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Electronic and steric effects of ligands as control elements for rhodium-catalyzed asymmetric hydrogenation ☆

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Abstract—Chiral diphosphine ligands analogous to bdpp have been synthesized and tested in order to study the effect of the electronic nature of the ligands in Rh-catalyzed asymmetric hydrogenation of some prochiral olefins. The results are compared with those obtained with the analogous unsubstituted ligand (bdpp). The rhodium-catalyzed asymmetric hydrogenation of olefins was influenced by ligand-based electronic effects, as well as substrate based ones. Excellent ee's (up to 98.3%) have been obtained in the rhodium-catalyzed hydrogenation of (*Z*)-α-acetamidocinnamic acids and esters.

1. Introduction

Asymmetric hydrogenation using soluble rhodium catalysts constitutes a key synthetic step in many industrial processes.[2] The precise control of molecular chirality plays an increasing role in chemistry, life science and material science. High activity, selectivity and stability, readily accessible ligands and enzyme-like stereocontrol are among the characteristic features of an ideal catalyst for practical asymmetric synthesis.[2]

In asymmetric catalysis bidentate phosphine ligands have been found to give excellent control in a number of catalytic asymmetric reactions. Chiral ligands based on a 2,4-pentane-2,4-diyl skeleton have found widespread application in asymmetric synthesis. The most well-known derivatives of this type are (2*S*,4*S*)-2,4-bis(diphenylphosphino)pentane[3] (*S*,*S*)-bdpp, sulfonated derivatives,[4] aryl-derivatives 4-CH_3-, 4-CF_3-, 3,5-CH_3-, 3,5-CF_3-bdpp,[5] (2*S*,4*S*)-pentane-2,4-diyl-bis(5*H*-dibenzo-[*b*]phosphindole)[6] [(*S*,*S*)-bdbpp], tetra-*p*-amino-functionalized [(*S*,*S*)-bdpp-(*p*NMe_2)$_4$],[7] 3-benzyl-bdpp,[8] (2*S*,4*S*)-2-(dibenzophospholyl)-4-(diphenylphosphino)pentane[9] or different diphosphite diastereomers, which contain stereogenic centres on the backbone as well as on the terminal groups.[10]

We and others have recently reported that the performance of enantioselective catalysts can be boosted by appropriate electronic tuning of the chiral ligand.[1,11,12] Electronic and steric effects in the rhodium diphosphinite catalyzed asymmetric hydrogenation were investigated. A series of electronically and sterically modified (*S*)-BINOL and (*S*)-H_8-BINOL ligands was synthesized and the effects on the catalytic performance were studied.

Phosphinite basicity was varied by using *p*-CH_3O, *p*-CH_3, *p*-H, *p*-CF_3, 3,5-$(CH_3)_2$, 3,5-$(CF_3)_2$ substituents on the diphenylphosphine moieties.[1] In the hydrogenation of dimethyl itaconate and methyl (*Z*)-α-acetamidocinnamate, an increase in enantioselectivity and activity was observed with increasing phosphinite basicity. Thus, the electronic tuning of the ligands offered a unique chance to improve the selectivity of such reactions. Herein, we report the first results concerning the electronic tuning of (*S*,*S*)-bdpp ligand. Targets were chosen both to probe the electronic effects of the ligands and the substrate.

2. Results and discussion

Having a reliable synthetic route for bpdp in hand,[3] the structurally similar analogues were obtained from

☆ First part of the series see Ref. 1.

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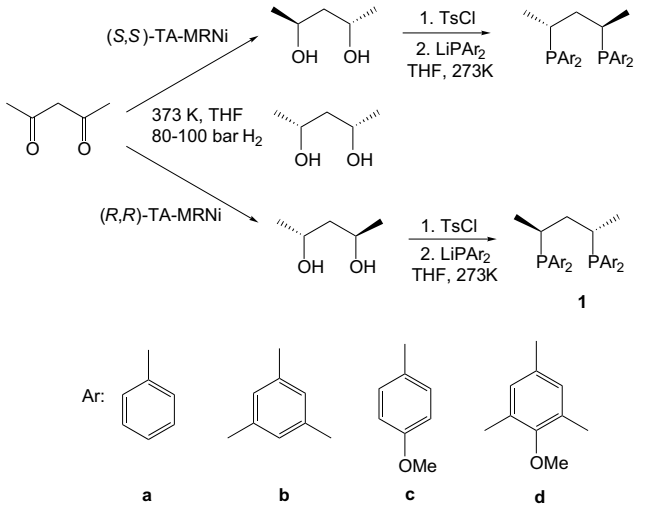
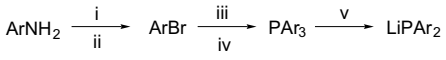
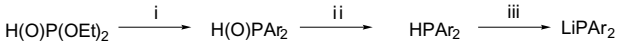


Scheme 1. General synthesis of ligands (TA = tartaric acid, MRNi modified Raney Ni).[2]



Scheme 2. Reagents and conditions: (i) $NaNO_2$, HBr, 0 °C; (ii) CuBr, 5 °C and then 120–140 °C; (iii) Mg, Et_2O, 20–30 °C; (iv) PCl_3, Et_2O, 0 °C; (v) Li, THF, room temperature.

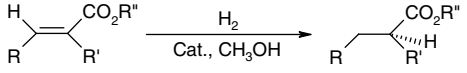


Scheme 3. Reagents and conditions: (i) ArMgBr, THF, 0 °C; (ii) $HSiCl_3$, Et_3N, xylol, rt, then 100 °C and then reflux; (iii) BuLi, hexane, −60 °C.

reaction of the corresponding lithium diarylphosphide with (2*S*,4*S*)-pentanediol ditosylate (Scheme 1).[13] The route for the preparation of diphenylphosphide and bis(3,5-dimethylphenyl)phosphide is shown in Scheme 2 for bis(4-methoxyphenyl)phosphide and bis(3,5-dimethyl-4-methoxyphenyl)phosphide in Scheme 3. Both nucleophilic attacks occurred with complete inversion at the stereogenic centres to give new homochiral diphosphines.[3,6] The complete enantioselectivity and diastereoselectivity of the double substitution is supported by the presence of only one singlet in the $^{31}P\{^1H\}$ NMR spectrum of the product.

The ionic catalysts $[Rh(NBD)(S,S)(P_2)]PF_6$ **4** were prepared by the reaction of phosphines with $[Rh(NBD)_2Cl_2]$ in methanol followed by the addition of the corresponding sodium salt of the anion.[14] For all diphosphine ligands, the formation of the [(diphosphines)Rh(NBD)]PF_6 complexes with square planar geometry was evidenced by the appearance of a doublet in the ^{31}P NMR spectra. The results show that itaconic acid and dimethyl itaconate containing electron-withdrawing groups show a better performance with less electron-rich phosphines in the order of **1a > 1b > 1c > 1d** (Table 1). Enantioselectivities range from 63.1% with **1a** to 8.4% with **1d**. It was noted that the enantioselectivity of the catalyst was sensitive to the solvent used. Higher ee values of **3a** and **3b** were achieved in aprotic and/or less polar solvents. In contrast, hydrogen pressure had a slight effect on the enantioselectivity, but a profound effect on the reaction rate. The ee of 70.8 % (entry 7) was obtained at 1 bar of H_2, but the value decreases to 63.1% (entry 1) at 20 bar.

To assess the advantages of using an electron-rich ligand with a broader range of olefins, we investigated the hydrogenation of (*Z*)-amidoacrylic acids and esters **2c**–**f**, which have more electron-rich double bonds (Scheme 4). In these cases the enantioselectivities were distinctly higher. When the aryl groups on the phosphorus of the phosphine ligand, which had phenyl groups replaced



2 **3**

a. R = H, R' = $CH_2CO_2CH_3$, R" = CH_3
b. R = H, R' = CH_2CO_2H, R" = H
c. R = C_6H_5, R' = $NHCOCH_3$, R" = H
d. R = C_6H_5, R' = $NHCOCH_3$, R" = CH_3
e. R = 4-CH_3O-C_6H_4, R' = $NHCOCH_3$, R" = H
f. R = 4-CH_3O-C_6H_4, R' = $NHCOCH_3$, R" = CH_3

Scheme 4. Asymmetric catalytic hydrogenation.

Table 1. Enantioselective Rh-catalyzed hydrogenation of **2a** and **2b**[a]

Entry	Substrate	Catalyst	Solvent	*t* (min)	$p(H_2)$ (bar)	Conv. (%)	Ee[b] (%)
1	**2a**	**4a**	CH_3OH	5	20	100	63.1 (*R*)
2	**2a**	**4b**	CH_3OH	5	20	100	49.4 (*R*)
3	**2a**	**4c**	CH_3OH	22	20	95.4	32.8 (*R*)
4	**2a**	**4d**	CH_3OH	45	20	76.6	8.4 (*R*)
5	**2a**	**4a**	CH_2Cl_2	15	20	100	71.1 (*R*)
6	**2a**	**4a**	THF	40	20	100	73.1 (*R*)
7	**2a**	**4a**	CH_3OH	10	1	34.1	70.8 (*R*)
8	**2b**	**4a**	CH_3OH	2	20	100	20.8 (*R*)
9	**2b**	**4a**	THF	25	20	100	48.5 (*R*)

[a] Reaction conditions: 23 °C; substrate/Rh ratio 500; catalyst preparation see text.
[b] The enantiomeric excess of the product was determined by GC analysis of the distilled product [Hewlett–Packard HP 4890 gas chromatograph, split/spitless injector, β-DEX 225, 30 m, internal diameter 0.25 mm, film thickness 0.25 μm, carrier gas: 100 kPa nitrogen, FID detector; the retention times of the enantiomers are 33.3 min (*S*), 36.9 min (*R*)]. Absolute configuration was determined by comparison with the known sign of the specific rotation.

Table 2. Enantioselective Rh-catalyzed hydrogenation of (*Z*)-α-acetamidocinnamic acids and esters **2c**–**f**[a]

Entry	Substrate	Catalyst	Solvent	S/C	*t* (min)	Conv. (%)	Ee (%)
1	**2c**	**4a**	CH_3OH	50	8	100	94.4 (*R*)
2	**2c**	**4b**	CH_3OH	50	2	100	97.2 (*R*)
3	**2c**	**4b**	CH_3OH	200	3	100	96.9 (*R*)
4	**2c**	**4c**	CH_3OH	50	2	100	82.2 (*R*)
5	**2c**	**4d**	CH_3OH	50	5	100	96.5 (*R*)
6	**2d**	**4a**	CH_3OH	100	3	100	78.0 (*R*)
7	**2d**	**4b**	CH_3OH	200	2	100	90.8 (*R*)
8	**2e**	**4b**	THF	100	8	100	93.3 (*R*)
9	**2e**	**4b**	CH_3OH	100	2	100	98.3 (*R*)
10	**2f**	**4b**	CH_3OH	50	11	100	91.3 (*R*)

[a] Reaction conditions: 15 °C; $p(H_2)$=1 bar; other experimental conditions see footnotes under Table 1. The enantiomeric excess was determined on CP-CHIRASIL-L-VAL column [25 m, internal diameter 0.25 mm, film thickness 0.12 μm, carrier gas: 100 kPa nitrogen, FID detector; the retention times of the enantiomers are 32.5 min (*R*), 34.2 min (*S*)].

with aryl groups with electron-donating groups, the enantioselectivity and the activity of catalyst were enhanced (Table 2).

Comparison of the effect of the asymmetric induction by **1a**–**d**, suggested that the electronic effect is one of the key elements that controls enantioselectivity. The electronic nature of the *para*-substituents on the phosphines and substrates has a significant effect not only on the enantioselectivity but also on the activity of the catalysts.

Phosphines with electron-donating substituents (Table 2, entries 2–5 and 7) gave higher catalytic activities than that of the unsubstituted bdpp (entries 1 and 6). Somewhat surprisingly, **4c** gave a low enantioselectivity, which we cannot explain at present. Comparison of substrates **2c** and **2e**, **2d** and **2f** is particularly revealing as the structural difference between these two compounds is minimal meaning that the electronic effect of the methoxy group can be clearly identified.

Substrates with electron-donating *para*-methoxy substituents, **2e** and **2f** gave 98.3%, and 91.3% ee, respectively. The unsubstituted substrates, **2c** and **2d** gave 96.9% and 90.8% ee, respectively. The special '3,5-dialkyl *meta* effect' has been well demonstrated.[15]

These results suggest that the strong electron-donating ability of the *para*-methoxy group of substrates as well as the electron-donating aryl groups of ligands promotes the rate of oxidative addition of hydrogen to rhodium and changes the reactivity pattern of the major and minor diastereomeric substrates complexes by increasing the electron density on the central Rh atom, thereby affecting the relative rate of oxidative additions.[12a]

3. Conclusion

In summary, we have employed electronic effects as a control element for enantioselectivity while the electronically modified ligands and substrates produced an improvement in the activity and selectivity in the hydrogenation of (*Z*)-α-acetamidocinnamic acids. Remarkably, a comparison of the effect of ligand basicity on asymmetric induction and activity of the catalytic system in the case of itaconic acid and (*Z*)-α-acetamidocinnamic acids reveals an opposite trend, implying that there is a change in the mechanism.

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13. *(2S,4S)-2,4-Bis[di(3,5-dimethylphenyl)phosphino]pentane* **1b**: Yield: 38%; mp 132–134 °C; $[\alpha]_D^{20} = -105.0$ (*c* 3.0, $CHCl_3$). $^{31}P\{^1H\}$ NMR (202.46 MHz, $CDCl_3$): $\delta = -0.13$ (s), ^1H NMR (500.13 MHz, $CDCl_3$): $\delta = 0.97$ (dd, $^3J(P,H) = 15.0$ Hz, $^3J(H,H) = 7.0$ Hz, 6H; CH_3), 1.37 (quint., $^3J(P,H) \sim {}^3J(H,H) \sim 7.2$ Hz, 2H; CH_2), 2.24 (s, 12H; diast. $ArCH_3$), 2.26 (s, 12H; diast. $ArCH_3$), 2.44 (sept., $^2J(P,H) \sim {}^3J(H,H) \sim 7.0$ Hz, 2H; CH), 6.91 (s, 4H; C_p), 7.04 (d, $^3J(P,H) = 7.6$ Hz, 8H; C_o). $^{13}C\{^1H\}$ NMR (75.46 MHz, $CDCl_3$): $\delta = 15.93$ (d, ^2J (P,C) = 16.5 Hz, CH_3), 21.31 (s, diast. $ArCH_3$), 21.32 (s, diast. $ArCH_3$), 27.11 (dd, $^1J(P,C) = 11.5$, $^3J(P,C) = 9.9$ Hz, CH), 36.70 (t, $^2J(P,C) = 18.7$ Hz, CH_2), 130.46 (s, diast. C_p), 130.51 (s, diast. C_p), 131.30 (d, $^2J(P,C) = 19.2$ Hz, diast. C_o), 131.41 (d, $^2J(P,C) = 19.2$ Hz, diast. C_o), 136.42 (d, $^1J(P,C) = 12.6$ Hz, diast. C_i), 137.05 (d, $^1J(P,C) = 13.7$ Hz, diast. C_i), 137.51 (d, $^3J(P,C) = 7.7$ Hz, C_m).
(2S,4S)-2,4-Bis[di(4-methoxyphenyl)phosphino]pentane **1c**: Yield: 48%; $^{31}P\{^1H\}$ NMR (202.46 MHz, $CDCl_3$): $\delta = -3.92$ (s), ^1H NMR (300.15 MHz, $CDCl_3$): $\delta = 0.93$ (dd, $^3J(P,H) = 15.6$ Hz, $^3J(H,H) = 6.9$ Hz, 6H; CH_3), 1.31 (quint., $^3J(P,H) \sim {}^3J$ (H,H) ~ 7.2 Hz, 2H; CH_2), 2.39 (sept., $^2J(P,H) \sim {}^3J$ (H,H) ~ 6.9 Hz, 2H; CH), 3.75 (s, 6H; diast. $ArOCH_3$), 3.77 (s, 6H; diast. $ArOCH_3$), 6.80 (m, 8H; C_o), 7.35 (m, 8H; C_m).
(2S,4S)-2,4-Bis[di(3,5-dimethyl-4-methoxyphenyl)phosphino]-pentane **1d**: Yield: 46%; mp 142–145 °C; $[\alpha]_D^{20} = -83.5$ (*c* 4.0, $CHCl_3$). $^{31}P\{^1H\}$ NMR (202.46 MHz, $CDCl_3$): $\delta = -3.02$ (s), ^1H NMR (300.15 MHz, $CDCl_3$): $\delta = 0.95$ (dd, $^3J(P,H) = 15.6$ Hz, $^3J(H,H) = 6.8$ Hz, 6H; CH_3), 1.32 (quint., ^3J (P,H) ~ ^3J(H,H) ~ 6.9 Hz, 2H; CH_2), 2.20 (s, 12H; diast. $ArCH_3$), 2.21 (s, 12H; diast. $ArCH_3$), 2.42 (sept., $^2J(P,H) \sim {}^3J(H,H) \sim 6.5$ Hz, 2H; CH), 3.67 (s, 6H; diast. $ArOCH_3$), 3.69 (s, 6H; diast. $ArOCH_3$), 7.07 (d, $^3J(P,H) = 5.4$ Hz, 4H; diast. C_o), 7.09 (d, $^3J(P,H) = 5.4$ Hz, 4H; diast. C_o), $^{13}C\{^1H\}$ NMR (125.76 MHz, $CDCl_3$): $\delta = 16.44$ (d, $^2J(P,C) = 16.9$ Hz, CH_3), 16.86 (s, diast. $ArCH_3$), 16.88 (s, diast. $ArCH_3$), 28.24 (dd, $^1J(P,C) = 12.1$, $^3J(P,C) = 8.5$ Hz, CH), 37.10 (t, $^2J(P,C) = 19.4$ Hz, CH_2), 60.18 (s, diast. OCH_3), 60.21 (s, diast. $ArOCH_3$), 131.05 (d, $^3J(P,C) = 4.8$ Hz, diast. C_m), 131.09 (d, $^1J(P,C) = 2.4$ Hz, C_i overlapped by the signal of C_m), 131.11 (d, $^3J(P,C) = 6.1$ Hz, diast. C_m), 134.45 (d, $^2J(P,C) = 18.2$ Hz, diast. C_o), 134.61 (d, $^2J(P,C) = 18.2$ Hz, diast. C_o), 158.00 (s, diast. $COCH_3$), 158.05 (s, diast. $COCH_3$).
14. *[Rh(NBD){(2S,4S)-2,4-bis[di(3,5-dimethylphenyl)phosphino]pentane}]PF_6* **4b**: Yield: 76%; $^{31}P\{^1H\}$ NMR (121.49 MHz, $CDCl_3$): $\delta = 24.48$ (d, ^1J(Rh,P) = 148.5 Hz), −145.53 (septet, $^1J(F,P) = 712.8$ Hz); ^1H NMR (500.13 MHz, $CDCl_3$): $\delta = 1.16$ (dd, $^3J(P,H) = 13.2$ Hz, $^3J(H,H) = 6.9$ Hz, 6H; CH_3), 1.65 (br s, 2H; H_1 $H_{1'}$), 1.91 (tt, $^3J(P,H) = 20.7$, $^3J(H,H) = 6.3$ Hz, 2H; CH_2), 2.34 (s, 12H; diast. $ArCH_3$), 2.42 (s, 12H; diast. $ArCH_3$), 2.76 (m, 2H; CH), 3.96 (m, 2H; H_2, H_5), 4.35 (m, 2H; H_4, H_7), 4.87 (m, 2H; H_3, H_6), 7.04 (s, 4H; H_p), 7.20 (s, 8H; H_o). Anal. Calcd for $C_{44}H_{54}F_6P_3Rh$: C 59.19%, H 6.09 %. Found: C 59.02, H 6.10.
[Rh(NBD){(2S,4S)-2,4-bis[Di(4-methoxyphenyl)phosphino]pentane}] PF_6 **4c**: Yield: 34%; $^{31}P\{^1H\}$ NMR (121.49 MHz, $CDCl_3$): $\delta = 23.93$ (d, ^1J(Rh,P) = 151.5 Hz), −145.40 (septet, $^1J(F,P) = 712.8$ Hz); ^1H NMR (300.15 MHz, $CDCl_3$): $\delta = 1.08$ (dd, $^3J(P,H) = 13.1$ Hz, $^3J(H,H) = 6.9$ Hz, 6H; CH_3), 1.58 (brs, 2H; H_1,$H_{1'}$), 1.73 (tt, $^3J(P,H) = 20.0$, $^3J(H,H) = 6.9$ Hz, 2H; CH_2), 2.66 (m, 2H; CH), 3.87 (s, 6H; diast. $ArOCH_3$), 3.88 (s, 6H; diast. $ArOCH_3$), 3.97 (m, 2H; H_2, H_5), 4.33 (m, 2H; H_4, H_7), 4.79 (m, 2H; H_3, H_6), 7.04 (d, $^3J(H,H) = 8.0$ Hz, 4H; diast. H_m), 7.07 (d, $^3J(H,H) = 8.0$ Hz, 4H; diast. H_m), 7.32 (m, 4H; diast. H_o), 7.67 (m, 4H; diast. H_o). Anal. Calcd for $C_{40}H_{46}F_6O_4P_3Rh$: C 52.87%, H 5.10%. Found: C 52.79, H 4.85.
[Rh(NBD){(2S,4S)-2,4-bis[di(3,5-dimethyl-4-methoxyphenyl)phosphino]pentane}]PF_6 **4d**: Yield: 48%; $^{31}P\{^1H\}$ NMR (121.49 MHz, $CDCl_3$): $\delta = 22.92$ (d, ^1J(Rh,P) = 150.0 Hz), −145.59 (septet, $^1J(F,P) = 712.8$ Hz); ^1H NMR (300.15 MHz, $CDCl_3$): $\delta = 1.10$ (dd, $^3J(P,H) = 13.5$ Hz, $^3J(H,H) = 6.9$ Hz, 6H; CH_3), 1.61 (br s, 2H; $H_1H_{1'}$), 1.84 (tt, $^3J(P,H) = 20.9$, $^3J(H,H) = 6.6$ Hz, 2H; CH_2), 2.23 (s, 12H; diast. $ArCH_3$), 2.33 (s, 12H; diast. $ArCH_3$), 2.65 (m, 2H; CH), 3.77 (s, 6H; diast. $ArOCH_3$), 3.80 (s, 6H; diast. $ArOCH_3$), 3.93 (m, 2H; H_2, H_5), 4.34 (m, 2H; H_4, H_7), 4.83 (m, 2H; H_3, H_6), 7.04 (d, $^3J(P,H) = 4.4$ Hz, 2H; diast. H_o), 7.06 (d, $^3J(P,H) = 4.4$ Hz, 2H; diast. H_o), 7.14 (d, $^3J(P,H) = 5.1$ Hz, 2H; diast. H_o), 7.16 (d, $^3J(P,H) = 5.1$ Hz, 2H; diast. H_o). Anal. Calcd for $C_{48}H_{62}F_6O_4P_3Rh$: C 56.92%, H 6.17%. Found: C 56.55, H 5.98.
15. (a) Guo, R.; Au-Yeng, T. T.-L.; Wu, J.; Choi, M. C. K.; Chan, A. S. C. *Tetrahedron: Asymmetry* **2002**, *13*, 2519; (b) Traubesinger, G.; Albinati, A.; Feiken, E.; Kunz, R. W.; Pregosin, P. S.; Tschoerner, M. *J. Am. Chem. Soc.* **1997**, *119*, 6315.