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New chiral ruthenium(II)–phosphinite complexes containing a ferrocenyl group in enantioselective transfer hydrogenations of aromatic ketones

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ABSTRACT

A new and versatile class of unsymmetrical ferrocenyl-phosphinite ligands possessing a stereogenic center has been prepared from commercially available, inexpensive aminoacids such as, D-, L-phenylglycine and D-, L-phenylalanine, through a concise synthetic procedure. These ligands are not very sensitive to air and moisture, and display good enantioselectivities in the ruthenium-catalyzed asymmetric transfer hydrogenation of acetophenone derivatives, in which up to 91% ee was obtained. A comparison of the catalytic properties of amino alcohols and other analogues based on a ferrocenyl backbone is also discussed briefly. The structures of these ligands and their corresponding complexes have been elucidated by a combination of multinuclear NMR spectroscopy, IR spectroscopy, and elemental analysis.

1. Introduction

The asymmetric reduction of ketones is a pivotal reaction for the preparation of chiral alcohols,[1] which form an extremely important class of intermediates for fine chemicals and pharmaceuticals.[2] Catalytic asymmetric synthesis using chiral metal complexes as catalyst precursors offers an ideal method for reducing ketones to chiral alcohols.[3] Over the past ten years, an efficient method has been developed for the catalytic transfer hydrogenation of ketones using chiral Rh(III), Ir(III), Ru(II), or lanthanoid complexes as catalyst precursors and *iso*-PrOH/KOH or HCOOH/Et_3N as a hydride source.[4] In particular, ruthenium(II)-catalyzed asymmetric transfer hydrogenation (ATH) has recently received much attention due to its operational simplicity and the use of non-hazardous hydrogen donors.[5]

Ferrocene ligands have attracted much attention due to their chemical features, namely diastereoselective metallation on the cyclopentadienyl ring[6] and retentive nucleophilic displacement at the benzylic position,[7] which allow for the preparation of a broad range of substituted derivatives. We have reported on the synthesis of new phosphinite ligands[8] and their application in ruthenium-catalyzed transfer hydrogenation reactions.[9] With the aim of designing an efficient and recoverable phosphinite ligands for the asymmetric transfer hydrogenations of ketones, we designed and synthesized a series of novel ferrocenyl-phosphinites and their Ru(II) complexes. Although some ferrocenyl amino alcohols, diamines, and phosphines have been employed successfully as ligands in the Ru(II)-promoted transfer hydrogenation of ketones,[10] a screening of catalytic activities of ferrocenyl-phosphinites in this reaction has not yet been reported. To the best of our knowledge, there is no report on the utility of these complexes including chiral phosphinites based on the ferrocenyl moiety in ruthenium catalyzed transfer hydrogenation reactions. On the basis of previous work,[12,13] we here report the results obtained in the asymmetric transfer hydrogenation of ketones using chiral phosphinite ligands based on the ferrocenyl moiety, possessing central chirality, as ligands. The synthesis and full characterization of neutral ruthenium(II)–phosphinites complexes are also reported.

2. Results and discussion

2.1. Synthesis and characterization of the amino alcohols, phosphinites, and their ruthenium(II) complexes

Initially, the synthesis of D-, L-phenylglycinol and D-, L-phenylalaninol was accomplished in one step from D-, L-phenylglycine or D-, L-phenylalanine according to procedures described in the literature,[11] using $NaBH_4$–I_2 in dry THF. The ferrocene based amino alcohols **1**–**4** were prepared by a condensation reaction, followed by reductive amination between ferrocenecarboxaldehyde[12] and the corresponding amino alcohols in the presence of a base catalyst as illustrated in Scheme 1. The ^1H NMR spectra of compounds **1**–**4** showed characteristic features: the α- and β-cyclopentadienyl

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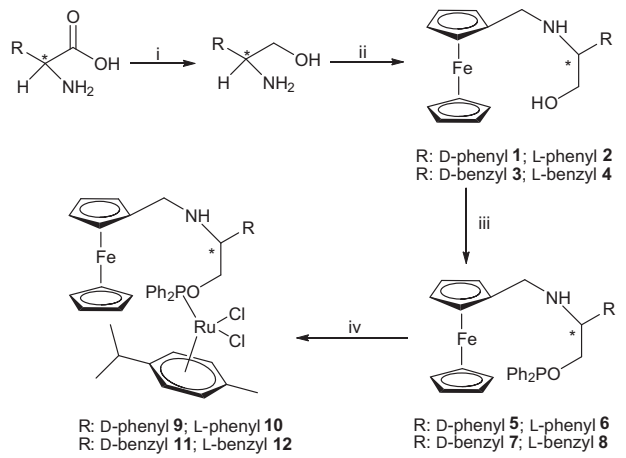


Scheme 1. Reagents and conditions: (i) $NaBH_4$–I_2, THF; (ii) ferrocenecarboxaldehyde, K_2CO_3, $CHCl_3$, $NaBH_4$, 1.5 h, for **1**–**4**; (iii) 1 equiv Ph_2PCl, 1 equiv Et_3N, toluene for **5**–**8**; (iv) 1/2 equiv $[Ru(\eta^6\text{-}p\text{-cymene})(\mu\text{-Cl})Cl]_2$, toluene for **9**–**12**.

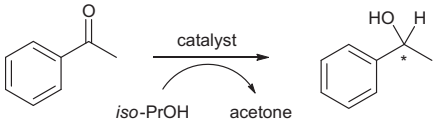
protons in the amino alcohols with relatively small non-resolved multiplets appeared at approximately δ 4.00–4.50 ppm. The magnetic non-equivalence of protons, which is caused by the diastereotopicity of the alpha and beta protons of ferrocene, as well as those of the carbon atoms of the monosubstituted Cp (cyclopentadienyl) ring was observed. The $^{13}C\text{-}\{^1H\}$ NMR spectra also exhibited the signals typical for monosubstituted ferrocenes. The structures of these ferrocene based chiral amino alcohols were consistent with the data obtained from ^1H NMR, ^{13}C NMR, IR spectra, and elemental analyses (for further details see Section 4).

Chiral phosphinite ligands **5**–**8** based on the ferrocenyl group, were synthesized by hydrogen abstraction from the described ferrocene based chiral amino alcohols **1**–**4**, by a base (Et_3N) and the subsequent reaction with 1 equiv of Ph_2PCl in anhydrous toluene under an inert argon atmosphere, respectively (Scheme 1). The progress of this reaction was conveniently followed by $^{31}P\text{-}\{^1H\}$ NMR spectroscopy. The signal of the starting material PPh_2Cl at δ 81.0 ppm disappeared and a new singlet appeared downfield due to the phosphinite ligands. The $^{31}P\text{-}\{^1H\}$ NMR spectra of **5**–**8** showed no unexpected features. The $^{31}P\text{-}\{^1H\}$ NMR spectra of the free ligands were[13] in agreement with the values previously observed for similar compounds, respectively.[14] A solution of the ligands in $CDCl_3$, prepared under anaerobic conditions, was stable up to 24 h and then decomposed very slowly to give an oxide and the hydrolysis product diphenylphosphinous acid, $Ph_2P(O)H$.[15] Furthermore, the $^{31}P\text{-}\{^1H\}$ NMR spectrum also displayed the formation of PPh_2PPh_2 and $P(O)Ph_2PPh_2$, as indicated by signals at approximately δ −15.6 ppm as a singlet and δ 35.4 ppm and δ −21.8 ppm as doublets with $^1J_{(PP)}$ 220 Hz, respectively, after 48 h.[16] The assignment of the ^1H chemical shifts was derived from 2D HH-COSY spectra and the appropriate assignment of the ^{13}C chemical shifts from DEPT and 2D HMQC spectra. Again, the magnetic non-equivalence of the protons as well as the carbon atoms of the monosubstituted Cp ring was observed (see Section 4). All products were fully characterized by spectroscopic methods: ^1H, ^{13}C NMR, IR spectra, and elemental analysis.

All of the ruthenium complexes were readily synthesized in good yields. The starting ruthenium(II) complex, $[Ru(\eta^6\text{-}p\text{-cymene})(\mu\text{-Cl})Cl]_2$, was prepared from the reaction of commercially available α-phellandrene (5-isopropyl-2-methylcyclohexa-1,3-diene) with $RuCl_3$.[17] Treatment of $[Ru(\eta^6\text{-}p\text{-cymene})(\mu\text{-Cl})Cl]_2$ with phosphinites **5**–**8** in 0.5:1 molar ratio in toluene resulted in the formation of mononuclear complexes **9**–**12** as orange-red crystalline solids. The reactions between Ru(II) precursor and phosphinite ligands were not affected by the molar ratio of $[Ru(\eta^6\text{-}p\text{-cymene})(\mu\text{-Cl})Cl]_2$ or the steric and electronic properties of the donor phosphorus atoms. The initial color change, that is, from clear orange to deep red, was attributed to the dimer cleavage most probably caused by the phosphinite ligand.[18] All of the complexes were isolated as indicated by singlets in the $^{31}P\text{-}\{^1H\}$ NMR spectra at δ 112.14, 112.46, 112.20, and 111.56 ppm for **9**–**12**, respectively, in line with the values previously observed for similar compounds.[19] The $^{31}P\text{-}\{^1H\}$ NMR spectra of the complexes showed single resonances at approximately δ 112 ppm with a coordination shift of approximately δ 3.0 ppm. In the ^1H and ^{13}C spectra of complexes **9**–**12**, the characteristic signals of mono- and unsubstituted ferrocene unit were observed.[20] The ^1H, ^{13}C NMR, IR spectroscopic data, and the elemental analysis data of the complexes were consistent with the proposed structures (see Section 4).

2.2. Asymmetric transfer hydrogenation of acetophenone derivatives with *iso*-PrOH

The encouraging performance of many ferrocene based bidendate phosphorus–chelate ligands[21] in recent years has led to a renewed interest in the development of chiral monodendate phosphorus containing ligands for their use in asymmetric hydrogenation reactions.[22] This resurgence in monodendate ligands is due to the ready accessibility of a range of diverse ligand structures, and often their lower cost compared to bidendate ligands.[23] Additionally, the most important advantage of chiral phosphinite ligands over the corresponding phosphorus-based ligands is the ease of preparation, which has led to substantial interest in the development of highly effective chiral monodendate phosphinite ligands for asymmetric catalysis.[24] Encouraged by our recent success in the development of new chiral and highly active ligands,[25] we initiated a study of the synthesis of a series of monodendate ferrocene based chiral phosphinite ligands, and investigated their efficiency in Ru(II)-catalyzed asymmetric transfer hydrogenations (Scheme 2).



Scheme 2. Hydrogen transfer from *iso*-PrOH to acetophenone.

In a preliminary study, these chiral complexes **9**–**12** were tested as catalyst precursors for the asymmetric transfer hydrogenation of acetophenone by *iso*-PrOH and the results are shown in Table 1. Catalytic experiments were carried out under an Ar atmosphere using standard Schlenk-line techniques. These systems catalyzed the reduction of acetophenone to the corresponding alcohol (*S*)-, (*R*)-1-phenylethanol in the presence of KOH as a promoter. To an *iso*-PrOH solution of Ru(II)-monodendate phosphinite complex, an appropriate amount of acetophenone and KOH/*iso*-PrOH solutions was added at room temperature. The solution was stirred for several hours and then monitored with capillary GC analysis. At room temperature, the transfer hydrogenation of acetophenone occurred very slowly[26] with low conversion (up to 15%, 24 h) and moderate to high enantioselectivity (up to 90% ee) (entries 1–4). During this period, the color changed from orange to deep red. Carrying out this reaction at room temperature and prolonging the reaction time (72 h) led to a slight decrease in enantioselectivity, as indicated by the catalytic results collected with **9**–**12** (entries 1 and 2[d]). Furthermore, as can be inferred from Table 1 (entries 5–8) the presence of a base is necessary to observe appreciable conversions. The choice of base, such as KOH and NaOH, had little influence on the conversion and enantioselectivity (entries 9 and

Table 1
Transfer hydrogenation of acetophenone with *iso*-PrOH catalyzed by Ru-ferrocenyl based monodendate phosphinite complexes **9**–**12**

Entry	Complex	S/C/KOH	Time	Conversion[f] (%)	ee[g] %	Configuration[h]	TOF[i] (h^{-1})
1	**9**[a]	100:1:5	24 h (72 h)[d]	10 (48)[d]	85 (81)[d]	(*R*)	>5
2	**10**[a]	100:1:5	24 h (72 h)[d]	15 (45)[d]	90 (88)[d]	(*S*)	>5
3	**11**[a]	100:1:5	24 h	11	86	(*R*)	>5
4	**12**[a]	100:1:5	24 h	9	82	(*S*)	>5
5	**9**[b]	100:1	1 h	<5	—	—	>5
6	**10**[b]	100:1	1 h	<5	—	—	>5
7	**11**[b]	100:1	1 h	<5	—	—	>5
8	**12**[b]	100:1	1 h	<5	—	—	>5
9	**9**[c]	100:1:5	20 min (20 min)[e]	99 (97)[e]	79 (78)[e]	(*R*)	297 (291)
10	**10**[c]	100:1:5	20 min (20 min)[e]	98 (97)[e]	83 (81)[e]	(*S*)	294 (291)
11	**11**[c]	100:1:5	30 min	99	70	(*R*)	198
12	**12**[c]	100:1:5	30 min	97	77	(*S*)	194
13	**10**	100:1:3[j]	20 min	95	77	(*R*)	285
14	**10**	100:1:5[k]	20 min	98	83	(*S*)	294
15	**10**	100:1:7[l]	20 min	94	79	(*R*)	282
16	**10**	100:1:9[m]	20 min	92	72	(*S*)	276

[a] Reaction conditions: At room temperature; acetophenone/Ru/KOH, 100:1:5.
[b] Refluxing in *iso*-PrOH; acetophenone/Ru, 100:1, in the absence of base.
[c] Refluxing in *iso*-PrOH; acetophenone/Ru/KOH, 100:1:5.
[d] At room temperature; acetophenone/Ru/KOH, 100:1:5, (72 h).
[e] Refluxing in *iso*-PrOH; acetophenone/Ru/NaOH, 100:1:5.
[f] Determined by GC (three independent catalytic experiments).
[g] Determined by capillary GC analysis using a chiral cyclodex B (Agilent) capillary column.
[h] Determined by comparison of the retention times of the enantiomers on the GC traces with literature values, an (*S*)- or (*R*)-configuration was obtained in all experiments.
[i] TOF = (mol product/mol cat.) × h^{-1}.
[j] Refluxing in *iso*-PrOH; acetophenone/Ru/KOH, 100:1:3.
[k] Refluxing in *iso*-PrOH; acetophenone/Ru/KOH, 100:1:5.
[l] Refluxing in *iso*-PrOH; acetophenone/Ru/KOH, 100:1:7.
[m] Refluxing in *iso*-PrOH; acetophenone/Ru/KOH, 100:1:9.

10[e]). In addition, optimization studies of the catalytic reduction of acetophenone in *iso*-PrOH showed that good activity was obtained with a base/ligand ratio of 5:1 (entries 13–16).

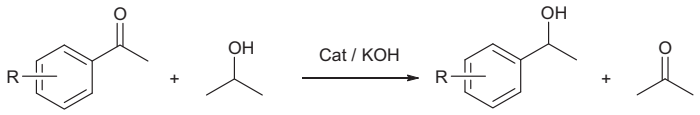
The reduction of acetophenone into (*S*)- or (*R*)-1-phenylethanol could be achieved in high yield by increasing the temperature up to 82 °C (Table 1, entries 9–12). Chiral phosphinite ligands containing a ferrocenyl moiety with an amino (NH) moiety showed much higher activity and enantioselectivity. A similar tendency was reported in earlier studies,[27] indicating that the NH functional moiety in the ligand played an important role in the ruthenium(II)–ligand catalytic system by H-bonding. The higher activity and enantioselectivity of the amino containing phosphinite ligand may also be due to the fact that the NH moiety can stabilize the catalytic transition state.[28] Furthermore, it is noteworthy that the catalytic systems **9**–**12** display the differences in reactivity. These results indicate that the structure of the monodendate phosphinite ligands is a crucial factor for accelerating the reaction. Compared to the other complexes, [(2*R*)-,(2*S*)-2-(ferrocenylmethylamino)-2-phenylethyldiphenylphosphinito(dichloro(η^6-*p*-cymene)ruthenium(II))], **9**–**10** appear to provide a more effective chiral environment around the ruthenium atom due to the presence of the phenyl moiety and the configuration. From these results, it could be reasonably argued that the absolute configuration of the product is governed by the ligand chirality (probably via chirality transfer to the metal).

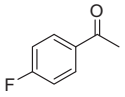
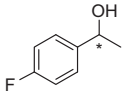
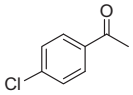
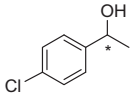
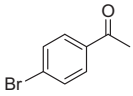
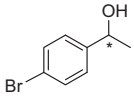
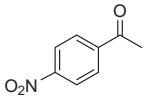
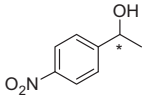
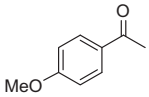
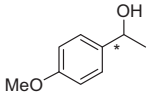
Due to its efficiency in the transfer hydrogenation of acetophenone, complexes **9**–**12** were further investigated in the transfer hydrogenation of substituted acetophenone derivatives; the results are summarized in Table 2. The catalytic reduction of acetophenone derivatives was tested with the conditions optimized for acetophenone. The results in Table 2 demonstrate that a range of acetophenone derivatives can be hydrogenated with good to high enantioselectivities. Complex **10** showed the highest activity with good enantioselectivity for most of the ketones listed in Table 2. Furthermore, the position and electronic properties of the ring substituents also influenced the hydrogenation results. The highest enantioselectivity was found for the transfer hydrogenation of *o*-methoxyacetophenone (91% ee). The introduction of electron-withdrawing substituents, such as F or NO_2, at the *para*-positions of the aryl ring of the ketone resulted in improved activity with good enantioselectivity (Table 2, entries 1–4, 13–16). The introduction of electron withdrawing substituents at the *para*-position of the aryl ring of the ketone decreased the electron density of the C=O bond so that the activity was improved, giving rise to easier hydrogenation.[29] The lowest enantioselectivity was observed in the transfer hydrogenation of *p*-methoxyacetophenone, which is probably due to the strong electron-donating effect of the methoxy group on the aryl ring of the ketone. The introduction of an electron-donating group such as methoxy group to the *p*-position decelerates the reaction, but introduced at the *o*-position, it increased the rate and improved the enantioselectivity. These results show that the activity and enantioselectivity of the Ru(II) catalysts are also sensitive to the substrate structure.

3. Conclusion

In conclusion, the work presented here explores the scope of Ru(II)-phosphinite ligands based on ferrocenyl moiety catalysts. These catalyst systems are effective for the asymmetric transfer hydrogenation (ATH) of acetophenone derivatives. High yields and moderate to good enantioselectivities were obtained by using the complexes as catalysts. The facile synthesis of the ligands and catalysts provides a useful method for the modular design of this type of compounds. Furthermore, the simplicity and efficiency make it an excellent choice of catalyst for the practical preparation of highly valued alcohols via the catalytic asymmetric transfer hydrogenation of ketones. Further studies of these ligands in catalytic reactions are currently underway.

Table 2
Asymmetric transfer hydrogenation results for substituted acetophenones catalyzed by Ru-ferrocenyl based monodendate phosphinite complexes **9**–**12**[a]



Entry	Catalyst	Substrate	Product	Time (min)	Conv[b]. (%)	ee[c] (%)	TOF[d] (h^{-1})	Config.[e]
1	**9**			15	97	74	388	(*R*)
2	**10**			15	98	80	392	(*S*)
3	**11**			20	98	76	294	(*R*)
4	**12**			20	96	72	288	(*S*)
5	**9**			20	98	75	294	(*R*)
6	**10**			20	99	80	297	(*S*)
7	**11**			30	97	78	194	(*R*)
8	**12**			30	98	74	196	(*S*)
9	**9**			20	98	73	294	(*R*)
10	**10**			20	99	79	297	(*S*)
11	**11**			30	98	74	196	(*R*)
12	**12**			30	99	75	198	(*S*)
13	**9**			15	98	77	392	(*R*)
14	**10**			15	98	81	392	(*S*)
15	**11**			20	98	75	294	(*R*)
16	**12**			20	97	72	291	(*S*)
17	**9**			30	96	80	192	(*R*)
18	**10**			30	99	91	198	(*S*)
19	**11**			60	98	82	98	(*R*)
20	**12**			60	98	73	98	(*S*)
21	**9**			60	96	70	96	(*R*)
22	**10**			60	99	79	99	(*S*)
23	**11**			120	98	67	49	(*R*)
24	**12**			120	97	63	49	(*S*)

[a] Catalyst (0.005 mmol), substrate (0.5 mmol), *iso*-PrOH (5 mL), KOH (0.025 mmol %), 82 °C, the concentration of acetophenone is 0.1 M.
[b] The purity of compounds was checked by NMR and GC (three independent catalytic experiments), yields are based on aryl ketone.
[c] Determined by capillary GC analysis using a chiral cyclodex B (Agilent) capillary column (30 m × 0.32 mm I.D. × 0.25 μm film thickness).
[d] TOF = (mol product/mol cat.) × h^{-1}.
[e] Determined by comparison of the retention times of the enantiomers on the GC traces with the literature values.

4. Experimental

4.1. Materials and methods

Unless otherwise mentioned, all reactions were carried out under an argon atmosphere using conventional Schlenk glassware. Solvents were dried using established procedures and distilled under argon immediately prior to use. Analytical grade and deuterated solvents were purchased from Merck. The starting materials D-, L-phenylglycine, D-, L-phenylalanine, PPh_2Cl, and Et_3N were purchased from Fluka and used as received. Ferrocenecarboxaldehyde,[30] and $[Ru(\eta^6\text{-}p\text{-cymene})(\mu\text{-Cl})Cl]_2$,[31] were prepared according to the literature. ^1H (at 400.1 MHz), ^{13}C (at 100.6 MHz), and $^{31}P\text{-}\{^1H\}$ NMR (at 162.0 MHz) spectra were recorded on a Bruker Avance 400 spectrometer, with TMS (tetramethylsilane) as an internal reference for ^1H NMR and ^{13}C NMR or 85% H_3PO_4 as the external reference for $^{31}P\text{-}\{^1H\}$ NMR. The IR spectra were recorded on a Mattson 1000 ATI UNICAM FT-IR spectrometer as KBr pellets. Elemental analysis was carried out on a Fisons EA 1108 CHNS-O instrument. Melting points were recorded by a Gallenkamp Model apparatus with open capillaries. GC analyses were performed on a Shimadzu GC 2010 Plus Gas Chromatograph equipped with cyclodex B (Agilent) capillary column (30 m × 0.32 mm I.D. × 0.25 μm film thickness). Racemic samples of alcohols were obtained by reduction of the corresponding ketones with $NaBH_4$ and used as authentic samples for ee determination. The GC parameters for asymmetric transfer hydrogenation of ketones are as follows; initial temperature, 50 °C; initial time 1.1 min; solvent delay, 4.48 min; temperature ramp 1.3 °C/min; final temperature, 150 °C; initial time 2.2 min; temperature ramp 2.15 °C/min; final temperature, 250 °C; initial time 3.3 min; final time, 44.33 min; injector port temperature, 200 °C; detector temperature, 200 °C, injection volume, 2.0 μL.

4.2. General procedure for the transfer hydrogenation of ketones

Typical procedure for the catalytic hydrogen-transfer reaction: a solution of ruthenium complexes **9**–**12** (0.005 mmol), KOH (0.025 mmol), and the corresponding ketone (0.5 mmol) in degassed *iso*-PrOH (5 mL) was refluxed until the reaction was completed. Next a sample of the reaction mixture was taken off, diluted with acetone, and analyzed immediately by GC, conversions obtained are related to the unreacted ketone.

4.3. Synthesis of amino alcohols based on the ferrocene backbone

4.3.1. (2*R*)-2-[(Ferrocenylmethyl)amino]-2-phenylethan-1-ol 1

Ferrocenecarboxaldehyde (856 mg, 4.0 mmol) and D-phenylglycinol (576 mg, 4.2 mmol) were dissolved in previously dried chloroform (40 mL; dried over K_2CO_3) and the resulting solution was heated at reflux under argon for 90 min. Next, the solution was allowed to cool to room temperature, the solvent was removed under reduced pressure and the red–brown residue immediately redissolved in dry methanol (40 mL; distilled from a MeONa solution). The methanolic solution was cooled in an ice bath and treated slowly with solid $NaBH_4$ (756 mg, 20 mmol over 30 min). After adding all of

the $NaBH_4$, the mixture was stirred at 0 °C for 1 h and at room temperature for a further 90 min. Next, the cooled mixture was quenched with an aqueous solution of NaOH (10%, 40 mL) and extracted with CH_2Cl_2 (2 × 40 mL). The combined organic layers were washed with brine (2 × 40 mL), dried over anhydrous magnesium sulfate, and evaporated, leaving the crude product as a yellow–brown solid. Subsequent purification of the residue by column chromatography (silica gel, dichloromethane–methanol 10:1) led to the development of two bands: the first (minor) one containing mostly ferrocenylmethanol, followed by the major band of the aminoalcohol. Careful evaporation of the second fraction afforded pure **1** as an amber oil, which slowly solidified to a brown solid (yield: 1.03 g, 77 %; mp: 78–79 °C); $[\alpha]_D^{20} = -42.8$ (*c* 1.2, MeOH); ^{1}H NMR (400.1 MHz, $CDCl_3$, ppm) δ: 2.10 (br, 2H, N**H** and O**H**), 3.29 (d, 1H, *J* = 12.6 Hz, C**H**$_2$NH, (a)), 3.43 (d, 1H, *J* = 12.6 Hz, C**H**$_2$NH, (b)), 3.48–3.53 (m, 1H, C**H**$_2$OH) (a)), 3.63–3.66 (m, 1H, C**H**$_2$OH) (b)), 3.75–3.79 (m, 1H, –C**H**NH), 4.01 (m, 5H, C_5**H**$_5$+2H, C_5**H**$_4$), 4.06 (m, 2H, C_5**H**$_4$), 7.12–7.33 (m, 5H, C_6**H**$_5$); ^{13}C NMR (100.6 MHz, $CDCl_3$, ppm) δ: 46.29 (**C**H$_2$NH), 63.98 (**C**HNH), 66.58 (**C**H$_2$OH), 67.79, 67.89, 68.09, 68.42 (**C**$_5$H$_4$), 68.49 (**C**$_5$H$_5$), 85.52 (*i*-**C**$_5$H$_4$), 127.32, 127.75, 128.73 (**C**$_6$H$_5$), 140.37 (*i*-**C**$_6$H$_5$); IR (KBr pellet in cm^{-1}) *v*: (N–H): 3281, (C-Cp): 3086, (C=C-Cp): 1455, (O–H): 3280; Anal. Calcd for $C_{19}H_{21}NOFe$ (335.27 g/mol): C, 67.87; N, 4.16; H, 6.29. Found: C, 67.82; N, 4.11; H, 6.24.

4.3.2. (2*S*)-2-[(Ferrocenylmethyl)amino]-2-phenylethan-1-ol 2

Ferrocenecarboxaldehyde (856 mg, 4.0 mmol) and L-phenylglycinol (576 mg, 4.2 mmol) were dissolved in previously dried chloroform (40 mL; dried over K_2CO_3) and the resulting solution was heated at reflux under argon for 90 min. Next, the solution was allowed to cool at room temperature, the solvent was removed under reduced pressure and the red–brown residue immediately re-dissolved in dry methanol (40 mL; distilled from a MeONa solution). The methanolic solution was cooled in an ice bath and treated slowly with solid $NaBH_4$ (756 mg, 20 mmol over 30 min). After adding all of the $NaBH_4$, the mixture was stirred at 0 °C for 1 h and at room temperature for a further 90 min. Next, the cooled mixture was quenched with an aqueous solution of NaOH (10%, 40 mL) and extracted with dichloromethane (2 × 40 mL). The combined organic layers were washed with brine (2 × 40 mL), dried over anhydrous magnesium sulfate, and evaporated, leaving the crude product as a yellow–brown solid. Subsequent purification of the residue by column chromatography (silica gel, dichloromethane–methanol 10:1) led to the development of two bands: the first (minor) one containing mostly ferrocenylmethanol, followed by the major band of the aminoalcohol. Careful evaporation of the second fraction afforded pure **2** as an amber oil, which slowly solidified to a brown solid (yield: 0.98 g, 73%; mp: 78–79 °C); $[\alpha]_D^{20} = +42.8$ (*c* 1.2, MeOH); ^{1}H NMR (400.1 MHz, $CDCl_3$, ppm) δ: 2.34 (br, 2H, N**H** and O**H**), 3.39 (d, 1H, *J* = 13.2 Hz, C**H**$_2$NH, (a)), 3.51–3.63 (m, 2H, C**H**$_2$NH (b) + C**H**$_2$OH (a)), 3.74 (dd, 1H, *J* = 4.2 and 11.0 Hz C**H**$_2$OH) (b)), 3.87 (dd, 1H, *J* = 4.4 and 8.8 Hz, –C**H**NH), 4.10 (m, 5H, C_5**H**$_5$ + 2H, C_5**H**$_4$), 4.18 (m, 2H, C_5**H**$_4$), 7.35–7.43 (m, 5H, C_6**H**$_5$); ^{13}C NMR (100.6 MHz, $CDCl_3$, ppm) δ: 46.31 (**C**H$_2$NH), 63.98 (**C**HNH), 66.64 (**C**H$_2$OH), 67.80, 67.90, 68.11, 68.43 (**C**$_5$H$_4$), 68.51 (**C**$_5$H$_5$), 86.45 (*i*-**C**$_5$H$_4$), 127.34, 127.72, 128.73 (**C**$_6$H$_5$), 140.37 (*i*-**C**$_6$H$_5$); IR (KBr pellet in cm^{-1}) *v*: (N–H): 3291, (C-Cp): 3087, (C=C-Cp): 1441, (O–H): 3320; Anal. Calcd for $C_{19}H_{21}NOFe$ (335.27 g/mol): C, 67.87; N, 4.16; H, 6.29. Found: C, 67.81; N, 4.10; H, 6.22.

4.3.3. (2*R*)-2-[(Ferrocenylmethyl)amino]-3-phenylpropan-1-ol 3

Ferrocenecarboxaldehyde (856 mg, 4.0 mmol) and D-phenylalaninol (635 mg, 4.2 mmol) were dissolved in previously dried chloroform (40 mL; dried over K_2CO_3) and the resulting solution was heated at reflux under argon for a further 90 min. Next, the solution was allowed to cool at room temperature, the solvent was removed under reduced pressure and the red–brown residue immediately re-dissolved in dry methanol (40 mL; distilled from a MeONa solution). The methanolic solution was cooled in an ice bath and treated slowly with solid $NaBH_4$ (756 mg, 20 mmol over 30 min). After adding all of the $NaBH_4$, the mixture was stirred at 0 °C for 1 h and at room temperature for a further 90 min. Next, the cooled mixture was quenched with an aqueous solution of NaOH (10%, 40 mL) and extracted with dichloromethane (2 × 40 mL). The combined organic layers were washed with brine (2 × 40 mL), dried over anhydrous magnesium sulfate, and evaporated, leaving a crude product as a yellow–brown solid. Subsequent purification of the residue by column chromatography (silica gel, dichloromethane–methanol 10:1) led to the development of two bands: the first (minor) one containing mostly ferrocenylmethanol, followed by the major band of the aminoalcohol. Careful evaporation of the second fraction afforded pure **3** as an amber oil, which slowly solidified to a brown solid (yield: 1.19 g, 81%; mp: 50–51 °C); $[\alpha]_D^{20} = +18.6$ (*c* 1.2, MeOH); ^{1}H NMR (400.1 MHz, $CDCl_3$, ppm) δ: 2.11 (br, 2H, (NH and OH)), 2.83–2.88 (m, 2H, C**H**$_2$Ph), 3.00–3.06 (m, 1H, C**H**NH), 3.39–3.45 (m, 2H, C**H**$_2$NH (a) + C**H**$_2$OH (a)), 3.54 (d, 1H, *J* = 13.2 Hz, C**H**$_2$NH (b)), 3.70 (dd, 1H, *J* = 3.8 and 10.6, C**H**$_2$OH (b)), 4.09 (m, 5H, C_5**H**$_5$ + 2H, C_5**H**$_4$), 4.16 (m, 2H, C_5**H**$_4$), 7.23–7.36 (m, 5H, C_6**H**$_5$); ^{13}C NMR (100.6 MHz, $CDCl_3$, ppm) δ: 38.26 (**C**H$_2$Ph) 46.07 (**C**H$_2$NH), 59.71 (**C**HNH), 62.38 (**C**H$_2$OH), 67.61, 67.64, 67.76, 67.86 (**C**$_5$H$_4$), 68.35 (**C**$_5$H$_5$), 86.85 (***i***-C$_5$H$_4$) 126.62, 128.72, 129.20 (**C**$_6$H$_5$), 138.52 (***i***-**C**$_6$H$_5$); IR (KBr pellet in cm^{-1}) *v*: (N–H): 3268, (C-Cp): 3084, (C=C-Cp): 1448; (O–H): 3305; Anal. Calcd for $C_{20}H_{23}NOFe$ (349.29 g/mol): C, 68.76; N, 4.02; H, 6.64. Found: C, 68.74; N, 3.99; H, 6.59.

4.3.4. (2*S*)-2-[(Ferrocenylmethyl)amino]-3-phenylpropan-1-ol 4

Ferrocenecarboxaldehyde (856 mg, 4.0 mmol) and L-phenylalaninol (635 mg, 4.2 mmol) were dissolved in previously dried chloroform (40 mL; dried over K_2CO_3) and the resulting solution was heated at reflux under argon for 90 min. Next, the solution was allowed to cool to room temperature, the solvent was removed under reduced pressure and the red–brown residue immediately re-dissolved in dry methanol (40 mL; distilled from a MeONa solution). The methanolic solution was cooled in an ice bath and treated slowly with solid $NaBH_4$ (756 mg, 20 mmol over 30 min). After adding all of the $NaBH_4$, the mixture was stirred at 0 °C for 1 h and at room temperature for a further 90 min. Next, the cooled mixture was quenched with an aqueous solution of NaOH (10%, 40 mL) and extracted with dichloromethane (2 × 40 mL). The combined organic layers were washed with brine (2 × 40 mL), dried over anhydrous magnesium sulfate, and evaporated, leaving the crude product as a yellow–brown solid. Subsequent purification of the residue by column chromatography (silica gel, dichloromethane–methanol 10:1) led to the development of two bands: the first (minor) one containing mostly ferrocenylmethanol, followed by the major band of the aminoalcohol. Careful evaporation of the second fraction afforded pure **4** as an amber oil, which slowly solidified to a brown solid. (Yield: 1.20 g, 82%; mp: 50–51 °C); $[\alpha]_D^{20} = -18.6$ (*c* 1.2, MeOH); ^{1}H NMR (400.1 MHz, $CDCl_3$, ppm) δ: 2.01 (br, 2H, NH and OH), 2.82–2.85 (m, 2H, C**H**$_2$Ph), 3.01–3.05 (m, 1H, C**H**NH), 3.40 (m, 1H, C**H**$_2$OH (a), 3.43 (d, 1H, *J* = 13.1 Hz, C**H**$_2$NH (a), 3.54 (d, 1H, *J* = 12.9 Hz, C**H**$_2$NH (b)), 3.70 (dd, 1H, C**H**$_2$OH (b)), 4.10 (m, 5H, C_5**H**$_5$ + 2H, C_5**H**$_4$), 4.16 (br s, 2H, C_5**H**$_4$), 7.23–7.36 (m, 5H, C_6**H**$_5$); ^{13}C NMR (100.6 MHz, $CDCl_3$, ppm) δ: 38.28 (**C**H$_2$Ph), 46.05 (**C**H$_2$NH), 59.68 (**C**HNH), 62.38 (**C**H$_2$OH), 67.60, 67.63, 67.76, 67.85 (**C**$_5$H$_4$), 68.35 (**C**$_5$H$_5$), 86.88 (*i*-**C**$_5$H$_4$), 126.62, 128.72, 129.20 (**C**$_6$H$_5$), 138.52 (*i*-**C**$_6$H$_5$); IR (KBr pellet in cm^{-1}) *v*: (N–H): 3268, (C-Cp): 3089, (C=C-Cp): 1448; (O–H): 3305; Anal. Calcd for $C_{20}H_{23}NOFe$ (349.29 g/mol): C, 68.76; N, 4.02; H, 6.64. Found: C, 68.73; N, 4.00; H, 6.58.

4.4. Synthesis of phosphinite ligands based on the ferrocene backbone and their ruthenium(II) complexes

4.4.1. (2*R*)-2-(Ferrocenylmethylamino)-2-phenylethyl diphenylphosphinite 5

(2*R*)-2-(Ferrocenylmethylamino)-2-phenylethan-1-ol **1** (100 mg 0.30 mmol) and triethylamine (30.4 mg, 0.30 mmol) were dissolved in dry toluene (20 mL) under an argon atmosphere. Next PPh_2Cl (66.1 mg, 0.30 mmol) was added dropwise with a syringe to this solution. The mixture was stirred at room temperature for 30 min. The white precipitate was then filtered under argon and the remaining organic phase was dried in vacuo to produce a white viscous oily compound **5** (yield: 0.135 g, 87%); $[\alpha]_D^{20} = -55.6$ (*c* 1.2, MeOH); ^{1}H NMR (400.1 MHz, $CDCl_3$, ppm) δ: 3.32 (d, 1H, *J* = 13.2 Hz, C**H**$_2$NH (a)), 3.50 (d, 1H, *J* = 13.2 Hz, C**H**$_2$NH (b)), 3.96–3.99 (m, 2H, C**H**$_2$OP), 4.12–4.18 (m, 1H, C**H**NH + 4H C_5**H**$_4$ + 5H, C_5**H**$_5$), 7.32–7.56 (m, 5H, C_6**H**$_5$ + 10H C_6**H**$_5$P); ^{13}C NMR (100.6 MHz, $CDCl_3$, ppm) δ: 46.37 (**C**H$_2$-NH), 63.52 (d, *J* = 8.0 Hz, **C**HNH), 67.59, 67.79, 68.02, 68.24 (**C**$_5$H$_4$), 68.42 (**C**$_5$H$_5$), 74.85 (d, *J* = 17.11 Hz, **C**H$_2$OP), 87.25 (***i***-**C**$_5$H$_4$), 127.67, 127.93, 128.54 (CH**C**$_6$H$_5$), 128.46 (d, *J* = 7.0 Hz, *m*-carbons of phenyls), 129.49 (s, *p*-carbons of phenyls), 130.59 (d, *J* = 21.6 Hz, *o*-carbons of phenyls), 140.23 (***i***-**C**$_6$H$_5$), 141.69 (t, *J* = 19.31 Hz, *i*-carbons of phenyls); ^{31}P-{^{1}H} NMR (162.0 MHz, $CDCl_3$, ppm) δ: 116.30 (s, O-**P**(Ph)$_2$); IR (KBr pellet in cm^{-1}) *v*: (N–H) = 3323, (C-Cp): 3058, (C=C-Cp): 1454, (P-Ph): 1443, (O–P): 1028; Anal. Calcd for $C_{31}H_{30}NOPFe$ (520.41 g/mol): C, 71.54; N, 2.69; H, 5.81. Found: C, 71.52; N, 2.67; H, 5.79.

4.4.2. (2*S*)-2-(Ferrocenylmethylamino)-2-phenylethyl diphenylphosphinite 6

(2*S*)-2-(Ferrocenylmethylamino)-2-phenylethan-1-ol **2** (100 mg 0.30 mmol) and triethylamine (30.4 mg, 0.30 mmol) were dissolved in dry toluene (20 mL) under an argon atmosphere. Next, PPh_2Cl (66.1 mg, 0.30 mmol) was added dropwise with a syringe to this solution. The mixture was stirred at room temperature for 30 min. The white precipitate was then filtered under argon and the remaining organic phase was dried in vacuo to produce a white viscous oily compound **6** (yield: 0.140 g, 90 %); $[\alpha]_D^{20} = +55.6$ (*c* 1.2, MeOH); ^{1}H NMR (400.1 MHz, $CDCl_3$, ppm) δ: 3.30 (d, 1H, *J* = 13.3 Hz, C**H**$_2$NH (a)), 3.47 (d, 1H, *J* = 13.3 Hz, C**H**$_2$NH (b)), 3.93–3.97 (m, 2H, C**H**$_2$OP), 4.11–4.16 (m, 1H, C**H**NH + 4H C_5**H**$_4$ + 5H, C_5**H**$_5$), 7.38–7.55 (m, 5H, C_6**H**$_5$ + 10H C_6**H**$_5$P); ^{13}C NMR (100.6 MHz, $CDCl_3$, ppm) δ: 46.36 (**C**H$_2$-NH), 63.52 (d, *J* = 7.10 Hz, **C**HNH), 67.56, 67.75, 67.98, 68.20 (**C**$_5$H$_4$), 68.39 (**C**$_5$H$_5$), 74.85 (d, *J* = 17.10 Hz, **C**H$_2$OP), 87.31 (***i***-**C**$_5$H$_4$), 127.63, 127.90, 128.50 (CH**C**$_6$H$_5$), 128.42 (d, *J* = 6.00 Hz, *m*-carbons of phenyls), 129.46 (s, *p*-carbons of phenyls), 130.56 (d, *J* = 22.1 Hz, *o*-carbons of phenyls), 140.27 (***i***-**C**$_6$H$_5$), 141.67 (t, *J* = 19.01 Hz, *i*-carbons of phenyls); ^{31}P-{^{1}H} NMR (162.0 MHz, $CDCl_3$, ppm) δ: 116.27 (s, O-**P**(Ph)$_2$); IR (KBr pellet in cm^{-1}) *v*: (N–H) = 3325, (C-Cp): 3060, (C=C-Cp): 1458, (P-Ph): 1440, (O–P): 1030; Anal. Calcd for $C_{31}H_{30}$-NOPFe (520.41 g/mol): C, 71.54; N, 2.69; H, 5.81. Found: C, 71.50; N, 2.65; H, 5.77.

4.4.3. (2*R*)-2-(Ferrocenylmethylamino)-3-phenylpropyl diphenylphosphinite 7

(2*R*)-2-(Ferrocenylmethylamino)-3-phenylpropan-1-ol **3** (100 mg 0.28 mmol) and triethylamine (29.0 mg, 0.28 mmol) were dissolved in dry toluene (20 mL) under an argon atmosphere. Next, PPh_2Cl (57.3 mg, 0.28 mmol) was added dropwise with a syringe to this solution. The mixture was stirred at room temperature for 30 min. The white precipitate was then filtered under argon and the remaining organic phase was dried in vacuo to produce a white viscous oily compound **7** (yield: 0.140 g, 92%); $[\alpha]_D^{20} = +25.4$ (*c* 1.2, MeOH); ^{1}H NMR (400.1 MHz, $CDCl_3$, ppm) δ: 2.84–2.89 (m, 1H, C**H**$_2$C$_6$H$_5$ (a)), 2.96–3.01 (m, 1H, C**H**$_2$C$_6$H$_5$ (b)), 3.22–3.25 (m, 1H, C**H**NH), 3.55 (d, 1H, *J* = 12.9 Hz, C**H**$_2$NH (a)), 3.64 (d, 1H, *J* = 12.9 Hz, C**H**$_2$NH (b)), 3.92–3.96 (m, 2H, C**H**$_2$OP), 4.09 (s, 5H, C_5**H**$_5$), 4.14–4.22 (m, 4H, C_5**H**$_4$), 7.25–7.50 (m, 5H, C_6**H**$_5$ + 6H, *p* and *m*-C_6**H**$_5$P), 7.60–7.66 (m, 4H, *o*-C_6**H**$_5$P); ^{13}C NMR (100.6 MHz, $CDCl_3$, ppm) δ: 38.44 (**C**H$_2$C$_6$H$_5$), 46.73 (**C**H$_2$NH), 59.88 (d, *J* = 8.0 Hz, **C**HNH), 67.65, 67.70, 67.97, 67.98 (**C**$_5$H$_4$), 68.41 (**C**$_5$H$_5$), 71.53 (d, *J* = 17.1 Hz, **C**H$_2$OP), 87.35 (***i***-**C**$_5$H$_4$), 128.34, 128.59, 129.15 (CH$_2$**C**$_6$H$_5$), 129.42 (d, *J* = 2.2 Hz, *m*-carbons of phenyls), 129.51 (s, *p*-carbons of phenyls), 130.60 (d, *J* = 21.6 Hz, *o*-carbons of phenyls), 137.94 (*i*-**C**$_6$H$_5$), 142.08 (d, *J* = 17.1 Hz, *i*-carbons of phenyls); ^{31}P-{^{1}H} NMR (162.0 MHz, $CDCl_3$, ppm) δ: 115.62 (s, O-**P**(Ph)$_2$); IR (KBr pellet in cm^{-1}) *v*: (N–H) = 3322, (C-Cp): 3068, (C=C-Cp): 1454, (P-Ph): 1435, (O–P): 1026; Anal. Calcd for $C_{32}H_{32}$-NOPFe (533.43 g/mol): C, 72.05; N, 2.62; H, 6.04. Found: C, 72.02; N, 2.59; H, 6.01.

4.4.4. (2*S*)-2-(Ferrocenylmethylamino)-3-phenylpropyl diphenylphosphinite 8

(2*S*)-2-(Ferrocenylmethylamino)-3-phenylpropan-1-ol **4** (100 mg 0.28 mmol) and triethylamine (29.0 mg, 0.28 mmol) were dissolved in dry toluene (20 mL) under an argon atmosphere. Next, PPh_2Cl (57.3 mg, 0.28 mmol) was added dropwise with a syringe to this solution. The mixture was stirred at room temperature for 30 min. The white precipitate was then filtered under argon and the remaining organic phase was dried in vacuo to produce a white viscous oily compound **8** (yield:0.142 g, 93 %); $[\alpha]_D^{20} = -25.4$ (*c* 1.2, MeOH); ^{1}H NMR (400.1 MHz, $CDCl_3$, ppm) δ: 2.81–2.86 (m, 1H C**H**$_2$-C_6H_5, (a)), 2.89–2.94 (m, 1H, C**H**$_2$C$_6$H$_5$, (b)), 3.19 (br, 1H, C**H**NH), 3.52 (d, 1H, *J* = 12.4 Hz, C**H**$_2$NH (a)), 3.61 (d, 1H, *J* = 12.4 Hz, C**H**$_2$NH (b)), 3.88 (br, 2H, C**H**$_2$OP), 4.05 (br, 5H, C_5**H**$_5$), 4.10–4.16 (m, 4H, C_5**H**$_4$), 7.19–7.41 (m, 5H, C_6**H**$_5$ + 6H, *p*- and *m*-C_6**H**$_5$P), 7.56 (m, 4H, *o*-C_6**H**$_5$P); ^{13}C NMR (100.6 MHz, $CDCl_3$, ppm) δ: 38.16 (**C**H$_2$C$_6$-H$_5$), 46.60 (**C**H$_2$NH), 59.77 (d, *J* = 7.0 Hz, **C**HNH), 67.67, 67.72, 68.07, 68.36 (**C**$_5$H$_4$), 68.46 (**C**$_5$H$_5$), 71.20 (d, *J* = 17.1 Hz, **C**H$_2$OP), 87.25 (***i***-**C**$_5$H$_4$), 128.31, 128.40, 128.53 (CH$_2$**C**$_6$H$_5$), 129.34 (s, *p*-carbons of phenyls), 129.43 (d, *J* = 7.0 Hz, *m*-carbons of phenyls), 130.54 (d, *J* = 21.6 Hz, *o*-carbons of phenyls), 138.72 (***i***-**C**$_6$H$_5$), 141.84 (d, *J* = 18.3 Hz, *i*-carbons of phenyls); ^{31}P-{^{1}H} NMR (162.0 MHz, $CDCl_3$, ppm) δ: 114.64 (s, O-**P**(Ph)$_2$); IR (KBr pellet in cm^{-1}) *v*: (N–H) = 3332, (C-Cp): 3054, (C=C-Cp): 1494, (P-Ph): 1435, (O–P): 1023; Anal. Calcd for $C_{32}H_{32}NOPFe$ (533.43 g/mol): C, 72.05; N, 2.62; H, 6.04. Found: C, 72.00; N, 2.57; H, 6.00.

4.4.5. (2*R*)-2-(Ferrocenylmethylamino)-2-phenylethyl diphenylphosphinito(dichloro(η^6-*p*-cymene)ruthenium(II)) 9

At first, $[Ru(\eta^6\text{-}p\text{-cymene})(\mu\text{-Cl})Cl]_2$ (91 mg, 0.15 mmol) and (2*R*)-2-(ferrocenylmethylamino)-2-phenylethyl diphenylphosphinite **5** (156 mg, 0.30 mmol) were dissolved in 20 mL of toluene and stirred for 1 h at room temperature. The volume was concentrated to ca. 1–2 mL under reduced pressure and the addition of petroleum ether (15 mL) gave **9** as a red solid. The product was collected by filtration and dried in vacuum (yield: 0.197 g, 80 %; mp: 113–115 °C); $[\alpha]_D^{20} = -43.2$ (*c* 1.2, MeOH); ^{1}H NMR (400.1 MHz, $CDCl_3$, ppm) δ: 1.07 (d, 6H, *J* = 7.6 Hz, (C**H**$_3$)$_2$CHPh of *p*-cymene), 1.79 (s, 3H, C**H**$_3$-Ph of *p*-cymene), 2.62 (m, 1H, C**H**- of *p*-cymene), 3.28 (d, 1H, *J* = 12.8 Hz, C**H**$_2$NH (a)), 3.47 (d, 1H, *J* = 12.8 Hz, C**H**$_2$NH (b)), 3.80–3.89 (m, 2H, C**H**$_2$OP + 1H C**H**NH), 4.09–4.12 (m, 2H, C_5**H**$_4$ + 5H C_5**H**$_5$), 4.20 (s, 2H, C_5**H**$_4$), 5.15–5.18 (m, 4H, aromatic protons of *p*-cymene), 7.29–7.39 (m, 6H, *m*- and *p*-protons of phenyls + 5H, (C_6**H**$_5$), 7.83–7.85 (m, 4H, *o*-protons of phenyls); ^{13}C NMR (100.6 MHz, $CDCl_3$, ppm) δ: 17.51 (**C**H$_3$-Ph of *p*-cymene), 21.84, ((**C**H$_3$)$_2$CH of *p*-cymene), 30.12 (**C**H- of *p*-cymene), 46.31 (**C**H$_2$NH), 62.22 (**C**HNH), 67.68, 67.92, 68.20, 68.42 (**C**$_5$H$_4$), 68.58 (**C**$_5$H$_5$), 71.41 (**C**H$_2$OP), 87.00 (***i***-**C**$_5$H$_4$), 87.41, 87.73, 90.39, 90.70 (aromatic carbons of *p*-cymene), 97.48, 111.46 (quaternary carbons of *p*-cymene), 127.73, 127.91, 127.98, (**C**$_6$H$_5$), 128.01 (s, *m*-carbons of phenyls), 130.95 (d, *J* = 11.0 Hz, *p*-carbons of phenyls), 132.49 (d,

J = 10.6 Hz, *o*-carbons of phenyls), 136.33 (d, J = 50.3 Hz, *i*-carbons of phenyls), 138.20 (***i***-$\underline{C}_6H_5$); ^{31}P-{^1H} NMR (162.0 MHz, $CDCl_3$, ppm) δ: 112.14 (s, O-$\underline{P}(Ph)_2$); IR (KBr pellet in cm^{-1}) ν: (N–H): 3281, (C-Cp): 3086, (C=C-Cp): 1455, (O–P): 1020, (C=C-Cp): 1465; Anal. Calcd for [$C_{41}H_{44}NOPFeRuCl_2$] (826.60 g/mol): C, 59.57; N, 1.69; H, 5.36. Found: C, 59.53; N, 1.65; H, 5.32.

4.4.6. (2*S*)-2-(Ferrocenylmethylamino)-2-phenylethyl diphenylphosphinito(dichloro(η^6-*p*-cymene)ruthenium(II)) 10

At first, [Ru(η^6-*p*-cymene)(μ-Cl)Cl]$_2$ (91 mg, 0.15 mmol) and (2*S*)-2-(ferrocenylmethylamino)-2-phenylethyl diphenylphosphinite **6** (156 mg, 0.30 mmol) were dissolved in 20 mL of toluene and stirred for 1 h at room temperature. The volume was concentrated to ca. 1–2 mL under reduced pressure and addition of petroleum ether (15 mL) gave **10** as a red solid. The product was collected by filtration and dried in vacuo (yield: 0.187 g, 76%; mp: 113–115 °C); $[\alpha]_D^{20} = +43.2$ (*c* 1.2, MeOH); ^1H NMR (400.1 MHz, $CDCl_3$, ppm) δ: 0.97 (br, 6H, ($\underline{C}H_3$)$_2$CHPh of *p*-cymene), 1.71 (s, 3H, $C\underline{H}_3$-Ph of *p*-cymene), 2.52 (m, 1H, $C\underline{H}$- of *p*-cymene), 3.22 (br, 1H, $C\underline{H}_2NH$ (a)), 3.39 (br, 1H, $C\underline{H}_2NH$ (b)), 3.80 (br, 2H, $C\underline{H}_2OP$ + 1H, $C\underline{H}NH$), 4.00–4.14 (m, 4H, $C_5\underline{H}_4$ + 5H, $C_5\underline{H}_5$) 5.08 (br, 4H, aromatic protons of *p*-cymene), 7.26 (br, 6H, *m*- and *p*-protons of phenyls + 5H, $C_6\underline{H}_5$), 7.75 (br, 4H, *o*-protons of phenyls); ^{13}C NMR (100.6 MHz, $CDCl_3$, ppm) ***δ***: 17.52 $\underline{C}H_3$-Ph of *p*-cymene), 21.82 (($\underline{C}H_3$)$_2$CH of *p*-cymene), 30.12 ($\underline{C}H$- of *p*-cymene), 46.26 ($\underline{C}H_2NH$), 62.18 (d, J = 7.1 Hz, $\underline{C}HNH$), 65.86, 67.73, 67.99, 68.43 ($\underline{C}_5H_4$), 68.69 ($\underline{C}_5H_5$), 71.25 ($\underline{C}H_2OP$), 86.90 (***i***-$\underline{C}_5H_4$), 87.44, 87.70, 90.41, 90.73 (aromatic carbons of *p*-cymene), 97.47, 111.41 (quaternary carbons of *p*-cymene), 127.98, 128.53, 130.89, 131.05, 132.46, 132.71, 136.03, 136.53 (carbons of phenyls); ^{31}P-{^1H} NMR (162.0 MHz, $CDCl_3$, ppm) δ: 112.46 (s, O-$\underline{P}(Ph)_2$); **IR** (KBr pellet in cm^{-1}) ν: (N–H): 3291, (C-Cp): 3087, (C=C-Cp): 1441, (P-Ph): 1442, (O–P): 1016, (C=C-Cp): 1465; Anal. Calcd for [$C_{41}H_{44}NOPFeRuCl_2$] (826.60 g/mol): C, 59.57; N, 1.69; H, 5.36. Found: C, 59.51; N, 1.63; H, 5.30.

4.4.7. (2*R*)-2-(Ferrocenylmethylamino)-3-phenylpropyl diphenylphosphinito(dichloro(η^6-*p*-cymene)ruthenium(II)) 11

At first, [Ru(η^6-*p*-cymene)(μ-Cl)Cl]$_2$ (87.6 mg, 0.143 mmol) and (2*R*)-2-(ferrocenylmethylamino)-3-phenylpropyl diphenylphosphinite **7** (154.7 mg, 0.28 mmol) were dissolved in 20 mL of toluene and stirred for 1 h at room temperature. The volume was concentrated to ca. 1–2 mL under reduced pressure and the addition of petroleum ether (15 mL) gave **11** as a red solid. The product was collected by filtration and dried in vacuo (yield: 0.197 g, 82%; mp: 104–106 °C); $[\alpha]_D^{20} = +33.9$ (*c* 1.2, MeOH); ^1H NMR (400.1 MHz, $CDCl_3$, ppm) δ: 0.97 (br, 6H, ($C\underline{H}_3$)$_2$-CH of *p*-cymene), 1.68 (s, 3H, $C\underline{H}_3$-Ph of *p*-cymene), 2.27 (br, 1H, $N\underline{H}$), 2.51 (br, 1H, -$C\underline{H}$ of *p*-cymene), 2.73 (br, 2H $C\underline{H}_2C_6H_5$), 2.94 (br, 1H, $C\underline{H}NH$), 3.33 (br, 1H, $C\underline{H}_2NH$, (a)), 3.40 (br, 1H, $C\underline{H}_2NH$, (b)), 3.65 (br, 1H, $C\underline{H}_2OP$ (a)), 3.74 (br, 1H, $C\underline{H}_2OP$ (b)) 3.92–4.05 (br, 4H, $C_5\underline{H}_4$ + 5H, $C_5\underline{H}_5$), 5.10 (br, 4H, aromatic protons of *p*-cymene), 7.05–7.32 (m, 6H, *m*- and *p*-protons of phenyls + 5H, $CH_2C_6\underline{H}_5$) 7.80 (d, 4H, J = 6.8 Hz, *o*-protons of phenyls); ^{13}C NMR (100.6 MHz, $CDCl_3$, ppm) ***δ***: 17.49 $\underline{C}H_3$Ph of *p*-cymene), 21.79, ($\underline{C}H_3$)$_2$CH of *p*-cymene), 30.12 ($\underline{C}H$- of *p*-cymene), 38.35 ($C\underline{H}_2$Ph), 46.65 ($\underline{C}H_2NH$), 58.79 ($\underline{C}HNH$), 67.83, 67.84 68.15, 68.46 ($\underline{C}_5H_4$), 68.41 ($\underline{C}_5H_5$), 70.36 ($\underline{C}H_2OP$), 87.22 (***i***-$\underline{C}_5H_4$), 87.48, 87.75, 90.27, 90.38 (aromatic carbons of *p*-cymene), 97.59, 111.67 (quaternary carbons of *p*-cymene), 126.51, 128.61, 129.28, ($CH_2\underline{C}_6H_5$), 127.97 (d, J = 9.9 Hz, *m*-carbons of phenyls), 130.99 (d, J = 18.0 Hz, *p*-carbons of phenyls), 132.6 (d, J = 10.3, *o*-carbons of phenyls), 137.19 (*i*-$CH_2\underline{C}_6H_5$), 138.35 (d, J = 52.0 Hz, *i*-carbons of phenyls); ^{31}P-{^1H} NMR (162.0 MHz, $CDCl_3$, ppm) δ: 112.20 (s, O-$\underline{P}(Ph)_2$); IR (KBr pellet in cm^{-1}) ν: (N–H): 3268, (C-Cp): 3084, (C=C-Cp): 1448, (P-Ph): 1442, (O–P): 1022, (C=C-Cp): 1465; Anal. Calcd for [$C_{42}H_{46}NOPFeRuCl_2$] (839.62 g/mol): C, 60.08; N, 1.66; H, 5.52. Found: C, 59.98; N, 1.60; H, 5.45.

4.4.8. (2*S*)-2-(Ferrocenylmethyl-amino)-3-phenylpropyl diphenylphosphinito(dichloro(η^6-*p*-cymene)ruthenium(II)) 12

At first, [Ru(η^6-*p*-cymene) (μ-Cl)Cl]$_2$ (87.6 mg, 0.143 mmol) and (2*S*)-2-(ferrocenylmethylamino)-3-phenylpropyl diphenylphosphinite **8** (154.7 mg, 0.28 mmol) were dissolved in 20 mL of toluene and stirred for 1 h at room temperature. The volume was concentrated to ca. 1–2 mL under reduced pressure and the addition of petroleum ether (15 mL) gave **12** as a red solid. The product was collected by filtration and dried in vacuum (yield: 0.204 g, 85 %; mp: 104–106 °C); $[\alpha]_D^{20} = -33.9$ (*c* 1.2, MeOH)]; ^1H NMR (400.1 MHz, $CDCl_3$, ppm) δ: 0.98 (m, 6H, ($C\underline{H}_3$)$_2$CH of *p*-cymene), 1.66 (s, 3H, $C\underline{H}_3$-Ph of *p*-cymene)), 2.25 (br, 1H, $N\underline{H}$), 2.57 (m, 1H, –$C\underline{H}$ of *p*-cymene), 2.70 (m, 2H, $C\underline{H}_2C_6H_5$), 2.97 (m, 1H, $C\underline{H}NH$), 3.40 (m, 2H, $C\underline{H}_2NH$), 3.61 (m, 1H, $C\underline{H}_2OP$ (a)), 3.71 (m, 1H, $C\underline{H}_2OP$ (b)), 3.96 (m, 2H, $C_5\underline{H}_4$ + 5H, $C_5\underline{H}_5$); 4.07 (m, 2H, $C_5\underline{H}_4$), 5.11 (m, 4H, aromatic protons of *p*-cymene), 7.25 (m, 5H, $CH_2C_6\underline{H}_5$); 7.29 (m, 6H, *m*- and *p*-protons of phenyls), 7.82 (m, 4H, *o*-protons of phenyls); ^{13}C NMR (100.6 MHz, $CDCl_3$, ppm) δ: 17.50 $\underline{C}H_3$-Ph of *p*-cymene), 21.80, ($\underline{C}H_3$)$_2$CH of *p*-cymene), 30.11 ($\underline{C}H$– of *p*-cymene), 38.38 ($C\underline{H}_2$Ph), 46.70 ($\underline{C}H_2NH$), 58.75 ($\underline{C}HNH$), 64.42 ($\underline{C}H_2OH$), 67.74, 67.84, 68.12, 68.43 ($\underline{C}_5H_4$), 68.43 ($\underline{C}_5H_5$), 87.32 (***i***-$\underline{C}_5H_4$), 87.46, 87.74, 90.28, 90.40 (aromatic carbons of *p*-cymene), 97.60, 111.65 (quaternary carbons of *p*-cymene), 127.82, 127.95, 128.71 ($CH_2\underline{C}_6H_5$), 130.92 (d, J = 10.0, *m*-carbons of phenyls), 132.08 (d, J = 10.1 Hz, *p*-carbons of phenyls), 133.12 (d, J = 11.0 *o*-carbons of phenyls), 136.92 (d, J = 50.3 Hz, *i*-carbons of phenyls), 137.40 (*i*-$CH_2\underline{C}_6H_5$); ^{31}P-{^1H} NMR (162.0 MHz, $CDCl_3$, ppm) δ: 111.56 (s, O-$\underline{P}$-$(Ph)_2$); IR (KBr pellet in cm^{-1}) ν: 3268, (C-Cp): 3089, (C=C-Cp): 1448, (P-Ph): 1442, (O–P): 1023, (C=C-Cp): 1465; Anal. Calcd for [$C_{42}H_{46}NOPFeRuCl_2$] (839.62 g/mol): C, 60.08; N, 1.66; H, 5.52. Found: C, 59.97; N, 1.61; H, 5.47.

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