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Note

Synthesis of a novel chiral ruthenium complex and its crystal structure

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Abstract

One novel chiral ruthenium complex was successfully synthesized from the reaction of chiral bidentate nitrogen ligand with $RuCl_3 \cdot 3H_2O$ in ethanol under reflux. Its unique crystal structure was unambiguously disclosed by X-ray analysis. The crystal is orthorhombic, space group $P2_12_12_1$ (no. 19), with $a = 13.337(2)$, $b = 15.088(2)$, $c = 8.878(2)$ Å, $V = 1786.4(5)$ Å^3, $Z = 4$, $D = 1.702$ g cm^{-3}. An interesting additional coordination from an oxygen atom of methoxy group to the Ru metal center was found in this novel ruthenium complex.

Keywords: Chiral ruthenium complex; Tridentate chiral ligand; Bidentate chiral ligand; Crystal structure; X-ray analysis

1. Introduction

Chiral chelating bidentate or tridentate nitrogen ligands have found wide-spread application in asymmetric homogeneous catalysis by transition metal complexes [1]. 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 [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 field [5]. 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 reaction. In this paper we wish to report the synthesis of a novel chiral bidentate pyrrolidine ligand having an N-pyridyl group and the preparation of its novel chiral ruthenium complex. Moreover, the crystal structure of this novel ruthenium complex, which was disclosed unambiguously by X-ray analysis will be reported in this paper as well.

2. Results and discussion

2.1. Synthesis of chiral ligand **3** and its ruthenium complex **4**

The new chiral bidentate nitrogen ligand **3** was synthesized from the reaction of chiral C_2-symmetric 2,5-disubstituted pyrrolidine (**1**) [6] with 2-(chloromethyl)-pyridine hydrochloride (**2**) in the presence of potassium carbonate in acetonitrile under reflux (Scheme 1). The compound **3** was obtained as a colorless oil and should be stored under an nitrogen atmosphere at low temperature (< -10°C) [7]. Its transition metal complex **4** was synthesized from the reaction of **3** with $RuCl_3 \cdot 3H_2O$ in ethanol at 80°C for 9 h under an argon

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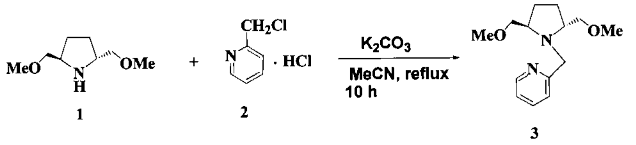
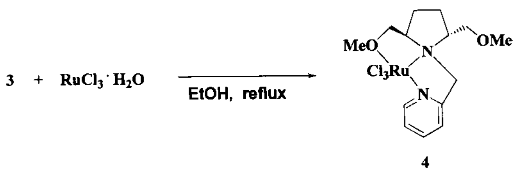


Scheme 1.



Scheme 2.

atmosphere (Scheme 2). We first confirmed its structure by microanalysis because Ru(III) complex **4** is a paramagnetic complex, therefore, its fine structure can not be determined by ^{1}H-NMR spectroscopic analysis.

2.2. Molecular structure of complex **4**

After tremendous efforts, the single crystal of novel ruthenium complex **4** was obtained by careful recrystallization from ethanol and diethyl ether (1:10). Thus finally its structure was disclosed unambiguously by X-ray analysis (Fig. 1). The crystal data was shown in Table 1. The bond lengths and bond angles were elucidated in Tables 2 and 3, respectively.

From Fig. 1, it is very clear that the bidentate nitrogen ligand **3** is actually a tridentate ligand because besides the two nitrogen atoms, the oxygen atom of methoxy group can also coordinate to the metal center to form an octahedral complex. As can be seen from Fig. 1 for ruthenium complex **4**, the bond length of two N–Ru coordination bonds are not identical [2.135(2) and 2.079(2) Å, respectively]. The coordination bond of the atom from pyrrolidine to Ru is slightly longer than the corresponding pyridine one. Furthermore, the bond length of O–Ru is 2.126(2) Å, which is very close to those of N–Ru bonds. This result strongly suggests that the additional coordination from oxygen atom to Ru metal is very similar to that of nitrogen atom to Ru. In fact, the octahedral ruthenium complex **4** is quite stable.

Concerned about the stable coordination bond of oxygen atom to Rh or Ru transition metal center, we often can find it in those ligands having Schiff base structures, such as salen type complexes, which are usually from the hydroxyl group of phenol to the metal center [8] and Doyle's chiral Rh complexes in which the oxygen atom of carbonyl group coordinate to the metal center [9]. In order to clarify the novelty of this ruthenium complex, we checked the scope and limitations of the coordination bond from heteroatom to Ru metal center. As a result, we did not find any other example related with the coordination of methoxy group to Ru metal center. Some examples were found that the oxy-

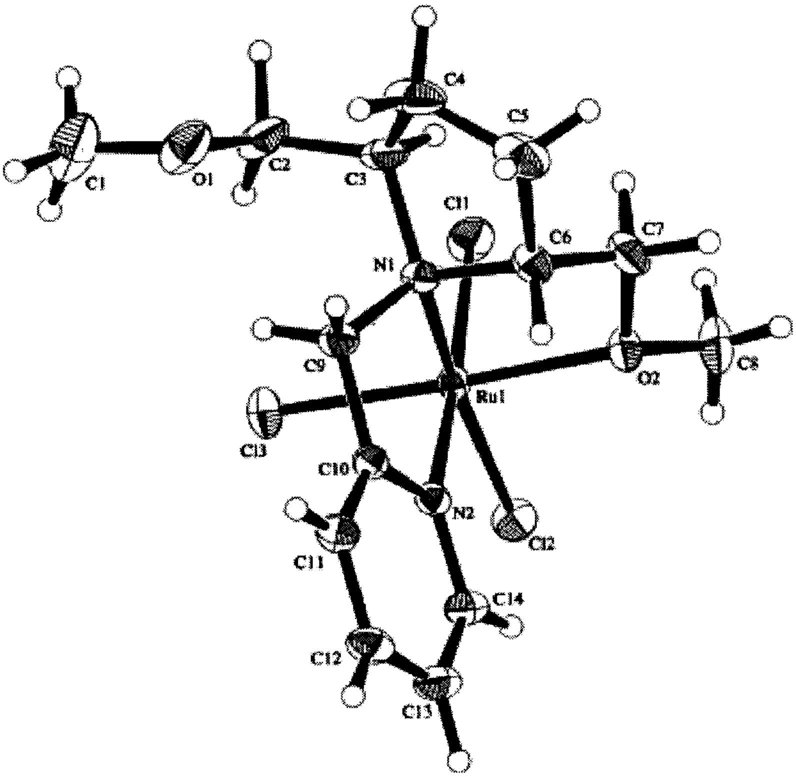


Fig. 1. The crystal structure of **4**.

gen atom from carbonyl group and sulfonyl group coordinated to the Ru center. For example, in $[Ru(CO)Cl\{MeOOC{=}C(CO_2Me)CH{=}CHCMe_3\}(PPh_3)_2]$ complex, the oxygen atom from carbonyl group coordinated to Ru with bond length 2.219(1) Å [10] and in $[Ru(O_3SC_6H_4{-}CH_3\text{-}p)_2(H_2O)(CO)(PPh_3)_2]$ complex the oxygen atom from sulfonyl group coordinated to Ru with bond length 2.165(5) Å [11]. Thus the bond length of the oxygen atom to the Ru center from the methoxy group (2.126(2) Å) is very similar to those from the carbonyl or sulfonyl group. Therefore, in this paper we first showed that the methoxy group on the side chain of pyrrolidine ring also can coordinate to the transition metal; even this kind of methoxy group has such flexibility. We believe that this finding could open a new way on the design of new chiral ligand and synthesis of novel chiral metal complexes. The combination of the coordination bond from nitrogen and oxygen atom to transition metal center can give us more insights about ligand coordination chemistry.

Table 1
Crystal data and summary of intensity data collection and structure refinement of **3**

Empirical formula	$C_{14}H_{22}Cl_3N_2O_2Ru$
Formula weight	457.77
Crystal color, habit	Orange, plate
Crystal dimensions (mm)	0.32 × 0.25 × 0.18
Crystal system	Orthorhombic
Lattice type	Primitive
Lattice parameters	
a (Å)	13.337(2)
b (Å)	15.088(2)
c (Å)	8.878(2)
V (Å^3)	1786.4(5)
Space group	$P2_12_12_1$ (no. 19)
Z	4
D_{calc} (g cm^{-3})	1.702
$F(000)$	924.00
μ(Mo–K$_\alpha$) (cm^{-1})	13.32
Diffractometer/scan	Rigaku AFC7R
Radiation, graphite monochromator (Å)	Mo–K$_\alpha$ ($\lambda = 0.71069$)
Crystal to detector distance (mm)	235
T (°C)	21.0
Scan type	ω–2θ
Scan rate	8.0° 1 min^{-1} (in ω)-up to five scans
$2\theta_{max}$ (°)	55.00
Scan width (°)	$(1.31 + 0.30 \tan \theta)$
Structure solution	Direct-methods (SIR92)
Refinement	Full-matrix least-squares
ρ-factor	0.0410
Reflection/parameter ratio	13.97
Residual: R; R_w	0.025; 0.033
Residual: R_1	0.025
Maximum shift/error in final cycle	0.00
Maximum peak in final difference map (e Å^{-3})	0.58
Minimum peak in final difference map (e Å^{-3})	−0.26

Table 2
Bond lengths (Å)

Atom	Atom	Distance
Ru(1)	Cl(1)	2.3479(8)
Ru(1)	Cl(2)	2.3724(8)
Ru(1)	Cl(3)	2.3095(8)
Ru(1)	O(2)	2.126(2)
Ru(1)	N(1)	2.135(2)
Ru(1)	N(2)	2.079(2)
O(1)	C(1)	1.364(8)
O(1)	C(2)	1.427(5)
O(2)	C(7)	1.422(4)
O(2)	C(8)	1.458(4)
N(1)	C(3)	1.518(4)
N(1)	C(6)	1.519(4)
N(1)	C(9)	1.499(4)
N(2)	C(10)	1.347(4)
N(2)	C(14)	1.345(4)
C(13)	C(14)	1.390(5)
C(12)	C(13)	1.371(5)
C(11)	C(12)	1.382(5)
C(10)	C(11)	1.385(4)
C(9)	C(10)	1.505(4)
C(6)	C(7)	1.510(5)
C(5)	C(6)	1.534(5)
C(4)	C(5)	1.517(8)
C(3)	C(4)	1.523(6)
C(2)	C(3)	1.512(6)

Table 3
Selected bond angles (°)

Atom	Atom	Atom	Angle
Cl(1)	Ru(1)	Cl(2)	91.14(3)
Cl(1)	Ru(1)	Cl(3)	91.72(4)
Cl(1)	Ru(1)	O(2)	88.12(7)
Cl(1)	Ru(1)	N(1)	97.17(7)
Cl(1)	Ru(1)	N(2)	175.15(7)
O(2)	Ru(1)	O(3)	91.50(3)
O(2)	Ru(1)	O(2)	91.36(6)
O(2)	Ru(1)	N(1)	168.83(7)
O(2)	Ru(1)	N(2)	93.68(7)
O(3)	Ru(1)	O(2)	177.14(7)
O(3)	Ru(1)	N(1)	95.67(7)
O(3)	Ru(1)	N(2)	87.57(7)
O(2)	Ru(1)	N(1)	81.52(9)
O(2)	Ru(1)	N(2)	92.36(9)
N(1)	Ru(1)	N(2)	78.13(9)

3. Conclusions

In conclusion, we have explored a new tridentate chiral ligand for the synthesis of novel chiral transition metal complex and disclosed its interesting structure by X-ray analysis. We expect that our results will develop a new strategy on the design of chiral ligands and the synthesis of chiral metal complexes. Further studies in this area are in progress in our laboratory.

4. Experimental

4.1. General procedures

M.p. values were obtained with a Yanagimoto micro melting point apparatus and are uncorrected. Optical rotations were determined for solution in 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}. ^1H-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 Hz. Mass spectra were recorded with a HP-5989 instrument and HRMS was measured by a Finnigan MA + mass spectrometer. Organic solvents used were dried by standard methods when necessary. All solid compounds reported in this paper gave satisfactory CHN microanalyses with an Italian Carlo-Erba 1106 analyzer. Commercially obtained reagents were used without further purification. All reactions were monitored by TLC with Huanghai $60F_{254}$ silica gel coated plates. Flash column chromatography was carried out using 300–400 mesh silica gel at increased pressure. The chiral starting material **1** was prepared according to the literature [6]. Compound **2** was purchased from Aldrich Co.

4.2. Preparation of N-(2′-pyridylmethyl)-(2R,5R)-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; ϕ, 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, $CHCl_3$); ^1H-NMR ($CDCl_3$, 300M) 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.

4.3. Preparation of chiral ruthenium complex (4)

This compound was synthesized by heating an ethanol solution (20 ml) of **3** (100 mg, 0.40 mmol) with $RuCl_3 \cdot 3H_2O$ (88 mg, 0.41 mmol) under argon atmosphere for 5 h. The solvent was removed under reduced pressure and the residue was purified by silica gel column chromatography (length, 20 cm; ϕ, 2 cm) to give the compound **4** as an orange solid (eluent: $CHCl_3$–EtOH = 10:1). 47 mg, 30%; m.p. (dec.) 203°C; $[\alpha]_D^{20}$ +169° (c 0.13, MeOH); Found: C, 43.43; H, 5.85; N. 7.40. $C_{14}H_{22}Cl_3N_2O_2Ru$ requires: C, 43.40; H, 5.72; N, 7.23%.

4.4. Crystallography

A suitable crystal with 0.32 × 0.25 × 0.18 mm^3 dimensions was mounted on the top of a glass capillary. Crystal data and details of data collection and structure refinement are given in Tables 1 and 2, respectively. Data were collected on a Rigak u AFC7R diffractometer with graphite-monochromated Mo–K_α radiation $\lambda = 0.71069$ Å using the ω–2θ technique at 20°C. A total of 4554 unique reflection was collected. The data were collected for Lorentz polarization effects. The structure was solved by direct methods and expanded using Fourier techniques [12]. The non-hydrogen atoms were refined anisotropically by full-matrix least-squares. All hydrogen atoms were included in calculated position. All calculations were performed using the TEXSAN crystallographic software package. Final R and R_w values were 0.025 and 0.033 for 4023 observed reflection.

5. Supplementary material

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 142912. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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