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Preparation and Characterization of A New Dinuclear Ruthenium Complex with BDPX Ligand and Its Catalytic Hydrogenation Reactions for Cinnamaldehyde

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A new anionic dinuclear ruthenium complex bearing 1,2-bis(diphenylphosphinomethyl)benzene (BDPX) $[NH_2Et_2][\{RuCl(BDPX)\}_2(\mu\text{-}Cl)_3]$ (**1**) was synthesized and its structure was determined by an X-ray crystallographic analysis. This result indicated that complex **1** consisted of an anion dinuclear BDPX-Ru and a cationic diethylammonium. The crystal belonged to monoclinic system, *C*2/*c* space group with a=3.3552(7) nm, b=1.8448(4) nm, c=2.4265(5) nm, β=101.89(3)° and Z=8. The catalytic hydrogenation activities and selectivities of complex **1** for cinnamaldehyde were investigated.

Keywords ruthenium complex, bidentate phosphine, hydrogenation, cinnamaldehyde

Introduction

Recently, dinuclear Ru complexes containing chelating bidentate phosphines (either chiral or non-chiral) have attracted more and more attention owing to their effective ability for catalytic hydrogenation of olefins and carbonyl groups under mild conditions. A great number of dinuclear Ru complexes with bidentate phosphines have been obtained.[1-10] In 1985 Ikariya *et al*.[1] prepared a chiral binuclear ruthenium complex $[Ru_2Cl_4(BINAP)_2]\bullet NEt_3$ by the reaction of (*S*)-BINAP with $[RuCl_2(COD)]_n$ in the presence of triethylamine in refluxing toluene solution. It is an excellent catalyst for the asymmetric hydrogenation of carbonyl compounds. A decade later, the X-ray diffraction of single crystal indicated that the structure of ruthenium complex with diphosphine ligand (*R*)-*p*-MeO-BINAP was not $[Ru_2Cl_4(P\text{-}P)_2]\bullet NEt_3$ but $[NH_2Et_2][\{RuCl[(R)\text{-}p\text{-}MeO\text{-}BINAP]\}_2(\mu\text{-}Cl)_3]$.[4] To the best of our knowledge, $[NH_2Et_2][\{RuCl[(R)\text{-}p\text{-}MeO\text{-}BINAP]\}_2(\mu\text{-}Cl)_3]$ in this kind of complexes was only confirmed by X-ray diffraction up to date. James proposed a formation mechanism of this kind of the anionic dinuclear ruthenium complexes by reacting NR_3 with $RuCl_2(dppb)(PPh_3)$ in refluxing benzene, but single crystal structure of the chelated ruthenium complex, which was synthesized by reacting diphosphine with $[RuCl_2(COD)]_n$ in the presence of NR_3, was not obtained.[10] In this regard, we have synthesized a new ruthenium complex containing BDPX [1,2-bis(diphenylphosphinomethyl)benzene]. The X-ray single-crystal analysis confirmed that the complex had the same structure as $[NH_2Et_2][\{RuCl[(R)\text{-}p\text{-}MeO\text{-}BINAP]\}_2(\mu\text{-}Cl)_3]$. The hydrogenation of carbon-carbon double bond in an organic compound is thermodynamically more favorable than the hydrogenation of an carbonyl group catalyzed by transition metal complexes,[11-16] therefore, it is still a challenging problem to synthesize catalysts for highly selective hydrogenation of α,β-unsaturated aldehyde to its corresponding unsaturated alcohol. That the ruthenium complex is used to hydrogenate selectively cinnamaldehyde was investigated in this paper.

Experimental

Materials

All synthetic reactions were carried out using standard Schlenk techniques under nitrogen atmosphere. Solvents were generally dried over appropriate drying agents, and distilled under nitrogen prior to use. $[RuCl_2(COD)]_n$, triethylamine, ethylenediamine and cinnamaldehyde were used as purchased without further purification. 1,2-Bis(diphenylphosphinomethyl)benzene (BDPX) was prepared according to the reported method.[17]

Analytical methods

The $^{31}P\{^1H\}$ NMR spectra in $CDCl_3$ were recorded on a Bruker ARX 300 spectrometer at room temperature

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and at 121.5 MHz for $^{31}P\{^{1}H\}$ NMR with 85% H_3PO_4 as external standard, and downfield shifts as positive value. Elemental analyses were performed by the Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences.

Catalytic hydrogenation

Appropriate amounts of the catalyst and substrate were introduced into a stainless steel autoclave (60 mL) equipped with a stirring bar. The autoclave was evacuated and flushed consecutively with hydrogen (99.995%) for five times, then filled with the hydrogen to the desired pressure. When the reaction mixture was heated to the desired temperature, stirring was started and reaction time was accounted. The reaction was quenched by immersing the reactor in a cold water-bath at the end of hydrogenation. The products were analyzed on a GC (HP 1890 II Series) with FID and a capillary column (SE-30, 30 m×0.25 mm), and the GC graphs were treated with an HP 3295 Integrator. The components were identified with authentic samples on GC.

Preparation of complex

A mixture of BDPX (192 mg, 0.40 mmol), $[RuCl_2(COD)]_n$ (112 mg, 0.40 mmol as monomeric form), toluene (10 mL) and triethylamine (1 mL) was refluxed for 8 h to give a clear reddish brown solution. At the end of reaction, 5 mL of *n*-hexane was added to the reaction solution and then it was put in refrigerator to generate some reddish brown crystals. The product was filtered, washed separately with ethanol and diethyl ether and dried under vacuum to give 0.15 g (54%) of red-brown product. $^{31}P\{^{1}H\}$ NMR ($CDCl_3$) δ: 41.7 (s). Anal. calcd for $C_{68}H_{68}NCl_5P_4Ru_2$: C 57.83, H 4.99, N 0.99; found C 57.88, H 5.01, N 1.09.

X-ray crystallographic analysis

The crystal used for X-ray diffraction was grown by gas diffusion of CH_2Cl_2 and *n*-hexane. The crystal (0.50 mm×0.28 mm×0.12 mm) covered with a thin layer of paraffin oil as a precaution against decomposition in air was mounted on a Rigaku RAXIS IIC imaging-plate diffractometer with a rotating-anode generator powered at 50 kV and 90 mA. Intensity data were collected at 293 K using graphite-monochromatized Mo Kα radiation (λ=0.071073 nm). Crystallographic data are summarized in Table 1.

Table 1 Crystal data and structure refinement for complex **1**

Empirical formula	$C_{68}H_{68}Cl_5NP_4Ru_2$•1.5H_2O
Formula weight	1421.53
Temperature/K	293(2)
Wavelength/nm	0.071073
Crystal habit	Orange plate
Crystal size/mm^3	0.50×0.28×0.12
Crystal system	Monoclinic
Space group	*C*2/*c*
Unit cell dimensions	*a*=3.3552(7) nm *b*=1.8448(4) nm, β=101.89(3)° *c*=2.4265(5) nm
Volume/nm^3	14.697(5)
Z	8
Density (calcd)/(Mg•m^{-3})	1.285
Absorption coefficient/mm^{-1}	0.718
F(000)	5816
θ range for data collection/(°)	2.03 to 25.06
Index ranges	$0\leqslant h\leqslant 39$, $0\leqslant k\leqslant 21$, $-28\leqslant l\leqslant 28$
Reflections collected	13204
Independent reflections	12971 (R_{int}=0.0612)
Observed reflections	6190 [$I>2\sigma(I)$]
Absorption correction	Semi-empirical
Maximum and minimum transmission	1.0000 and 0.8342
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	12971/4/740
Goodness-of-fit on F^2	0.986
Final *R* indices [$I>2\sigma(I)$]	R_1=0.0690, wR_2=0.1810
R indices (all data)	R_1=0.1863, wR_2=0.2212
Extinction coefficient	0.000000(9)
Largest and mean Δ/σ	0.541, 0.023
Largest differential peak and hole/(e•nm^{-3})	0.930×10^3 and −0.684×10^3

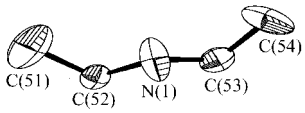


Figure 1 ORTEP drawing of the complex cation. Hydrogen atoms are omitted for clarity.

Results and discussion

Structure of complex

$[NH_2Et_2][\{RuCl(BDPX)\}_2(\mu\text{-}Cl)_3]$ was very sensitive to air oxidation in solution. When its solution was exposed to air, its color changed from reddish brown to green in a few minutes. A singlet at δ 41.7 in $^{31}P\{^{1}H\}$ NMR spectrum indicated that all four phosphorus atoms in the complex were of the same chemical environment. The results of X-ray single-crystal diffraction analysis of the complex are shown in Table 2, Figures 1 and 2.

These results exhibit that the complex consists of an anionic dinuclear BDPX-Ru species, and a diethylam monium cation, and each complex molecule contains 1.5 mol of H_2O in approximate crystal. The anionic structure reveals that the two-ruthenium atoms are bridged by three chloride ions, with an approximate near-twofold axis through the bridging chloride Cl(2). The coordination geometry about each ruthenium center can be described as a distorted octahedron. The struc-

Table 2 Selected bond lengths (10^{-1} nm) and bond angles (°)

Ru (1)—P(1)	2.2655(11)	Ru(2)—P(1')	2.2701(10)
Ru(1)—P(2)	2.2406(11)	Ru(2)—P(2')	2.2685(11)
Ru(1)—Cl(1)	2.4906(11)	Ru(2)—Cl(1)	2.4920(10)
Ru(1)—Cl(2)	2.4105(10)	Ru(2)—Cl(2)	2.4328(10)
Ru(1)—Cl(3)	2.4891(11)	Ru(2)—Cl(3)	2.4899(11)
Ru(1)—Cl(4)	2.4248(11)	Ru(2)—Cl(5)	2.4191(10)
Cl(1)-Ru(1)-P(1)	91.04(4)	Cl(1)-Ru(2)-P(1')	92.28(3)
Cl(1)-Ru(1)-P(2)	172.15(3)	Cl(1)-Ru(2)-P(2')	167.92(3)
Cl(2)-Ru(1)-P(1)	104.70(4)	Cl(2)-Ru(2)-P(1')	97.92(4)
Cl(2)-Ru(1)-P(2)	93.86(4)	Cl(2)-Ru(2)-P(2')	104.41(3)
Cl(3)-Ru(1)-P(1)	168.98(4)	Cl(3)-Ru(2)-P(1')	171.82(4)
Cl(3)-Ru(1)-P(2)	95.19(4)	Cl(3)-Ru(2)-P(2')	89.49(3)
Cl(4)-Ru(1)-P(1)	88.95(4)	Cl(5)-Ru(2)-P(1')	86.59(4)
Cl(4)-Ru(1)-P(2)	91.73(4)	Cl(5)-Ru(2)-P(2')	86.55(4)
P(1)-Ru(1)-P(2)	94.60(4)	P(1')-Ru(2)-P(2')	98.66(4)
Cl(1)-Ru(1)-Cl(2)	79.41(3)	Cl(1)-Ru(2)-Cl(2)	78.96(3)
Cl(1)-Ru(1)-Cl(3)	79.71(3)	Cl(1)-Ru(2)-Cl(3)	79.67(3)
Cl(1)-Ru(1)-Cl(4)	93.82(4)	Cl(1)-Ru(2)-Cl(5)	89.01(3)
Cl(2)-Ru(1)-Cl(3)	79.65(3)	Cl(2)-Ru(2)-Cl(3)	79.21(4)
Cl(2)-Ru(1)-Cl(4)	164.75(3)	Cl(2)-Ru(2)-Cl(5)	167.27(3)
Cl(3)-Ru(1)-Cl(4)	85.73(4)	Cl(3)-Ru(2)-Cl(5)	94.67(4)
Ru(1)-Cl(1)-Ru(2)	83.87(3)	Ru(1)-Cl(2)-Ru(2)	86.87(4)
Ru(1)-Cl(3)-Ru(2)	83.95(4)		

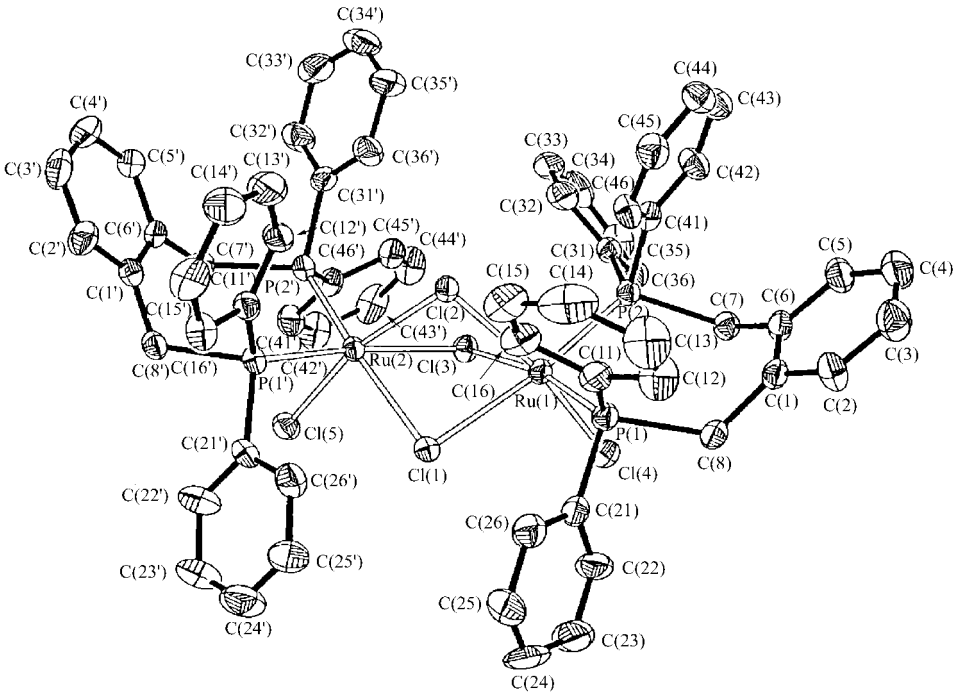


Figure 2 ORTEP drawing of the anionic part of complex **1**. Hydrogen atoms are omitted for clarity.

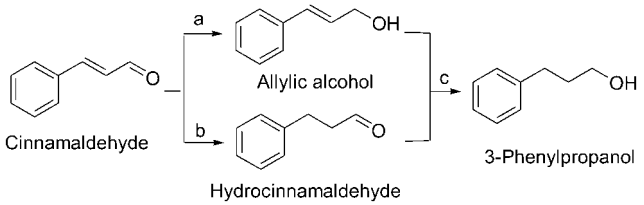
ture of the complex is very close to that of $[NH_2Et_2][\{RuCl[(R)\text{-}p\text{-MeO-BINAP}]\}_2(\mu\text{-}Cl)_3]$ (**2**). The Ru—Ru distance (0.333 nm) of complex **1** is equal to that found for complex **2**, but the bite angle of P-Ru-P (av. ~ 96.7°) for complex **1** is wider than that (91.8°) for complex **2**. The Ru—Cl bond length (0.242 nm) for the bridging chloride Cl(2) *trans* to terminal chlorides is shorter than those (0.249 nm) of the bridging chloride atoms *trans* to phosphine atoms. This might result from the weaker *trans* influence of the chloro ligand compared to that of the phosphine ligand, thus producing a larger Ru-Cl(2)-Ru bond angle (86.9°) compared to the

other two Ru-Cl-Ru angles (av. ~83.9°). In this complex the average Ru-Cl-Ru bond angle is 84.9°, which is larger than the bridging angle (70.5°) of two regular octahedron sharing one face,[18] and hence the two ruthenium atoms are further apart than they will be in a regular cofacial bioctahedron. Indeed, the separation of the ruthenium centers (0.333 nm) is well outside the range (0.228—0.295 nm) usually observed for a Ru—Ru bond,[19-26] but is comparable to those (0.3115—0.337 nm) reported for face-sharing bioctahedral ruthenium complexes having the Ru(μ-Cl)$_3$Ru unit.[8-9, 18, 27-30]

Hydrogenation of cinnamaldehyde by complex 1

The hydrogenation routes of cinnamaldehyde are shown in Scheme 1.

Scheme 1 Hydrogenation routes of cinnamaldehyde



The influence of reaction conditions such as temperature, pressure, reaction time, and the presence of ethylenediamine was investigated. The results of the hydrogenation of cinnamaldehyde catalyzed by complex **1** are summarized in Table 3. The selectivity for the hydrogenation of cinnamaldehyde to cinnamyl alcohol reached 69.2% as the reaction temperature increased to 70 ℃, but the selectivity of cinnamyl alcohol reduced to 24.9% gradually as the conversion of cinnamaldehyde increased to 100%. This could be explained that the further hydrogenation of the unsaturated alcohol as well as saturated aldehyde proceeded rapidly at higher temperature (100 ℃), which led to the lower selectivity.

When the hydrogen pressure was raised from 1 to 4 MPa, maintaining constant temperature (80 ℃), the selectivity for the unsaturated alcohol almost remained constant (about 70%). The conversion of cinnamaldehyde became higher with prolonging the reaction time, but the selectivity for cinnamyl alcohol reduced considerably because of the further hydrogenation of cinnamyl alcohol. When methanol was used as solvent, the catalytic activity was much higher than in toluene and an almost complete conversion of cinnamaldehyde (99.5%) could be reached in short time or at mild reaction temperature, but the selectivity was only 39.0%. Using ethanol as solvent showed the similar results, however the conversion was a little lower (86.0%) and the selectivity for cinnamyl alcohol was some higher (52.2%). When tetrahydrofuran was used as solvent, both the conversion of cinnamaldehyde (24.4%) and the selectivity for cinnamyl alcohol (54.5%) became much lower than when toluene was used.

An interesting observation was that the conversion of cinnamaldehyde increased drastically when ethylenediamine was introduced to the catalysis system (Table 4), and the color of the reaction mixture was deep red at the end of hydrogenation reaction, in contrast to light yellow in the absence of ethylenediamine. When molar ratio of ethylenediamine/complex came to 2 (*i.e.*, ethylenediamine equivomolar to ruthenium atom), a much higher conversion of cinnamaldehyde was obtained. However, when more ethylenediamine was introduced, the catalytic activity remained essentially unchanged. From these results it is suggested that in the presence of ethylenediamine the formation of an active

Table 3 Catalytic hydrogenation of cinnamaldehyde[a]

Entry	Temp./℃	*p*/MPa	Time/h	Conv./%	Distribution of products/%		
					Hydrocinnamaldehyde	3-Phenylpropanol	Cinnamyl alcohol
1	60	3	3	14.3	26.6	9.1	64.3
2	70	3	3	21.4	24.3	6.5	69.2
3	80	3	3	50.6	12.9	18.3	68.8
4	90	3	3	72.4	7.1	27.6	64.6
5	100	3	3	100	1.3	73.8	24.9
6	80	1	3	26.8	19.4	10.1	70.5
7	80	2	3	36.5	16.7	13.7	69.6
8	80	4	3	53.0	15.8	17.9	66.3
9	80	3	1	17.7	28.8	4.6	61.6
10	80	3	6	64.1	9.7	22.3	68.0
11	80	3	12	96.5	1.7	42.7	55.6
12[b]	80	3	3	99.5	17.0	44.0	39.0
13[c]	80	3	3	86.0	14.5	33.3	52.2
14[d]	80	3	3	24.4	32.8	12.7	54.5

[a] Reaction conditions: catalyst concentration 5×10^{-4} mol•dm^{-3}, cinnamaldehyde 1.0 mL, toluene 9.0 mL; [b] methanol as solvent (9.0 mL); [c] ethanol as solvent (9.0 mL); [d] THF as solvent (9.0 mL).

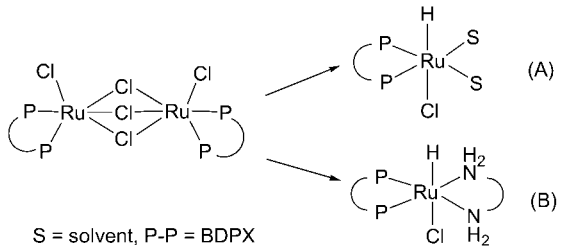
Table 4 Hydrogenation of cinnamaldehyde in the presence of $NH_2CH_2CH_2NH_2$ [a]

Ethylenediamine/complex (molar ratio)	Conversion/%	Distribution of products/%		
		Hydrocinnamaldehyde	3-Phenylpropanol	Cinnamyl alcohol
0	50.6	12.9	18.3	68.8
1	63.5	8.1	17.6	74.3
2	83.9	5.5	27.5	67.0
4	89.7	3.8	28.6	67.6
8	83.1	4.8	22.4	72.8

[a] Reaction conditions: catalyst concentration 5×10^{-4} mol•dm^{-3}, cinnamaldehyde 1.0 mL, toluene 9.0 mL, temperature 80 ℃, pressure 3 MPa, reaction time 3 h.

species would be accompanied by a structural change from a binuclear to a mononuclear unit containing an ethylenediamine ligand (Scheme 2B),[31,32] and in absence of ethylenediamine the structural change of the-complex might still take place in alcohol solution, possibly accompanying the formation of the solvent-coordinated hydride active species (Scheme 2A).[33,34]

Scheme 2 Possible catalytically active species formed in a catalytic system without ethylenediamine (A) and in the presence of ethylenediamine (B)



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