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Reversal in enantioselectivity for the palladium-catalyzed asymmetric allylic substitution with novel metallocene-based planar chiral diphosphine ligands

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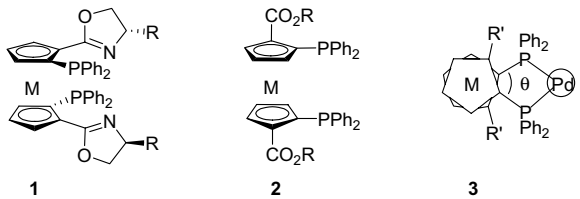
Abstract

The novel C_2-symmetric metallocene-based ligands with only planar chirality were synthesized easily and applied in palladium-catalyzed asymmetric allylic substitution with excellent enantioselectivity and high catalytic activity. When two ester groups on Cp rings of the metallocene were replaced by hydroxymethyl groups, opposite configuration of the product was obtained with high catalytic activity and excellent enantioselectivity. The opposite configuration of products was also obtained when the hydroxyl groups were protected as esters or ethers. These results might be attributed to the different configuration of the diphosphine ligands–Pd(II) complexes.

The steric properties of ligands employed in asymmetric metal catalysis are crucial for efficient transfer of chirality and control of the absolute configuration of newly formed stereocenters in the reaction. The preparation of two enantiomers generally requires access to the ligands with opposite absolute configurations. If a chiral ligand from a natural product exists in only one enantiomeric form, access to compounds derived from the opposite enantiomer may be limited. To obtain products of opposite configuration, one promising strategy would be the ability to prepare ligands from the same chiral starting material via simple modification of the structure. This means to prepare opposite enantiomers with the ligands possessing identical chiral scaffolds. There are some reports related to this strategy.[1] But to the best of our knowledge, there has not been any report on the reversal in enantioselectivity with modified ligands with planar chirality.

Metallocene-based chiral ligands designed for asymmetric synthesis have attracted much scientific attention over the past decades.[2] We had reported the synthesis of C_2-symmetric chiral metallocene-based ligands, 1,1′-bis(oxazolinyl)-2,2′-diphenylphosphino metallocene (**1**, Fig. 1), and their application for Pd-catalyzed asymmetric allylic alkylation with excellent enantioselectivity (up to 99% ee).[3] This type of ligands afford a C_2-symmetric 1:2 P,N-chelation complex with palladium(II). Subsequently, the oxazoline moiety was removed by ring-opening followed by ester transformation to give C_2-symmetric metallocene with only planar chirality (**2**, Fig. 1).[4] It was shown that the twist angle in the complexes of these metallocene diphosphine ligands with palladium(II), which could be adjusted by changing M and/or R′ group on Cp rings,



1 **2** **3**

M: (**a**=Fe, **b**=Ru)

Fig. 1.

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had a pivotal influence on the asymmetric allylic substitutions (**3**, Fig. 1).[4c]

To further explore the effects of twist angle on asymmetric catalysis, novel metallocene-based diphosphine ligands (**4**–**6**, Fig. 2) with different kind of substituents adjacent to diphenylphosphine group were synthesized. Furthermore, their application in Pd-catalyzed asymmetric allylic substitution was studied.

Ligands **4**–**6** were synthesized easily via the reduction of ester amide **7**[4] followed by protecting the hydroxyl group as shown in Scheme 1. Thus, treating **7** with $LiAlH_4$ in THF afforded 1,1′-dihydroxymethyl-2,2′-diphenylphosphino metallocene (**4**).[5,6] Alcohol **4** could be converted to **5** and **6** via esterification and etherification, respectively.[7–10] They have identical chiral scaffold but different substituents adjacent to diphenylphosphine group with **2**.

The transition-metal-catalyzed asymmetric allylic amination has become an invaluable tool for synthetic chemists, as these types of amines are otherwise difficult to prepare.[11] Because of the ubiquity of the chiral amine unit in biologically active compounds, we studied the palladium-catalyzed asymmetric allylic amination using ligands **4** as chiral ligands. To our surprise, the reversal in enantioselectivity in this reaction was observed comparing to that resulted by **2**, though they have identical chiral scaffold. Then, we studied this reaction in details and the results are summarized in Table 1.

As shown in Table 1, ligands **2** gave excellent enantioselectivity (99% ee, *S*-configuration) in this reaction (Table 1, entries 1–4). When **4** was used as chiral ligands, high catalytic activity and moderate enantioselectivity were obtained (Table 1, entries 5 and 6). However, to our surprise, the opposite *R*-configuration of the product was obtained as the major isomer. To optimize the reaction conditions, the effect of solvents was taken into account first of all. Improved results were obtained with both toluene and THF (Table 1, entries 7–12), and **4a** showed better ee than **4b** in these two solvents. Temperature affected the enantioselectivity as well. The ee values were increased (81% ee in THF and 76% ee in toluene) at 0 °C with **4a** as the ligands (Table 1, entries 13 and 14). The enantioselectivity was further improved in THF and up to 88% ee was obtained at −78 °C with **4a** (Table 1, entries 15–17). However, the enantioselectivity was somewhat reduced at lower temperature in toluene with **4b** (Table 1, entry 18).

It was reported that the hydroxyl group in the ligands was interacting via a hydrogen bond with the nucleophile.[13] To explain the results mentioned above, the hydroxyl groups in **4** were converted to ether and ester groups to give the corresponding ligands **5** and **6**, respectively. The absolute configuration of product remains *R*-configuration

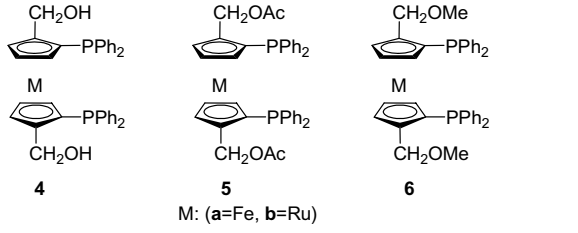
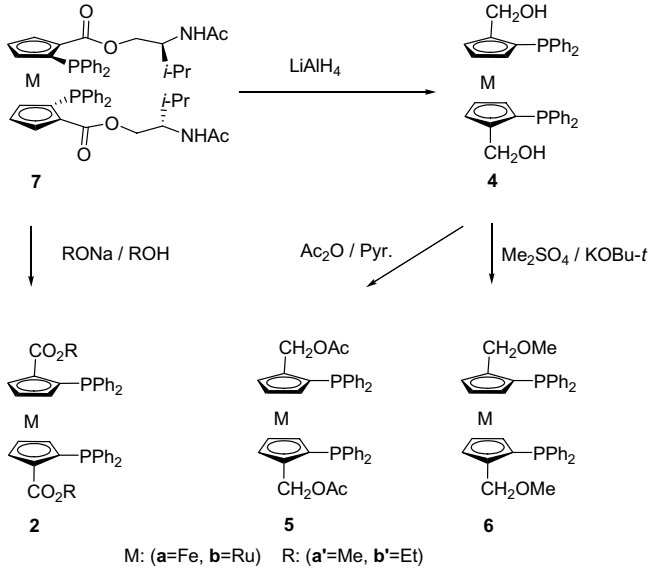
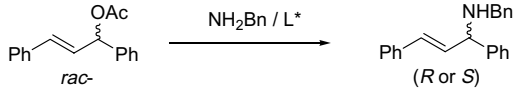


Fig. 2.



Scheme 1.

Table 1
Asymmetric allylic amination of 1,3-diphenyl-2-propenyl acetate with benzylamine[a]



Entry	Ligands	Solvent	T (°C)	Time (min)	ee[b,c] (%)
1[d]	**2aa′**	Toluene	0	240	99 (*S*)
2[d]	**2ab′**	Toluene	0	240	99 (*S*)
3[d]	**2ba′**	CH_2Cl_2	−25	90	99 (*S*)
4[d]	**2bb′**	CH_2Cl_2	−25	180	99 (*S*)
5	**4a**	CH_2Cl_2	20	20	55 (*R*)
6	**4b**	CH_2Cl_2	20	20	60 (*R*)
7	**4a**	Toluene	20	20	70 (*R*)
8	**4b**	Toluene	20	20	69 (*R*)
9	**4a**	THF	20	20	70 (*R*)
10	**4b**	THF	20	20	67 (*R*)
11	**4a**	DMF	20	20	28 (*R*)
12	**4b**	DMF	20	20	46 (*R*)
13	**4a**	THF	0	30	81 (*R*)
14	**4a**	Toluene	0	30	76 (*R*)
15	**4a**	THF	−10	120	86 (*R*)
16	**4a**	THF	−25	8 h	87 (*R*)
17	**4a**	THF	−78	72 h	88 (*R*)
18	**4a**	Toluene	−10	60	61 (*R*)

[a] Molecular ratio: $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$/ligand/substrate/benzylamine = 1/2.2/200/600; reactions were conducted under nitrogen with more than 95% yield; the catalysts were prepared by treating $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ with ligands in suitable solvent at 20 °C for 1 h before use.

[b] Determined by the HPLC using chiral OJ-H column.

[c] The absolute configuration was determined according to the literature.[12]

[d] See Ref. 4.

even if **5** and **6** were used as chiral ligands (Table 2, entries 1–4). These results indicated that the hydroxyl group in **4** was not crucial for the reversal in configuration of the products.

Furthermore, to investigate if the reversal was caused by the hydrogen bond between the nucleophile (NH_2Bn) and the oxygen atom in ligands **4–6**, we also carried out the Pd-catalyzed asymmetric allylic alkylation with dimethyl malonate as a nucleophile. The results were shown in Table 3.

As shown in Table 3, the reversal in enantioselectivity was still observed when chiral ligands **4** and **5** were used. Up to 73% ee value was obtained when **5b** was used as the ligand at −78 °C. These results indicated that the possible hydrogen bond between the nucleophile and the ligands was not crucial for the reversal in configuration either.

We tried to find an explanation by X-ray analysis, but failed to obtain a single crystal of any of these ligands with Pd(II) after much effort. It was known that the complex of **2** with Pd(II) existed as the configuration **3** by X-ray analysis of the single crystal in our previous research.[4c] It was deduced that the configuration of the complexes of **4–6** with Pd(II) might exist as **8** (Fig. 3). This is possible because the steric interaction between the phenyl group and methylene group in R′ in complex **8** for ligands **4**, **5** and **6** is much smaller than that between the phenyl group and the carbonyl group in R′ for ligand **2**, which would make the formation of complex **8** easier than that of complex **3** for **4–6**. The opposite configuration of **8** from **3** might be responsible for the reversed configuration of the product.

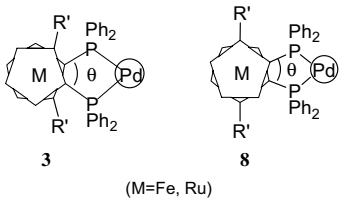
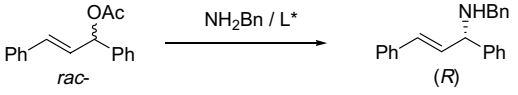


Fig. 3.

In summary, novel C_2-symmetric metallocene-based ligands with only planar chirality were synthesized and applied in the palladium-catalyzed asymmetric allylic amination. Modification of the substituents adjacent to the diphenylphosphine group on the Cp rings can switch the configuration of the product in this amination with excellent enantioselectivity and high catalytic activity. This phenomenon of the reversal was also observed in the asymmetric allylic alkylation. These results might be attributed to the different configuration of the complexes of the diphosphine ligands with Pd(II).

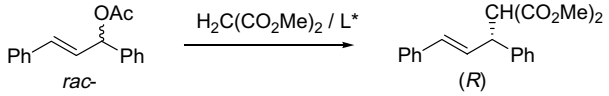
Table 2
Asymmetric allylic amination of 1,3-diphenyl-2-propenyl acetate with benzylamine[a]



Entry	Ligands	Solvent	T (°C)	Time (min)	ee[b,c] (%)
1	**5a**	CH_2Cl_2	20	20	33 (*R*)
2	**5b**	CH_2Cl_2	20	20	42 (*R*)
3	**6a**	CH_2Cl_2	20	20	22 (*R*)
4	**6b**	CH_2Cl_2	20	20	44 (*R*)

[a] Molecular ratio: $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$/ligand/substrate/benzylamine = 1/2.2/200/600; reactions were conducted under nitrogen with more than 95% yield; the catalysts were prepared by treating $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ with ligands in suitable solvent at 20 °C for 1 h before use.
[b] Determined by the HPLC using chiral OJ-H column.
[c] The absolute configuration was determined according to the literature.[12]

Table 3
Asymmetric allylic alkylation of 1,3-diphenyl-2-propenyl acetate with dimethyl malonate[a]



Entry	Ligands	Solvent	T (°C)	Time (min)	ee[b,c] (%)
1	**4a**	CH_2Cl_2	rt	20	8 (*R*)
2	**4b**	CH_2Cl_2	rt	20	22 (*R*)
3	**5a**	CH_2Cl_2	rt	20	2 (*R*)
4	**5b**	CH_2Cl_2	rt	20	45 (*R*)
5	**5b**	CH_2Cl_2	−78	8 h	73 (*R*)

[a] Molecular ratio: $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$/ligand/substrate/benzylamine = 2.5/6.0/200/600; reactions were conducted under nitrogen with more than 95% yield; The catalysts were prepared by treating $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ with ligands in CH_2Cl_2 solvent at 20 °C for 1 h before use.
[b] Determined by the HPLC using chiral OD-H column.
[c] The absolute configuration was determined according to the literature.[14]

Acknowledgments

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5. **4a** mp 136–137 °C. $[\alpha]_{27}^{D}$ −444.3 (*c* 0.825, $CHCl_3$); ^1H NMR ($CDCl_3$, 400 Hz): δ 3.46 (br s, 2H), 3.55 (s, 2H), 3.97 (br s, 2H), 4.27 (d, $J = 13.6$ Hz, 2H), 4.56 (d, $J = 13.2$ Hz, 2H), 4.62 (br s, 2H), 7.09–7.13 (m, 4H), 7.22–7.34 (m, 12H), 7.39–7.43 (m, 4H); ^{13}C NMR ($CDCl_3$, 100 Hz): δ 59.63, 59.72, 71.74, 71.76, 72.22, 72.26, 72.77, 72.79, 72.81, 72.83, 74.89, 74.96, 96.08, 96.30, 128.39, 128.48, 128.56, 128.61, 129.58, 132.27, 132.45, 134.83, 135.04, 136.31, 136.39, 138.77, 138.86; ^{31}P NMR ($CDCl_3$, 162 Hz, 85% H_3PO_4): δ −22.47; MS (MALDI): *m*/*z* 615 [M+1$^+$] (100); HRMS calcd for $C_{36}H_{32}O_2P_2Fe$ 614.1231, found 614.12215.
6. **4b** mp 155–157 °C. $[\alpha]_{27}^{D}$ −488.1 (*c* 1.08, $CHCl_3$); ^1H NMR ($CDCl_3$, 400 Hz): δ 3.23 (br s, 2H), 3.92 (br s, 2H), 4.23 (br s, 2H), 4.23 (d, $J = 13.2$ Hz, 2H), 4.49 (dd, $J = 1.6$, 13.6 Hz, 2H), 4.99 (br s, 2H), 7.22–7.26 (m, 6H), 7.28–7.31 (m, 10H), 7.34–7.38 (m, 4H); ^{13}C NMR ($CDCl_3$, 100 Hz): δ 58.87, 58.95, 73.94, 75.36, 75.38, 75.72, 75.74, 75.77, 75.78, 79.94, 80.03, 99.47, 99.70, 128.23, 128.31, 128.58, 128.63, 128.69, 129.43, 132.31, 132.50, 134.64, 134.83, 136.49, 136.55, 138.80, 138.89; ^{31}P NMR ($CDCl_3$, 162 Hz, 85% H_3PO_4): δ −21.67; MS (MALDI): *m*/*z* 661 [M+1$^+$] (100); HRMS calcd for $C_{36}H_{32}O_2P_2Ru$ 660.0915, found 660.09156.
7. **5a** mp 140–142 °C. $[\alpha]_{27}^{D}$ −306.0 (*c* 0.415, $CHCl_3$); ^1H NMR ($CDCl_3$, 400 Hz): δ 1.64 (s, 6H), 3.32 (br s, 2H), 4.27 (br s, 2H), 4.54 (br s, 2H), 4.95 (d, $J = 12$ Hz, 2H), 5.11 (d, $J = 11.6$ Hz, 2H), 7.06–7.10 (m, 4H), 7.20–7.23 (m, 10H), 7.27–7.35 (m, 6H); ^{13}C NMR ($CDCl_3$, 100 Hz): δ 20.61, 61.39, 61.49, 73.14, 73.17, 73.56, 73.60, 75.33, 75.36, 78.81, 78.92, 87.77, 88.02, 128.14, 128.16, 128.22, 128.34, 128.42, 129.52, 132.43, 132.61, 134.78, 134.99, 136.39, 136.48, 139.35, 139.45, 170.71; ^{31}P NMR ($CDCl_3$, 162 Hz, 85% H_3PO_4): δ −23.71; MS (MALDI): *m*/*z* 699 [M+1$^+$] (100); HRMS calcd for $C_{40}H_{36}O_4P_2Fe$ 698.1457, found 698.14328.
8. **5b** mp 139–140 °C. $[\alpha]_{27}^{D}$ −390.5 (*c* 0.28, $CHCl_3$); ^1H NMR ($CDCl_3$, 400 Hz): δ 1.66 (s, 6H), 3.84 (br s, 2H), 4.43 (t, $J = 2.4$ Hz, 2H), 4.78 (d, $J = 12.4$ Hz, 2H), 4.93 (br s, 2H), 4.96 (dd, $J = 2.4$, 12.4 Hz, 2H), 7.20–7.30 (m, 20H); ^{13}C NMR ($CDCl_3$, 100 Hz): δ 20.68, 61.01, 61.10, 75.35, 76.80, 76.84, 78.18, 78.21, 83.47, 83.60, 91.23, 91.50, 128.13, 128.20, 128.25, 128.31, 129.27, 132.56, 132.74, 134.50, 134.71, 136.87, 136.94, 139.45, 139.56, 170.69; ^{31}P NMR ($CDCl_3$, 162 Hz, 85% H_3PO_4): δ −23.10; MS (MALDI): *m*/*z* 745 [M+1$^+$] (100); HRMS calcd for $C_{40}H_{36}O_4P_2Ru$ 744.1139, found 744.11269.
9. **6a** mp 144–146 °C. $[\alpha]_{27}^{D}$ −412.5 (*c* 0.885, $CHCl_3$); ^1H NMR ($CDCl_3$, 400 Hz): δ 3.17 (s, 6H), 3.28 (br s, 2H), 4.11 (t, $J = 2.4$ Hz, 2H), 4.28 (d, $J = 11.2$ Hz, 2H), 4.41 (dd, $J = 2.8$, 11.2 Hz, 2H), 4.47 (br s, 2H), 7.07–7.11 (m, 4H), 7.19–7.25 (m, 10H), 7.28–7.32 (m, 2H), 7.35–7.39 (m, 4H); ^{13}C NMR ($CDCl_3$, 100 Hz): δ 58.26, 69.27,69.37, 72.67, 72.70, 72.84, 72.87, 75.08, 75.12, 90.49, 90.74, 127.82, 128.07, 128.13, 128.27, 128.36, 129.40, 132.16, 132.33, 135.02, 135.23, 137.14, 137.22, 139.97, 140.06; ^{31}P NMR ($CDCl_3$, 162 Hz, 85% H_3PO_4): δ −22.75; MS (MALDI): *m*/*z* 643 [M+1$^+$] (100); HRMS calcd for $C_{38}H_{36}O_2P_2Fe$ 642.1556, found 642.15345.
10. **6b** mp 166–167 °C. $[\alpha]_{27}^{D}$ −438.3 (*c* 0.545, $CHCl_3$); ^1H NMR ($CDCl_3$, 400 Hz): δ 3.18 (s, 6H), 3.84 (br s, 2H), 4.07 (d, $J = 11.2$ Hz, 2H), 4.27 (t, $J = 2.4$ Hz, 2H), 4.33 (dd, $J = 2.4$, 11.2 Hz, 2H), 4.85 (m, 2H), 7.22–7.28 (m, 16H), 7.32–7.36 (m, 4H); ^{13}C NMR ($CDCl_3$, 100 Hz): δ 58.15, 68.93, 69.02, 74.98, 76.28, 76.32, 77.92, 77.95, 82.23, 82.35, 93.56, 93.83, 127.94, 128.07, 128.15, 128.18, 128.22, 129.21, 132.30, 132.47, 134.77, 134.99, 137.73, 137.80, 140.05, 140.15; ^{31}P NMR ($CDCl_3$, 162 Hz, 85% H_3PO_4): δ −22.48; MS (MALDI): *m*/*z* 689 [M+1$^+$] (100); HRMS calcd for $C_{38}H_{36}O_2P_2Ru$ 688.1234, found 688.12286.
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