Asymmetric Synthesis of Metallocenes through Enantioselective Addition of Organolithium Reagents to 6-(Dimethylamino)fulvene

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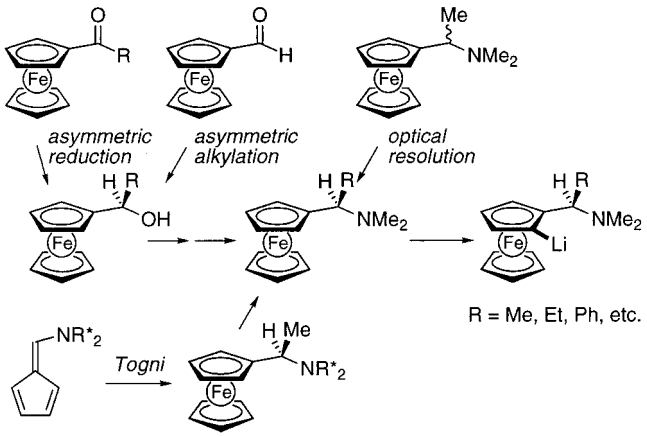
Enantioselective addition of aryllithiums **2a**−**d** (Ar = Ph (**a**), 2-MeC_6H_4 (**b**), 2-$MeOC_6H_4$ (**c**), 1-naphthyl (**d**)) to 6-(dimethylamino)fulvene (**1**) in the presence of (−)-sparteine in toluene at −78 °C generated chiral cyclopentadienyllithiums (**4**) substituted with an *N*,*N*-dimethylamino(aryl)-methyl group, where the enantioselectivities are 51, 91, 90, and 83% for **4a**, **4b**, **4c**, and **4d**, respectively. Treatment of the chiral cyclopentadienides **4** with $FeCl_2$ or $Fe(acac)_2$ gave ferrocenes, which contain an *N*,*N*-dimethylamino(aryl)methyl side chain on both of the cyclopentadienyl rings. The enantiomeric purity of the chiral ferrocenes **7** thus obtained is 99% ee or higher for those containing a 2-MeC_6H_4 (**7b**) or a 2-$MeOC_6H_4$ (**7c**) group.

Introduction

It is well documented that enantiomerically enriched ferrocene derivatives are powerful chiral auxiliaries in asymmetric reactions.[1] Of the chiral ferrocene auxiliaries, chiral ferrocenylphosphines have been used most widely and successfully as chiral ligands for transition metal-catalyzed asymmetric reactions including hydrogenation, allylic alkylation, cross-coupling, and aldol-type reactions.[2,3] One of the unique features of the ferrocene-based chiral auxiliaries is that most of them possess the ferrocene planar chirality, which is usually introduced by the diastereoselective ortho-lithiation of ferrocenes containing an *N*,*N*-dimethylamino group at the α-position of the chiral side chain[4] or some other chiral ortho-directing groups.[5] A typical example is *N*,*N*-dimethyl-1-ferrocenylethylamine,[6] which is a key intermediate for the preparation of several types of chiral ferrocenylphosphines, ppfa,[2,7] bppfa,[2,7] trap,[8] josiphos,[9] and so on.[1,3] The ferrocenes containing an *N*,*N*-dimethylamino group at the α stereogenic carbon center have been obtained by optical resolution of the racemate[6] or by way of optically active alcohols prepared by asymmetric reduction of ketones[10] or asymmetric alkylation of ferrocenecarboxaldehyde[11] (Scheme 1). Togni reported another useful method for their preparation through generation of a chiral cyclopentadienyllithium by diastereoselective addition of methyllithium to a fulvene substituted with a chiral amino group.[12] Here we report an enantioselective version of the asymmetric addition, which is practically useful for the preparation of chiral ferrocenes (90% ee) containing *N*,*N*-dimethylamino and aryl groups at the α stereogenic carbon center.

Scheme 1



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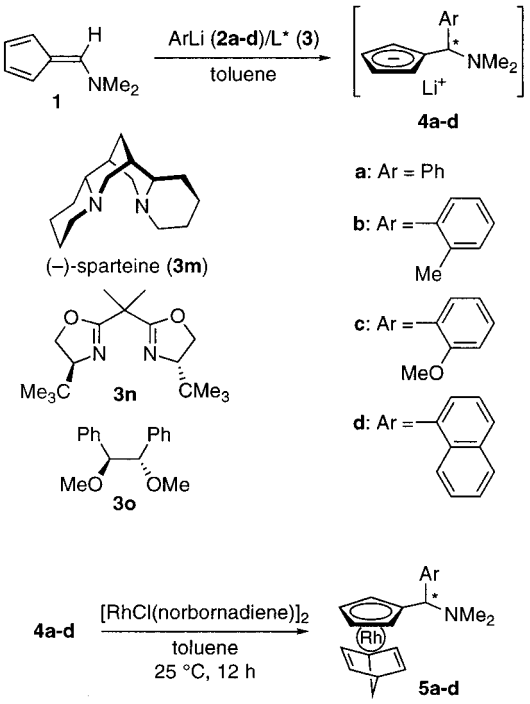
Scheme 2



Results and Discussion

For the asymmetric addition of an aryllithium **2** to 6-(dimethylamino)fulvene (**1**)[13] forming lithium cyclopentadienide (**4**) substituted with an *N*,*N*-dimethylamino(aryl)methyl group, several reaction conditions were examined for high enantioselectivity and high yield. The cyclopentadienide **4** was converted to a cyclopentadienylrhodium(I) **5** by treatment with $[RhCl(norbornadiene)]_2$ (Scheme 2), because the reaction-forming rhodium complex **5** is fast at a low temperature and analysis of its enantiomeric purity is easy with HPLC equipped with a chiral stationary-phase column. A typical reaction procedure is shown for the addition of 2-methylphenyllithium (**2b**) in the presence of (−)-sparteine (**3m**) (entry 6 in Table 1). To a solution of (−)-sparteine (**3m**) (0.48 mmol) in toluene was added, at −78 °C, a cyclohexane/ether (1/1) solution of 2-methylphenyllithium (**2b**) (0.48 mmol), which was prepared from 2-methylphenyl bromide and lithium metal and made free from lithium bromide. A solution of 6-(dimethylamino)fulvene (**1**) (0.40 mmol) in toluene was added, and the mixture was stirred at −78 °C for 7 h. At the same temperature was added $[RhCl(norbornadiene)]_2$ (0.48 mmol Rh), and the whole mixture was stirred at room temperature for 12 h. Aqueous workup followed by chromatography on alumina gave 92% yield of cyclopentadienylrhodium(I) complex **5b**, which is an (*R*)-isomer of 91% ee. The *R* configuration was determined by correlation with known chiral ferrocene (*R*,*R*)-**7b**[10b,14] (vide infra). The enantioselectivity observed here is much higher than the 17% ee reported for the asymmetric reduction of 6-methyl-6-phenylfulvene that is only one precedent of enantioselective reaction of fulvene derivatives.[15] In addition to the high enantioselectivity obtained with 2-methylphenyllithium (**2b**), the results summarized in Table 1 contain several significant features. (1) The enantioselectivity is high (over 90%) for the reaction of aryllithiums **2b** and **2c**, which contain ortho-substituents (entries 6 and 12). The addition of 2-methoxyphenyllithium also proceeded with high enantioselectivity (90% ee), though the reaction is slow (entry 11). (2) Sparteine (**3m**)[16,17] is more effective than chiral bisoxaoline **3n** and diether **3o** especially for the reaction of 2-methylphenyllithium (**2b**) (entries 6, 10, and 11). (3) The use of toluene as a solvent is important for the high enantioselectivity, the reaction in THF giving the racemic product (entry 7).[18] (4) Lithium bromide, generated at the preparation of aryllithiums from aryl bromides and lithium metal, must be removed for the high enantioselectivity (entry 8). (5) The enantioselectivity is higher at lower reaction temperatures (entries 1−3). (6) Unfortunately, the asymmetric addition requires a stoichiometric amount of the chiral base, the use of a catalytic amount of sparteine under the present reaction conditions giving the addition product with much lower enantioselectivity (entry 9).

Table 1. Asymmetric Addition of Aryllithium 2 to 6-(Dimethylamino)fulvene (1) in the Presence of Chiral Ligand 3[a]

entry	ArLi **2**	ligand **3**	temp (°C)	time (h)	product **5** yield (%)[b]		% ee[c]
1	**2a**	**3m**	−78	7	**5a**	93	51 (*R*)
2	**2a**	**3m**	−70	7	**5a**	99	42 (*R*)
3	**2a**	**3m**	−40	7	**5a**	99	25 (*R*)
4	**2a**	**3n**	−78	7	**5a**	51	62 (*R*)
5	**2a**	**3o**	−78	7	**5a**	54	23 (*S*)
6	**2b**	**3m**	−78	7	**5b**	92	91 (*R*)
7[d]	**2b**	**3m**	−78	7	**5b**	86	0 (*R*)
8[e]	**2b**	**3m**	−78	7	**5b**	82	23 (*R*)
9[f]	**2b**	**3m**	−78	7	**5b**	81	8 (*R*)
10	**2b**	**3n**	−78	7	**5b**	77	20 (*R*)
11	**2b**	**3o**	−78	7	**5b**	92	10 (*R*)
12	**2c**	**3m**	−78	15	**5c**	83	90 (*R*)
13	**2d**	**3m**	−78	7	**5d**	92	83 (*R*)

[a] Reaction was carried out with **1** (0.40 mmol) and aryllithium **2** (0.48 mmol) in the presence of a chiral ligand **3** (0.48 mmol) in 1.0 mL of toluene at a given temperature, and then $[RhCl(nbd)]_2$ (0.48 mmol Rh) was added at −78 °C. [b] Isolated yield of rhodium complex **5** by column chromatography on alumina (8/1 hexane/ethyl acetate). [c] Enantiomeric purity was determined by HPLC analysis with a chiral stationary phase column (Chiralcel OD-H, 100/1 hexane/2-propanol for **5a** and **5b**, 200/1 for **5c**, and 300/1 for **5d**). Absolute configurations of **5a** and **5b** were determined by correlation with ferrocenes **7a** and **7b** (see text). For **5c** and **5d**, configurations were assigned by consideration of similarity of the reaction pathway. [d] In THF. [e] In the presence of lithium bromide. [f] In the presence of 20 mol % (−)-sparteine (**3m**).

The cyclopentadienyllithiums **4**, which were generated by the enantioselective addition of aryllithiums **2** in the presence of (−)-sparteine at −78 °C, were used for the

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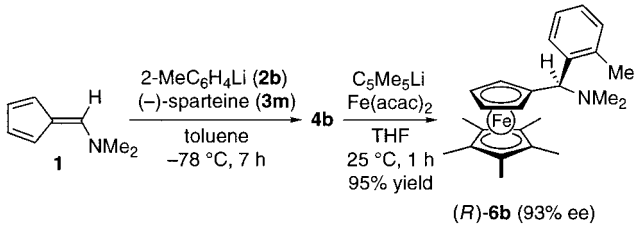
Scheme 3



Scheme 4

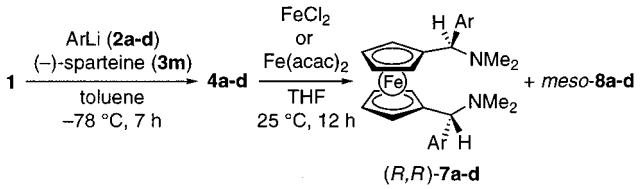


Table 2. Asymmetric Synthesis of Ferrocene 7 by Asymmetric Addition of Aryllithium 2 to 6-(Dimethylamino)fulvene (1) in the Presence of (−)-Sparteine (3m) Followed by Treatment with $FeCl_2$ or $Fe(acac)_2$[a]

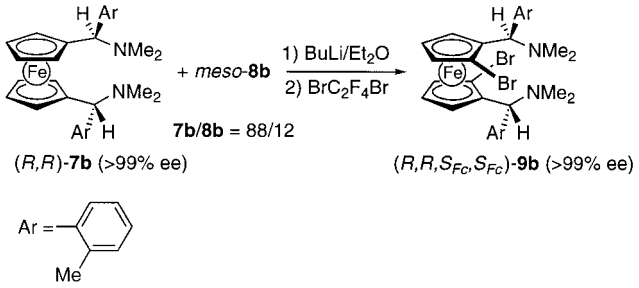
		results			calculation[b]	
entry	ArLi **2**	yield[c] of **7** and **8** (%)	ratio of **7**:**8**	% ee[d] of **7**	ratio of **7**:**8**	% ee of **7**
1	**2a**	99	63:37	78 (*R*,*R*)	63:37	80 (*R*,*R*)
2	**2b**	94	88:12	>99 (*R*,*R*)	91:9	99.6 (*R*,*R*)
3[e]	**2c**	80	90:10	99 (*R*,*R*)	90:10	99.4 (*R*,*R*)
4	**2d**	68	92:8	*f*	85:11	98 (*R*,*R*)

[a] Aryllithium **2** was added to **1** in the presence of (−)-sparteine (**3m**) at −78 °C. The cyclopentadienyllithium **4** generated was added to a THF solution of $FeCl_2$. [b] Calculation was made on the basis of enantiomeric purities of 51, 91, 90, and 83% ee for **4a**, **4b**, **4c**, and **4d**, respectively, obtained from data shown in Table 1. [c] Isolated yield by silica gel chromatography (5/4/1 hexane/Et_2O/Et_3N). [d] Determined by HPLC analysis with a chiral stationary phase column (Chiralcel OD-H, 100/1/0.1 hexane/2-propanol/triethylamine). [e] $Fe(acac)_2$ was used in place of $FeCl_2$. [f] Not determined.

asymmetric synthesis of ferrocene derivatives (Schemes 3 and 4). Thus, treatment of **4b** with FeCp*(acac) (Cp* = pentamethylcyclopentadienyl), which is generated in situ from $Fe(acac)_2$ and Cp*Li,[12,19] gave 95% yield of ferrocene **6b**. Its enantiomeric purity as determined by HPLC analysis was 93%, essentially the same as that of the rhodium complex **5b**, indicating that the enantiomeric purity of the cyclopentadienide **4b** is transferred to rhodium(I) and iron(II) without loss of its purity at the substitution reaction with the electrophiles.

The reaction of **4** with $FeCl_2$ or $Fe(acac)_2$ gave high yields of ferrocenes containing the chiral side chain on both cyclopentadienyl rings. As expected, the ferrocenes consist of chiral and meso isomers **7** and **8**, respectively. The ratio of **7** to **8** and the enantiomeric excess of the chiral isomer **7** obtained here are in good agreement with the values calculated from the enantiomeric excess of the cyclopentadienyllithium **4** on the assumption that both enantiomers of **4** are statistically incorporated into the ferrocene (Table 2). Thus, cyclopentadienyllithium **4a** (51% ee) generated by the asymmetric addition of phenyllithium **2a** gave (*R*,*R*)-**7a**[14] of 78% ee and **8a** in a ratio of 63:37, the calculated values being 80% ee and 63:37

Scheme 5



(entry 1). The enantiomeric purities of chiral ferrocenes (*R*,*R*)-**7b** and (*R*,*R*)-**7c** resulting from the asymmetric addition of 2-methylphenyllithium (**2b**) and 2-methoxyphenyllithium (**2c**), respectively, are extremely high (99% ee or higher) as it is expected from the calculation based on 90−91% ee of cyclopentadienyllithiums **4b** and **4c** (entries 2 and 3).

The mixture of (*R*,*R*)-**7b** (>99% ee) and **8b** (88:12 ratio), obtained by the reaction shown in entry 2 in Table 2, was subjected to the ortho-lithiation with butyllithium in ether followed by treatment of the dilithiated ferrocene with 1,2-dibromotetrafluoroethane to give, after silica gel chromatography, 60% isolated yield (based on **7b**) of dibromide (*R*,*R*,S_{Fc},S_{Fc})-**9b** as a diastereomerically pure product. The dibromide **9b** is a useful synthetic intermediate to chiral ferrocene derivatives represented by C_2-symmetric chiral bisphosphines.[10]

Conclusion

We have described the first successful example of enantioselective addition to a fulvene generating a chiral cyclopentadienide anion, which was realized in the reaction of aryllithiums with 6-(dimethylamino)fulvene in the presence of (−)-sparteine. The chiral cyclopentadienyllithiums were efficiently transferred onto iron(II) giving ferrocenes substituted with an *N*,*N*-dimethylamino group at the α position of the side chain. The enantiomeric excesses of the ferrocenes are very high, up to 91% ee for those containing one chiral side chain and 99% ee or higher for those containing two chiral side chains, one on each of the cyclopentadienyl rings. The chiral ferrocenes obtained here are versatile synthetic intermediates that can be converted into various types of chiral ferrocene derivatives through diastereoselective ortholithiation.[1,2,10]

Experimental Section

General. All manipulations were carried out under a nitrogen atmosphere. Nitrogen gas was dried by passage through P_2O_5. Chemical shifts for NMR spectra are reported in δ parts per million referenced to an internal tetramethylsilane standard for ^1H NMR and chloroform-*d* (δ 77.0) for ^{13}C NMR.

Materials. Rhodium complex $[RhCl(norbornadiene)]_2$[20] and 6-(dimethylamino)fulvene (**1**)[13] were prepared according to the reported procedures. Phenyllithium (**2a**) in cyclohexane/ether (1/1) was purchased commercially.

Preparation of Aryllithiums. 2-Methylphenyllithium (**2b**) and 2-methoxyphenyllithium (**2c**) were prepared from the corresponding aryl bromides and lithium metal in ether under standard procedures.[21] To the ether solution was added an equivalent volume of cyclohexane, and the white powder of

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(21) Jones, R. G.; Gilman, H. *Org. React.* **1951**, *6*, 339.

precipitated lithium bromide was removed by filtration through a glass wool plug.

1-Naphthyllithium (**2d**) was generated by lithiation of 1-bromonaphthalene with *n*-butyllithium in ether.

Asymmetric Addition of Aryllithium 2 to 6-(Dimethylamino)fulvene (1). (A) Reaction of the Cyclopentadienide 4 with [RhCl(nbd)]$_2$. The reaction conditions and results are summarized in Table 1. A typical procedure is given for the reaction of 2-methylphenyllithium (**2b**) in the presence of (−)-sparteine (**3m**) giving [1-(dimethylamino)-1-(2-methylphenyl)methyl-η^5-cyclopentadienyl](η^4-norbornadiene)rhodium (Rh[η^5-$C_5H_4CH(NMe_2)(2\text{-}MeC_6H_4)$](nbd), **5b**) (entry 6 in Table 1). To a solution of (−)-sparteine (112 mg, 0.48 mmol) in dry toluene (0.8 mL) was added a solution of 2-methylphenyllithium (0.74 M in cyclohexane/ether (1/1), 0.64 mL, 0.48 mmol) at −78 °C. After the solution was stirred at room temperature for 10 min and then cooled to −90 °C, a solution of 6-(dimethylamino)fulvene (**1**, 48.4 mg, 0.40 mmol) in dry toluene (0.2 mL) was added dropwise over 10 min. The reaction mixture was stirred at −78 °C for 7 h, and then [RhCl(nbd)]$_2$ (109 mg, 0.48 mmol Rh) was added. The reaction mixture was stirred at room temperature for 12 h, and then water (5 mL) was added. The mixture was extracted with ether. The combined extracts were washed with saturated aqueous sodium chloride and dried over anhydrous magnesium sulfate. The solvent was evaporated, and the residue was chromatographed on alumina (8/1 hexane/ethyl acetate) to give a mixture of **5b** and a considerable amount of (−)-sparteine. Removal of (−)-sparteine by distillation under reduced pressure gave 161.5 mg (92% yield) of Rh[η^5-$C_5H_4CH(NMe_2)(2\text{-}MeC_6H_4)$](nbd) (**5b**).

Spectral and analytical data for the rhodium complexes **5** are shown below. **Rh[η^5-$C_5H_4CH(NMe_2)Ph$](nbd) (5a)**: ^{1}H NMR ($CDCl_3$) δ 0.80 (s, 2H), 2.13 (s, 6H), 2.67 (s, 2H), 2.77 (s, 2H), 3.06 (s, 2H), 3.69 (s, 1H), 4.93 (s, 1H), 5.13 (s, 1H), 5.21 (s, 2H), 7.22 (t, J = 7.5 Hz, 1H), 7.32 (t, J = 7.5 Hz, 2H), 7.45 (d, J = 7.5 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 28.19 (d, J = 10.2 Hz), 29.33 (d, J = 10.2 Hz), 44.86, 46.17 (d, J = 2.5 Hz), 56.87 (d, J = 6.7 Hz), 71.65, 82.07 (d, J = 4.7 Hz), 84.09 (d, J = 4.1 Hz), 85.54 (d, J = 4.1 Hz), 86.46 (d, J = 4.1 Hz), 108.53 (d, J = 5.2 Hz), 126.69, 127.85, 127.93, 144.85. Anal. Calcd for $C_{21}H_{24}NRh$: C, 64.13; H, 6.15. Found: C, 63.87; H, 6.07. $[\alpha]^{20}_D$ +57 (*c* 1.0, $CHCl_3$) for (*R*)-**5a** of 51% ee. Chiral HPLC conditions: Chiralcel OD-H, 100/1 hexane/2-propanol. **Rh[η^5-$C_5H_4CH(NMe_2)(2\text{-}MeC_6H_4)$](nbd) (5b)**: ^{1}H NMR ($CDCl_3$) δ 0.78 (s, 2H), 2.11 (s, 6H), 2.46 (s, 2H), 2.62 (s, 3H), 2.87 (s, 2H), 3.03 (s, 2H), 4.02 (s, 1H), 4.87 (s, 1H), 4.93 (s, 1H), 5.13 (s, 1H), 5.38 (s, 1H), 7.09 (t, J = 7.8 Hz, 1H), 7.18 (m, 2H), 7.61 (d, J = 7.8 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 20.53, 28.94 (d, J = 10.3 Hz), 29.42 (d, J = 10.3 Hz), 44.99, 46.20 (d, J = 2.6 Hz), 56.86 (d, J = 6.6 Hz), 66.01, 81.89 (d, J = 4.1 Hz), 82.57 (d, J = 4.1 Hz), 85.57 (d, J = 4.1 Hz), 86.96 (d, J = 3.6 Hz), 109.60 (d, J = 4.6 Hz), 125.73, 126.17, 126.52, 130.08, 135.18, 144.09. Anal. Calcd for $C_{22}H_{26}NRh$: C, 64.87; H, 6.43. Found: C, 64.84; H, 6.44. $[\alpha]^{20}_D$ +45 (*c* 1.0, $CHCl_3$) for (*R*)-**5b** of 91% ee. Chiral HPLC conditions: Chiralcel OD-H, 100/1 hexane/2-propanol. **Rh[η^5-$C_5H_4CH(NMe_2)(2\text{-}MeOC_6H_4)$](nbd) (5c)**: ^{1}H NMR ($CDCl_3$) δ 0.78 (s, 2H), 2.12 (s, 6H), 2.70 (s, 2H), 2.74 (s, 2H), 3.02 (s, 2H), 3.88 (s, 3H), 4.36 (s, 1H), 4.90 (s, 1H), 5.17 (s, 1H), 5.23 (s, 1H), 5.28 (s, 1H), 6.87 (d, J = 7.4 Hz, 1H), 6.95 (t, J = 7.4 Hz, 1H), 7.18 (t, J = 7.4 Hz, 1H), 7.59 (d, J = 7.4, 1H); ^{13}C NMR ($CDCl_3$) δ 28.73 (d, J = 6.6 Hz), 28.81 (d, J = 6.6 Hz), 44.54, 46.16 (d, J = 2.5 Hz), 55.33, 56.79 (d, J = 6.7 Hz), 61.01, 81.93 (d, J = 4.1 Hz), 83.98 (d, J = 4.1 Hz), 85.18 (d, J = 4.1 Hz), 87.29 (d, J = 4.1 Hz), 107.93 (d, J = 5.1 Hz), 110.31, 120.35, 127.32, 128.14, 132.86, 156.34. Anal. Calcd for $C_{22}H_{26}NORh$: C, 62.42; H, 6.19. Found: C, 62.55; H, 6.28. $[\alpha]^{20}_D$ +10 (*c* 1.0, $CHCl_3$) for (*R*)-**5c** of 90% ee. Chiral HPLC conditions: Chiralcel OD-H, 200/1 hexane/2-propanol. **Rh[η^5-$C_5H_4CH(NMe_2)$(1-naphthyl)](nbd) (5d)**: ^{1}H NMR ($CDCl_3$) δ 0.53 (s, 2H), 2.11 (s, 2H), 2.19 (s, 6H), 2.39 (s, 2H), 2.64 (s, 2H), 4.66 (s, 1H), 4.91 (s, 1H), 4.98 (s, 1H), 5.13 (s, 1H), 5.31 (s, 1H), 7.46−7.49 (m, 2H), 7.52 (t, J = 8.1 Hz, 1H), 7.59 (t, J = 8.1 Hz, 1H), 7.76 (d, J = 8.1 Hz, 1H), 7.87 (d, J = 8.1 Hz, 1H), 8.66 (d, J = 8.1 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 29.04 (d, J = 10.3 Hz), 29.19 (d, J = 10.3 Hz), 45.35, 45.77 (d, J = 2.5 Hz), 56.55 (d, J = 6.6 Hz), 66.44, 82.45 (d, J = 4.1 Hz), 82.74 (d, J = 4.1), 85.62 (d, J = 4.1 Hz), 86.32 (d, J = 4.1 Hz), 110.21 (d, J = 4.6 Hz), 124.10, 124.34, 125.18, 125.29, 126.91, 128.84, 131.67, 134.08, 142.29. Anal. Calcd for $C_{25}H_{26}NRh$: C, 67.72; H, 5.91. Found: C, 67.76; H, 5.89. $[\alpha]^{20}_D$ −219 (*c* 0.3, $CHCl_3$) for (*R*)-**5d** of 83% ee. Chiral HPLC conditions: Chiralcel OD-H, 300/1 hexane/2-propanol.

(B) Reaction of the Cyclopentadienide 4b with Fe(acac)$_2$ and Lithium Pentamethylcyclopentadienide. To a stirred brown suspension of Cp*Fe(acac) (prepared in situ from $[Fe(acac)_2]_n$ (780 mg, 3.1 mmol) and LiCp* (3.1 mmol) in 10 mL of THF)[17] was added, at 0 °C, a solution of lithium cyclopentadienide **4b** (which was generated in situ from 6-(dimethylamino)fulvene (**1**) (375 mg, 3.1 mmol) in toluene (5 mL) and 2-methylphenyllithium (**2b**) (5.0 mL, 3.7 mmol) in the presence of (−)-sparteine (**3m**) (865 mg, 3.7 mmol)). The resulting green suspension was stirred for 1 h at room temperature and then poured into ca. 20 mL of water. The reaction mixture was extracted with ether. The combined extracts were washed with water and dried over anhydrous magnesium sulfate. The solvent was evaporated and the residue was chromatographed on silica gel (hexane/diethyl ether/triethylamine = 5/4/1) to give 1.18 g (95% yield) of Fe[η^5-$C_5H_4CH(NMe_2)(2\text{-}MeC_6H_4)$]($\eta^5$-$C_5Me_5$) (**6b**).

Spectral and analytical data for the ferrocene **6b** are shown below. **Fe[η^5-$C_5H_4CH(NMe_2)(2\text{-}MeC_6H_4)$]($\eta^5$-$C_5Me_5$) (6b)**: ^{1}H NMR ($CDCl_3$) δ 1.82 (s, 15H), 2.17 (s, 6H), 2.51 (s, 3H), 3.37 (s, 1H), 3.57 (s, 1H), 3.63 (s, 1H), 4.01 (s, 1H), 5.00 (s, 1H), 7.01 (d, J = 7.0 Hz, 1H), 7.09 (t, J = 7.0 Hz, 1H), 7.13 (t, J = 7.0 Hz, 1H), 7.17 (d, J = 7.0, 1H); ^{13}C NMR ($CDCl_3$) δ 9.32, 11.03, 20.56, 42.12, 62.42, 70.51, 70.60, 71.67, 72.24, 79.86, 124.86, 126.48, 130.21, 130.50, 133.68, 136.59. Anal. Calcd for $C_{25}H_{33}NFe$: C, 74.44; H, 8.25. Found: C, 74.40; H, 8.45. $[\alpha]^{20}_D$ +89 (*c* 0.56, $CHCl_3$) for (*R*)-**6b** of 93% ee. Chiral HPLC conditions: Chiralcel OD-H, 100/1 hexane/2-propanol.

(C) Reaction of the Cyclopentadienide 4 with FeCl$_2$ Giving Ferrocene 7. The reaction conditions and results are summarized in Table 2. A typical procedure is given for the reaction of 2-methylphenyllithium (**2b**) in the presence of (−)-sparteine (**3m**) giving 1,1′-bis[1-(dimethylamino)-1-(2-methylphenyl)methyl]ferrocenes, Fe[η^5-$C_5H_4CH(NMe_2)(2\text{-}MeC_6H_4)$]$_2$, **7b** and **8b** (entry 2 in Table 2). To a solution of (−)-sparteine (2.10 g, 9.0 mmol) in dry toluene (10 mL) was added a solution of 2-methylphenyllithium (0.74 M in cyclohexane/ether (1/1), 12 mL, 9.0 mmol) at −78 °C. After the solution was stirred at room temperature for 10 min and cooled to −90 °C, a solution of 6-(dimethylamino)fulvene (**1**) (907 mg, 7.5 mmol) in dry toluene (4 mL) was added dropwise at −90 °C over 10 min. The reaction mixture was stirred at −78 °C for 7 h, and the reaction mixture was added to a suspension of $FeCl_2$ (562 mg, 4.4 mmol) in dry THF *via cannula*. The mixture was stirred at room temperature for 12 h, and water (10 mL) was added. The mixture was extracted with ether. The combined extracts were washed with aqueous sodium chloride solution and dried over anhydrous magnesium sulfate. The solvent was evaporated, and the residue was chromatographed on silica gel (5/4/1 hexane/ether/triethylamine) to give 1.72 g (94% yield) of a mixture of (*R*,*R*)-Fe[η^5-$C_5H_4CH(NMe_2)(2\text{-}MeC_6H_4)$]$_2$ (**7b**) and *meso*-Fe[η^5-$C_5H_4CH(NMe_2)(2\text{-}MeC_6H_4)$]$_2$ (**8b**) in a ratio of 88:12.

Spectral and analytical data for the ferrocene derivatives **7** and **8** are shown below. **(*R*,*R*)-Fe[η^5-$C_5H_4CH(NMe_2)(2\text{-}MeC_6H_4)$]$_2$ (7b)**: ^{1}H NMR ($CDCl_3$) δ 1.96 (s, 12H), 2.55 (s, 6H), 3.21 (s, 2H), 3.51 (s, 2H), 3.73 (s, 2H), 3.81 (s, 2H), 3.87 (s, 2H), 7.15−7.25 (m, 4H), 7.26 (t, J = 7.7 Hz, 2H), 7.49 (d, J = 7.7 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 20.73, 44.48, 66.18, 66.82, 67.34, 69.92, 71.32, 90.96, 126.05, 126.54, 127.55, 130.06, 134.87, 142.55. Anal. Calcd for $C_{30}H_{36}N_2Fe$: C, 74.99; H, 7.55. Found: C, 74.77; H, 7.55 (a mixture of isomers **7b** and **8b**). $[\alpha]^{20}_D$ +123 (*c* 1.0, $CHCl_3$) for a mixture of (*R*,*R*)-**7b** of >99% ee and *meso*-**8b** in a ratio of 88:12. (lit.[10b] $[\alpha]^{23}_D$ +120.1 (*c* 1.29, $CHCl_3$) for (*R*,*R*)-**7b**). ***meso*-Fe[η^5-$C_5H_4CH(NMe_2)(2\text{-}MeC_6H_4)$]$_2$ (8b)**: ^{1}H NMR ($CDCl_3$) δ 1.93 (s, 12H), 2.52 (s, 6H), 3.37 (s, 2H), 3.39 (s, 2H), 3.47 (s, 2H), 3.81 (s, 2H), 3.97 (s, 2H), 7.20−7.15 (m, 4H), 7.28 (t, J = 7.5 Hz, 2H), 7.60 (d, J = 7.5 Hz,

2H); ^{13}C NMR ($CDCl_3$) δ 20.66, 44.52, 66.07, 67.03, 67.11, 69.76, 71.32, 91.15, 125.96, 126.47, 127.42, 130.16, 135.10, 142.80. **(*R,R*)-Fe[η^5-$C_5H_4CH(NMe_2)Ph]_2$ (7a)**: ^{1}H NMR ($CDCl_3$) δ 1.97 (s, 12H), 3.48 (s, 4H), 3.56 (s, 2H), 3.58 (s, 2H), 3.87 (s, 2H), 7.41−7.26 (m, 10H); ^{13}C NMR ($CDCl_3$) δ 44.38, 67.52, 67.58, 69.95, 71.22, 72.23, 90.26, 126.85, 127.83, 128.23, 143.24; $[\alpha]^{20}_D$ +84 (*c* 1.0, $CHCl_3$) for a mixture of isomers **7a** of 78% ee and *meso*-**8a** in a ratio of 63:37 (lit.[10c] $[\alpha]^{20}_D$ +103 (*c* 1.0, $CHCl_3$) for a mixture of isomers **7a** of 99% ee and *meso*-**8a** in a ratio of 91:9). ***meso*-Fe[η^5-$C_5H_4CH(NMe_2)Ph]_2$ (8a)**: ^{1}H NMR ($CDCl_3$) δ 1.94 (s, 12H), 3.43 (s, 4H), 3.55 (s, 2H), 3.58 (s, 2H), 3.89 (s, 2H), 7.41−7.26 (m, 10H); ^{13}C NMR ($CDCl_3$) δ 44.27, 67.08, 67.70, 69.14, 71.67, 71.97, 126.89, 127.87, 128.35, 143.43. **(*R,R*)-Fe[η^5-$C_5H_4CH(NMe_2)(2\text{-}MeOC_6H_4)]_2$ (7c)**: ^{1}H NMR ($CDCl_3$) δ 1.98 (s, 12H), 3.44 (s, 2H), 3.44 (s, 2H), 3.52 (s, 2H), 3.93 (s, 6H), 4.07 (s, 2H), 4.39 (s, 2H), 6.92 (d, J = 7.7 Hz, 2H), 7.01 (t, J = 7.7 Hz, 2H), 7.27−7.25 (m, 2H), 7.38 (t, J = 7.7 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 44.11, 55.28, 61.22, 67.58, 67.89, 69.93, 71.58, 89.62, 110.12, 120.47, 127.53, 128.77, 131.33, 156.48. Anal. Calcd for $C_{30}H_{36}N_2O_2Fe$: C, 70.31; H, 7.08. Found: C, 70.21; H, 7.13 (a mixture of isomers **7c** and **8c**). $[\alpha]^{20}_D$ −45 (*c* 0.93, $CHCl_3$) for a mixture of (*R,R*)-**7c** of 99% ee and *meso*-**8c** in a ratio of 90:10. ***meso*-Fe[η^5-$C_5H_4CH(NMe_2)(2\text{-}MeOC_6H_4)]_2$ (8c)**: ^{1}H NMR ($CDCl_3$) δ 1.96 (s, 12H), 3.44 (s, 2H), 3.47 (s, 2H), 3.49 (s, 2H), 3.93 (s, 6H), 4.07 (s, 2H), 4.29 (s, 2H), 6.94 (d, J = 7.5 Hz, 2H), 7.05 (t, J = 7.5 Hz, 2H), 7.28−7.25 (m, 2H), 7.56 (d, J = 7.5 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 44.11, 55.32, 61.22, 67.47, 67.58, 69.54, 72.04, 89.90, 110.21, 120.27, 127.53, 128.64, 131.69, 156.71. **(*R,R*)-Fe[η^5-$C_5H_4CH(NMe_2)(1\text{-naphthyl})]_2$ (7d)**: ^{1}H NMR ($CDCl_3$) δ 1.94 (s, 12H), 3.09 (s, 2H), 3.12 (s, 2H), 3.38 (s, 2H), 3.54 (s, 2H), 4.31 (s, 2H), 7.48 (t, J = 8.0 Hz, 2H), 7.51 (t, J = 8.0 Hz, 2H), 7.60−7.58 (m, 4H), 7.78 (d, J = 8.0 Hz, 2H), 7.89 (d, J = 8.0 Hz, 2H), 8.57 (br, 2H); ^{13}C NMR ($CDCl_3$) δ 44.77, 66.99, 66.99, 67.41, 69.40, 71.42, 90.77, 124.41, 125.23, 125.36, 125.39, 127.23, 128.99, 131.81, 133.81, 140.01. Anal. Calcd for $C_{36}H_{36}N_2Fe$: C, 78.26; H, 6.57. Found: C, 78.06; H, 6.56 (a mixture of **7d** and **8d**). $[\alpha]^{20}_D$ −59 (*c* 0.91, $CHCl_3$) for (*R*)-**7d** for a mixture of (*R,R*)-**7d** and *meso*-**8d** in a ratio of 92:8. ***meso*-Fe[η^5-$C_5H_4CH(NMe_2)(1\text{-naphthyl})]_2$ (8d)**: ^{1}H NMR ($CDCl_3$) δ 1.91 (s, 12H), 3.03 (s, 2H), 3.13 (s, 2H), 3.24 (s, 2H), 3.67 (s, 2H), 4.09 (s, 2H), 7.49 (t, J = 8.0 Hz, 2H), 7.52 (t, J = 8.0 Hz, 2H), 7.67−7.56 (m, 4H), 7.85 (d, J = 8.0 Hz, 2H), 7.92 (d, J = 8.0 Hz, 2H), 8.49 (br, 2H); ^{13}C NMR ($CDCl_3$) δ 44.77, 66.92, 66.92, 67.41, 69.05, 71.58, 90.77, 124.38, 125.23, 125.36, 125.39, 127.23, 128.84, 131.86, 133.81, 140.26.

Ortho-Lithiation of Ferrocene (*R,R*)-7b Giving Dibromide (*R,R,S*$_{Fc}$,*S*$_{Fc}$)-9b. To a mixture of **7b** and **8b** (100 mg, 0.20 mmol, **7b**/**8b** = 88/12) in dry ether (1.7 mL) was added *n*-butyllithium (1.54 M, 0.64 mL, 1.0 mmol) at 0 °C. The reaction mixture was stirred at room temperature for 6 h, and 1,2-dibromotetrafluoroethane (0.31 g, 1.2 mmol) was added at 0 °C. The reaction mixture was stirred at 40 °C for 1 h, and then water (5 mL) was added. The reaction mixture was extracted with ether. The combined extracts were washed with aqueous sodium hydrogen carbonate solution and dried over anhydrous magnesium sulfate. The solvent was evaporated, and the residue was chromatographed on silica gel (5/4/0.1 hexane/diethyl ether/triethylamine) gave 76 mg (60% yield) of (*R,R,S*$_{Fc}$,*S*$_{Fc}$)-Fe[η^5-2-$BrC_5H_3CH(NMe_2)(2\text{-}MeC_6H_4)]_2$ (**9b**). **(*R,R,S*$_{Fc}$,*S*$_{Fc}$)-Fe[η^5-2-$BrC_5H_3CH(NMe_2)(2\text{-}MeC_6H_4)]_2$ (9b)**: ^{1}H NMR ($CDCl_3$) δ 1.94 (s, 12H), 2.63 (s, 6H), 3.17 (s, 2H), 3.57 (s, 2H), 3.64 (s, 2H), 4.11 (s, 2H), 7.21−7.18 (m, 4H), 7.36−7.33 (m, 2H), 7.49 (d, J = 7.7 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 21.00, 44.22, 62.78, 67.15, 70.51, 74.15, 82.71, 90.71, 126.35, 127.10, 127.40, 130.16, 135.13, 142.91. Anal. Calcd for $C_{30}H_{34}N_2Br_2Fe$: C, 56.45; H, 5.37. Found: C, 56.71; H, 5.42. $[\alpha]^{20}_D$ +196 (*c* 1.0, $CHCl_3$) for (*R*)-**9b**.

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