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The synthesis of new chiral rhodium complexes and their crystal structures

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Two novel chiral rhodium complexes were successfully synthesized from the reaction of chiral bidentate nitrogen ligands with $RhCl_3{\cdot}3H_2O$ in ethanol under reflux. Their unusual crystal structures were unambiguously obtained by X-ray analysis. Copyright © 2001 John Wiley & Sons, Ltd.

KEYWORDS: chiral rhodium complex; tridentate chiral ligand; bidentate chiral ligand; crystal structure

INTRODUCTION

Chiral chelating bidentate or tridentate nitrogen ligands have found widespread application in asymmetric homogeneous catalysis by transition metal complexes.[1–4] The most famous 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 *et al.*[5] Their rhodium and ruthenium complexes can attain excellent enantioselection in the hydrosilylative reduction of ketones[6–8] and cyclopropanation of olefins.[9] Recently this catalytic system has been developed as a chiral Lewis acid catalyst for the enantioselective allylation of aldehydes, one of the most challenging and attractive research fields.[10] These exciting results stimulated us to explore new chiral bidentate or tridentate nitrogen ligands and their novel rhodium and ruthenium complexes which can be used for asymmetric reactions. We previously reported in a short communication that a new chiral bidentate pyrrolidine ligand having an *N*-pyridyl group can form a novel chiral rhodium complex that can effectively catalyze the allylation of arylaldehydes with allylstannane and its unusual structure was clearly disclosed by X-ray analysis although the enantiomeric excess (ee) achieved was only about 5%.[11] We believe that the low enantioselectivity of this new catalyst is simply because the chiral complex broke the C_2-symmetry element of the chiral ligand. However, its crystal structure is unique from the view-point of coordination chemistry. In this paper, therefore, we wish to report the full details for the synthesis of these kinds of novel chiral rhodium complex and their crystal structures.

RESULTS AND DISCUSSION

Synthesis of chiral ligands 3 and 5 and their rhodium complexes 6 and 7

The chiral bidentate nitrogen ligands **3** and **5** were synthesized from the reaction of chiral C_2-symmetric 2,5-disubstituted pyrrolidine **1**[12] with either 2-(chloromethyl)-pyridine hydrochloride **2** or 2-(chloromethyl)quinoline hydrochloride **4** respectively in the presence of potassium carbonate in acetonitrile under reflux (Scheme 1). Compounds **3** and **5** were obtained as colorless oils and they should be stored under nitrogen atmosphere at low temperature ($<-10\,°C$). Compounds **3** and **5** gradually become brown in color if they are exposed to air at room temperature for only 1 day. This phenomenon may be related to the partial oxidation of amines by air. Many liquid amines suffer this problem; however, they can still be used for the next reaction. Their transition metal complexes **6** and **7** were synthesized from the reaction of **3** and **5** with $RhCl_3{\cdot}3H_2O$ in ethanol at 80 °C for 9 h under argon atmosphere (Scheme 2). After purification by silica gel column chromatography (eluent: $CHCl_3/EtOH = 10/1$), the complexes **6** and **7** were obtained as yellow solids. Their structures were first determined by ^1H NMR spectroscopic analysis, since the rhodium(III) complexes are diamagnetic materials, and then were further confirmed by microanalysis.

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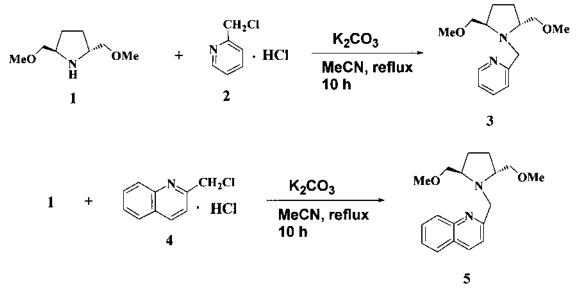
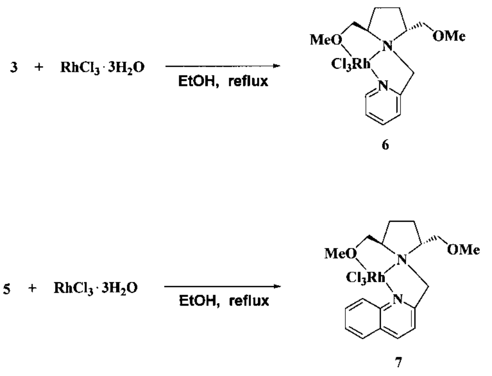


Scheme 1.



Scheme 2.

Molecular structure of complex 4

The single crystals of these novel rhodium complexes **6** and **7** were obtained by careful recrystallization from ethanol and diethyl ether (2:1), and their crystal structures were unambiguously disclosed by X-ray analysis (Figs 1 and 2). The crystal data for **6** and **7** are shown in Tables 1 and 2 respectively. The bond lengths of complexes **6** and **7** are given in Tables 3 and 4 respectively.

From Figs 1 and 2, it is very clear that the two nitrogen and one oxygen ligands in **3** and **5** form a tridentate ligand: besides the two nitrogen atoms, the oxygen atom of the methoxy group can also coordinate to the metal center to form an octahedral complex. The bond lengths of the two *N*—Rh are not identical [2.017(4) Å (pyridine to rhodium) and 2.106(4) Å (pyrrolidine to rhodium) for **6**; 2.105(4) Å (quinoline to rhodium) and 2.083 Å (pyrrolidine to rhodium) for **7**]. Furthermore, the bond lengths of O—Rh are 2.106 Å for **6** and 2.082(4) Å for **7**, which are very close to those of the corresponding *N*—Rh bonds. This result strongly suggests that the additional coordination from oxygen atom to rhodium metal is very similar to that of the nitrogen atom to rhodium.

In fact, based on the ^{1}H NMR spectroscopic analysis (de = 100%), only one diastereomer of **6** or **7** was formed. Namely, the methoxy group was coordinated to the metal center from only from one side, giving octahedral complexes **6** or **7**. In connection with the stable coordination bond of the

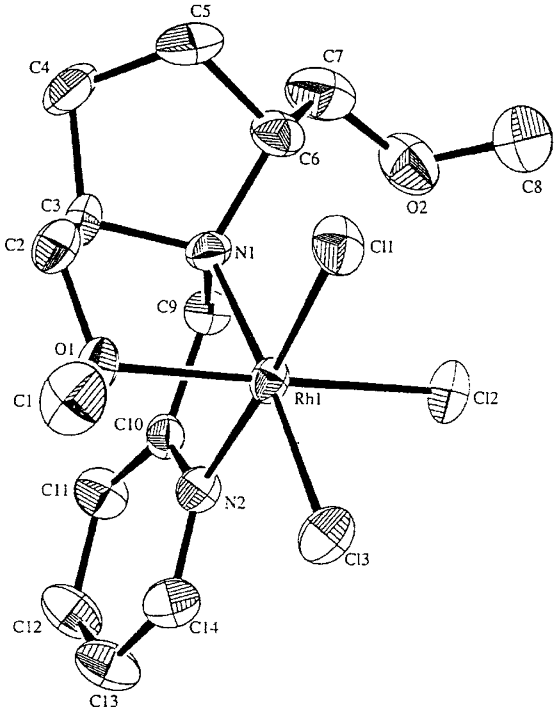


Figure 1. The crystal structure of chiral rhodium complex **6**.

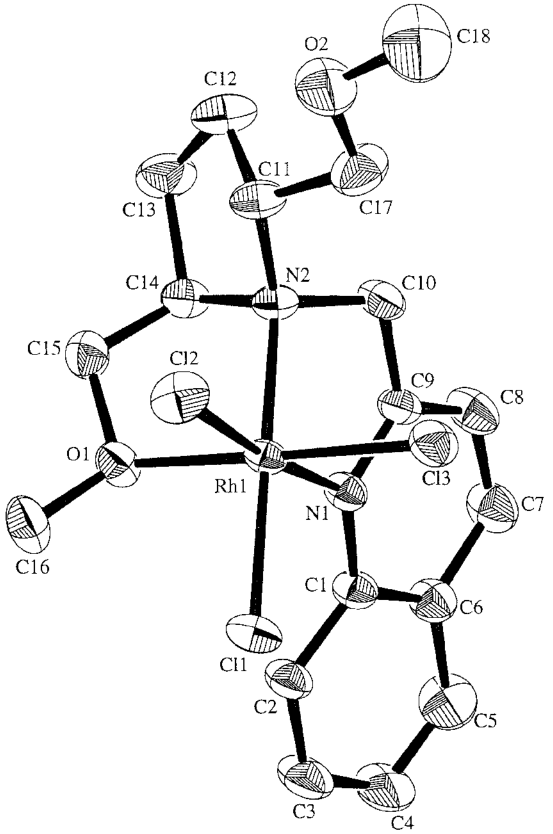


Figure 2. The crystal structure of chiral rhodium complex **7**.

Table 1. Crystal data and summary of intensity data collection and structure refinement of **6**

Empirical formula	$C_{14}H_{22}Cl_3N_2O_2Rh$
Formula weight	459.60
Crystal color, habit	red, prismatic
Crystal dimensions (mn^3)	$0.20 \times 0.20 \times 0.30$
Crystal system	monoclinic
Lattice type	primitive
Lattice parameters	
a (Å)	7.808(1)
b (Å)	13.878(2)
c (Å)	15.938(3)
V (Å^3)	1723.4(5)
β (deg)	93.68(1)
Space group	$P2_1$ (#4)
Z value	2
D_{calc} (g cm^{-3})	1.771
$F_{(000)}$	928.00
μ(Mo Kα) (cm^{-1})	14.60
Diffractometer/scan	Rigaku AFC7R
Radiation, graphite monochromator	Mo Kα ($\lambda = 0.710\ 69$ Å)
Crystal to detector distance (mm)	235
Temperature (°C)	20.0
Scan type	ω–2θ
Scan rate (deg min^{-1})	16.0 (in ω) — up to four scans
$2\theta_{max}$ (deg)	55.0
Scan width (deg)	$1.10 + 0.30 \tan \theta$
Structure solution	Direct methods (SHELXS86)
Refinement	Full-matrix least-squares
ρ-factor	0.02
Reflection/parameter ratio	8.34
Residuals: R; R_w	0.027; 0.033
Max shift/error in final cycle	0.05
Maximum peak in final diff. map (e$^-$Å^{-3})	0.54
Minimum peak in final diff. map (e$^-$Å^{-3})	−0.47

oxygen atom to the rhodium or ruthenium transition metal center, we often can find stability in those ligands having Schiff base structures from the hydroxyl group of phenol to the metal center,[13,14] such as in salen-type complexes and in Doyle's chiral rhodium complexes, in which the oxygen atom of the carbonyl group coordinates to the metal center.[15,16] In this paper we have shown that the methoxy group on the side chain of the pyrrolidine ring can also coordinate to the transition metal and so this methoxy group has such flexibility.

In conclusion, we have explored new tridentate chiral ligands for the synthesis of novel chiral transition metal complexes and obtained their structures by X-ray analysis. We expect that our results will help to develop new strategies for the design of chiral ligands and the synthesis of chiral metal complexes. Further studies in this area are in progress in our laboratory.

EXPERIMENTAL

General

Melting points were obtained with a Yanagimoto micro melting point apparatus and are uncorrected. Optical rotations were determined for solution in $CHCl_3$ or MeOH at 20 °C by using a Perkin–Elmer-241 MC polarimeter; $[\alpha]_D$ values are given in units of 10^{-1} deg cm^2 g^{-1}. ^{1}H NMR spectra were recorded on a Bruker AM-300 spectrometer for solution in $CDCl_3$ with tetramethylsilane (TMS) as internal standard; J values are in hertz. Mass spectra were recorded with an HP-5989 instrument and high resolution mass spectrometry (HRMS) was undertaken with a Finnigan MA + mass spectrometer. The organic solvents used were dried by standard methods when necessary. All solid compounds reported in this paper gave satisfactory CHN microanalyses with a Carlo-Erba 1106 analyzer. Commer-

Table 2. Crystal data and summary of intensity data collection and structure refinement of **7**

Empirical formula	$C_{18}H_{24}O_2N_2Cl_3Rh$
Formula weight	509.66
Crystal color, habit	red, prismatic
Crystal dimensions (mm^3)	0.20 × 0.20 × 0.30
Crystal system	monoclinic
Lattice type	Primitive
Lattice parameters	
a (Å)	8.409(2)
b (Å)	13.098(2)
c (Å)	18.453(7)
V (Å^3)	2009.2(9)
β (deg)	98.70(3)
Space group	$P2_1$ (#14)
Z value	4
D_{calc} (g cm^{-3})	1.685
$F_{(000)}$	1032.00
μ(Mo Kα) (cm^{-1})	12.62
Diffractometer/scan	Rigaku AFC7R
Radiation, graphite monochromator	Mo Kα (λ = 0.71069 Å)
Crystal to detector distance (mm)	235
Temperature (°C)	20.0
Scan type	ω–2θ
Scan rate (deg min^{-1})	16.0 (in ω) — up to four scans
$2\theta_{\max}$ (deg)	51.0
Scan width	$1.37 + 0.30 \tan \theta$
Structure solution	Direct methods (SHELXS86)
Refinement	Full-matrix least-squares
ρ-factor	0.03
Reflection/parameter ratio	7.93
Residuals: R; R_w	0.028; 0.037
Max shift/error in final cycle	0.01
Maximum peak in final diff. map (e$^-$ Å^{-3})	1.05
Minimum peak in final diff. map (e$^-$ Å^{-3})	−0.89

cially obtained reagents were used without further purification. All reactions were monitored by thin-layer chromatography with Huanghai 60F$_{254}$ silica gel coated plates. Flash column chromatography was carried out using 300–400 mesh silica gel. The chiral starting material **1** was prepared according to the literature.[12] Compounds **2** and **4** were purchased from Aldrich Co.

Preparation of *N*-(2′-pyridylmethyl)-(2*R*,5*R*)-bis(methoxymethyl)pyrrolidine (3)

This compound was prepared from the reaction of **1** (200 mg, 1.26 mmol) with 2-(chloromethyl)pyridine hydrochloride **2** (248 mg, 1.51 mmol) in the presence of potassium carbonate (180 mg, 1.30 mmol) in acetonitrile (15 ml) under reflux for 10 h. The solvent was removed under reduced pressure. The residue was washed with water and extracted with ether (3 × 20 ml) and dried over Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by flash chromatography (length: 30 cm; diameter: 2 cm; eluent: EtOAc:petroleum ether = 1:4) to give **3** (210 mg, 67%) as 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.

Preparation of *N*-(2′-quinolylmethyl)-(2*R*,5*R*)-bis(methoxymethyl)pyrrolidine (5)

This compound was prepared in the same manner as that described above (228 mg, 60%); a colorless oil; $[\alpha]_D^{18}$ + 45.8 (c 0.89, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.56–1.96 (2H, m), 1.97–2.35 (2H, m), 3.25 (6H, s, OMe), 3.22–3.50 (6H, m), 4.28 (2H, d, J 1.9), 7.50 (1H, td, J 8.1, 1.0), 7.71 (1H, t, J 8.6), 7.73 (1H, t, J 8.6), 7.79 (1H, td, J 8.3, 1.0), 8.07 (1H, d, J 8.3), 8.11

Table 3. Bond lengths of **6**

Atom	Atom	Distance (Å)
Rh(1)	Cl(1)	2.349(2)
Rh(1)	Cl(2)	2.288(2)
Rh(1)	Cl(3)	2.343(2)
Rh(1)	O(1)	2.106(4)
Rh(1)	N(1)	2.106(5)
Rh(1)	N(2)	2.017(5)
O(1)	C(1)	1.454(9)
O(1)	C(2)	1.459(8)
O(2)	C(7)	1.41(1)
O(2)	C(8)	1.40(1)
N(1)	C(3)	1.509(8)
N(1)	C(6)	1.542(8)
N(1)	C(9)	1.511(9)
N(2)	C(10)	1.348(8)
N(2)	C(14)	1.339(8)
C(2)	C(3)	1.533(10)
C(3)	C(4)	1.514(10)
C(4)	C(5)	1.52(1)
C(5)	C(6)	1.53(1)
C(6)	C(7)	1.53(1)
C(9)	C(10)	1.493(9)
C(10)	C(11)	1.375(9)
C(11)	C(12)	1.404(9)
C(12)	C(13)	1.37(1)
C(13)	C(14)	1.377(10)

(1H, d, *J* 8.6); MS (EI) *m/z* (%) 301 (MH^+) 255 (100.0), 158 (65.5), 143 (79.3); HRMS (EI) found: 301.1904 (MH^+). $C_{18}H_{25}N_2O_2$ requires 301.1916.

Preparation of chiral rhodium complex 6

This compound was synthesized by heating an ethanol solution (20 ml) of **3** (100 mg, 0.40 mmol) with $RhCl_3{\cdot}3H_2O$ (105 mg, 0.41 mmol) under argon atmosphere for 9 h. The solvent was removed under reduced pressure and the residue was purified by silica gel column chromatography (length: 20 cm; diameter: 2 cm) to give the compound **4** as a red solid (eluent: $CHCl_3/EtOH = 10/1$); 102 mg, 50%; mp 203 °C (dec.); $[\alpha]_D^{20} + 208$(*c* 0.13, CH_2Cl_2); ^1H NMR ($CDCl_3$, 300 MHz) δ 2.10–2.30 (3H, m), 2.50–2.65 (1H, m), 3.05–3.30 (2H, m, CH), 3.37 (3H, s, OMe), 3.72 (3H, s, OMe), 3.76 (1H, dd, *J* 11.2, 3.7), 3.94 (1H, dd, *J* 11.2, 11.2), 4.0 (1H, d, *J* 15.3), 4.70–4.82 (2H, dm, *J* 11.2), 5.40 (1H, d, *J* 15.3), 7.51 (2H, dd, *J* 13.4, 7.3), 7.92 (1H, t, *J* 7.0), 9.73 (1H, d, *J* 5.8). Anal. Found: C, 36.43; H, 4.85; N. 5.93; $C_{14}H_{22}Cl_3N_2O_2Rh$ requires: C, 36.59; H, 4.83; N, 6.10%.

Preparation of chiral rhodium complex 7

This compound was synthesized in the same manner as that described above as a red solid; 47 mg, 30%; mp 273 °C (dec.); $[\alpha]_D^{20} + 176$ (*c* 0.14, CH_2Cl_2); ^1H NMR (DMSO-d_6, 300 MHz) δ 2.0–2.70 (4H, m), 3.05–3.30 (2H, m, CH), 3.46 (3H, s, OMe), 3.73 (3H, s, OMe), 3.76 (1H, dd, *J* 11.2, 1.7), 4.0–4.12 (1H, m), 4.48 (1H, dd, *J* 11.2, 11.2), 4.60 (1H, d, *J* 16.5), 4.80–5.0 (1H, m), 5.53 (1H, d, *J* 16.5), 7.74 (2H, d, *J* 8.1), 7.88 (1H, t, *J* 9.0), 8.09 (1H, d, *J* 8.1), 8.63 (1H, d, *J* 8.1); 9.76 (1H, d, *J* 9.0). Anal. Found: C, 42.40; H, 4.80; N. 5.43; $C_{18}H_{24}Cl_3N_2O_2Rh$ requires: C, 42.42; H, 4.75; N, 5.50%.

Table 4. Bond lengths of **7**

Atom	Atom	Distance (Å)
Rh(1)	Cl(1)	2.365(1)
Rh(1)	Cl(2)	2.321(1)
Rh(1)	Cl(3)	2.312(2)
Rh(1)	O(1)	2.082(4)
Rh(1)	N(1)	2.105(4)
Rh(1)	N(2)	2.083(4)
O(1)	C(15)	1.442(7)
O(1)	C(16)	1.450(7)
O(2)	C(17)	1.388(8)
O(2)	C(18)	1.42(1)
N(1)	C(1)	1.399(6)
N(1)	C(9)	1.328(6)
N(2)	C(10)	1.493(7)
N(2)	C(11)	1.528(7)
N(2)	C(14)	1.517(8)
C(1)	C(2)	1.412(7)
C(2)	C(3)	1.378(8)
C(3)	C(4)	1.391(10)
C(4)	C(5)	1.357(10)
C(5)	C(6)	1.411(8)
C(6)	C(7)	1.421(8)
C(7)	C(8)	1.354(9)
C(8)	C(9)	1.399(8)
C(9)	C(10)	1.502(7)
C(11)	C(12)	1.524(10)
C(12)	C(13)	1.51(1)
C(13)	C(14)	1.550(8)
C(14)	C(15)	1.499(8)

Crystallography

Suitable crystals with 0.20 × 0.20 × 0.30 mm^3 dimensions for **6** and **7** were mounted on the top of a glass capillary. Data were collected on a Rigaku AFC7R diffractometer with graphite-monochromated MoKα radiation $\lambda = 0.710\,69$ Å using the ω–2θ technique at 20 °C. The data were corrected for Lorentz polarization effects. Their structures were solved by direct methods and expanded using Fourier techniques.[17] The non-hydrogen atoms were refined anisotropically by full-matrix least squares. All hydrogen atoms were included in calculated positions. All calculations were performed using the TEXSAN crystallographic software package. Final R and R_w values for **6** were 0.027 and 0.033 for 3319 observed reflections. Final R and R_w values for **7** were 0.028 and 0.037 for 3711 observed reflections. Their crystal structures have been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition numbers: CCDC 149245 and 149246.

Acknowledgements

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