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Transfer hydrogenation of acetophenone promoted by (arene)ruthenium(II) reduced Schiff base complexes: an X-ray structure of [(η^6-*p*-cymene)RuCl(OC_6H_4-2-$CH_2NHC_6H_4$-*p*-Me)]

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Abstract

Arene ruthenium(II) reduced Schiff base complexes of formulation [(η^6-*p*-cymene)RuCl(L^n)] (**1**–**5**, $n = 1$–5) were prepared by reacting [(η^6-*p*-cymene)$RuCl_2$]$_2$ with HL^n in the presence of sodium carbonate in CH_2Cl_2. The complexes contain an η^6-*p*-cymene group, a chloride and a bidentate chelating N,O-donor ligand. The molecular structure of [(η^6-*p*-cymene)RuCl(OC_6H_4-2-$CH_2NHC_6H_4$-*p*-Me)] (**1**) has been determined by X-ray crystallography. The complexes are found to be catalytically active for transfer hydrogenation of acetophenone to (±)1-phenylethanol in the presence of KOH and isopropanol showing percent conversion of 98 with the catalysts having a bulky substituent adjacent to the O- and N-donor sites of the auxiliary ligand. © 2001 Published by Elsevier Science Ltd.

Keywords: Arene ruthenium; Crystal structure; Transfer hydrogenation; Catalysis; Reduced Schiff base

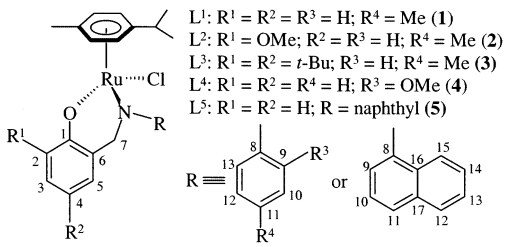
1. Introduction

Half-sandwich (η^6-arene)ruthenium(II) complexes are of current interest in the development of new catalytic systems for organic transformation reactions and in asymmetric induction studies [1–3]. Recent reports have shown that ruthenium-based complexes are effective catalysts for transfer hydrogenation of ketones in the presence of an organic hydrogen donor like 2-propanol [4–10]. It has been observed that the auxiliary ligand having a NH moiety plays an important role in the catalytic process involving a hydride intermediate species [4]. The present work stems from our interest to study the catalytic behavior of (*p*-cymene)ruthenium(II) complexes having a N,O-donor chelating, reduced Schiff base auxiliary ligand. Herein we report the synthesis, structure and properties of [(η^6-*p*-cymene)RuCl(L^n)] ($n = 1$–5) (Scheme 1). The crystal structure of complex **1** has been determined by X-ray crystallographic study.

2. Experimental

2.1. Materials and methods

All reactions were carried out in dry solvent under a dinitrogen atmosphere. Dichloromethane, *n*-hexane, methanol, petroleum ether (b.p. 40–60 °C) and isopropanol were distilled from appropriate drying agents and deoxygenated prior to use. Acetophenone was distilled under vacuum. The ligands (HL^n) were prepared



Scheme 1.

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by reducing the Schiff bases [11] using sodium borohydride (Aldrich make) in methanol. The precursor complex $[(\eta^6\text{-}p\text{-cymene})RuCl_2]_2$ was synthesized following a literature method [12]. Elemental analysis was performed on a Perkin–Elmer 2400 CHN analyzer. ^1H NMR spectra were recorded on Bruker 200 MHz and Bruker AMX 400 MHz spectrometer using $CDCl_3$ as a solvent and tetramethylsilane as an internal standard.

2.2. Preparation of $[(\eta^6\text{-}p\text{-cymene})RuCl(L^n)]$ ($n = 1$–5, **1**–**5**)

The complexes were prepared using a general procedure in which 0.33 mmol of $[(\eta^6\text{-}p\text{-cymene})RuCl_2]_2$ (200 mg) was reacted with 0.66 mmol of HL^n in the presence of 1.5 mmol of sodium carbonate (160 mg) in 15 cm^3 CH_2Cl_2 under stirring condition at 25 °C for 3 h. The mixture was filtered and the filtrate was reduced to 5 cm^3 and the product was precipitated by addition of *n*-hexane. The solid was isolated, washed with *n*-hexane and finally dried under vacuum. Yield ranged between 85 and 90%.

2.3. Hydrogenation of acetophenone

A general procedure was followed for the catalytic hydrogenation of acetophenone. In a typical reaction, 0.05 mmol of the catalyst (**1**–**5**) was reacted with 0.125 mmol of KOH and 5 mmol of acetophenone (0.6 cm^3) under refluxing condition in 5 cm^3 isopropanol for 6 h. The reaction mixture was cooled to ambient temperature. The catalyst was removed by addition of 15 cm^3 of petroleum ether (b.p. 40–60 °C) followed by filtration and neutralization with dilute HCl. The petroleum ether layer was separated and passed through anhydrous sodium sulfate. The crude mixture containing the hydrogenated product, (±)-1-phenylethanol and the unreacted acetophenone was obtained by distilling the solvent. Percentage conversion was calculated by comparing the methyl proton signals of acetophenone (s, δ 2.62 ppm) and (±)-1-phenylethanol (d, δ 1.50 ppm, $J = 6.8$ Hz) in the ^1H NMR spectrum of the mixture in $CDCl_3$ (s, singlet; d, doublet).

2.4. Crystallographic analysis

Single crystals of **1**, suitable for X-ray studies, were obtained by using a diffusion technique in which a dichloromethane solution of the complex was layered below *n*-hexane in a Schlenk tube under a dinitrogen atmosphere. An orange rectangular shaped crystal of dimensions $0.32 \times 0.20 \times 0.18$ mm was mounted on a glass fiber with epoxy cement. Unit cell dimensions were obtained by angular settings of 25 reflections in the range $7.5° < \theta < 15.9°$. Intensities of reflections ($0 \le h \le 11$; $0 \le k \le 17$; $-18 \le l \le 18$) within the range $4° \le 2\theta \le 50°$ were measured in a ω–2θ scan mode on a CAD-4 diffractometer equipped with graphite monochromated Mo Kα radiation ($\lambda = 0.7107$ Å). Out of a total 3826 unique reflections collected at 20 °C, 2901 reflections with $I > 2\sigma(I)$ were used for the refinement of the structure. The intensity data were corrected for Lorentz and polarization effects.

The structure was solved by Patterson's heavy-atom method, which revealed the position of ruthenium atom in the asymmetric unit. The remaining atoms were located in successive difference Fourier syntheses. Refinement of the structure was made by the full-matrix least-squares procedures. An empirical absorption correction was made on obtaining the complete structural model [13]. The transmission coefficients were in the range 0.77–0.86. All non-hydrogen atoms were refined anisotropically. The hydrogen atom positions were generated and assigned isotropic thermal parameters riding to the atoms they were bonded. The final refinement was converged to $R = 0.0350$; $R_w = 0.0771$ with the weighting scheme: $w = 1/[\sigma^2(F_o^2) + (0.0340P)^2 + 2.8307P]$ using 253 parameters, where $P = (F_o^2 + 2F_c^2)/3$. The maximum shift/e.s.d., goodness-of-fit and the highest peak were 0.001, 1.063 and 0.63 e $Å^{-3}$, respectively. All calculations were carried out using SHELX system of programs [14].

2.4.1. Crystal data for $[(\eta^6\text{-}p\text{-cymene})RuCl(OC_6H_4\text{-}2\text{-}CH_2NHC_6H_4\text{-}p\text{-}Me)]$

$C_{24}H_{28}NOClRu$: $M = 482.6$, monoclinic, $P2_1/c$, $a = 9.609(7)$, $b = 14.552(4)$, $c = 15.608(4)$ Å, $\beta = 94.90(3)°$, $V = 2175(2)$ $Å^3$, $F(000) = 988$, $Z = 4$, $D_{calc} = 1.47$ g cm^{-3}, μ(Mo Kα) = 8.58 cm^{-1}.

3. Results and discussion

3.1. Synthesis and structure

Complexes **1**–**5** are prepared in high yield from a reaction of $[(\eta^6\text{-}p\text{-cymene})RuCl_2]_2$ with the anionic N,O-donor reduced Schiff base ligands. The complexes are moderately stable in the solid state and unstable in solution phase. They are characterized from elemental analysis and ^1H NMR spectral data (Table 1). The ^1H NMR data suggest a 1:1 ratio of the *p*-cymene and the reduced Schiff base in the monomeric complexes (Fig. 1). The methyl singlet and the isopropyl methyl protons (two doublets) of the *p*-cymene ligand appear in the ranges 1.7–2.1 and 1.1–1.3 ppm, respectively. Complex **2**, however, shows a single doublet at 1.24 ppm for the isopropyl methyl protons. The isopropyl CH proton appears as a septet in the range 2.7–2.9 ppm. Four doublets observed in the range 3.58–5.2 ppm are assignable to the *p*-cymene ring protons. The other spectral features are characteristic of the N,O-donor

Table 1
Analytical [a] and ^{1}H NMR [b] data of [(η^6-*p*-cymene)RuCl(L^n)] ($n = 1$–5, **1**–**5**)

Complex	Analysis (%)			^{1}H NMR (ppm, multiplicity, H_x, $^3J_{HH}$ (Hz))	
	C	H	N	L^n	*p*-Cymene
1	59.6 (59.7)	5.7 (5.8)	2.8 (2.9)	2.41 (s, Me), 3.65 (d, H_{7A}, 10.0), 4.34 (d, H_{7B}, 10.0), 4.35 (t, NH, 10.2), 6.49 (t, H_4, 7.5), 6.79 (d, H_5, 7.4), 6.90 (d, H_2, 7.4), 7.01 (t, H_3, 7.5), 7.09–7.34 (2d, $H_{9,10,12,13}$, 8.8)	1.21–1.29 (2d, CH*Me*$_2$, 6.0), 2.04 (s, Me), 2.86 (sp, *CH*Me$_2$, 6.8), 4.30–5.10 (4d, four ring H, 6.0)
2	58.3 (58.5)	5.7 (5.9)	2.7 (2.7)	2.40 (s, Me), 3.65 (d, H_{7A}, 11.0), 3.88 (s, OMe), 4.23 (t, NH, 10.4), 5.15 (d, H_{7B}, 10.0), 6.44–6.79 (m, H_{3-5}), 7.28 (2d, $H_{9,10,12,13}$, 8.4)	1.24 (d, CH*Me*$_2$, 6.8), 2.02 (s, Me), 2.91 (sp, *CH*Me$_2$, 7.0), 4.18–5.04 (4d, four ring H, 5.8)
3	64.6 (64.9)	7.5 (7.3)	2.4 (2.4)	1.19 (s, CMe$_3$), 1.64 (s, CMe$_3$), 3.55 (d, H_{7A}, 10.4), 4.37 (t, NH, 10.4), 5.26 (d, H_{7B}, 10.4), 6.64 (s, H_5), 7.13 (s, H_3), 7.28 (m, $H_{9,10,12,13}$)	1.16–1.25 (2d, CH*Me*$_2$, 7.2), 2.05 (s, Me), 2.87 (sp, *CH*Me$_2$, 6.0), 4.14–5.14 (4d, four ring H, 5.8)
4	57.6 (57.8)	5.5 (5.6)	2.6 (2.8)	3.83 (s, OCH$_3$), 3.70 (d, H_{7A}, 10.0), 3.72 (t, NH, 10.2), 4.51 (d, H_{7B}, 10.0), 6.75 (m, $H_{4,5}$), 6.91(m, $H_{2,3}$), 7.1–7.3 (m, H_{10-13})	1.19–1.23 (2d, CH*Me*$_2$, 6.8), 2.07 (s, Me), 2.80 (sp, *CH*Me$_2$, 7.0), 4.65–5.05 (4d, four ring H, 6.2)
5	62.6 (62.5)	5.6 (5.4)	2.8 (2.7)	3.44 (d, H_{7A}, 11.0), 4.17 (t, NH, 10.0), 5.39 (d, H_{7B}, 10.8), 6.1–6.9 (m, H_{2-5}), 7.0–8.1 (m, H_{9-15})	1.03–1.14 (2d, CH*Me*$_2$, 7.0), 1.72 (s, Me), 2.78 (sp, *CH*Me$_2$, 7.0), 3.58–4.70 (4d, four ring H, 5.8)

[a] Calculated values are in parentheses.
[b] 200 MHz (**1**–**4**); 400 MHz (**5**); solvent, $CDCl_3$; s, singlet; d, doublet; t, triplet; sp, septet; m, multiplet. H_x corresponds to the carbon number C_x of the reduced Schiff base ligand as shown in Scheme 1.

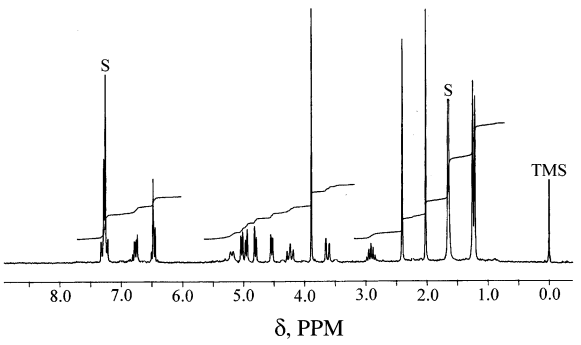


Fig. 1. A 200 MHz ^{1}H NMR spectrum of [(η^6-*p*-cymene)RuCl(L^2)] (**2**) in $CDCl_3$ (S, solvent peaks).

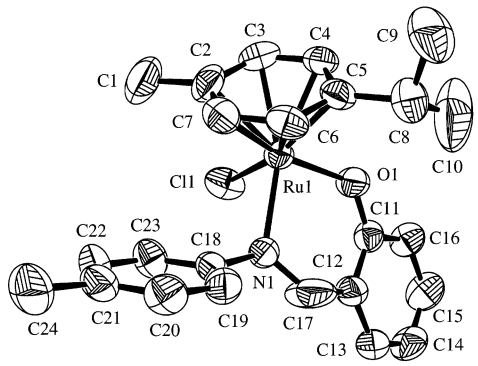


Fig. 2. An ORTEP view of [(η^6-*p*-cymene)RuCl(OC_6H_4-2-$CH_2NHC_6H_4$-*p*-Me)] (**1**) showing the thermal ellipsoids at 50% probability level along with the atom numbering scheme.

Table 2
Selected bond lengths (Å) and bond angles (°) for [(η^6-*p*-cymene)RuCl(OC_6H_4-2-$CH_2NHC_6H_4$-*p*-Me)] (**1**) (C^0, the centroid of the η^6-*p*-cymene ring)

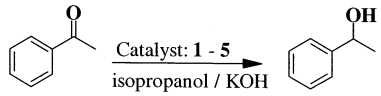
Bond lengths			
Ru(1)–O(1)	2.050(3)	Ru(1)–C(2)	2.187(5)
Ru(1)–N(1)	2.136(3)	Ru(1)–C(4)	2.195(4)
Ru(1)–C(6)	2.172(4)	Ru(1)–C(5)	2.200(4)
Ru(1)–C(7)	2.174(4)	Ru(1)–Cl(1)	2.450(1)
Ru(1)–C(3)	2.181(4)	Ru(1)–C^0	1.673(5)
Bond angles			
O(1)–Ru(1)–N(1)	87.02(12)	N(1)–Ru(1)–C^0	131.51(18)
O(1)–Ru(1)–Cl(1)	84.75(11)	Cl(1)–Ru(1)–C^0	128.99(16)
N(1)–Ru(1)–Cl(1)	81.87(10)	O(1)–Ru(1)–C^0	126.56(19)

reduced Schiff base ligand. The methyl and the methoxy protons of the bidentate ligand appear as singlets near 2.4 and 3.9 ppm, respectively.

The complex [(η^6-*p*-cymene)RuCl(L^1)] has been structurally characterized by X-ray crystallography. An ORTEP [15] view of the complex is shown in Fig. 2. Selected bond distances and bond angles are given in Table 2. The complex has an essentially octahedral coordination geometry. The *p*-cymene ring carbons occupy one face of the octahedron leaving the other three sites to be coordinated by a chloride and the chelating N,O-donor reduced Schiff base ligand. The structural features correspond well to the analogous Schiff base ruthenium(II) complexes [16,17].

3.2. Catalytic properties

The catalytic hydrogenation of acetophenone in the presence of **1**–**5** has been studied in isopropanol–KOH medium using a mole ratio of 1:2.5:100 for the catalyst, KOH and the ketone in 5 cm^3 of isopropanol (Eq. (1)). The percent conversion is 70 and 72 for the complexes **1** and **2**, respectively. While complexes **3** and **4** show percent conversion of 98, the same is 93 for complex **5**. The high conversion rate could be due to the presence of bulky substituents adjacent to the donor atom of the reduced Schiff base ligands. Complex **3** has a bulky *t*-butyl group in the *ortho*-position of the phenolato ring. Complexes **4** and **5** have bulky groups like OMe at the *ortho*-position of the phenyl ring or the naphthyl group attached to the amine nitrogen.



(1)

Noyori and co-workers have shown that the true catalyst in the hydrogenation reaction is formally a 16-electron intermediate species [4]. The active catalyst precursor is, however, a hydride 18-electron species in a kinetically controlled reaction pathway. The role of KOH is to generate the catalyst from the chloro precursor and the reaction mediates through the hydride species. The steric bulk of the auxiliary ligand plays an important role in this hydrogenation process. It is likely that the NH proton of the auxiliary ligand is sufficiently acidic to undergo a facile elimination of HCl in the presence of KOH. This results in the formation of a reactive 16-electron species in which the metal is bound to both anionic oxygen and nitrogen atoms in addition to the *p*-cymene ring (6-electron donor). The stability of the planar geometry of this formally 16-electron neutral species may depend on the steric constraints generated by the bulky substituents or groups of the auxiliary ligand in the kinetically controlled reaction process.

4. Conclusions

We have prepared a series of (arene)ruthenium(II) reduced Schiff base complexes that are catalytically active in the hydrogenation of acetophenone to (±)-1-phenylethanol. The steric bulk of the auxiliary ligand has profound effect on the transfer hydrogenation process resulting high percent conversion. The complexes **3**–**5** having bulky substituents or groups attached to

the donor atoms of the auxiliary ligand show percent conversion > 90.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre (CCDC), CCDC No. 160646 for compound **1**. 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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