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Pentamethylated and Pentaphenylated Azaferro- and Azaruthenocenes: Simple and General Methodology for the Preparation of Enantiopure Derivatives

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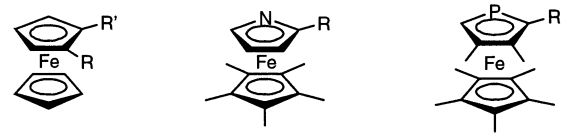
A methodology for the enantioselective synthesis of planar chiral 2-substituted 1′,2′,3′,4′,5′-pentamethylazaferro- and azaruthenocenes is reported. The key step is the introduction of an enantiopure chiral sulfoxide auxiliary via a selective *ortho*-lithiation with subsequent chromatographic separation of the resulting diastereomers. Cleaving off the sulfoxide auxiliary by treatment with *t*-BuLi generates an optically pure anion which may be quenched with a variety of electrophiles to give the optically pure azametallocene derivatives. In addition, it was attempted to extend the methodology to encompass 1′,2′,3′,4′,5′-pentaphenyl derivatives. It was, however, not possible to attach the chiral sulfoxide auxiliary onto the pentaphenylated azaferrocene, and for the azaruthenocene case, only one diastereomer could be isolated. Most importantly, the sulfoxide group could be cleaved off and the resulting chiral azaruthenocenyl anion was quenched with paraformaldehyde and iodine, resulting in products with ee values of 85% and 99%, respectively.

Introduction

The ferrocene moiety has been established as an efficient and generally applicable backbone in chiral ligands during the past decades.[1,2] The chirality of the ferrocene complex may arise from stereogenic centers or from a 1,2- or 1,3-disubstitution pattern on the ferrocene core (planar chirality), and several methods for preparing nonracemic ferrocene derivatives have been developed.[3] Planar chirality in ligands and in catalysts has been shown to be an important control element for the outcome of various enantioselective catalytic reactions as has the cooperativity between planar and central chirality.[4−10] Aza- or phosphaferrocenes require only one substituent in the 2- or 3-position for the compound to be chiral due to the presence of a heteroatom, and planar chiral aza- and phosphaferrocenyl groups have also been shown to be very efficient chiral controllers both as catalysts themselves and as ligands for catalysts.[11−21,23]



Planar Chiral Ferrocene | Planar Chiral Azaferrocene | Planar Chiral Phosphaferrocene

The versatility in applications of both azaferrocenes and phosphaferrocenes as nucleophilic catalysts and ligands has been well established, primarily through the elegant work of Fu and co-workers. Planar chiral azaferrocenes have successfully been applied as catalysts in kinetic resolution of secondary alcohols,[17] in the addition of alcohols to ketenes,[18] in the rearrangement reaction of O-acylated azalactones,[19] and as ligands in the addition of dialkylzinc and diarylzinc to aldehydes.[20] Furthermore, we are aware of one study comparing the reactivity of pentamethylated azaruthenocene with that of pentamethylated azaferrocene; however, the issue of comparing

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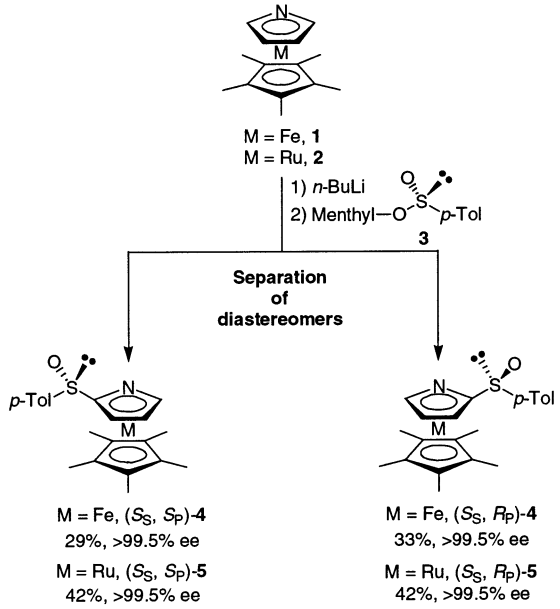
azaferrocenes and azaruthenocenes with respect to enantioselectivity was not addressed.[21] Also, a study has been published comparing planar chiral ferrocenyl ligands with ruthenocenyl equivalents in asymmetric catalysis.[22]

In ferrocene chemistry there exist several sophisticated methods for enantio- or diastereoselective synthesis,[23] but until now, no generally applicable method has been available for the preparation of optically pure azaferro- and azaruthenocenes without the use of chiral HPLC. We have thus focused our efforts on developing a synthetic methodology for the construction of such compounds in enantiomerically pure form. Here we present a simple, general, and practical method for the preparation of a multitude of novel chiral enantiopure azaferrocenyl and azaruthenocenyl compounds. The methodology is based upon the introduction of a removable chiral auxiliary to the azametallocene backbone and simple separation of the resulting diastereomers which then act as precursors to optically pure 2-azametallocenyl anions, building blocks for the preparation of a variety of enantiopure azametallocene derivatives.

Results and Discussion

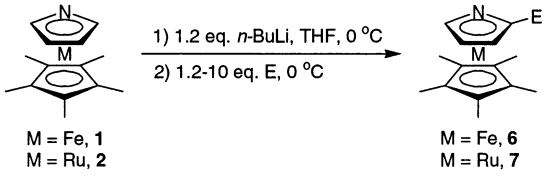
***ortho*-Lithiation Strategy.** The first step in the synthesis and resolution of the new chiral building blocks involves a regioselective *ortho*-lithiation of the pentamethylated azaferrocene **1**[17] or azaruthenocene **2**[21] giving solely the 2-lithiated isomer. Early reports on the selective *ortho*-lithiation of azaferrocenes describe problems with concomitant 1′,2-dilithiations as well as monolithiation of the Cp ring.[24−26] By using pentamethylated azaferrocenes, these problems are conveniently avoided, since only monolithiation should be possible. The anion is then trapped by the addition of (−)-(1*R*,2*S*,5*R*)-menthyl-(*S*)-*p*-toluenesulfinate (**3**), giving a mixture of two enantiopure sulfoxide diastereomers. Previous attempts to add directly lithiated metallocenes and related benzene chromium tricarbonyl complexes to **3** gave partly racemized products with ee values of 6−89%. The best procedure involved cannulation of the metalated ferrocene to a 2-fold excess of the sulfinate ester **3**, giving the product in 83% ee.[27−29] We found that, in the case of azaferrocenes, simple addition of the solid sulfinate ester **3** to the anion at −78 °C followed by warming the reaction mixture to room temperature was sufficient to get the enantiomerically pure addition products. The fact that no racemization takes place in our reactions is due, we presume, to the ortho stabilizing effect of the nitrogen atom, which ensures a clean lithiation process. The lithiation procedure was previously established by us for the azaferrocene case,[30] and we have now applied it with equal success in the azaruthenocene case. The diastereomers are easily separated by standard column chromatography, giving the enantiopure sulfoxides in total yields of 61% (29% and 32% of the two diastereomers) and 84% (42% of each diastereomer) for the azaferro- and azaruthenocene cases, respectively (Scheme 1). Furthermore, the absolute stereochemistries of the novel compounds were determined by crystal structures of azaferrocene sulfoxides (S_S,S_P)-**4** and (S_S,R_P)-**4**, which were also reported in the previous communication.[30]

SCHEME 1



To further establish the scope of the regioselective *ortho*-lithiation, racemic anions were generated by direct lithiation of the parent azametallocene **1** or **2** using *n*-BuLi at 0 °C followed by quench with a selection of electrophiles (Table 1).

TABLE 1. Scope of the Regioselective *ortho*-Lithiation and Entrapment with Electrophiles



entry	metal	electrophile, E	product	yield, %
1	Fe	I_2	**6a**	43
2	Fe	$(CH_2O)_n$	**6b**	49
3	Fe	Ph_2CO	**6c**	56
4	Fe	$ClPPh_2$	**6d**	41
5	Fe	*n*-Bu_3SnCl	**6e**	59
6	Fe	TMSCl	**6f**	60
7	Ru	I_2	**7a**	44
8	Ru	$(CH_2O)_n$	**7b**	57
9	Ru	Ph_2CO	**7c**	35
10	Ru	$ClPPh_2$	**7d**	35
11	Ru	Ph-I, cat.	**7e**	34

As evident from Table 1, a range of different complexes may be obtained using this lithiation procedure. The reactions are easily carried out, and yields are generally

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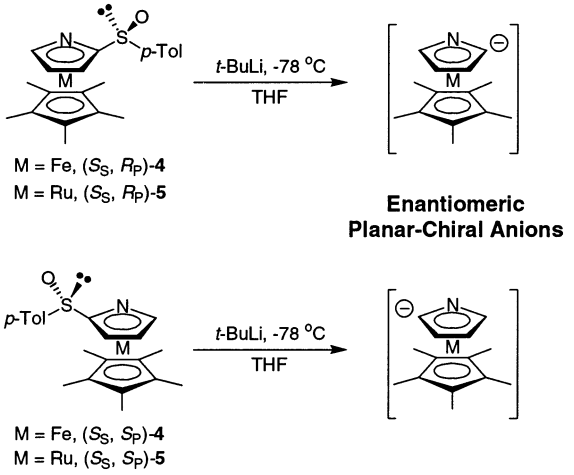
SCHEME 2

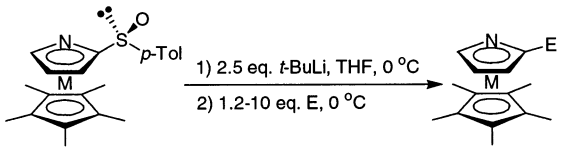


moderate. For all reactions 1.2 equiv of the electrophile gave a clean reaction within minutes at 0 °C except for the synthesis of the hydroxymethylene derivatives, where a large excess (10 equiv) of the less reactive paraformaldehyde was used in order to get a decent yield (entries 2 and 8). For the ruthenocene case it was even possible to perform a Negishi-type cross-coupling reaction with phenyl iodide (entry 11) using a $Pd_2(dba)_3/(P(2\text{-}Fur)_3)_4$ mixture as catalyst. To the best of our knowledge, this is the first example of a successful cross-coupling reaction on these compounds. It is worth mentioning that most of the derivatives prepared could not be resolved by chiral HPLC using some of the most common analytical columns (Daicel OD-H, AD, OJ), adding to the value of this novel procedure (vide infra).

Enantiopure Derivatives. After having established the scope of the regioselective *ortho*-lithiation, we set out to apply the methodology for the preparation of enantiopure derivatives. The key feature in the methodology is the generation of optically pure azametallocene anions which are stable at low temperatures. It has been demonstrated by Kagan et al. that the selective removal of the sulfoxide group from a chiral 1,2-disubstituted ferrocene can be accomplished by treatment with *tert*-butyllithium at −78 °C without any racemization.[27] A similar cleavage can be performed on our azaferro- and azaruthenocenes, yielding optically pure anions which may be trapped by various electrophiles with complete retention of enantiopurity (Scheme 2).

The same range of electrophiles was used as that for the racemic case, though it was not possible to prepare enantiopure **7e**. Our knowledge of the absolute configuration of the azaferrocene sulfoxides **4** allows us to assign absolute stereochemistry to the products obtained from quench of the optically pure anion. Since we have not been able to grow crystals of azaruthenocenes **5** suitable for X-ray structure analysis, we assign absolute stereochemistry in that series by analogy to the azaferrocene series **4** and **6a**−**f**. This is a safe approach, since the chromatographic behaviors of the two series as well as the optical rotations of the diastereoisomers are very similar. Moreover, the optical rotations of all of the enantiomerically pure derivatives prepared are of the same sign, apart from that of one ruthenocene compound with a value close to zero (see Experimental Section for details). The enantiomeric purities of all the novel metallocenes were determined where possible using standard chiral HPLC or NMR with chiral shift reagents. In all cases ee values > 99% were found, even for the reactions where the poor paraformaldehyde electrophile was used.

TABLE 2. Enantiopure Azaferro- and Azaruthenocene Derivatives



M = Fe, (S_S, S_P)-**4**
M = Fe, (S_S, R_P)-**4**
M = Ru, (S_S, S_P)-**5**
M = Ru, (S_S, R_P)-**5**

M = Fe, (S_P)-**6**
M = Fe, (R_P)-**6**
M = Ru, (S_p)-**7**
M = Ru, (R_p)-**7**

entry	metal	electrophile, E	product, yield
1	Fe	I_2	(S_p)-**6a**, 52%
			(R_p)-**6a**, 68%
2	Fe	$(CH_2O)_n$	(S_p)-**6b**, 58%
			(R_p)-**6b**, 54%
3	Fe	Ph_2CO	(S_p)-**6c**, 79%
			(R_p)-**6c**, 55%
4	Fe	$ClPPh_2$	(S_p)-**6d**, 50%
			(R_p)-**6d**, 38%
5	Fe	*n*-Bu_3SnCl	(S_p)-**6e**, 39%
			(R_p)-**6e**, 35%
6	Fe	TMSCl	(S_p)-**6f**, 74%
			(R_p)-**6f**, 60%
7	Ru	I_2	(S_p)-**7a**, 62%
			(R_p)-**7a**, 53%
8	Ru	$(CH_2O)_n$	(S_p)-**7b**, 45%
			(R_p)-**7b**, 46%
9	Ru	Ph_2CO	(S_p)-**7c**, 73%
			(R_p)-**7c**, 76%

As evident from Table 2, many different kinds of planar chiral azametallocenes are now available for the synthetic community. The simplicity and scope of the methodology, that is, generation and quench of the optically pure anion, open the possibility of preparing a wide variety of other planar chiral azametallocenes with known absolute stereochemistry and applying these as catalysts or ligands for catalysts.

Pentaphenylazametallocenes. The methodology described above allows for the easy preparation of pentamethylated azaferro- and azaruthenocene derivatives. We next wanted to explore whether it would be possible to extend the use of the methodology to encompass pentaphenylated azaferro- and azaruthenocenes, thus dramatically changing the steric bulk of the azametallocene backbone. To that end, the parent pentaphenylated azaferrocene **9** was prepared as well as the pentaphenylated azaruthenocene **12** (Scheme 3). Azaferrocene **9** was prepared in a similar way to that of **1**, that is, abstraction of the proton from pentaphenylcyclopentadiene **8** with *n*-BuLi and cannulation of the lithium salt to a suspension of $FeCl_2$ in THF, followed by addition of K-pyrrolide. Azaruthenocene **12** was prepared in a slightly different manner, namely by reaction of $[Cp^{\varphi}*Ru(CO)_2Br]$[31−32] (**10**) ($Cp^{\varphi}*$ = pentaphenylcyclopentadienyl) with K-pyrrolide.

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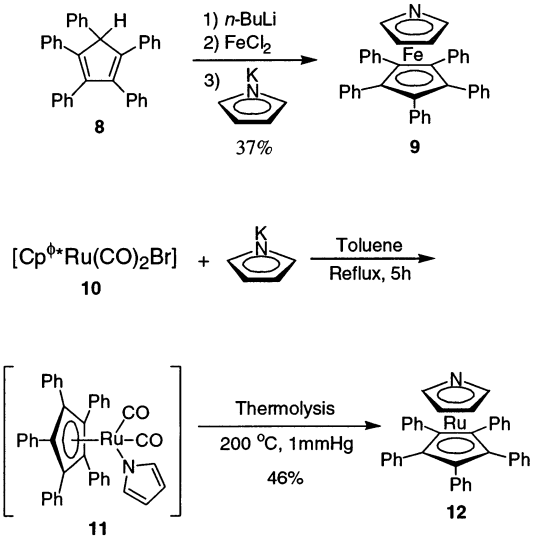
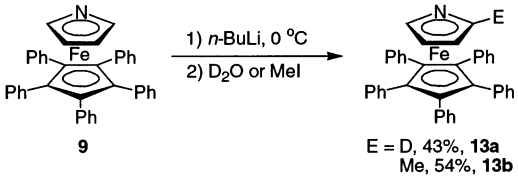
SCHEME 3



However, even prolonged reflux of a solution of [Cp$^{\varphi}$*-$Ru(CO)_2Br$] (**10**) and K-pyrrolide would only furnish pyrrolide bound η^1 to ruthenium (**11**, according to crude NMR), and solvent removal followed by thermolysis of the crude mixture was necessary to get the desired azaruthenocene in 46% yield. This is in good agreement with previously reported syntheses of the nonaza analogues pentaphenylferrocene[33−34] and pentaphenylruthenocene.[35]

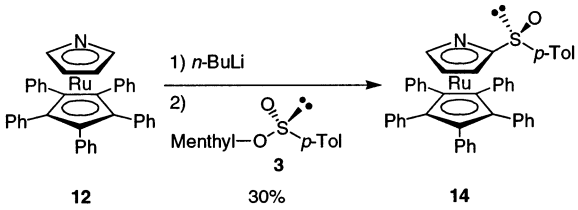
When attempting to introduce the chiral sulfoxide auxiliary to azaferrocene **9**, we found it impossible, most likely due to steric interactions from the Cp$^{\varphi}$* unit. In fact, we were able to incorporate only deuterium (**13a**) and a methyl group (**13b**), but not TMS, thus showing that the lithiation procedure works but also rendering probable that it is indeed sterics that is responsible for the impossibility of incorporating the sulfoxide auxiliary (eq 1). Also, **13b** could not be separated from unreacted



(1)

9 by normal flash chromatography and was isolated as a mixture of the two in a ratio of approximately 4:1.

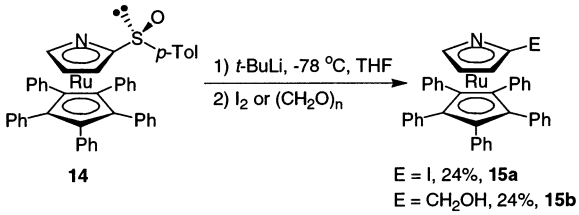
On comparing the crystal structures of the nonaza analogues 1,2,3,4,5-pentaphenylferro- and ruthenocene,[34,35] we noticed that the mean distance between the metallocene planes increases by ∼0.3 Å on going from Fe to Ru. We speculated that this increase in distance could be enough for the introduction of the sulfoxide auxiliary in the ruthenocene case. We were pleased to learn that the reaction worked well; however, we were surprised to observe that only one diastereomer could be isolated using the standard conditions established for the pentamethyl case (eq 2).[36] The diastereomer formed was



(2)

found to be enantiomerically pure according to chiral HPLC. The fact that only one diastereomer was formed may be due to a steric preference for attack of one side of the ruthenocene complex in particular. We expect the sulfur atom to possess (*S*)-stereochemistry, but the absolute stereochemistry of the planar chirality is unknown.

With the ruthenocene sulfoxide **14** in hand, what remained was to attempt cleavage of the sulfoxide group. Treatment with *t*-BuLi resulted in the expected removal of the sulfoxide moiety and generation of the chiral anion. This in turn was trapped by iodine (**15a**) and paraformaldehyde (**15b**) in yields of 24% for both cases and ee values of 99% and 85%, respectively (eq 3). To our



(3)

surprise, this was the first time we observed <99% ee in the product obtained from cleaving off the sulfoxide group. This is most probably due to the combined effects of steric hindrance from the five phenyl groups and the fact that paraformaldehyde is a rather poor electrophile under the conditions used.

Conclusion

We have developed a short and generally applicable route to planar chiral azaferro- and azaruthenocenes incorporating the Cp* (Cp* = pentamethylcyclopentadienyl) moiety. The methodology is based upon a selective *ortho*-lithiation and subsequent introduction of a chiral auxiliary to allow easy separation of the enantiopure pair of diastereomers formed in the reaction. The chiral sulfoxide auxiliary may conveniently be removed by treatment with *t*-BuLi to generate an optically pure anion which is stable at low temperatures and may be quenched with a variety of electrophiles, providing enantiopure azametallocene derivatives. Upon introducing the more sterically hindered Cp$^{\varphi}$* moiety, it was not possible to introduce the sulfoxide auxiliary in the case of the azaferrocenes. For the azaruthenocene case, introduction of the sulfoxide group gave only one diastereomer, which

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(36) Small amounts of material formed from lithiation of the phenyl groups was sometimes observed.

could be purified by normal column chromatography. The sulfoxide group could be cleaved off by standard treatment with *t*-BuLi to generate the chiral anion, which was quenched with iodine and paraformaldehyde to yield the desired pentaphenylated azaruthenocene derivatives.

The simplicity and general nature of this methodology make it an attractive route toward planar chiral azametallocenes. We expect that the overall methodology may also be applied to other related organometallic structures containing the pyrrolide or similar compounds with ortho stabilizing atoms.

Experimental Section

All reactions were carried out under an atmosphere of dry nitrogen in flame- or oven-dried glassware with magnetic stirring. All solvents were distilled prior to use. THF was distilled from sodium/benzophenone under nitrogen. *t*-BuLi (1.7 M solution in pentane), *n*-BuLi (1.6 M solution in hexane), n-Bu_3SnCl, Me_3SiCl, Ph_2PCl, iodine, benzophenone, and paraformaldehyde were purchased and used without further purification. Ph-I was distilled prior to use. Compounds **1**, **2,** and **3** were prepared according to literature procedures.[17,21,37] Purification of reaction products was carried out by flash chromatography using silica gel (0.040−0.063 mm, 230−400 mesh). Deactivation of silica gel was performed by stirring with a 2% solution of Et_3N in hexane for 5 min followed by filtration and washing with EtOAc (twice) and then hexane. The azametallocenes presented here may be purified using standard silica gel, but the inherent acidity of the silica leads to some decomposition and coloration of the column. Prior deactivation of the silica gel is therefore preferred. Analytical thin-layer chromatography was performed on Merck silica gel 60 F_{254} plates. Azaferrocenes could be seen directly as yellow-brown spots, whereas azaruthenocenes are conveniently visualized by spraying with iodine vapor.

^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were recorded on a 300 MHz NMR spectrometer at ambient temperature. Chemical shifts are reported in ppm using undeuterated solvent residues as internal standard (benzene-d_6: ^{13}C at 128.06 ppm and ^{1}H at 7.16 ppm). Multiplicity (br = broad, s = singlet, d = doublet, t = triplet, p = pentet, dd = doublet of doublets, m = multiplet), integration, and coupling constants are reported.

(S_S,S_P)-2-*p*-Tolylsulfinyl-1′,2′,3′,4′,5′-pentamethylazaferrocene, (S_S,S_P)-4, and (S_S,R_P)-2-*p*-Tolylsulfinyl-1′,2′,3′,4′,5′-pentamethylazaferrocene, (S_S,R_P)-4. 1′,2′,3′,4′,5′-Pentamethylazaferrocene (**1;** 514 mg, 2.00 mmol) was dissolved in dry THF (4 mL) in an oven-dried Schlenk tube and cooled to 0 °C. 1.1 equiv of *n*-BuLi (2.20 mmol, 1.38 mL, 1.6 M) was added dropwise via syringe and the mixture stirred for 30 min, after which time it had become a deep red suspension of the 2-lithio salt. The mixture was cooled to −78 °C, and 1.2 equiv of (−)-(1*R*,2*S*,5*R*)-menthyl (*S*)-*p*-toluenesulfinate (**3;** 711 mg, 2.4 mmol) was added in one portion to the deep red solution. After 2 min the cooling bath was removed and stirring was continued until the reaction had reached rt (15−20 min) and the solution had become homogeneous. The major part of the solvent was evaporated in vacuo and the residue then immediately worked up on a standard flash column (25% CH_2Cl_2, 25% Et_2O, 50% pentane ≫ 50% CH_2Cl_2, 50% Et_2O). The yellow-brown (S_S,S_P)-**4** isomer is contained in the first fractions using the low polarity solvent mixture. After elution of the first diastereoisomer, the solvent mixture was changed to the more polar mixture and the second product (S_S,R_P)-**4** eluted (second yellow-brown band on the column). Occasionally a third weak yellow band of **1** elutes between the two diastereoisomers. The solvent was evaporated immediately after column chromatography, since some minor precipitation occurred in the fractions containing (S_S,R_P)-**4** on prolonged standing. The two products are obtained as yellow-brown solids in a total yield of 62%: (S_S,S_P)-**4** (226 mg, 0.57 mmol, 29%) with >99.5% ee according to HPLC analysis (Daicel Chiralcel OD-H, 10% *i*-PrOH in hexane, 0.5 mL/min; t_r(major) = 12.1, t_r(minor) = 10.9 (the minor enantiomer could not be observed)) and (S_S,R_P)-**4** (263 mg, 0.67 mmol, 33%) with >99.5% ee according to HPLC analysis (Daicel Chiralcel OD-H, 10% *i*-PrO in hexane, 0.5 mL/min; t_r(minor) = 23.0 (the minor enantiomer could not be observed), t_r(major) = 26.9). Crystals suitable for X-ray analysis were obtained from a Et_2O/pentane solution stored at −15 °C.

(S_S,S_P)-**4**: ^{1}H NMR (300 MHz, benzene-d_6) δ 7.78 (d, 2H, J = 8.0), 6.77 (d, 2H, J = 7.8), 4.78 (s, 1H), 4.73 (s, 1H), 3.80 (s, 1H), 1.90 (s, 15H), 1.83 (s, 3H). ^{13}C NMR (75 MHz, benzene-d_6) δ 144.94, 140.32, 129.73, 124.29, 113.52, 94.37, 82.74, 76.29, 69.06, 21.02, 10.94. MS (EI): *m*/*z* (%) 395 (M^+, 41), 379 (53), 314 (32), 189 (57), 133 (57), 119 (100), 91 (62). $[\alpha]^{20}_D$ = +315 (benzene, c = 0.24).

(S_S,R_P)-**4**: ^{1}H NMR (300 MHz, benzene-d_6) δ 7.67 (d, 2H, J = 7.8), 6.77 (d, 2H, J = 7.8), 4.81 (s, 1H), 4.10 (s, 1H), 3.77 (s, 1H), 1.90 (s, 15H), 1.85 (s, 3H). ^{13}C NMR (75 MHz, benzene-d_6) δ 144.28, 140.29, 129.63, 125.01, 112.69, 94.67, 83.17, 76.27, 73.59, 21.07, 11.12. MS (EI): *m*/*z* (%) 395 (M^+, 16), 379 (79), 314 (14), 189 (60), 133 (48), 119 (100), 91 (59). $[\alpha]^{20}_D$ = +625 (benzene, c = 0.13).

In a similar manner the racemates of the two diastereoisomers were prepared using a 50:50 mixture of (+)- and (−)-**3**.

(S_S,S_P)-2-*p*-Tolylsulfinyl-1′,2′,3′,4′,5′-pentamethylazaruthenocene, (S_S,S_P)-5, and (S_S,R_P)-2-*p*-Tolylsulfinyl-1′,2′,3′,4′,5′-pentamethylazaruthenocene, (S_S,R_P)-5. 1′,2′,3′,4′,5′-Pentamethylazaruthenocene (**2**; 250 mg, 0.826 mmol) was dissolved in dry THF (3 mL) in an oven-dried Schlenk tube and cooled to 0 °C. 1.1 equiv of *n*-BuLi (0.992 mmol, 0.62 mL, 1.6 M) was added dropwise via syringe and the mixture stirred for 30 min to give a yellow suspension of the 2-lithio salt. The mixture was cooled to −78 °C, and 1.2 equiv of (−)-(1*R*,2*S*,5*R*)-menthyl (*S*)-*p*-toluenesulfinate (**3;** 292.1 mg, 0.992 mmol) was added in one portion to the yellow suspension. After 2 min the cooling bath was removed, and stirring was continued until the reaction had reached rt (15−20 min) and the solution had become homogeneous. The solvent was evaporated in vacuo and the residue then immediately worked up on a standard flash column (deactivated silica, CH_2Cl_2/EtOAc/pentane 1:1:8 ≫ CH_2Cl_2/EtOAc 1:9). The yellow (S_S,S_P)-**5** isomer is contained in the first fractions, and the second product (S_S,R_P)-**5** is collected after changing to the high polarity mixture. Occasionally a third weak band of **2** elutes between the two diastereoisomers. The solvent was evaporated immediately after column chromatography, and the two products are obtained as yellow solids in a total yield of 84%: (S_S,S_P)-**5** (151.5 mg, 0.34 mmol, 42%) with >99.5% ee according to HPLC analysis (Daicel Chiralcel OD-H, 10% *i*-PrOH in hexane, 0.5 mL/min; t_r(major) = 11.2 (the minor enantiomer was not observed)) and (S_S,R_P)-**5** (151.8 mg, 0.34 mmol, 42%) with >99.5% ee according to HPLC analysis (Daicel Chiralcel OD-H, 10% *i*-PrOH in hexane, 0.5 mL/min; t_r(major) = 31.5 (the minor enantiomer was not observed)).

(S_S,S_P)-**5**: ^{1}H NMR (300 MHz, benzene-d_6) δ 7.81 (d, 2H, J = 8.1), 7.77 (d, 2H, J = 8.1), 5.25 (d, 1H, J = 0.7), 5.16 (d, 1H, J = 2.3), 4.24 (m, 1H), 1.88 (s, 18H). ^{13}C NMR (75 MHz, benzene-d_6) δ 145.2, 140.3, 129.8, 124.3, 116.2, 96.1, 87.4, 78.0, 72.2, 21.1, 11.8. MS (EI): *m*/*z* (%) 443 (M + 2, 48), 441 (M^+, 91), 440 (M − 1, 60), 439 (M − 2, 43), 438 (M − 3, 35), 435 (M − 6, 14), 362 (44), 360 (77), 359 (44), 358 (37), 357 (32), 354 (20), 237 (59), 235 (79), 233 (100), 231 (99), 230 (72), 229 (59), 228 (59), 227 (38), 91 (39). HRMS: Calcd for $C_{21}H_{25}NORuS$ 441.0700, found 441.0691. $[\alpha]^{20}_D$ = +258 (benzene, c = 0.19).

(S_S,R_P)-**5**: ^{1}H NMR (300 MHz, benzene-d_6) δ 7.77 (d, 2H, J = 8.4), 6.84 (d, 2H, J = 8.4), 5.23 (d, 1H, J = 0.7), 4.65 (dd, 1H, J = 2.2, 0.7), 4.25 (dd, 1H, J = 2.2, 0.7), 1.89 (s, 18H). ^{13}C NMR (75 MHz, benzene-d_6) δ 143.9, 140.3, 129.6, 125.2, 116.1,

(37) Solladié, G. *Synthesis* **1981**, 185−196.

96.4, 87.7, 77.7, 75.9, 21.1, 11.9. MS (EI): *m/z* (%) 443 (M + 2, 49), 441 (M^+, 86), 440 (M − 1, 60), 439 (M − 2, 37), 438 (M − 3, 33), 435 (M − 6, 13), 362 (42), 360 (68), 359 (51), 358 (37), 357 (30), 354 (20), 237 (60), 235 (75), 233 (99), 231 (100), 230 (72), 229 (59), 228 (49), 227 (33), 91 (30). HRMS: Calcd for $C_{21}H_{25}NORuS$ 441.0700, found 441.0699. $[\alpha]^{20}_D = +440$ (benzene, $c = 0.20$).

General Procedure for the Synthesis of Racemic Azaferrocene and Azaruthenocene Derivatives. 1′,2′,3′,4′,5′-Pentamethylazametallocene **1** (50 mg, 0.194 mmol) or **2** (50 mg, 0.165 mmol) was dissolved in THF (1 mL) in a Schlenk tube and cooled to 0 °C. *n*-BuLi (1.2 equiv, 1.6 M in hexane) was added dropwise via syringe and the solution stirred for 30 min, after which time the electrophile was added either neat (1.2 equiv: *n*-Bu_3SnCl, $ClPPh_2$, TMSCl, Ph_2CO. 10 equiv: $(CH_2O)_n$) or as a solution in dry THF (0.5 mL) (I_2). The reaction mixture was stirred for an additional 30 min at 0 °C, after which time the product was worked up by flash column chromatography using suitable mixtures of Et_2O/pentane or EtOAc/hexane as eluent (5% MeOH in EtOAc was used for **6b** and **7b**).

2-Iodo-1′,2′,3′,4′,5′-pentamethylazaferrocene (6a). Yield, 32.3 mg (0.084 mmol, 43%); orange solid. ^{1}H NMR (300 MHz, benzene-d_6) δ 4.69 (s, 1H), 3.96 (s, 1H), 3.60 (s, 1H), 1.70 (s, 15H). ^{13}C NMR (75 MHz, benzene-d_6) δ 93.4, 82.1, 80.3, 75.9, 65.8, 10.4. MS (EI): *m/z* (%) 383 (M^+, 100), 255 (13), 134 (78), 119 (91).

2-Hydroxymethyl-1′,2′,3′,4′,5′-pentamethylazaferrocene (6b). Yield, 27.5 mg (0.096 mmol, 49%); orange solid. ^{1}H NMR (300 MHz, benzene-d_6) δ 5.03 (br s, 1H), 4.80 (d, 1H, $J = 12.2$), 4.68 (s, 1H), 4.66 (d, 1H, $J = 12.2$), 3.86 (d, 1H, $J = 2.1$), 3.72 (d, 1H, $J = 2.1$), 1.77 (s, 15H). ^{13}C NMR (75 MHz, benzene-d_6) δ 105.7, 91.5, 81.1, 75.7, 72.7, 59.8, 10.9. MS (EI): *m/z* (%) 287 (M^+, 24), 269 (68), 190 (100), 188 (48), 174 (20), 134 (26), 119 (26).

2-Diphenylhydroxymethyl-1′,2′,3′,4′,5′-pentamethylazaferrocene (6c). Yield, 47.7 mg (0.109 mmol, 56%); orange solid. ^{1}H NMR (300 MHz, benzene-d_6) δ 7.88 (d, 2H, $J = 6.9$ Hz), 7.0 (m, 8H), 4.86 (s, 1H), 4.77 (s, 1H), 4.09 (s, 1H), 3.90 (s, 1H), 1.60 (s, 15H). ^{13}C NMR (75 MHz, benzene-d_6) δ 151.2, 146.0, 127.9, 127.8, 127.6, 127.4, 126.9, 126.7, 113.9, 91.5, 81.4, 77.9, 76.0, 71.9, 11.1. MS (EI): *m/z* (%) 439 (M^+, 3), 421 (33), 304 (78), 287 (29), 231 (58), 230 (100), 119 (37), 105 (31), 77 (22).

2-Diphenylphosphinyl-1′,2′,3′,4′,5′-pentamethylazaferrocene (6d). Yield, 35.0 mg (0.080 mmol, 41%); orange solid. ^{1}H NMR (300 MHz, benzene-d_6) δ 8.00 (m, 2H), 7.70 (m, 2H), 7.18 (m, 6H), 5.25 (s, 1H), 4.14 (s, 1H), 4.11 (s, 1H), 1.84 (s, 15H). ^{13}C NMR (75 MHz, benzene-d_6) δ 140.4 (d, $J_{C-P} = 12.0$), 139.5 (d, $J_{C-P} = 12.0$), 134.9 (d, $J_{C-P} = 20.2$), 134.5 (d, $J_{C-P} = 20.2$), 128.8, 128.7, 128.5, 128.2 (C_{para}-hidden in solvent signals), 96.4 (d, $J_{C-P} = 5.7$), 81.4, 78.8, 78.6, 76.9, 11.1. MS (EI): *m/z* (%) 441 (M^+, 100), 307 (24), 256 (26), 229 (20), 173 (25), 133 (37).

2-Tri-*n*-butylstannyl-1′,2′,3′,4′,5′-pentamethylazaferrocene (6e). Yield, 62.8 mg (0.115 mmol, 59%); orange oil. ^{1}H NMR (300 MHz, benzene-d_6) δ 5.19 (s, 1H), 4.04 (dd, 1H, $J = 2.2$, 0.9), 3.93 (d, 1H, $J = 2.2$), 1.86 (s, 15H), 1.74 (m, 6H), 1.45 (m, 6H), 1.30 (m, 6H), 0.97 (t, 9H, $J = 7.4$). ^{13}C NMR (75 MHz, benzene-d_6) δ 99.1, 96.8, 80.9, 80.3, 76.1, 29.7, 27.9, 14.0, 11.6, 10.8. MS (EI): *m/z* (%) 547 (M^+, 41), 545 (34), 543 (20), 490 (37), 488 (28), 486 (15), 376 (100), 374 (82), 372 (41), 257 (63), 255 (33), 253 (26), 186 (39), 184 (25), 182 (15), 133 (54), 119 (28).

2-Trimethylsilyl-1′,2′,3′,4′,5′-pentamethylazaferrocene (6f). Yield, 38.4 mg (0.117 mmol, 60%); orange solid. ^{1}H NMR (300 MHz, benzene-d_6) δ 5.14 (s, 1H), 4.00 (s, 1H), 3.91 (s, 1H), 1.80 (s, 15H), 0.41 (s, 9H). ^{13}C NMR (75 MHz, benzene-d_6) δ 97.8, 97.4, 78.8, 77.1, 11.5, −0.2. MS (EI): *m/z* (%) 329 (M^+, 100), 190 (66), 188 (53), 174 (30), 133 (25).

2-Iodo-1′,2′,3′,4′,5′-pentamethylazaruthenocene (7a). Yield, 31.0 mg (0.072 mmol, 44%); light brown solid. ^{1}H NMR (300 MHz, benzene-d_6) δ 5.17 (s, 1H), 4.58 (dd, 1H, $J = 2.1$, 0.7), 4.10 (dd, 1H, $J = 2.1$, 1.0), 1.74 (s, 15H). ^{13}C NMR (75 MHz, benzene-d_6) δ 95.9, 86.4, 83.8, 77.9, 59.5, 11.2. MS (EI): *m/z* (%) 431 (M + 2, 57), 429 (M^+, 100), 428 (M − 1, 57), 427 (M − 2, 48), 426 (M − 3, 41), 423 (M − 6, 21), 304 (22), 302 (56), 300 (66), 298 (55), 297 (48), 296 (40), 294 (23), 293 (15), 234 (29), 232 (39), 231 (57), 230 (48). HRMS: Calcd for $C_{14}H_{18}INRu$ 428.9527, found 428.9541.

2-Hydroxymethyl-1′,2′,3′,4′,5′-pentamethylazaruthenocene (7b). Yield, 31.2 mg (0.094 mmol, 57%); off-white solid. ^{1}H NMR (300 MHz, benzene-d_6) δ 5.37 (br s, 1H, −OH), 5.28 (s, 1H), 4.58 (d, 1H, $J = 12.4$), 4.50 (d, 1H, $J = 2.1$), 4.45 (d, 1H, $J = 12.4$), 4.29 (dd, 1H, $J = 2.1$, 0.7), 1.79 (s, 15H). ^{13}C NMR (75 MHz, benzene-d_6) δ 109.8, 93.6, 85.7, 77.4, 76.0, 59.7, 11.8. MS (EI): *m/z* (%) 335 (M + 2, 32), 333 (M^+, 67), 332 (M − 1, 34), 331 (M − 2, 37), 330 (M − 3, 29), 327 (M − 6, 10), 256 (41), 254 (71), 253 (42), 252 (29), 238 (47), 236 (100), 234 (87), 233 (76), 232 (61), 230 (57).

2-Diphenylhydroxymethyl-1′,2′,3′,4′,5′-pentamethylazaruthenocene (7c). Yield, 28.1 mg (0.058 mmol, 35%); off-white solid. ^{1}H NMR (300 MHz, benzene-d_6) δ 7.83 (d, 2H, $J = 7.8$), 7.60 (d, 2H, $J = 7.8$), 7.10 (m, 6H), 5.25 (d, 1H, $J = 0.9$), 4.66 (dd, 1H, $J = 2.4$, 0.9), 4.33 (dd, 1H, $J = 2.4$, 0.9), 4.20 (s, 1H), 1.69 (s, 15H). ^{13}C NMR (75 MHz, benzene-d_6) δ 149.9, 146.4, 127.8, 127.8, 127.4, 127.7, 126.9, 126.8, 119.7, 93.5, 86.1, 77.6, 77.5, 75.9, 11.9. MS (EI): *m/z* (%) 485 (M^+, 3), 469 (20), 467 (42), 466 (33), 465 (22), 461 (6), 234 (37), 232 (100), 230 (30).

2-Diphenylphosphinyl-1′,2′,3′,4′,5′-pentamethylazaruthenocene (7d). Yield, 28 mg (0.058 mmol, 35%); light brown solid. ^{1}H NMR (300 MHz, benzene-d_6) δ 8.04 (dt, 2H, $J = 8.1$, 1.2), 7.63 (dt, 2H, $J = 8.1$, 1.2), 7.06 (m, 6H), 5.56 (s, 1H), 4.65 (d, 1H, $J = 2.2$), 4.44 (dd, 1H, $J = 2.2$, 0.9), 1.72 (s, 15H). ^{13}C NMR (75 MHz, benzene-d_6) δ 141.1 (d, $J_{C-P} = 11.4$), 139.1 (d, $J_{C-P} = 11.4$), 135.1 (d, $J_{C-P} = 20.8$), 133.7 (d, $J_{C-P} = 19.5$), 128.8, 128.5, 128.2, 128.1, 102.3, 102.2, 98.1 (d, $J_{C-P} = 5.3$), 86.0, 82.1 (d, $J_{C-P} = 25.5$), 78.4, 78.4, 11.9, 11.9. MS (EI): *m/z* (%) 489 (M + 2, 53), 487 (M^+, 97), 486 (100), 485 (68), 484 (53), 483 (27), 481 (18), 412 (9), 410 (20), 408 (13), 404 (7), 304 (10), 302 (18), 300 (13), 235 (13), 234 (18), 231 (25), 228 (18), 183 (19), 172 (24).

2-Phenyl-1′,2′,3′,4′,5′-pentamethylazaruthenocene (7e). Pentamethylazaruthenocene (**2;** 50 mg, 0.165 mmol) was dissolved in THF (1 mL). *n*-BuLi (0.12 mL, 1.6 M, 0.198 mmol, 1.2 equiv) was added dropwise at 0 °C, giving a yellow suspension of the 2-lithio salt, which was stirred for 30 min before addition of a solution of $ZnCl_2$ (0.40 mL, 0.5 M in THF, 0.198 mmol, 1.2 equiv). The resulting clear yellow solution was stirred for another 10 min before Ph-I (40.4 mg, 0.198 mmol, 1.2 equiv) and a preformed solution of $Pd_2(dba)_3$ (8.54 mg, 8.25 μmol, 10 mol %) and P(2-furyl)$_3$ (7.66 mg, 0.033 mmol) in dry THF (0.5 mL) were added. The reaction mixture was allowed to reach rt before heating to a gentle reflux for 1 h. The reaction mixture was then applied directly to column chromatographic workup (deactivated silica, hexane/EtOAc 4:1) to give 21.2 mg of **7e** (0.056 mmol, 34%) as a light brown solid.

^{1}H NMR (300 MHz, benzene-d_6) δ 7.77 (dd, 2H, $J = 8.4$, 1.5), 7.22 (m, 2H), 7.05 (m, 1H), 5.52 (s, 1H), 4.92 (dd, 1H, $J = 2.2$, 0.6), 4.56 (dd, 1H, $J = 2.2$, 0.9), 1.64 (s, 15H). ^{13}C NMR (75 MHz, benzene-d_6) δ 136.4, 128.5, 126.5, 125.2, 107.0, 94.8, 85.4, 77.8, 73.0, 11.3. MS (EI): *m/z* (%) 381 (M + 2, 44), 379 (M^+, 83), 377 (55), 376 (51), 375 (23), 373 (14), 234 (17), 232 (21), 231 (18), 190 (15), 143 (22), 115 (33), 84 (100). HRMS: Calcd for $C_{20}H_{23}NRu$ 379.0874, found 379.0870.

General Procedure for the Synthesis of Enantiopure Azametallocene Derivatives. (−)-(S_P)-2-Iodo-1′,2′,3′,4′,5′-pentamethylazaferrocene, (−)-(S_P)-6a. (S_S,S_P)-**4** (36 mg, 0.091 mmol) was dissolved in THF and cooled to −78 °C. 2.5 equiv of *t*-BuLi (0.23 mmol, 0.134 mL, 1.7 M) was added dropwise via syringe and the brownish suspension stirred 5 min before adding iodine (57.8 mg, 0.23 mmol in 0.5 mL of THF). The brown-black homogeneous solution was worked up

by flash column chromatography (20%−50% Et_2O in pentane). Yield, 18.0 mg (0.047 mmol, 52%) with 99% ee according to HPLC analysis (Daicel Chiralcel OD-H, 10% *i*-PrOH in hexane, 0.5 mL/min; t_r(minor) = 11.1, t_r(major) = 13.7).

^{1}H NMR (300 MHz, benzene-d_6) δ 4.69 (s, 1H), 3.96 (s, 1H), 3.60 (s, 1H), 1.70 (s, 15H). ^{13}C NMR (75 MHz, benzene-d_6) δ 93.4, 82.1, 80.3, 75.9, 65.8, 10.4. MS (EI): *m*/*z* (%) 383 (M^+, 100), 255 (13), 134 (78), 119 (91). $[\alpha]^{20}_D$ = −88 (benzene, *c* = 0.35).

(+)-(R_P)-2-Iodo-1′,2′,3′,4′,5′-pentamethylazaferrocene, (+)-(R_P)-6a. (S_S,R_P)-**4** (36 mg, 0.091 mmol) was used in the synthesis, giving 23.6 mg (0.062 mmol, 68%) of (+)-(R_P)-**6a** with 99% ee according to HPLC analysis (Daicel Chiralcel OD-H, 10% *i*-PrOH in hexane, 0.5 mL/min; t_r(major) = 10.8, t_r(minor) = 13.7). $[\alpha]^{20}_D$ = +77 (benzene, *c* = 0.12).

(+)-(S_P)-2-Hydroxymethyl-1′,2′,3′,4′,5′-pentamethylazaferrocene, (+)-(S_P)-6b. (S_S,S_P)-**4** (30 mg, 0.076 mmol) was used in the synthesis, giving 12.6 mg (0.044 mmol, 58%) of (+)-(S_P)-**6b** with 98% ee according to HPLC analysis (Daicel Chiralcel OD-H, 10% *i*-PrOH in hexane, 0.5 mL/min; t_r(major) = 11.4, t_r(minor) = 20.1).

^{1}H NMR (300 MHz, benzene-d_6) δ 5.03 (br s, 1H), 4.80 (d, 1H, *J* = 12.3), 4.68 (s, 1H), 4.66 (d, 1H, *J* = 12.2), 3.86 (d, 1H, *J* = 2.1), 3.72 (d, 1H, *J* = 2.1), 1.77 (s, 15H). ^{13}C NMR (75 MHz, benzene-d_6) δ 105.7, 91.5, 81.0, 75.7, 72.7, 59.8, 10.9. MS (EI): *m*/*z* (%) 287 (M^+, 24), 269 (68), 190 (100), 188 (48), 174 (20), 134 (26), 119 (26). HRMS: Calcd for $C_{15}H_{21}FeNO$ 287.0973, found 287.0972. $[\alpha]^{20}_D$ = +50 (benzene, *c* = 0.11).

(−)-(R_P)-2-Hydroxymethyl-1′,2′,3′,4′,5′-pentamethylazaferrocene, (−)-(R_P)-6b. (S_S,R_P)-**4** (50 mg, 0.126 mmol) was used in the synthesis, giving 17.5 mg (0.068 mmol, 54%) of (−)-(R_P)-**6b**. HRMS: Calcd for $C_{15}H_{21}FeNO$ 287.0973, found 287.0971. $[\alpha]^{20}_D$ = −49 (benzene, *c* = 0.28).

(+)-(S_P)-2-Diphenylhydroxymethyl-1′,2′,3′,4′,5′-pentamethylazaferrocene, (+)-(S_P)-6c. (S_S,S_P)-**4** (100 mg, 0.253 mmol) was used in the synthesis, giving 87.7 mg (0.200 mmol, 79%) of (+)-(S_P)-**6c**. ^{1}H NMR (300 MHz, benzene-d_6) δ 7.88 (dd, 2H, *J* = 8.4, 1.5), 7.23−6.86 (m, 8H), 4.90 (s, 1H), 4.78 (s, 1H), 4.09 (dd, 1H, *J* = 2.4, 0.6), 3.90 (dd, 1H, *J* = 2.4, 0.6), 1.60 (s, 15H). ^{13}C NMR (75 MHz, benzene-d_6) δ 151.2, 146.1, 127.9, 127.8, 127.6, 127.5, 126.9, 126.7, 113.9, 91.5, 81.3, 77.8, 76.0, 71.8, 11.1. MS (EI): *m*/*z* (%) 439 (M^+, 3), 421 (28), 305 (20), 304 (99), 231 (53), 230 (100), 119 (34), 105 (26), 77 (21). HRMS: Calcd for $C_{27}H_{29}FeNO$ 439.1599, found 439.1597. $[\alpha]^{20}_D$ = +159 (benzene, *c* = 0.39).

(−)-(R_P)-2-Diphenylhydroxymethyl-1′,2′,3′,4′,5′-pentamethylazaferrocene, (−)-(R_P)-6c. (S_S,R_P)-**4** (100 mg, 0.253 mmol) was used in the synthesis, giving 60.9 mg (0.139 mmol, 55%) of (−)-(R_P)-**6c**. HRMS: Calcd for $C_{27}H_{30}FeNO$ (M + H) 440.1677, found 440.1667. $[\alpha]^{20}_D$ = −146 (benzene, *c* = 0.32).

(−)-(S_P)-2-Diphenylphosphinyl-1′,2′,3′,4′,5′-pentamethylazaferrocene, (−)-(S_P)-6d. (S_S,S_P)-**4** (50 mg, 0.126 mmol) was used in the synthesis, giving 28.0 mg (0.063 mmol, 50%) of (−)-(S_P)-**6d**. ^{1}H NMR (300 MHz, benzene-d_6) δ 7.91 (t, 2H, *J* = 6.6), 7.60 (t, 2H, *J* = 6.6), 7.08 (m, 6H), 5.15 (s, 1H), 4.04 (s, 1H), 4.00 (s, 1H), 1.74 (s, 15H). ^{13}C NMR (75 MHz, benzene-d_6) δ 140.5 (d, J_{C-P} = 11.5), 139.4 (d, J_{C-P} = 11.5), 134.9 (d, J_{C-P} = 20.2), 134.5 (d, J_{C-P} = 20.2), 128.8, 128.7, 128.5, 128.2, 99.4, 96.4 (d, J_{C-P} = 5.5), 81.4, 78.9 (d, J_{C-P} = 18.3), 76.9, 76.9, 11.2, 11.1. MS (EI): *m*/*z* (%) 441 (M^+, 100), 307 (24), 256 (26), 133 (41). HRMS: Calcd for $C_{26}H_{28}FeNP$ 441.1309, found 441.1309. $[\alpha]^{20}_D$ = −35 (benzene, *c* = 0.26).

(+)-(R_P)-2-Diphenylphosphinyl-1′,2′,3′,4′,5′-pentamethylazaferrocene, (+)-(R_P)-6d. (S_S,R_P)-**4** (50 mg, 0.126 mmol) was used in the synthesis, giving 21.2 mg (0.048 mmol, 38%) of (+)-(R_P)-**6d**. HRMS: Calcd for $C_{26}H_{28}FeNP$ 441.1309, found 441.1305. $[\alpha]^{20}_D$ = +26 (benzene, *c* = 0.26).

(−)-(S_p)-2-Tri-*n*-butylstannyl-1′,2′,3′,4′,5′-pentamethylazaferrocene, (−)-(S_P)-6e. (S_S,S_P)-**4** (50 mg, 0.126 mmol) was used in the synthesis, giving 26.7 mg (0.049 mmol, 39%) of (−)-(S_P)-**6e**. ^{1}H NMR (300 MHz, benzene-d_6) δ 5.20 (s, 1H), 4.05 (d, 1H, *J* = 2.1 Hz), 3.93 (d, 1H, *J* = 2.1), 1.87 (s, 15H), 1.73 (m, 6H), 1.44 (sextet, 6H, *J* = 7.2), 1.31 (p, 6H, *J* = 7.2), 0.97 (t, 9H, *J* = 7.2). ^{13}C NMR (75 MHz, benzene-d_6) δ 99.2, 97.0, 80.9, 80.3, 76.1, 29.7, 27.9, 14.0, 11.6, 10.9. MS (EI): *m*/*z* (%) 547 (M^+, 27), 490 (26), 376 (100), 257 (63), 186 (37), 133 (48). HRMS: Calcd for $C_{26}H_{45}NFeSn$ 547.1923, found 547.1924. $[\alpha]^{20}_D$ = −61 (benzene, *c* = 0.27).

(+)-(R_P)-2-Tri-*n*-butylstannyl-1′,2′,3′,4′,5′-pentamethylazaferrocene, (+)-(R_P)-6e. (S_S,R_P)-**4** (50 mg, 0.126 mmol) was used in the synthesis, giving 24.1 mg (0.044 mmol, 35%) of (+)-(R_P)-**6e**. HRMS: Calcd for $C_{26}H_{45}NFeSn$ 547.1923, found 547.1906. $[\alpha]^{20}_D$ = +49 (benzene, *c* = 0.28).

(−)-(S_P)-2-Trimethylsilyl-1′,2′,3′,4′,5′-pentamethylazaferrocene, (−)-(S_P)-6f. (S_S,S_P)-**4** (50 mg, 0.126 mmol) was used in the synthesis, giving 30.8 mg (0.094 mmol, 74%) of (−)-(S_P)-**6f**. ^{1}H NMR (300 MHz, benzene-d_6) δ 5.14 (s, 1H), 4.00 (d, 1H, *J* = 1.8), 3.91 (d, 1H, *J* = 1.8), 1.80 (s, 15H), 0.42 (s, 9H). ^{13}C NMR (75 MHz, benzene-d_6) δ 97.8, 97.5, 80.2, 78.7, 77.1, 11.5, −0.2. MS (EI): *m*/*z* (%) 329 (M^+, 100), 190 (93), 188 (60), 174 (34), 133 (23). HRMS: Calcd for $C_{17}H_{27}FeNSi$ 329.1262, found 329.1264. $[\alpha]^{20}_D$ = −108 (benzene, *c* = 0.37).

(+)-(R_P)-2-Trimethylsilyl-1′,2′,3′,4′,5′-pentamethylazaferrocene, (+)-(R_P)-6f. (S_S,R_P)-**4** (50 mg, 0.126 mmol) was used in the synthesis, giving 24.4 mg (0.075 mmol, 60%) of (+)-(R_P)-**6f**. HRMS: Calcd for $C_{17}H_{27}FeNSi$ 329.1262, found 329.1267. $[\alpha]^{20}_D$ = +126 (benzene, *c* = 0.27).

(−)-(S_P)-2-Iodo-1′,2′,3′,4′,5′-pentamethylazaruthenocene, (−)-(S_P)-7a. (S_S,S_P)-**5** (50 mg, 0.113 mmol) was used in the synthesis, giving 30.2 mg (0.071 mmol, 62%) of (−)-(S_P)-**7a**. ^{1}H NMR (300 MHz, benzene-d_6) δ 5.17 (s, 1H), 4.59 (dd, 1H, *J* = 2.2, 0.6), 4.10 (dd, 1H, *J* = 2.2, 0.9), 1.74 (s, 15H). ^{13}C NMR (75 MHz, benzene-d_6) δ 95.9, 86.4, 83.8, 77.9, 59.5, 11.2. MS (EI): *m*/*z* (%) 431 (M + 2, 53), 429 (M^+, 100), 428 (M − 1, 56), 427 (M − 2, 47), 426 (M − 3, 38), 423 (M − 6, 22), 304 (18), 302 (41), 300 (51), 298 (48), 297 (39), 296 (31), 232 (36), 231 (48), 230 (42), 150 (16), 149 (24), 148 (22). HRMS: Calcd for $C_{14}H_{18}INRu$ 428.9527, found 428.9517. $[\alpha]^{20}_D$ = −47 (benzene, *c* = 0.29).

(+)-(R_P)-2-Iodo-1′,2′,3′,4′,5′-pentamethylazaruthenocene, (+)-(R_P)-7a. (S_S,R_P)-**5** (50 mg, 0.113 mmol) was used in the synthesis, giving 25.8 mg (0.060 mmol, 53%) of (+)-(R_P)-**7a**. HRMS: Calcd for $C_{14}H_{18}INRu$ 428.9527, found 428.9535. $[\alpha]^{20}_D$ = +46 (benzene, *c* = 0.29).

(S_P)-2-Hydroxymethyl-1′,2′,3′,4′,5′-pentamethylazaruthenocene, (S_P)-7b. (S_S,S_P)-**5** (100 mg, 0.227 mmol) was used in the synthesis, giving 33.6 mg (0.101 mmol, 45%) of (S_P)-**7b** with 99% ee according to HPLC analysis (Daicel Chiralcel OD-H, 10% *i*-PrOH in hexane, 0.8 mL/min; t_r(major) = 6.5, t_r(minor) = 12.3). ^{1}H NMR (300 MHz, benzene-d_6) δ 5.22 (s, 1H), 5.20 (br s, 1H, −OH), 4.55 (d, 1H, *J* = 12.3, CHOH), 4.49 (d, 1H, *J* = 1.8), 4.47 (d, 1H, *J* = 12.3, CHOH), 4.28 (d, 1H, *J* = 1.8), 1.81 (s, 15H). ^{13}C NMR (75 MHz, benzene-d_6) δ 109.7, 93.6, 85.7, 77.4, 75.8, 59.9, 11.8. MS (EI): *m*/*z* (%) 335 (M + 2, 31), 333 (M^+, 61), 332 (M − 1, 36), 331 (M − 2, 33), 330 (M − 3, 28), 327 (10), 256 (35), 254 (60), 253 (37), 252 (26), 251 (25), 238 (46), 236 (100), 234 (82), 233 (78), 230 (56), 228 (33). HRMS: Calcd for $C_{15}H_{21}NORu$ 333.0667, found 333.0680. $[\alpha]^{20}_D$ = 0 (benzene, *c* = 0.21).

(+)-(R_P)-2-Hydroxymethyl-1′,2′,3′,4′,5′-pentamethylazaruthenocene, (+)-(R_P)-7b. (S_S,R_P)-**5** (50 mg, 0.113 mmol) was used in the synthesis, giving 17.4 mg (0.052 mmol, 46%) of (+)-(R_P)-**7b** with 99% ee according to HPLC analysis (Daicel Chiralcel OD-H, 10% *i*-PrOH in hexane, 0.8 mL/min; t_r(major) = 12.3, t_r(minor) = 6.5). HRMS: Calcd for $C_{15}H_{21}NORu$ 333.0667, found 333.0671. $[\alpha]^{20}_D$ = +9 (benzene, *c* = 0.20).

(+)-(S_P)-2-Diphenylhydroxymethyl-1′,2′,3′,4′,5′-pentamethylazaruthenocene, (+)-(S_P)-7c. (S_S,S_P)-**5** (100 mg, 0.227 mmol) was used in the synthesis, giving 80.0 mg (0.166 mmol, 73%) of (+)-(S_P)-**7c**. ^{1}H NMR (300 MHz, benzene-d_6) δ 7.83 (d, 2H, *J* = 7.2), 7.56 (d, 2H, *J* = 7.2), 7.14 (m, 10H), 5.19 (s, 1H), 4.66 (d, 1H, *J* = 2.4), 4.44 (s, 1H), 4.33 (d, 1H, *J* = 2.4), 1.70 (s, 15H). ^{13}C NMR (75 MHz, benzene-d_6) δ 150.0, 146.5, 127.9, 127.8, 127.7, 127.4, 126.9, 126.8, 119.5, 93.4, 86.1,

77.6, 77.4, 75.8, 11.9. MS (EI): *m*/*z* (%) 469 (M + 2, 29), 467 (M^+, 54), 466 (M − 1, 43), 465 (M − 2, 30), 464 (M − 4, 23), 461 (M − 6, 9), 236 (26), 234 (39), 233 (46), 232 (100), 230 (37), 183 (12), 105 (13), 77 (17). HRMS: Calcd for $C_{27}H_{30}NORu$ (M + H) 486.1371, found 486.1358. $[\alpha]^{20}_D = +57$ (benzene, *c* = 0.46).

(−)-(*R*$_P$)-2-Diphenylhydroxymethyl-1′,2′,3′,4′,5′-pentamethylazaruthenocene, (−)-(*R*$_P$)-7c. (*S*$_S$,*R*$_P$)-**5** (100 mg, 0.227 mmol) was used in the synthesis, giving 84.0 mg (0.173 mmol, 76%) of (−)-(*R*$_P$)-**7c**. HRMS: Calcd for $C_{27}H_{29}NORu$ 485.1293, found 485.1294. $[\alpha]^{20}_D = -67$ (benzene, *c* = 0.38).

1′,2′,3′,4′,5′-Pentaphenylazaferrocene (9). Pentaphenylcyclopentadiene **8** (1.85 g, 4.14 mmol) was dissolved in dry toluene (40 mL) and heated to 100 °C. *n*-BuLi (2.85 mL 1.6 M, 4.56 mmol) was added dropwise, during which a tan solid precipitated. After stirring for 30 min, the oil bath was removed and the solvent removed under reduced pressure. The resulting solid was dissolved in dry THF (20 mL) under nitrogen to give a clear brown solution which was slowly cannulated into a suspension of $FeCl_2$ in THF (20 mL). The reaction mixture was stirred for 1 h, after which time a suspension of K-pyrrolide in THF (10 mL) was slowly added. The brown solution was stirred for 1 h and then filtered through a short silica column which was rinsed with EtOAc until no more orange color was visible. The solvents were removed in vacuo and the resulting solid purified by flash column chromatography (CH_2Cl_2/hexane 1:1 ≫ CH_2Cl_2). Yield: 0.877 g (1.54 mmol, 37%) of an orange solid.

^{1}H NMR (300 MHz, benzene-d_6) δ 7.37 (m, 10H), 6.96 (m, 15H), 5.35 (s, 2H), 4.32 (s, 2H). ^{13}C NMR (75 MHz, benzene-d_6) δ 135.8, 132.9, 127.9, 126.9, 96.1, 88.5, 78.4. MS (EI): *m*/*z* (%) 569 (M + 2, 14), 567 (M^+, 100), 499 (5), 446 (8). Anal. Calcd for $C_{39}H_{29}FeN$: C, 82.54; H, 5.15; N, 2.47. Found C, 82.42; H, 5.28; N, 2.36.

1′,2′,3′,4′,5′-Pentaphenylazaruthenocene (12). [Cp$^{\varphi}$*Ru(CO)$_2$Br] (**10**; 1.00 g, 1.47 mmol) was placed in a Schlenk tube with K-Pyrrolide (308 mg, 2.93 mmol, 2 equiv), and dry toluene (10 mL) was added. The resulting suspension was refluxed for 5 h, during which time the suspension turned orange-brown in color. The solvent was removed in vacuo and the solid residue placed in a 200 °C oil bath under vacuum (2 mmHg) for 1 h. The resulting grayish solid was worked up by column chromatography (deactivated silica, CH_2Cl_2/hexane 1:1≫ CH_2Cl_2 ≫ 5% EtOAc in CH_2Cl_2) to give a tan solid. Yield: 400 mg (0.652 mmol, 45%).

^{1}H NMR (300 MHz, benzene-d_6) δ 7.31 (m, 10H), 6.90 (dd, 15H, *J* = 1.8, 5.1), 5.69 (s, 2H), 4.69 (s, 2H). ^{13}C NMR (75 MHz, benzene-d_6) δ 135.4, 133.1, 127.7, 127.0, 98.4, 94.4, 80.6. MS (EI): *m*/*z* (%) 615 (M + 2, 58), 613 (M^+, 100), 612 (M − 1, 83), 611 (M − 2, 56), 610 (M − 3, 40), 607 (M − 6, 14), 547 (6), 545 (14), 543 (13). HRMS: Calcd for $C_{39}H_{29}NRu$ 613.1343, found 613.1332.

2-Deutero-1′,2′,3′,4′,5′-Pentaphenylazaferrocene (13a). 1′,2′,3′,4′,5′-Pentaphenylazaferrocene (**9**; 50 mg, 0.088 mmol) was placed in a Schlenk tube and dissolved in THF (1.5 mL). The solution was cooled to 0 °C, and *n*-BuLi (0.106 mmol, 0.076 mL, 1.4 M, 1.2 equiv) was added dropwise via syringe. The reaction mixture was stirred for 25 min, giving a dark red-brown solution before addition of D_2O (8.8 mg, 0.44 mmol). Stirring was continued for 2 h while the temperature gradually reached room temperature. The solvent was removed in vacuo and the residue directly worked up by column chromatography (deactivated silica, CH_2Cl_2/hexane 1:1 ≫ CH_2Cl_2) to give **13a** as a red solid. Yield: 21.5 mg (43%). Data given for **13a:** ^{1}H NMR (300 MHz, benzene-d_6) δ 7.37 (m, 10H), 6.96 (m, 15H), 5.35 (s, 1H), 4.32 (s, 2H).

2-Methyl-1′,2′,3′,4′,5′-Pentaphenylazaferrocene (13b). 1′,2′,3′,4′,5′-Pentaphenylazaferrocene (**9**; 50 mg, 0.088 mmol) was placed in a Schlenk tube and dissolved in THF (1.5 mL). The solution was cooled to 0 °C, and *n*-BuLi (0.106 mmol, 0.076 mL, 1.4 M, 1.2 equiv) was added dropwise via syringe. The reaction mixture was stirred for 25 min, giving a dark red-brown solution before addition of MeI (62.5 mg, 0.44 mmol, 27 μL). Stirring was continued for 2 h while the temperature gradually reached room temperature. The solvent was removed in vacuo and the residue directly worked up by column chromatography (deactivated silica, CH_2Cl_2/hexane 1:1 ≫ CH_2Cl_2) to give a mixture of **13b** and **9** (4:1) as a red solid. Yield: 27.6 mg. Data given for **13b**: ^{1}H NMR (300 MHz, benzene-d_6) δ 7.38 (m, 10H), 6.96 (m, 15H), 5.36 (s, 1H), 4.33 (d, 1H, *J* = 2.1), 4.14 (s, 1H), 2.06 (s, 3H). ^{13}C NMR (75 MHz, benzene-d_6) δ 135.7, 132.9, 127.9, 126.9, 107.0, 95.1, 88.2, 79.0, 76.7, 14.1. MS (EI): *m*/*z* (%) 581 (M^+, 100), 567 (15), 501 (15), 365 (12), 289 (22). HRMS: Calcd for $C_{40}H_{31}FeN$ 581.1806, found 581.1818.

2-*p*-Tolylsulfinyl-1′,2′,3′,4′,5′-pentaphenylazaruthenocene (14). 1′,2′,3′,4′,5′-Pentaphenylazaruthenocene **12** (197 mg, 0.322 mmol) was placed in a Schlenk tube and dissolved in THF (3 mL). The solution was cooled to 0 °C, and *n*-BuLi (0.39 mmol, 0.24 mL, 1.6 M, 1.2 equiv) was added dropwise. The reaction mixture was stirred for 25 min, giving a dark red-brown solution which was cooled to −78 °C followed by addition of (−)-(1*R*,2*S*,5*R*)-menthyl (*S*)-*p*-toluenesulfinate (**3;** 113.8 mg, 0.386 mmol, 1.2 equiv). Stirring was continued at −78 °C for 30 min, after which time the cooling bath was removed, allowing the reaction mixture to reach room temperature. The solvent was removed in vacuo and the residue directly worked up by column chromatography (deactivated silica, CH_2Cl_2 ≫ 5% EtOAc in CH_2Cl_2) to give **14** as a yellow solid with >99.5% ee according to HPLC analysis (Daicel Chiralcel OD-H, 20% *i*-PrOH in hexane, 0.5 mL/min; t_r(major) = 18.9, t_r(minor) = 13.3 (according to racemic sample, the enantiomer was not observed)). Yield: 72.9 mg (0.097 mmol, 30%).

^{1}H NMR (300 MHz, benzene-d_6) δ 7.46 (d, 2H, *J* = 8.4), 7.31 (m, 10H), 6.92 (m, 15H), 6.80 (d, 2H, *J* = 8.4), 5.57 (s, 1H), 4.84 (d, 1H, *J* = 2.2), 4.57 (dd, 1H, *J* = 2.2, 0.7), 1.93 (s, 3H). ^{13}C NMR (75 MHz, benzene-d_6) δ 143.0, 141.1, 134.5, 133.1, 129.9, 128.6, 127.8, 127.3, 126.0, 119.0, 100.6, 95.5, 82.4, 78.2, 21.2. MS (EI): *m*/*z* (%) 753 (M + 2, 30), 751 (M^+, 51), 736 (62), 735 (100), 734 (79), 733 (61), 671 (27), 669 (45), 668 (28), 545 (25), 367 (20), 91 (30). HRMS: Calcd for $C_{46}H_{35}NORuS$ 751.1483, found 751.1488. $[\alpha]^{20}_D = +47$ (benzene, *c* = 0.49).

General Procedure for the Synthesis of Enantiopure Pentaphenylated Azaruthenocene Derivatives. (+)-2-Iodo-1′,2′,3′,4′,5′-pentaphenylazaruthenocene (15a). Sulfoxide **14** (50 mg, 0.067 mmol) was dissolved in THF (1.5 mL) and cooled to −78 °C before treatment with *t*-BuLi (0.102 mL, 1.65 M, 0.17 mmol, 2.5 equiv) for 5 min. I_2 (42.2 mg, 0.17 mmol) was then added, and after stirring another 5 min, the solution was allowed to warm to room temperature. After stirring for 1 h at room temperature, the solvent was evaporated and the residue directly applied to flash column chromatography (CH_2Cl_2/hexane 1:1 ≫ CH_2Cl_2) to afford 11.9 mg (0.016 mmol, 24%) of a pale yellow solid with 99% ee according to HPLC analysis (Daicel Chiralcel OD-H, 1% *i*-PrOH in hexane, 0.8 mL/min; t_r(major) = 18.8, t_r(minor) = 11.6).

^{1}H NMR (300 MHz, benzene-d_6) δ 7.26 (m, 10H), 6.92 (m, 15H), 5.42 (d, 1H, *J* = 0.7), 4.85 (m, 1H), 4.40 (m, 1H). ^{13}C NMR (75 MHz, benzene-d_6) δ 134.4, 133.0, 127.8, 127.2, 99.3, 95.1, 87.4, 82.0, 66.1. MS (EI): *m*/*z* (%) 741 (M + 2, 53), 739 (M^+, 100), 738 (M − 1, 57), 736 (M − 3, 33), 733 (M − 6, 13), 612 (13), 306 (22). HRMS: Calcd for $C_{39}H_{28}INRu$ 739.0310, found 739.0324. $[\alpha]^{20}_D = +159$ (benzene, *c* = 0.21).

(+)-2-Hydroxymethyl-1′,2′,3′,4′,5′-pentaphenylazaruthenocene (15b). Sulfoxide **14** (42.1 mg, 0.056 mmol) was used in the synthesis, giving 8.7 mg (0.0135 mmol, 24%) of (+)-**15b** as a tan solid with 85% ee according to HPLC analysis (Daicel Chiralcel OD-H, 10% *i*-PrOH in hexane, 0.5 mL/min; t_r(major) = 17.8, t_r(minor) = 11.1). ^{1}H NMR (300 MHz, benzene-d_6) δ 7.28 (m, 10H), 6.89 (m, 15H), 5.58 (s, 1H), 4.92 (d, 1H, *J* = 1.8), 4.65 (d, 1H, *J* = 1.8), 4.55 (dd, 1H, *J* = 12.9, 5.4), 4.45 (dd, 1H, *J* = 12.9, 6.7), 2.33 (t, 1H, *J* = 6.0, −OH). ^{13}C NMR (75 MHz, benzene-d_6) δ 135.1, 132.9, 127.9, 127.1,

113.6, 97.7, 94.3, 81.7, 79.0, 60.2. MS (EI): *m*/*z* (%) 645 (M + 2, 37), 643 (M^+, 69), 642 (M − 1, 42), 641 (M − 2, 41), 640 (M − 3, 26), 637 (M − 6, 9), 566 (29), 564 (52), 545 (39), 543 (31), 542 (23), 463 (10), 363 (18), 96 (69), 80 (33), 28 (100). HRMS: Calcd for $C_{40}H_{31}NORu$ 643.1449, found 643.1460. $[\alpha]^{20}_D = +53$ (benzene, $c = 0.77$).

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Supporting Information Available: ^1H and ^{13}C NMR spectra for compounds **5** (both diastereomers), **6b**−**6f** (both enantiomers), and **7a**−**7c** (both enantiomers), racemic **7d** and **7e**, and compounds **9**, **12**, **13a**−**b**, **14**, and **15a**−**b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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