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Synthesis of a biferrocene diphosphine ligand with only planar chirality and its application in the Rh-catalyzed asymmetric hydrogenation of β-keto sulfones

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Abstract—A new type of biferrocene diphosphine ligand bearing only planar chirality was developed and used in Rh(I)-catalyzed asymmetric hydrogenation of β-keto sulfones, giving the corresponding optically active β-hydroxy sulfones in excellent yields and in 72.4–97.9% ee.
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1. Introduction

Optically active β-hydroxy sulfones are useful chiral synthons for the synthesis of biologically active molecules such as γ-butenolides,[1] γ-butyrolactones,[1,2] 2,5-disubstituted tetrahydrofuran,[3] and δ-valerolactones.[4] Many methods have been developed so far for the preparation of optically active β-hydroxy sulfones, such as kinetic resolution of racemic β-hydroxy sulfones[5] and asymmetric reduction of β-keto sulfones, including baker's yeast-mediated reduction.[6] CBS catalyzed borane reduction,[7] and $NaBH_4/Me_3$-SiCl catalyzed reduction using polymer-supported chiral sulfonamide as a ligand.[8] Although asymmetric hydrogenation of the C=X bond has been one of the most important reaction in asymmetric catalysis,[9] there are a few reports on the metal catalyzed asymmetric hydrogenation of β-keto sulfones.[1,10] On the other hand, since the pioneering work of Hayashi and Kumada in 1974 on the synthesis of the first chiral ferrocenyl phosphine,[11] the planar chiral 1,2-disubstituted ferrocene unit has become one of the most useful backbones in the design of new ligands for asymmetric catalysis.[12] Recently, many ligands with the biferrocene structure have been synthesized,[13] some of which were applied to the asymmetric hydrogenation reactions. Among them, the diphosphine ligand PhTRAP developed by Ito and his co-workers has been proven to be very efficient in enantioselective hydrogenation.[13h] During studies on the applications of ferrocene ligands in asymmetric catalysis,[14] we synthesized a biferrocene diphosphine ligand and used it successfully in the Rh-catalyzed asymmetric hydrogenation of β-keto sulfones. We reported herein this Rh-catalyzed enantioselective hydrogenation of β-keto sulfones using a bisferrocenyl diphosphine ligand (*R*,*R*)-**5** with only planar chirality.[12a,c,15]

2. Synthesis of ligand (*R*,*R*)-5

From the readily available (*S*)-*p*-tolylsulfinylferrocene **1**,[16] compound (S_{Fc},S_S)-**2** was synthesized according to the literature with enantiomeric purity of over 99% ee after recrystallization using a chiral sulfoxide as an *ortho*-directing group.[16] Treatment of (S_{Fc},S_S)-**2** with *t*-BuLi at −78 °C, followed by the addition of DMF provided phosphino-formyl ferrocene (*R*)-**3**.[17] The reaction of (*R*)-**3** with lithiated (S_{Fc},S_S)-**2** in THF at −78 °C afforded biferrocene methanol (*R*,*R*)-**4**, subsequent removal of the borane on phosphine by treating with DABCO in toluene at 60 °C provided target ligand (*R*,*R*)-**5** (Scheme 1). It is noteworthy that ligand (*R*,*R*)-**5** bears only planar chirality on each ferrocene skeleton. It is stable, and no change was found from NMR after exposing it in air for several months, albeit it is unstable under acidic conditions.

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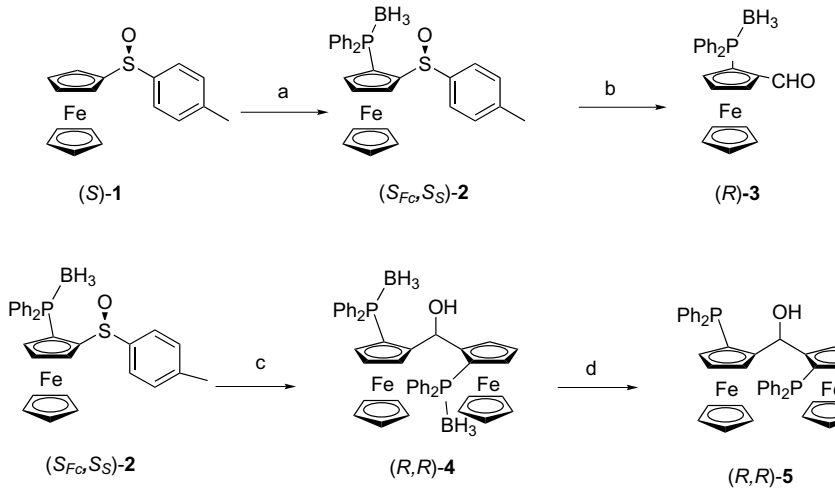
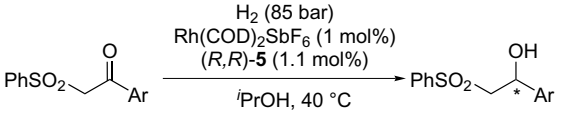


Scheme 1. Synthesis of biferrocene ligand (*R*,*R*)-**5**. Reagents and conditions: (a) (1) LDA, THF, −78 °C; (2) PPh_2Cl, −78 °C; (3) $BH_3{\cdot}Me_2S$, −78 °C to rt, 65%; (b) (1) *t*-BuLi, THF, −78 °C; (2) DMF, −78 °C, 44%; (c) (1) *t*-BuLi, THF, −78 °C; (2) (*R*)-**3**, −78 to 0 °C; (d) DABCO, toluene, 60 °C, 89% (c+d).

3. Results and discussion

The reaction of $Rh(COD)_2SbF_6$ with (*R*,*R*)-**5** formed a Rh complex, which was used as a catalyst in the asymmetric hydrogenation of β-keto sulfones **1**–**8** (Eq. 1, Table 1). Thus, treatment of 2-(phenylsulfonyl)acetophenone **1** with hydrogen (20 bar, 50 °C, 18 h) in the presence of $Rh(COD)_2SbF_6$ (1 mol %) and ligand (*R*,*R*)-**5** (1.1 mol %) in methanol led to β-hydroxy sulfone **9** in almost quantitative yield and with moderate enantioselectivity (entry 1). When raising the H_2 pressure to 85 bar in isopropanol, the product was obtained in quantitative yield with much higher enantioselectivity (95.6% ee, entry 2). However, raising the reaction temperature from 40 to 60 °C led to a drop of enantioselectivity from 95.6% to 91.2% ee (entry 3 vs entry 2).

When the optimized reaction condition (85 bar H_2, 40 °C in isopropanol) was applied to other β-keto sulfones **2**–**8** with different substituents on the aromatic ring of the Ph group, enantioselectivities ranging from 72.4% to 97.9% ee were obtained with excellent conversion. When the substituent on the aromatic ring was an electron-donating group (e.g., *p*-methyl, *p*-methoxy, *o*-methyl), lower enantioselectivities were obtained (entries 4, 5, 6 vs entry 2). On the other hand, when there was an electron-withdrawing group on the aromatic ring, slightly higher enantioselectivities were obtained (entries 7, 8, 9, 10 vs entry 2). These results showed that the electron density of the aromatic ring has some effect on the enantioselectivity of the reduction, but the reason is still obscure at the moment.



1 Ar=C_6H_5, **2** Ar=*p*-Me-C_6H_4, **3** Ar=*o*-Me-C_6H_4, **4** Ar=*p*-MeO-C_6H_4, **5** Ar=*p*-Cl-C_6H_4, **6** Ar=*m*-Cl-C_6H_4, **7** Ar=*p*-F-C_6H_4, **8** Ar=*p*-Br-C_6H_4

9 Ar=C_6H_5, **10** Ar=*p*-Me-C_6H_4, **11** Ar=*o*-Me-C_6H_4, **12** Ar=*p*-MeO-C_6H_4, **13** Ar=*p*-Cl-C_6H_4, **14** Ar=*m*-Cl-C_6H_4, **15** Ar=*p*-F-C_6H_4, **16** Ar=*p*-Br-C_6H_4 (1)

4. Conclusion

We have developed a novel biferrocene diphosphine ligand with only planar chirality. When it was applied in the

Table 1. Rhodium-catalyzed hydrogenation of β-keto sulfones[a]

Entry	Substrate	Solvent	H_2 (bar)	Time (h)	*T* (°C)	Conv[b] (%)	ee[c] (%)
1	**1**	MeOH	20	18	50	>99	56
2	**1**	^{i}PrOH	85	24	40	>99	95.6
3	**1**	^{i}PrOH	85	12	60	>99	91.4
4	**2**	^{i}PrOH	85	12	40	>99	91.2
5	**3**	^{i}PrOH	85	12	40	>99	72.4
6	**4**	^{i}PrOH	85	12	40	>99	82.9
7	**5**	^{i}PrOH	85	12	40	>99	97.9
8	**6**	^{i}PrOH	85	12	40	>99	97.1
9	**7**	^{i}PrOH	85	12	40	>99	96.0
10	**8**	^{i}PrOH	85	12	40	>99	97.0

[a] Reaction and conditions: $Rh(COD)_2SbF_6$/(*R*,*R*)-**5**/sub = 1/1.1/100.
[b] Determined by ^{1}H NMR.
[c] Ee was determined by HPLC.

rhodium-catalyzed enantioselective hydrogenation of β-keto sulfones, high enantioselectivities and nearly quantitative conversions were achieved. Further modification of the ligand and application in asymmetric catalysis are in progress.

5. Experimental

5.1. General

All NMR spectra were measured in $CDCl_3$ using a Bruker AMX-300 instrument [300 MHz (^{1}H), 75 MHz (^{13}C), 121.46 MHz (^{31}P)], and chemical shifts are expressed in parts per million relative to internal $CHCl_3$ (7.26 ppm for ^{1}H, 77.0 ppm for ^{13}C, and 85% H_3PO_4 as the external reference for ^{31}P). IR spectrum was recorded on a Shimadzu IR-400 using KBr pellets. All manipulations involving air-sensitive reagents were carried out under an argon atmosphere. The hydrogenation reactions were performed in a 300 mL stainless steel autoclave. All solvents were treated using standard procedures before use.

5.1.1. Preparation of (*R*)-3. To a solution of (S_{Fc},S_S)-**2** (3 g, 5.75 mmol) in THF (60 mL) was added dropwise *tert*-BuLi (4.2 mL, 6.3 mmol, 1.5 M in pentane) at −78 °C during 10 min, and the resulting red-orange solution was stirred at −78 °C for 10 min before addition of 5 mL DMF (65 mmol). After stirring at the same temperature for 2 h, the light colored solution was quenched with 20 mL of water. The aqueous layer was extracted with CH_2Cl_2 (10 mL × 2), and the combined organic phase was dried over Na_2SO_4, concentrated, and purified by silica gel column chromatography (elution: petroleum ether/EtOAc/CH_2Cl_2 20/5/2). The product was then recrystallized at −20 °C to give 1.0 g of (*R*)-**3** as red crystals, Yield: 44%. Mp 140–142 °C; $[\alpha]_D^{20} = -556$ (*c* 0.2, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.5 (br, 3H), 4.26 (m, 1H), 4.40 (s, 5H), 4.83 (br, 1H), 5.26 (br, 1H), 7.35–7.70 (m, 10H), 10.24 (s, 1H); MS (EI) *m*/*z* (rel) 412 (M^+, 5.94), 398 (100), 369 (38), 399 (27), 332 (24), 183 (23), 370 (22), 304 (20), 170 (18); IR (KBr) 2392 (w), 1664 (s), 1437 (w), 1410 (w), 1247 (w); ^{31}P NMR (121.46 MHz, $CDCl_3$): δ 11.63 (m); Anal. Calcd for $C_{23}H_{22}BPOFe$: C, 67.04; H, 5.38; Found: C, 66.85; H, 5.29.

5.1.2. Preparation of (*R*,*R*)-5. To a solution of (S_{Fc},S_S)-**2** (783 mg, 1.55 mmol) in dry THF (30 mL) was added dropwise *tert*-BuLi (4.2 mL, 6.3 mmol, 1.5 M in pentane) at −78 °C during 10 min, and the resulting red-orange solution was stirred at −78 °C for 10 min. Then a solution of (*R*)-**3** (487 mg, 1.22 mmol) in dry THF (15 mL) was added dropwise. After stirring at the same temperature for 1 h, the light yellow solution was quenched with 10 mL of water at 0 °C. The aqueous layer was extracted with EtOAc (10 mL × 2), and the combined organic phases were dried over anhydrous Na_2SO_4, concentrated. The crude product was dissolved in 20 mL of toluene, and DABCO (1.8 g, 8.18 mmol) was added. The reaction mixture was stirred for 4 h at 60 °C. After the reaction mixture was cooled to about 30 °C, toluene was removed under reduced pressure, the crude product was purified by basic Al_2O_3 column chromatography (elution: petroleum ether/EtOAc 50/1) to give 830 mg of the product (*R*,*R*)-**5** as a yellow solid. Yield: 89%. Mp 190–192 °C; $[\alpha]_D^{20} = +400$ (*c* 0.215, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.48 (s, 1H), 3.51 (s, 1H), 3.59–3.66 (m, 3H), 4.01 (s, 5H), 4.03 (s, 5H), 4.16 (s, 1H), 4.28 (s, 1H), 5.60–5.63 (m, 1H), 6.92–7.55 (m, 20H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 139.66, 139.56, 139.18, 139.10, 137.19, 137.10, 137.02, 136.93, 135.41, 135.32, 135.13, 135.04, 132.56, 132.54, 132.34, 132.31, 129.15, 129.05, 128.01, 127.98, 127.91, 127.87, 127.57, 127.52, 127.46, 127.43, 98.09, 97.89, 97.77, 97.60, 73.87, 73.80, 72.78, 73.70, 72.65, 72.55, 71.66, 71.60, 70.97, 70.91, 70.32, 70.12, 69.99, 69.69, 69.57, 69.46, 69.06, 69.00, 68.92, 68.89, 68.75, 68.48; ^{31}P NMR (121.46 MHz, $CDCl_3$): δ −26.37, −28.20; MS (MALDI) *m*/*z* (rel) 767 (M^+−H), 769 (M^++H); IR (KBr) 1712 (w), 1478 (w), 1433 (w), 695 (m); HRMS (ESI): calcd for $C_{45}H_{38}OFe_2P_2$ [M^++H] 769.1182, found: 769.1169.

5.2. General procedure for the asymmetric hydrogenation of β-keto sulfones

To a 10 mL tube were added $Rh(COD)_2SbF_6$ (2.8 mg, 0.005 mmol) and (*R*,*R*)-**5** (4.3 mg, 0.0055 mmol). The tube was then transferred into a dry box in a dry nitrogen atmosphere and the mixture was dissolved in degassed isopropanol (2 mL). After the reaction mixture was stirred for 30 min at room temperature, keto sulfone (0.5 mmol) was added. The reaction was carried out in an autoclave at the desired hydrogen pressure and temperature for a designated period of time. After removal of the solvent, the residue was purified by silica gel chromatography to afford the β-hydroxysulfone (over 99% conversion of β-keto sulfones were obtained in all reactions indicated by ^{1}H NMR).

5.2.1. 1-Phenyl-2-(phenylsulfonyl)ethanol 9. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 3.30 (dd, $J = 1.8$, 14.4 Hz, 1H), 3.50 (dd, $J = 10.2$, 14.4 Hz, 1H), 3.75 (s, 1H), 5.26 (d, $J = 9.6$ Hz, 1H), 7.28–7.95 (m, 10H). HPLC (Chiralpak AD-H) elution with *i*-PrOH/hexane = 30/70, flow rate: 1.0 mL/min, $\lambda = 254$ nm, retention times: t_1 11.25 min, t_2 13.38 min.

5.2.2. 1-(4′-Methylphenyl)-2-(phenylsulfonyl)ethanol 10. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 2.31 (s, 3H), 3.32 (dd, $J = 2.1$, 15 Hz, 1H), 3.50 (dd, $J = 9.6$, 14.1 Hz, 1H), 3.63 (d, $J = 2.7$ Hz, 1H), 5.23 (d, $J = 9.6$ Hz, 1H), 7.10–7.18 (m, 4H), 7.55–7.71 (m, 3H), 7.94–7.96 (m, 2H). HPLC (Chiralpak AD-H) elution with *i*-PrOH/hexane = 40/60, flow rate: 0.3 mL/min, $\lambda = 254$ nm, retention times: t_1 35.04 min, t_2 38.75 min.

5.2.3. 1-(2′-Methylphenyl)-2-(phenylsulfonyl)ethanol 11. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 2.06 (s, 3H), 3.24 (dd, $J = 1.2$, 14.4 Hz, 1H), 3.43 (dd, $J = 9.6$, 14.7 Hz, 1H), 3.67 (d, $J = 1.5$ Hz, 1H), 5.43 (d, $J = 8.1$ Hz, 1H), 7.06–7.23 (m, 3H), 7.47–7.73 (m, 4H), 7.96–8.00 (m, 2H). HPLC (Chiralpak AD-H) elution with *i*-PrOH/hexane = 40/60, flow rate: 0.6 mL/min, $\lambda = 254$ nm, retention times: t_1 15.51 min, t_2 17.92 min.

5.2.4. 1-(4′-Methoxyphenyl)-2-(phenylsulfonyl)ethanol 12. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 3.30 (dd, $J = 1.8$, 16.8 Hz, 1H), 3.50 (dd, $J = 10.2$, 14.4 Hz, 1H), 3.63 (d, $J = 1.8$ Hz, 1H), 3.76 (s, 3H), 5.22 (br, 1H), 6.80–6.85 (m, 2H), 7.17–7.22 (m, 2H), 7.55–7.92 (m, 3H), 7.92–7.96 (m, 2H). HPLC (Chiralpak OJ-H) elution with *i*-PrOH/hexane = 40/60, flow rate: 0.6 mL/min, $\lambda = 254$ nm, retention times: t_1 40.75 min, t_2 51.23 min.

5.2.5. 1-(4′-Chlorophenyl)-2-(phenylsulfonyl)ethanol 13. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 3.30 (dd, $J = 1.8$, 14.1 Hz, 1H), 3.46 (dd, $J = 9.9$, 14.4 Hz, 1H), 3.79 (d, $J = 2.1$ Hz, 1H), 5.26 (d, $J = 7.5$ Hz, 1H), 7.21–7.30 (m, 4H), 7.57–7.72 (m, 3H), 7.93–7.96 (m, 2H). HPLC (Chiralpak OJ-H) elution with *i*-PrOH/hexane = 40/60, flow rate: 0.8 mL/min, $\lambda = 254$ nm, retention times: t_1 20.02 min, t_2 21.87 min.

5.2.6. 1-(3′-Chlorophenyl)-2-(phenylsulfonyl)ethanol 14. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 3.31 (dd, $J = 1.8$, 13.5 Hz, 1H), 3.46 (dd, $J = 9.3$, 14.1 Hz, 1H), 3.84 (d, $J = 2.4$ Hz, 1H), 5.25 (d, $J = 6.9$ Hz, 1H), 7.14–7.30 (m, 4H), 7.56–7.72 (m, 3H), 7.92–7.95 (m, 2H). HPLC (Chiralpak AD-H) elution with *i*-PrOH/hexane = 30/70, flow rate: 0.6 mL/min, $\lambda = 254$ nm, retention times: t_1 14.96 min, t_2 18.09 min.

5.2.7. 1-(4′-Flurophenyl)-2-(phenylsulfonyl)ethanol 15. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 3.30 (dd, $J = 2.1$, 13.8 Hz, 1H), 3.47 (dd, $J = 9.3$, 13.8 Hz 1H), 3.79 (s, 1H), 5.26 (d, $J = 9.9$ Hz, 1H), 6.96–7.01 (m, 2H), 7.24–7.28 (m, 2H), 7.56–7.71 (m, 3H), 7.92–7.95 (m, 2H). HPLC (Chiralpak AD-H) elution with *i*-PrOH/hexane = 30/70, flow rate: 0.6 mL/min, $\lambda = 254$ nm, retention times: t_1 19.45 min, t_2 21.67 min.

5.2.8. 1-(4′-Bromophenyl)-2-(phenylsulfonyl)ethanol 16. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 3.30 (dd, $J = 2.4$, 14.7 Hz, 1H), 3.46 (dd, $J = 9.6$, 14.1 Hz 1H), 3.81 (d, $J = 1.8$, 1H), 5.25 (dd, $J = 2.4$ and 9.6 Hz, 1H), 7.15–7.19 (m, 2H), 7.42–7.46 (m, 2H), 7.57–7.73 (m, 3H), 7.93–7.95 (m, 2H). HPLC (Chiralpak OJ-H) elution with *i*-PrOH/hexane = 40/60, flow rate: 0.6 mL/min, $\lambda = 254$ nm, retention times: t_1 29.71 min, t_2 33.07 min.

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