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A New Stereoselective Approach to Chiral Ferrocenyl Ligands for Asymmetric Catalysis

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Optically active 6-(dialkylamino)fulvenes, derived from (*R*)-(1-phenylethyl)amine, (*R*)-(1-cyclohexylethyl)amine, and *O*-methylephedrine, respectively, were used to prepare chiral cyclopentadienyl synthons. The addition of MeLi to these fulvenes, affording the corresponding dialkyl(1-cyclopentadienylethyl)amines, was found to occur with high diastereoselectivity, the maximum being 87%, which was obtained with a fulvene derived from (*R*)-(1-cyclohexylethyl)amine. The reaction of the resulting cyclopentadienyllithium salt with the Cp*Fe^{II}− and MeCpFe^{II}−fragments (generated *in situ* from [Fe(acac)$_2$]$_n$) afforded the diastereomerically enriched heteroleptic ferrocenyl amines. These were converted by reaction with HNMe$_2$ in acetic acid to the corresponding optically active (75% ee) dimethylamino derivatives (*S*)-**7** and (*S*)-**16**, respectively. Diastereospecific lithiation with BuLi and reaction with ClPPh$_2$ of the last two compounds gave the phosphines (*S*)-(*R*)-**9** and (*S*)-(*R*)-**17**. Retentive substitution of the dimethylamino group using dicyclohexylphosphine, 9-phosphabicyclo[3.3.1]nonane, pyrazole, or 3,5-dimethylpyrazole in acetic acid afforded the corresponding P,P- and P,N-chelating ligands, which were obtained optically pure after recrystallization. The optical purity was checked by HPLC using a chiral stationary phase. The absolute configuration at the newly formed stereogenic center was determined to be *S* by an X-ray crystallographic study of the pyrazole derivative (*S*)-(*R*)-Cp*FeC$_5$H$_3$CH(Me)-{(N$_2$C$_3$H$_3$)PPh$_2$}-1,2 ((*S*)-(*R*)-**13**). Crystals of (*S*)-(*R*)-**13** are orthorhombic, space group $P2_12_12_1$, with a = 8.586(4) Å, b = 16.224(9) Å, c = 20.054(2) Å, and Z = 4. Crystals of racemic Cp*FeC$_5$H$_3$CH(Me){(PC$_8$H$_{14}$)PPh$_2$}-1,2 ((*S**)-(*R**)-**12**) are triclinic, space group $P\bar{1}$, with a = 11.265(4) Å, b = 11.666(4) Å, c = 13.870(4) Å, and Z = 2.

Introduction

Chiral ferrocenyl diphosphines are among the most successful ligands used in asymmetric catalysis.[1] A very important feature of many of these ferrocene-based ligands is the presence of a stereogenic, functionalized side chain which can be modeled to fulfill specific purposes, in particular to act as a source of secondary interactions with substrates,[2] compound **1** in Chart 1 being a prototype. Whereas most of these ligands contain two identical diphenylphosphino fragments attached at the 1,1′-positions on the ferrocene core, we recently showed that it is possible to create new structures when one of the phosphorus substituents replaces the side chain.[3] Ligand **2** (josiphos) has been shown to impart high to very high degrees of enantioselection to several transition-metal-catalyzed reactions, by virtue of its two sterically and electronically different ligating groups. Currently, the key intermediate in virtually all the synthetic procedures to optically active ferrocenyl ligands is dimethyl(1-ferrocenylethyl)amine (**3**), a compound whose enantiomers can both be obtained in optically pure form by conventional methods from the racemate.[4] However, the use of amine **3** has certain drawbacks. (1) In all its subsequent reactions it is not possible to selectively activate (substitute) the "lower" Cp ring (η^5-C$_5$H$_5$), since metalation or electrophilic substitution will take place preferentially at the "upper", already functionalized Cp. (2) A consequence is that 1,1′-diphosphino derivatives will contain two equal PR$_2$ groups, because these will have to be introduced in a one-pot procedure.[5] (3) The methyl group at the stereogenic center in **3** is a specific feature of this compound, derivatives containing other substituents not being known or being less easily accessible.[6]

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(4) (a) Marquarding, D.; Klusacek, H.; Gokel, G.; Hoffmann, P.; Ugi, I. *J. Am. Chem. Soc.* **1970**, *92*, 5389−5393. (b) Gokel, G. W.; Marquarding, D.; Ugi, I. K. *J. Org. Chem.* **1972**, *94*, 3052−3058. (c) Gokel, G. W.; Ugi, I. K. *J. Chem. Educ.* **1972**, *49*, 294−296.

(5) Hayashi, T.; Mise, T.; Fukushima, M.; Kagotani, M.; Nagashima, M.; Hamada, Y.; Matsumoto, A.; Kawakami, S.; Konishi, M.; Yamamoto, K.; Kumada, M. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 1138−1151.

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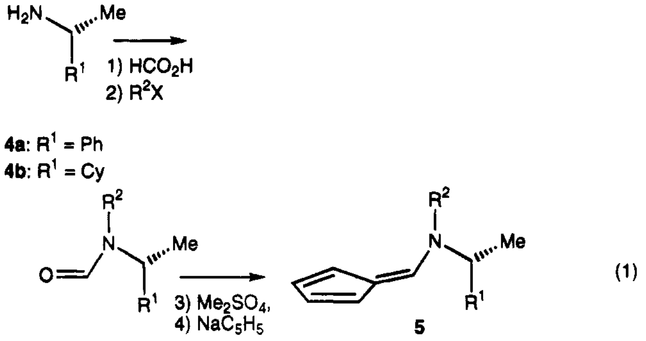
Our goal was to avoid these disadvantages by devising a new preparative method for compounds related to **3**, in particular seeking (1) more synthetic flexibility and (2) a stereoselective approach. The key feature of our strategy was to construct 1,1′-di- or polysubstituted ferrocenes starting from optically active Cp synthons and a suited iron(II) precursor.

This account provides full synthetic details for the preparation of new optically active ferrocenyl amines, as well as their derivatization to novel ligands for transition-metal-catalyzed asymmetric reactions.

Results and Discussion

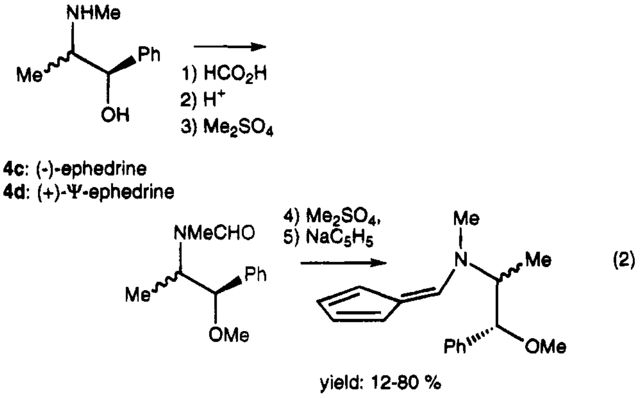
Synthesis. Optically Active Fulvenes and Their Use as Cyclopentadienyl Synthons. With cheap, optically pure amines from the chiral pool as starting materials, *i.e.* (*R*)-(+)-1-(phenylethyl)amine (**4a**), (*R*)-(−)-(1-cyclohexylethyl)amine (**4b**), (−)-ephedrine (**4c**), or the diastereoisomeric (+)-Ψ-ephedrine (**4d**), the fulvenes **5** can be obtained in 10−64% overall yield in a four- to five-step procedure (eqs 1 and 2). All reaction steps have been reported previously for related starting materials and successively involve (1) N-formylation, with neat formic acid,[7] (2) N-methylation (for **5a,b**) or O-methylation (for **5c,d**) employing dimethyl sulfate and a phase-transfer catalyst,[8] (3) O-methylation of the amide with dimethyl sulfate,[9] and (4) reaction with cyclopentadienylsodium.[10] Among the final products, compounds **5a−c** are nicely crystalline yellow solids that can be stored in air, while the others are yellow oils that slowly turn black on exposure to air. Especially the ephedrine-derived fulvenes **5e,f** tend to decompose and consequently were found to be of little use for the ferrocene syntheses reported here.



4a: R^1 = Ph
4b: R^1 = Cy

5

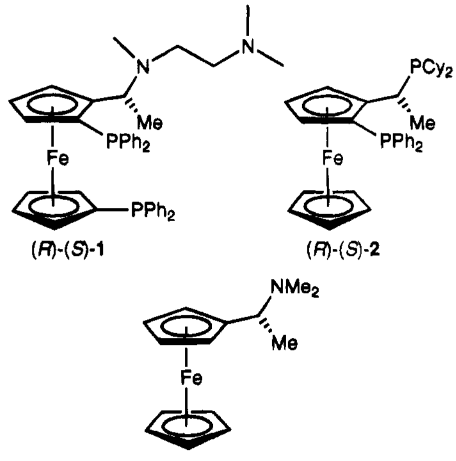
R^1	R^2	R^{2}X	product	yield (%)
Ph	Me	Me_2SO_4	**5a**	45
Cy	Me	Me_2SO_4	**5b**	64
Cy	Et	Et_2SO_4	**5c**	52
Cy	CH_2Ph	$ClCH_2Ph$	**5d**	30



4c: (-)-ephedrine
4d: (+)-Ψ-ephedrine

(*R*)-(*S*)-**5e**
(*S*)-(*S*)-**5f**

Chart 1

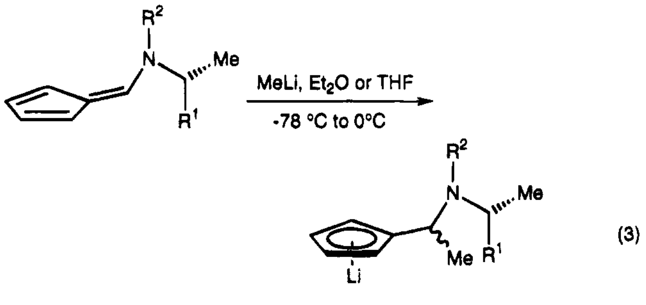


(*R*)-(*S*)-**1**

(*R*)-(*S*)-**2**

(*R*)-**3**

The new fulvenes can be converted quantitatively into cyclopentadienyls by addition of MeLi to the C_5H_4=CHN double bond (eq 3). This reaction with MeLi transforms the fulvene carbon atom at position 6 into a new stereogenic center, thus leading to two possible diastereoisomeric forms of the products. The NMR spectra of hydrolyzed samples taken from the reaction mixtures indicate that, with the fulvenes **5b−f**, the addition of MeLi can be performed with a varying degree of diastereoselectivity (*vide infra*), whereas fulvene **5a** affords the two diastereomeric cyclopentadienyl salts in nearly equal amounts.



quantitative yields

In order to get more insight into the diastereoselectivity of the cyclopentadienyl generation shown in eq 3, reaction mixtures of **5a−f** with LiMe in Et_2O or THF were quenched with an anhydrous iron(II) salt, either $FeCl_2$ or $[Fe(acac)_2]_n$.[11] These afforded mixtures of the diastereomeric ferrocenes **6a−f** quantitatively, as shown in Scheme 1. As a result of the newly generated stereogenic center, three diastereomeric forms of these homoleptic ferrocenes can be formed. Attempts to determine the relative amounts of the ferrocene mixtures by HPLC analysis were unsuccessful. Careful

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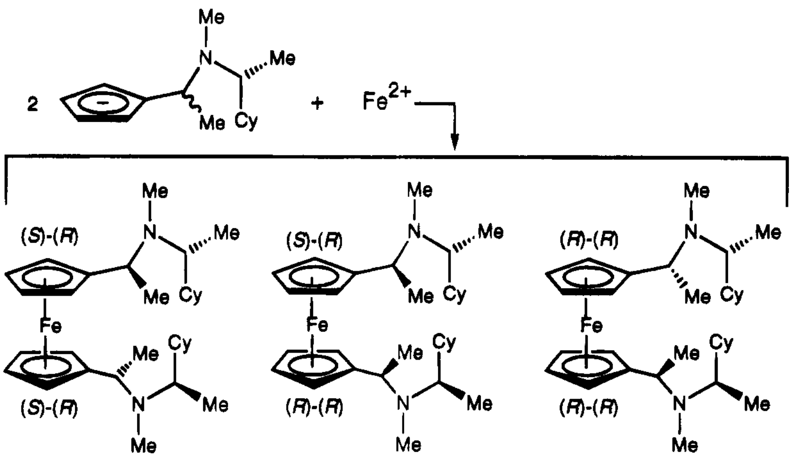
(6) (a) Wally, H.; Kratky, C.; Weissensteiner, W.; Widhalm, M.; Schlögl, K. *J. Organomet. Chem.* **1993**, *450*, 185−192. (b) Wally, H.; Widhalm, M.; Weissensteiner, W.; Schlögl, K. *Tetrahedron: Asymmetry* **1993**, *4*, 285−288. (c) Jedlicka, B.; Kratky, C.; Weissensteiner, W.; Widhalm, M. *J. Chem. Soc., Chem. Commun.* **1993**, 1329−1330. (d) Yamamoto, K.; Wakatsuki, J.; Sugimoto, R. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 1132−1137.

Scheme 1



(76 %) (S,R)-(S,R)'-**6b** Diastereomer A

(22 %) (S,R)-(R,R)'-**6b** Diastereomer B

(<2 %) (R,R)-(R,R)'-**6b** Diastereomer C

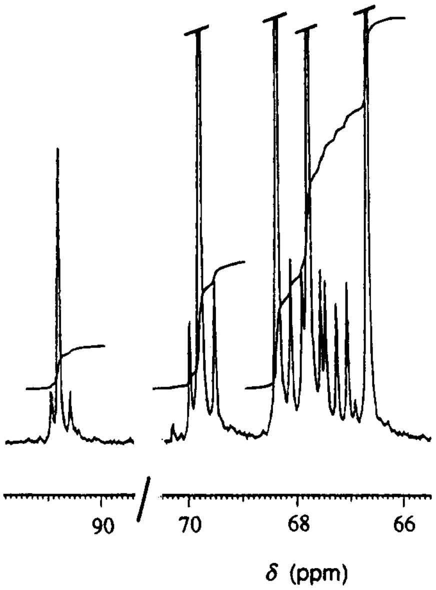


Figure 1. Cp region of the ^{13}C NMR spectrum (62.90 MHz, $CDCl_3$) of the diastereomeric mixture of compounds **6b**. The 5 major peaks are due to the isomer (*S*)-(*R*)-(*S'*)-(*R'*)-**6b** (pairwise equivalent Cp carbon atoms, diastereomer A), and the 10 small peaks arise from the isomer (*S*)-(*R*)-(*R'*)-(*R'*)-**6b** (nonequivalent Cp carbon atoms, diastereomer B). The concentration of the isomer (*R*)-(*R*)-(*R'*)-(*R'*)-**6b** (diastereomer C) is too low (<2%) for this compound to be identified.

analysis of high-resolution ^{13}C NMR spectra (see Figure 1), however, enabled us to assign reliable numbers to the product distribution. This analysis pointed out that, depending on the fulvene employed, the solvent, and the temperature, the reaction mixture contains up to 85%

Table 1. Diastereoselectivity of Cyclopentadienyl Generation from (*R*)-$C_5H_4CH{=}CHNR^1CHMeR^2$ (5) and MeLi[a]

fulvene	R^1	R^2	solvent	temp (°C)	ds (%)[b]
5a	Me	Ph	THF	0	50
5b	Me	Cy	Et_2O	20	80
5b	Me	Cy	THF	0	87
5b	Me	Cy	THF	−78	85[c]
5c	Et	Cy	THF	0	80
5d	CH_2Ph	Cy	THF	0	65
5e	Me	(*S*)-CH(OMe)Ph	THF	0	75
5f[d]	Me	(*S*)-CH(OMe)Ph	THF	0	80

[a] Unless otherwise specified, the reactions proceed with complete conversion within 1 h. [b] Values obtained by integration of the ^{13}C NMR resonances of the cyclopentadienyl carbons and/or the ^{1}H NMR resonances of the CH*Me* units from mixtures of homoleptic ferrocene derivatives of type **6** (see text). Only the two major diastereoisomers A and B, as illustrated in Scheme 1 for **6b**, are taken into account. % ds = [((% diastereomer A) + $^1/_2$(% diastereomer B))/((% diastereomer A) + (% diastereomer B))] × 100. [c] Only ca. 5% conversion after 18 h. [d] Reaction with (*S*)-$C_5H_4CH{=}CHNR^1CHMeR^2$.

of the diastereoisomer (*S*)-(*R*)-(*S*)'-(*R*)'-**6** (for the assignment of the absolute configuration of the new stereogenic center, see the discussion of the solid-state structure of derivative **12**, below). The diastereoselectivity of the underlying cyclopentadienyl generations are summarized in Table 1.

Although the synthesis of ferrocenes from fulvenes has been known for more than 30 years,[12] the high degree of diastereoselectivity in the reaction of **5b–f** with MeLi as reported here is, to our knowledge, unprecedented. Past attempts to stereochemically control related reactions did not provide any practical procedures. A typical example of the previous "state of the art" is the reaction of the prochiral fulvene $C_5H_4{=}C(Ph)Me$ with $LiAlH_4$/quinine, which is reported to give the cyclopentadienyl species $[C_5H_4CH(Ph)Me]^-$ with 17% ee.[13]

Heteroleptic Ferrocenyl Amines. 1′,2′,3′,4′,5′-Pentamethyl Derivatives. [Cp*Fe(acac)] (Cp* = $C_5Me_5^-$, acac = acetylacetonate) has been reported to be a convenient starting material for the synthesis of some mixed-Cp ferrocenes.[14] We used *in situ* generated

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(7) Huisgen, R.; Rüchardt, C. *Justus Liebigs Ann. Chem.* **1956**, *601*, 21–39.

(8) (a) Gajda, T.; Koziara, A.; Zawadski, S.; Zwierzak, A. *Synthesis* **1979**, *11*, 549-552. (b) Note: though a similar procedure has been reported for the alkylation of alcohols with Me_2SO_4 (Merz, A. *Angew. Chem.* **1973**, *85*, 868–869), we obtained best results for the ephedrine O-methylation employing the procedure given for N-alkylation in ref 8a).

(9) Bredereck, H.; Effenberger, F.; Simchen, G. *Angew. Chem.* **1961**, *73*, 493.

(10) Hafner, K.; Vöpel, K. H.; Ploss, G.; König, C. *Ann. Chem.* **1963**, *661*, 52–75.

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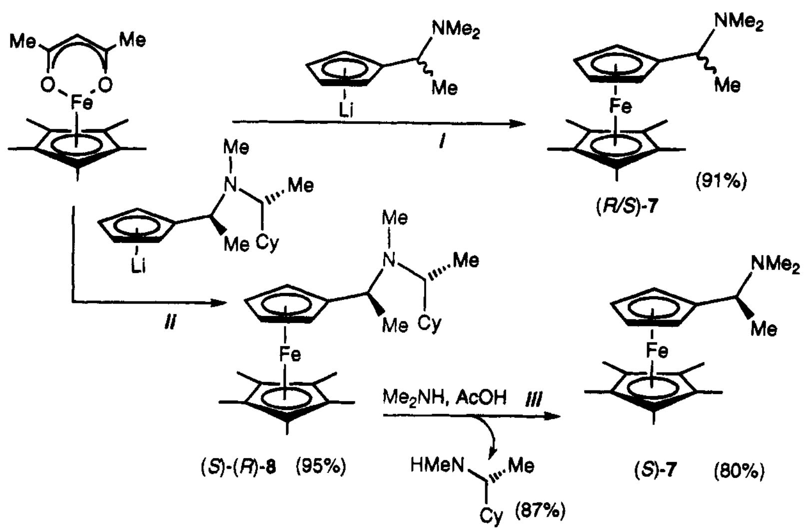
(12) Knox, G. R.; Munro, J. D.; Pauson, P. L.; Smith, G. H.; Watts, W. E. *J. Chem. Soc.* **1961**, 4619–4624.

(13) Leblanc, J. C.; Moise, C. *J. Organomet. Chem.* **1976**, *120*, 65–71.

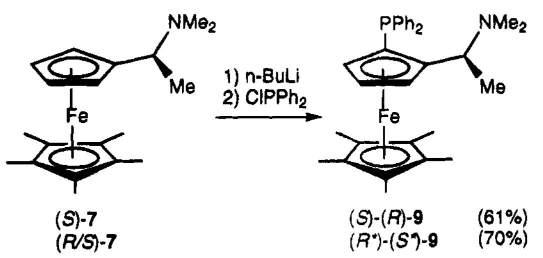
Scheme 2



[Cp*Fe(acac)] for the synthesis of new ferrocenyl amines as shown in Scheme 2. Racemic (ferrocenylethyl)amine **7** can be prepared in high yield (Scheme 2, route *i*) by transmetalation of [Cp*Fe(acac)] with racemic Li[C_5H_4-CH(Me)NMe_2] (prepared *in situ* from 6-(dimethylamino)fulvene and LiMe). Attempts to classically resolve racemic **7** with (*R*)-(+)-tartaric acid, in analogy to the method reported for the resolution of (*R*/*S*)-dimethyl-(1-ferrocenylethyl)amine,[4] were unsuccessful due to the very high solubility of the complexes in organic solvents. An alternative procedure to give optically pure **7** has therefore been developed using the chiral fulvene **5b**.

The related reaction of [Cp*Fe(acac)] with Li[C_5H_4-(*S*)-CH(Me)NMe-(*R*)-CH(Me)Cy] (prepared from **5b** as shown in eq 3) gives the ferrocenyl amine **8** in 95% chemical yield and 87% ds (Scheme 2, route *ii*). From this material, optically enriched dimethyl(1-ferrocenylethyl)amine ((*S*)-**7**; ee = 75%) can be prepared in 80% yield by substitution of the NMe-(*R*)-CH(Me)Cy unit of **8** with $HNMe_2$ (Scheme 2, route *iii*), a reaction that is easily achieved in acetic acid at 60 °C, with retention of configuration, as reported previously for the analogous compounds containing the unsubstituted Cp ligand.[3a] Interestingly, the chiral amine auxiliary used in the synthesis of fulvene **5b** can be recovered from the reaction mixture as (*R*)-N(Me)CH(Me)Cy in 87% yield.

Ferrocenylphosphines. Attempts to *ortho*-lithiate the optically enriched ferrocenyl amine (*S*)-(*R*)-**8** using *n*-BuLi, MeLi, or LDA were unsuccessful because of the low reactivity of compound **8**. This low reactivity is tentatively ascribed to the presence of sterically demanding substituents at the nitrogen center, which could severely disfavor chelation in the ferrocenyllithium intermediate. From a practical point of view this constitutes a disadvantage of the present methodology, since it requires a further synthetic step, i.e., the conversion of derivative (*S*)-(*R*)-**8** to the corresponding dimethylamine (*S*)-**7**. Thus, lithiation of the ferrocenyl amine **7** with *n*-BuLi can be achieved with high stereoselectivity and the lithiated ferrocene reacts easily with chlorodiphenylphosphine to give the optically enriched (diphenylphosphino)ferrocenyl amine (*S*)-(*R*)-**9** (eq 4).



(4)

The diastereoselectivity of this reaction must be greater than 99%, as the (*S*)-(*S*) diastereoisomer could never be identified. The racemate (*S**)-(*R**)-**9** readily crystallizes from hexane or MeOH, while the enantiomerically pure compound (*S*)-(*R*)-**9** is an oil that does not crystallize at room temperature.[15] Traces of the enantiomer (*R*)-(*S*)-**9**, which result from incomplete diastereoselectivity in the synthesis of (*S*)-(*R*)-**8**, can therefore be readily removed by crystallization as the racemate (*S**)-(*R**)-**9**. In such a way, (*S*)-(*R*)-**9** can be obtained nearly enantiomerically pure (>95% ee).

Attempts to convert the (diphenylphosphino)ferrocenyl amine (*S*)-(*R*)-**9** into the corresponding 1-ferrocenylethyl acetate by reaction with acetic anhydride met with complications. Treatment of the monophosphine (*S*)-(*R*)-**9** in acetic anhydride at 100 °C, as reported for the classical ferrocenyl ligands,[5] leads to quantitative formation of the vinyl complex (*R*)-**10** (Scheme 3, route *i*). Obviously, under these conditions, deprotonation of the intermediate ferrocenyl carbocation is much faster than the nucleophilic attack of the acetate anion. Under different conditions, however, the dimethylamino fragment of the derivative (*S*)-(*R*)-**9** can be easily substituted by both phosphine and amine functionalities. Thus, reaction with dicyclohexylphosphine in acetic acid at 60 °C affords the diphosphino ferrocene derivative (*S*)-(*R*)-**11** and the analogous reaction with the bicyclic aliphatic phosphine 9-phospha[3.3.1]bicyclononane ("phobane")[16] gives the novel bidentate ligand (*S*)-(*R*)-**12** (Scheme 3, routes *ii* and *v*). The phobane fragment gives us the

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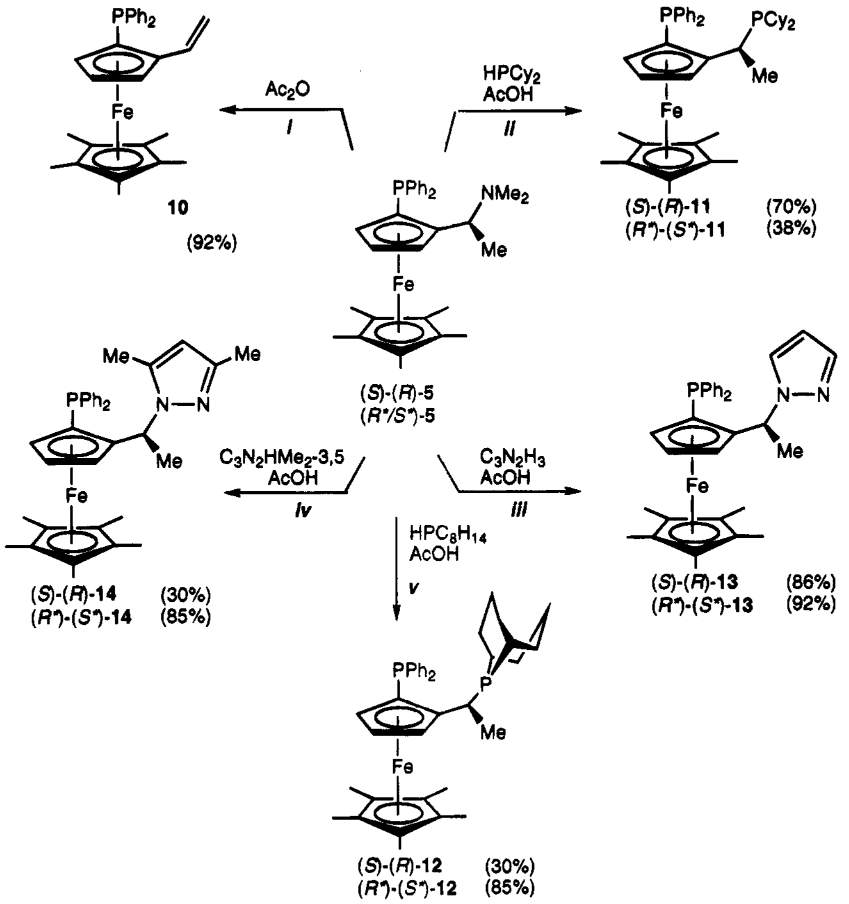
(14) (a) Bunel, E. E.; Valle, L.; Manriquez, J. M. *Organometallics* **1985**, *4*, 1680–1682. (b) Paciello, R. A.; Manriquez, J. M.; Bercaw, J. E. *Organometallics* **1990**, *9*, 260–265. (c) Herberich, G. E.; Englert, U.; Marken, F. M.; Hoffmann, P. *Organometallics* **1993**, *12*, 4039–4045.

(15) For a discussion of this aspect, see: Pratt Brock, C.; Schweizer, W. B.; Dunitz, J. D. *J. Am. Chem. Soc.* **1991**, *113*, 9811–9820.

(16) (a)Harris, T. V.; Pretzer, W. R. *Inorg. Chem.* **1985**, *24*, 4437–4439. (b) Weferling, N. *Z. Anorg. Allg. Chem.* **1987**, *548*, 55–62 and references cited therein.

Scheme 3



opportunity to construct ligands with a conformationally rigid, compact, and electron-rich trialkylphosphine moiety. As has been shown previously,[3a] the combination of sterically and electronically different phosphino groups in the same molecule can drastically modify the properties of the corresponding transition-metal catalysts. An interesting practical aspect of the synthesis of the phobane complex **12** is that it can be prepared using phobane from a technical source that contains ca. 35% of 9-phospha[4.2.1]bicyclononane, together with substantial quantities of phosphine oxides. Since no convenient method exists for the purification of technical phobane, its synthetic applications are very limited. We found, however, that direct use of a ca. 10-fold excess of this technical-grade material allows clean synthesis of **12** without formation of the isomer derived from the 9-phospha[4.2.1]bicyclononane. Furthermore, the novel (diphenylphosphino)ferrocenyl pyrazoles (*S*)-(*R*)-**13** and (*S*)-(*R*)-**14** could also be prepared in moderate to high yield under similar conditions from the corresponding pyrazoles (Scheme 3, routes *iii* and *iv*). All these new ligands were obtained in good yields in crystalline form. For compounds (*S*)-(*R*)-**11**–**14** both the racemic ((*S**)-(*R**)) and the optically pure forms ((*S*)-(*R*)) have been prepared. The racemates can be readily separated by HPLC on a chiral stationary phase (see Table 2). This provides a useful reference to establish the optical purities of crystalline (*S*)-(*R*)-**11**, (*S*)-(*R*)-**12**, (*S*)-(*R*)-**13**, and (*S*)-(*R*)-**14** (98, 100, 100, and 100% ee, respectively). A typical chromatogram showing the separation of the two enantiomers of derivative **13** is shown in Figure 2.

1′-Methylferrocenyl Ligands. The synthesis of heteroleptic ferrocenes with a *mono*(cyclopentadienyl)-iron(II) derivative as the starting material, as described above for [Cp*Fe(acac)], is seriously hampered by the inaccessibility of such simple *mono*cyclopentadienyl compounds. Attempts to prepare $MeC_5H_4FeC_5H_4CH(Me)N(Me)CH(Me)Cy$ (**14**) by *sequentially* adding THF solutions of $Li[MeC_5H_4]$ and $Li[C_5H_4CH(Me)N(Me)CH(Me)Cy]$ to $[Fe(acac)_2]_n$ at −78 °C invariably gave rise to homoleptic ferrocenes only. Similar results were obtained when, instead of $[Fe(acac)_2]_n$, the related, monomeric complex $[Fe(t\text{-}BuCOCHCO\text{-}t\text{-}Bu)_2]$[17] was used. A successful, though less elegant, approach to other heteroleptic ferrocenes is feasible when solutions of both cyclopentadienyl salts are mixed prior to adding them to $[Fe(acac)_2]_n$. Though nearly statistical mixtures of both possible homoleptic and heteroleptic ferrocenes result from this procedure, variations in the relative amounts of the cyclopentadienyls allow for good use of one of these Cp's. An illustration of this approach is shown in Scheme 4, where the product distribution for the reaction of 3 equiv of $Li[MeC_5H_4]$ and 1 equiv of $Li[C_5H_4CH(Me)N(Me)CH(Me)Cy]$ with $[Fe(acac)_2]_n$ has been calculated (assuming equal reactivity of both cyclopentadienyls) to incorporate 84% of the more precious, chiral cyclopentadienyl in the desired heteroleptic product. The reaction of a 3:1 *mixture* of $Li[MeC_5H_4]$ and $Li[C_5H_4CH(Me)N(Me)CH(Me)Cy]$ with $[Fe(acac)_2]_n$ leads to a mixture of ferrocenes that contains mainly $Fe(C_5H_4Me)_2$ and the desired product $(C_5H_4Me)FeC_5H_4CH(Me)N(Me)CH(Me)Cy$ (**15**). Com-

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[17] (a) Linn, B. O.; Hauser, C. R. *J. Am. Chem. Soc.* **1956**, *78*, 6066–6070. (b) Fackler, J. P.; Hollah, D. G.; Buckingham, D. A.; Henry, J. T. *Inorg. Chem.* **1965**, *4*, 920–921. (c) Buckingham, D. A.; Gorges, R. C.; Henry, J. T. *Aust. J. Chem.* **1967**, *20*, 281–296.

Table 2. Separation of Ferrocenylphosphines by HPLC[a]

compd	solvent	flow (mL min^{-1})	ret time (min)	enantiomer	R_s[b]
11	hexane/*i*-PrOH (99.5:0.5)	1.0	5.8	(*R*)-(*S*)-**11**	1.1
			6.3	(*S*)-(*R*)-**11**	
12	hexane/*i*-PrOH (99.3:0.7)	0.4	9.2	(*R*)-(*S*)-**12**	0.5
			9.4	(*S*)-(*R*)-**12**	
13	hexane/*i*-PrOH (98.0:2.0)	1.0	8.0	(*R*)-(*S*)-**13**	7.1
			14.4	(*S*)-(*R*)-**13**	
14	hexane/*i*-PrOH (98.0:2.0)	1.0	4.8	(*R*)-(*S*)-**14**	2.2
			5.5	(*S*)-(*R*)-**14**	

[a] Measurements were made on a Hewlett-Packard 1050 Series chromatograph using a 25 cm Daicel Chiralcel ODH column: T = 25 °C (isothermic); detection 254 nm. [b] The resolution R_s is defined as $R_s = 2(t_{R2} - t_{R1})/(w_1 + w_2)$, where t_R is the retention time and w is the peak width at half-height.

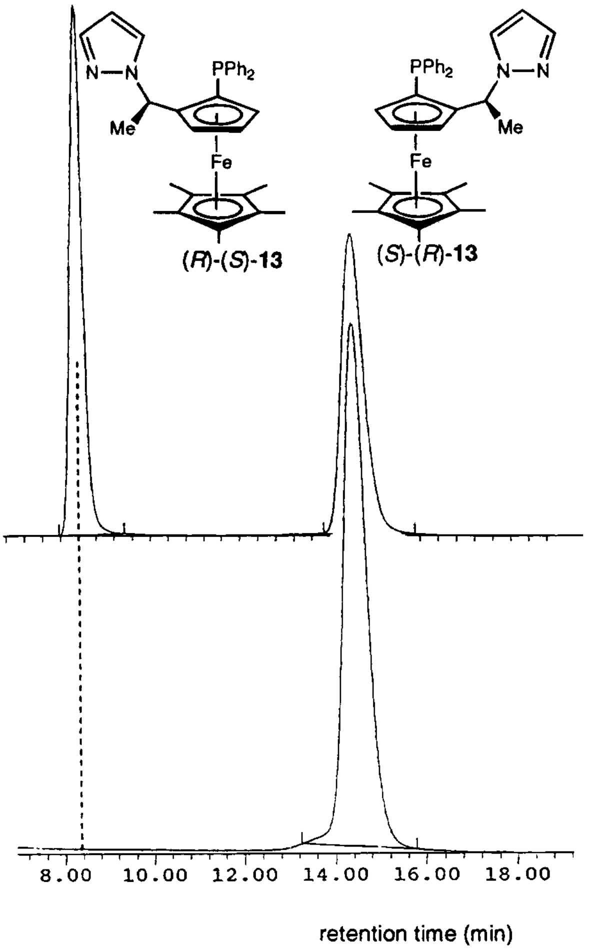

Figure 2. HPLC chromatograms (Daicel Chiralcel OD-H, hexane/*i*-PrOH (98:2 v/v), flow = 1 mL·min^{-1}) of racemic (top) and enantiomerically pure (bottom) **13**.

pound **15** is difficult to isolate from this mixture by conventional column chromatography but may be converted *in situ* to its dimethylamine analogue (*S*)-**16**, which can be readily isolated and purified by column chromatography. The conversion of **15** to (*S*)-**16** can be effected by treatment with Me$_2$NH·HCl and NaOAc in acetic acid at 60 °C (Scheme 5, step *i*). The final utilization of the chiral fulvene in the two-step synthesis of (*S*)-**16** gives an acceptable 66% yield.

Lithiation of the ferrocenyl amine (*S*)-**16** with butyllithium can be achieved like that of its Cp* analogue (*S*)-**7**, and the lithiated ferrocene can be easily converted with chlorodiphenylphosphine to give the (diphenylphosphino)ferrocenyl amine (*S*)-(*R*)-**17** in 60% yield (Scheme 5, step *ii*). Subsequently, the dimethylamine derivative (*S*)-(*R*)-**17** can be smoothly converted to the diphosphine (*S*)-(*R*)-**18** via reaction with dicyclohexylphosphine at 60 °C. The yellow microcrystalline (*S*)-(*R*)-**18** is isolated in 70% yield (Scheme 5, step *iii*).

Solid-State Structure of Racemic (*S)-(*R**)-$\mathrm{Cp^*FeC_5H_3CH(Me)\{(PC_8H_{14})PPh_2\}}$-1,2 ((*S**)-(*R**)-12).** In order to establish the incorporation of the phospha[3.3.1]bicyclononyl isomer from technical grade phobane in the structure of (*S**)-(*R**)-**12** and to elucidate conformational characteristics of this complex, an X-ray structural analysis was carried out. Suitable crystals of (*S**)-(*R**)-**12** were obtained from ethanol. A selection of bond lengths and angles is given in Table 3, and a view of the molecule is shown in Figure 3. Crystal data are collected in Table 4, and the final atomic coordinates are given in Table 5. No bond length shows significant deviation from normal values.[18] The most interesting features of this structure involve conformational aspects. Thus, the presence of the Cp* ligand forces the two phenyl substituents on P(1) to take axial and equatorial positions, respectively (see the torsion angle C(2)−C(1)−P(1)−C(16) of 87.0(5)°). The axial phenyl ring indirectly dictates, at least in part, the conformation of the stereogenic side chain. Thus, in order to avoid severe intermolecular contacts, the phosphabicyclononyl (phobyl) fragment points away from P(1) (torsion angle C(1)−C(2)−C(6)−P(2) = −164.0(5)°). This leads to an endo-axial position of the methyl group C(7), which is located 0.92 Å below the Cp ring and is also at a relatively short distance from the iron atom (3.73 Å). As a consequence, C(6) is lifted above the Cp plane by 0.24 Å. Because of this distortion and although C(3), C(2), C(6), and P(2) are essentially coplanar (within 0.08 Å, see also the torsion angle defined by these four atoms of 3°), P(2) is situated 0.65 Å above the Cp ring. That the molecule suffers from some intramolecular crowding is also reflected by the opening up of the ferrocene core, such that the two planes defined by the Cp rings form an angle of 9.3(5)°. The bending of the sandwich is also manifested by the differing distances between corresponding pairs of Cp−Cp* carbon atoms, varying from 3.15 Å for C(4)−C(4′) to 3.51 Å for C(2)−C(2′). Furthermore, the two Cp rings are not perfectly eclipsed, being rotated by ca. 11° against each other, but the iron atom is equidistant from the Cp rings (1.66 Å). Finally, the two phosphacyclohexane rings of the phobyl fragment display an almost perfect chair conformation.

Solid-State Structure of (*S*)-(*R*)-$\mathrm{Cp^*FeC_5H_3CH(Me)\{(N_2C_3H_3)PPh_2\}}$-1,2 ((*S*)-(*R*)-13). In order to establish the absolute configuration of optically active (*S*)-(*R*)-**13**, an X-ray structural analysis of this compound was carried out. Suitable crystals were obtained from a hot MeOH solution of (*S*)-(*R*)-**12** that was allowed to slowly cool down to −20 °C. The molecular structure involves the packing of four discrete monomeric molecules in the unit cell. An ORTEP drawing of (*S*)-(*R*)-**12** along with the adopted numbering scheme is shown in Figure 4; selected bond distances and angles are given in Table 6. Table 4 collects relevant crystal and data

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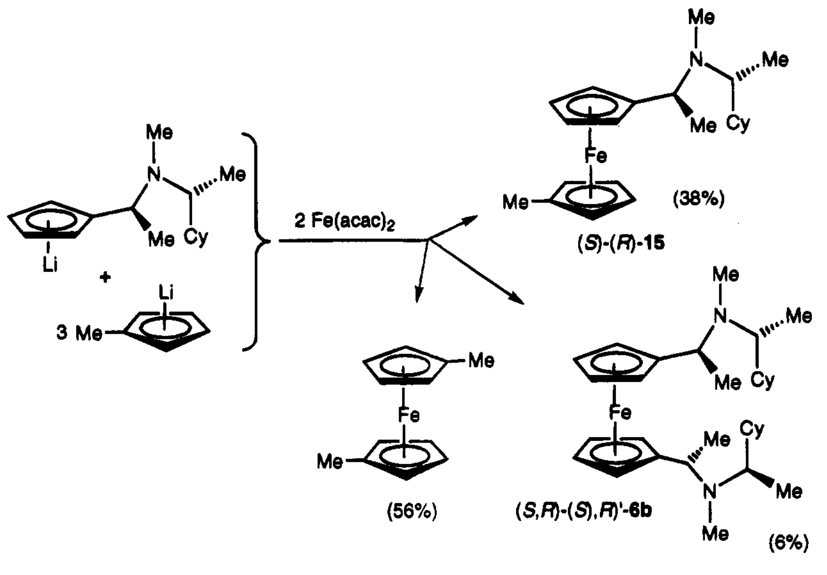
[18] (a) Orpen, A. G.; Brammer, L.; Allen, F. H.; Kennard, O.; Watson, D. G.; Taylor, R. *J. Chem. Soc., Dalton Trans.* **1989**, Supplement S1-S83. (b) Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. *J. Chem. Soc., Perkin Trans 2* **1987**, Supplement S1−S19. (c) The positions of the substituents at C(6) correspond qualitatively to what is usually found in related ferrocenyl compounds.[3c]

Scheme 4



Scheme 5

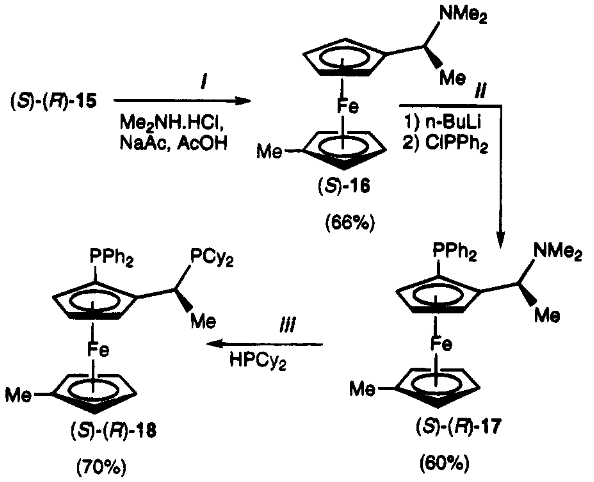


Table 3. Selected Bond Distances (Å) and Angles (deg) for (S^*)-(R^*)-$Cp^*FeC_5H_3CH(Me)\{(PC_8H_{14})PPh_2\}$-1,2 ($(S^*)$-$(R^*)$-**12**)[a]

	Bond Distances		
P(1)–C(1)	1.824(3)	P(1)–C(16)	1.834(5)
P(1)–C(17)	1.839(3)	C(2)–C(6)	1.517(4)
C(6)–P(2)	1.870(3)	P(2)–C(8)	1.855(3)
P(2)–C(12)	1.845(5)	C(2)–C(6)	1.517(4)
C(6)–C(7)	1.540(6)	Fe–Cp*[b]	1.664(5)
Fe–Cp[b]	1.660(5)		
	Bond Angles		
C(2)–C(1)–P(1)	123.5(2)	C(5)–C(1)–P(1)	129.2(2)
C(1)–P(1)–C(16)	101.7(2)	C(1)–P(1)–C(22)	103.3(1)
C(16)–P(1)–C(22)	99.6(2)	C(1)–C(2)–C(6)	124.7(3)
C(3)–C(2)–C(6)	127.6(3)	C(2)–C(6)–C(7)	115.1(3)
C(7)–C(6)–P(2)	107.6(2)	C(6)–P(2)–C(8)	102.6(1)
C(6)–P(2)–C(12)	105.3(2)	C(8)–P(2)–C(12)	93.2(2)

[a] Numbers in parentheses following the bond distances and angles are standard deviations in the least-significant digits. [b] Distance from the plane defined by the Cp (and Cp*) ring to the iron atom. Fe–C distances range from 2.027(5) to 2.092(4) Å for the "upper" Cp and from 2.039(4) to 2.075(5) Å for Cp*.

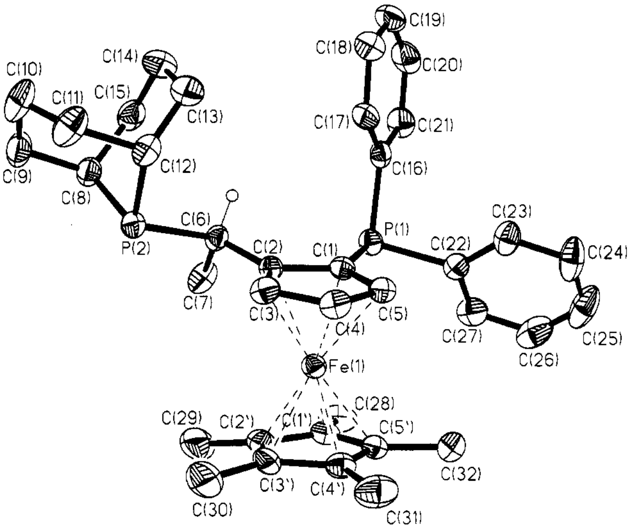


Figure 3. Structure of racemic (S^*)-(R^*)-$Cp^*FeC_5H_3CH(Me)\{(PC_8H_{14})PPh_2\}$-1,2 ($(S^*)$-$(R^*)$-**12**) in the crystal: ORTEP drawing with 50% probability thermal ellipsoids.

collection parameters, whereas final atomic coordinates are given in Table 7. All bond distances and angles fall in the expected range.[18] The X-ray structure shows that the configuration at C(6) is *S*, while the planar chirality at the disubstituted Cp ring has *R*-handedness. *Because all the substitution reactions at C(6) discussed above occur with retention of configuration,*[4b] *one can now unambiguously assign the absolute configuration S to the pseudo-benzylic center of all derivatives of this series.*

The relative positions of the substituents at C(6) correspond to what is usually found in related ferrocenyl compounds.[3c] Thus, the pyrazolyl fragment is in a pseudoaxial orientation (torsion angle C(3)–C(2)–C(6)–N(1) = −96.9(4)°, and the distance of N(1) from the least-squares plane defined by C(1)–C(5) is 1.444(3) Å) and the methyl group (C(10)) is located slightly below the above-mentioned plane (torsion angle C(3)–C(2)–C(6)–C(10) = 27.2(5)° and a distance of 0.487(5) Å). A slight tilt of 6.7° between the two Cp rings is observed and may be ascribed to steric hindrance of the Cp substituents.

The pseudoequatorial position of one of the phenyl rings may be dictated by the relatively close contact between C(22) and C(28). Simple molecular models show that (1) a pseudoaxial position can be excluded because of unacceptably short intermolecular contacts (Ph–Cp*) and (2) any change in conformation obtained by rigid rotation around the P–C(17) axis leads again to unacceptable Van der Waals contacts (less than 3.1

Table 4. Experimental Data for the X-ray Diffraction Study of 12 and 13

compd	(*S*)-(*R*)-**12**	(*S*)-(*R*)-**13**
formula	$C_{37}H_{46}FeP_2$	$C_{32}H_{35}FeN_2P$
mol wt	608.5	534.47
crystal dimens (mm)	0.2 × 0.2 × 0.3	0.45 × 0.40 × 0.12
data collecn *T* (°C)	20	25
cryst syst	triclinic	orthorhombic
space group	$P\bar{1}$	$P2_12_12_1$
a (Å)	11.265(4)	8.586(4)
b (Å)	11.666(4)	16.224(9)
c (Å)	13.870(4)	20.054(2)
V (Å³)	1622.2(9)	2793.7(4)
Z	2	4
ϱ(calcd) (g·cm^{-3})	1.246	1.273
μ (cm^{-1})	5.87	6.176
F(000)	648	1128
diffractometer	Nonius CAD4	Syntex P21
radiation	Mo Kα (graphite monochromator), $\lambda = 0.710\,69$ Å	
measd rflns	$0 \le h \le 12, -12 \le k \le 12, -14 \le l \le 14$; $+h,+k,+l$ ($15.0 < \theta < 25.0°$)	$+h,+k,+l$; $-h,-k,-l$ ($2.5 < \theta < 15.0°$)
2θ range (deg)	3.0−45.0	5.0−50.0
scan type	ω	$\omega/2\theta$
scan width (deg)	1.10	$1.10 + 0.35 \tan \theta$
bkgd time (s)	0.3 × scan time	0.5 × scan time
max scan speed (deg·min^{-1})	9.0	5.6
no. of indep data collected	4261	3469
no. of obsd rflns (n_o)	3537 ($\lvert F_o^2\rvert > 3.0\sigma(\lvert F\rvert^2)$)	2578 ($\lvert F_o^2\rvert > 4.0\sigma(\lvert F\rvert^2)$)
transmissn coeff		0.9531−0.9977
no. of params refined (n_v)	361	325
quantity minimized	$\sum w(F_o - F_c)^2$	$\sum w(\lvert F_o\rvert - 1/k\lvert F_c\rvert)^2$
weighting scheme	$w^{-1} = \sigma^2(F) + 0.0000F^2$	$w = [\sigma^2(F_o)]^{-1\,a}$
R^b	0.038	0.031
$R_w{}^c$	0.035	0.042
GOF^d	3.06	1.149

[a] $\sigma(F_o) = [\sigma^2(F_o)^2 + f^4(F_o)^2]^{1/2}/2F_o$, with $f = 0.060$. [b] $R = \sum(\lvert\lvert F_o\rvert - (1/k)\lvert F_c\rvert\rvert)/\sum\lvert F_o\rvert$. [c] $R_w = \sum w(\lvert\lvert F_o\rvert - (1/k)\lvert F_c\rvert\rvert)^2/[\sum w\lvert F_o\rvert^2]^{1/2}$. [d] GOF $= [\sum w(\lvert F_o\rvert - (1/k)\lvert F_c\rvert)^2/(n_o - n_v)]^{1/2}$.

Table 5. Final Positional Parameters (×10⁴) and Equivalent Isotropic Displacement Coefficients (×10³)[a] for (*S)-(*R**)-12[b]**

atom	*x*	*y*	*z*	U_{eq}, Å²
Fe(1)	2470(1)	4577(1)	7949(1)	39(1)
P(1)	5384(1)	5623(1)	7200(1)	45(1)
P(2)	1418(1)	8728(1)	6556(1)	48(1)
C(5)	3435(3)	4686(3)	8990(3)	45(2)
C(4)	2185(3)	5029(3)	9252(3)	48(2)
C(1)	3846(3)	5539(3)	7945(3)	39(2)
C(3)	1789(3)	6084(3)	8386(3)	47(2)
C(3′)	1020(3)	3929(4)	7732(3)	55(2)
C(2)	2799(3)	6427(3)	7560(3)	38(2)
C(2′)	1831(4)	4285(3)	6775(3)	54(2)
C(6)	2863(3)	7625(3)	6571(3)	43(2)
C(22)	6232(3)	4125(3)	7962(3)	47(2)
C(4′)	1661(3)	2963(3)	8527(3)	48(2)
C(23)	6475(3)	3826(4)	8987(3)	60(2)
C(17)	5312(3)	7283(3)	8266(3)	54(2)
C(30)	308(3)	4435(4)	7865(4)	93(3)
C(5′)	2864(3)	2753(3)	8058(3)	44(2)
C(16)	5971(3)	6698(3)	7607(3)	44(2)
C(8)	1860(3)	10222(3)	5486(3)	54(2)
C(1′)	2981(3)	3569(3)	6969(3)	49(2)
C(15)	3083(3)	10553(3)	5561(3)	63(2)
C(31)	1107(4)	2258(4)	9653(3)	80(2)
C(27)	6689(3)	3268(4)	7476(3)	65(2)
C(28)	4089(3)	3605(4)	6135(3)	75(2)
C(19)	6949(5)	8424(4)	8053(4)	77(3)
C(9)	767(4)	11241(3)	5493(3)	71(2)
C(12)	1398(3)	9300(3)	7622(3)	58(2)
C(14)	3185(4)	10644(4)	6611(3)	79(3)
C(7)	3127(3)	7428(3)	5511(3)	65(2)
C(11)	318(4)	10361(4)	7540(3)	80(2)
C(21)	7164(3)	6976(4)	7186(3)	62(2)
C(25)	7532(4)	1835(5)	9031(5)	98(3)
C(20)	7642(4)	7825(4)	7420(4)	78(3)
C(10)	425(4)	11529(4)	6508(3)	86(3)
C(24)	7119(4)	2688(5)	9512(4)	82(2)
C(18)	5778(4)	8158(4)	8487(3)	70(2)
C(29)	1460(4)	5121(4)	5695(3)	102(3)
C(26)	7319(4)	2112(5)	8026(5)	90(3)
C(13)	2607(4)	9677(4)	7629(3)	73(2)
C(32)	3850(3)	1764(3)	8625(3)	70(2)

[a] Equivalent isotropic *U* values are defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor. [b] Esd's on the last significant digit are given in parentheses.

Å). As a result of these interactions, the second Ph ring is forced in a pseudoaxial position, as shown by the torsion angle C(11)−P−C(1)−C(2) of 85.4(3)°. The planes defined by this second Ph ring and the pyrazole fragment make an angle of 14.9(4)°. This angle and the interplanar distances (in the range between 3.4 and 3.5 Å) are consistent with an attractive intramolecular stacking interaction.[19]

Conclusions

We have demonstrated that it is possible to prepare chiral, optically active ferrocenyl ligands, thereby exploiting the diastereoselective addition of alkyllithium reagents to optically pure aminofulvenes derived from the chiral pool. The chiral auxiliaries employed can be partially recovered and reused. This strategy offers a method for the synthesis of derivatives which are not accessible by conventional functionalization reactions of the preformed ferrocene core, thus opening a new avenue for the modification of known ferrocenyl ligands. In particular, the Cp* derivatives **9** and **11** provide an opportunity to study the effect of the enhanced steric bulk of the "lower" Cp ring on the conformation of the chelate ring of their transition-metal complexes and, hence the effect on stereoselectivity of homogeneously catalyzed reactions. Furthermore, the combination of phosphine and pyrazolyl ligands to give a chiral P,N-chelating unit of types **13** and **14** had not been realized before. We are currently studying the coordination chemistry of our new ligands, as well as their application in asymmetric catalysis. Furthermore, we are extending our synthetic strategy to the corresponding ruthenocene derivatives. The results of these studies will be reported in due course.

Experimental Section

General Considerations. All reactions with air- or moisture-sensitive materials were carried out under Ar using standard Schlenk techniques. Freshly distilled, dry, and oxygen-free solvents were used throughout. Routine ^{1}H (250.133 MHz), ^{13}C (62.90 MHz), and ^{31}P NMR (101.26 MHz) spectra were recorded with a Bruker AM 250 spectrometer. Chemical shifts are given in ppm, and coupling constants (*J*) are given in Hz. Merck silica gel 60 (70−230 mesh) was used for column chromatography. Optical rotations were measured with a Perkin-Elmer 241 polarimeter using 10 cm cells. HPLC measurements were made on a Hewlett-Packard 1050 Series chromatograph using a 25 cm Daicel Chiralcel ODH column (see Figure 2 and Table 2). Elemental analyses were performed by the "Mikroelementar-analytisches Laboratorium

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(19) Togni, A.; Hobi, M.; Rihs, G.; Rist, G.; Albinati, A.; Zanello, P.; Zech, D.; Keller, H. *Organometallics* **1994**, *13*, 1224−1234 and references cited therein.

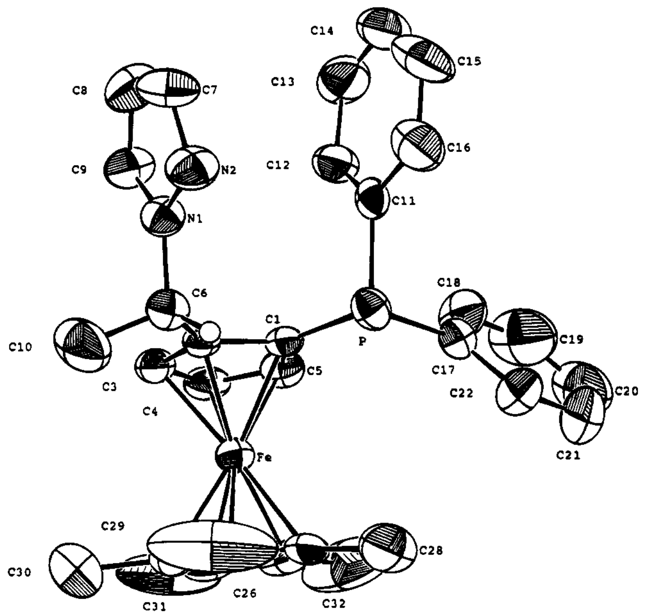

Figure 4. Structure of (*S*)-(*R*)-$Cp^*FeC_5H_3CH(Me)\{(N_2C_3H_3)PPh_2\}$-1,2 (*S*)-(*R*)-**13**) in the crystal: ORTEP drawing with 50% probability thermal ellipsoids. The H atom at C(6) is at a calculated position.

Table 6. Selected Bond Distances (Å) and Angles (deg) for (*S*)-(*R*)-$Cp^*FeC_5H_3CH(Me)\{(N_2C_3H_3)PPh_2\}$-1,2 ((*S*)-(*R*)-13)[a]

	Bond Distances		
P−C(1)	1.819(4)	P−C(11)	1.835(5)
P−C(17)	1.845(5)	C(2)−C(6)	1.509(6)
C(6)−N(1)	1.478(5)	N(1)−N(2)	1.342(5)
C(6)−C(10)	1.477(6)	Fe−Cp*[b]	1.671(1)
Fe−Cp[b]	1.657(1)		
	Bond Angles		
C(1)−C(2)−C(3)	107.6(4)	C(1)−C(2)−C(6)	125.8(4)
C(3)−C(2)−C(6)	126.5(4)	N(1)−C(6)−C(2)	110.1(3)
N(1)−C(6)−C(10)	109.2(4)	C(2)−C(6)−C(10)	115.3(4)
N(2)−N(1)−C(6)	119.5(4)	N(2)−N(1)−C(9)	111.6(4)
C(1)−P−C(11)	102.6(2)	C(1)−P−C(17)	102.7(2)
C(11)−P−C(17)	99.3(2)	P−C(1)−C(2)	121.9(3)
P−C(1)−C(5)	69.2(2)	C(2)−C(1)−C(5)	107.0(4)

[a] Numbers in parentheses following the bond distances and angles are standard deviations in the least-significant digits. [b] Distance from the plane defined by the Cp (and Cp*) ring to the iron atom; Fe−C distances range from 2.031(5) to 2.072(5) Å for the "upper" Cp and from 2.047(4) to 2.067(4) Å for the Cp*.

der ETH". The enantiomerically pure compounds **4a−d** were purchased from Fluka AG und used as received. The ee values of the ferrocene products are either inferred from the diastereoselectivity of the nucleophile addition to the fulvene derivatives, as determined by NMR (see Table 1), or measured by HPLC (see Table 2), as appropriately stated.

(*R*)-PhCH(Me)N(Me)CH=C_5H_4 (5a). A colorless mixture of (*R*)-Ph(Me)CHN(Me)CHO (34.6 g, 0.212 mol) and Me_2SO_4 (21 mL, 0.22 mol) was heated to 110 °C for 1.5 h and then slowly added to a solution of $Na[C_5H_5]$ (27 g, 0.30 mol) in THF (150 mL). The resulting green suspension was heated to reflux for 5 min and filtered in air and the darkening residue washed with 3 × 150 mL of THF. The solvent was removed from the combined filtrates *in vacuo*, and the resulting black tar was extracted with 2 × 500 mL of hot hexane. The combined yellow extracts were concentrated to ca. 300 mL and stored overnight at −20 °C, causing the product to crystallize as yellow needles: yield 20 g (45%), $[\alpha]^{22}_D = +136$ (c = 1.0, $CHCl_3$). ^1H NMR ($CDCl_3$, 298 K): δ 7.45 (s, 1H, C*H*=C_5H_4), 7.40−7.21 (m, 5H, Ph), 6.57 (m, 2H, C_5H_4), 6.49 (m, 1H, C_5H_4), 6.40 (m, 1H, C_5H_4), 4.76 (br s, 1H, C*H*MeN), 3.01 (s, 3H, NMe), 1.68 (d, 3H, CH*Me*N, ^3J(HH) = 7). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 298 K): δ 147.0 (=CHN), 139.7, 129.0, 128.2, 126.8, 125.6, 125.0 (Ph), 120.0, 117.3, 116.3, 114.6 (C_5H_4), 35.9 (NMe), 18.7 (CH*Me*N). Note: no resonance was observed that could be assigned to *C*HMeN. Anal. Calcd for $C_{15}H_{17}N$: C, 85.26; H, 8.11; N, 6.63. Found: C, 84.99; H, 7.92; N, 6.56.

Table 7. Final Positional Parameters and Equivalent Temperature Factors[a] for (*S*)-(*R*)-13[b]

atom	*x*	*y*	*z*	B_{eq}, Å^2
Fe	0.63105(6)	0.46306(3)	0.80055(3)	2.901(9)
P	0.9519(1)	0.52501(7)	0.89474(5)	3.43(2)
N(1)	1.0120(4)	0.3026(3)	0.8759(2)	3.39(7)
N(2)	1.1676(4)	0.3095(2)	0.8785(2)	4.37(8)
C(1)	0.7773(4)	0.4632(2)	0.8824(2)	2.82(7)
C(2)	0.7816(4)	0.3848(2)	0.8486(2)	2.95(8)
C(3)	0.6267(5)	0.3518(2)	0.8490(2)	3.63(8)
C(4)	0.5292(5)	0.4084(3)	0.8815(2)	3.90(9)
C(5)	0.6204(5)	0.4768(2)	0.9021(2)	3.82(8)
C(6)	0.9253(4)	0.3432(2)	0.8214(2)	3.58(9)
C(7)	1.2080(5)	0.2597(3)	0.9281(2)	5.2(1)
C(8)	1.0839(6)	0.2228(3)	0.9574(2)	5.4(1)
C(9)	0.9583(5)	0.2505(3)	0.9224(2)	4.5(1)
C(10)	0.8974(7)	0.2829(3)	0.7674(2)	7.1(1)
C(11)	1.0338(5)	0.4820(2)	0.9717(2)	3.26(8)
C(12)	0.9552(6)	0.4363(3)	1.0180(2)	4.7(1)
C(13)	1.0266(7)	0.4083(3)	1.0768(2)	5.9(1)
C(14)	1.1779(6)	0.4264(3)	1.0871(2)	6.5(1)
C(15)	1.2607(6)	0.4703(3)	1.0422(3)	6.6(1)
C(16)	1.1893(5)	0.4977(3)	0.9841(2)	5.1(1)
C(17)	0.8732(5)	0.6225(2)	0.9282(2)	3.97(9)
C(18)	0.7845(7)	0.6286(3)	0.9843(2)	6.1(1)
C(19)	0.7282(8)	0.7037(3)	1.0055(3)	8.5(2)
C(20)	0.7595(9)	0.7728(3)	0.9696(3)	10.2(2)
C(21)	0.8492(8)	0.7691(3)	0.9148(3)	8.8(2)
C(22)	0.9092(6)	0.6943(3)	0.8934(2)	5.9(1)
C(23)	0.6655(6)	0.5631(3)	0.7395(2)	5.8(1)
C(24)	0.6961(5)	0.4902(3)	0.7036(2)	4.7(1)
C(25)	0.5584(5)	0.4442(2)	0.7044(2)	4.43(9)
C(26)	0.4462(5)	0.4868(3)	0.7398(2)	5.1(1)
C(27)	0.5126(7)	0.5597(3)	0.7611(2)	5.8(1)
C(28)	0.775(1)	0.6331(4)	0.7452(3)	16.1(2)
C(29)	0.8404(6)	0.4713(6)	0.6658(3)	11.9(2)
C(30)	0.5313(9)	0.3640(3)	0.6674(3)	9.4(2)
C(31)	0.2815(6)	0.4608(5)	0.7506(3)	12.0(2)
C(32)	0.429(1)	0.6275(4)	0.8010(3)	16.5(2)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $B_{eq} = {}^4/_3[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2.3)]$. [b] Esd's on the last significant digit are given in parentheses.

(*R*)-CyCH(Me)N(Me)CH=C_5H_4 (5b). The procedure is the same as that for (*R*)-PhCH(Me)N(Me)CH=C_5H_4, except that 43.8 g (0.259 mol) of (*R*)-Cy(Me)CHN(Me)CHO and 24.5 mL (0.259 mol) of Me_2SO_4 were converted with 30 g (0.34 mol) of $Na[C_5H_5]$ to give 36.2 g (64%) of the product, which crystallized as large yellow needles. $[\alpha]^{22}_D = -118$ (c = 1.3, $CHCl_3$). ^1H NMR ($CDCl_3$, 298 K): δ 7.26 (s, 1H, C*H*=C_5H_4), 6.60 (m, 2H, C_5H_4), 6.46 (m, 1H, C_5H_4), 6.37 (m, 1H, C_5H_4), 3.32 (q, 1H, C*H*MeN, ^3J(HH) = 7), 3.29 (s, 3H, NMe), 2.00−1.06 (m, 11H, Cy), 1.42 (d, 3H, CH*Me*N, ^3J(HH) = 7). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 298 K): δ 148.0 (=CHN), 124.3, 124.2, 118.9, 115.8, 114.2 (C_5H_4), 69.1 (*C*HMeN), 41.4 (NMe), 34.2, 30.0, 29.6, 25.8, 25.7, 25.5 (Cy), 16.7 (CH*Me*N). Anal. Calcd for $C_{15}H_{21}N$: C, 82.89; H, 10.67; N, 6.44. Found: C, 82.91; H, 10.44; N, 6.40.

(*R*)-CyCH(Me)N(Et)CH=C_5H_4 (5c). The procedure is the same as that for (*R*)-PhCH(Me)N(Me)CH=C_5H_4, except that 10.9 g (58 mmol) of (*R*)-Cy(Me)CHN(Et)CHO and 6.0 mL (63 mmol) of Me_2SO_4 were converted with 6.2 g (70 mmol) of $Na[C_5H_5]$ to give 7.0 g (52%) of the microcrystalline, yellow product. $[\alpha]^{22}_D = -104$ (c = 1.5, $CHCl_3$). ^1H NMR ($CDCl_3$, 298 K): δ 7.14 (s, 1H, C*H*=C_5H_4), 6.53 (m, 2H, C_5H_4), 6.43 (m, 1H, C_5H_4), 6.33 (m, 1H, C_5H_4), 3.63 (dq, 2H, C*H*$_2$CH$_3$), 3.10 (m, 1H, C*H*MeN), 1.63−0.87 (m, 11H, Cy), 1.37 (t, 3H, CH$_2$C*H*$_3$), 1.33 (d, 3H, CH*Me*N). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 298 K): δ 146.4 (=CHN), 125.2, 118.7, 113.8 (C_5H_4), 69.5 (*C*HMeN), 44.5 (NCH_2), 42.5 (NCH_2CH_3), 30.4, 30.0, 26.1, 26.9, 25.8, 18.3

(Cy), 12.3 (CH*Me*N). Anal. Calcd for $C_{16}H_{25}N$: C, 83.06; H, 10.89; N, 6.05. Found: C, 83.34; H, 10.62; N, 6.11.

(*R*)-CyCH(Me)N(CH_2Ph)CH=C_5H_4 (5d). The procedure is the same as that for (*R*)-PhCH(Me)N(Me)CH=C_5H_4, except that 22 g (90 mmol) of (*R*)-Cy(Me)CHN(CH_2Ph)CHO and 9.5 mL (100 mmol) of Me_2SO_4 were converted with 18 g (200 mol) of Na[C_5H_5]. The product is purified by flash chromatography over Al_2O_3 followed by precipitation from hexane at −78 °C. The resulting yellow solid melts upon warming to room temperature: yield ca. 30%. $[\alpha]^{22}_D$ = −128 (*c* = 1.6, $CHCl_3$). ^1H NMR ($CDCl_3$, 298 K): δ 7.37 (m, 6H, C*H*=C_5H_4 and Ph), 6.50 (m, 2H, C_5H_4), 6.46 (m, 1H, C_5H_4), 6.39 (m, 1H, C_5H_4), 5.04 and 4.76 (br AB, 2H, C*H*$_2$Ph, ^2J(HH) = 16), 3.17 (br q, 1H, C*H*MeN), 1.94−0.85 (m, 11H, Cy), 1.31 (d, 3H, CH*Me*N, ^3J(HH) = 7). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 298 K): δ 146.8 (=CHN), 128.8, 127.6, 127.4, 125.7, 125.4, 119.4, 114.1 (C_5H_4 and Ph), 66.9 (*C*HMeN), 54.8 (N*C*H$_2$Ph), 42.7, 30.4, 29.8, 26.1, 26.0, 25.9 (Cy), 18.1 (CH*Me*N). Anal. Calcd for $C_{21}H_{27}N$: C, 85.95; H, 9.27; N, 4.77. Found: C, 85.75; H, 8.97; N, 4.64.

(*R*)-(*S*)-PhCH(OMe)CH(Me)N(Me)CH=C_5H_4 (5e). The procedure is the same as that for (*R*)-PhCH(Me)N(Me)CH=C_5H_4, except that 1.2 g (5.8 mmol) of (*R*)-(*S*)-PhCH(OMe)CH(Me)N(Me)CHO and 0.6 mL (6.3 mmol) of Me_2SO_4 were converted with 0.9 g (10 mmol) of Na[C_5H_5] to give 1.3 g (80%) of the product, which precipitated as an yellow oil from hexane at −20 °C. $[\alpha]^{22}_D$ = +97 (*c* = 1.0, $CHCl_3$). ^1H NMR ($CDCl_3$, 298 K): δ 7.33 (m, 5H, Ph), 7.18 (s, 1H, C*H*=C_5H_4), 6.53 (m, 2H, C_5H_4), 6.40 (m, 1H, C_5H_4), 6.35 (m, 1H, C_5H_4), 4.22 (d, 1H, C*H*(OMe), ^3J(HH) = 6), 3.60 (br quintet, 1H, C*H*MeN, ^3J(HH) = 6), 3.22 (s, 3H, OMe), 3.09 (s, 3H, NMe), 1.38 (d, 3H, CH*Me*N, ^3J(HH) = 7). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 298 K): δ 146.8 (=CHN), 137.9, 128.2, 127.8, 126.9, 126.5, 124.6, 124.4, 118.9, 114.4 (C_5H_4 and Ph), 85.7 (OMe), 67.7 and 56.6 [O*C*H(Me) and N*C*H(Me)], 36.8 (NMe), 14.0 (CH*Me*N). Anal. Calcd for $C_{17}H_{21}NO$: C, 79.96; H, 8.29; N, 5.49. Found: C, 73.40; H, 8.15; N, 4.83.

(*R*)-(*S*)-PhCH(OMe)CH(Me)N(Me)CHO. The procedure is the same as that reported for PhCH(Me)NMeCHO,[8] except that 26.2 g (0.14 mol) of (*R*)-(*S*)-PhCH(OH)CH(Me)N(H)CHO was converted with 19.1 g (0.50 mol) of NaOH, 11.2 g (0.081 mol) of K_2CO_3, and 26 mL (0.27 mol) of Me_2SO_4 using 5.3 g of the phase-transfer catalyst Bu_4NHSO_4: yield: 25.07 g (86%) of pale yellow oil. ^1H NMR ($CDCl_3$, 298 K): major isomer, δ 7.76 (s, 1H, CHO), 7.35−7.20 (m, 5H, Ph), 4.10 (d, 1H, C*H*(OMe), ^3J(HH) = 7), 3.64 (quintet, 1H, C*H*MeN, ^3J(HH) = 7), 3.22 (s, 3H, OMe), 2.73 (s, 3H, NMe), 1.35 (d, 3H, CH*Me*N, ^3J(HH) = 7). Characteristic ^1H NMR resonances for the minor isomer are δ 7.93 (CHO), 2.87 (NMe), and 1.18 (CH*Me*N).

(*R*)-(*S*)-PhCH(OH)CH(Me)N(Me)CHO. A mixture of 17.1 g (0.10 mol) of (−)-ephedrine and 30 mL (0.80 mol) of formic acid is stirred at 60 °C overnight. Excess formic acid is removed *in vacuo,* and to the resulting oil are subsequently added water (100 mL) and concentrated HCl (5 mL). The solution is heated to 60−80 °C for 30 min. After workup involving addition of NaOH to pH 10, extraction with 2 × 100 mL of toluene, drying on $MgSO_4$, and removal of the solvent *in vacuo*, 16.4 g (82%) of product is obtained as a colorless oil. ^1H NMR ($CDCl_3$, 298 K): major isomer, δ 7.79 (s, 1H, CHO), 7.32 (m, 5H, Ph), 4.67 (d, 1H, C*H*(OH), ^3J(HH) = 7), 3.69 (quintet, 1H, C*H*MeN, ^3J(HH) = 7), 2.74 (s, 3H, NMe), 1.38 (d, 3H, CH*Me*N, ^3J(HH) = 7). Characteristic ^1H NMR resonances for the minor isomer are δ 7.99 (CHO), 2.79 (NMe), and 1.23 (CH*Me*N).

(*S*)-(*S*)-PhCH(OMe)CH(Me)N(Me)CH=C_5H_4 (5f). The procedure is the same as that for (*R*)-PhCH(Me)N(Me)CH=C_5H_4, except that 9.08 g (43.8 mmol) of (*S*)-(*S*)-PhCH(OMe)CH(Me)N(Me)CHO and 4.2 mL (44 mmol) of Me_2SO_4 were converted with 7.4 g (84 mmol) of Na[C_5H_5] to give 1.29 g (12%) of the product, which precipitated as an yellow oil from hexane at −20 °C. $[\alpha]^{22}_D$ = +169 (*c* = 0.87, $CHCl_3$). ^1H NMR ($CDCl_3$, 298 K): δ 7.35 (m, 6H, Ph and C*H*=C_5H_4), 6.59 (m, 2H, C_5H_4), 6.47 (m, 1H, C_5H_4), 6.37 (m, 1H, C_5H_4), 4.09 (d, 1H, C*H*(OMe), ^3J(HH) = 6), 3.63 (br quintet, 1H, C*H*MeN, ^3J(HH) = 6), 3.17 (s, 3H, OMe), 3.25 (s, 3H, NMe), 1.09 (d, 3H, CH*Me*N, ^3J(HH) = 7). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 298 K): δ 148.2 (=CHN), 138.1, 128.5, 128.3, 127.2, 126.7, 124.6, 119.0, 116.4, 114.5 (C_5H_4 and Ph), 85.5 (OMe), 68.0 and 56.8 [O*C*H(Me) and N*C*H(Me)], 35.9 (NMe), 15.9 (CH*Me*N). Anal. Calcd for $C_{17}H_{21}NO$: C, 79.96; H, 8.29; N, 5.49. Found: C, 72.27; H, 8.01; N, 4.79.

(*S*)-(*R*)-Fe(C_5H_4CH(Me)N(Me)CH(Me)Cy)$_2$ ((*S*)-(*R*)-6b). A THF solution of Li[C_5H_4CH(Me)N(Me)CH(Me)Cy] (from 1.83 g (8.43 mmol) of C_5H_4=CHN(Me)CH(Me)Cy and 6.5 mL of 1.6 M MeLi (10 mmol) in 50 mL of THF) was added to [Fe(acac)$_2$]$_n$ (2.16 g, 8.47 mmol) in 20 mL of THF at −78 °C. The resulting brown solution was warmed to room temperature, stirred for another 15 min, and then poured into 100 mL of water. The resulting organic layer and hexane extracts from the aqueous layer were combined, washed with 2 × 20 mL of water, dried over $MgSO_4$, and concentrated *in vacuo* to afford a red oil. The oil was chromatographed on silica (30 × 2.5 cm column) using hexane (containing 5% NEt_3) as the eluent. Removal of the solvent from the product fraction *in vacuo* left 2.98 g (68%) of the product as a red oil that was pure by ^1H NMR. The product can be obtained analytically pure by crystallization from MeOH. $[\alpha]^{22}_D$ = +90 (*c* = 1.13, $CHCl_3$). ^1H NMR ($CDCl_3$, 298 K): δ 4.09, 4.04, 4.01, 3.97 (s, 4 × 2H, C_5H_4), 3.70 (q, 2H, CpC*H*(Me)N, ^3J(HH) = 7), 2.34 (quintet, 2H, C*H*(Me)Cy, ^3J(HH) = 7), 2.03 (s, 6H, NMe), 1.39 (d, 6H, CpCH(*Me*)N, ^3J(HH) = 7), 0.65 (d, 6H, CH(*Me*)Cy, ^3J(HH) = 7), 2.00−0.75 (m, 22H, Cy). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 298 K): δ 90.7 (C_5H_4, *ipso* C), 69.9, 68.4, 67.8, 66.8 (C_5H_4), 58.3, 57.6 (*C*HMeN), 42.2 (NMe), 31.9, 31.2, 29.9, 26.9, 26.7, 26.7 (Cy), 17.0, 13.2 (CH*Me*N). Anal. Calcd for $C_{32}H_{52}N_2Fe$: C, 73.83; H, 10.07; N, 5.38. Found: C, 73.98; H, 9.82; N, 5.35.

(*R*)-(*S*)-(*R*)-Fe(C_5H_4CH(Me)N(Me)CH(Me)CH(OMe)Ph)$_2$ ((*R*)-(*S*)-(*R*)-6e). A THF solution of Li[C_5H_4CH(Me)N(Me)CH(Me)CH(OMe)Ph] (from 1.27 g (4.97 mmol) of C_5H_4=CHN(Me)CH(Me)CH(OMe)Ph and 4.0 mL of 1.6 M MeLi (6.4 mmol) in 50 mL of THF at 0 °C) was quenched with 0.95 g (7.5 mmol) of $FeCl_2$. Workup as described for (*S*)-(*R*)-Fe(C_5H_4CH(Me)N(Me)CH(Me)Cy)$_2$ afforded a red oil that was purified by flash chromatography on alumina using THF as the eluent: yield 0.81 g (55%) of red oil. The product can be obtained analytically pure by crystallization from EtOH at −20 °C. $[\alpha]^{22}_D$ = −76 (*c* = 0.56, $CHCl_3$). ^1H NMR ($CDCl_3$, 298 K): δ 7.26 (m, 10H, Ph), 3.85 (m, 8H, C_5H_4), 3.51 (2H, br s, C*H*(OMe)), 3.39 (q, 2H, CpC*H*(Me)N, ^3J(HH) = 7), 3.19 (s, 6H, OMe), 2.80 (quintet, 2H, N(Me)C*H*(Me)CH(OMe), ^3J(HH) = 7), 2.09 (s, 6H, NMe), 1.07 and 0.83 (both d, 2 × 6H, CH(*Me*), ^3J(HH) = 7). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 298 K): δ 142.0, 127.7, 127.4, 127.0, 126.9 (Ph), 90.0 (C_5H_4, *ipso* C), 70.1, 68.3, 67.4, 66.4 (C_5H_4), 87.3 (OMe), 59.4, 58.0, 57.1 (both *C*HMeN and *C*H(OMe)), 32.0 (NMe), 16.1, 12.1 (CH*Me*N). Anal. Calcd for $C_{36}H_{48}N_2O_2Fe$: C, 72.47; H, 8.11; N, 4.70. Found: C, 72.46; H, 8.00; N, 4.69.

Racemic $Cp^*FeC_5H_4CH(Me)NMe_2$ ((*R*/*S*)-7). To a vigorously stirred brown THF suspension of [Cp^*Fe(acac)] (prepared *in situ* from [Fe(acac)$_2$]$_n$ (7.41 g, 29.1 mmol) and LiCp^* (4.39 g (30.9 mmol)) in 100 mL of THF) was added, at ca. 0 °C, a yellow suspension of Li[$C_5H_4CH(Me)NMe_2$] (prepared *in situ* from C_5H_4=CHNMe$_2$ (3.75 g, 30.5 mmol in 50 mL of Et_2O) and MeLi (20 mL of a 1.6 M solution (32 mmol) in Et_2O)). The resulting green suspension was stirred for 15 min at 20 °C and then than poured into ca. 200 mL of water and acidified by addition of ca. 3 mL of concentrated HCl. The aqueous phase was washed with 2 × 50 mL of Et_2O, then made basic by the addition of KOH, and subsequently extracted with 3 × 100 mL of Et_2O. The combined Et_2O fractions were dried on $MgSO_4$, and the solvent was removed in *vacuo*, leaving 9.18 g (91%) of a red oil. The product can be obtained analytically pure after purification by chromatography on a silica column using THF (containing 1% of NEt_3) as the eluent.

(*S*)-$\mathrm{Cp^*FeC_5H_4CH(Me)NMe_2}$ ((*S*)-7). To a cooled (ca. −10 °C) yellow solution of (*S*)-$\mathrm{Cp^*FeC_5H_4CH(Me)N(Me)CH(Me)Cy}$ ((*S*)-8; 11.49 g, 27.1 mmol) in $\mathrm{NHMe_2}$ (25 mL) was slowly added 45 mL of AcOH. The resulting solid was heated for 30 min at 75 °C, giving a clear dark yellow solution. Water (250 mL) was added and the resulting suspension made basic by careful addition of 17 g of NaOH. The aqueous phase was extracted with 3 × 200 mL of hexane. The combined hexane layers were dried on $\mathrm{MgSO_4}$, and the solvent was removed *in vacuo*, leaving 10.43 g of a red oil. From this oil, 3.32 g (87%) of NH(Me)CH(Me)Cy was removed by bulb to bulb transfer at 75 °C for 2 h at 0.1 Torr. The remaining red oil (7.11 g, 80%) is virtually pure product. (It contains traces (<3%) of NH(Me)CH(Me)Cy and the side product $\mathrm{Cp^*FeC_5H_4CH{=}CH_2}$ but can be used in the syntheses described below without any further purification.) $[\alpha]^{22}_{\mathrm{D}}$ = +7.4 (*c* = 1.6, $\mathrm{CHCl_3}$), 75% ee. ^{1}H NMR ($\mathrm{CDCl_3}$, 298 K): δ 3.65−3.58 (m, 5H, $\mathrm{C_5H_4}$ and *C*HMeN), 2.04 (s, 6H, $\mathrm{NMe_2}$), 1.86 (s, 15H, $\mathrm{C_5Me_5}$), 1.30 (d, 3H, CH*Me*N, ^3J(HH) = 8). ^{13}C{^{1}H} NMR ($\mathrm{CDCl_3}$, 298 K): δ 87.2 ($\mathrm{C_5H_4}$, *ipso* C), 79.2 ($\mathit{C}_5\mathrm{Me_5}$), 72.1, 71.2, 70.8, 68.2 ($\mathrm{C_5H_4}$), 56.8 (*C*HMeN), 40.0 ($\mathrm{NMe_2}$), 13.3 (CH*Me*N), 10.9 ($\mathrm{C_5}\mathit{Me}_5$). Anal. Calcd for $\mathrm{C_{19}H_{29}NFe}$: C, 69.73; H, 8.93; N, 4.28. Found: C, 69.48; H, 8.78; N, 4.06.

(*S*)-(*R*)-$\mathrm{Cp^*FeC_5H_4CH(Me)N(Me)CH(Me)Cy}$ ((*S*)-(*R*)-8). To a stirred brown suspension of $\mathrm{Cp^*Fe(acac)}$ (prepared *in situ* from $\mathrm{[Fe(acac)_2]_{\mathit{n}}}$ (7.84 g, 30.7 mmol) and $\mathrm{LiCp^*}$ (4.38 g (30.8 mmol) in 100 mL of THF)) was added, at ca. 0 °C, a yellow suspension of $\mathrm{Li[C_5H_4CH(Me)N(Me)CH(Me)Cy]}$ (prepared *in situ* from $\mathrm{C_5H_4{=}CHN(Me)CH(Me)Cy}$ (6.83 g (31.5 mmol) in 50 mL of THF and 22 mL of a 1.6 M MeLi solution in $\mathrm{Et_2O}$ (35 mmol)). The resulting green suspension was stirred for 15 min at 20 °C and then poured into ca. 200 mL of water in which ca. 5 g of KOH was dissolved, this solution was subsequently extracted with 2 × 500 mL of $\mathrm{Et_2O}$. The combined $\mathrm{Et_2O}$ extracts were dried on $\mathrm{MgSO_4}$ and the solvent removed *in vacuo*, leaving 13.5 g (ca. 100%) of crude product. The product can be obtained analytically pure after purification by chromatography on a silica column using toluene (containing 1% of $\mathrm{NEt_3}$) as the eluent. The product is a red oil; yield 12.4 g (95%). $[\alpha]^{22}_{\mathrm{D}}$ = +26 (*c* = 1.35, $\mathrm{CHCl_3}$). ^{1}H NMR ($\mathrm{CDCl_3}$, 298 K): δ 3.74 (m, 2H, Cp*CH*(Me)N and $\mathrm{C_5H_4}$), 3.59 (m, 3H, $\mathrm{C_5H_4}$), 2.38 (m, 1H, *CH*(Me)Cy), 1.93 (s, 3H, NMe), 1.88 (s, 15H, $\mathrm{C_5Me_5}$), 1.29 (d, 3H, CpCH(*Me*)N, ^3J(HH) = 7), 0.77 (d, 3H, CH(*Me*)Cy, ^3J(HH) = 7), 1.85−0.85 (m, 11H, Cy). ^{13}C{^{1}H} NMR ($\mathrm{CDCl_3}$, 298 K): δ 90.7 ($\mathrm{C_5H_4}$, *ipso* C), 79.3 ($\mathit{C}_5\mathrm{Me_5}$), 72.3, 71.9, 70.8, 68.6 ($\mathrm{C_5H_4}$), 59.1, 55.9 (*C*HMeN), 42.3 (NMe), 30.8, 30.3, 29.5, 26.9, 26.8, 26.7 (Cy), 14.5, 13.7 (CH*Me*N), 11.0 ($\mathrm{C_5}\mathit{Me}_5$). Anal. Calcd for $\mathrm{C_{26}H_{41}NFe}$: C, 73.75; H, 9.76; N, 3.31. Found: C, 73.53; H, 9.72; N, 3.21.

Racemic (R^*)-(S^*)-$\mathrm{Cp^*FeC_5H_3(CH(Me)NMe_2)PPh_2}$-1,2 ($(R^*)$-$({}^*S)$-9). To a solution of $\mathrm{Cp^*FeC_5H_4CH(Me)NMe_2}$ (5.68 g, 17.3 mmol) in ca. 50 mL of $\mathrm{Et_2O}$ was added a solution of 1.6 M *n*-BuLi in hexane (15 mL, 24 mmol). The resulting slightly turbid orange solution was stirred overnight. Subsequent careful addition of $\mathrm{ClPPh_2}$ (5 mL, 27 mmol) resulted in a yellow suspension that was heated to reflux for 1 h. Aqueous saturated $\mathrm{NaHCO_3}$ (50 mL) was slowly added with cooling in an ice bath. The resulting organic layer and $\mathrm{Et_2O}$ extracts from the aqueous layer were combined, washed with 2 × 20 mL of water, dried over $\mathrm{MgSO_4}$, and concentrated *in vacuo* to afford an orange powder. This powder was subjected to column chromatography on $\mathrm{Al_2O_3}$ using toluene/hexane (1:3 v/v, containing 5% $\mathrm{NEt_3}$) as the eluent. Finally, the product was recrystallized from ca. 50 mL of hot hexane: yield 6.22 g (70%) of orange, microcrystalline product.

(*S*)-(*R*)-$\mathrm{Cp^*FeC_5H_3(CH(Me)NMe_2)PPh_2}$-1,2 ((*S*)-(*R*)-9). The procedure is the same as that for racemic $\mathrm{Cp^*FeC_5H_3(CH(Me)NMe_2)PPh_2}$-1,2 except that 2.43 g (7.42 mmol) of (*S*)-$\mathrm{Cp^*FeC_5H_4CH(Me)NMe_2}$ (75% ee) is converted with 6.5 mL of 1.6 M *n*-BuLi (10 mmol) and 2.5 mL (13 mmol) of $\mathrm{ClPPh_2}$. Crystallization from hexane or MeOH gives 0.55 g (14%) of virtually racemic ($[\alpha]^{22}_{\mathrm{D}}$ = +23) product, while the enantiomerically pure (HPLC) material (2.32 g, 61%) is obtained as a red oil by subsequent removal of the solvent *in vacuo*. $[\alpha]^{22}_{\mathrm{D}}$ = +276 (*c* = 0.48, $\mathrm{CHCl_3}$). ^{1}H NMR ($\mathrm{CDCl_3}$, 298 K): δ 7.74 (m, 2 H, $\mathrm{PPh_2}$), 7.28 (m, 3 H, $\mathrm{PPh_2}$), 7.12 (m, 5 H, $\mathrm{PPh_2}$), 3.85 (br q, 1H, *C*HMeN, ^3J(HH) = 8), 3.81 (m, 3H, $\mathrm{C_5H_3}$), 1.65 (s, 15H, $\mathrm{C_5Me_5}$), 1.51 (s, 6H, $\mathrm{NMe_2}$), 1.05 (d, 3H, CH*Me*N, ^3J(HH) = 8). ^{13}C{^{1}H} NMR ($\mathrm{CDCl_3}$, 298 K): δ 142.7−126.5 ($\mathrm{PPh_2}$), 95.3, 75.5, 73.9, 73.8, 73.4 ($\mathrm{C_5H_3}$), 80.0 ($\mathit{C}_5\mathrm{Me_5}$), 55.9 (*C*HMeN), 38.4 ($\mathrm{NMe_2}$), 10.9 ($\mathrm{C_5}\mathit{Me}_5$), 7.4 (CH*Me*). ^{31}P NMR ($\mathrm{CDCl_3}$, 298 K): δ −26.7 (s, $\mathrm{PPh_2}$). Anal. Calcd for $\mathrm{C_{31}H_{38}NFeP}$: C, 72.80; H, 7.49; N, 2.74. Found: C, 79.09; H, 7.39; N, 2.68.

Racemic $\mathrm{Cp^*FeC_5H_3(CH{=}CH_2)PPh_2}$-1,2 (10). A solution of $\mathrm{Cp^*FeC_5H_3(CH(Me)NMe_2)PPh_2}$-1,2 (0.69 g, 1.3 mmol) in 1 mL of acetic anhydride was kept at 100 °C for 2 h. The resulting dark red solution was stored at −20 °C overnight, giving large red crystals of analytically pure product: yield 0.56 g (92%). ^{1}H NMR ($\mathrm{CDCl_3}$, 298 K): δ 7.62 (m, 2 H, $\mathrm{PPh_2}$), 7.34 (m, 3 H, $\mathrm{PPh_2}$), 7.17 (m, 3 H, $\mathrm{PPh_2}$), 7.04 (m, 2 H, $\mathrm{PPh_2}$), 6.38 (dd, 1H, *C*H=$\mathrm{CH_2}$, J_{cis} = 10.1, J_{trans} = 16.7), 5.20 and 5.05 (both d, 2 × 1H, CH=$\mathit{C}\mathrm{H_2}$, J_{cis} = 10.1, J_{trans} = 16.7, J_{gem} = 10.1), 4.09, 3.90, 3.47 (m, 3 × 1H, $\mathrm{C_5H_3}$), 1.73 (s, 15H, $\mathrm{C_5Me_5}$). ^{13}C{^{1}H} NMR ($\mathrm{CDCl_3}$, 298 K): δ 136.5−127.6 (nonquaternary C of $\mathrm{PPh_2}$), 117.1 (*C*H=$\mathrm{CH_2}$), 111.0 (CH=$\mathit{C}\mathrm{H_2}$), 74.6, 74.2, 70.8 ($\mathrm{C_5H_4}$), 10.7 ($\mathrm{C_5}\mathit{Me}_5$). ^{31}P NMR ($\mathrm{CDCl_3}$, 298 K): δ −25.6 (s, $\mathrm{PPh_2}$). Anal. Calcd for $\mathrm{C_{29}H_{31}FeP}$: C, 74.68; H, 6.70. Found: C, 74.68; H, 6.88.

(*S*)-(*R*)-$\mathrm{Cp^*FeC_5H_3CH(Me)PCy_2(PPh_2)}$-1,2 ((*S*)-(*R*)-11). A yellow solution of (*S*)-(*R*)-$\mathrm{Cp^*FeC_5H_3(CH(Me)NMe_2)PPh_2}$-1,2 (0.51 g, 1.0 mmol) and $\mathrm{HPCy_2}$ (0.3 mL, 1 mmol) in acetic acid (ca. 5 mL) was heated at 75 °C for 1 h. The solvent was subsequently removed *in vacuo* and the sticky residue triturated with 20 mL of ethanol. The resulting yellow solid was filtered off and washed with 2 × 5 mL of ethanol, giving 0.33 g (50%) of the product. From the combined and concentrated (ca. 5 mL) ethanol fractions, another batch of microcrystalline yellow product (0.13 g, 20%) could be obtained at −20 °C: total yield 0.46 g (70%). $[\alpha]^{22}_{\mathrm{D}}$ = +426 (*c* = 0.34, $\mathrm{CHCl_3}$), ca. 100% ee (HPLC).

Racemic (R^*)-(S^*)-$\mathrm{Cp^*FeC_5H_3CH(Me)PCy_2(PPh_2)}$-1,2 ($(R^*)$-$(S^*)$-11). The procedure is the same as above, except that 0.51 g (1.0 mmol) of (S^*)-(R^*)-9 and 0.25 mL (1.1 mmol) of $\mathrm{HPCy_2}$ were reacted to give 0.25 g (38%) of microcrystalline yellow product. ^{1}H NMR ($\mathrm{CDCl_3}$, 298 K): δ 7.71 (m, 2H, $\mathrm{PPh_2}$), 7.30 (m, 3H, $\mathrm{PPh_2}$), 7.06 (m, 5H, $\mathrm{PPh_2}$), 3.86, 3.82, 3.76 (m, 3H, $\mathrm{C_5H_3}$), 2.93 (br q, *C*HMeP, ^3J(HH) = 7), 1.61 (s, 15H, $\mathrm{C_5Me_5}$), 1.50 (dd, 3H, CH*Me*P, ^3J(HH) = 7.2, ^3J(PH) = 3.0), 1.93−0.82 (m, 22 H, $\mathrm{PCy_2}$). ^{13}C{^{1}H} NMR ($\mathrm{CDCl_3}$, 298 K): δ 137.0−126.4 (nonquaternary C of $\mathrm{PPh_2}$), 80.12 ($\mathit{C}_5\mathrm{Me_5}$), 99.2, 74.0, 73.2 ($\mathrm{C_5H_3}$), 33.3−26.5 ($\mathrm{PCy_2}$), 16.0 (CH*Me*P), 11.1 ($\mathrm{C_5}\mathit{Me}_5$). ^{31}P NMR ($\mathrm{CDCl_3}$, 298 K): δ 11.1 (d, $\mathrm{PCy_2}$, ^4J(PP) = 64), −28.3 (d, $\mathrm{PPh_2}$, ^4J(P,P) = 64). Anal. Calcd for $\mathrm{C_{41}H_{54}P_2Fe}$: C, 74.09; H, 8.19. Found: C, 73.97; H, 8.33.

(*S*)-(*R*)-$\mathrm{Cp^*FeC_5H_3CH(Me)PC_8H_{14}(PPh_2)}$-1,2 ((*S*)-(*R*)-12). A yellow solution of (*S*)-(*R*)-$\mathrm{Cp^*FeC_5H_3(CH(Me)NMe_2)}$-$\mathrm{PPh_2}$-1,2 (1.47 g, 2.87 mmol) and $\mathrm{HPC_8H_{14}}$ (10 g, 74 mmol) in acetic acid (ca. 10 mL) was heated at 60 °C for 1 h. The solvent was subsequently removed *in vacuo* and the sticky, smelly residue subjected twice to flash chromatography over $\mathrm{Al_2O_3}$ using toluene as the eluent. Subsequent crystallization from EtOH (50 mL) at −20 °C for 4 days gave 0.33 g (19%) of analytically pure, orange, microcrystalline product. $[\alpha]^{22}_{\mathrm{D}}$ = +285 (*c* = 0.62, $\mathrm{CHCl_3}$), ca. 100% ee (HPLC).

Racemic (S^*)-(R^*)-$\mathrm{Cp^*FeC_5H_3CH(Me)PC_8H_{14}(PPh_2)}$-1,2 ($(S^*)$-$(R^*)$-12). The procedure is the same as above, except that $\mathrm{Cp^*FeC_5H_3(CH(Me)NMe_2)PPh_2}$-1,2 (0.62 g, 1.2 mmol) and $\mathrm{HPC_8H_{14}}$ (2.7 g, 19 mmol) were reacted to give 0.58 g (79%) of orange product that crystallized readily as large needles from hot EtOH. ^{1}H NMR ($\mathrm{CDCl_3}$, 298 K): δ 7.68 (m, 2H, $\mathrm{PPh_2}$), 7.34 (m, 2H, $\mathrm{PPh_2}$), 7.23 (m, 6H, $\mathrm{PPh_2}$), 4.13, 3.74, 3.52 (br s, 3H, $\mathrm{C_5H_3}$), 2.43 (dq, *C*HMeP, ^3J(HH) = 7, ^2J(PH) = 6), 1.76 (s, 15H, $\mathrm{C_5Me_5}$), 1.64 (dd, 3H, CH*Me*P, ^3J(HH) = 7, ^3J(PH) = 6), 2.05−0.95 (m, 14 H, $\mathrm{PC_8H_{14}}$). ^{13}C{^{1}H} NMR ($\mathrm{CDCl_3}$, 298 K):

δ 139.9–128.0 (nonquaternary C of PPh_2), 80.6 (C_5Me_5), 73.9, 72.9, 72.4 (C_5H_3), 32.6–21.3 (PC_8H_{14}), 18.9 ($CH\mathit{Me}P$), 11.6 ($C_5\mathit{Me}_5$). ^{31}P NMR ($CDCl_3$, 298 K): δ −22.0 (br s, PC_8H_{14}), −25.3 (br s, PPh_2). Anal. Calcd for $C_{37}H_{46}P_2Fe$: C, 73.03; H, 7.62. Found: C, 73.19; H, 7.70.

Racemic (R^*)-(S^*)-$Cp^*FeC_5H_3CHMe\{(N_2C_3H_3)PPh_2\}$-1,2 ($(R^*)$-$(S^*)$-13). The procedure is the same as above, except that $Cp^*FeC_5H_3(CH(Me)NMe_2)PPh_2$-1,2 (0.92 g, 1.8 mmol) and pyrazole (1.9 g, 28 mmol) reacted to give 0.88 g (92%) of crude yellow product that was pure by ^{1}H NMR. The compound can be obtained analytically pure in 52% yield by crystallization from hot MeOH.

(S)-(R)-$Cp^*FeC_5H_3CH(Me)\{(N_2C_3H_3)PPh_2\}$-1,2 ($(S)$-$(R)$-13). The procedure is the same as above, except that (S)-(R)-$Cp^*FeC_5H_3(CH(Me)NMe_2)PPh_2$-1,2 (0.30 g, 0.59 mmol) and pyrazole (0.65 g, 9.6 mmol) reacted to give 0.27 g (86%) of crude yellow product. The compound can be obtained analytically pure in 44% yield by crystallization from hot MeOH. $[\alpha]^{22}_D$ = +450 (c = 0.71, $CHCl_3$), 100% ee (HPLC). ^{1}H NMR ($CDCl_3$, 298 K): δ 7.63 (m, 2H, PPh_2), 7.32 (m, 3H, PPh_2), 6.94 (m, 5H, PPh_2 and o-H of $N_2C_3H_3$), 6.64 (t, 2H, PPh_2), 5.55 (dq, 1H, $C\mathit{H}MeN$, ^3J(HH) = 6.8, ^3J(PH) = 2.3), 5.36 (t, 1H, p-H of $N_2C_3H_3$), 4.25, 4.00, 3.78 (q, t, br s, respectively, 3H, C_5H_3), 1.80 (d, 3H, $CH\mathit{Me}N$, ^3J(HH) = 6.8), 1.72 (s, 15H, C_5Me_5). ^{13}C{^{1}H} NMR ($CDCl_3$, 298 K): δ 139.4-126.8 (PPh_2 and o-C of N_2C_3), 80.7 (C_5Me_5), 103.9 (p-C of $N_2\mathit{C}_3$), 75.4, 74.6, 73.5 (C_5H_3), 55.5 ($\mathit{C}HMeN$), 21.3 ($CH\mathit{Me}N$), 11.1 ($C_5\mathit{Me}_5$). ^{31}P NMR ($CDCl_3$, 298 K): δ −29.8 (s, PPh_2). Anal. Calcd for $C_{32}H_{35}N_2FeP$: C, 71.91; H, 6.60; N, 5.24. Found: C, 71.68; H, 6.56; N, 5.14.

Racemic (R^*)-(S^*)-$Cp^*FeC_5H_3CHMe\{(N_2C_3HMe_2$-3,5)-$PPh_2\}$-1,2 ($(R^*)$-$(S^*)$-14). A yellow solution of $Cp^*FeC_5H_3(CH(Me)NMe_2)PPh_2$-1,2 (0.68 g, 1.3 mmol) and 3,5-dimethylpyrazole (1.74 g, 18.1 mmol) in 5 mL of AcOH was heated to 70 °C for 30 min. Water (60 mL) was added, and the resulting suspension was made basic by careful addition of 4.2 g of NaOH, followed by extraction with hexane (100 mL). The hexane extract was dried on $MgSO_4$ and the solvent removed *in vacuo*, leaving a crude product that was crystallized from ca. 100 mL of hot $EtOH/H_2O$ (5:1) to give 0.62 g (85%) of microcrystalline yellow product.

(S)-(R)-$Cp^*FeC_5H_3CH(Me)\{(N_2C_3HMe_2$-3,5)$PPh_2\}$-1,2 ($(S)$-$(R)$-14). The procedure is the same as above, except that (S)-(R)-$Cp^*FeC_5H_3(CH(Me)NMe_2)PPh_2$-1,2 (0.61 g, 1.2 mmol) and 3,5-dimethylpyrazole (2.0 g, 21 mmol) reacted to give 0.20 g (30%) of crude yellow product. The compound can be obtained analytically pure in ca. 10% yield by crystallization from hot MeOH. $[\alpha]^{22}_D$ = +435 (c = 0.63, $CHCl_3$), 100% ee (HPLC). ^{1}H NMR ($CDCl_3$, 298 K): δ 7.61 (m, 2H, PPh_2), 7.30 (m, 3H, PPh_2), 6.93 (m, 3H, PPh_2), 6.70 (dt, 2H, PPh_2), 5.37 (dq, $C\mathit{H}MeN$, ^3J(HH) = 6.9, ^2J(PH) = 1.6), 4.89 (s, 1H, N_2C_3H), 4.22, 3.93, 3.70 (q, t, br s, respectively, 3 × 1H, C_5H_3), 2.16, 1.81 (s, 2 × 3H, $N_2C_3H\mathit{Me}_2$), 1.73 (s, 15H, C_5Me_5), 1.70 (d, 3H, $CH\mathit{Me}N$, ^3J(HH) = 6.9). ^{13}C{^{1}H} NMR ($CDCl_3$, 298 K): δ 137.0–126.7 (PPh_2), 80.4 (C_5Me_5), 104.3 (p-C of $N_2C_3HMe_2$), 75.1, 74.7, 74.4 (C_5H_3), 51.5 ($\mathit{C}HMeN$), 20.3, 13.5 ($N_2C_3H\mathit{Me}_2$), 11.5 ($CH\mathit{Me}N$), 11.1 ($C_5\mathit{Me}_5$). ^{31}P NMR ($CDCl_3$, 298 K): δ −29.1 (s, PPh_2). Anal. Calcd for $C_{34}H_{39}N_2FeP$: C, 72.60; H, 6.99; N, 4.98. Found: C, 72.10; H, 7.10; N, 4.69.

(S)-$C_5H_4MeFeC_5H_4CH(Me)NMe_2$ ((S)-16). Freshly prepared THF solutions of $Li[C_5H_4CH(Me)N(Me)CH(Me)Cy]$ (from 8.48 g (39.0 mmol) of $C_5H_4{=}CHN(Me)CH(Me)Cy$ and 27 mL of 1.6 M MeLi (43 mmol) in 100 mL of THF) and $Li[C_5H_4Me]$ (from 9.36 g (117 mmol) of MeC_5H_5 and 86 mL of 1.6 M MeLi (138 mmol) in 100 mL of THF) were mixed and then directly added to a stirred suspension of $[Fe(acac)_2]_n$ (20.99 g, 82.31 mmol) in 30 mL of THF at −78 °C. The resulting brown suspension was warmed to room temperature and stirred for 15 min. The mixture was poured into 1 L of water and extracted with 2 × 500 mL of hexane. The hexane fractions were washed with 3 × 50 mL of water and subsequently dried on $MgSO_4$. Removal of the solvent *in vacuo* left 22.8 g of a crude mixture of ferrocenes that was heated with 36.8 g (0.451 mol) of $NHMe_2{\cdot}HCl$ and 49.4 g (0.602 mol) of NaOAc suspended in 100 mL of acetic acid for 18 h at 55 °C. To this mixture was added water (300 mL), and the undesired $Fe(C_5H_4Me)_2$ was washed away with 3 × 200 mL of hexane. The aqueous phase was subsequently made basic by careful addition of NaOH and extracted with 1 L of hexane, and the hexane extract was washed with 3 × 100 mL of water and dried on $MgSO_4$. The solvent was removed from the extract *in vacuo*, and NH(Me)CH(Me)Cy (3.57 g, 65%) was removed from the red, oily residue by distillation at 100 °C/1 Torr. Finally, the residue was purified by chromatography on silica (20 × 2.5 cm column) using THF containing 5% of NEt_3 as eluent: yield 7.0 g (66%) of red oil. $[\alpha]^{22}_D$ = −19° (c = 0.96, $CHCl_3$), 75% ee. ^{1}H NMR ($CDCl_3$, 298 K): δ 4.00 (m, 8H, both C_5H_4), 3.59 (q, 1H, $C\mathit{H}MeN$, ^3J(H,H) = 7), 2.08 (s, 6H, NMe_2), 1.98 (s, 3H, $C_5H_4\mathit{Me}$), 1.48 (d, 3H, $CH\mathit{Me}N$, ^3J(H,H) = 7). ^{13}C{^{1}H} NMR ($CDCl_3$, 298 K): δ 125.4 (C_5H_4CHMe, *ipso* C), 84.0 (C_5H_4Me, *ipso* C), 70.1–67.2 (C_5H_4), 58.5 ($\mathit{C}HMeN$), 40.6 (NMe_2), 30.3 ($C_5H_4\mathit{Me}$), 16.0 ($CH\mathit{Me}N$). Anal. Calcd for $C_{15}H_{21}NFe$: C, 66.44; H, 7.81; N, 5.17. Found: C, 66.53; H, 7.56; N, 5.09.

(S)-(R)-$(C_5H_4Me)FeC_5H_3(CH(Me)NMe_2)PPh_2$-1,2 ($(S)$-$(R)$-17). To a solution of (S)-$(C_5H_4Me)FeC_5H_4CH(Me)NMe_2$ (75% ee, 3.04 g, 11.2 mmol) in ca. 50 mL of Et_2O was added a solution of 1.6 M n-BuLi in hexane (9.5 mL, 15 mmol). The resulting slightly turbid orange solution was stirred at room temperature overnight. Subsequent careful addition of $ClPPh_2$ (3.5 mL, 19 mmol) resulted in a yellow suspension that was heated to reflux for 1 h. Aqueous saturated $NaHCO_3$ (25 mL) was slowly added with cooling in an ice bath. The resulting organic layer and toluene extracts from the aqueous layer were combined, washed with 2 × 20 mL of water, dried over $MgSO_4$, and concentrated *in vacuo* to afford a red oil. The oil was chromatographed on alumina (30 × 2.5 cm column) using first 500 mL of hexane/toluene 3:1 v/v), which allowed elution of impurities. Finally, the product was eluted with toluene/THF (1:1, containing 5% of NEt_3). Removal of the solvent from the product fraction *in vacuo* left 3.03 g (60%) of a pure, red oil. $[\alpha]^{22}_D$ = +235 (c = 0.72, $CHCl_3$), 75% ee. ^{1}H NMR ($CDCl_3$, 298 K): δ 7.60 (m, 2 H, PPh_2), 7.26 (m, 3 H, PPh_2), 7.17 (m, 5 H, PPh_2), 4.35–3.70 (m, 8H, C_5H_3, C_5H_4, and $C\mathit{H}MeN$), 1.76 (s, 6H, NMe_2), 1.69 (s, $C_5H_4\mathit{Me}$), 1.25 (d, 3H, $CH\mathit{Me}N$, ^3J(HH) = 7). ^{13}C{^{1}H} NMR ($CDCl_3$, 298 K): δ 141.3–126.9 (PPh_2), 77.5–69.3 (nonquaternary C of C_5H_3 and C_5H_4), 56.8 ($\mathit{C}HMeN$), 38.9 (NMe_2), 13.9 ($C_5H_4\mathit{Me}$), 9.2 ($CH\mathit{Me}N$). ^{31}P NMR ($CDCl_3$, 298 K): δ −23.6 (s, PPh_2). Anal. Calcd for $C_{27}H_{30}NFeP$: C, 71.22; H, 6.64; N, 3.08. Found: C, 71.72; H, 6.59; N, 3.07.

(S)-(R)-$(C_5H_4Me)FeC_5H_3CH(Me)PCy_2(PPh_2)$-1,2 ($(S)$-$(R)$-18). A yellow solution of (S)-(R)-$(C_5H_4Me)FeC_5H_3(CH(Me)$-$NMe_2)PPh_2$-1,2 (75% ee, 1.33 g, 2.92 mmol) and $HPCy_2$ (0.65 mL, 3.2 mmol) in acetic acid (ca. 5 mL) was heated at 75 °C for 3 h. The solvent was subsequently removed *in vacuo* and the sticky residue dissolved in 10 mL of hot ethanol. Microcrystals that fell out of this solution overnight at −20 °C were filtered off and washed with 2 × 2 mL of ethanol, giving 0.89 g (50%) of the product. From the combined and concentrated (ca. 2 mL) ethanol fractions, another batch of microcrystalline yellow product (0.13 g, 20%) could be obtained at −20 °C: total yield 1.02 g (70%). $[\alpha]^{22}_D$ = +340 (c = 0.72, $CHCl_3$), 75% ee. ^{1}H NMR ($CDCl_3$, 298 K): δ 7.65 (m, 2H, PPh_2), 7.36 (m, 3H, PPh_2), 7.22 (m, 5H, PPh_2), 4.23, 3.95, 3.53 (m, 2H, 3H, 2H, respectively, C_5H_3 and C_5H_4), 3.22 (dq, $C\mathit{H}MeP$, ^3J(HH) = 7.2, ^2J(P,H) = 3.2), 1.68 (dd, 3H, $CH\mathit{Me}P$, ^3J(HH) = 7.2, ^3J(P,H) = 5.8), 1.93–0.82 (m, 22 H, PCy_2). ^{13}C{^{1}H} NMR ($CDCl_3$, 298 K): δ 136.0–126.9 (nonquaternary C of PPh_2), 71.7 ($\mathit{C}HMeP$), 70.3 (C_5H_4Me), 70.0, 69.4, 69.0 (nonquaternary C of C_5H_3), 33.0–25.9 (PCy_2), 17.8 ($C_5H_4\mathit{Me}$), 14.0 ($CH\mathit{Me}P$). ^{31}P NMR ($CDCl_3$, 298 K): δ 15.1 (d, PCy_2, ^4J(PP) = 30), −26.5 (d, PPh_2, ^4J(PP) = 30). Anal. Calcd for $C_{37}H_{46}P_2Fe$: C, 73.03; H, 7.62. Found: C, 73.23; H, 7.51.

X-ray Crystallographic Study of Racemic 12 and (S)-(R)-13. Selected crystallographic and other relevant data are listed in Table 4. Unit cell dimensions for (S)-(R)-**13** were obtained by a least-squares fit of the 2θ values of 25 high-order reflections ($9.5 < \theta < 15.9°$). Data were measured with variable scan speed to ensure constant stastistical precision on the collected intensities. One standard reflection was measured every 120 reflections for racemic **12**. For (*S*)-(*R*)-**13** 3 standard reflections were used to check the stability of the crystal and of the experimental conditions and measured every 1 h; no significant variation was detected. The orientation of the crystal was checked by measuring 3 other reflections every 300 measurements.

For (*S*)-(*R*)-**13**, reflections were collected in the quadrant $\pm h,+k,+l$, but up to $(\sin \theta)/\lambda = 0.364$ the Bijvoet pairs were measured. Data were corrected for Lorentz and polarization factors and, empirically, for absorption (azimuthal (Ψ) scans of three reflections having $\chi > 87°$, $11.96 < \theta < 16.89°$).[20] The standard deviations on intensities were calculated in terms of statistics alone, while those on F_o were calculated as reported in Table 4.

For both compounds, the structure was solved by a combination of direct and Fourier methods and refined by full-matrix least squares using anisotropic displacement parameters for all atoms. The contribution of the hydrogen atoms in their idealized position (Riding model with fixed isotropic $U = 0.080$ Å^2 for **12;** C−H = 0.95 Å and $B = 1.3$ [B(carbon)] Å^2 for (*S*)-(*R*)-**13**) was taken into account but not refined. No extinction correction was deemed necessary. The scattering factors used, corrected for the real and imaginary parts of the anomalous dispersion were taken from the literature.[21] Upon convergence (no parameter shift $> 0.2\sigma(p)$), the final Fourier difference map showed no significant peaks. All calculations were carried out by using the Siemens SHELXTL PLUS system for **12** and the Enraf-Nonius MOLEN crystallographic programs[22] for (*S*)-(*R*)-**13**. The handedness of the crystal of (*S*)-(*R*)-**13** was tested by refining the two enantiomorphs. The two sets of coordinates gave significantly different values for the agreement factors, based on Hamilton's test[23] ($R_w = 0.042$, $R = 0.031$ and $R_w = 0.053$, $R = 0.038$, respectively), thus establishing the absolute configuration of the molecule. Final atomic coordinates and equivalent thermal factors are given in Tables 5 (for **12**) and 7 (for **13**).

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Supplementary Material Available: For compounds **12** and **13,** tables giving calculated positional parameters for the hydrogen atoms, anisotropic displacement parameters, bond distances, and bond angles (16 pages). Ordering information is given on any current masthead page.

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