Pergamon

Tetrahedron: *Asymmetry* 10 (1999) 2071–2074

TETRAHEDRON:
ASYMMETRY

Two novel chiral rhodium complexes as catalysts for the enantioselective allylation of arylaldehydes

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Received 11 May 1999; accepted 1 June 1999

Abstract

Two novel chiral rhodium complexes were successfully synthesized from the reaction of a new class of bidentate nitrogen ligands with $RhCl_3{\cdot}3H_2O$ in ethanol under reflux. The crystal structure of **4a** was unambiguously established by X-ray analysis. Their corresponding cationic metal complexes prepared in situ from the reaction of **4a** or **4b** with $AgBF_4$ catalyze the enantioselective allylation of arylaldehydes with allylstannane in 5–50% ee.
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Chiral chelating bidentate or tridentate nitrogen ligands have found widespread application in asymmetric homogeneous catalysis by transition metal complexes.[1] The most well-known catalyst ligands are the chiral C_2-symmetric 2,6-bis(oxazolinyl)phenyl group (Phebox) and 2,6-bis(oxazolinyl)pyridyl group (Pybox), prepared by Nishiyama.[2] Their rhodium and ruthenium complexes can attain excellent enantioselection in the hydrosilylative reduction of ketones[3] and cyclopropanation of olefins.[4] Recently, this catalytic system has been developed as chiral Lewis acid catalysts for the enantioselective allylation of aldehydes, one of the most challenging and attractive research fields.[5] These exciting results stimulated us to explore a new class of bidentate or tridentate nitrogen ligands and their rhodium and ruthenium complexes for asymmetric reactions. In this paper we wish to report the synthesis of a new class of chiral bidentate pyrrolidine ligands having an *N*-pyridyl group and their rhodium complex-catalyzed enantioselective allylation of *p*-chlorobenzaldehyde. The crystal structure of this novel chiral rhodium complex **4a** was established by X-ray analysis.

The new class of bidentate nitrogen ligands **3a** and **3b**[6] was synthesized from the reaction of chiral C_2-symmetric 2,5-disubstituted pyrrolidines **1a** and **1b**[7] with 2-(chloromethyl)pyridine hydrochloride **2** in the presence of potassium carbonate in acetonitrile under reflux (Scheme 1). Their rhodium complexes were then synthesized from the reaction of **3a** or **3b** with $RhCl_3{\cdot}3H_2O$ in ethanol at 80°C for 9 h (Scheme 1). The solvent was removed under reduced pressure and the yellow solid obtained, purified

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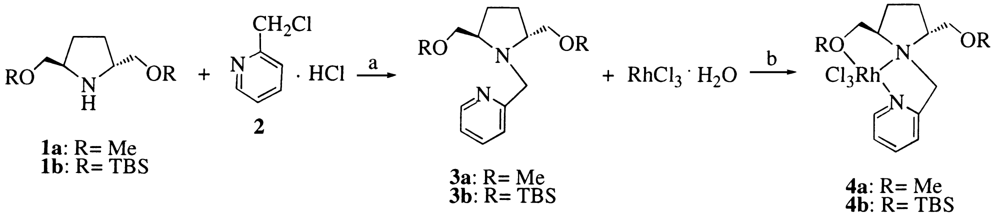
PII: S0957-4166(99)00229-3

by silica gel column chromatography to give an air-stable and dichloromethane-soluble yellow solid (eluent chloroform:ethanol=5:1). Their structures were confirmed by microanalysis.[8] Moreover, a single crystal of the rhodium complex **4a** was obtained by careful recrystallization from ethanol and diethyl ether (2:1) and its crystal structure was established by X-ray analysis (Fig. 1).[9]



Scheme 1. Conditions: (a) K_2CO_3, MeCN, reflux, 10 h; 64% for R=Me, 50% for R=TBS. (b) EtOH, reflux, 9 h; 50% for R=Me, 26% for R=TBS

From Fig. 1, it is very clear that the bidentate nitrogen ligand **3a** is actually a tridentate ligand because, besides the two nitrogen atoms, the oxygen atom of the methoxy group can also coordinate to the metal center to form an octahedral complex. This is probably why this rhodium complex **4a** is so air-stable. Concerning the additional coordination of the oxygen atom in chiral ligand **3b**, we speculate that the sterically bulky *tert*-butyldimethylsilyl group on the 2,5-position of C_2-symmetric pyrrolidine would impede this kind of coordination and eventually influence the crystal structure of rhodium complex **4b**. Unfortunately, however, to date we have not been able to obtain a single crystal of **4b**. The bond lengths of two N–Rh coordination bonds are not identical [2.106(5) Å and 2.017(5) Å, respectively]. The coordination bond of the nitrogen atom from pyrrolidine to Rh is slightly longer than the corresponding pyridine one. Furthermore, the bond length of O–Rh is 2.106(4) Å, which is very close to those of N–Rh bonds. This result strongly suggests that the additional coordination from the oxygen atom to Rh is very similar to that of the nitrogen atom to Rh and that this metal complex is quite stable.

These two novel chiral rhodium complexes were used for the enantioselective allylation of arylaldehydes. We found that neither **4a** nor **4b** catalyze the allylation of arylaldehydes with allylstannane, but that their cationic metal complexes prepared from the reaction of **4a** or **4b** with $AgBF_4$ in situ can promote the allylation effectively to give the chiral alcohols (Scheme 2).

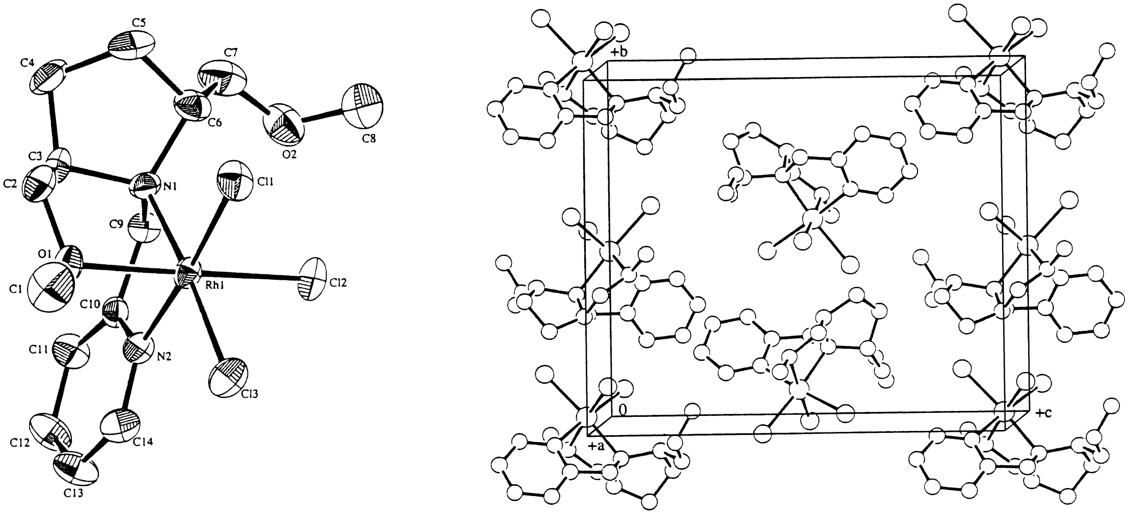
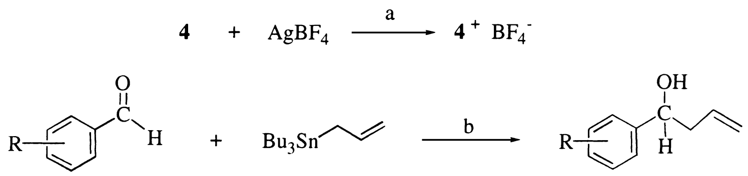


Figure 1.



Scheme 2. Conditions: (a) CH_2Cl_2 or THF, 0°C, 2 h. (b) **4**$^+$ BF_4^- (10 mol%), CH_2Cl_2 or THF, 0°C–rt, 12 h

Table 1

Enantioselective allylation of arylaldehydes using allyltributyltin in the presence of 10 mol% chiral catalysts **4a**$^+$ BF_4^- and **4b**$^+$ BF_4^-

R	Cat.	Solvent	Yield (%)[a]	ee (%)[b]
H	**4a**	CH_2Cl_2	80	6
H	**4b**	CH_2Cl_2	50	40
H	**4b**	THF	40	35
p-Cl	**4a**	CH_2Cl_2	88	5
p-Cl	**4b**	THF	30	40
p-Cl	**4b**	CH_2Cl_2	40	40
p-Me	**4b**	CH_2Cl_2	54	46
p-MeO	**4b**	CH_2Cl_2	50	50

a) Isolated Yields; b) Determined by chiral HPLC.

The results are summarized in Table 1. The ee is only 5% using 10 mol% of **4a** as the chiral catalyst, but when using sterically bulky rhodium complex **4b**, the ee can reach 40–50%;[10] dichloromethane and THF are good solvents for this reaction. In the meantime, it should be emphasized here that in our reaction system, $AgBF_4$ itself cannot catalyze the allylation of aldehydes, although Yamamoto has reported that a BINAP-derived chiral silver complex can achieve the enantioselective allylation of arylaldehydes.[11] In addition, we found that **4a** itself can directly catalyze the hydrogenation of acetophenone with 20% ee in the presence of water, but its cationic metal complex in the hydrosilylation of acetophenone is sluggish.

In conclusion, we have explored a novel chiral rhodium complex system and established its structure by X-ray analysis. Although the ees are not as high as the chiral C_2-symmetric 2,6-bis(oxazolinyl)phenyl group (Phebox) and 2,6-bis(oxazolinyl)pyridyl group (Pybox),[2] these results at least suggest that they have potential as catalysts for asymmetric reactions. Perhaps, with chemical modification in the ligand structure, higher enantioselectivity can be obtained. Further studies in this area are in progress in our laboratory.

Acknowledgements

We thank Prof. Albert S. C. Chan and the National Natural Sciences Foundation of China for financial support.

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6. Physical data for **3a**: a colorless oil; $[\alpha]_D^{20}$ +70.4 (c 0.98, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.56–1.96 (2H, m), 1.97–2.35 (2H, m), 3.31 (6H, s), 3.26–3.50 (6H, m), 4.14 (2H, s), 7.13 (1H, t, J=6.3), 7.47–7.62 (1H, m), 7.64 (1H, dt, J=7.6, 2.0), 8.51 (1H, d, J=4.4); MS (EI) m/z (%) 251 $(MH)^+$, 205 (100.0), 186 (12.4), 173 (9.6); [HRMS (EI) found: 249.1617 $[(M-H)^+]$. $C_{14}H_{21}N_2O_2$ requires: 249.1603]. Physical data for **3b**: a colorless oil; $[\alpha]_D^{20}$ +38.3 (c 1.29, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.01 (6H, s, SiMe), 0.02 (6H, s, SiMe), 0.85 (18H, s, CMe_3), 1.56–1.96 (2H, m), 1.97–2.35 (2H, m), 3.16–3.25 (2H, m), 3.42–3.65 (4H, m), 4.14 (2H, s), 7.11 (1H, t, J=6.3), 7.47–7.62 (1H, m), 7.64 (1H, dt, J=7.6, 2.0), 8.51 (1H, d, J=4.4); MS (EI) m/z (%) 452 $(MH)^+$, 436 (4.1), 357 (10.2), 305 (100.0); [HRMS (EI) found: 451.3099 $(M)^+$. $C_{24}H_{46}N_2O_2Si_2$ requires: 450.3098].
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8. Physical data for compound **4a**: a yellow solid; mp 203°C (dec.); $[\alpha]_D^{20}$ +208 (c 0.125, CH_2Cl_2); [found: C, 36.43; H, 4.85; N. 5.93. $C_{14}H_{22}N_2O_2Cl_3Rh$ requires: C, 36.59; H, 4.83; N, 6.10%]. Physical data for compound **4b**: a yellow solid; mp 193°C (dec.); $[\alpha]_D^{20}$ +66 (c 0.110, CH_2Cl_2); [found: C, 43.72; H, 6.95; N, 4.60. $C_{24}H_{46}N_2Si_2O_2Cl_3Rh$ requires: C, 43.67; H, 7.02; N, 4.24%].
9. Crystal data for **4a**: empirical formula: $C_{28}H_{44}O_4N_4Cl_6Rh_2$; formula weight: 919.21; crystal color, habit: red, prismatic; crystal dimensions: 0.20×0.20×0.30 mm; crystal system: monoclinic; lattice type: primitive; lattice parameters: a=7.808(1) Å, b=13.878(2) Å, c=15.938(3) Å, β=93.68(1) Å, V=1723.4(5) Å^3; space group: $P2_1$ (#4); Z_{value}=2; D_{calc}=1.771 g/cm^3; F_{000}=928.00; μ(MoKα)=14.60 cm^{-1}.
10. The ee was determined by chiral HPLC (Chiralcel OJ).
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