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Enantiopure Ruthenocenes Cp*Ru(1,2-$C_5H_3R^1R^2$) with a Planar Chiral Cyclopentadienyl Ligand and a Pentamethylcyclopentadienyl Spectator Ligand[‡]

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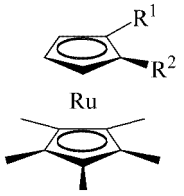
Keywords: Ruthenium / Ruthenocene / Sandwich complexes / Planar chirality / (*S*)-2-(methoxymethyl)pyrrolidine

Kreutzberger's synthesis was used to produce 6-(morpholino)-fulvene (**7a**) from 1,3,5-triazine, cyclopentadiene and morpholine (94 %). Likewise with (*S*)-2-(methoxymethyl)pyrrolidine (HSMP) the 6-[(*S*)-2-(methoxymethyl)pyrrolidino] analogue **7b** was obtained (62 %). Hydride addition from $NaBHEt_3$ in toluene afforded the cyclopentadienides $Na[C_5H_4CH_2–N(C_2H_4)_2O]$ (**8a**) (83 %) and $Na(C_5H_4CH_2–SMP)$ (**8b**) (90 %). Cp*Ru($C_5H_4CH_2$–SMP) (**5**) was synthesized from $[Cp^*RuCl]_4$ and **8b** (84 % yield). The related methyleneiminium salt $[Cp^*Ru(C_5H_4CH{=}SMP)]PF_6$ (**9**) was made from $[Cp^*Ru(MeCN)_3]PF_6$ and **7b** and could be transformed into **5** by hydride addition from $LiAlH_4$ in THF. Diastereoselective lithiation of **5** with Li*s*Bu in Et_2O/cyclohexane and subsequent quenching with electrophiles E–X gave enantiomerically pure (*de* > 98 %), 1,2-disubstituted complexes Cp*Ru(E–$C_5H_3CH_2$–SMP) **10a–i** with E = F, Cl, Br, I, Me, CD_3, $SiMe_3$, PPh_2, $Au(PPh_3)$ as oils. The chiral auxiliary was removed from **10a**, **b**, and **f** by quaternization with MeI and subsequent reductive cleavage with $LiAlH_4$ in THF to afford the exclusively planar chiral complexes Cp*Ru(1-E-2-MeC_5H_3) **14a** (E = F), **14b** (E = Cl), and **14f** (E = CD_3). The complexes **14a**,**b**,**f** no longer possess central chirality. The crystal structure of **12**, a LiI adduct of **10f**, gave the absolute configuration via internal reference to the (*S*)-stereochemistry of the SMP group. The absolute configuration of the planar chiral complex **14b** was determined from the anomalous X-ray dispersion of the crystals of **14b**.

Introduction

In this paper we describe a synthetic route to ruthenocenes Cp*Ru(1,2-$C_5H_3R^1R^2$) (**1**) that have a planar chiral cyclopentadienyl ligand and a pentamethylcyclopentadienyl (Cp*) spectator ligand, but do not possess any further element of chirality in the substituents R^1 and R^2.



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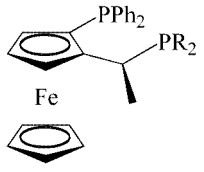
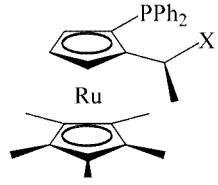
Planar chiral ferrocenes[2,3] have found application as excellent chiral ligands in homogeneous asymmetric catalysis. For instance, the industrial production of (+)-biotine makes use of the chiral ferrocene-based ligand **2**,[4,5] and the herbicide (*S*)-metolachlor® is produced with the help of the closely related ligand **3**.[5,6] The quest for chiral ligands which are optimized for specific catalytic processes has led to the development of a large family of chiral pentamethylferrocenes[5b] and a group of similar chiral pentamethylruthenocenes;[7] the complexes Cp*Ru[1,2-C_5H_3(PPh_2)-(CHXMe)] (**4**) (X = e.g. NMe_2, PCy_2) may serve as examples.[7b] All these complexes are deceptively similar to ruthenocenes of type **1**; however, they possess a center of chirality in one of the sidechains as the distinguishing feature.



2, R = *t*Bu

3, R = 3,5-$Me_2C_6H_3$



4, X = NMe_2, PCy_2

Although the chemistry of the ruthenocenes is much less developed than that of the ferrocenes a number of planar chiral and enantiopure ruthenocenes are known. There are essentially three methods to produce such complexes. i) The first planar chiral, more or less enantiopure ruthenocenes

[‡] This work is part of a dissertation.[1]

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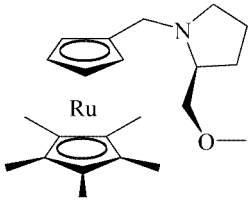
were made by the group of K. Schlögl using the classical method of resolution of racemates.[8] Chiral HPLC has also been used as a modern and efficient resolution method.[9] ii) The second method is the diastereoselective *ortho*-metalation, discovered by I. Ugi et al. as highly stereoselective derivatization reactions of the two [(1-dimethylamino)ethyl]-ferrocene – or (1-ferrocenylethyl)dimethylamine – enantiomers.[10] In this way T. Hayashi et al. synthesized the ruthenocene derivatives $Ru(C_5H_4PPh_2)[C_5H_4(PPh_2)\{CHR(NMe_2)\}]$ (R = Me, Et),[11] and A. Togni et al. synthesized the pentamethylruthenocenes **4**.[7b] iii) Finally, as U. Koelle et al. demonstrated more recently, enantioselective reaction of planar chiral cyclopentadienides with suitable chiral sources of the Cp^*Ru^+ fragment may also give chiral, enantiomerically enriched pentamethylruthenocene derivatives.[12]

We now return to the goal of this work, the development of a synthetic route to complexes of type **1**. We decided to use the method of diastereoselective *ortho*-metalation with the (*S*)-2-(methoxymethyl)pyrrolidino (≡ SMP) group as *ortho*-directing chiral auxiliary. Ruthenium was preferred to iron because ruthenocenes are more robust than ferrocenes. Thus, the synthesis of complex **5** assumes a central role in this work. It seemed reasonable and most promising, to introduce the Cp*Ru group as late as possible, for instance by treating $[Cp^*RuCl]_4$[13] with a salt of the (as yet unknown) chiral cyclopentadienide $\mathbf{6}^-$. Once complex **5** was available, we studied the *ortho*-metalation of **5** and the subsequent quenching with electrophiles, and finally the removal of the chiral auxiliary.



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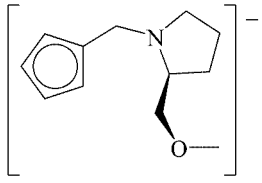
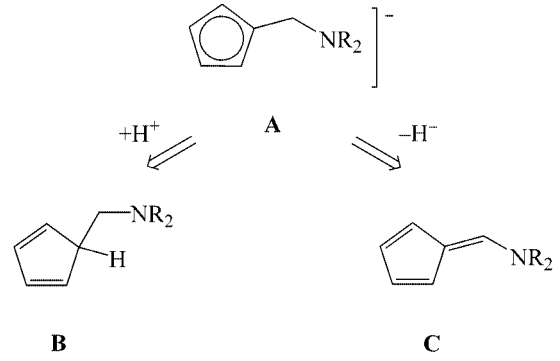


$\mathbf{6}^-$

Results and Discussion

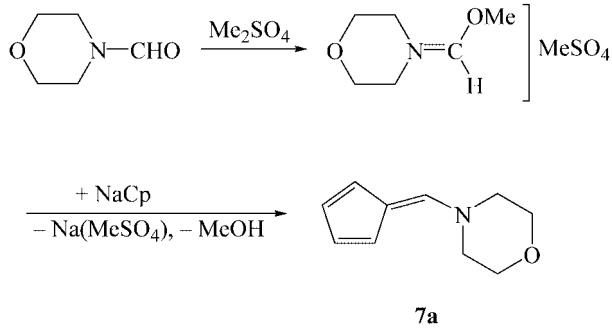
Ligand Precursors

From a retrosynthetic point of view [(dialkylamino)-methyl]cyclopentadienides **A** (such as $\mathbf{6}^-$) are related to [(dialkylamino)methyl]cyclopentadienes **B** (via formal proton addition) and alternatively to 6-(dialkylamino)fulvenes **C** (via formal hydride abstraction)[14] (Scheme 1). The constitution of the cyclopentadienes **B** is reminiscent of products of Mannich condensation reactions. Experimentally, Mannich condensations with cyclopentadienes are stricken with low chemoselectivity. In favorable situations fulvenes are obtained,[15] and under some more special conditions Diels–Alder products are formed.[16] The alternative to use 6-(dialkylamino)fulvenes **C** seemed more promising. Especially the 6-(dimethylamino) derivative $C_5H_4{=}CH(NMe_2)$ is a well known compound which may undergo hydride addition from $LiAlH_4$ to form the corresponding cyclopentadienide.[17]



Scheme 1.

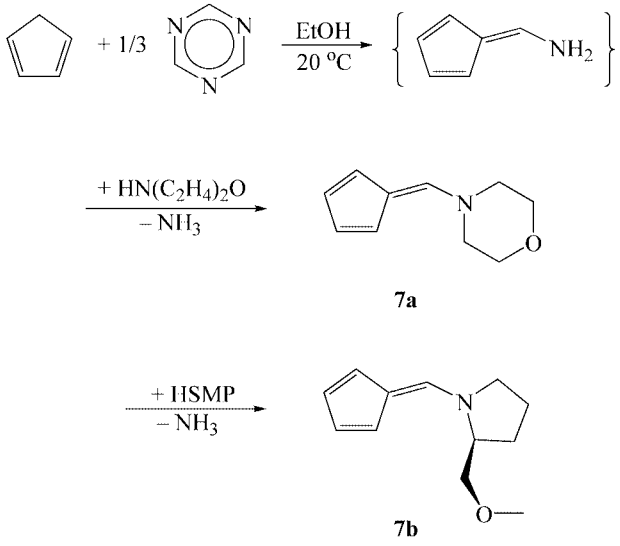
We first consider the syntheses of 6-(dialkylamino)fulvenes **C**. The 6-morpholino compound **7a** served as a testing ground. There are essentially three fulvene syntheses: the historical Thiele synthesis,[18] Hafner's synthesis of 6-(dimethylamino)fulvene,[19] and Kreutzberger's synthesis.[20] An attempt to apply Thiele's synthesis, i.e. the direct base-catalyzed condensation of cyclopentadiene with a carbonyl compound,[18a] to formylmorpholide, using an improved procedure,[18b] failed altogether; the dominating process was the dimerization of cyclopentadiene. Hafner's more forcing synthesis (Scheme 2) produced the desired 6-(morpholino) derivative **7a**, but the yield dropped from the 74% obtained for the 6-(dimethylamino)fulvene[19] to unsatisfactory 16% for **7a**. Kreutzberger's method[20] (Scheme 3) uses 1,3,5-triazine[21] as a synthon for formamide and presumably produces 6-aminofulvene as the primary product; this then undergoes nucleophilic substitution[22] of the amino group with morpholine and gave 6-(morpholino)fulvene **7a** as golden-brownish, analytically pure microcrystals in near quantitative isolated yield (94%). Compound **7a** has been mentioned in the literature, but has not been described in any detail.[23]



7a

Scheme 2.

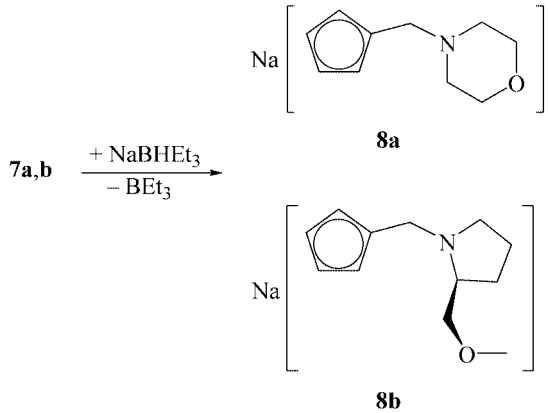
Our observations suggest that Kreutzberger's synthesis should be the best option for the preparation of the (*S*)-2-(methoxymethyl)pyrrolidino analogue **7b**. When it was applied to (*S*)-2-(methoxymethyl)pyrrolidine (HSMP),[24] **7b**



Scheme 3.

was obtained as a yellow to red, analytically pure oil in good yield (62%).

The second task was the hydride addition to the 6-aminofulvenes **7a**,**b** which turned out to be more difficult than in the case of 6-(dimethylamino)fulvene.[17] The reaction of **7b** with $LiAlH_4$ in THF mainly produced LiC_5H_4Me, indicating an undesired substitution of the amide group with a hydride. We found, however, that the milder reagent $NaBHEt_3$ in toluene effected a smooth addition of hydride (Scheme 4). In the case of **7a** the reaction was fast at 0 °C and markedly exothermic. The triethylborane also formed was in part bonded to the nitrogen of the morpholine ring; it was removed by washing the raw product with diethyl ether to give the salt $Na[C_5H_4CH_2–N(C_2H_4)_2O]$ (**8a**) in high yield (83%), but still contaminated with small amounts of BEt_3 (^1H and ^{11}B NMR). The analogous reaction in the SMP series gave $Na(C_5H_4CH_2–SMP)$ (**8b**), again in high yield (90%), but at a much lower rate at ambient temperature. Both salts are highly air-sensitive.



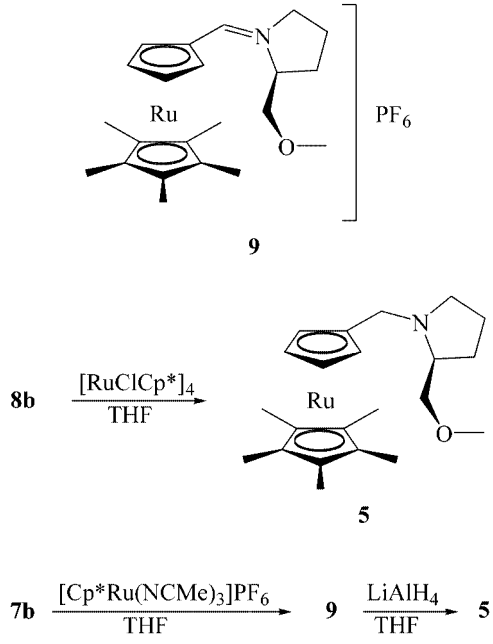
Scheme 4.

The cyclopentadienides **8a**,**b** show surprisingly low solubilities, and only strong donor solvents such as DMF and DMSO give moderately concentrated solutions which tend to decompose at ambient temperature within hours to days. Only solutions in liquid ammonia did not show decomposition, even after several days. Functionalized cyclopentadienides with N- and/or O-donor centers often have the structure of a coordination polymer.[25] This could well be the cause of the observed low solubilities of **8a**,**b**.

Pentamethylruthenocenes with a SMP-Methyl Side Chain

The Starting Material 5

Complex **5** was synthesized from $[Cp^*RuCl]_4$[13] and the sodium cyclopentadienide **8b** in THF (Scheme 5). It is a golden yellow, chemically and thermally robust oil which could not be crystallized. Complex **5** can also be made by a two-step procedure. In the first step a slight excess of the fulvene **7b** is treated with $[Cp^*Ru(MeCN)_3]PF_6$[26] to produce the (ruthenocenylmethylene)iminium salt **9** (Scheme 5). An excess of **7b** can be removed by recrystallization of the material **9** from acetone/ether or from THF/ether. In the second step hydride addition from $LiAlH_4$ in THF smoothly transforms complex **9** into the desired complex **5**. This alternative has not been optimized.



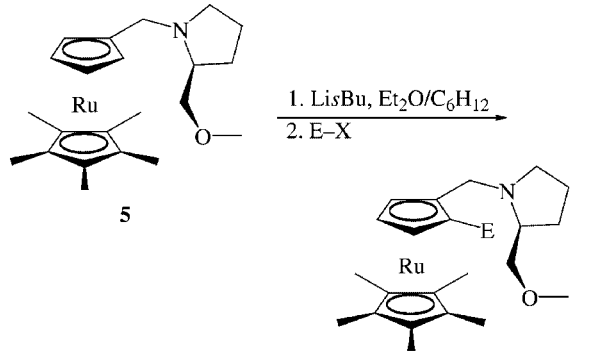
Scheme 5.

Lithiation and Derivatization of 5

We now turn to the diastereoselective lithiation of **5**. Lithiations of ruthenocenes are known to be faster and less selective than those of ferrocenes and may give rise to homo- and heteroannular di- and even trilithiations.[8a,27] In the case of **5** the presence of the Cp* ligand greatly reduces the resulting problems.

All lithiation reactions were conducted under standardized conditions. Complex **5** was used as 0.1 M solution in diethyl ether at –78 °C and the lithiations were performed with titrated[28] ca. 1.5 M Li*s*Bu solutions in cyclohexane

at –78 °C, usually in a 1:1.7 ratio. After mixing the reagents the reaction mixture was stirred at –78 °C for 3.5 h. A quenching reagent E–X was then added at –78 °C and the mixture was warmed to ambient temperature (Scheme 6). All products Cp*Ru[1-E-2-(SMP–CH_2)C_5H_3] **10a**–**i** are very pale yellow, almost colorless oils. They were analyzed mainly with the help of ^{1}H NMR spectroscopy (500 MHz). In no case could we detect a second diastereomer; hence the diastereomeric excess should be better than 98%. In all cases an admixture of starting material was present as impurity; for more details see below and Experimental Section.



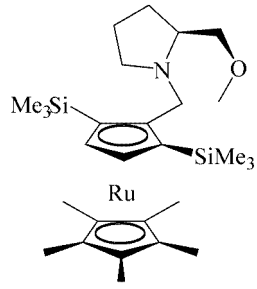
	a	b	c	d	e	f	g	h	i
E =	F	Cl	Br	I	Me	CD_3	SiMe3	PPh2	Au(PPh3)

Scheme 6.

The stereochemistry of complexes **1** may be specified in one of two ways:[29] either by specifying the *planar* chirality of the $C_5H_3R^1R^2$ ring as originally proposed by Schlögl,[30] or by specifying the *central* chirality of the ring carbon bearing the highest ranking substituent with the help of the CIP rules.[31] As we shall prove below, the SMP–CH_2 group of the complexes **10a**–**i** has the role of R^1 in the illustration of complex **1**, and E occupies the position of R^2. For most substituents E we have therefore (S_P)-stereochemistry for the planar chirality;[32] only the low-ranking groups Me and CD_3 of **10e**,**f** leave the higher priority to the SMP–CH_2 group thus implying (R_P)-stereochemistry.

A few details concerning specific cases should be mentioned here. The fluororuthenocene **10a** was obtained by electrophilic fluorination[33] with *N*-fluoro-*N*,*N*-bis(benzenesulfonyl)imide.[34] The higher homologues **10b**, **10c**, and **10d** were obtained with C_2Cl_6, 1,2-$C_2H_4Br_2$, and 1,2-$C_2H_4I_2$, respectively, as source of the halogen. The iodo compound **10d** seems to form an adduct with LiI (cf. below compound **12**), but an aqueous workup step smoothly removed the coordinated LiI. Iodomethane was used to synthesize **10e** and likewise CD_3I gave **10f**, using again an aqueous workup procedure. In the case of **10b** the metalation conditions were varied with the aim to find out the optimum procedure. It was found that temperatures below –78 °C (without change of other parameters) resulted in incomplete lithiation and a higher admixture of starting material **5** in the product. On the other hand, when the lithiation mixture was warmed up to 40 °C and then was cooled again to –78 °C before the addition of the quenching reagent, the admixture of **5** in the product was no longer seen.

The remaining examples are more complex. Quenching with $SiClMe_3$ under the usual conditions gave **10g** and in addition a doubly silylated product **11** in a 3:1 ratio. This by-product could largely be suppressed if the temperature of the quenching mixture was increased more slowly (for instance in 14 h vs. the usual 1.5 h) from –78 °C to ambient temperature. This observation suggests that a transmetalation step is coming into play in this system. In the cases **10h**,**i** byproducts (inter alia P*s*BuPh$_2$[35] in the case of **10h** and *s*BuAu(PPh$_3$)[36] in the case of **10i**) formed from the excess of Li*s*Bu, which were difficult to remove; their formation can be suppressed if the lithiation reagent is used in near equivalent quantity, but then the metalation remains incomplete and the product becomes contaminated by larger admixtures (up to 25%) of starting material **5**. These difficulties were aggravated by the fact that none of the products **10a**–**i** could be crystallized.



11

First Proof of the Product Stereochemistry: the Structure of the LiI Adduct [10f(LiI)]$_2$

Quite serendipitously we obtained crystals of a lithium iodide adduct [**10f**(LiI)]$_2$ (≡ **12**), when we intended to synthesize **10f** and used a non-aqueous workup procedure. This

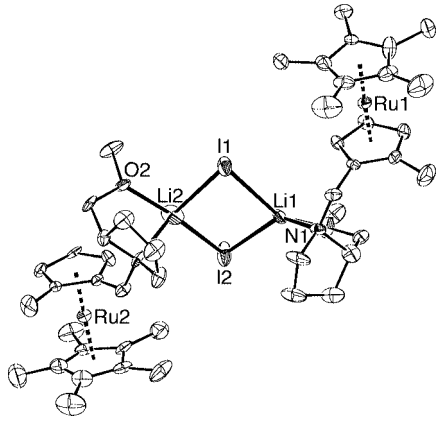


Figure 1. Molecular structure of the LiI adduct **12** (PLATON plot[38] at the 30% probability level). Selected distances [Å]: Ru1–Cp 2.147(13), Ru2–Cp 2.167(12), Ru1–Cp* 2.157(14), Ru2–Cp* 2.138(15).

allowed us to determine the stereochemistry of the directed *ortho*-lithiation of **5** via *internal reference* to the (*S*)-stereochemistry of the chiral auxiliary group SMP. Compound **12** crystallizes in the monoclinic, noncentrosymmetric space group $P2_1$. The crystal consists of dinuclear molecules. Inspection of Figure 1 shows that the planar chiral cyclopentadienyl rings in **12** are coordinated to the Ru atom with (R_P)-stereochemistry.[37]

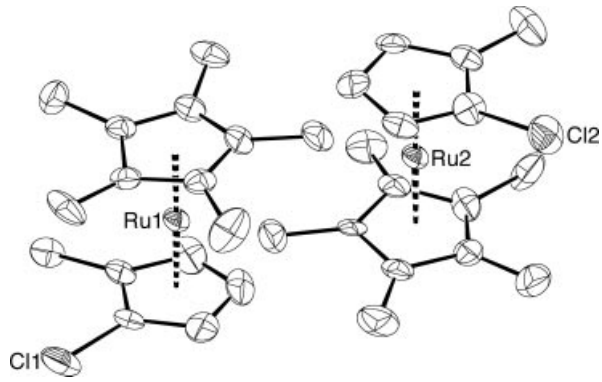
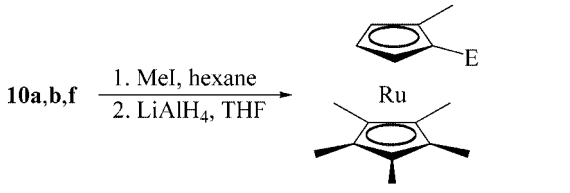


Figure 2. Structure of (S_P)-Cp*Ru(1-Cl-2-MeC_5H_3) (**14b**) (PLATON plot[38] at the 50% probability level). Selected distances [Å]: Ru1–Cp 2.184(12), Ru2–Cp 2.174(12), Ru1–Cp* 2.180(11), Ru2–Cp* 2.165(11), Cl1–C11 1.767(12), Cl2–C31 1.748(11).

Planar Chiral Pentamethylruthenocenes

The removal of the chiral auxiliary group SMP is the next step in our strategy. We give three examples, the replacement of the SMP group in **10a**, **b** and **f** with hydride (Scheme 7). This replacement is achieved in a two-step reaction sequence. In the first step iodomethane was added to give ammonium iodides **13a**,**b**,**f** which were mixtures of diastereomers. As these compounds are of no interest by themselves we give only a minimal description in the Experimental Section. Early in ferrocene chemistry it was found that the NMe_3 group of [CpFe($C_5H_4CH_2NMe_3$)]I is readily amenable to nucleophilic substitution reactions, for instance with CN^- ion.[39] In this vein the tertiary amine moiety *N*-Me–SMP in **13a**,**b**,**f** could readily be substituted with hydride from $LiAlH_4$ in THF. Thus we obtained the planar chiral ruthenocenes Cp*Ru(1-E-2-MeC_5H_3) **14a** (E = F), **14b** (E = Cl), and **14f** (E = CD_3) as enantiomerically pure, crystalline compounds in high yields. It should be emphasized that these complexes possess the planar chirality of the 1,2-disubstituted cyclopentadienyl ring as the sole element of chirality.



14a, E = F; **14b**, E = Cl; **14f**, E = CD_3

Scheme 7.

Second Proof of the Product Stereochemistry: the Structure of the 1-Cl-2-Me Derivative 14b

The structure of **14b** was determined with the aim to confirm the assigned absolute configuration of the planar chiral ruthenocenes **14a**,**b**,**f** by measuring the anomalous dispersion of the X-ray radiation. Complex **14b** crystallizes in the triclinic space group *P*1 with two independent molecules in the unit cell.[37] The pseudocentrosymmetric arrangement of these molecules (Figure 2) is understandable in view of the roughly similar space filling requirements for a Cl atom and Me substituents.[40] The absolute configuration was found to be the (S_P)-configuration in agreement with the result from the structure determination for **12**.

It could be argued that picking a single crystal from a crystalline sample is unsafe: a crystal of the nonrepresentative stereoisomer might unfortunately be chosen. In the present work this is a most unlikely scenario. In the case of the complexes **10a**–**i** we have never observed any indication for the presence of the alternative stereoisomer. As we have two independent determinations of the configuration the unlikely unfortunate choice would have to have occurred twice. And last not least, in the case of **14b** it would be required that the two enantiomers do form a conglomerate. The very nature of the pseudocentrosymmetric structure of **14b** renders the possibility of conglomerate formation for **14b**/***ent*-14b** unlikely. We would rather expect the formation of racemic crystals or of a solid solution.

Concluding Remarks

In this paper we have established a synthetic route to enantiomerically pure ruthenocenes with a pentamethylcyclopentadienyl spectator ligand and with exclusively planar chirality. The absolute configuration of the metalation product has been determined by two independent methods. As may be seen from the experimental details the choice of the SMP group as a chiral auxiliary was not a very fortunate one, as all complexes **10a**–**i** were oils which did not show any tendency to crystallize. This was a severe disadvantage practically, and might be due to the fact that the SMP group is a five-membered saturated ring. Rings of this type are mechanically soft, and the pending methoxymethyl group adds further conformational flexibility. A six-membered ring as chiral auxiliary might be more recommendable.

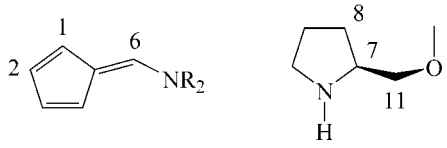
It should be noted that complex **5** could also be used to synthesize bidentate chiral ligands which would potentially be useful as chiral ligands in homogeneous catalysis. The first coordinating sidearm could be introduced as in the synthesis of the phosphanyl derivative **10h** which in itself is already a potentially useful, bidentate *N*,*P* ligand. Furthermore, the SMP group can not only be replaced with hydride (as in this work), but also with other nucleophiles such as

amino or phosphanyl functionalities which would again provide a second coordinating site.

In earlier work we had used achiral (pentamethylcyclopentadienyl)ruthenium sandwich complexes to show that certain ring-ligand transfer reactions take place via triple-decker intermediates.[41] If enantiomerically pure, planar chiral pentamethylruthenocenes were used in such studies, they would give additional, specific and stringent insights into the mechanism and the stereochemistry of ring-ligand transfer reactions. We do, however, not have the means to elaborate these ideas any further.

Experimental Section

General Remarks: All manipulations were carried out under nitrogen or argon using standard Schlenk techniques. 'Vacuum' corresponds to ca. 10^{-6} bar, unless stated otherwise. Solvents were dried by conventional methods,[42] freed from oxygen and stored under nitrogen. Alumina (ICN Alumina N, activity 1), kieselguhr (Merck), silica gel (Merck, Kieselgel 60, 0.063–0.200 mm), molecular sieves (Merck, 4 Å), and seasand were freed from oxygen and water by heating in a vacuum (10^{-6} bar) to 300 °C for 24 h and then stored under nitrogen. Alumina was deactivated before use by controlled addition of water (5%, degassed). IR spectra were recorded on a Nicolet Avatar 360 FT IR spectrometer using NaCl cuvettes with PTFE stoppers. Mass spectra were recorded on a Finnigan MAT 95 (EI, CI, SIMS) or on a Nermag R10/10 spectrometer (DCI). NMR spectra were measured on a Varian VXR 500 Unity (^{1}H, 500.0 MHz; ^{7}Li, 194.2 MHz; ^{11}B, 160.3 MHz; ^{13}C, 125.6 MHz; ^{19}F, 470.1 MHz; ^{29}Si, 99.3 MHz; ^{31}P, 202.3 MHz) in most cases. Chemical shifts are given in ppm; they were referenced to TMS for ^{1}H and ^{13}C. ^{2}H NMR spectra were measured using the deuterated solvent as internal reference; since $\delta(^1H)$ of the natural solvent is equal to $\delta(^2H)$ of the deuterated solvent,[43] the chemical shift of the natural solvent could be taken as reference value. Assignments were based on APT spectra, 2D experiments (COSY, HETCOR, HMQC, HMBC), and on ^{1}H{^{1}H} NOE difference spectra. In the documentation of the NMR spectra the numbering follows the chemical numbering Scheme in most instances; for fulvenes the traditional numbering is used and for the pyrrolidine ring of SMP arbitrary numbers are defined as shown below.



Synthesis of 6-Morpholinofulvene (7a) – Method A: a) (Methoxy)-morpholinocarbenium methyl sulfate: *N*-Formylmorpholide (11.35 g, 98.6 mmol) was placed in a 50 mL three-necked flask equipped with a dropping funnel and a reflux condenser. Dimethyl sulfate (12.44 g, 98.6 mmol) was added dropwise with stirring at 55 °C. Stirring was continued at 75 °C for 2 h, and the reaction mixture turned dark brown and became rather viscous. b) **7a**: A 100-mL three-necked flask equipped with a dropping funnel and a reflux condenser was charged with NaCp (98.6 mmol) in THF (70 mL) and cooled to –10 °C. The carbenium methyl sulfate was then added with stirring at such a rate that the temperature did not rise above –5 °C. The mixture was then warmed up to ambient temperature overnight. Pentane (40 mL) was added. The solid material was filtered off and washed with CH_2Cl_2 and pentane until the filtrate was nearly colorless. The volatiles were removed from the collected filtrates in a vacuum, and the resulting dark residue was crystallized from EtOH/H_2O (1:1) or from hexane to afford **7a** (2.59 g, 16%) as air-stable, orange-yellow platelets; m.p. 75 °C; highly soluble in polar organic solvents, soluble in toluene, moderately soluble in cold hexane, insoluble in water. $C_{10}H_{13}NO$ (163.2): calcd. C 73.59, H 8.03, N 8.58; found C 73.77, H 8.03, N 8.44. MS (EI): *m*/*z* (%) = 163 (100) [M^+, $C_{10}H_{13}NO^+$], 79 (44) [$C_6H_7^+$], 58 (97) [$C_2H_4NO^+$]. ^{1}H NMR (500 MHz, [D$_6$]DMSO, 25 °C): δ = 3.37 (br., $\nu_{1/2}$ = 14 Hz, 2 CH_2N, gives rise to a multiplet at 90 °C), 3.69 (m, 2 CH_2O), 6.03 (m, 2-H), 6.24 (m, 1-H), 6.28 (m, 3-H), 6.44 (dt, 4-H), 7.28 (br. s, 6-H), coupling constants from simulation: $^3J_{12}$ = 4.50, $^4J_{13}$ = 1.88, $^4J_{14}$ = 2.15, $^4J_{16}$ = 0.15, $^3J_{23}$ = 2.51, $^4J_{24}$ = 1.39, $^5J_{26}$ = 0.25, $^3J_{34}$ = 4.77, $^5J_{36}$ = 0.88, $^4J_{46}$ = 0.42 Hz; the line-broadening of the signals for 6-H, CH_2N and CH_2O is caused by hindered rotation around the bond N–C-6. ^{13}C{^{1}H} NMR (125.6 MHz, [D$_6$]DMSO, 25 °C): δ = 147.94 (C-6), 125.40 (C-1), 124.47 (C-3), 118.13 (C-2), 115.50 (C-5), 113.65 (C-4), 65.76 (CH_2O, $\nu_{1/2}$ = 17 Hz; $\nu_{1/2}$ = 0.8 Hz at 90 °C), 49.64 (CH_2N, $\nu_{1/2}$ = 215 Hz; $\nu_{1/2}$ = 4.9 Hz at 90 °C). For NMR spectroscopic data in C_6D_6 and CD_2Cl_2 see ref.[1].

Synthesis of 6-Morpholinofulvene (7a) – Method B: A Schlenk flask equipped with a gas outlet was charged with freshly distilled cyclopentadiene (6.61 g, 100 mmol), morpholine (17.4 g, 200 mmol), and ethanol (absolute, 10 mL). Solid 1,3,5-triazine[21] (3.24 g, 40.0 mmol) was then added with efficient stirring at 0 °C, and stirring was continued at ambient temperature for 24 h. A yellow, glistening suspension formed. Water was added to complete the precipitation of the product. The solid was collected on a frit, washed several times with water (a total of 300 mL), and dried in a high vacuum for 12 h, to give **7a** (15.3 g, 94%) as a golden-brownish, analytically pure [elemental analysis (CHN), NMR] microcrystalline powder; m.p. 77 °C, other data as above.

6-[(*S*)-2-(Methoxymethyl)pyrrolidino]fulvene (7b): As described above for **7a** the reaction of cyclopentadiene (4.29 g, 64.9 mmol), HSMP[24] (14.95 g, 129.8 mmol), ethanol (absolute, 13 mL), and 1,3,5-triazine[21] (2.10 g, 26.0 mmol) produced a dark red oil. Ethanol (5 mL) was added and thereafter water (60 mL). The mixture was vigorously shaken and then kept standing until the phases had separated. The upper turbid, yellow phase was removed with the help of a syringe and the lower, oily, dark red organic phase was washed twice with water. The organic phase was then kept in a high vacuum with occasional shaking to remove the more volatile components. After about 60 h a film of the oil no longer gave off bubbles, and the residue was pure (NMR) **7b** (7.73 g, 62%); could not be crystallized; highly soluble in the common soft and/or polar organic solvents, soluble in Et_2O, moderately soluble in hot hexane. Chromatography on alumina (5% H_2O) with pentane/ether (1:4) gave particularly pure samples, but also resulted in high losses of material. $C_{12}H_{17}NO$ (191.3): calcd. C 75.35, H 8.96, N 7.32; found C 75.49, H 9.01, N 7.19. MS (EI): *m*/*z* (%) = 191 (20) [M^+], 146 (36) [M^+ – CH_2OMe], 70 (100) [$C_4H_8N^+$]. ^{1}H NMR (500 MHz, CD_2Cl_2, 25 °C): δ = 1.81 (br., $\nu_{1/2}$ = 22.0 Hz, 1 H, 8-H), 2.07 (m, 8-H + 2 9-H), 3.36 (s, OMe), 3.44 (m, CH_2O), 3.65 (m, CH_2N), 3.96 (br., $\nu_{1/2}$ = 18.0 Hz, 7-H), 6.22 (m, 2-H), 6.37 (m, 1-H), 6.43 (m, 3-H), 6.48 (m, 4-H), 7.50 (br., $\nu_{1/2}$ = 7.5 Hz, 6-H). ^{13}C{^{1}H} NMR (125.6 MHz, CD_2Cl_2, 25 °C): δ = 24.60 (C-9), 27.86 (C-8), 50.54 (C-10), 59.27 (OMe), 63.94 (C-7), 75.45 (CH_2O), 114.71 (C-4), 118.14 (C-5), 119.46 (C-2), 124.00 (C-1), 124.53 (C-3), 144.92 (C-6).

Sodium (Morpholinomethyl)cyclopentadienide Na[$C_5H_4CH_2$–$N(C_2H_4)_2O$] (8a): A Schlenk tube was charged with toluene

(30 mL) and **7a** (0.918 g, 5.63 mmol), and cooled to 0 °C. A solution of $NaBHEt_3$ in toluene (1 M, 6.19 mL, 6.19 mmol) was added dropwise with vigorous stirring. The cooling bath was then removed, and stirring was continued at ambient temperature for 20 h. The volatiles were then removed in a vacuum and the solid residue was kept in a high vacuum for 24 h. This raw product contained (inter alia) triethylborane (0.32 equiv.) coordinated to morpholino groups [$\delta(^{11}B)$ = 4 and –2 ppm, two conformers] and borates [$NaBHEt_3$: $\delta(^{11}B)$ = –13 ppm; $NaBEt_4$: $\delta(^{11}B)$ = –16 ppm; in [D_7]-DMF or [D_6]DMSO].[44] The triethylborane could not be removed in a high vacuum at 80 °C. The residue was dispersed in diethyl ether (10 mL) with the help of an ultrasonic bath; when the solid had settled again, the supernatant liquid was removed with a syringe. This procedure was repeated twice with ether and three time with pentane. Drying the solid in a high vacuum overnight left **8a** (0.87 g, 83%, with 0.04 eq BEt_3) as a light brown to ochre colored, extremely air-sensitive solid; soluble in DMF, DMSO and liquid ammonia, and moderately soluble in MeCN, slowly decomposing in solution. ^1H NMR (500 MHz, [D_7]DMF, 25 °C): δ = 2.34 (br., $\nu_{1/2}$ = 21.8 Hz, 2 CH_2N), 3.35 (s, $C_5H_4CH_2$), 3.52 ("t", br, "J" = 4.58 Hz, 2 CH_2O), AA′BB′ system: 5.54 ("t", 3-/4-H), 5.56 ("t", 2-/5-H), $N = J_{12} + J_{13}$ = 2.44 Hz; protons of residual BEt_3: –0.04 (q, BCH_2Me), 0.71 (t, BCH_2), ^3J = 7.94 Hz. $^{13}C\{^1H\}$ NMR (125.6 MHz, [D_7]DMF, 25 °C): δ = 54.38 (NCH_2), 61.65 ($C_5H_4CH_2$), 67.51 (CH_2O), 102.91 (C-3,4), 105.41 (C-2,5), 114.19 (C-1). $^{11}B\{^1H\}$NMR (160.3 MHz, [D_7]DMF, 25 °C, ext. $BF_3{\cdot}OEt_2$): δ = 4.1, –2.0.

Sodium {[(*S*)-2-(Methoxymethyl)pyrrolidino]methyl}cyclopentadienide, Na($C_5H_4CH_2$–SMP) (8b): A Schlenk tube was charged with toluene (3 mL) and **7b** (0.676 g, 3.53 mmol). A solution of $NaBHEt_3$ in toluene (1 M, 3.89 mL, 3.89 mmol) was added dropwise with vigorous stirring, and stirring was continued for 20 h. Further workup as described for **8a** (but with 5 mL volumes of solvent) afforded **8b** (0.684 g, 90%, with 0.018 eq BEt_3) as a light brown to ochre colored, extremely air-sensitive solid; soluble in liquid ammonia, slightly soluble in MeCN and THF, slowly decomposing in solution. There is no improved solubility in DME, TMEDA or in the presence of 15-crown-5. Prolonged washing of **8b** with ether removed the residual triethylborane completely, but also drastically reduced the yield. ^1H NMR (500 MHz, [D_8]THF, 25 °C): δ = 1.47 (m, 1 H, 8-H), 1.56 (m, 2 H, 9-H), 1.78 (m, 1 H, 8-H), 2.37 (m, 1 H, 10-H), 2.74 (m, 7-H), 2.96 (m, 1 H, 10-H), 3.11 (dd, ^2J = 9.46, $^3J_{7,11}$ = 6.10 Hz, 1 H, 11-H), 3.19 (d, ^2J = 9.46 Hz, 1 H, 11-H), 3.25 (s, OMe), AB system $C_5H_4CH_2$: 3.44 (d) and 3.66 (d), ^2J = 12.51 Hz; 5.60 (s, C_5H_4). $^{13}C\{^1H\}$ NMR (125.6 MHz, [D_8]THF, 25 °C): δ = 23.46 (C-9), 28.88 (C-8), 55.19 (C-10), 56.43 ($C_5H_4CH_2$), 58.72 (OMe), 62.62 (C-7), 76.47 (CH_2O), 103.26 (C-3,4), 104.36 (C-2,5), 116.45 (C-1).

Cp*Ru($C_5H_4CH_2$–SMP) (5): A suspension of **8b** (1.615 g, 7.50 mmol) in THF (10 mL) was cooled to –78 °C and [Cp*RuCl]$_4$[13] (2.039 g, 1.876 mmol), also suspended in THF (10 mL), was added. The mixture was stirred and was warmed up to ambient temperature within 4 h and stirring was continued for 2 h. Then the volatiles were removed in a vacuum. The red-brown oily residue was extracted with pentane (15 mL), the solution was separated from solid material by filtration through kieselguhr, which was then washed and extracted with several portions of pentane (a total of 35 mL). Removal of the pentane in a vacuum left a raw product which was contaminated with BEt_3, which had come into the system as a contaminant of **8b**. It was dissolved in diethyl ether (15 mL) and a saturated aqueous solution of NaF (5 mL) was added. After vigorous shaking the two phases were separated, the aqueous phase was extracted several times with diethyl ether (a total of 25 mL); the combined ethereal solutions were dried with Na_2SO_4, filtered and the solvents evaporated to dryness. The yellow-brownish, oily residue was heated in a high vacuum ($5{\cdot}10^{-7}$ bar); above 160 °C a yellow oil was condensed over a short (!) bridge into a small flask. The product **5** (2.70 g. 84%) is a viscous yellow oil, highly soluble in all common organic solvents (except MeOH), insoluble in perfluoropentane and water. $C_{22}H_{33}NORu$ (428.6): calcd. C 61.65, H 7.76, N 3.27; found C 61.79, H 7.95, N 3.34. MS (EI): m/z (%) = 429 (15) [M^+], 315 (100) [M^+ – SMP]. ^1H NMR (500 MHz, CD_2Cl_2, 25 °C): δ = 1.49–1.55 (m, 1 H, 8-H), 1.59–1.66 (m, 2 9-H), 1.77–1.85 (m, 1 H, 8-H), 1.89 (s, Cp*), 2.22 (m, 1 H, 10-H), 2.60 (m, 1 H, 7-H), 2.89 (m, 1 H, 10-H), 2.95 (d, ^2J = 12.97 Hz, 1 H, 6-H), 3.17 (dd, ^2J = 9.33, $^3J_{7,11}$ = 6.52 Hz, 1 H, 11-H), 3.31 (s, OMe), 3.34 (dd, ^2J = 9.33, $^3J_{7,11'}$ = 4.94 Hz, 1 H, 11-H′), 3.36 (d, ^2J = 12.97 Hz, 1 H, 6-H), 4.08 (m, 2-/5-H), 4.10 (m, 3-/4-H). $^{13}C\{^1H\}$ NMR (125.6 MHz, CD_2Cl_2, 25 °C): δ = 12.07 (C_5Me_5), 23.11 (C-9), 29.09 (C-8), 53.43 ($C_5H_4CH_2$), 54.36 (C-10), 59.06 (OMe), 61.96 (C-7), 73.12 and 72.97 (C-3,4), 74.65 and 74.45 (C-2,5), 77.02 (CH_2O), 85.12 (C_5Me_5), 85.48 (C-1).

[Cp*Ru(C_5H_4CH=SMP)]PF_6 (9): To a Schlenk tube charged with [Cp*Ru(MeCN)$_3$]PF_6[26] (0.581 g, 1.151 mmol) was added a solution of **7b** (0.227 g, 1.186 mmol) in THF (15 mL). The resulting reaction mixture was heated to reflux temperature for 24 h. The volatiles were removed in a vacuum. The residue was powdered at liquid nitrogen temperature and was warmed to ambient temperature in a high vacuum. This procedure was repeated several times and left **9** (0.660 g, 100%) as dark red-brown powder; m.p. 155 °C, rather soluble in CH_2Cl_2, THF and acetone, sparingly soluble in ether, decomposes in MeOH. The product may be crystallized as dark yellow needles by layering of acetone solutions with ether. $C_{22}H_{32}F_6NOPRu$ (572.54): calcd. C 46.15, H 5.63, N 2.45; found C 46.19, H 5.62, N 2.56. MS (DCI, NH_3) m/z (%) = 428 (85) [M^+], 116 (100) [H_2SMP^+]. ^1H NMR (500 MHz, CD_2Cl_2, 25 °C): δ = 1.91 (s, Cp*), 1.92–2.00 (m, 1 H, 8-H), 2.19–2. 34 (m, 3 H, 8-H′ + 2 9-H), 3.40 (s, OMe), 3.36–3.48 (m, CH_2N), 3.55 (dd, ^2J = 10.68, $^3J_{7,11}$ = 7.63 Hz, 1 H, 11-H), 3.68 (dd, ^2J = 10.68, $^3J_{7,11}$ = 3.36 Hz, 1 H, 11-H′), 4.26 (m, 7-H), C_5H_4: 4.78 (ddd, 1-H), 4.86 (ddd, 4-H), 4.93 (ddd, 2-H), 4.95 (ddd, 3-H), simulated with $^3J_{12}$ = $^3J_{34}$ = 2.75, $^3J_{23}$ = 2.67, $^4J_{13}$ = $^4J_{14}$ = $^4J_{24}$ = 1.14 Hz; 8.28 (br., $\nu_{1/2}$ = 4.2 Hz, 6-H). $^{13}C\{^1H\}$ NMR (125.6 MHz, CD_2Cl_2, 25 °C): δ = 11.86 (C_5Me_5), 24.52 (C-9), 27.53 (C-8), 53.01 (CH_2N), 59.34 (OMe), 68.08 (C-7), 73.64 (CH_2O), 75.01 (C-5), 76.34 and 76.70 (br., C-1,4), 82.87 and 82.92 (C-2,3), 90.32 (C_5Me_5), 162.95 (C-6).

Synthesis of 5 by Hydride Addition to Complex 9: A solution of **9** in THF (20 mL) was prepared as described above from [Cp*Ru(MeCN)$_3$]PF_6[26] (0.550 g, 1.090 mmol) and **7b** (0.210 g, 1.099 mmol). A solution of $LiAlH_4$ in THF (1 M, 1.090 mL) was added dropwise at –78 °C. The mixture was then warmed to ambient temperature and stirred at that temperature for 7 d. Water (2 mL) was added, then the mixture was evaporated to dryness. The residue was extracted with several portions of pentane (a total 50 mL). The combined, lemon yellow extracts were filtered through kieselguhr. Removal of the pentane left a very pure (NMR) sample of **5** (0.24 g, 50%, yield not optimized).

Lithiation of 5: Complex **5** was used as 0.1 M solution in diethyl ether at –78 °C. A titrated solution of Li*s*Bu in cyclohexane[28] (ca. 1.5 M) was added at –78 °C within 30 s. The ratio **5**/Li*s*Bu was usually 1:1.7 The reaction mixture was kept stirring at –78 °C for 3.5 h. Then the quenching reagent E–X was added, still at –78 °C, and the mixture was warmed to ambient temperature. Stoichiometric quantities are specified below.

(S_P)-Cp*Ru[1-F-2-(SMP–CH_2)C_5H_3] (10a): A solution of **5** in diethyl ether (0.298 g, 0.695 mmol, 1.39 mL) was cooled to –78 °C

and a solution of Li*s*Bu in cyclohexane (1.58 M, 0.748 mL, 1.181 mmol) (ratio 1:1.70) was added at –78 °C within 20–30 s. The mixture was stirred at –78 °C for 3.5 h. Then a suspension of *N*-fluoro-*N*,*N*-bis(benzenesulfonyl)imide [$(PhSO_2)_2NF$] (0.3835 g, 1.216 mmol) in diethyl ether (a total of 10 mL) was added. The reaction mixture was warmed to ambient temperature within 2.5 h and stirring was then continued for 12 h. The volatiles were removed in a high vacuum and the residue was extracted with several portions of pentane (a total of 25 mL). The combined solutions were passed through kieselguhr and carefully freed of all volatiles to leave **10a** (0.233 g, 75%) as pale yellow oil, de > 98%, 8% admixture of **5** (only the ring protons 1-H – 4-H of **5** are not hidden by signals of **10a**). MS (EI): *m*/*z* (%) = 447 (9) [M^+], 333 (100) [M^+ – SMP]. Further comment: $(PhSO_2)_2NF$ should be colorless. The commercial product (Aldrich) was dissolved in CH_2Cl_2; the solution was passed through kiesel gel (Kieselgel 60, Merck), freed from solvent and carefully dried in a high vacuum. ^1H NMR (500 MHz, CD_2Cl_2, 25 °C): δ = 1.90 (s, Cp*), 3.01 (d, 1 H, 2-CH_2), 3.66 (d, 1 H, 2-CH_2), ^2J(2-CH_2) = 13.42 Hz; 3.846 (dddd, 4-H), 3.897 (dd, 3-H), 4.338 (dddd, 5-H), $^3J(^{19}F,5\text{-H})$ = 3.74, $^3J_{34}$ = 2.52, $^3J_{45}$ = 2.51, $^4J(^{19}F,4\text{-H})$ = 0.61, $^4J(^{19}F,3\text{-H})$ = 0.50, $^4J_{35}$ = 1.29, ^4J(3-H,2-CH_2) = 0.25, ^5J(4-H,2-CH_2) = 0.53, ^5J(5-H,2-CH_2) = 0.57 Hz; SMP fragment: 1.50–1.57 (m, 1 H, 8-H), 1.61–1.68 (m, 2 H, 9-H,H′), 1.78–1.86 (m, 1 H, 8-H′), 2.25 (ddd, br, 1 H, 10-H), 2.67 (br. m, 7-H), 2.95 (ddd, br, 1 H, 10-H′), 3.20 (dd, ^2J = 9.46, $^3J_{7,11}$ = 6.41 Hz, 1 H, 11-H), 3.31 (s, OMe), 3.36 (dd, ^2J = 9.46, $^3J_{7,11'}$ = 5.19 Hz, 1 H, 11-H′). $^{13}C\{^1H\}$ NMR (125.6 MHz, CD_2Cl_2, 25 °C): δ = 11.69 (C_5Me_5), 23.15 (C-9), 29.04 (C-8), 49.42 (d, $^3J_{FC}$ = 3.9 Hz, C-6), 54.31 (C-10), 59.05 (OMe), 61.76 (C-7), 62.32 (d, $^2J_{FC}$ = 15.9 Hz, C-5), 66.26 (d, $^3J_{FC}$ = 3.9 Hz, C-4), 69.68 (d, $^3J_{FC}$ = 2.7 Hz, C-3), 73.72 (small, d, $^2J_{FC}$ = 14.3 Hz, C-2), 77.02 (C-11), 86.29 (C_5Me_5), 133.81 (d, $^1J_{FC}$ = 267.9 Hz, C-1). ^{19}F NMR (470.1 MHz, CD_2Cl_2, 25 °C): δ = –196.8 vs. ext. $CFCl_3$; when measured at 188.1 MHz a doublet was seen with $^3J(^{19}F,5\text{-H})$ = 3.5 Hz.

(S_P)-Cp*Ru[1-Cl-2-(SMP–CH_2)C_5H_3] (10b): The reaction of **5** (59.5 mg, 138.8 μmol), Li*s*Bu (1.65 M, 143 μL, 236 μmol), and C_2Cl_6 (82.2 mg, 347 μmol) gave **10b** (64.0 mg, 100%) as pale yellow oil; de > 98%, ca. 2% admixture of **5** (the signal at δ = 1.893 ppm of the Cp* ligand of **5** was the only impurity signal seen). MS (EI): *m*/*z* (%) = 463 (7) [M^+], 349 (100) [M^+ – SMP], 316 (17) [$RuC_{16}H_{22}^+$]. ^1H NMR (500 MHz, CD_2Cl_2, 25 °C): δ = 1.85 (s, Cp*), 2.91 (d, 1 H, 2-CH_2), 3.59 (d, 1 H, 2-CH_2), ^2J(2-CH_2) = 13.18 Hz; 4.09 (ddd, 4-H), 4.15 (dd, 3-H), 4.34 (ddd, 5-H), $^3J_{34}$ = 2.47, $^3J_{45}$ = 2.38, $^4J_{35}$ = 1.29, ^4J(3-H,2-CH_2) = 0.25, ^5J(4-H,2-CH_2) = 0.40, ^5J(5-H,2-CH_2) = 0.55 Hz; SMP fragment: 1.51–1.57 (m, 1 H, 8-H), 1.60–1.70 (m, 2 H, 9-H,H′), 1.80 –1.90 (m, 1 H, 8-H′), 2.20 (ddd, ^2J = 9.06, $^3J_{9,10} \approx 9.3$ $^3J_{9',10} \approx$Hz, 1 H, 10-H), 2.66 (m, 7-H), 2.99 (ddd, ^2J = 9.06, $^3J_{9,10'}$ = 6.68, $^3J_{9',10'}$ = 2.38 Hz, 1 H, 10-H′), 3.21 (dd, ^2J = 9.33, $^3J_{7,11}$ = 6.40 Hz, 1 H, 11-H), 3.32 (s, OMe), 3.42 (dd, ^2J = 9.33, $^3J_{7,11'}$ = 4.90 Hz, 1 H, 11-H′). $^{13}C\{^1H\}$ NMR (125.6 MHz, CD_2Cl_2, 25 °C): δ = 11.29 (C_5Me_5), 23.12 (C-9), 29.06 (C-8), 50.71 ($C_5H_4CH_2$), 54.57 (C-10), 59.06 (OMe), 62.32 (C-7), 70.98 (C-4), 73.59 (C-3), 73.79 (C-5), 77.15 (CH_2O), 83.57 (C-2), 86.39 (C_5Me_5), 92.11 (C-1).

(S_P)-Cp*Ru[1-Br-2-(SMP–CH_2)C_5H_3] (10c): The reaction of **5** (70.5 mg, 164.5 μmol), Li*s*Bu (1.65 M, 170 μL, 280 μmol), and 1,2-$C_2H_4Br_2$ (54.1 mg, 288 μmol) gave **10c** (83.3 mg, 100%) as pale yellow oil; de > 98%, ca. 5% admixture of **5** (NMR). MS (EI): *m*/*z* (%) = 507/509 (5) [M^+], 393/395 (100) [M^+ – SMP], 315 (22) [$RuC_{16}H_{21}^+$]. ^1H NMR (500 MHz, CD_2Cl_2, 25 °C): δ = 1.84 (s, Cp*), 3.55 (d, 1 H, 2-CH_2), 2.95 (d, 1 H, 2-CH_2), ^2J(2-CH_2) = 13.26 Hz; 4.132 (ddd, 4-H), 4.170 (dd, 3-H), 4.358 (ddd, 5-H), $^3J_{34}$ = 2.29, $^3J_{45}$ = 2.38, $^4J_{35} \approx 1.2$, ^5J(4-H,2-CH_2) = 0.40, ^5J(5-H,2-CH_2) = 0.55 Hz; SMP fragment: 1.554–1.716 (m, 3 H, 8-/9-H,H′), 1.80–1.89 (m, 1 H, 8-H′), 2.22 (ddd, $^2J \approx 9.35$, $^3J_{9,10} \approx 9.40$, $^3J_{9',10} \approx 7.46$ Hz, 1 H, 10-H), 2.68 (m, 7-H), 3.02 (ddd, $^2J \approx 9.2$, $^3J_{9,10'} \approx 7.2$, $^3J_{9',10'} \approx 2.0$ Hz, 1 H, 10-H′), 3.25 (dd, ^2J =.38, $^3J_{7,11}$ = 6.18 Hz, 1 H, 11-H), 3.34 (s, OMe), 3.45 (dd, ^2J = 9.38, $^3J_{7,11'}$ = 4.72 Hz, 1 H, 11-H′). $^{13}C\{^1H\}$ NMR (125.6 MHz, CD_2Cl_2, 25 °C): δ = 11.21 (C_5Me_5), 23.05 (C-9), 28.93 (C-8), 51.49 ($C_5H_4CH_2$), 54.55 (C-10), 59.12 (OMe), 62.31 (C-7), 72.33 (C-4), 73.97 (C-3), 75.99 (C-5), 76.76 (CH_2O), 79.17 (C-1), 84.53 (C-2), 86.54 (C_5Me_5).

(S_P)-Cp*Ru[1-I-2-(SMP–CH_2)C_5H_3] (10d): The reagents were **5** (141.8 mg, 331 μmol), Li*s*Bu (1.65 M, 211 μL, 347 μmol), and 1,2-$C_2H_4I_2$ (93.3 mg, 331 μmol). The reaction mixture was kept at ambient temperature for 50 h. Then the volatiles were removed in a vacuum. the residue was treated with diethyl ether (5 mL) and then with water (5 mL) and vigorously shaken. The aqueous phase was extracted with two portions of ether (5 mL each). The combined ethereal phases were dried with $MgSO_4$ and carefully freed from all volatiles to leave **10d** (99.4 mg, 54%) as a brown oil; de > 98%, ca. 2% admixture of **5** (^1H NMR: δ = 1.893 ppm, Cp* ligand of **5**). MS (EI): *m*/*z* (%) = 555 (7) [M^+], 441 (100) [M^+ – SMP], 315 (21) [$RuC_{16}H_{21}^+$]. ^1H NMR (500 MHz, CD_2Cl_2, 25 °C): δ = 1.81 (s, Cp*), 2.85 (d, 1 H, 2-CH_2), 3.432 (d, 1 H, 2-CH_2), ^2J(2-CH_2) = 13.17 Hz; 4.138 (dd, 3-H), 4.151 (ddd, 4-H), 4.35 (ddd, 5-H), $^3J_{34}$ = 2.42, $^3J_{45}$ = 2.38, $^4J_{35}$ = 1.23, ^5J(4-H,2-CH_2) = 0.55, ^5J(5-H,2-CH_2) = 0.60 Hz; SMP fragment: 1.51–1.57 (m, 1 H, 8-H), 1.61–1.68 (m, 2 H, 9-H,H′), 1.80–1.88 (m, 1 H, 8-H′), 2.16 (ddd, 1 H, 10-H), 2.63 (m, 7-H), 3.00 (ddd, 1 H, 10-H′), 3.22 (dd, ^2J = 9.33, $^3J_{7,11}$ = 6.41 Hz, 1 H, 11-H), 3.33 (s, OMe), 3.52 (dd, ^2J = 9.33, $^3J_{7,11'}$ = 4.94 Hz, 1 H, 11-H′). $^{13}C\{^1H\}$ NMR (125.6 MHz, CD_2Cl_2, 25 °C): δ = 11.04 (C_5Me_5), 23.06 (C-9), 29.09 (C-8), 45.25 (C-1), 53.37 ($C_5H_4CH_2$), 54.77 (C-10), 59.07 (OMe), 62.71 (C-7), 74.13 (C-3), 74.35 (C-4), 77.27 (CH_2O), 80.41 (C-5), 86.41 (C_5Me_5), 87.27 (C-2).

(R_P)-Cp*Ru[1-(SMP–CH_2)-2-MeC_5H_3] (10e): The reagents were **5** (83.2 mg, 194 μmol), Li*s*Bu (1.58 M, 209 μL, 330 μmol), and MeI (48.2 mg, 340 μmol). Workup as described for **10d** (with Na_2SO_4 for drying) gave **10e** as yellow-brown oil; de > 98%, ca. 5% admixture of **5** (^1H NMR: δ = 1.893 ppm, Cp* ligand of **5**). The yield was not determined; cf. however the data for **10f**. MS (EI): *m*/*z* (%) = 443 (15) [M^+], 329 (100) [M^+ – SMP]. ^1H NMR (500 MHz, CD_2Cl_2, 25 °C): δ = 1.84 (s, Cp*), 2.78 (d, 1 H, 2-CH_2), 3.54 (d, 1 H, 2-CH_2), ^2J(2-CH_2) = 12.82 Hz; 4.013 (dd, 4-H), 4.029 (m, 3-H), 4.041 (dd, 5-H), $^3J_{34} \approx 2.4$, $^3J_{45}$ = 2.14, $^4J_{35}$ = 1.22 Hz; SMP fragment: 1.49–1.54 (m, 1 H, 8-H), 1.60–1.64 (m, 2 H, 9-H,H′), 1.75 (s, 2-Me), 1.80 –1.88 (m, 1 H, 8-H′), 2.14 (ddd, 1 H, 10-H), 2.61 (m, 7-H), 2.94 (m, 1 H, 10-H′), 3.22 (dd, ^2J = 9.15, $^3J_{7,11}$ = 6.10 Hz, 1 H, 11-H), 3.32 (s, OMe), 3.39 (dd, ^2J = 9.15, $^3J_{7,11'}$ = 5.19 Hz, 1 H, 11-H′). $^{13}C\{^1H\}$ NMR (125.6 MHz, CD_2Cl_2, 25 °C): δ = 11.66 (2-Me), 11.69 (C_5Me_5), 23.14 (C-9), 29.08 (C-8), 52.03 ($C_5H_4CH_2$), 54.74 (C-10), 59.05 (OMe), 62.50 (C-7), 71.45 (C-4), 74.92 (C-3), 75.29 (C-5), 77.48 (CH_2O), 84.66(C_5Me_5), 84.92(small, C-1), 85.25(small, C-2).

(S_P)-Cp*Ru[1-(SMP–CH_2)-2-$CD_3C_5H_3$] (10f): The reagents were **5** (0.448 g, 1.045 mmol), Li*s*Bu (1.58 M, 0.992 mL, 1.567 mmol), and CD_3I (0.235 g, 1.62 mmol). Workup as described for **10d** (with Na_2SO_4 as drying agent) gave **10f** (0.421 g, 100%) as yellow oil; de > 98%, ca. 3% admixture of **5** (^1H NMR: δ = 1.893 ppm, Cp* ligand of **5**). MS (EI): *m*/*z* (%) = 463 (3) [M^+ – H + CD_3], 446 (14) [M^+], 349 (24) [M^+ – SMP – H + CD_3], 332 (100) [M^+ – SMP]. ^1H NMR (500 MHz, CD_2Cl_2, 25 °C): δ = 1.84 (s, 15 H, Cp*), 2.79 (d, 1 H, 2-CH_2), 3.53 (d, 1 H, 2-CH_2), ^2J(2-CH_2) = 12.90 Hz; 4.009 (ddd, 4-H), 4.023 (ddd, 3-H), 4.038 (dd, 5-H), $^3J_{34}$ = 2.29, $^3J_{45} \approx$

2.20, $^4J_{35} \approx 1.45$, ^5J(3-H,2-CH_2) = 0.6, ^5J(4-H,2-CH_2) = 0.37 Hz; SMP fragment: 1.48–1.54 (m, 1 H, 8-H), 1.60–1.66 (m, 2 H, 9-H,H′), 1.81–1.87 (m, 1 H, 8-H′), 2.14 (ddd, 1 H, 10-H), 2.62 (m, 7-H), 2.94 (m, 1 H, 10-H′), 3.21 (dd, ^2J = 9.24, $^3J_{7,11}$ = 6.23 Hz, 1 H, 11-H), 3.32 (s, OMe), 3.391 (dd, ^2J = 9.06, $^3J_{7,11'}$ = 5.21 Hz, 1 H, 11-H′). ^{2}H{^{1}H} NMR (61.4 MHz, CD_2Cl_2, 25 °C): δ = 1.74 (CD_3) vs. $\delta(CD_2Cl_2)$ = 5.330. ^{13}C{^{1}H} NMR (125.6 MHz, CD_2Cl_2, 25 °C): δ = 11.66 (C_5Me_5), 23.12 (C-9), 29.06 (C-8), 52.01 ($C_5H_4CH_2$), 54.71 (C-10), 59.03 (OMe), 62.48 (C-7), 71.45 (C-4), 74.91 (C-5), 75.27 (C-3), 77.45 (CH_2O), 84.66 (C_5Me_5), 84.77 (small, C-1), 85.26 (small, C-2); in a ^{13}C NMR spectrum the 2-CD_3 group can be seen as a septet: δ = 10.96 [sept, $^1J(^{13}C–^2H)$ = 19.2 Hz, CD_3].

(S_P)-Cp*Ru[1-(Me_3Si)-2-(SMP–CH_2)C_5H_3] (10g) and Cp*Ru[1,3-(Me_3Si)$_2$-2-(SMP–CH_2)C_5H_2] (11): The reagents were **5** (87.5 mg, 204 μmol), Li*s*Bu (1.65 M, 210 μL, 347 μmol), and $SiClMe_3$ (38.8 mg, 357 μmol). Workup as described for **10d** (with Na_2SO_4 as drying agent) gave a yellow oil (99.4 mg) which consisted of **10g** and **11** in a 3:1 ratio; unconsumed starting material **5** could not be detected. When only a small excess of Li*s*Bu was used, the formation of **11** could be suppressed and some unconsumed **5** was found. MS (EI) *m*/*z* (%): 573 (< 0.5) [**11**$^+$], 501 (12) [**10g**$^+$], 459 (2%) [**11**$^+$ – SMP], 428 (16) [**10g**$^+$ – $SiMe_3$], 387 (100) [**10g**$^+$ – SMP], 316 (27) [$RuC_{16}H_{22}^+$].

Data for 10g: ^{1}H NMR (500 MHz, CD_2Cl_2, 25 °C): δ = 1.87 (s, Cp*), 2.55 (d, 1 H, 2-CH_2), 3.66 (d, 1 H, 2-CH_2), ^2J(2-CH_2) = 12.21 Hz; 4.03 (m, 5-H), 4.08 (dd, 3-H), 4.10 (dd, 4-H), $^3J_{34}$ = $^3J_{45}$ = 2.14, $^4J_{35}$ = 1.22 Hz; 0.17 [s, $^2J(^{29}Si,^1H)$ = 6.41 Hz, $SiMe_3$]; SMP fragment: 1.45–1.61 (m, 3 H, 8-/9-H,H′), 1.83–1.97 (m, 1 H, 8-H′), 2.00 (ddd, 1 H, 10-H), 2.45 (m, 7-H), 2.75 (m, 1 H, 10-H′), 3.21 (dd, ^2J = 9.16, $^3J_{7,11}$ = 6.11 Hz, 1 H, 11-H), 3.300 (s, OMe), 3.47 (dd, ^2J = 9.16, $^3J_{7,11'}$ = 5.50 Hz, 1 H, 11-H′). ^{13}C{^{1}H} NMR (125.6 MHz, CD_2Cl_2, 25 °C): δ = 0.21 [$^1J(^{29}Si–^{13}C)$ = 51.5 Hz, $SiMe_3$], 12.25 (C_5Me_5), 22.73 (C-9), 29.33 (C-8), 54.46 (C-10), 54.69 ($C_5H_4CH_2$), 58.95 (OMe), 63.94 (C-7), 75.01 (C-4), 76.71 (small, C-1), 77.30 (CH_2O), 78.89 (C-5), 79.48 (C-3), 84.96 (C_5Me_5), 91.00 (small, C-2). ^{29}Si{^{1}H} NMR (99.3 MHz, CD_2Cl_2, 25 °C): δ = –5.3 vs. ext. $SiMe_4$, measured as ^{1}H/^{29}Si HMQC NMR spectrum.

Data for 11: ^{1}H NMR (500 MHz, CD_2Cl_2, 25 °C): δ = 1.85 (s, Cp*), 2.75 (d, 1 H, 2-CH_2), 3.51 (d, 1 H, 2-CH_2), ^2J(2-CH_2) = 12.51 Hz; 4.00–4.15 (4-/5-H); 0.197 (s, $SiMe_3$), 0.208 (s, $SiMe_3$); SMP fragment: 1.45–1.61 (m, 3 H, 8-/9-H,H′), 1.83–1.97 (m, 1 H, 8-H′), 2.08 (ddd, 1 H, 10-H), 2.45 (m, 7-H), 2.67 (m, 1 H, 10-H′), 3.17 (dd, ^2J = 9.16, $^3J_{7,11}$ = 6.40 Hz, 1 H, 11-H), 3.27 (s, OMe), 3.41 (dd, ^2J = 9.16, $^3J_{7,11'}$ = 5.49 Hz, 1 H, 11-H′); several signals are hidden by the corresponding signals of the main product **10g**. ^{13}C{^{1}H} NMR (125.6 MHz, CD_2Cl_2, 25 °C): δ = 0.65 and 1.52 *ppm*(1-/3-$SiMe_3$), 12.41 (C_5Me_5), 22.67 (C-9), 29.36 (C-8), 53.97 and 54.39 ($C_5H_4CH_2$ and C-10), 58.86 (OMe), 64.36 (C-7), 76.90 (CH_2O), 80.45 and 81.38 (C-4,5), 81.23 and 81.43 (small, C-1,3), 84.87 (C_5Me_5), 95.20 (small, C-2). ^{29}Si{^{1}H} NMR (99.3 MHz, CD_2Cl_2, 25 °C): δ = –5.7 vs. ext. $SiMe_4$, measured as ^{1}H/^{29}Si HMQC NMR spectrum.

(S_P)-Cp*Ru[1-(Ph_2P)-2-(SMP–CH_2)C_5H_3] (10h): The reagents were **5** (0.272 g, 0.635 mmol), Li*s*Bu (1.41 M, 653 μL, 0.921 mmol), and $PClPh_2$ (0.8974 *M* in hexane, 1.097 mL, 0.984 mmol). After warming the reaction mixture to ambient temperature within 1.5 h, the volatiles were removed in a high vacuum. The yellow oily residue was extracted with several portions of ether. The combined extracts were filtered through kieselguhr and carefully freed of solvent. The residue was heated in a high vacuum (oil diffusion pump, ca. 10^{-9} bar) for several hours; above 80 °C P*s*BuPh_2 was condensed over a short (!) bridge into a small flask. This procedure finally left **10h** (0.327 g, 84%) as a dark yellow, extremely viscous oil; soluble in CH_2Cl_2, THF, and ether, only moderately soluble in pentane; de > 98, ca. 15% admixture of **5** (^{1}H NMR); the P-containing compounds were **10h** (90%), residual P*s*BuPh_2 (ca. 4%), and phosphane oxides (ca. 6%) (^{31}P NMR). MS (EI) *m*/*z* (%): 613 (1) [M$^+$], 499 (3) [M$^+$ – SMP], 429 (15) [**5**$^+$], 315 (100) [$C_{16}H_{21}Ru^+$]. ^{1}H NMR (500 MHz, CD_2Cl_2, 25 °C): δ = 1.80 (s, Cp*), 2.64 (d, 1 H, 2-CH_2), 3.87 [dd, $^4J(^{31}P,2\text{-CH})$ = 2.44 Hz, 1 H, 2-CH_2], ^2J(2-CH_2) = ^2J = 12.21 Hz; 4.01 (ddd, 5-H), 4.217 (dddd, 4-H), 4.235 (ddd, 3-H), $^3J(^{31}P,5\text{-H})$ = 0.54, $^3J_{34}$ = 2.29, $^3J_{45}$ = 2.36, $^4J(^{31}P,3\text{-H})$ = 1.15, $^4J(^{31}P,4\text{-H})$ = 0.68, $^4J_{35}$ = 1.22, ^5J(4-H,2-CH_2) = 0.38 Hz; PPh2 group: 7.17–7.19 (m, 3 H), 7.22 –7.26 (m, 2 H), 7.29–7.31 (m, 3 H), 7.56 –7.59 (m, 2 H); SMP fragment: 0.97–1.16 (m, 2 H, 8-/9-H), 1.34–1.404 (m, 1 H, 9-H′), 1.59–1.67 (m, 1 H, 8-H′), 1.83–1.91 (m, partially overlapped by Cp* signal of **5**, 1 H, 10-H), 2.38 (m, 7-H), 2.61 (dd, ^2J = 9.16, $^3J_{7,11}$ = 7.63 Hz, 1 H, 11-H), 2.69 ("t"m, 1 H, 10-H′′), 3.25 (s, OMe), 3.80 (dd, ^2J = 9.16, $^3J_{7,11'}$ = 4.58 Hz, 1 H, 11-H′). ^{13}C{^{1}H} NMR (125.6 MHz, CD_2Cl_2, 25 °C): δ = 11.85 (C_5Me_5), 22.67 (C-9), 29.32 (C-8), 52.86 (d, $^3J_{PC}$ = 7.1 Hz, $C_5H_4CH_2$), 53.92 (C-10), 58.85 (OMe), 63.06 (C-7), 74.55 (s, C-4), 75.77 (d, $^2J_{PC}$ = 4.9 Hz, C-5), 76.81(d,$^6J_{PC}$= 2.2 Hz, CH_2O), 78.86(d,$^3J_{PC}$ = 3.3 Hz,C-3),78.91 (d,small,$^2J_{PC}$ = 9.3 Hz,C-2), 85.71 (C_5Me_5), 90.74 (d, small, $^1J_{PC}$ = 26.8 Hz, C-1), 8 signals of PPh_2 group 127.4–142.4. ^{31}P{^{1}H} NMR (202.3 MHz, CD_2Cl_2, 25 °C): δ = –24.03 vs. ext. H_3PO_4 (85%).

(S_P)-Cp*Ru[1-{(Ph_3P)Au}-2-(SMP–CH_2)C_5H_3] (10i): The reagents were **5** (72.3 mg, 169 μmol), Li*s*Bu (1.65 M, 107 μL, 177 μmol; only 1.05 equiv. !), and AuCl(PPh_3) (83.5 mg, 169 μmol). The metalation solution was kept at –78 °C for 12 h, was then warmed to ambient temperature within 13 h, and was cooled again to –78 °C. The gold reagent was added as a fine powder. The reaction mixture was warmed to ambient temperature and kept at that temperature for 3 h. Further workup as described for **10a** gave **10i** (0.115 g, 77%) as a yellow oil; de > 98%, ca. 25% admixture of **5** (NMR). MS (EI): *m*/*z* (%) = 887 (0.03) [M$^+$], 429 (8) [**5**$^+$], 315 (49) [$C_{16}H_{21}Ru^+$], 262 (100) [PPh_3^+]. ^{1}H NMR (500 MHz, CD_2Cl_2, 25 °C): δ = 1.92 (s, Cp*), 2.995 (d, overlapping with 10-/11-H, 1 H, 2-CH_2), 3.57 (d, 1 H, 2-CH_2), ^2J(2-CH_2) = 12.51 Hz; 3.97 (m, 5-H), 4.16 (m, 4-H), 4.22 (m, 3-H); PPh3: 7.47–7.541–(m, 9 H), 7.60–7.64 (m, 6 H); SMP fragment: 1.49–1.57 (m, 1 H, 8-H), 1.59–1.67 (m, 2 H, 9-H,H′), 1.74–1.80 (m, 1 H, 8-H′), 2.37 (ddd, 1 H, 10-H), 2.80 (m, 7-H), 2.97 (d, OMe), 2.995 (dd, overlapping with signals of 2-CH_2 and 10-H′, ^2J = 9.16, $^3J_{7,11} \approx 1.2$ Hz, 1 H, 11-H), 3.006 (m, overlapping with signals of 2-CH_2 and 11-H, 1 H, 10-H′), 3.41 (dd, ^2J = 9.15, $^3J_{7,11'}$ = 3.96 Hz, 1 H, 11-H′). ^{13}C{^{1}H} NMR (125.6 MHz, CD_2Cl_2, 25 °C): δ = 12.95 (C_5Me_5), 23.35 (C-9), 29.51 (C-8), 54.92 (C-10), 57.28 (s, $C_5H_4CH_2$), 58.82 (OMe), 61.85 (C-7), 74.23 (d, $^4J_{PC}$ = 6.5 Hz, C-4), 75.26 (d, $^4J_{PC}$ = 6.1 Hz, C-3), 77.14 (CH_2O), 80.96 (d, $^3J_{PC}$ = 5.5 Hz, C-5), 84.55 (C_5Me_5), 92.41 (d, small, $^3J_{PC}$ = 6.1 Hz, C-2), 111.24 (d, small, $^2J_{PC}$ = 121.8 Hz, C-1), 4 signals of PPh_3 group 129.4–134.7. ^{31}P{^{1}H} NMR (202.3 MHz, CD_2Cl_2, 25 °C): δ = 47.46 vs. ext. H_3PO_4 (85%); δ = 44.7 for *s*Bu$Au(PPh_3)$ when present as an impurity.

The Dimer [(R_P)-Cp*Ru{1-(LiI·SMP–CH_2)-2-$CD_3C_5H_3$}]$_2$ (12): Reagents and reaction as described for **10f**. After warming up to ambient temperature the reaction mixture was kept at that temperature for 0.5 h. The volatiles were then removed in a high vacuum. The foamy residue was extracted with 5–10 portions of hexane (5 mL each). The combined solutions were filtered through kieselguhr. Crystallization set in spontaneously and was completed by cooling to –26 °C for 15 h. The mother liquor was removed and the crystals were dried in a vacuum maintaining low temperature during the whole procedure. This gave **12** (0.54–0.60 g, 90–100%)

as yellowish, almost colorless, rather hygroscopic needles; m.p. 165 °C (dec.); only slightly soluble in hexane. NMR spectra similar to those of **10f**.

(S_P)-Cp*Ru(1-F-2-MeC$_5$H$_3$) (14a): a) A solution of **10a** (0.233 g, 0.522 mmol) and excess MeI (0.50 mL, 8.0 mmol) in hexane (10 mL) was kept at ambient temperature for 10 d. The precipitate was collected, washed with hexane (2 × 3 mL), and dried in a high vacuum to give **13a** (0.251 g, 82%) as ochre-colored powder. The minor stereomer was best seen in the ^{19}F NMR (376.3 MHz, [D$_6$]-DMSO) spectrum which displayed two signals at $\delta(^{19}F)$ = –194.2 and –196.6 ppm vs. ext. $CFCl_3$ in a 8:1 ratio. b) A Schlenk tube was charged with **13a** (0.251 g, 0.427 mmol) and THF (16 mL). A solution of $LiAlH_4$ in THF (1 M, 0.64 mL, 0.64 mmol) was added at ambient temperature, and the mixture was heated to reflux temperature for 50 h. Then the reaction mixture was hydrolyzed with water (2.5 mL) and dried in a vacuum. The residue was extracted with several portions of pentane (a total of 40 mL). The combined extracts were filtered through kieselguhr and dried with $MgSO_4$. The concentrated solution was chromatographed on a column (7 cm long, 1 cm diameter) of alumina (5% H_2O) and eluted with pentane (a total of 20 mL). Careful removal of the solvent left **14a** (80 mg, 56%) as white crystals containing 2% (NMR) of Cp*Ru(C$_5$H$_4$Me);[45] m.p. 43 °C. $C_{16}H_{21}FRu$ (333.4): calcd. C 57.64, H 6.35; found C 57.53, H 6.48. MS (EI): *m/z* (%) = 334(100) [M$^+$],319(47) [M$^+$–Me],316(28) [$C_{16}H_{22}Ru^+$]. ^{1}H NMR (500 MHz, CD_2Cl_2, 25 °C): δ = 1.82 (s, 2-Me), 1.90 (s, Cp*), 3.78 (ddd, $^4J_{FH}$ = 0.76 Hz, 4-H), 3.81 (m, 3-H), 4.28 (ddd, $^3J_{FH}$ = 3.82 Hz, 5-H), $^3J_{34}$ = $^3J_{45}$ = 2.52, $^4J_{35}$ = 1.22 Hz. ^{13}C{^{1}H} NMR (125.6 MHz, CD_2Cl_2, 25 °C): δ = 9.56 (d, $^3J_{FH}$ = 2.8 Hz, 2-Me), 11.58 (C$_5$*Me*$_5$), 61.48 (d, $^2J_{FC}$ = 16.4 Hz, C-5), 65.43 (d, $^3J_{FC}$ = 4.4 Hz, C-4), 69.16 (d, $^3J_{FC}$ = 2.7 Hz, C-3), 73.42 (d, $^2J_{FC}$ = 14.2 Hz, C-2), 85.98 (*C*$_5$Me$_5$), 134.02 (d, $^1J_{FC}$ = 266.5 Hz, C-1). ^{19}F NMR (470.1 MHz, CD_2Cl_2, 25 °C): δ = –198.05 [d, $^3J(^{19}F,5\text{-H})$ = 3.7 Hz] vs. ext. $CFCl_3$.

(S_P)-Cp*Ru(1-Cl-2-MeC$_5$H$_3$) (14b): a) A solution of **10b** (1.890 g, 4.082 mmol) in pentane (60 mL) was treated with excess MeI (2.50 mL, 41 mmol). Workup after 13 d and as described for **13a** gave **13b** (2.47 g; 100%) as colorless solid. In the NMR spectra a second set of signals with ca. 2% relative intensity was seen indicating the presence of a second stereomer in 50:1 ratio. b) A Schlenk tube charged with **13b** (2.47 g, 4.08 mmol), THF (150 mL), and a solution of $LiAlH_4$ in THF (1 M, 6.12 mL, 6.12 mmol) was heated to reflux temperature for 50 h. After hydrolysis with water (20 mL, dropwise addition) all volatiles were removed in a vacuum. The residue was extracted with several portions of Et_2O (a total of 100 mL). The combined ethereal solutions were filtered through kieselguhr and dried with $MgSO_4$. The drying agent was filtered off and washed with diethyl ether (2 × 10 mL). Removal of the solvent left **14b** (1.14 g, 80%) as an off-white solid, contains 4% (NMR) of Cp*Ru(C$_5$H$_4$Me);[45] may be sublimed at 120 °C/10^{-6} bar, m.p. 103 °C. The compound may be recrystallized as needles by cooling pentane solutions to –30 °C. $C_{16}H_{21}ClRu$ (349.9): calcd. C 54.93, H 6.05, Cl 10.13; found C 54.73, H 6.16, Cl 9.98. MS (EI): *m/z* (%) = 350 (77) [M$^+$], 315 (100) [M$^+$ – Cl]. ^{1}H NMR (500 MHz, CD_2Cl_2, 25 °C): δ = 1.78 (s, 2-Me), 1.84 (s, Cp*), 4.02 (dd, 4-H), 4.05 (ddq, 3-H), 4.29 (dd, 5-H), $^3J_{34}$ = 2.47, $^3J_{45}$ = 2.38, $^4J_{35}$ = 1.28, ^4J(3-H,2-Me) = 0.46 Hz. ^{13}C{^{1}H} NMR (125.6 MHz, CD_2Cl_2, 25 °C): δ = 11.04 (2-Me), 11.15 (C$_5$*Me*$_5$), 70.16 (C-5), 72.73 (C-4), 73.01 (C-3), 83.36 (C-2), 86.03 (*C*$_5$Me$_5$), 92.33 (C-1).

(S_P)-Cp*Ru(1-CD$_3$–2-MeC$_5$H$_3$) (14f): a) A solution of **10f** (412 mg, 0.925 mmol) in hexane (10 mL) was treated with MeI (0.30 mL, 4.8 mmol). Workup as described for **13a** gave **13f** (0.503 g, 93%) as a colorless powder. In the NMR spectra a second set of signals with ca. 2% relative intensity was present. This was best seen for the *N*-Me group [$\delta(^1H)$ = 2.78 and 2.99 ppm, $\delta(^{13}C)$ = 41.64 and 48.83 ppm, with the low-field signals assigned to the minor stereomer]. b) The reaction of **10f** (0.503 g, 0.856 mmol) in THF (32 mL) with $LiAlH_4$ in THF (1 M, 1.28 mL, 1.28 mmol) gave, after workup as described for **14b**, the product **14f** (0.231 g, 81%) as a white solid; m.p. 95 °C. The compound may be recrystallized from very concentrated pentane solutions by cooling to –30 °C. $C_{17}H_{21}D_3Ru$ (332.5): calcd. C 61.42, H(D) 7.28 (for, 24 "H" atoms; after combustion D is detected with the same weight as H); found C 61.45, H 7.40. MS (EI): *m/z* (%) = 333 (100) [M$^+$], 318 (40) [M$^+$ – Me]. ^{1}H NMR (500 MHz, CD_2Cl_2, 25 °C): δ = 1.71 (s, 2-Me), 1.83 (s, Cp*), 3.946 (t, 4-H), 3.974 (d, 3-/5-H), $^3J_{34}$ = $^3J_{45}$ = 2.45 Hz. ^{2}H{^{1}H} NMR (61.4 MHz, CD_2Cl_2, 25 °C): δ = 1.69 (CD_3) vs. $\delta(CD_2Cl_2)$ = 5.330. ^{13}C{^{1}H} NMR (125.6 MHz, CD_2Cl_2, 25 °C): δ = 11.49 (2-Me), 11.54 (C$_5$*Me*$_5$), 70.74 (C-4), 74.36 (C-3,5), 84.36 (*C*$_5$Me$_5$), 84.53 (small, C-2), C-1 not observed; in a ^{13}C NMR spectrum (i.e. without proton decoupling) the 1-CD_3 group can be seen as a septet: δ = 10.53 [sept, $^1J(^{13}C,^2H)$ = 19.7 Hz].

Crystal Structure Determinations of 12 and of 14b: Geometry and intensity data were collected with an ENRAF-Nonius CAD4 diffractometer (Mo-*K*α radiation, 0.71073 Å, graphite monochromator). A summary of crystal data, data collection parameters and convergence results is compiled in Table 1. A numerical absorption correction[46] was applied to the intensity data of **12**, and an empirical correction based on azimuthal scans[47] to those of **14b**. The structures were solved by direct methods[48] and subsequent Fourier difference syntheses, and were refined on intensities.[49] Non-hydro-

Table 1. Crystal data, data collection parameters, and convergence results for **12** and **14b**.

	12	**14b**
Empirical formula	$C_{46}H_{70}I_2Li_2N_2O_2Ru_2$	$C_{16}H_{21}ClRu$
Formula weight	1152.86	349.85
Crystal system	monoclinic	triclinic
Space group	$P2_1$ (4)	$P\bar{1}$ (1)
a [Å]	9.0982(13)	7.610(2)
b [Å]	14.319(3)	8.298(2)
c [Å]	19.624(3)	13.361(2)
α [°]		94.21(2)
β [°]	102.888(11)	96.69(2)
γ [°]		114.46(2)
V [Å^3]	2492.2(7)	755.8(3)
Z	2	2
$d_{calcd.}$ [g/cm^3]	1.536	1.537
F(000)	1152	356
μ [mm^{-1}]	1.880	1.195
Absorption correction	Numerical	empirical
Max./min. transmission	0.93/0.49	0.73/0.58
θ range [°]	2–26	3–28
Temperature [K]	223	213
Scan mode	ω–2θ	ω–2θ
Crystal size [mm]	0.45 × 0.18 × 0.04	0.50 × 0.40 × 0.27
Reflections collected	11914	9283
unique	9746	6896
observed $I > 2\sigma(I)$	4318	6298
Variables	519	337
R_1,[a] observed (all data)	0.0779 (0.2021)	0.0562 (0.0641)
wR_2,[b] observed (all data)	0.0945 (0.1072)	0.1493 (0.1543)
GOF[c]	0.966	1.142
Max./min. resid. dens. [e/Å^3]	0.816/–0.712	2.656/–1.480

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$, where $w = 1/[\sigma^2(F_o^2) + (aP)^2]$ and $P = [\max(F_o^2,0) + 2F_c^2]/3$. [c] GOF = $[\Sigma w(F_o^2 - F_c^2)^2/\Sigma(n-p)]^{1/2}$.

gen atoms were assigned anisotropic displacement parameters and hydrogen atoms were included as riding in standard geometry. The structure of **14b** contains two symmetrically independent molecules of the same planar chirality; pseudo inversion relates the chloro substituent on one molecule to the methyl group of the other moiety and vice versa; all remaining atoms closely match a non-crystallographic inversion. It is therefore no surprise that during refinement of this structure high correlations were encountered, and that similarity and rigid bond restraints were required to ensure physically reasonable molecular geometries and displacement parameters. We note that, despite a clearly acentric intensity distribution in the diffraction pattern, refinement in the centrosymmetric super group $P\bar{1}$ initially proceeds smoothly, but converges at unsatisfactory agreement factors (wR_2 ca. 0.28), and results in apparently disordered substituents in the chloro methyl ring ligand. CCDC-272905 (for **12**) and CCDC-272906 (for **14b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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