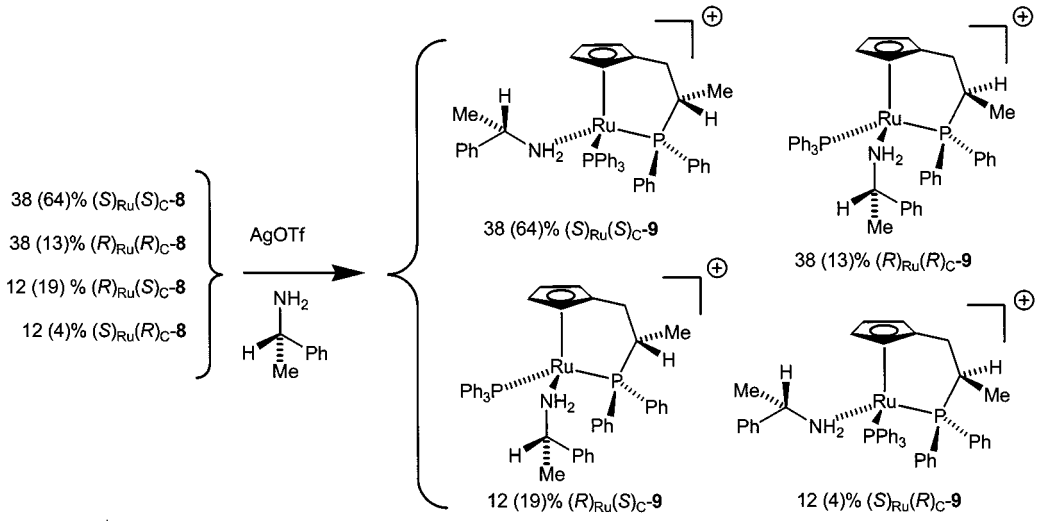


8, *cis*- diastereomer (77%) **8**, *trans*- diastereomer (23%)

Figure 2. Selected ^{1}H NMR data of **8**; the $^2J_{HH}$ coupling of 13.7 Hz in *trans*-**8** is averaged from the measured data (13.5, 13.8 Hz)

behaviour although exchange between the two diastereomers takes several days in chlorobenzene.[18] It was found that the rate of the isomerisation is very solvent-dependent, consistent with dissociation of Cl^- being the rate-determining step (pathway A in Scheme 6) and not decomplexation of the PPh_3 ligand (pathway B in Scheme 6). It also suggests that interconversion of the *cis*- and *trans*-diastereomers of the intermediate cations $[Ru]^+$ is faster than Ru−Cl bond dissociation. It was further found that the presence of extra PPh_3 did not slow down the reaction rate of the *trans-cis* interconversion of **8** in $CDCl_3$, confirming that phosphane dissociation does not trigger the conversion (Figure 4). Despite this, dissociation of PPh_3 in **8** probably does occur. In the related compound $[RuCl(\eta^5\text{-Cp})(PPh_3)_2]$ dissociation of PPh_3 occurs with a rate constant of 5×10^{-6} s^{-1} (thf, 21°C), which is of the same magnitude as chloride dissociation in **8** (4.8×10^{-6} s^{-1}, thf, 23°C).[19] If phosphane dissociation in **8** occurs with a similar rate, then this means that the interconversion of the *cis*- and *trans*- isomers (i.e. site exchange of the chloride) of the intermediate $[RuCl(\eta^5{:}\eta^1\text{-}C_5H_4CH_2CH(Me)PPh_2)]$ is very slow.

In another experiment the *trans-cis* interconversion of **8** was monitored in $CDCl_3$ in the presence of Et_3NHCl (Figure 4). It was expected that when Ru−Cl dissociation is rate-determining for the conversion, then adding Cl^- should slow down the conversion. Actually, the presence of



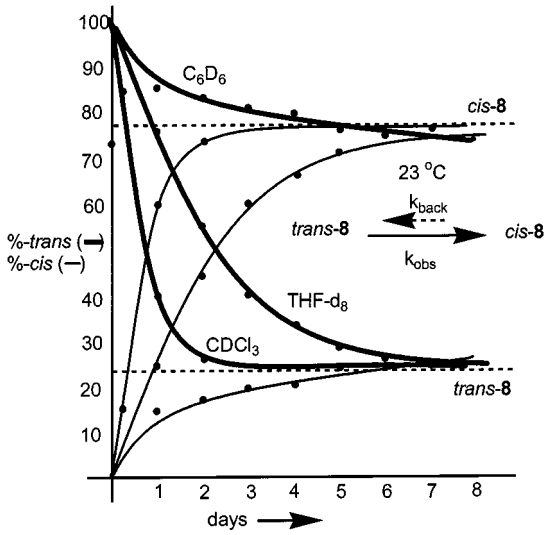
Scheme 5. Preparation of the amine complex **9** as a mixture of 4 diastereomers

Table 5. Selected ^{1}H, ^{13}C and ^{31}P NMR data for the four diastereomers of $\{Ru[\eta^5{:}\eta^1\text{-}C_5H_4CH_2CH(Me)PPh_2](PPh_3)[(R)\text{-}H_2NCH(Me)Ph)]\}\{O_3SCF_3\}$ (**9**)[a]

Isomer	C_5H_4	PCCH_3	CHPPh$_2$	PPh$_3$
$(S)_{Ru}(S)_C$	4.20, 4.37, 4.71, 5.67	0.96 (dd, 6.8 and 13.4 Hz)	72.8 (d, 29 Hz)	49.6 (d, 29 Hz)
$(R_{Ru}(R)_C$	4.20, 4.50,..	0.96?	78.7 (d, 29 Hz)	51.8 (d?)
$(R)_{Ru}(S)_C$	3.85, 4.47, 4.61, 5.09	0.77 (dd, 6.6 and 13.1 Hz)	74.2 (d, 28 Hz)	52.2 (d, 28 Hz)
$(S)_{Ru}(R)_C$	3.85, 4.62, 5.09?, 5.44	0.79?	76.1 (d, 28 Hz)	53.6 (d, 28 Hz)

Isomer	PCCH_3	CH_2	PCH	C_5H_4	C_5H_4	C_5H_4	C_5H_4	CNH_2	$NCCH_3$
$(S)_{Ru}(S)_C$	14.3 (d, 7 Hz)	30.2 (d, 4 Hz)	56.9 (d, 30 Hz)	61.4 (s)	74.7 (d, 9 Hz)	81.9 (d, 9 Hz)	89.2 (s)	58.6	25.8
$(R)_{Ru}(R)_C$	14.1 (d, 7 Hz)	30.2 (d, 4 Hz)	58.1 (d, 30 Hz)	60.7 (s)	74.8 (d, 9 Hz)	80.2 (d, 9 Hz)	88.2 (s)	59.0	26.6
$(R)_{Ru}(S)_C$	16.0 (d, 7 Hz)	28.8 (d, 7 Hz)	53.5 (dd, 30 and 4 Hz)	65.0 (s)	72.2 (d, 10 Hz)	82.5 (d, 6 Hz)	83.2 (d, 4 Hz)	59.6	27.3
$(S)_{Ru}(R)_C$	15.9 (d, 7 Hz)	29.2 (d, 7 Hz)	51.0 (dd, 29 and 4 Hz)	65.6 (s)	71.5 (d, 10 Hz)	80.9 (d, 6 Hz)	84.1 (d, 6 Hz)	61.8	27.3?

[a] In $CDCl_3$; coupling to phosphorous in parentheses.



solvent	polarity (E_t-value)	k_{obs}	k_{back}
$CDCl_3$	39.1	13×10^{-6}	3.6×10^{-6}
thf-d_8	37.4	4.8×10^{-6}	1.4×10^{-6}
C_6D_6	34.8	0.3×10^{-6}	0.08×10^{-6}

($K = 77/23 = 3.35 = k_{obs}/k_{back}$)

Figure 3. Equilibration of the *trans*- and *cis*-diastereomers of **8** in different solvents

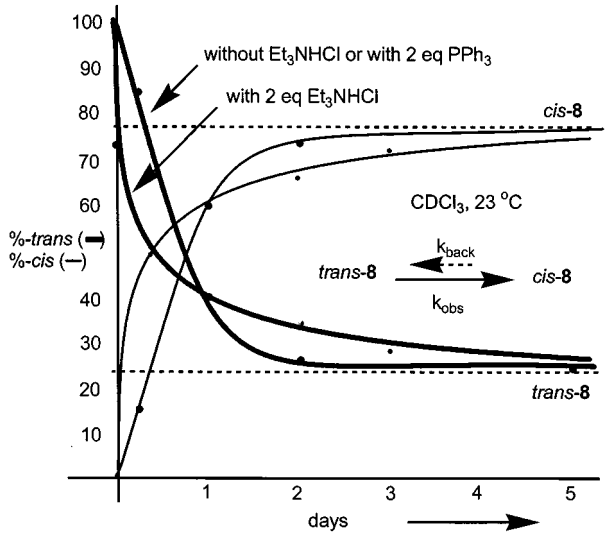
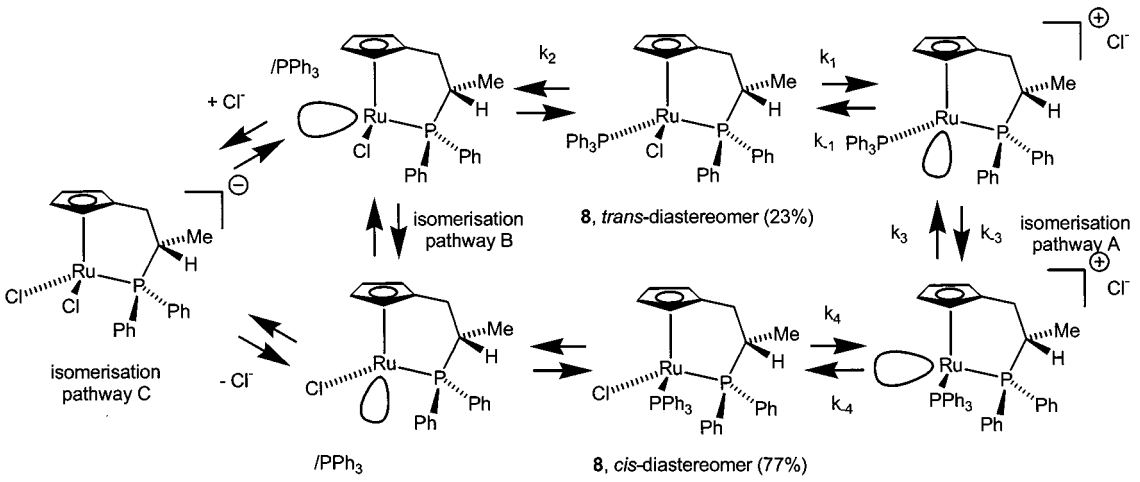


Figure 4. Equilibration of the *trans*- and *cis*-diastereomers of **8** in $CDCl_3$ in the presence of either PPh_3 or Et_3NHCl

other diastereotopic site. This, however, would imply that $Ru-PPh_3$ dissociation becomes rate-determining, and that this dissociation is in fact faster than Ru−Cl dissociation.

In order to study the relative reactivity of *cis*- and *trans*-**8** in more detail we investigated the substitution reactions of **8** with NaBr or NaI. This reaction results in quantitative formation of [RuBr{η^5:η^1-$C_5H_4CH_2CH(Me)PPh_2$}(PPh_3)] (**11**) or [RuI{η^5:η^1-$C_5H_4CH_2CH(Me)PPh_2$}(PPh_3)] (**12**) (see Tables 1 and 2). The reaction was monitored by NMR spec-



Scheme 6. Interconversion of the *trans* and *cis* diastereomers of **8**

Et_3NHCl *enhances* the rate. One reason might be that the slowing down due to the presence of extra Cl^- is counterbalanced by the enhanced polarity of the solvent (a salt effect). It is also possible that Et_3NH^+ labilizes the Ru−Cl bond by forming a hydrogen bond. Another explanation is that a third mechanism is operative for the conversion (pathway C in Scheme 6): after dissociation of PPh_3 from **8** the intermediate [RuCl(η^5:η^1-$C_5H_4CH_2CH(Me)PPh_2$] is trapped by Cl^- forming the anion [$RuCl_2$(η^5:η^1-$C_5H_4CH_2CH(Me)PPh_2$]$^-$ which than loses Cl^- from the troscopy in $CDCl_3$ (Figure 5 and 6). After the reaction was complete, the *cis*/*trans* ratio of **11** and **12** is about the same as in **8**. The presence of 3 equivalents of PPh_3 during the reaction with NaI does not change the reaction profile so that, again, $Ru-PPh_3$ dissociation is not expected to play a role in these substitution reactions. The rate of reaction of **8** is about the same for both substitutions, and is also of a similar magnitude as the *cis*/*trans* conversion of **8**. Although the reactions are heterogenic, it again suggests that Cl^- dissociation is the rate-determining step. For both substi-

tutions the minor *trans*-diastereomer of **8** reacts about three times as fast as the *cis*-diastereomer. This is also in agreement with the rate constants for Cl^- dissociation in *cis*- and *trans*-**8** (Figure 3). As the *cis*-diastereomer has about three times the abundance of the *trans*-isomer, at the beginning of the reaction the *cis*- and *trans*-diastereomers of the cation $[Ru]^+$ should have about equal abundance. As a result, a relatively large proportion of the *trans*-diastereomers of **11** and **12** is formed (Figure 5 and 6). For the reaction with NaI the amount of *trans*-**12** after 2 days is even larger (42%) than the initial amount of *trans*-**8** (23%). This is probably due to the fact that, as *trans*-**8** reacts and disappears about three times faster than *cis*-**8**, the *cis*/*trans* equilibrium of **8** is out of balance and *cis*-$[Ru]^+$ will convert into *trans*-$[Ru]^+$. Then, after both *cis*- and *trans*-**8** have been consumed, the *cis*/*trans* ratio of **12** changes until equilibrium has been reached after about a week. From the profile in Figure 6 it is estimated that I^- dissociation in *trans*- and *cis*-**12** in $CDCl_3$ is about three times as slow ($k_1 = 4.3 \times 10^{-6}$, $k_{-1} = 1.5 \times 10^{-6}$ s^{-1}) as Cl^- dissociation in **8** (see Figure 3). This "peaking" of the abundance of the *trans*-diastereomer is not observed during the reaction of **8** with NaBr. We think that exchange between the *cis*/*trans* diastereomers in **11** is faster than for **12**, and that equilibrium is reached before **8** has completely reacted.

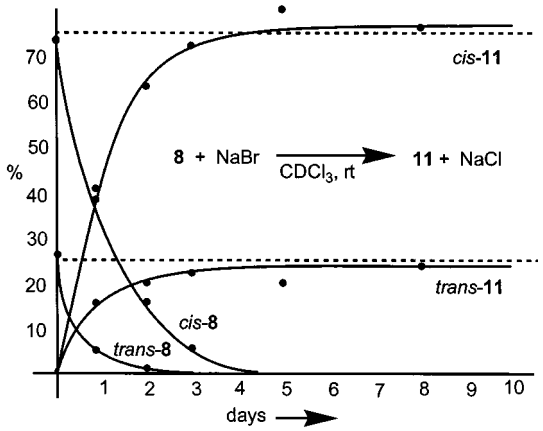


Figure 5. Reaction of **8** with NaBr in $CDCl_3$

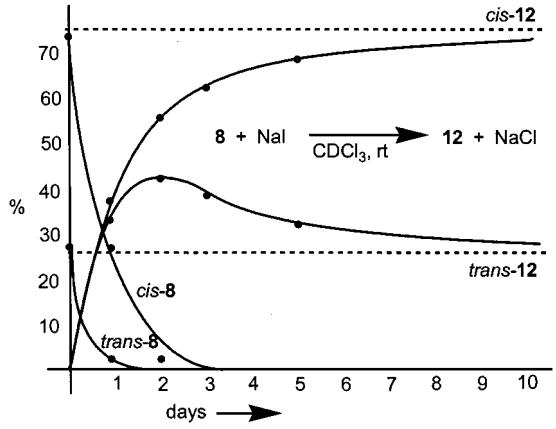


Figure 6. Reaction of **8** with NaI in $CDCl_3$

Conclusions

The experiments presented above confirm that the *cis*- and *trans*-diastereomers of the Cp/phosphane complex **8** (and **11**, **12**) exchange through Cl^- dissociation with intermediate formation of the cations *cis*- and *trans*-**[Ru]**$^+$. The rate of Cl^- dissociation in *trans*-**8** is about 3 times as large as in *cis*-**8**. Furthermore, the cations **[Ru]**$^+$ are too electron rich to develop significant Lewis acidity for asymmetric catalysis. Further modifications of the functionalized Cp-ligands should lead to the formation of only one diastereomer upon coordination, as in the ferrocene-based Cp/phosphane ligand designed by Hidai, mentioned earlier.[7b] Thus, the presence of two, possibly counteracting, diastereotopic sites on the catalyst is not very promising for obtaining high enantioselectivity. Another solution might be the separation of the diastereomers. However, this is only meaningful when the ruthenium complexes are configurationally stable at the metal center. The situation may be improved by using π-acceptor ligands which at the same time would increase the Lewis acidity. In future work, we will concentrate on other coordination environments and transition metals to avoid the diastereomer problem.

Experimental Section

General: All manipulations were carried out under an atmosphere of argon using Schlenk techniques. Solvents were dried and degassed by conventional procedures prior to use. − ^1H and ^{13}C NMR: Varian Gemini 300. − The ^1H and ^{13}C NMR spectra were measured in $CDCl_3$ unless stated otherwise ($CHCl_3$: $\delta_H = 7.24$; $CDCl_3$: $\delta_C = 77.0$) − Mass spectra: AMD Intectra 402, EI-MS, 70 eV; only the primary signal of a mixture of isotopes is given. − Combustion analyses (C,H): CHNS-932 LECO analyzer. The Cp/ether ligands were prepared according to ref.[5c] and their Me_3Si-derivatives according to ref.[5d]

[RuCl{η^5-$C_5H_4CH_2CH_2O$[(1*R*)-fenchyl]}$(PPh_3)_2$] (3d): A suspension of $RuCl_2(PPh_3)_3$ (2.00 g, 2.1 mmol) and {C_5H_4-(CH_2CH_2Ofenchyl)($SiMe_3$)} (1.1 g, 3.5 mmol) in 100 mL of toluene was refluxed for 5 h. After cooling to room temperature the mixture was concentrated and chromatographed (Fluka: silica gel 60, toluene/THF, 9:1). Concentration of the extracts afforded a yellow-orange air stable powder that was washed once with a little pentane. Yield: 1.60 g (1.92 mmol, 91%). − $C_{53}H_{55}ClOP_2Ru$ (906.5): calcd. C 70.2, H 6.1; found C 68.9, H 6.5. − (EI) MS for **3d**, and also for **3a**−**c**, do not show fragments for M; main fragments are due to PPh_3 (262, 183, 108, 78); a fragment with low abundance was recognized as the metallocene Cp'_2Ru (for **3d**: *m*/*z* = 592), obviously a result of rearrangement.

[RuCl{η^5-$C_5H_4CH_2CH_2O$[(1*R*)-menthyl]}{$PPh_3)_2$] (3c): As for **3d**. Yield: 95%. − $C_{53}H_{57}ClOP_2Ru$ (908.5): calcd. C 70.0, H 6.3; found C 70.0, H 5.8.

[RuCl[η^5-$C_5H_4CH_2CH_2OMe$](PPh$_3$)$_2$] (3a). − Method 1: A suspension of $RuCl_2(PPh_3)_3$ (1.0 g, 1.1 mmol) and 0.3 $C_5H_5CH_2CH_2OMe$ (0.3 g, 2.5 mmol) in degassed ethanol was refluxed overnight under argon. The solvent was then replaced by toluene and the mixture heated to reflux for a few hours. Concentration and chromatograpy (Fluka: silica gel 60, toluene/THF, 15:1) afforded a yellow-orange powder (0.4 g, 45%). − **Method 2:** As for **3d**. Yield: 90%. − $C_{44}H_{41}ClOP_2Ru$ (784.3): calcd. C 67.4, H 5.3; found C 67.1, H 5.4.

[RuCl{η^5-$C_5H_4CH_2CH_2O$[(1*S*)-isobornyl]}$(PPh_3)_2$]: As for **3a**, method 1. Yield: 40%. $C_{53}H_{55}ClOP_2Ru$ (906.5): calcd. C 70.2, H 6.1; found C 68.4, H 5.9.

[Ru(O_3SCF_3){η^5-$C_5H_4CH_2CH_2OR$}$(PPh_3)_2$] {R = Me (4a), isobornyl (4b) or menthyl (4c)}: In a typical experiment 0.10 g of **3** was reacted with a slight excess of AgO_3SCF_3 in 10 mL of CH_2Cl_2. After stirring for 10 min at room temperature the solution was filtered over Celite, and evaporated to dryness. The triflates were unstable in solution, and were therefore characterized by their ^{1}H, ^{13}C, and ^{31}P NMR spectra measured immediately after their preparation.

C_5H_4{CH_2CH_2S[(1*R*)-neomenthyl]}($SiMe_3$): A solution of (*S*)-(+)-neomenthanethiol[10b,c] (8.6 g, 50 mmol) in 50 mL of THF was stirred in the presence of excess potassium metal at room temperature overnight. The solution of the resulting potassium thiolate was decanted and spiro[2.4]hepta-4,6-diene[10d] (4.6 g, 50 mmol) was added at 0°C. After stirring for 5 h at 45°C, the reaction mixture was cooled to −78°C and 6 mL (excess) of $ClSiMe_3$ was added. After stirring for 2 h, solvent was evaporated and the residue extracted with a mixture of water and pentane. The pentane extracts were collected, dried over Na_2SO_4, filtered and evaporated to dryness affording the oily title compound in quantitative yield and high purity. − $C_{20}H_{36}SSi$ (336.7): calcd. C 71.4, H 10.8, S 9.5; found C 70.5, H 10.3, S 9.1.

[RuCl{η^5-$C_5H_4CH_2CH_2S$[(1*R*)-neomenthyl]}$(PPh_3)_2$] (5): A mixture of $RuCl_2(PPh_3)_3$ (4.79 g, 5.0 mmol) and C_5H_4{CH_2CH_2S[(1*R*)-neomenthyl]}($SiMe_3$) (1.68 g, 5.0 mmol) in CH_2Cl_2 was stirred overnight at room temperature. The solvent was then evaporated and the residue washed once with pentane. The orange product was isolated by exhaustive extraction with diethyl ether. Yield: 2.96 g (64%). − $C_{53}H_{57}ClP_2RuS$ (924.6): calcd. C 68.9, H 6.2, S 3.5; found C 67.6, H 6.6, S 3.3. − ^{1}H NMR: δ = 0.85, 0.87, 0.91 (all d, 3 × 3 H, neomenthyl), 2.5−2.7 (m, 4 H, CCH_2CH_2S), 3.14 (1 H, SC*H*), 3.27, 3.31, 3.99, 4.01 (C_5H_4). − ^{13}C NMR: δ = 20.9, 21.1, 22.2 ($C_{7,9,10}$), 25.9 (CCH_2), 26.3 (C_8), 27.3 (C_5), 29.9 (C_1), 31.8 (SCH_2), 35.4 (C_6), 40.7 (C_2), 46.5 (C_3), 48.9 (C_4), 76.4, 76.9, 80.0(br), 80.3(br) (C_5H_4).^{31}P NMR: δ = 40.0.

[Ru(O_3SCF_3){η^5-$C_5H_4CH_2CH_2S$[(1*R*)-neomenthyl]}$(PPh_3)_2$] (6): A solution of **6** was generated from **5** as described for **4**. Complex **6** decomposes within a few hours at room temperature in $CDCl_3$ and was therefore only characterized by NMR spectroscopy. Selected NMR spectroscopic data: ^{1}H NMR: δ = 0.61, 0.88, 0.98 (all d, 3 × 3 H, neomenthyl), 2.17, 2.44 (m, 2 × 1 H, CCH_2), 2.53 (1 H, SC*H*), 3.59, 3.97 (m, 2 × 1 H, SCH_2), 4.04, 4.19, 4.50, 4.55 (C_5H_4). − ^{13}C NMR: δ = 20.4, 21.2, 23.7 ($C_{7,9,10}$), 23.9 (CCH_2), 26.4 (C_5), 28.6, 29.1 ($C_{1,8}$), 31.8 (C_6), 36.6 (C_2), 47.2 (C_4), 49.9 (C_3), 53.9 (SCH_2), 76.0, 76.8, 79.8, 82.7 (C_5H_4). − ^{31}P NMR: δ = 33.1 (d, *J* = 36 Hz), 42.8 (d, *J* = 36 Hz).

(*S*)-$HOCH_2CH(Me)PPh_2$: A solution of Ph_2PLi and PhLi was prepared by reacting PPh_3 (29.95 g, 114 mmol) and lithium shavings (3.0 g, 430 mmol) in 200 mL of THF at room temperature overnight. The bright orange solution was then filtered and cooled to −70°C upon which *(R)*-$HOCH_2CH(Me)Cl$ (9.9 g, 105 mmol) was added. The solution was slowly raised to room temperature and stirred overnight. The resulting colorless solution was evaporated to dryness. Water and 100 mL of CH_2Cl_2 were added (in air), and 3 M HCl was added until the mixture was just neutral (ca 40 mL). The organic layer was separated, dried over Na_2SO_4 and evaporated to dryness affording 27.2 g (100%) of a very viscous colorless oil. Except for some trace amounts of $Ph_2P(O)H$, this material was virtually pure. − $C_{15}H_{17}OP$ (244.3): calcd. C 73.8, H 7.0; found C 72.7, H 7.0. − $[\alpha]_D$ (*c* = 3.2, CH_2Cl_2) +4.5° (*ee* ≈ 60%; *S*/*R* ≈ 80:20). Actually, the optical purity is 66% as was found after complexation to ruthenium (vide infra). − ^{1}H NMR: δ = 1.09 (dd, $^3J_{HH}$ = 6.9 Hz, $^3J_{HP}$ = 13.9 Hz, 3 H, CH_3), 2.61 (m, 1 H, C*H*CH_3), 3.54 (ddd, $^2J_{HH}$ = 10.9 Hz, $^3J_{HH}$ = 7.6 Hz, $^3J_{HP}$ = 7.6 Hz, 1 H, OCH_2), 3.70 (ddd, $^2J_{HH}$ = 10.9 Hz, $^3J_{HH}$ = 4.6 Hz, $^3J_{HP}$ = 8.9 Hz, 1 H, OCH_2), 7.32 (m, 6 H, Ph), 7.50 (m, 4 H, Ph). − ^{13}C NMR ($CDCl_3$): δ = 13.71 (d, $^2J_{CP}$ = 13.1 Hz, *C*H_3), 33.64 (s, *C*CH_3), 65.16 (d, $^2J_{CP}$ = 19.8 Hz, O*C*H_2), 128.7, 129.6, 133.7 (m, Ph). − ^{31}P NMR: δ = −9.2.

[RuCl{η^5:η^1-$C_5H_4CH_2CH(Me)PPh_2$}(PPh_3)] (racemic) (8): To a solution of (*S*)-$HOCH_2CH(Me)PPh_2$ (22.4 g, 92 mmol) was added 100 mL of a 1 M solution of BH_3 in THF at −30°C. After stirring for 1 h at room temperature the solvent was removed affording crude (*S*)-$HOCH_2CH(Me)PPh_2(BH_3)$ as a very viscous colorlous oil (23.3 g, ≈ 100%). − ^{1}H NMR: δ = 1.15 (dd, $^3J_{HH}$ = 7.0 Hz, $^3J_{HP}$ = 15.7 Hz, 3 H, CH_3), 2.82 (m, 1 H, C*H*CH_3), 3.6−3.8 (m, 2 H, OCH_2), 7.42 (m, 6 H, Ph), 7.73 (m, 4 H, Ph). − ^{13}C NMR ($CDCl_3$): δ = 11.88 (sbr, *C*H_3), 31.61 (d, $^1J_{CP}$ = 34.9 Hz, *C*CH_3), 63.17 (d, $^2J_{CP}$ = 6.6 Hz, O*C*H_2), 128.7, 131.3, 132.5 (m, Ph). − ^{31}P NMR: δ = 19.8. − A solution of the borane-adduct (6.85 g, 26.6 mmol) and Et_3N (6.0 mL, 43 mmol) in 80 mL of CH_2Cl_2 was cooled to −30°C upon which $MeSO_2Cl$ (3.0 mL, 39 mmol) was added. The thick suspension was stirred for a few hours at room temperature. Addition of water resulted in the formation of two clear layers. The CH_2Cl_2 layer was washed with water several times, then separated, dried over Na_2SO_4 and evaporated to dryness affording 8.77 g (26.1 mmol, ca 98%) of (*S*)-$MeSO_3CH_2CH(Me)PPh_3(BH_3)$ as a light-brown viscous oil. − ^{1}H NMR: δ = 1.20 (dd, $^3J_{HH}$ = 6.9 Hz, $^3J_{HP}$ = 15.4 Hz, 3 H, CCH_3), 2.84 (s, 3 H, SCH_3), 3.10 (m, 1 H, C*H*CH_3), 4.21 (ddd, $^2J_{HH}$ = 10.2 Hz, $^3J_{HH}$ = 6.8 Hz, $^3J_{HP}$ = 9.6 Hz, 1 H, OCH_2), 4.35 (ddd, $^2J_{HH}$ = 10.2 Hz, $^3J_{HH}$ = 4.7 Hz, $^3J_{HP}$ = 6.6 Hz, 1 H, OCH_2), 7.46 (m, 6 H, Ph), 7.65−7.85 (m, 4 H, Ph). − ^{13}C NMR ($CDCl_3$): δ = 11.79 (sbr, *C*H_3), 29.50 (d, $^1J_{CP}$ = 34.9 Hz, *C*CH_3), 37.26 (s, S*C*H_3), 70.24 (d, $^2J_{CP}$ = 11.8 Hz, O*C*H_2), 129.0, 131.7, 132.4 (m, Ph). − ^{31}P NMR: δ = 20.0. − A solution of CpLi was generated by adding 26 mL of a 1.61 M solution of *n*BuLi (42 mmol) in hexane to a solution of 3.5 mL (42 mmol) of freshly cracked CpH in 60 mL of THF with ice-cooling. Then, the above mentioned mesylate (26.1 mmol) was added at −20°C and the dark brown reaction mixture was stirred overnight at room temperature. Solvents were removed and the residue was extracted into CH_2Cl_2. Filtration and removal of solvent afforded 7.91 g of a dark brown oil, mainly containing (*S*)-$C_5H_5CH_2CH(Me)PPh_2(BH_3)$ as a mixture of two regioisomers. − ^{1}H NMR: δ = 1.06 (dd, $^3J_{HH}$ = 7.0 Hz, $^3J_{HP}$ = 16.4 Hz, 3 H, CH_3), 2.3−3.0 {m, C*H*CH_3, CCH_2, Cp(aliphatic), 5 H}, 6.01 (s), 6.17 (s), 6.23 (d, *J* = 5.4 Hz), 6.31−6.40 {m, Cp(olefinic), 3H in total}, 7.41 (m, 6 H, Ph), 7.74 (m, 4 H, Ph). − ^{13}C NMR: δ = 13.23/13.33 (sbr, *C*H_3), 28.03 (d, $^1J_{CP}$ = 36.0 Hz)/28.70 (d, $^1J_{CP}$ = 35.6 Hz, *C*CH_3), 30.56 (d, $^2J_{CP}$ = 3.7 Hz)/31.41 (d, $^2J_{CP}$ = 4.1 Hz, *C*H_2CP), 41.09/42.91 {Cp(aliphatic)}, 133.60/134.03 {Cp(olefinic CH)}, 143.58 (d, $^3J_{CP}$ = 13.6 Hz)/145.63 {d, $^3J_{CP}$ = 14.2 Hz, Cp(olefinic)}, other Cp signals hidden by Ph signals, 128.4 (m), 130.8 (m), 132.2 (m, all Ph). − ^{31}P NMR: δ = 24.8. − This oil was dissolved in 30 mL of degassed pyrrolidine and heated at 70−80°C for 30 min. After removal of solvent the residue was extracted with warm pentane (ca 150 mL in total), and filtered over Celite. Removal of solvent afforded 3.95 g (ca 13 mmol) of (*S*)-$C_5H_5CH_2CH(Me)PPh_2$ as a yellow oil. This material could not be distilled without decomposition and was therefore used without further purification. − ^{1}H NMR: δ = 0.99 (dd, $^3J_{HH}$ = 6.8 Hz, $^3J_{HP}$ = 15.0 Hz, 3 H, CH_3), 2.0−2.9 (m, C*H*CH_3, CCH_2, 3 H), 2.94 {s, Cp(aliphatic), 2 H}, 6.02 (s), 6.18 (s), 6.25 (d, *J* = 4.2 Hz),

6.40 {s, Cp(olefinic), 3H in total}, 7.32 (m, 6 H, Ph), 7.51 (m, 4 H, Ph). – ^{13}C NMR: δ = 16.16 (d, $^2J_{CP}$ = 16.3 Hz)/16.28 (d, $^2J_{CP}$ = 16.4 Hz, *C*H$_3$), 29.87 (d, $^2J_{CP}$ = 10.3 Hz)/30.67 (d, $^2J_{CP}$ = 10.3 Hz, *C*H$_2$CP), 33.59 (d, $^1J_{CP}$ = 19.0 Hz)/34.49 (d, $^1J_{CP}$ = 19.3 Hz, *C*CH$_3$), 41.26/43.48 {Cp(aliphatic)}, other Cp signals hidden by Ph signals, 128.3 (m), 128.7 (m), 133.6 (m, all Ph). – ^{31}P NMR: δ = −0.4. – A suspension of $RuCl_2(PPh_3)_3$ (3.1 g, 3.2 mmol) and 1.83 g of the above oil in 50 mL of degassed ethanol was refluxed overnight. Then, ethanol was replaced by toluene and the mixture was heated to reflux for another few hours. Workup by chromatography (see above) afforded 0.68 g {1.0 mmol, 8% based on $HOCH_2CH(Me)PPh_3$} of racemic [RuCl{η^5:η^1-$C_5H_4CH_2CH(Me)PPh_2$}(PPh_3)] as a 77:23 mixture of diastereomers (NMR) as an orange powder. – $C_{38}H_{35}ClP_2Ru$ (689.6): calcd. C 66.1, H 5.1; found C 64.3, H 5.3. – MS; *m*/*z*(%): 690 (30) [M$^+$], 428 (100) [M$^+$ – PPh_3], 393 (100), [M$^+$ – Cl – PPh_3], 315 (5) [M$^+$ – Cl – PPh_3 – Ph].

Determination of the Enantiopurity of [RuCl{η^5:η^1-C_5H_4-$CH_2CH(Me)PPh_2$}(PPh_3)]. Formation of {Ru[η^5:η^1-$C_5H_4CH_2CH$-$(Me)PPh_2$][(***S*****)-H$_2$**NCH(Me)Ph](PPh_3)}{O_3SCF_3} (9): A solution of **8** (0.10 g, 0.14 mmol) in 2.0 mL of dry $CDCl_3$ was treated with AgO_3SCF_3 (0.04 g, 0.16 mmol) and (*S*)-$H_2NCH(Me)Ph$ (0.12 g, 1 mmol). After stirring for 30 min the silver salts were removed by filtration and the resulting yellow-green solution was analyzed by NMR spectroscopy. The salt **9** is present as a 38:38:12:12 mixture of isomers and is therefore completely racemic.

[RuCl{η^5:η^1-$C_5H_4CH_2CH(Me)PPh_2$}(PPh_3)] (*S* enriched) (8): A mixture of (*S*)-$HOCH_2CH(Me)PPh_2$ (*S*/R ≈ 80:20, see above, 6.0 g, 24.7 mmol) and Et_3NHCl (6.3 g, 46 mmol) in 150 mL of degassed acetonitrile was cooled to −30°C, upon which PCl_3 (4.0 mL, 46 mmol) was added. The resulting bright yellow suspension was stirred for 2 days at 50−60°C. Solvent was removed in vacuo and CH_2Cl_2 and degassed water were added. The CH_2Cl_2 layer was washed with water, filtered and dried over $CaCl_2$. Filtration and removal of solvent afforded 6.24 g of an oily substance mainly containing (*S*)-$ClCH_2CH(Me)PPh_2$ (up to 30% of $Ph_2P(O)H$ may be present due to the partial formation of Ph_2PCl during the chlorination procedure and subsequent hydrolysis). – ^{1}H NMR: δ = 1.18 (dd, $^3J_{HH}$ = 6.8 Hz, $^3J_{HP}$ = 14.6 Hz, 3 H, C*H*$_3$), 2.69 (m, 1 H, C*H*CH$_3$), 3.32 (ddd, $^2J_{HH}$ = 10.4 Hz, $^3J_{HH}$ = 3.1 Hz, $^3J_{HP}$ = 10.4 Hz, 1 H, OC*H*$_2$), 3.68 (ddd, $^2J_{HH}$ = 10.4 Hz, $^3J_{HH}$ = 4.6 Hz, $^3J_{HP}$ = 8.9 Hz, 1 H, OC*H*$_2$), 7.32 (m, 6 H, Ph), 7.50 (m, 4 H, Ph). – ^{13}C NMR ($CDCl_3$): δ = 15.09 (d, $^2J_{CP}$ = 16.2 Hz, *C*H$_3$), 33.72 (d, $^1J_{CP}$ = 13.8 Hz, *C*CH$_3$), 49.07 (d, $^2J_{CP}$ = 26.9 Hz, O*C*H$_2$), 128.8, 130.6, 132.5 (m, Ph). – ^{31}P NMR: δ = −5.1. – This oil was added to a solution of CpLi generated from mixing 21 mL of a 1.61 M solution of *n*BuLi (34 mmol) in hexane and a solution of 3.0 mL (36 mmol) of CpH in 50 mL of THF. This mixture was refluxed for 2 days. Then, 1 mL of water was added and the mixture was evaporated to dyness. Extraction with pentane afforded 2.17 g (ca 7 mmol) of (*S*)-$C_5H_5CH_2CH(Me)PPh_2$ as a yellow oil. Reaction with $RuCl_2(PPh_3)_3$ (3.3 g, 3.4 mmol) and workup as described above afforded 1.17 g of **8** {1.7 mmol, 8% based on $HOCH_2CH(Me)PPh_2$}. The reaction with AgO_3SCF_3 and (*S*)-$H_2NCH(Me)Ph$ (vide supra) afforded a 64:13:19:4 mixture of isomers of **9** and therefore the enantiomeric excess of the Cp-Ligand was 66% (64 + 19−13−4; *S*/*R* = 83:17) which is an agreement with the estimated enantiopurity of the starting product $HOCH_2CH(Me)PPh_2$ of 60% (vide supra).

X-ray Structure Determination of *rac*, *trans*-8: Orange crystals suitable for an X-ray diffraction study were grown within a few days from a saturated ether solution at room temperature. There were two crystal forms. Crystallographic and experimental details are summarized in Table 3. No absorption corrections were made. The structures were solved by direct methods (SHELXS-86)[20a] and refined by full-matrix least squares against F^2 (SHELXL-97).[20b] All non-hydrogen atoms were refined anisotropically, hydrogen atoms isotropically. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-117007 (triclinic *rac, trans*-**8**) and 117006 (monoclinic *rac, trans*-**8**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ {fax: (internat.) + 44-1223/336-033, E-mail: deposit@ccdc.cam.ac.uk}.

Reaction of Racemic 8 with NaBr: A solution of **8** (0.08 g, 0.12 mmol) in 1.0 mL of dry $CDCl_3$ was treated with NaBr (0.10 g, 1.0 mmol) of and stirred at room temperature. The reaction was monitored by NMR spectroscopy. After 1 week the reaction was complete. The solution was filtered and evaporated to dryness affording orange-brown RuBr[η^5:η^1-$C_5H_4CH_2CH(Me)PPh_2$](PPh_3) (**11**) as a 76:24 mixture of diastereomers. MS; *m*/*z*(%): 736 (20) [M$^+$], 474 (90) [M$^+$ – PPh_3], 393 (100), [M$^+$ – Br – PPh_3], 315 (5) [M$^+$ – Br – PPh_3 – Ph].

Reaction of Racemic 8 with NaI: The reaction with NaI was performed analogously. The reaction was complete after about 2 weeks. The brown RuI[η^5:η^1-$C_5H_4CH_2CH(Me)PPh_2$](PPh_3) (**12**) was obtained as a 73:27 mixture of diastereomers. MS; *m*/*z*(%): 782 (20) [M$^+$], 520 (100) [M$^+$ – PPh_3], 393 (95), [M$^+$ – I – PPh_3], 315 (5) [M$^+$ – I – PPh_3 – Ph]. Neither the rate of the reaction nor the product formation was changed when the reaction was conducted in the presence of 3 equiv. of added PPh_3 per Ru (NMR monitoring).

Catalysis. Diels−Alder reaction: To a solution of *S*-enriched **8** (0.08 g, 13 μmol) in 10 mL of CH_2Cl_2 was added an excess of AgO_3SCF_3 (0.18 g). After stirring for 10 min the resulting red-brown suspension was filtered over Celite and cooled to −60°C. Then, *i*Pr_2NEt (9 μL, 50 μmol), cyclopentadiene (1.8 mL, 22 mmol) and methacrolein (1.0 mL, 12.2 mmol) were added. The clear yellow solution was stirred at −4°C. Samples were taken regularly over a period of a few days. They were quenched by flash chromatography over silica gel. Volatiles were removed in vacuo (without heating) and the residue was analyzed by ^{1}H NMR spectroscopy. The Diels−Alder product 2-formyl-2-methyl-bicyclo[2.2.1]hept-5-ene could not be found;[5b] instead the gradual formation of dicyclopentadiene was observed.

Supporting Information: ^{1}H, ^{13}C and ^{31}P NMR spectroscopic data for **3** and **4**. A drawing of the assignment of the ^{1}H and ^{13}C NMR spectroscopic data of **8**.

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[21] *Cis* or *trans* in these compounds refers to the relative positions of the substituents on the two stereogenic centers; at the chiral carbon center Me has higher priority than H and on ruthenium Cl has higher priority than PPh_3. Priority sequence around ruthenium is $C_5H_4R > Cl > PPh_3 > Ph_2PR$.

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