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Ligand electronic effects in the palladium catalyzed asymmetric allylic alkylation reaction with planar chiral diphosphine-oxazoline ferrocenyl ligands

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Abstract

A series of planar chiral diphosphine-oxazoline ferrocenyl ligands with different electronic properties were successfully used in the asymmetric allylic substitutent reaction. The enantioselectivity of this reaction was affected by the electronic nature of the ligands. When the electronic effect was coincident with the steric effect of ligand, a higher ee value was observed.

Keywords: Electronic effect; Asymmetric; Alkylation; Planar chirality; Ferrocenyl-derived ligands

1. Introduction

The palladium catalyzed asymmetric allylic substitution reaction [1] has been demonstrated to be useful in the syntheses of valuable small molecules and complex natural products [2]. A number of chiral ligands have been successfully used in the palladium catalyzed allylic substitutions. Much effort has been made to elucidate crucial factors for the enantioselection of this reaction [1,4] especially with 1,3-diphenyl-prop-2-enyl acetate[3] as a model substrate. Consequently, the variations in the different donor atoms and steric demands of the ligands were exploited to examine the differentiation between isomeric allylic species as well as enantiotopic allylic termini, which might be observed by the configuration and the enantiomeric excess of the substitution products [3c,5]. We recently reported the syntheses of a series of new planar chiral diphosphine-oxazoline ferrocenyl ligands (*S,Sp*)-**1**–**5** and their successful application in the asymmetric intermolecular Heck reaction. The regioselectivity as well as the enantioselectivity of this reaction were strongly affected by the electronic effect of ligands [6a–c]. Similar electronic effects of cyclophane ligands in the asymmetric alkylation reaction were also examined [6d]. In a program aimed at the synthesis and applications of ferrocenyl ligands in asymmetric catalysis [7,8], we also sought to examine the effect of these ligands in the asymmetric allylic alkylation reaction. We found that these ligands have been shown to not only show high reactivity and enantioselectivity, but also exhibit definite electronic effects on the enantioselectivity in this reaction (see Scheme 1).

2. Results and discussion

As shown in Scheme 2, ligands (*S,Sp*)-**8a**, (*S,Sp*)-**8b**, and (*S,Sp*)-**9** were synthesized using similar procedure for the synthesis of ligands (*S,Sp*)-**1**–**5** from ferrocenyloxazoline derivatives (*S*)-**6** [6b]. Ligands (*S,Sp*)-**8a** and

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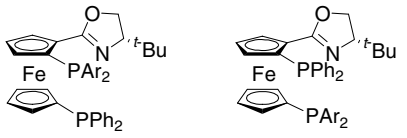


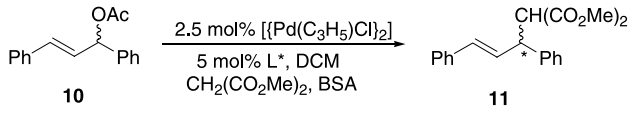
(S,Sp)-1		Ar = -C_6H_5
(S,Sp)-2a	**(S,Sp)-2b**	Ar = 3,5-$(CF_3)_2$-C_6H_3
(S,Sp)-3a	**(S,Sp)-3b**	Ar = 3,5-$(CH_3)_2$-C_6H_3
(S,Sp)-4a	**(S,Sp)-4b**	Ar = 4-(CF_3)-C_6H_4
(S,Sp)-5a	**(S,Sp)-5b**	Ar = 4-(MeO)-C_6H_4

Scheme 1.

(*S,Sp*)-**8b**, which contain a cyclohexylphosphine components, may have different properties to the other diphosphine-oxazoline ferrocenyl ligands.

To examine the catalytic efficiency of these ligands in the palladium catalyzed allylic alkylation reaction of 1,3-diphenyl-2-propenyl acetate **10**, the reaction was studied in dry dichloromethane at room temperature in the presence of $[\eta^3$-$(C_3H_5)PdCl]_2$ and the ligand in 1:1 ratio. The nucleophile was generated from dimethyl malonate in the presence of *N,O*-bis-(trimethylsilyl)acetamide (BSA) and a catalytic amount of potassium acetate (Scheme 3) [9].

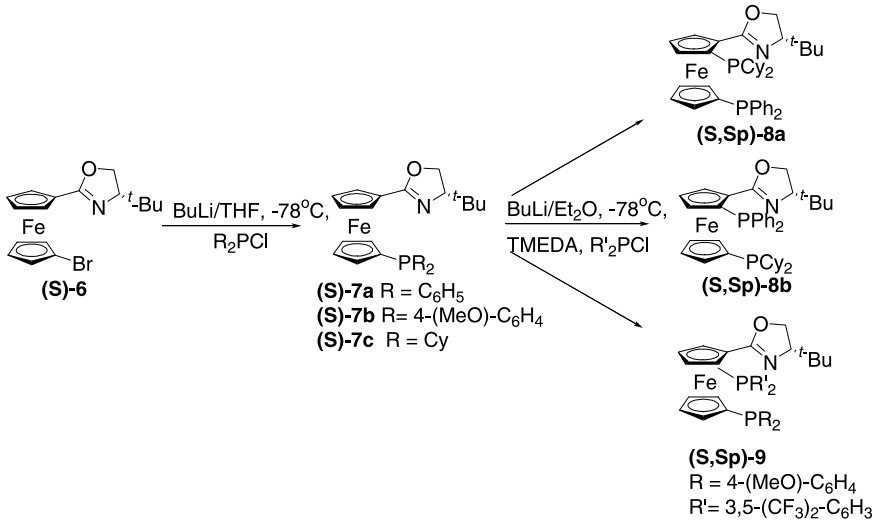
From the results in Table 1, it was established that the reaction proceeded very quickly in almost quantitative yield with ligand (*S,Sp*)-**1** at ambient temperature with moderate ee value (78.6%). However, when no more potassium acetate was added to the reaction system, little change was observed on the ee value and reaction time, which is rather different from that reported in the literature [9]. When the reaction temperature was decreased to 0 °C, the ee value of product **11** was increased to 81.6% (entry 2, Table 1). However, further lowering of the temperature will also decrease the ee value. Therefore, the rest of the reaction



Scheme 3.

was carried out at 0 °C. The results were also compiled in Table 1, which showed that all these ligands, although with different electronic effect substitutents, have very high reactivities. Almost all reactions can be completed in quantitative yield within 1 h. The electronic effect of ligands indeed affected the enantioselectivity of this reaction. When electronic withdrawing ligands were applied to this reaction, the ee values were increased (entries 3, 4, 7 and 8 in Table 1). The best ee value 90.1% was observed with ligand (*S,Sp*)-**2a**, which contains four strongly electron-withdrawing trifluoromethyl groups on the phenyl rings of the phosphine attached to the upper Cp ring (entry 3, Table 1). However, when electron-donating ligands were used, lower ee values of the product were found (entries 5, 6, 9 and 10, Table 1), especially, for ligand (*S,Sp*)-**5a**, which contains two electron-donating methoxy groups on the phenyl rings of the phosphine attached to the upper Cp ring. When strongly electron-donating ligands (*S,Sp*)-**8a** and (*S,Sp*)-**8b**, which contained cyclohexyl groups on either of the phosphine, were applied in the asymmetric allylic alkylation, almost racemic product could be obtained. And 24 h were needed to complete the reaction, when ligand (*S,Sp*)-**8a** was used.

With the aid of ^{31}P NMR spectroscopy the possible intermediate in the asymmetric allylic alkylation reaction was investigated and it was shown that these diphosphine-oxazoline ligands function as bidentate



Scheme 2.

Table 1
Electronic effect of the ligands on the palladium catalyzed asymmetric allylic alkylation reaction[a]

Entry	Ligand	Time (h)	Yield (%)[b]	ee (*S*) (%)[c]
1[d]	(*S,Sp*)-**1**	0.5	98	78.6
2	(*S,Sp*)-**1**	0.75	98	81.6
3	(*S,Sp*)-**2a**	1	99	**90.1**
4	(*S,Sp*)-**2b**	1	99	84.3
5	(*S,Sp*)-**3a**	0.5	99	75.1
6	(*S,Sp*)-**3b**	1	99	83.5
7	(*S,Sp*)-**4a**	1	99	82.3
8	(*S,Sp*)-**4b**	1	99	84.3
9	(*S,Sp*)-**5a**	1	98	69.2
10	(*S,Sp*)-**5b**	0.5	100	70
11	(*S,Sp*)-**8a**	24	90	5.2
12	(*S,Sp*)-**8b**	1	98	8.6
13	(*S,Sp*)-**9**	<0.5	100	**91.5**

[a] *Condition*: 2.5 mol% $[Pd\eta^3\text{-}(C_3H_5)Cl]_2$, 5 mol% Ligands, 100 mol% 1,3-diphenyl-2-propenyl acetate (**8**), 300 mol% $CH_2(CO_2Me)_2$, 300 mol% BSA at 0 °C.

[b] Isolated yield based on 1,3-diphenyl-2-propenyl acetate (**8**).

[c] Determined by HPLC (Chiralcel OJ column) and the absolute configuration of product was assigned through comparison of the sign of specific rotations with the literature data [9].

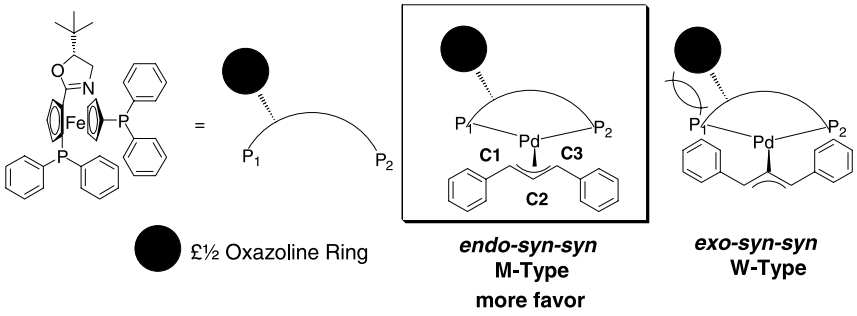
[d] The reaction was carried out at 25 °C.

ligands. The chemical shifts of the two phosphorus nuclei in the ligand (*S,Sp*)-**1** were −16.86 and −17.16 ppm in CD_2Cl_2. After reacting with $[\eta^3\text{-}(C_3H_5)PdCl]_2$ and 1,3-diphenyl-2-propenyl acetate **10** for 1 h, the corresponding phosphorus signals of major isomer were shifted to down field region (42.04 ppm, d, $J = 29.3$ Hz and 36.80 ppm, d, $J = 29.3$ Hz), and that of the minor isomer were shifted to 25.06 and 15.53 ppm.

According to the generally accepted mechanism of the asymmetric allylic alkylation reaction, a chiral π-allylic complex would be formed when Pd(0) was added to allylic acetate [1]. The absolute configuration of product was determined by the configuration of this chiral π complex. For the complex formed by these diphosphine-oxazoline ferrocenyl ligands, there are two possible orientations for the π-allyl moiety with respect to the coordination plane defined by the Pd, P1 and P2, and the structures are designated as W-type and M-type in Scheme 4. There are a strong steric repulsion between the allylic phenyl ring and the oxazoling ring of ligand in W-type intermediate. Therefore, W-type isomer was not the predominant configuration in the reaction. While in M-type configuration, the nucleophile would attack the allylic terminal carbon C3 because of the steric effect of oxazoling ring, the absolute configuration of product would be S, which is consistent with the experiment results.

The attacking point will also be determined by the *trans* effect of P1 or P2. When the electronic density on the P1 was lower than that on the P2 (that is, there is an electron-withdrawing group on the phenyl rings of the phosphine attached to the uppr Cp ring, just like ligand (*S,Sp*)-**2a**), the electronic charge on allylic termini C3 would be more positive than that on C1 for the *trans* effect, and hence should be more easily susceptible to the nucleophilic attack. In this case, the electronic effect of ligand was concordant with the steric effect of oxazoline ring; a higher enantioseletivity could be obtained. Therefore, when ligand (*S,Sp*)-**2a** was applied in the reaction, up to 90% ee was observed (entry 3, Table 1). However, when the electronic density on P1 was richer than P2, the electronic charge on C3 would be more negative than C1, so C1 would be attacked more easily for electronic effect, which was not matched with steric effect of ligand. Therefore, a lower ee value could be obtained with such type ligands, for example, when ligand (*S,Sp*)-**5a** was applied in this reaction, only 69.2% ee could be observed (entry 9, Table 1).

If this explanation is true, on enlarging the difference of the charge density of two phosphine of the ligand and matching of these two effects, a better ee value may be observed. Therefore, ligand (*S,Sp*)-**9** which contains four strongly electron-withdrawing trifurormethyl group on the phenyl rings of P1 and two electron-donating methoxy group on the phenyl rings of P2, was synthesized from (*S*)-**7** (Scheme 2). When the ligand (*S,Sp*)-**9** was applied in the asymmetric allylic substitutent reaction, a higher ee value 91.5% was observed (entry 13, Table 1), although not as high as we expected.



Scheme 4.

3. Conclusions

A series of planar chiral diphosphine-oxazoline ferrocenyl ligands with different electronic properties was successfully applied to palladium catalyzed asymmetric allylic substitutions of rac-1,3-diphenyl-2-propenyl acetate. The enantioselectivity of this reaction was affected by the electronic nature of the ligands. A higher ee value could be observed, when the electronic effect was coincident with the steric effect of ligand.

4. Experimental

4.1. General methods

All reactions and manipulations were performed in argon atmosphere using standard Schlenk techniques. Anhydrous solvents were transferred by oven-dried syringe. Bis-(μ-chloro)(1,3-diphenyl-η^3-allyl) dipalladium was prepared by a known method [10]. The commercially available reagents were used as received without further purification. Flaskware was flame dried under the stream of argon. Melting points are uncorrected. NMR spectra were recorded at room temperature in $CDCl_3$ or CD_2Cl_2 with 300 MHz (^1H), 121MHz (^{31}P) and 288 MHz (^{19}F) instrument. The chemical shifts were relative to TMS (as an internal reference) for ^1H NMR, 85% H_3PO_4 (as an external reference) for ^{31}P NMR and CF_3COOH (as an external reference) for ^{19}F NMR. IR spectra were recorded in KBr and measured in inverse centimeters, using a Shimadze IR-440 infrared spectrophotometer. Mass spectra were recorded on HP5989A mass spectrometer. Elemental analyses were carried out on a Foss-Heraus Vario instrument by Analytical and Testing Center of SIOC, Chinese Academy of Sciences.

4.2. 1-dicyclohexylphosphino-1′-[(S)-tert-butyl-2,5-oxazolinyl]-ferrocene (S)-7c

Compound (*S*)-**6** (195 mg, 0.5 mmol) was dissolved in fresh distilled THF (4 mL) under argon and cooled to −78°C. At this temperature, *n*-BuLi (0.38 mL, 0.6 mmol, 1.6 M in *n*-hexane) was added, and then the resulting deep red solution was stirred for 30 min. Choro-dicyclohexylposphine (0.7 mmol) was then added, and the resulting mixture was continually stirred and warm to room temperature over 30 min. The reaction mixture was diluted with ether (20 mL) washed with saturated aqueous $NaHCO_3$, and dried over Na_2SO_4. The solvent was removed under reduced pressure, and the resulting residue was chromatographed on silica gel with ethyl acetate: petroleum (1:5) as eluent to give 236 mg of (*S*)-**7c** (93% yield) as an orange solid, m.p. 40°C; $[\alpha]_D^{20} = -80^\circ$ $(c, 0.255, CHCl_3)$; ^1H NMR (300 MHz, $CDCl_3$/TMS): δ 0.96 (s, 9H), 1.00–1.38 (m, 10H), 1.67–2.00 (m, 12H), 3.90 (dd, J = 10.1, 7.6 Hz, 1 H), 4.14–4.23 (m, 3H), 4.24–4.28 (m, 1H), 4.28–4.43 (m, 4H), 4.70 (s, 1H), 4.76 (m, 1H); ^{31}P NMR (161 MHz, $CDCl_3$): δ − 7.20 (s, 1P); MS (EI) *m*/*z* (%): 508 (M^+, 38.85), 507 (M − 1, 31.92), 425 (42.44), 343 (78.22), 242 (100.0); IR (KBr, cm^{-1}): 2922, 2848, 1663, 1487, 1448, 1265, 1195, 1115, 1018, 971, 931, 508; Anal. Calc. for $C_{29}H_{42}FeNOP$: C, 68.64; H, 8.43; N, 2.76. Found: C, 68.53; H, 8.39; N, 2.53%.

4.3. 1-diphenylphosphino-1′-[(S)-tert-butyl-2,5-oxazolinyl]-2′-(Sp)-di-cyclohexyl-phosphino-ferrocene (S,Sp)-8a

A solution of (*S*)-**7a** [7] (248 mg, 0.5 mmol) and TMEDA (0.1 mL, 0.7 mmol) in ether (6 mL) under argon was cooled −78°C. To this resultant solution was added *n*-BuLi (0.4 mL, 0.64 mmol). After this solution was stirred at −78°C for 2 h. choro-dicyclohexylposphine (0.8 mmol) was then added, the dry ice bath was removed, The resulting mixture was continually stirred for 20 min, and quenched with saturated $NaHCO_3$, diluted with ether, washed with brine, dried over $MgSO_4$, filtered and evaporated under reduced pressure. The resulting residue was purified by column chromatography with ethyl acetate: petroleum (1:10) as an eluent to afford 297 mg of compound (*S,Sp*)-**8a** as a yellow powder (86% yield). $[\alpha]_D^{20} = 186.7^\circ$ $(c, 0.35, CHCl_3)$; ^1H NMR (300 MHz, $CDCl_3$/TMS): δ 0.92 (s, 9H), 1.20–1.43 (m, 8H), 1.43–1.62 (m, 7H), 1.63–1.95 (m, 7H), 2.34 (d, J = 12.2 Hz, 1 H), 3.85 (t, J = 9.78 Hz, 1H), 4.00 (s, 1H), 4.07 (t, J = 8.9 Hz, 1H), 4.21(s, 1H), 4.30–4.37 (m, 2H), 4.37–4.44 (m, 2H), 4.89 (s, 1H), 7.24–7.40 (m, 10H); ^{31}P NMR (161 MHz, $CDCl_3$): δ − 9.65 (s, 1P), −17.45 (s, 1P); MS(EI) *m*/*z* (%): 691 (M^+, 3.39), 610 (44.33), 609 (100.0), 526 (16.55), 382 (15.51); IR (KBr, cm^{-1}): 2922, 2848, 1660, 1478, 1434, 1133, 1027, 980, 829, 742, 696, 503; Anal. Calc. for $C_{41}H_{51}FeNOP_2$: C, 71.20; H, 7.34; N, 2.03; Found: C, 71.58; H, 7.63; N, 1.99%.

4.4. 1-dicyclohexylphosphino-1′-[(S)-tert-butyl-2,5-oxazolinyl]-2′-(Sp)-diphenyl-phosphino-ferrocene (S,Sp)-8b

After directed diastereoselective *ortho*-lithiation of (*S*)-**7c**, the resulting mixture was treated with choro-diphenyl-posphine as described above. After chromatography (ethyl acetate:petroleum = 1:10) of the crude product, (*S,Sp*)-**8b** was obtained as a yellow powder (68% yield). $[\alpha]_D^{20} = -68^\circ$ $(c, 0.415, CHCl_3)$; ^1H NMR (300 MHz, $CDCl_3$/TMS): δ 0.76 (s, 9H), 0.80–1.45 (m, 10H), 1.45–1.98 (m, 12H), 2.05 (m, 1 H), 3.60 (s, 1H), 3.80 (dt, J = 28.6, 8.1 Hz, 2H), 4.01 (m, 1H), 4.16–4.26 (m, 3H), 4.51 (s, 1H), 4.94 (m, 1H), 7.18–7.48 (m, 10H); ^{31}P NMR (161 MHz, $CDCl_3$): δ − 15.13 (s, 1P),

−16.85 (s, 1P); MS(EI) *m/z* (%): 691 (M^+, 68.75), 692 (M + 1, 75.75), 609 (100.0), 608 (92.10), 572 (39.39); IR (KBr, cm^{-1}): 2926, 2851, 1663, 1479, 1448, 1434, 1141, 1027, 979, 829, 742, 696, 501; Anal. Calc. for $C_{41}H_{51}FeNOP_2$: C, 71.20; H, 7.34; N, 2.03; Found: C, 71.56; H, 7.38; N, 1.78%.

4.5. 1-bis-[4-methoxyl]-phosphino-1′-[(S)-tert-butyl-2,5-oxazolinyl]-2′-(Sp)-bis-[3,5-trifluoromethyl]-phenyl-phosphino-ferrocene (S,Sp)-9

After directed diastereo-selective *ortho*-lithiation of (*S*)-**7b** [6b],the resulting mixture was treated with choro-bis-[3,5-dimethyl]-phenyl-posphine as described above. After chromatography (ethyl acetate:petroleum = 1:10) of the crude product, (*S,Sp*)-**9** was obtained as a yellow powder (85% yield). m.p. 61°C; $[\alpha]_D^{20} = -241.2^\circ$ $(c, 0.65, CHCl_3)$; ^1H NMR (300 MHz, $CDCl_3$/TMS): δ 0.85 (s, 9H), 3.24 (m, 1 H), 3.60 (dd, J = 9.8, 7.5 Hz, 1H), 3.79 (d, J = 3.2 Hz, 6H), 3.80 (m, 1H), 4.10 (dt, J = 29.0, 2.9 Hz, 2H), 4.35–4.46 (m, 3H), 4.47 (s, 1H), 4.97 (m, 1H), 6.77 (dd, J = 22.0, 7.9 Hz, 4H), 7.11 (m, 4H), 7.58 (d, J = 6.5 Hz, 2H), 7.78 (t, J = 5.9 Hz, 3H), 7.89 (s, 1H); ^{31}P NMR (161 MHz, $CDCl_3$): δ − 16.44 (s, 1P), −21.66 (s, 1P); ^{19}F NMR (282 MHz, $CDCl_3$): δ 13.11 (d, J = 17.3 Hz, 6F); MS(EI) *m/z* (%): 1012 (M^+, 87.78), 1011 (M − 1, 100.0), 955 (36.82), 954 (33.90), 381 (69.79); IR (KBr, cm^{-1}): 2959, 1662, 1595, 1499, 1354, 1279, 1249, 1181, 1136, 1033, 981, 898, 828, 704, 682, 534; Anal. Calc. for $C_{49}H_{39}F_{12}FeNO_3P_2$: C, 55.80; H, 3.89; N, 1.38; Found: C, 56.04; H, 4.22; N, 1.50%.

4.6. General procedure for palladium-catalyzed allylic alkylation

A mixture of ligand (0.02 mmol) and $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ (3.7 mg, 0.01 mmol) in 2 mL dry dichloromethane was stirred at room temperature for 1 h and the resulting yellow solution was added potassium acetate (2 mg, 0.02 mmol) and allylic acetate **10** (100 mg, 0.4 mmol). After stirring for another 30 min, dimethyl malonate (0.12 mL, 1.2 mmol) and BSA (0.3 mL, 1.2 mmol) were added. The reaction were carried out at room temperature and monitored by TLC for the disappearance of acetate **10**. The reaction mixture was diluted with ether, washed with saturated aq. NH_4Cl solution and then dried over $MgSO_4$. After removal of the solvent, the residue was purified by chromatography column on silica gel with ethyl acetate:petroleum (1:10) as an eluent to afford pure product **11**. ^1H NMR ($CDCl_3$) δ 3.52 (s, 3H), 3.70 (s, 3H), 3.95 (d, J = 10.8 Hz, 1H), 4.27 (dd, J = 8.8 Hz, 10.8 Hz, 1H), 6.30 (dd, J = 8.8 Hz, 15.8 Hz, 1H), 6.44 (d, J = 15.8 Hz, 1H), 7.19–7.34 (m, 10H). The enantiomeric excess was determined by HPLC analysis (Chiralcel OD, hexane:isopropanol (80:20); flow rate = 0.7 mL/min.; t_R = 18.7 min, t_S = 20.4 min.). The absolute configuration of the product was assigned by comparing the sign of its specific rotation with the literature data [9].

Acknowledgements

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