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Palladium-catalyzed asymmetric allylic substitution with a cyclopentadienide: asymmetric synthesis of metallocenes

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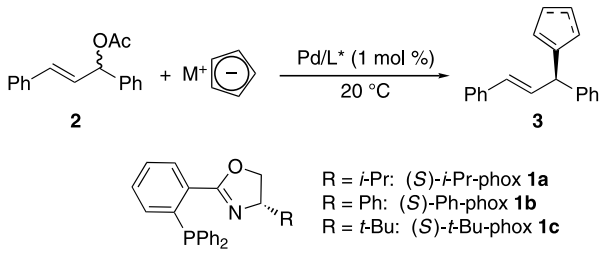
Abstract—Asymmetric synthesis of a chiral cyclopentadiene (98% ee) was realized for the first time by palladium-catalyzed asymmetric allylation of sodium cyclopentadienide in dioxane. The cyclopentadiene was readily converted into chiral metallocenes of iron, zirconium, and titanium, whose enantiomeric excesses are over 99%.

1. Introduction

Palladium-catalyzed allylic alkylation is one of the most widely and frequently used carbon–carbon bond forming reactions catalyzed by transition metal complexes because of its wide range of reactivity, high catalytic activity, and easy manipulation.[1] Catalytic asymmetric allylic alkylation protocols have been developed by the application of a number of chiral ligands.[2] The carbon nucleophiles successfully used for the asymmetric allylic alkylation have been limited mostly to enolate anions derived from β-dicarbonyl compounds represented by malonate esters. On the other hand, we have been interested in the asymmetric synthesis of enantiomerically enriched metallocenes.[3] Some of the chiral ferrocene derivatives are useful as chiral ligands for metal-catalyzed asymmetric reactions[4] and chiral zirconocenes and titanocenes[5] are used as catalysts for several types of asymmetric reactions such as carbometallation of alkenes.[6] Herein, we wish to report that cyclopentadienide can participate in the palladium-catalyzed asymmetric allylic alkylation as a nucleophile giving high yields of an allyl-substituted cyclopentadiene containing a stereogenic carbon center at the α position with high enantioselectivity and that the chiral cyclopentadiene obtained is converted into homochiral metallocenes. Rather surprisingly, there have been very few reports on the use of cyclopentadienides as nucleophiles in palladium-catalyzed allylic alkylation.[7,8]

2. Results and discussion

It is well-documented that chiral 2-(2-diphenylphosphinophenyl)oxazolines (phox, **1**)[9,10] are among the most enantioselective ligands for the palladium-catalyzed asymmetric substitution reactions of allylic esters represented by 1,3-diphenyl-2-propenyl acetate **2**. For example, the reaction of **2** with a sodium salt of dimethyl malonate in the presence of *i*-Pr-phox **1a** as a chiral ligand has been reported to proceed with over 94% enantioselectivity.[9c] Attempts to apply the reaction conditions used for dimethyl malonate to the reaction of sodium cyclopentadienide as a nucleophile (Scheme 1) resulted in low enantioselectivity, though the reaction proceeds smoothly to give 1,3-diphenyl-2-propenylcyclopentadiene **3** in high yields. Thus, the reaction of acetate **2** with sodium cyclopentadienide (4 equiv. to **2**), generated from cyclopentadiene and sodium hydride, in the presence of 1 mol% of a palladium catalyst coordinated with *i*-Pr-phox **1a** or Ph-



Scheme 1. Palladium-catalyzed asymmetric allylic alkylation with cyclopentadienides.

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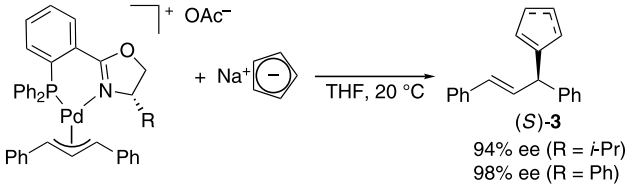
Table 1. Palladium-catalyzed asymmetric allylic substitution of **2** with cyclopentadienide[a]

Entry	Ligand L*	Solvent	M in M^+Cp^-	Yield (%) of **3**[b]	% ee of **3**[c]
1	(*S*)-*i*-Pr-phox **1a**	THF	Na	76	71 (*S*)
2	(*S*)-Ph-phox **1b**	THF	Na	79	71 (*S*)
3[d]	(*S*)-*i*-Pr-phox **1a**	THF	Na	77	94 (*S*)
4[d]	(*S*)-Ph-phox **1b**	THF	Na	78	98 (*S*)
5	(*S*)-*i*-Pr-phox **1a**	Dioxane	Na	80	94 (*S*)
6	(*S*)-Ph-phox **1b**	Dioxane	Na	80	98 (*S*)
7	(*S*)-*t*-Bu-phox **1c**	Dioxane	Na	85	81 (*S*)
8	(*R*)-Binap	Dioxane	Na	78	31 (*S*)
9	(*S*)-Ph-phox **1b**	Dioxane	Li	79	93 (*S*)
10	(*S*)-Ph-phox **1b**	Dioxane	K	80	94 (*S*)

[a] All reactions were carried out with allyl acetate **2** (0.40 mmol), M^+Cp^- (1.6 mmol), and 1 mol% of palladium catalyst generated from $[PdCl(\pi\text{-}C_3H_5)]_2$ and a chiral ligand in a solvent (1.6 mL) at 20°C for 50 h under nitrogen.
[b] Isolated yield by silica gel chromatography (ethyl acetate/hexane = 1/10).
[c] Determined by HPLC analysis with a chiral stationary phase column (Chiralcel OD-H (hexane/2-propanol = 500/1)).
[d] A solution of Na^+Cp^- (1.6 mmol) in THF was added over a period of 12 h.

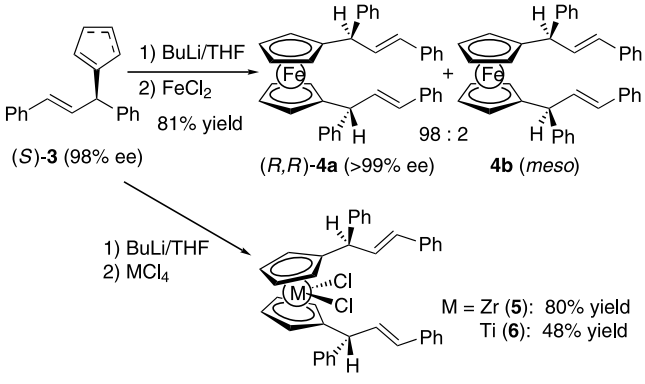
phox **1b** in THF (1.0 mol/L of sodium cyclopentadienide) at 20°C was completed in 20 min to give (*S*)-**3** with 71% ee (entries 1 and 2 in Table 1). The *S* absolute configuration was assigned by analogy of the present reaction to that using dimethyl malonate.[7b,9] The alkylation product **3** consists of two olefinic isomers at the cyclopentadiene moiety in about 1.6 to 1 ratio. The use of a large excess of sodium cyclopentadienide is important, a considerable amount of diallylated cyclopentadienes being formed with one or two equivalents of the cyclopentadienide. In our studies, we found that the enantioselectivity is strongly dependent on the concentration of the nucleophile, the highest enantioselectivity being observed at lower concentrations of sodium cyclopentadienide. Slow addition of the THF solution of sodium cyclopentadienide over a period of 12 h to the solution containing the catalyst Pd/*i*-Pr-phox **1a** and allyl ester **2** gave the product **3** of 94% ee (entry 3). The slow addition of cyclopentadienide in the presence of Ph-phox **1b** ligand gave the product **3** with the highest enantiomeric purity (98% ee) (entry 4). More conveniently, the reaction with the high enantioselectivity can be carried out in dioxane, where the concentration of sodium cyclopentadienide is kept low (0.05 mol/L measured by the titration with hydrochloric acid) due to the low solubility of the cyclopentadienide in dioxane. Thus, a mixture of **2** (0.40 mmol), sodium cyclopentadienide (1.6 mmol), and Pd/*i*-Pr-phox **1a** or Pd/Ph-phox **1b** catalyst (1 mol% Pd) in dioxane (1.6 mL) was stirred at 20°C for 50 h to give the allylation product (*S*)-**3** of 94% or 98% ee, respectively (entries 5 and 6).

Stoichiometric reaction of the isolated π-allylpalladium complex, [Pd(1,3-diphenyl-π-allyl)(**1b**)]$^+$OAc$^-$[11] with sodium cyclopentadienide in THF at 20°C gave (*S*)-**3** in 76% yield and 98% enantiomeric purity (Scheme 2). The enantiomeric purity of **3** is the same as that of **3** obtained in the catalytic reaction at low cyclopentadienide concentration (entries 4 and 6 in Table 1) and it is much higher than that of **3** with the high concentration of the cyclopentadienide in THF (entry 2 in Table 1). These results indicate that an equilibrium between the diastereomeric π-allylpalladium complexes must be reached before the nucleophilic attack of the cyclopentadienide anion to achieve high enantioselectivity in the catalytic reaction. This is in contrast to the reaction with dimethyl malonate where high enantioselectivity is observed in the reaction under high concentration conditions.[9]



Scheme 2. Stoichiometric reaction of π-allylpalladium complexes with sodium cyclopentadienide.

The lithium cyclopentadienide, generated from allylated cyclopentadiene (*S*)-**3** (98% ee) with butyllithium in THF, was allowed to react with $FeCl_2$ to give a high yield of ferrocene **4** containing the chiral allylic side chain on both cyclopentadienyl rings (Scheme 3). As expected from the calculation based on the assumption that both enantiomers of the cyclopentadienide are



Scheme 3. Synthesis of chiral metallocenes from the cyclopentadiene (*S*)-**3**.

statistically incorporated into the ferrocene, isomer **4a** and *meso*-isomer **4b** were formed in a ratio of 98:2 and **4a** was almost enantiomerically pure. The ee of **4a** calculated on the basis of 98% ee for **3** is 99.98% ee. In a similar manner, treatment of the lithium cyclopentadienide with $ZrCl_4$ and $TiCl_4$ gave zirconocene **5** and titanocene **6**, respectively. As a preliminary experiment, 5 mol% of a zirconocene ditriflate prepared from **5** catalyzes the asymmetric Diels–Alder reaction of 3-((*E*)-2-butenoyl)oxazolidinone with cyclopentadiene[12] in nitromethane at −30°C to give a quantitative yield of the cycloaddition product with 40% ee.

In summary, we have succeeded, for the first time, in the palladium-catalyzed asymmetric allylic alkylation with sodium cyclopentadienide with high enantioselectivity (98% ee). The chiral cyclopentadiene was converted into metallocenes of iron, zirconium, and titanium, whose enantiomeric excesses are essentially 100%. The chiral metallocenes obtained here will have broad applications as chiral ligands or chiral catalysts in catalytic asymmetric reactions.

3. Experimental

3.1. General

All manipulations were carried out under a nitrogen atmosphere. Nitrogen gas was dried by passage through P_2O_5. NMR spectra were recorded on a JEOL JNM LA-500 spectrometer (500 MHz for ^1H and 125 MHz for ^{13}C). Chemical shifts are reported in δ ppm referenced to an internal tetramethylsilane standard for ^1H NMR and chloroform-*d* (δ 77.0) for ^{13}C.

3.2. Materials

Palladium complex, $[Pd(OAc)(1,3\text{-diphenyl-}\pi\text{-allyl})]_2$ was prepared by the reaction of $[PdCl(1,3\text{-diphenyl-}\pi\text{-allyl})]_2$ with AgOAc according to the reported procedures,[13] and it was converted into [Pd(1,3-diphenyl-π-allyl)(phox (**1**))]OAc by addition of phox ligand.[11b] Phosphino-oxazoline ligands ((*S*)-Ph-phox, (*S*)-*i*-Pr-phox, (*S*)-*t*-Bu-phox) were prepared according to the reported procedures.[9,10a] THF, dioxane, toluene, diethyl ether were dried over sodium benzophenone ketyl and distilled prior to use.

3.3. Palladium-catalyzed asymmetric allylic substitution of 1,3-diphenyl-2-propenyl acetate, *dl*-2 with sodium cyclopentadienide

The reaction conditions and results are shown in Table 1. A typical procedure is given for the reaction with (*S*)-Ph-phox **1b** in dioxane (entry 6). To a solution of $[PdCl(\pi\text{-}C_3H_5)]_2$ (0.7 mg, 0.002 mmol), (*S*)-2-[2-(diphenylphosphino)phenyl]-4-phenyloxazoline (**1b**, (*S*)-Ph-phox) (1.7 mg, 0.004 mmol) in dioxane (0.8 mL) was added 1,3-diphenyl-2-propenyl acetate **2** (100 mg, 0.40 mmol). A slurry of sodium salt of cyclopentadiene (1.60 mmol) prepared from cyclopentadiene and sodium hydride in dioxane (0.8 mL) was added and the mixture was stirred at 20°C for 50 h. Water (5 mL) was added and the mixture was extracted with ether. The combined extracts were washed with aqueous sodium chloride and dried over anhydrous magnesium sulfate. The solvent was evaporated and the residue was chromatographed on silica gel (hexane/ethyl acetate = 10/1) to give 82.4 mg (80% yield) of 1,3-diphenyl-2-propenylcyclopentadiene **3**, which consists of two olefinic isomers at the cyclopentadiene moiety in about 1.6 to 1. On standing at room temperature, the cyclopentadiene **3** undergoes slow polymerization. The enantiomeric purity was determined to be 98% ee by HPLC analysis with Chiralcel OD-H (hexane/2-propanol = 500/1). $[\alpha]_D^{20}$ +2.1 (*c* 1.38, $CHCl_3$) for a mixture of the isomers.

Spectral and analytical data for 1,3-diphenyl-2-propenylcyclopentadiene **3** are shown below. **Major isomer**: ^1H NMR ($CDCl_3$) δ 3.02 (s, 2H), 4.60 (d, J = 7.6 Hz, 1H), 6.09 (d, J = 1.5 Hz, 1H), 6.26 (s, 1H), 6.39 (d, J = 15.2 Hz, 1H), 6.44 (s, 1H), 6.56 (dd, J = 15.2, 7.6 Hz, 1H), 7.18–7.37 (m, 10H): ^{13}C NMR ($CDCl_3$) δ 41.23, 49.63, 126.26 (2C), 126.43, 127.17, 128.18, 128.41 (2C), 128.46 (2C), 128.48 (2C), 130.68, 131.91, 132.46, 133.90, 137.41, 142.61, 148.36. **Minor isomer**: ^1H NMR ($CDCl_3$) δ 2.90 (s, 2H), 4.61 (d, J = 8.2 Hz, 1H), 6.31 (s, 1H), 6.33 (s, 1H), 6.36 (d, J = 15.2 Hz, 1H), 6.40 (s, 1H), 6.57 (dd, J = 15.2, 8.2 Hz, 1H), 7.18–7.37 (m, 10H); ^{13}C NMR ($CDCl_3$) δ 42.59, 50.59, 126.24 (2C), 126.40, 127.20, 127.83, 128.44 (2C), 128.46 (2C), 128.48 (2C), 130.45, 131.94, 132.09, 134.04, 137.38, 143.52, 150.77. Anal. calcd for $C_{20}H_{18}$: C, 92.98; H, 7.02. Found: C, 93.07; H, 7.12%.

3.4. Reaction of the 1,3-diphenyl-2-propenylcyclopentadienide with $FeCl_2$ giving ferrocene 4

To a suspension of $FeCl_2$ (100 mg, 0.80 mmol) in THF (1.6 mL) at −78°C was added a cold solution of lithium 1,3-diphenyl-2-propenylcyclopentadienide (424 mg, 1.60 mmol) prepared from (*S*)-1,3-diphenyl-2-propenylcyclopentadiene **3** (98% ee) and *n*-butyllithium in THF (1.6 mL). The mixture was allowed to warm to ambient temperature over a period of 6 h with stirring and then kept at ambient temperature for 12 h. Water (10 mL) was added, and the mixture was extracted with ether. The combined extracts were washed with aqueous sodium chloride and dried over anhydrous magnesium sulfate. The solvent was evaporated and the residue was chromatographed on silica gel (hexane/ethyl acetate = 10/1) to give 368 mg (81% yield) of $Fe[\eta^5\text{-}C_5H_4CHPh(CH{=}CHPh)]_2$ ((*R*,*R*)-**4a**/*meso*-**4b** = 98:2): **(*R*,*R*)-Fe[η^5-$C_5H_4CHPh(CH{=}CHPh)]_2$, 4a**: ^1H NMR ($CDCl_3$) δ 4.03 (s, 2H), 4.16 (s, 4H), 4.21 (s, 2H), 4.50 (d, J = 7.9 Hz, 2H), 6.32 (d, J = 15.9 Hz, 2H), 6.63 (dd, J = 15.6, 7.9 Hz, 2H), 7.22–7.40 (m, 20H); ^{13}C NMR ($CDCl_3$) δ 48.89 (2C), 67.97 (2C), 68.27 (2C), 68.49 (2C), 69.22 (2C), 91.73 (2C), 126.21 (4C), 126.34 (2C), 127.17 (2C), 128.17 (4C), 128.27 (4C), 128.53 (4C), 129.84 (2C), 133.17 (2C), 137.43 (2C), 144.03 (2C). Anal. calcd for $C_{40}H_{34}Fe$: C, 83.96; H, 6.02. Found: C, 84.21; H, 6.01%. $[\alpha]_D^{20}$ −249 (*c* 1.0, $CHCl_3$).

3.5. Reaction of the 1,3-diphenyl-2-propenylcyclopentadienide with $ZrCl_4$ giving zirconocene 5

To a suspension of $ZrCl_4$ (1.4 g, 6.3 mmol) in toluene (50 mL) was added at −78°C a cold solution of 3.2 g (12.7 mmol) of lithium 1,3-diphenyl-2-propenylcyclopentadienide prepared from (*S*)-1,3-diphenyl-2-propenylcyclopentadiene **3** (98% ee) and *n*-butyllithium in THF (50 mL). The mixture was allowed to warm to ambient temperature over a period of 6 h with stirring and then kept at 70°C for 12 h. Solvent was removed in vacuo. ^{1}H NMR spectroscopy of a sample of the residue revealed that the diastereomeric complexes were formed in a ratio of 98:2. Methylene chloride (50 mL) was added to the residue, and the precipitated lithium chloride was removed by filtration. Solvent of the clear filtrate was removed in vacuo, and diethyl ether (30 mL) was added. Concentration of the solution in vacuo brought about crystallization to give 3.3 g (80% yield) of the pure isomer **5**. **(*R*,*R*)-$ZrCl_2$[η^5-C_5H_4CHPh-(CH=CHPh)]$_2$**, **5**: ^{1}H NMR ($CDCl_3$) δ 5.11 (d, J=7.3 Hz, 2H), 5.94 (s, 2H), 6.05 (s, 2H), 6.18 (d, J=3.0 Hz, 2H), 6.28 (d, J=15.7 Hz, 2H), 6.46 (s, 2H), 6.57 (dd, J=15.7, 7.3 Hz, 2H), 7.22–7.40 (m, 20H); ^{13}C NMR ($CDCl_3$) δ 48.93 (2C), 113.24 (2C), 113.98 (2C), 115.23 (2C), 117.27 (2C), 126.34 (4C), 126.94 (2C), 127.44 (2C), 128.53 (4C), 128.62 (4C), 128.82 (4C), 131.58 (4C), 136.00 (2C), 136.97 (2C), 142.22 (2C). Anal. calcd for $C_{40}H_{34}ZrCl_2$: C, 70.98; H, 5.06. Found: C, 71.11; H, 5.27%. $[\alpha]_D^{20}$ −119 (*c* 1.0, $CHCl_3$).

3.6. Reaction of the 1,3-diphenyl-2-propenylcyclopentadienide with $TiCl_4$ giving titanocene 6

To a suspension of 710 mg (3.8 mmol) of $TiCl_4$ in 50 mL of toluene was added at −78°C a cold solution of 2.0 g (7.7 mmol) of lithium 1,3-diphenyl-2-propenylcyclopentadienide prepared from (*S*)-1,3-diphenyl-2-propenylcyclopentadiene **3** (98% ee) and *n*-butyllithium in 50 mL of THF. The mixture was allowed to warm to ambient temperature over a period of 6 h with stirring and then kept at 70°C for 12 h. Solvent was removed in vacuo. ^{1}H NMR spectroscopy of a sample of the residue revealed that the diastereomeric complexes were formed in a ratio of 98:2. Methylene chloride (50 mL) was added to the reaction mixture. The solution was filtered from the precipitated lithium chloride. Solvent of the clear filtrate was removed in vacuo and diethyl ether (30 mL) was added. Concentration of the solution in vacuo brought about crystallization to give 1.2 g (48% yield) of the pure diastereomer **6**. **(*R*,*R*)-$TiCl_2$[η^5-C_5H_4CHPh(CH=CHPh)]$_2$, 6**: ^{1}H NMR ($CDCl_3$) δ 5.22 (d, J=7.3 Hz, 2H), 6.00 (s, 2H), 6.03 (s, 2H), 6.27 (d, J=15.8 Hz, 2H), 6.33 (s, 2H), 6.58 (dd, J=15.8, 7.3 Hz, 2H), 6.64 (s, 2H), 7.18–7.35 (m, 20H): ^{13}C NMR ($CDCl_3$) δ 49.55 (2C), 116.28 (2C), 119.08 (2C), 119.44 (2C), 122.56 (2C), 126.34 (4C), 127.04 (2C), 127.47 (2C), 128.52 (4C), 128.66 (4C), 129.04 (4C), 131.48 (2C), 131.71 (2C), 136.95 (2C), 139.82 (2C), 141.74 (2C). Anal. calcd for $C_{40}H_{34}TiCl_2$: C, 75.84; H, 5.41. Found: C, 75.70; H, 5.26%. $[\alpha]_D^{20}$ +133 (*c* 1.0, $CHCl_3$).

3.7. Diels–Alder reaction catalyzed by chiral zirconocene triflate complex

3-((*E*)-2-Butenoyl)oxazolidinone (141 mg, 1.00 mmol) and zirconocene bis-(triflate) complex prepared in situ from (*R*,*R*)-**5** (33.7 mg, 0.05 mmol) and silver triflate (25.6 mg, 0.10 mmol) were combined and dissolved in CH_3NO_2 (2.0 mL). After the solution was cooled to −30°C, cyclopentadiene (0.2 mL) was added via syringe. After 50 min at this temperature, TLC analysis (silica gel, CH_2Cl_2) revealed the complete consumption of 3-((*E*)-2-butenoyl)oxazolidinone. The mixture was quenched with saturated aqueous NH_4Cl and diluted with CH_2Cl_2 and water. The aqueous layer was extracted with CH_2Cl_2 and the combined organic layers were dried over anhydrous Na_2SO_4. Removal of the solvent in vacuo gave the crude adduct in 99% yield with 40% ee. (Chiral HPLC conditions: Chiralcel OD-H (hexane/2-propanol = 500/1)).

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