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Synthesis, characterization, and application to transfer hydrogenation of η^6 -(3,4,5-trimethoxybenzyl)- η^1 -N-heterocyclic carbene–ruthenium complex

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A new chelating ruthenium complex was synthesized using an electron-rich olefin and $[\text{RuCl}_2(p\text{-cymene})_2]$ and characterized structurally and spectroscopically. The structure of the complex was verified using X-ray crystallography. The complex displayed high activities in transfer hydrogenation.

Keywords: Transfer hydrogenation reaction; N-Heterocyclic carbene; Ruthenium; Chelating carbene

1. Introduction

Transfer hydrogenation, a potentially useful protocol for the reduction of ketones and aldehydes to their corresponding alcohols, has been extensively studied [1]. A large number of studies have appeared with transition metal-catalyzed enantioselective hydrogenation of ketones using 2-propanol or formic acid under basic conditions [2, 3], because the method has advantages, such as low cost, ease of handling, and high solubility of 2-propanol or formic acid as a hydrogen-donor reagent. The most active and versatile homogeneous catalytic *sec*-alcohol/ketone oxidation/reduction systems are the metal–ligand bifunctional ruthenium complexes developed by Noyori and co-workers [4–6]. A variety of related ligands and transition metal complex catalysts have been developed for this purpose [7, 8]. One of these ruthenium complexes is Ru(NHC) (NHC: N-heterocyclic carbene). N-heterocyclic carbene ligands appear particularly suited to this purpose, in that their ruthenium(II) complexes possess high thermal and hydrolytic stability [9].

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Recently, our research group has focused on N-heterocyclic carbene derivative ligands and their metal complexes with synthesis, characterization, crystal structure, and catalytic activity [10–14]. In this contribution, we pursue further work on the synthesis and characterization of chelating ruthenium(II) complex $[\text{RuCl}_2\{\eta^1\text{-CN}(\text{CH}_2\{\eta^6\text{-C}_6\text{H}_2(\text{OMe})_{3-3,4,5}\})\text{CH}_2\text{CH}_2\text{N}(\text{CH}_2\text{CH}_2\text{OMe})\}]$. The crystal structure of this new complex as well as its applications in transfer hydrogenation is described.

2. Experimental

2.1. Materials

Syntheses were carried out using standard Schlenk techniques under an inert argon atmosphere with previously dried solvents. The starting complex $[\text{RuCl}_2(p\text{-cymene})_2]$ was prepared by known methods [15]. Electron-rich olefin **1** was prepared according to Lappert's procedure [16].

2.2. Measurements

^1H - and ^{13}C -NMR spectra were performed in CDCl_3 using a Varian As 400 Merkur spectrometer operating at 400 MHz (^1H), 100 MHz (^{13}C). Chemical shifts (δ) are given in parts per million relative to TMS, coupling constants (J) in Hertz. Infrared (IR) spectra were recorded as KBr pellets from 400 to 4000 cm^{-1} on a ATI UNICAM 1000 spectrometer. Melting points were measured in open capillary tubes with an Electrothermal-9200 melting point apparatus and are uncorrected. Elemental analyses were performed by the Turkish Research Council (Ankara, Turkey) Microlab. All reactions were monitored on an Agilent 6890 N GC system by GC-FID with a HP-5 column of 30 m length, 0.32 mm diameter, and 0.25 μm film thickness.

2.3. Synthesis of $[\text{RuCl}_2\{\eta^1\text{-CN}(\text{CH}_2\{\eta^6\text{-C}_6\text{H}_2(\text{OMe})_{3-3,4,5}\})\text{CH}_2\text{CH}_2\text{N}(\text{CH}_2\text{CH}_2\text{OMe})\}]$ (**1**)

A solution of the electron-rich olefin (338 mg, 0.55 mmol) and ruthenium complex $[\text{RuCl}_2(p\text{-cymene})_2]$ (306 mg, 0.5 mmol) in degassed toluene (15 mL) was heated under reflux for 24 h. After the reaction mixture had been cooled at 25°C, *n*-hexane (15 mL) was added, and the formed solid was filtered and recrystallized from dichloromethane/hexane (10:20 mL) to give **1** as brown crystals. Yield 398 mg (83%); m.p. > 350°C; $\nu_{(\text{CN})} = 1510 \text{ cm}^{-1}$. ^1H NMR (399.9 MHz, CDCl_3) $\delta = 3.24$ (s, 3H, $\text{CH}_2\text{CH}_2\text{OCH}_3$), 3.56 and 3.89 (t, 4H, $J = 4.4$ Hz, $\text{NCH}_2\text{CH}_2\text{N}$), 3.69 and 3.93 (m, 4H, $\text{CH}_2\text{CH}_2\text{OCH}_3$), 3.93 and 3.98 (s, 9H, $\text{CH}_2\text{C}_6\text{H}_2(\text{OCH}_3)_{3-3,4,5}$), 4.16 (s, 2H, $\text{CH}_2\text{C}_6\text{H}_2(\text{OCH}_3)_{3-3,4,5}$), 4.78 (s, 2H, 4H, $\text{CH}_2\text{C}_6\text{H}_2(\text{OCH}_3)_{3-3,4,5}$). ^{13}C NMR (100.5 MHz, CDCl_3) $\delta = 48.7$ and 50.6 ($\text{NCH}_2\text{CH}_2\text{N}$), 49.8 ($\text{CH}_2\text{C}_6\text{H}_2(\text{OCH}_3)_{3-3,4,5}$), 51.7 ($\text{CH}_2\text{CH}_2\text{OCH}_3$), 54.7 and 56.5 ($\text{CH}_2\text{C}_6\text{H}_2(\text{OCH}_3)_{3-3,4,5}$), 58.3 ($\text{CH}_2\text{CH}_2\text{OCH}_3$), 74.6 ($\text{CH}_2\text{CH}_2\text{OCH}_3$), 99.2, 105.1, 109.9, 133.4, 138.4, and 153.0 ($\text{CH}_2\text{C}_6\text{H}_2(\text{OCH}_3)_{3-3,4,5}$), 201.9 (Ru=C) ppm. Anal. Calcd for $\text{C}_{16}\text{H}_{24}\text{Cl}_2\text{N}_2\text{O}_4\text{Ru}$ (480.35) (%): C, 40.01; H, 5.04; N, 5.83. Found (%): C, 40.10; H, 5.17; N, 5.85.

2.4. Typical procedure for transfer hydrogenation of ketones with **1**

Complex **1** (0.01 mmol), substrate (1.00 mmol), KOBu^t (5 mmol%), and 2-propanol (10 mL) were added to a Schlenk tube under argon. The solution was heated at 80°C for 12 h. The solvent was then removed under reduced pressure and the crude product was purified by column chromatography on silica gel (60–120 mesh) using ethylacetate/*n*-hexane (1 : 5) as eluent to afford the *sec*-alcohols. Purity of compounds is checked by NMR and conversion and ratios were monitored by gas chromatography (GC) and gas chromatography–mass spectrometry (GC–MS).

2.5. Crystallography

For the crystal structure determination, a single crystal of **1** was used for data collection on a four-circle Rigaku R-AXIS RAPID-S diffractometer equipped with a 2-D area IP detector. The graphite-monochromated Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$) and oscillation scans technique with $\Delta\omega = 5^\circ$ for one image were used for data collection, by varying ω with three sets of different χ and φ values. Hundred and eight images for six different runs covering about 99.8% of the Ewald spheres were performed. The lattice parameters were determined by least-squares methods on the basis of all reflections with $F^2 > 2\sigma(F^2)$. Integration of the intensities, correction for Lorentz and polarization effects and cell refinement were performed using Crystal Clear software [17]. The structure was solved by direct methods using SHELXS97 [18] in the WinGX package [19] and refined using SHELXL97 [18]. All non-hydrogen atoms were refined, first with isotropic and then with anisotropic thermal displacement parameters by full-matrix least-squares. All hydrogens were placed geometrically and refined as riding with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. PLATON drawing [20] of the molecule with 50% probability displacement thermal ellipsoids and atomic-numbering scheme is shown in figure 1. PLATON drawing [20] of the hydrogen-bonding geometry is shown in figure 2. The crystal and experimental data are given in table 1; final atomic parameters are given in Supplementary material. Selected bonds and angles are given in table 2.

3. Results and discussion

3.1. Synthesis and characterization

The reaction of the electron-rich olefin with $[\text{RuCl}_2(p\text{-cymene})]_2$ in dry toluene resulted in **1** as a crystalline solid (scheme 1). The spectroscopically pure Ru(NHC) complex, which is very stable in the solid state, was characterized by analytical and spectroscopic techniques. FT-IR spectroscopy, ¹H- and ¹³C-NMR spectroscopy, and elemental analysis data of **1** confirm the proposed structure.

The ¹³C-NMR spectrum of the title compound shows characteristic coordinated carbene signal at 201.9 ppm, in the typical range observed for Ru–NHC complexes. The IR data for **1** clearly indicate the presence of the C–N with a ν_{CN} vibration at 1510 cm^{-1} .

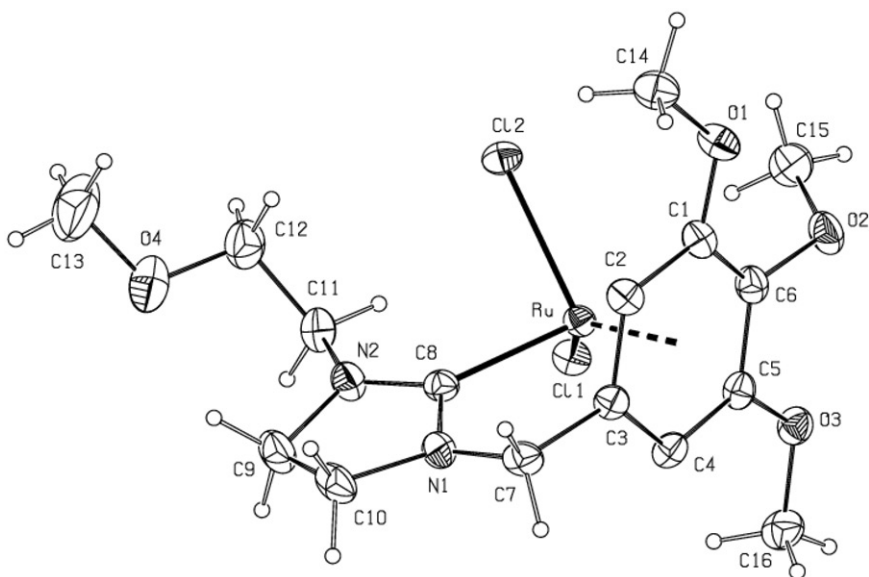


Figure 1. PLATON drawing of **1** with 50% probability displacement thermal ellipsoids and atomic-numbering scheme.

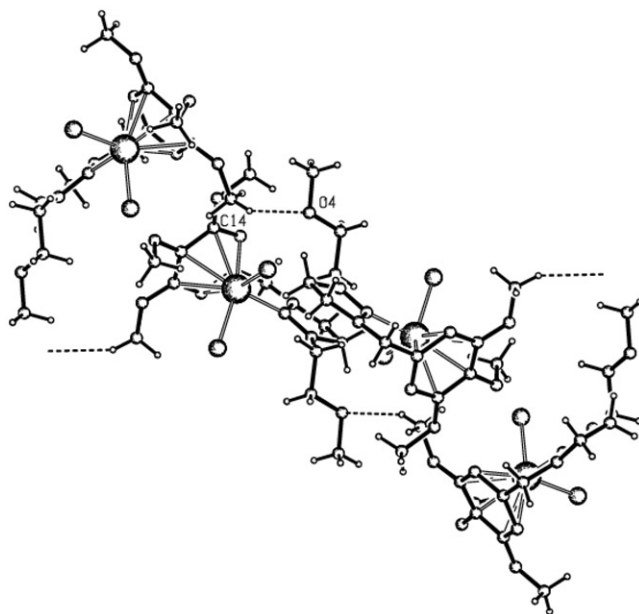


Figure 2. PLATON drawing of the hydrogen-bonding geometry.

3.2. X-ray crystal structure of **1**

The molecular structure of **1** was confirmed by the single-crystal X-ray structure determination; the atom-numbering scheme is shown in figure 1. The coordination

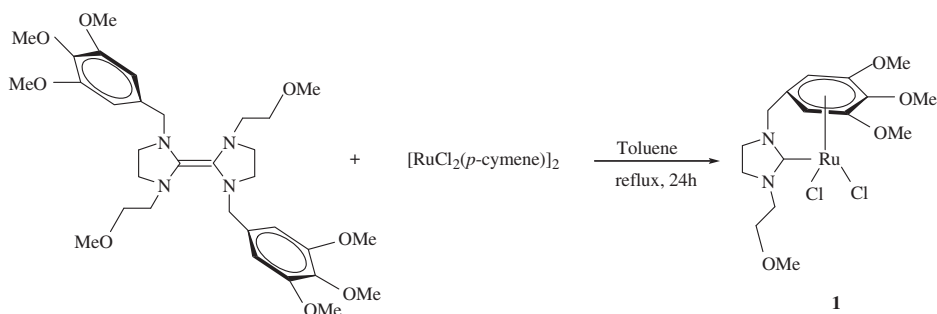
Table 1. Crystal and experimental data.

Chemical formula	C ₁₆ H ₂₂ Cl ₂ N ₂ O ₄ Ru
Formula weight	478.33
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>
Unit cell dimensions (Å, °)	
<i>a</i>	7.9100 (12)
<i>b</i>	20.8560 (13)
<i>c</i>	11.6410 (12)
α	92.069 (2)
Volume (Å ³), <i>Z</i>	1919.2 (4), 4
Calculated density (g cm ⁻³)	1.655
Absorption coefficient (mm ⁻¹)	1.118
<i>F</i> (000)	968
Crystal size (mm ³)	0.25 × 0.20 × 0.25
θ_{\max} (°)	26.40
Index range	$-8 \leq h \leq 9$; $-26 \leq k \leq 26$; $-14 \leq l \leq 14$
Number of reflections used	3868 ($I \geq 2\sigma(I)$)
Number of parameters	230
<i>R</i> _{int}	0.066
<i>R</i>	0.0396
<i>R</i> _w	0.0936
Goodness-of-fit	1.11
$\Delta\rho_{\min}, \Delta\rho_{\max}$ (e Å ⁻³)	-0.678, 0.695

Table 2. Selected bond lengths (Å) and angles (°).

	Ru	Cg ^a	1.7193(16)
	Ru	C1/1	2.4335(10)
	Ru	C1/2	2.4089(11)
	Ru	C8	2.038(4)
Cg	Ru	C1/1	124.47(5)
Cg	Ru	C1/2	125.97(6)
Cg	Ru	C8	120.72(12)
C1/1	Ru	C1/2	89.43(3)
C1/1	Ru	C8	94.01(11)
C1/2	Ru	C8	91.71(11)

^aCg is centroid of six-membered (C1–C6) ring.

Scheme 1. Preparation of (η^6 -arene- η^1 -carbene)RuCl₂.

around Ru is distorted octahedral. **1** crystallizes in the monoclinic space group $P21/n$ with ruthenium coordinated by heterocyclic carbene of the benzimidazole ring, two chlorides, and the η^6 -(3,4,5-trimethoxybenzyl) ring. There is a centroid (C_g) of the ring involving C1–C6. The distance between Ru and C_g is 1.7193(16) Å. The bond lengths between Ru and C1–C6 range from 2.090(4) to 2.320(4) Å. The bond angles around Ru range from 89.43(3)° [C1–Ru–C1] to 125.97(6)° [C $_g$ –Ru–C1]. There are three methoxy groups connected to C_g ring. The C=O and O–Me bond lengths are [1.327(5), 1.441(5) Å], [1.378(4), 1.409(6) Å], and [1.346(4), 1.420(15) Å], respectively. The dihedral angle between C_g and N1/C8/N2/C9/C10 ring is 91.74(13)°. The maximum deviations from mean plane of the atoms for C_g and N1/C8/N2/C9/C10 are –0.033(5) Å for C6 and 0.093(5) Å for C10, respectively. The important torsion angles are –68.9(5)° for N2/C11/C12/O4 and 177.0(2)° for C11/C12/O4/C13. There are intermolecular hydrogen bonds between oxygen and methyl [C14–H14A 0.96 Å, H14A \cdots O4ⁱ 2.49(5) Å, C14 \cdots O4ⁱ 3.383(6) Å, C14–H14A \cdots O4ⁱ 154(4)°, symmetry code $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$].

3.3. Catalytic properties

3.3.1. Procedure for the transfer hydrogenation of ketones. Transfer hydrogenation has high atom efficiency, no need of pressure, and economic as well as environmental advantages. Different carbene or carbene–phosphine systems containing Rh [21], Ir [22], and Ru [23, 24] have been reported. Due to economical benefit of ruthenium compared to rhodium or iridium and the advantages of phosphine-free systems, it is important to search for more active ruthenium carbene catalysts. We report the application of a ruthenium–NHC catalytic system in reduction of different acetophenone derivatives. To determine the most suitable reaction conditions for transfer hydrogenation, we studied the reactivity of acetophenones (1.0 mmol) in the presence of 0.01 mmol catalyst at 80°C. The use of bases such as Cs₂CO₃, K₃PO₄, and KOBu^t resulted in reasonable conversions to the products. KOBu^t afforded somewhat better selectivity. We have demonstrated higher yields from Ru–NHC-catalyzed transfer hydrogenation of ketones (table 3, entries 1, 3, and 5) such as *p*-bromo acetophenone and acetophenones. Transfer hydrogenation has been further explored for catalytic potential in the reduction of other aryl and alkyl ketones with reaction conditions similar to those used in the transfer hydrogenation of acetophenone [22–25].

4. Conclusion

This investigation demonstrates the synthesis and characterization of a chelating Ru–NHC complex whose structures were confirmed by ¹H-NMR, ¹³C-NMR, IR, elemental analysis, and X-ray diffraction. The complex showed activity in transfer hydrogenation. Our studies are focused on developing ruthenium (NHC) complex catalysts that display good catalytic activity under even milder reaction conditions, such as C–H activation and transfer hydrogenation reactions.

Table 3. Catalytic transfer hydrogenation with **1** for acetophenones with 2-propanol.

Entry	Substrate	Product	Yield % ^a
1			97
2			78
3			94
4			82
5			98

^aReaction conditions: 1.0 mmol of acetophenone, 5.0 mmol% KOBu^t, 0.01 mmol Ru catalyst, 2-propanol (10 mL), 12 h at 80°C; purity of compounds was checked by NMR and all reactions were monitored by GC and GC-MS.

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