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Tetrahedron Letters
Tetrahedron Letters 48 (2007) 585–588

# The synthesis of novel $C_2$-symmetric P,N-chelation ruthenocene ligands and their application in palladium-catalyzed asymmetric allylic substitution

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Received 16 September 2006; revised 13 November 2006; accepted 20 November 2006
Available online 12 December 2006

**Abstract**—Novel air-stable $C_2$-symmetric tetrasubstituted ruthenocene-based ligands were readily synthesized and used for palladium-catalyzed asymmetric allylic substitution showing excellent enantioselectivity and high catalytic activity.
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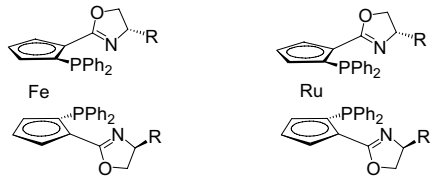
Ferrocene-based chiral ligands designed for asymmetric synthesis have attracted tremendous scientific interest over the past decades,[1] with some having been successfully applied in industrial processes.[2] The reason as to why these ligands were a versatile class of compounds is that structural modification can be readily made by introduction of a desired functional group on the cyclopentadienyl rings according to the demand of the reaction type. Among the vast variety of ferrocene-based ligands, the design and the preparation of $C_2$-symmetry planar chiral ferrocenes are of great importance in the development of transition metal-catalyzed enantioselective reactions.[3,4] Several years ago, the Ikeda group reported the $C_2$-symmetric ferrocene-based ligands 1,1′-bis(oxazolinyl)-2,2′-diphenylphosphino ferrocene **1** (Fig. 1). This type of ligands afford interesting complexation behavior with palladium(II) and excellent enantioselectivity for palladium-catalyzed asymmetric allylic substitution.[3] Since then, many $C_2$-symmetry tetrasubstituted chiral ferrocene ligands have been developed showing excellent enantioselectivity for asymmetric synthesis.[4]




**1** (a: R=*i*-Pr, b: *t*-Bu) **2** (a: R=*i*-Pr, b: *t*-Bu)

**Figure 1.**

Comparing with chiral ferrocene ligands, the chiral ruthenocene ligands have received much less attention. To the best of our knowledge, there are few reports on chiral ruthenocene ligands.[5] It is known that the distances between the two cyclopentadienyl rings in ferrocene and ruthenocene are 3.32 and 3.68 Å, respectively (Fig. 2).[6] The longer distance by about 10% in ruthenocene than their ferrocene analogs would be expected to present different complexation behavior with transition metals. These ligands will probably give rise to different enantioselectivity and catalytic activity in catalyzed asymmetric synthesis too. Considering these presumptions, we report herein the preparation of the novel $C_2$-symmetric tetrasubstituted ruthenocene compounds, their complexation behavior with palladium(II) and application in palladium-catalyzed asymmetric allylic substitution.

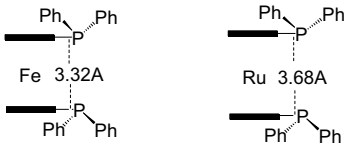



**Figure 2.**

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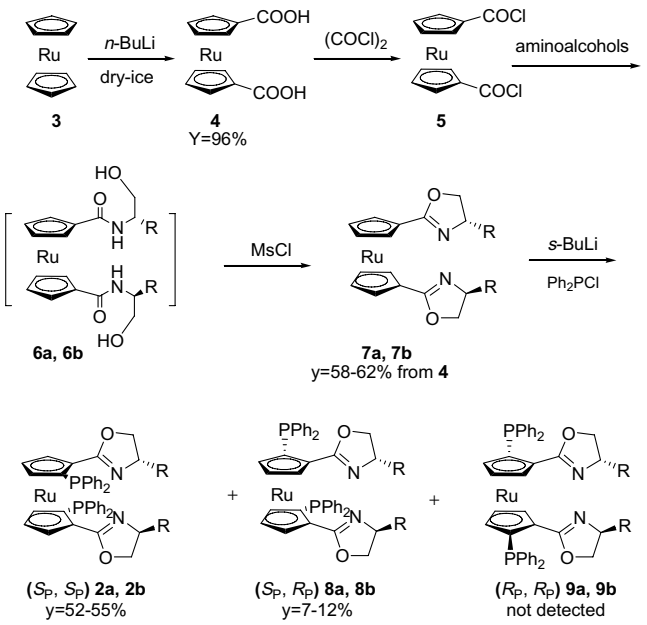
doi:10.1016/j.tetlet.2006.11.121




**Scheme 1.** **a**: R = *i*-Pr, **b**: R = *t*-Bu.

Compound **2** can be easily prepared from **3** via five steps (Scheme 1). Thus, treatment of **3** with 4 equiv *n*-butyllithium and 2.6 equiv TMEDA in *n*-hexane for 19 h gave lithiated compound, which followed by carboxylation reaction and acidification afford 1,1′-dicarboxylic ruthenocene **4** in 96% yield. This acid then reacted with 8 equiv oxallyl chloride in dichloromethane to give the 1,1′-dichlorocarbonylruthenocene **5**. Without any purification, **5** was directly reacted with 2.4 equiv chiral aminoalcohol and then treated with 2.6 equiv methyl sulfonyl chloride in 'one-pot' to afford the 1,1′-bis[(*S*)-4-substituted oxazolin-2-yl]-ruthenocene **7** in 58–62% overall yields from **4**. Compound **7** which was treated with 2.6 equiv of *sec*-butyllithium in THF at −78°C for a period of 2 h and then for 20 min at 0 °C. The dilithiated species were then reacted with 2.6 equiv of chlorodiphenylphosphine at 0 °C for 3 h. Thus, **2**[7,8] was obtained as a major product with yields of 52–55% and ($S_P$,$R_P$)-**8**[9] was also isolated as a minor product with yields of 7–12%. ($R_P$,$R_P$)-**9** could not be detected in this procedure. The absolute configuration of the product was deduced according to that of compound **1**.[3a]

To our delight, the obtained tetrasubstituted ruthenocene compound **2** is more air-stable than **1**. In the case of the preparation of **1**, work up and purification with column chromatography had to be done under argon all the time.[3a] During this work, no oxidation of phosphorus atoms in **2** could be detected upon exposure to air during synthesis. Furthermore, **2** can be stored in air atmosphere for more than ten months without any change.

Next, the complexation of **2a** with palladium(II) in acetonitrile-$d_3$ was examined. When **2a** was mixed with 1 equiv of dichlorobis(acetonitrile)palladium(II) in acetonitrile-$d_3$, three components including **2a** were observed by $^1$H NMR and $^{31}$P NMR. Finally, the mixture gave a single $C_2$-symmetric 1:2 P,N-chelation complex (**10**)[10] but not P,P-chelation complex (**11**) (Fig. 3), after an additional 1 equiv of palladium(II) had been added. We also tried to investigate the complexation of **2a** with 1,3-diphenylallylpalladium(II) chloride dimer, but the $^1$H NMR and $^{31}$P NMR were complicated and difficult to conclusively analyze.

With the novel $C_2$-symmetric tetrasubstituted ruthenocene compounds in hand, we first applied them in the palladium-catalyzed asymmetric allylic substitution (Scheme 2).[11] All of these ligands afforded high enantioselectivity for the palladium-catalyzed asymmetric allylic substitution of *rac*-1,3-diphenyl-2-propenyl acetate, similar to that of the corresponding ferrocene compounds.[3b] In addition, higher catalytic activity was observed since all reactions were completed within 30 min at room temperature in dichloromethane. However, it took 6 h for this reaction when **1** was used.[3b] The results are shown in Table 1.

The influence of reaction conditions and structure of ligands upon the allylic substitution were taken into

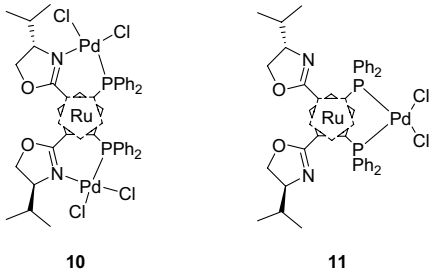
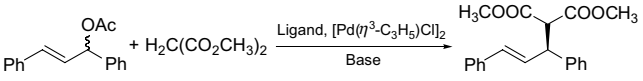



**Figure 3.**




**Scheme 2.**

**Table 1.** Allylic substitution of 1,3-diphenyl-2-propenyl acetate with dimethyl malonate[a]

| Entry | Ligand | *T* (°C) | Time | ee[b] (%) | Enantiomer[c] |
|---|---|---|---|---|---|
| 1[d] | **2a** | rt | 3 h | 82 | (*S*)-(−) |
| 2 | **2a** | rt | 0.5 h | 92 | (*S*)-(−) |
| 3[e] | **2a** | rt | 0.5 h | 82 | (*S*)-(−) |
| 4 | **2a** | 0 | 20 h | 92 | (*S*)-(−) |
| 5 | **2a** | −25 | 20 h | 92 | (*S*)-(−) |
| 6 | **2a** | 40 | 10 min | 92 | (*S*)-(−) |
| 7 | **2b** | rt | 0.5 h | 98 | (*S*)-(−) |

[a] Molecular ratio: $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$/ligand/substrate/BSA/$H_2C(CO_2Me)_2$ = 2.5/3.0/100/300/300. Reactions were conducted under nitrogen in $CH_2Cl_2$ at room temperature and all reactions gave above 95% isolated chemical yields. The catalyst was prepared by treating $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ with ligands in $CH_2Cl_2$ at 20 °C for 1 h before use.

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

[c] Assigned through comparison of the sign of specific rotations with the literature data.[12]

[d] NaH was used as a base.

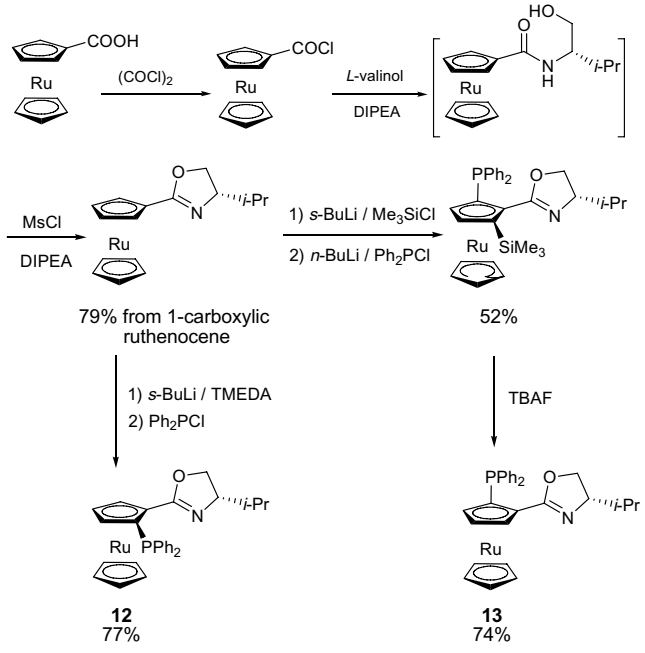
[e] THF was used as solvent.

account. First of all, the effect of the base on the catalytic reaction was examined. Primarily, when sodium hydride was used as the base, 82% ee was obtained. The enantioselectivity was enhanced to 92% ee if the base was changed to BSA (Table 1, entries 1 and 2). The solvent also affected the enantioselectivity. When using THF instead of dichloromethane, the enantioselectivity decreased to 82% ee (Table 1, entries 2 and 3). However, the temperature had no effect on the enantiometric excess in this substitution (Table 1, entries 2, 4–6).

It was shown that the substituent R on the oxazolinyl ring had much effect on the enantioselectivity and a bulkier group gave a better ee value. When **2b** having *tert*-butyl group was used as a chiral ligand, up to 98% ee was obtained in the allylic substitution (Table 1, entry 7).

In order to examine whether the planar chirality had effect on the catalytic reaction, the 1,2-substituted ruthenocene ligands **12** and **13** were also synthesized as shown in Scheme 3. Compounds **12**[13] and **13**[14] were easily prepared from 1-carboxylic ruthenocene via steps 4–6 with overall yields of 30–61%, and then employed in the palladium-catalyzed asymmetric allylic substitution (Table 2).

It was found that the $C_2$-symmetric tetrasubstituted ruthenocene ligand **2** had better enantioselectivity and higher activity than both **12** and **13** in the palladium-catalyzed asymmetric allylic substitution (Table 2), although it was not clear whether the process was affected by electric or/and steric effects, especially in view of the small amount of P,P-chelation complex. Meanwhile, it could be concluded that the planar chirality had an influence on the enantioselectivity and catalytic activity in this substitution (Table 2, entries 2 and 3).




**Scheme 3.**

**Table 2.** The effect of planar chirality to the allylic substitution[a]

| Entry | Ligand | Base | Solvent | Time (h) | ee[b] (%) | Enantiomer[c] |
|---|---|---|---|---|---|---|
| 1 | **2a** | BSA | $CH_2Cl_2$ | 0.5 | 92 | (*S*)-(−) |
| 2 | **12** | BSA | $CH_2Cl_2$ | 1 | 87 | (*S*)-(−) |
| 3 | **13** | BSA | $CH_2Cl_2$ | 1.5 | 59 | (*S*)-(−) |

[a] Molecular ratio: $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$/ligand/substrate/BSA/$H_2C(CO_2Me)_2$ = 2.5/6.0/100/300/300. Reactions were conducted under nitrogen in $CH_2Cl_2$ at room temperature and all reactions gave above 95% isolated chemical yields. The catalyst was prepared by treating $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ with ligands in $CH_2Cl_2$ at 20 °C for 1 h before use.
[b] Determined by the HPLC using chiral OD-H column.
[c] Assigned through comparison of the sign of specific rotations with the literature data.[12]

In summary, we have prepared the novel $C_2$-symmetric tetrasubstituted ruthenocene ligand **2** and applied it in the palladium-catalyzed asymmetric allylic substitution. Comparing to the corresponding ferrocene ligand **1**, much higher catalytic activity and comparable excellent enantioselectivities were observed. Furthermore, it was found that these novel ligands were rather stable toward air, which makes them suitable for commercial processes. Studies of the tetrasubstituted ruthenocene ligand **2** and the 1,2-substituted ruthenocene ligands **12** and **13** showed that the planar chirality has an influence on the enantioselectivity and catalytic activity in this substitution. Structural modifications of these ligands are currently being conducted in our laboratories.

## Acknowledgments

This work was partly supported by the Excellent Young Teachers Program of MOE, PRC and the National Natural Science Foundation of China (No. 20572070).

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7. Data for **2a**: mp 178–180 °C; $[\alpha]_D^{27}$ −263.6 (*c* 0.61, $CHCl_3$); $^1H$ NMR ($CDCl_3$, 400 Hz): $\delta$ 0.60 (d, $J = 6.8$ Hz, 6H), 0.86 (d, $J = 6.8$ Hz, 6H), 1.65–1.71 (m, 2H), 3.67 (t, $J = 8$ Hz, 2H), 3.82 (br s, 2H), 3.89–3.91 (m, 2H), 4.23–4.27 (dd, $J = 8$, 9.6 Hz, 2H), 4.67 (br s, 2H), 5.41 (br s, 2H), 7.17–7.32 (m, 20H); $^{13}C$ NMR ($CDCl_3$, 100 Hz): $\delta$ 17.4, 19.1, 32.1, 69.6, 72.2, 75.8, 77.4, 78.0, 78.1, 81.9, 82.1, 84.5, 84.8, 128.1, 128.2, 128.3, 128.4, 128.5, 128.9, 132.8, 133.0, 134.4, 134.6, 137.9, 138.0, 139.2, 139.3, 163.3, 163.4; $^{31}P$ NMR ($CDCl_3$, 162 Hz, 85% $H_3PO_4$): $\delta$ −16.85; MS (MALDI): *m*/*z* 823 [M+1$^+$] (100); HRMS calcd for $C_{46}H_{47}N_2O_2P_2Ru$ 823.2151, found 823.2154.
8. Data for **2b**: mp 150–151 °C; $[\alpha]_D^{27}$ −282.9 (*c* 1.04, $CHCl_3$); $^1H$ NMR ($CDCl_3$, 400 Hz): $\delta$ 0.70 (s, 18H), 3.71–3.80 (m, 4H), 3.82 (br s, 2H), 4.15 (t, $J = 8.4$ Hz, 2H), 4.72 (br s, 2H), 5.36 (br s, 2H), 7.12–7.29 (m, 20H); $^{13}C$ NMR ($CDCl_3$, 100 Hz): $\delta$ 25.9, 33.7, 68.7, 76.2, 76.3, 76.4, 77.7, 78.2, 78.3, 82.0, 82.2, 84.0, 84.2, 128.1, 128.2, 128.3, 128.4, 128.5, 128.8, 132.7, 132.9, 134.4, 134.6, 137.9, 138.0, 139.4, 139.5, 162.8; $^{31}P$ NMR ($CDCl_3$, 162 Hz, 85% $H_3PO_4$): $\delta$ −16.93; MS (MALDI): *m*/*z* 851 [M+1$^+$] (100); HRMS calcd for $C_{48}H_{51}N_2O_2P_2Ru$ 851.2464, found 851.2473.
9. Data for **8a**: mp 87–88 °C; $[\alpha]_D^{27}$ −62.9 (*c* 0.44, $CHCl_3$); $^1H$ NMR ($CDCl_3$, 400 Hz): $\delta$ 0.49–0.54 (m, 9H), 0.71 (d, $J = 6.8$ Hz, 3H), 1.36–1.43 (m, 1H), 1.48–1.56 (m, 1H), 3.38 (t, $J = 8.4$ Hz, 1H), 3.70–3.72 (m, 1H), 3.76–3.80 (m, 1H), 3.85–3.94 (m, 2H), 3.96–4.02 (m, 1H), 4.16 (br s, 2H), 4.78–4.80 (q, $J = 2.8$ Hz, 2H), 5.26 (br s, 1H), 5.29 (br s, 1H), 7.59–7.43 (m, 20H); $^{13}C$ NMR ($CDCl_3$, 100 Hz): $\delta$ 17.4, 18.0, 18.1, 18.9, 31.9, 32.7, 69.5, 69.6, 72.1, 72.3, 76.4, 76.7, 77.3, 77.8, 78.6, 78.7, 78.8, 78.9, 128.1, 128.21, 128.25, 128.27, 128.32, 128.38, 128.42, 128.49, 128.5, 128.8, 128.9, 132.6, 132.8, 132.9, 133.0, 134.6, 134.8, 134.9, 135.1, 162.9, 163.0; $^{31}P$ NMR ($CDCl_3$, 162 Hz, 85% $H_3PO_4$): $\delta$ −16.77, −15.72; MS (MALDI): *m*/*z* 823 [M+1$^+$] (100); HRMS calcd for $C_{46}H_{47}N_2O_2P_2Ru$ 823.2151, found 823.2159.
10. Data for **10**: $^1H$ NMR ($CD_3CN$, 400 Hz): $\delta$ 0.85 (d, $J = 6.8$ Hz, 6H), 0.95 (d, $J = 6.8$ Hz, 6H), 2.77–2.86 (m, 2H), 3.84 (br s, 2H), 3.88 (br s, 2H), 4.38 (t, $J = 9.2$ Hz, 2H), 4.46–4.48 (m, 2H), 5.12–5.15 (m, 2H), 5.16 (br s, 2H), 7.25–7.96 (m, 20H); $^{31}P$ NMR ($CD_3CN$, 162 Hz, 85% $H_3PO_4$): $\delta$ 18.09.
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13. Data for **12**: mp 136–138 °C; $[\alpha]_D^{27}$ −97.51 (*c* 0.46, $CHCl_3$); $^1H$ NMR ($CDCl_3$, 400 Hz): $\delta$ 0.67 (d, $J = 6.8$ Hz, 3H), 0.79 (d, $J = 6.8$ Hz, 3H), 1.64–1.68 (m, 1H), 3.67 (t, $J = 7.6$ Hz, 1H), 3.79–3.84 (m, 1H), 3.94 (br s, 1H), 4.16–4.20 (dd, $J = 8$, 10 Hz, 1H), 4.59 (s, 5H), 4.67 (br s, 1H), 5.31 (br s, 1H), 7.27–7.40 (m, 10H); $^{13}C$ NMR ($CDCl_3$, 100 Hz): $\delta$ 17.7, 18.7, 32.2, 69.7, 72.1, 72.8, 74.3, 73.1 (5C), 76.5, 76.6, 79.5 (d, $J = 18$ Hz), 81.7 (d, $J = 17.6$ Hz), 128.0, 128.1, 128.2, 128.3, 128.4, 128.9, 132.6, 132.8, 134.6, 134.8, 138.3 (d, $J = 13.6$ Hz), 139.8 (d, $J = 14.5$ Hz); $^{31}P$ NMR ($CDCl_3$, 162 Hz, 85% $H_3PO_4$): $\delta$ −14.94; MS (MALDI): *m*/*z* 528 [M+1$^+$] (100); HRMS calcd for $C_{28}H_{29}NOPRu$ 528.1025, found 528.1041.
14. Data for **13**: mp 169–171 °C; $[\alpha]_D^{27}$ +130.47 (*c* 0.46, $CHCl_3$); $^1H$ NMR ($CDCl_3$, 400 Hz): $\delta$ 0.62 (d, $J = 6.8$ Hz, 3H), 0.64 (d, $J = 6.8$ Hz, 3H), 1.51–1.57 (m, 1H), 3.86–4.00 (m, 3H), 4.60 (s, 5H), 4.67 (br s, 1H), 5.30 (br s, 1H), 7.26–7.42 (m, 10H). $^{13}C$ NMR ($CDCl_3$, 100 Hz): $\delta$ 18.0, 18.1, 32.6, 69.7, 72.1, 72.5, 73.1 (5C), 74.4, 76.8, 76.9, 79.2 (d, $J = 18.3$ Hz), 81.5 (d, $J = 16$ Hz), 128.0, 128.1, 128.2, 128.3, 128.4, 128.8, 132.6, 132.9, 134.8, 135.0, 138.4 (d, $J = 12$ Hz), 139.6 (d, $J = 11.5$ Hz); $^{31}P$ NMR ($CDCl_3$, 162 Hz, 85% $H_3PO_4$): $\delta$ −15.74: MS (MALDI): *m*/*z* 528 [M+1$^+$] (100); HRMS calcd for $C_{28}H_{29}NOPRu$ 528.1025, found 528.1036.