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Half-sandwich ruthenium(II) complexes containing 4-substituted aniline derivatives: structural characterizations and catalytic properties in transfer hydrogenation of ketones

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Abstract
Four half-sandwich Ru(II) complexes (1)–(4) with the general formulae [Ru(η^6-*p*-cymene)(L)Cl_2] were synthesized by the reaction of one equivalent of the Ru(II) *p*-cymene dimer with two equivalents of a *p*-substituted aniline derivative L (where L is *p*-methyl, *p*-isopropyl, *p*-methoxy, or *p*-hydroxy aniline). The structures of complexes (2)–(4) were determined by single-crystal X-ray diffraction studies. The structural analysis revealed piano-stool geometry at the Ru(II) ions which are coordinated to the η^6-*p*-cymene, two chloride anions and the amine group of the aniline ligand. In the structure of (2)–(4), the coordinated chloride ions make intermolecular hydrogen bonding with the $–NH_2$ group of an adjacent molecules (NH–Cl) resulting in hydrogen bond networks. The catalytic activities of the complexes in transfer hydrogenation of acetophenone were studied. Complex [Ru(η^6-*p*-cymene)(*p*-methylaniline)Cl_2] (1) showed the best catalytic performance in the transfer hydrogenation of acetophenone. The presence and positions of methyl and bromide groups on the acetophenone have an impact on the catalytic activity in transfer hydrogenation properties of the complex (1). Moreover, catalytic activity of the complex (1) is significantly higher in the transfers hydrogenation of cyclohexanone than 2-hexanone.

Introduction

Reduction of aldehydes and ketones to alcohols is an important transformation for the production of many industrial chemicals such as esters, acetals, and acids, which are commonly used in the chemical industry and in pharmaceutical applications [1–4]. Metal hydride reduction (often with $NaBH_4$ and $LiAlH_4$), direct hydrogenation, and catalytic transfer hydrogenation are the three general methods used to achieve this transformation. Hydride reagents are very effective; however, the metal hydride reduction produces stoichiometric amounts of waste requiring appropriate disposal, which is neither environmentally nor economically sustainable [5–8]. Direct hydrogenation is also a popular method that provides clean reaction and proceeds in high yield, yet it has some drawbacks such as the use of hydrogen gas and requirement for high-pressure reactors [8, 9]. Catalytic transfer hydrogenation has been developed in order to overcome those disadvantages [10]; the hydrogen atoms transferred in the reaction are generally provided from another molecule (hydrogen donor), which also acts as a solvent in the presence of a catalyst [11]. Suitable hydrogen donors include propan-2-ol, glycerol and formic acid/triethylamine mixtures [12–14]; propan-2-ol is usually preferred due to its lower environmental impact and because many catalysts can survive even in refluxing 2-propanol [15]. While aluminium alkoxide was previously used to catalyze the reduction of ketones to the corresponding alcohols, more recent powerful catalysts for transfer hydrogenation of ketones are based on transition metals such as rhodium, iridium, and ruthenium [16–18]. The development of novel catalysts for catalytic transfer hydrogenation of ketones is now focussed on the use of ruthenium-based complexes as ruthenium is relatively cheaper than rhodium and iridium. However, in many cases the Ru-catalysts required are complicated and require multi-step ligand design [19–26]. Noyori and co-workers reported extremely efficient ruthenium bifunctional catalyst [$RuCl_2$(diphosphane)(diamine)] for the enantioselective reduction of ketones in the presence of a base [27]. This pioneering catalytic system has allowed the preparation of alcohols with high optical purity [28]. In this catalytic system, the proper matching of a chiral ruthenium diphosphine

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with the correct enantiomer of diamine is the key point for enantioselective catalysts [29]. It was discussed that the presence of primary amino donors is important for the catalytic cycle where the hydride on ruthenium and proton on nitrogen attack the polar bond [30].

Due to the importance of the primary amine group in the catalytic transfer hydrogenation of ketones, we prepared four half-sandwich Ru(II) complexes (1)-(4) derived from [Ru(η^6-*p*-cymene)Cl_2]$_2$ and *p*-substituted aniline derivatives with the general formulae [Ru(η^6-*p*-cymene)(L)Cl_2] (where L is *p*-methyl, *p*-isopropyl, *p*-methoxy, or *p*-hydroxy aniline) and used as catalysts for the transfer hydrogenation of ketones. The complexes were characterized by FT-IR, UV–Vis. and ^{1}H-NMR spectroscopies, and the structures of (2)–(4) were determined by X-ray crystallography.

Experimental

Starting materials [Ru(η^6-*p*-cymene)Cl_2]$_2$, *p*-methylaniline, *p*-isopropyl aniline, *p*-methoxy aniline, and *p*-hydroxyl aniline were purchased from commercial sources and used as received. FT-IR spectra of the complexes recorded taken on a PerkinElmer Spectrum 100 FT-IR, and FT-IR spectra are given in the supplementary documents (Figs. S1–S4). The UV–Vis. absorption spectra were recorded on a PerkinElmer Lambda 45 spectrophotometer. ^{1}H-NMR spectra were measured on Bruker Avance III 400 MHz spectrometer using d_6-DMSO as solvent. Catalytic conversion of ketones to alcohols was monitored by GC using a YL6500 Instrument.

Synthesis of the complexes

The para-substituted aniline derivative (0.326 mmol) in ethanol (5 mL) was added dropwise to a refluxing solution of [Ru(η^6-*p*-cymene)Cl_2]$_2$ (100 mg, 0.16 mmol) in ethanol (15 mL). The reaction solutions were refluxed for 24 h. Upon cooling to 298 K, the solvent volume was reduced to 5 mL. Red crystals formed in three days and were filtered and dried in air.

[Ru(η^6-*p*-cymene)(*p*-methylaniline)Cl_2] (1): Yield: 84%, Colour: Red, M.p.: 229 °C (decomposed), Elemental analysis (Calculated for $C_{17}H_{23}NCl_2Ru$): C: 49.40, H: 5.61; N: 3.39; Found: C: 49.18, H: 5.42, N: 3.11, ^{1}H-NMR: 1.21 (6H, d, C(CH_3)$_2$ *p*-cymene), 2.10 (3H, s, Ph–CH_3 *p*-cymene), 2.12 (3H, s, Ph–CH_3 aniline), 2.83 (1H, septet, CH(CH_3)$_2$ *p*-cymene), 4.84 (2H, s, NH_2 aniline), 5.82 (4H, d, CH *p*-cymene), 6.48 (2H, d, (CH aniline), 6.83 (2H, d, (CH aniline), FT-IR (cm^{-1}): 3323, 3200, 3120, 3040, 2956, 2861 1610, 1578, 1515, 1467, 1375, 1225, 1135, 1105,1086, 1049, 876, 819, 7450, 668, 546, 450.

[Ru(η^6-*p*-cymene)(*p*-isopropylaniline)Cl_2] (2): Yield 82%, Colour: Red, M.p. 199 °C (decomposed), Elemental analysis (Calculated for $C_{19}H_{27}NCl_2Ru$): C: 51.70, H: 6.17; N: 3.17; Found: C: 51.22, H: 6.02, N: 3.02, ^{1}H-NMR: 1.13 (6H, d, C(CH_3)$_2$ aniline), 1.20 (6H, d, C(CH_3)$_2$ *p*-cymene), 2.09 (3H, s, Ph–CH_3 *p*-cymene), 2.71 (1H, septet, CH(CH_3)$_2$ *p*-cymene), 2.84 (1H, septet, CH(CH_3)$_2$ *p*-cymene), 4.88 (2H, s, NH_2 aniline) 5,79 (4H, d, CH *p*-cymene), 6.50 (2H, d, CH aniline), 6.87 (2H, d, CH aniline). FT-IR (cm^{-1}): 3203, 3104, 2953, 2865, 1608, 1600, 1505, 1465, 1378, 1230, 1119, 1053,1005, 882, 839, 568.

[Ru(η^6-*p*-cymene)(*p*-methoxyaniline)Cl_2] (3): Yield: 87%, Colour: Red, M.p. 199 °C (decomposed), Elemental analysis (Calculated for $C_{17}H_{23}NOCl_2Ru$): C: 47.56, H: 5.40; N: 3.26; Found: C: 47.31, H: 5.12, N: 3.01, ^{1}H-NMR: 1.19 (6H, d, C(CH_3)$_2$ *p*-cymene), 2.09 (3H, s, Ph–CH_3 *p*-cymene), 2.84 (1H, septet, CH(CH_3)$_2$ *p*-cymene), 3.62 (3H, s, OCH_3), 4.75 (2H, s, NH_2), 5.81 (4H, d, CH *p*-cymene), 6.64 (2H, d, CH aniline), 6.66 (2H, d, CH aniline). FT-IR (cm^{-1}): 3283, 3810, 3100, 2947, 1596, 1579, 1510, 1453, 1305, 1247, 1167, 1096, 1024, 876, 827, 736, 544.

[Ru(η^6-*p*-cymene)(*p*-hydroxyaniline)Cl_2] (4): Yield: 85%, Colour: Red, M.p.: 195 °C (decomposed), Elemental analysis (Calculated for $C_{16}H_{21}NOCl_2Ru$): C: 46.27, H: 5.10; N: 3.37; Found: C: 46.05, H: 4.95, N: 3.12, ^{1}H-NMR: 1.20 (6H, d, C(CH_3)$_2$ *p*-cymene), 2.09 (3H, s, Ph–CH_3 *p*-cymene), 2.82 (1H, septet, CH(CH_3)$_2$ *p*-cymene),4.43(2H, s, NH_2 aniline), 5.81 (4H, d, CH *p*-cymene), 6.41–6.43(4H, d, CH aniline), 8.34 (1H, b, OH aniline). FT-IR (cm^{-1}): 3341, 3255, 3187, 3101, 2960, 1612, 1600, 1569, 1501, 1511, 1458, 1375, 1357, 1255, 1214, 1119, 834, 803, 759, 663,573, 542.

X-ray crystallography

X-ray crystallographic data for complexes (**2**)-(**4**) were collected at 293 (2) K on a Bruker D8 QUEST diffractometer using Mo-$K\alpha$ radiation ($\lambda = 0.71073$ Å). Data reduction was performed using Bruker SAINT [31, 32]. SHELXT 2018/2 was used to solve and SHELXL-2018/3 to refine the structures [33, 34]. The structures were solved by direct methods and refined on F^2 using all the reflections. All the non-hydrogen atoms were refined using anisotropic atomic displacement parameters, and hydrogen atoms bonded to carbon, nitrogen, and oxygen atoms were inserted at calculated positions using a riding model and refined with temperature factors. The crystal data and refinement details are given in Table 1. Hydrogen bond parameters are given in the supplementary file (Tables S1–S3).

Transfer hydrogenation of ketones

The acetophenone derivative (1 mmol) was dissolved in in 2-propanol (9.4 mL) followed by addition of base and catalyst (5 mg). The reaction mixture was stirred at 82 °C. Samples from the reaction solution were collected periodically,

Table 1 X-ray crystallographic data for the compounds

Complex	(2)	(3)	(4)
Formulae	$C_{19}H_{27}Cl_2NRu$	$C_{17}H_{23}Cl_2Nru$	$C_{16}H_{21}Cl_2NORu$
Molecular weight	441.38	429.33	415.31
Temperature	293(2) K	293(2) K	293(2) K
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å
Crystal system	*Triclinic*	*Monoclinic*	*Monoclinic*
Space group	*P-1*	*C2/c*	*$P2_1/n$*
Unit cell parameters	a = 7.81510(10) Å α = 96.0000(10)°	a = 15.8030(5) Å α = 90°	a = 9.9076(4) Å α = 90°
	b = 9.04110(10) Å β = 98.9440(10)°	b = 27.4023(6) Å β = 97.455(3)°	b = 28.1896(11) Å β = 105.837(5)°
	c = 15.4559(2) Å γ = 108.2440(10)°	c = 17.5361(5) Å γ = 90°	c = 12.5573(6) Å γ = 90°
Volume ($Å^3$)	1010.81(2)	7529.6(4)	3374.0(3)
Z	2	16	8
Density(calc.) (Mg/m^3)	1.450	1.515	1.635
Absorption coefficient (mm^1)	1.039	1.117	1.244
Crystal size (mm^3)	0.22 × 0.15 × 0.11	0.15 × 0.11 × 0.09	0.16 × 0.14 × 0.13
Ref. collected	14,026	51,662	13,183
Independent ref	4751 [R(int) = 0.0282]	9208 [R(int) = 0.0467]	7627 [R(int) = 0.0602]
Final R values [I > 2sigma(I)]	R1 = 0.0251, wR2 = 0.0624	R1 = 0.0417, wR2 = 0.0815	R1 = 0.0697, wR2 = 0.1700
R indices (all data)	R1 = 0.0276, wR2 = 0.0643	R1 = 0.0597, wR2 = 0.0880	R1 = 0.1083, wR2 = 0.2023
Completeness to θ = 25.242°	99.8%	99.8%	99.1%
CCDC Number	1,956,820	1,956,821	1,956,822

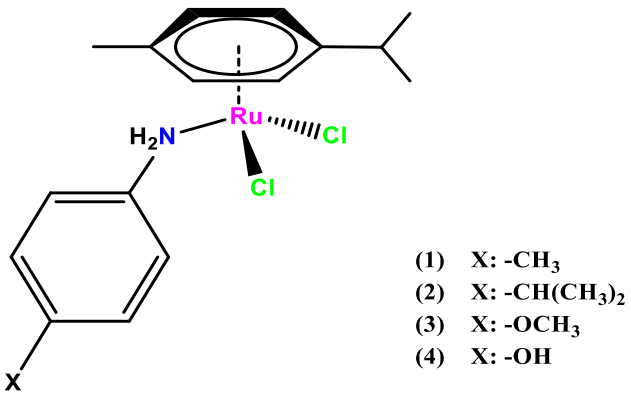


Fig. 1 The structures of half-sandwich Ru(II) (**1**)–(**4**) complexes

and conversion rates were determined on GC using a HP-5 column.

Results and discussion

In this work, four mononuclear Ru(II) complexes were obtained from the reaction of one equivalent of $[Ru(\eta^6\text{-}p\text{-cymene})Cl_2]_2$ dimer with two equivalents of *p*-substituted aniline derivatives [*p*-methyl, *p*-isopropyl, *p*-methoxy, or *p*-hydroxyl aniline] (Fig. 1) in high yield and purity. The structures of the synthesized complexes were determined by ^{1}H-NMR, FT-IR (Figs. S1–S4) and elemental analysis. Single crystals of the synthesized complexes were obtained, and their structures were illuminated by single-crystal X-ray diffraction studies.

In order to characterize the new complexes, ^{1}H-NMR spectra were recorded in d_6-DMSO solvent (Figs. S5–S8). Hydrogen signals due to the *p*-cymene ligands were observed in similar regions in each complex. The hydrogen signals due to the isopropyl ($–CH(CH_3)_2$) group in the *p*-cymene ligand were observed as multiplets (CH septet and $–CH_3$ doublet) in the ranges 1.20–1.21 and 2.82–2.84 ppm, respectively. The methyl group hydrogens ($–CH_3$) on *p*-cymene ligand were observed as singlets at around 2.09–2.12 ppm. Multiplets at 5.79–5.82 ppm are due to the aromatic hydrogens of *p*-cymene. The coordinated NH_2 groups in the aniline ligands resulted in broad signals in the range 4.43–4.88 ppm. In the spectrum of $[Ru(\eta^6\text{-}p\text{-cymene})(p\text{-methylaniline})Cl_2]$ (1), the singlet signal at 2.12 ppm is due to the methyl group hydrogens on the aniline ring. A doublet at 1.13 and a septet at 2.71 ppm are seen in the spectrum of $[Ru(\eta^6\text{-}p\text{-cymene})(p\text{-isopropylaniline})Cl_2]$ (2) due to the isopropyl hydrogens on the aniline ring (CH and CH_3), respectively. The methoxy group hydrogens on the aniline ring in the spectrum of $[Ru(\eta^6\text{-}p\text{-cymene})(p\text{-methoxyaniline})Cl_2]$ (3) are seen as a singlet at 3.62 ppm. The phenolic OH hydrogen in the spectrum of $[Ru(\eta^6\text{-}p\text{-cymene})(p\text{-hydroxyaniline})Cl_2]$ (4) appears as a singlet at 8.34 ppm. The ^{1}H NMR spectra and integration suggest that there were no significant organic impurities in the samples.

UV–Vis absorption spectra of the complexes were studied in MeOH (10^{-4} mol L^{-1}), and the spectra of the complexes are shown in Fig. S9. The complexes exhibit two broad absorption bands: the first band was observed in the 370–550 nm range and can be assigned to π-π* electronic transitions; weaker band observed at 550–700 nm is assigned to the ligand–metal charge transfer transition.

Molecular structures of complexes (2)–(4)

The structure of complex (1) was previously reported [36]. Here, we report the structures of complexes (2)–(4) for the first time. Quality crystals of complexes (2)–(4) suitable for single-crystal X-ray diffraction study were obtained from slow evaporation of solvent from the reaction solution over a few days. The X-ray crystallographic data for complexes (2)-(4) are summarized in Table 1. The structure of (2) was solved in triclinic unit cell, while the structures of complexes (3) and (4) were solved in monoclinic unit cell. The asymmetric unit of (2) contains a single molecule; however, there are two independent molecules in the asymmetric units of complexes (3) and (4). The structures of the complexes are shown in Fig. 2. The bond lengths and angles in the independent molecules are almost identical with different orientation of methoxy group in (3) and opposite alignment of the phenol unit in (4). In the structures of all three complexes, each Ru(II) coordinates to the η^6-*p*-cymene, two chloride anions and the amine group of *p*-substituted aniline ligands with piano-stool geometry. The ruthenium Ru(II) ion is *π*-bonded to the *p*-cymene ligand. The Ru–C distances in the complexes are in the range of 2.139(7) and 2.2284(19) Å (Table 2) and the distance between the centroid of phenyl ring (C1/C6) and Ru(II) is about 1.66 Å which is similar to those reported Ru(II) η^6-arene complexes [35, 36]. The Cl–Ru–Cl and Cl–Ru–N bond angles are comparable with the literature values [35, 36].

Although the coordination cores of the complexes are similar, the molecular packing shows distinct features due to different intermolecular interactions. In the structure of complex (2), the coordinated chloride ions are involved in intermolecular hydrogen bonding with the NH_2 group of an adjacent molecule (NH–Cl) and these hydrogen bond contacts make 1D hydrogen bond chains along the *ac* plane (Fig. S10). The hydrogen bonded chains are further linked by CH–Cl interactions. In the structure of complex (3), while one of the coordinated chloride ions (Cl1) makes an intermolecular hydrogen bond with the $–NH_2$ group of an adjacent molecule (Cl–HN), the other chloride ion (Cl2) makes two hydrogen bonds with the $–NH_2$ groups of two adjacent molecules. These hydrogen bond contacts connect four complex molecules into hydrogen bond cluster (Fig. S11a). The hydrogen bonded clusters are further linked by Cl–HC and O–HC (Fig. S11b). In the structure of complex (4), the phenol units of the two independent complex molecules make different hydrogen bonding interactions. While the phenol unit (O1H) of complex containing Ru1 involves only one hydrogen bonding interaction (as donor) with the coordinated chloride (Cl4) anion of an adjacent molecule, the phenol unit (O2H) of the other molecule containing Ru2 makes two hydrogen bonds (as donor with the coordinated chloride (Cl3) anion of an adjacent molecule and as acceptor with the amine NH_2 group of a neighbouring molecule forming a 2D hydrogen bond network (Fig. S12).

Catalytic studies

The catalytic activities of the half-sandwich Ru(II) complexes were investigated in transfer hydrogenation reactions. In order to determine the best catalysts among the complexes, the acetophenone 1-phenylethanol reduction was chosen as a model reaction. It was performed with 100:1 substrate/complex ratios in the presence of a base (0.1 mol L^{-1} NaOH) with isopropanol as a solvent and hydrogen source (Fig. 3). The reactions were stirred at 82 °C for 90 min. and samples from the reaction solutions were subjected to GC analysis to determine percentage (%) conversion. The catalytic performances of the complexes for acetophenone 1-phenylethanol transformation are given in Table S4. The data showed that the substituent groups in the *para* position of the aniline ligands have an impact in the catalytic transfer hydrogenation reaction. Complex (1) exhibited the highest catalytic activity for acetophenone 1-phenylethanol with 56% conversion at the end of 90 min. Therefore, complex (1) was chosen to optimize the catalytic reaction conditions. The effects of base type, amounts, and substituent groups on the ketone compounds were studied in order to establish the best catalytic conditions. The lowest activity (17%) of compound (4) may be assigned to the phenolic –OH group in the para position of aniline ligand. The phenolic group can involve in hydrogen bonding interaction with acetophenone, which can hinder the interaction of the metal centre with the substrate.

In the catalytic transfer hydrogenation reactions, a base additive is used in order to stimulate metal hydride formation to initiate transfer hydrogenation reactions [37]. The Ru(II)-based catalytic transfer hydrogenation mechanism was well established in the literature [38]. The N–H functionality is important as they activate the C = O double bond towards H^- acceptance through N–H–O hydrogen bonding interactions [39]. In the absence of a base, the same reaction occurs with only very small conversion rates. Bases NaOH, KOH, NaO^{i}Pr, or KO^{t}Bu (0.4 mL, 0.1 mol L^{-1}) were used for acetophenone reduction to 1-phenylethanol under the reaction conditions described above (Table S5). It was seen that the introduction of a base to the reaction vessel considerably increases the conversion rate. The conversion rates were found to vary in the following order

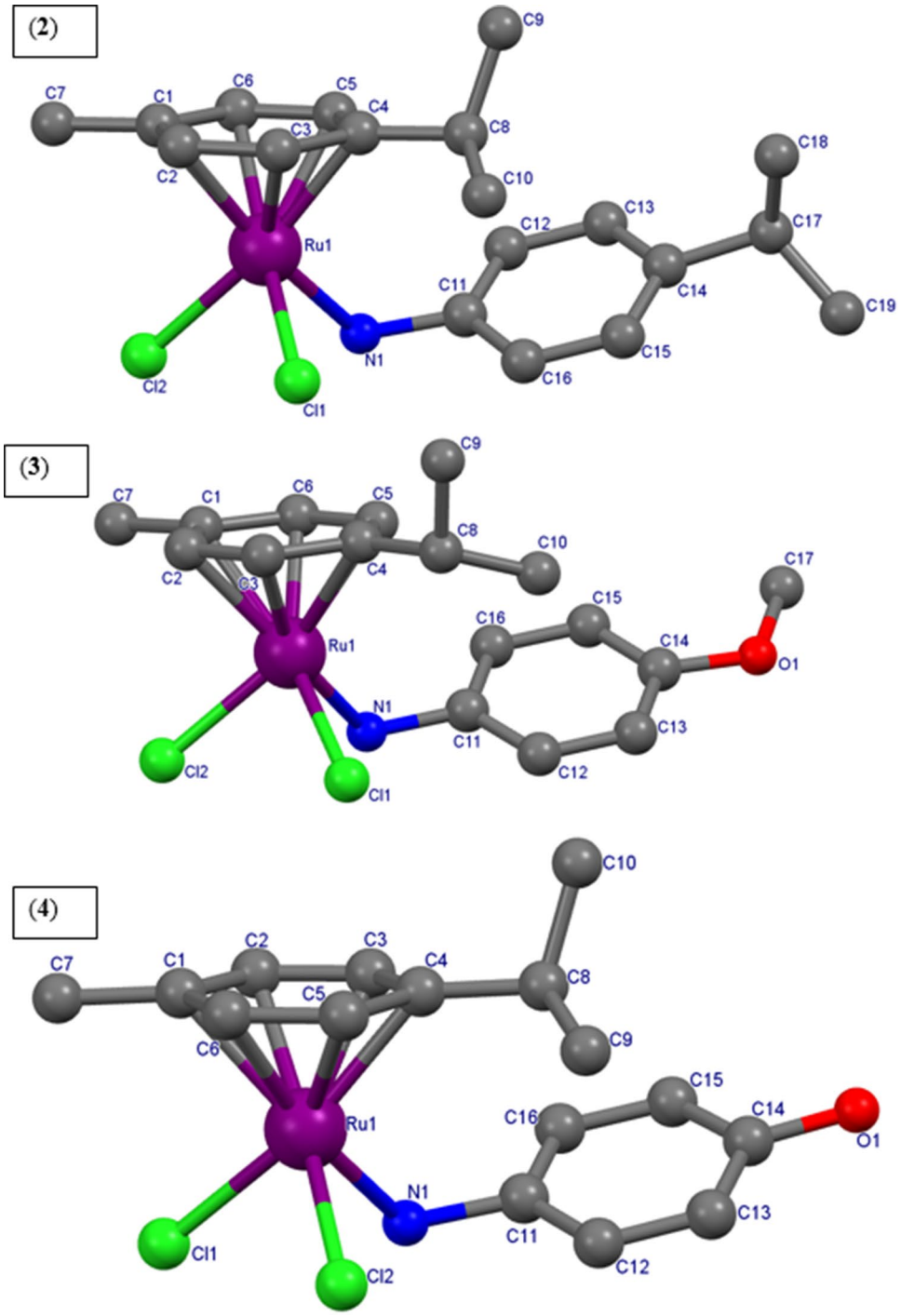


Fig. 2 Molecular structures of the complexes (**2**)–(**4**) with atom numbering. Hydrogen atoms are omitted for clarity

$KO^tBu > NaOH > KOH > NaO^iPr$. The amount of base also influences the catalytic activity of the complex. Increasing the amount of base KO^tBu ($0.1 mol L^{-1}$) from 0.2 to 0.6 mL improved catalytic activity observed in the presence of 0.6 mL KO^tBu (Table S6), but further increase in the amount of base did not affect the catalytic activity.

The catalytic activity of the complex (1) was investigated for transfer hydrogenation reactions of acetophenone derivatives containing different substituent groups (Table 3). Methyl groups ($–CH_3$) at the *ortho*, *meta*, and *para* positions of the acetophenone phenyl ring were tested, and % conversions (from ketone to corresponding alcohol) were measured at the end of four hours. The electron-donating methyl group at the *ortho*, *meta*, and *para* positions slightly decreased the catalytic activity when compared to the non-substituted acetophenone. The presence and position of a bromide group on the acetophenone also had an impact on the catalytic activity. Although the bromide group has electron withdrawing

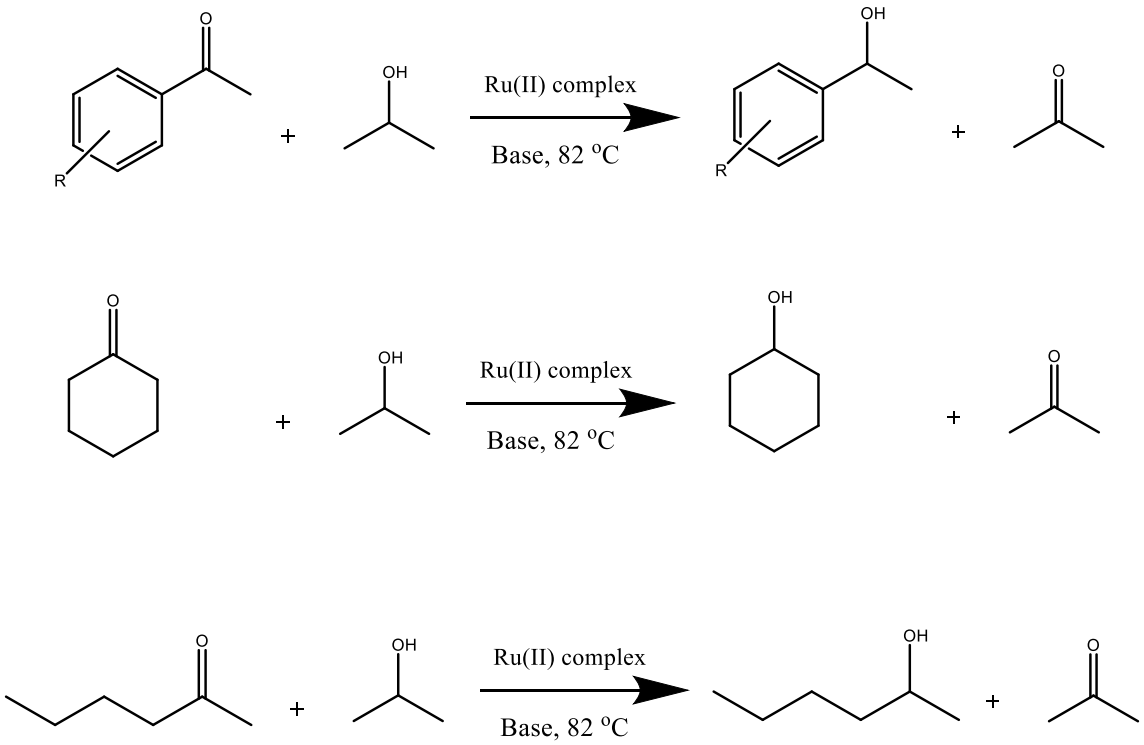


Fig. 3 Catalytic transfer hydrogenation reaction of acetophenone derivatives

Table 2 Selected bond lengths (Å) and angles (°) for complexes

	(2)	(3)	(4)
Ru(1)-C(1)	2.2284(19)	2.192(4)	2.221(7)
Ru(1)-C(2)	2.1924(19)	2.175(4)	2.171(7)
Ru(1)-C(3)	2.1514(19)	2.171(4)	2.139(7)
Ru(1)-C(4)	2.1864(19)	2.202(4)	2.221(7)
Ru(1)-C(5)	2.1420(19)	2.160(4)	2.165(7)
Ru(1)-C(6)	2.1885(19)	2.148(4)	2.198(8)
Ru(1)-N(1)	2.1793(15)	2.179(3)	2.164(6)
Ru(1)-Cl(1)	2.4024(5)	2.4181(9)	2.4167(18)
Ru(1)-Cl(2)	2.4189(5)	2.4104(10)	2.4208(19)
Cl(1)-Ru(1)-Cl(2)	87.078(18)	88.05(4)	86.78(7)
N(1)-Ru(1)-Cl(1)	83.65(4)	84.93(8)	79.39(16)
N(1)-Ru(1)-Cl(2)	80.28(4)	80.64(8)	84.05(17)

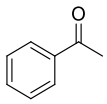
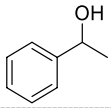
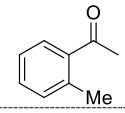
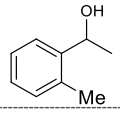
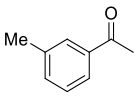
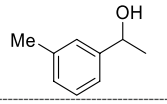
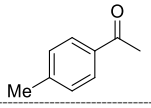
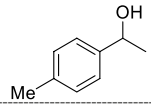
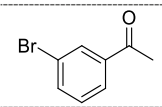
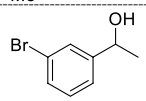
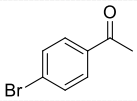
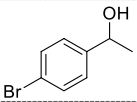
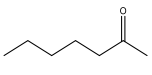
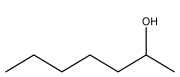
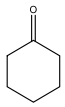
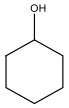
properties, the bromide group at the *para* position of acetophenone did not significantly change the %conversion when compared to the *para* methyl-substituted acetophenone. However, when the bromide group is located at the *meta* position, the catalytic activity dropped dramatically and 53% conversion was obtained at the end of four hours.

Complex [Ru(η^6-*p*-cymene)(*p*-methylaniline)Cl_2] (1) was further investigated for its catalytic activity in transfer hydrogenation of aliphatic (2-hexanone) and its cyclic analogue (cyclohexanone) (Fig. 3). The catalytic conversion values for 2-hexanone to product 2-hexanol and cyclohexanone to product cyclohexanol for complex (1) are given in Table 3. For transfer hydrogenation of 2-hexanone, %conversion was 67% at the end of four hours. Under the same reaction conditions, the conversion of cyclohexanone to cyclohexanol was almost completed (98%).

Conclusions

In summary, in the course of this work, we prepared four half-sandwich Ru(II) complexes using simple *p*-substituted aniline derivatives and characterized them by spectroscopic and analytical methods. The solid-state structures of complexes (2)–(4) were investigated by single-crystal X-ray diffraction studies. In each case, the Ru(II) centre shows a piano-stool geometry and coordination sphere consists of a η^6-*p*-cymene, two chloride anions and the amine group of *p*-substituted aniline ligands. Though the coordination geometry and bond distances around the Ru(II) centre are similar, the complex molecules showed distinct intermolecular interactions. The catalytic properties of the synthesized half-sandwich complexes were studied for transfer hydrogenation reactions of ketones. The complexes were found to catalyze the transfer hydrogenation of acetophenone derivatives, cyclic and acyclic ketones in the presence of isopropanol (as hydrogen source) and a base. Complex

Table 3 Transfer hydrogenation of ketones catalyzed by complex (1)*

Ketone	Product	Time (hour)	% Conversion**
		4h	96
		4h	90
		4h	90
		4h	85
		4h	53
		4h	87
		4 h	67
		4 h	98

*: Reaction conditions: ketone, (1.0 mmol), i–PrOH (9.4 mL), KOtBu (0.6 mL, 0.1 M), 0.5 mg complex (1) and 82 °C. **: GC yield

[Ru(η^6-*p*-cymene)(*p*-methylaniline)Cl_2] (1) showed the highest catalytic activity for transfer hydrogenation of acetophenone. The substituent groups and their positions on the acetophenone are important factors for the catalytic activity. Complex (1) was found to catalyze the transfer hydrogenation of cyclic (cyclohexanone) and acyclic (2-hexanone) ketones. The activity of the complex (1) is significantly higher for transfer hydrogenation of cyclohexanone than acyclic analogue 2-hexanone.

Supplementary Information The online version contains supplementary material available at https://doi.org/10.1007/s11243-021-00461-9.

References

1. Magano J, Dunetz JR (2012) Org Process Res Dev 16:1156
2. Ikemoto T, Ito T, Hashimoto H, Kawarasaki T, Nishiguchi A, Mitsudera H (2000) Org Process Res Dev 4:520
3. Fuenfschilling PC, Hoehn P, Mutz J (2007) Org Process Res Dev 11:13
4. Xia H, Xu S, Hu H, An J, Li C (2018) RSC Adv 8:30875
5. Foubelo F, Nájera C, Yus M (2015) Tetrahedron: Asymmetry 26:769
6. Breuer M, Ditrich K, Habicher T, Hauer B, Keßeler M, Stürmer R, Zelinski T (2004) Angew Chem Int Ed 43:788
7. Stefane B, Pozgan F (2016) Top Curr Chem 374:1
8. Palmer MJ, Wills M (1999) Tetrahedron: Asymmetry 10:2045
9. Ikarıya T, Blacker AJ (2007) Acc Chem Res 40:1300
10. Gladiali S, Alberico E (2006) Chem Soc Rev 35:226
11. Wang D, Astruc D (2015) Chem Rev 115:6621
12. Ohkuma T, Utsumi N, Tsutsumi K, Murata K, Sandoval C, Noyori R (2006) J Am Chem Soc 1288:724
13. Noyori R, Hashiguchi S (1997) Acc Chem Res 30:97
14. Díaz-álvarez AE, Cadierno V (2013) Appl Sci 3:55
15. Baráth E (2018) Catalysts 8:671
16. Peris E, Crabtree RH (2004) Coord Chem Rev 248:2239
17. Hillier AC, Lee HM, Stevens ED, Nolan SP (2001) Organometallics 20:4246
18. Gierz V, Urbanaite A, Seyboldt A, Kunz D (2012) Organometallics 31:7532
19. Cheung FK, Lin C, Minissi F, Criville AL, Graham MA, Fox DJ, Wills M, Park A (2007) Org Lett 9:4659
20. Pelagatti P, Carcelli M, Calbiani F, Cassi C, Elviri L, Pelizzi C, Rizzotti U, Rogolino D, Generale C, Analitica C, Fisica C (2005) Organometallics 24:5836
21. Fern FE, Puerta MC, Valerga P (2011) Organometallics 30:5793
22. Dayan O, Demirmen S, Özdemir N (2015) Polyhedron 85:926

23. Li K, Niu J, Yang M, Li Z, Wu L, Hao X, Song M (2015) Organometallics 34:1170
24. Singh P, Singh AK (2010) Organometallics 29:6433
25. Alonso DA, Brandt P, Nordin SJM, Andersson PG, Uni V, Copenhagen D.-, March RV (1999) J Am Chem Soc 121:9580
26. Soriano ML, Jalón FA, Manzano BR, Maestro M (2009) Inorganica Chim Acta 362:4486
27. Sandoval CA, Ohkuma T, Muñiz K, Noyori R (2003) J Am Chem Soc 125(44):13490
28. Ohkuma T, Takeno H, Honda Y, Noyori R (2001) Adv Synth Catal 343(4):369
29. Ohkuma T, Ooka H, Yamakawa M, Ikariya T, Noyori R (1996) J Org Chem 61(15):4872
30. Kitamura M, Ohkuma T, Inoue S, Sayo N, Kumobayashi H, Akutagawa S, Ohta T, Takaya H, Noyori R (1988) J Am Chem Soc 110(2):629
31. Bruker (1998). APEX2 and SAINT. Bruker AXS Inc., Madison, Wisconsin, USA.
32. Bruker (2009). SADABS. Bruker AXS Inc., Madison, Wisconsin, USA
33. Sheldrick GM (2008) Acta Crystallogr Sect A Found Crystallogr 64:112
34. Sheldrick GM (2015) Acta Crystallogr C 71:3
35. Bacchi A, Loffi C, Pagano P, Pelagatti P, Scè F (2015) J Organomet Chem 778:1
36. Tyagi D, Binnani C, Rai RK, Dwivedi AD, Gupta K, Li PZ, Zhao Y, Singh SK (2016) Inorg Chem 55(12):6332
37. Otsuka T, Ishii A, Dub PA, Ikariya T (2013) J Am Chem Soc 135:9600
38. Dub PA, Ikariya T (2013) J Am Chem Soc 135:2604
39. Dub PA, Gordon JC (2018) Nat Rev Chem 2:396