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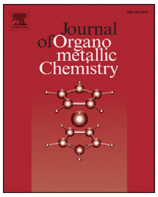

Efficient and recyclable Ru(II) arene thioamide catalysts for transfer hydrogenation of ketones: Influence of substituent on catalytic outcome

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Six cationic ruthenium(II) arene thioamide complexes with the general molecular formula [Ru(η^6-*p*-cymene)(PPh$_3$)(L)]$^+$ [where, L = pyridine-2-thioamide and its derivatives] have been successfully synthesized from the reaction of [Ru(η^6-*p*-cymene)Cl$_2$]$_2$ with chelating thioamide ligands and PPh$_3$ in methanol in 1:2 M ratio respectively. All the complexes were isolated as their BPh$_4^-$salts and were fully characterized by analytical and spectral (FT-IR, UV-Vis and^{1}H-NMR) methods. The solid-state structure of one of the complexes, [Ru(η^6-*p*-cymene)(PPh$_3$)(L4)]BPh$_4$ (**4**) (L4 = *N*-(2, 4, 6-Trimethylphenyl)pyridine-2-thiocarboxamide) has been established by X-ray single crystal diffraction which indicates a pseudo-octahedral (piano-stool) coordination geometry is present in the complex. The ruthenium(II) complexes have been examined for the transfer hydrogenation of various aromatic, heterocycle and cyclic ketones. The formation of ruthenium(II) hydride is confirmed by ^{1}H- NMR and is proposed as the catalytic intermediate in this reaction. Under the optimized conditions, these ruthenium complexes served as excellent catalyst precursors which smoothly reduce the ketones with conversion up to 100%. The influence of other variables on the transfer hydrogenation reaction such as solvent, base, temperature, time, catalyst loading and substrate scope is also reported. Furthermore, the catalyst could be easily recovered and reused at least three times without obvious loss of conversions.

1. Introduction

Although the direct hydrogenation of ketones is more widely applied, transfer hydrogenation (TH) is an attractive alternative method. So far, the TH reaction has been extensively studied and continues to generate a high degree of interest, given the need to develop environmentally friendly and simple processes [1]. The development of new and effective catalytic systems for TH reaction by simple solvent as the proton source like 2-proponal and formaldehyde continues to be the focus of many efforts designed to develop new technologies for future industrial applications [2–4]. There has been rapid growth in the various transition metal complexes such as rhodium [5,6], iridium [7], iron [8], rhenium and osmium [9] employed for the TH of ketones. However, ruthenium complexes are found to be excellent catalysts TH of ketones and there by particular attention has been devoted to them [10]. The most outstanding results have been obtained by Noyori's group who discovered and developed the catalyst [RuCl$_2$(diphosphine)(diamine)] with >99% yield [11]. In continuous, several works have been reported on TH reactions catalysed by ruthenium complexes containing various chelating ligands [12–16]. Cationic 1-(2-methylpyridine)phosphole cymene ruthenium chloride catalysed TH has been reported with moderate to excellent conversions [17]. In addition, Ru(II) benzene complexes containing tridendate chelating ligands have been reported as catalysts for the reduction of ketones to the corresponding alcohols with conversion is up to 98% within 5–7 h [18] Ruthenium complexes of the type [RuCl$_2$(*p*-cymene)(1,3-dialkyl-imidazolidin-2-ylidene)] complexes have been used as efficient catalysts for TH of ketones with excellent yields [19].

Arene ruthenium(II) complexes containing different ligands such as Schiff bases [20], aryl azo [21], pincer [22], carbene [23] and tripodal [24] are known in the literature. However, arene ruthenium complexes bearing thioamides containing–NHS unit are

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relatively less. Thioamides (tautomeric forms **Ia** and **Ib)** are versatile ligands which can coordinate to metal as neutral thione or in their deprotonated thiol form (Scheme 1). It has been found in the literature that the thiocarboxamide ligands are known to coordinate metal ions usually in a bidentate fashion with an N,S donor forming a five membered chelate ring. However, sulphur containing SCS pincers have gained recognition because of the added stability *via* tridentate coordination imparts to the formation of pincer complex. In terms of sulphur Lewis base donors, thioamides are a relatively unexplored compound class in the design of ligands. Palladium(II), gold(III), and platinum(II) complexes have been reported for the bidentate coordination [25]. Arene ruthenium metallacycles containing anionic chelating thioamides have been reported [26]. Recently, deprotonation-induced structural changes in ruthenium pincer complexes with secondary thioamide groups have been reported [27].

With the objective of promoting the catalysts for TH reactions, we focus our interest on synthesis of ruthenium(II) arene complexes and its catalytic application towards TH reaction [28]. Herein, we describe the report on synthesis of ruthenium(II) arene *p*-cymene complexes containing pyridine-2-thioamide ligands and triphenylphosphine. The composition of the complexes has been established by analytical and spectral (IR, UV-Vis, and NMR) methods. The molecular structure of complex **4** has been determined by diffraction analysis on single crystals. Further, the new cationic ruthenium complexes were demonstrated to be efficient catalysts for the TH of the various aromatic/heterocycle and aliphatic ketones to their corresponding secondary alcohols.

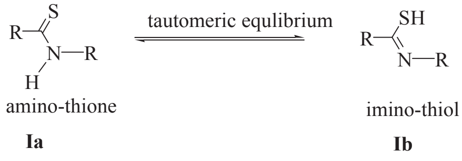
2. Experimental section

2.1. Materials

Commercially available $RuCl_3 \cdot 3H_2O$ was used as supplied from Loba Chemie. All the reagents used were chemically pure and analytical grade. The solvents were freshly distilled using the standard procedures. 2-methyl pyridine, sulphur, aniline derivatives and the ketones used for catalysis were purchased from Sigma-Aldrich and were used as received. The precursor complex $[Ru(\eta^6\text{-}p\text{-cymene})Cl_2]_2$ [29] and the substituted pyridine-2-thioamide ligands [30] were prepared by the literature reports.

2.2. Physical measurements

Melting points were recorded in the Boetius micro-heating table and are uncorrected. The analysis of carbon, hydrogen, nitrogen and sulphur were performed at Sophisticated Test and Instrumentation Centre (STIC), Cochin University of Science and Technology, Kochi. Infrared spectra of complexes were recorded in KBr pellets with a Perkin-Elmer 597 spectrophotometer in the range 4000–400 cm^{-1}. Electronic spectra of the complexes were recorded in CH_2Cl_2 solution with a Cary 300 Bio UV–Vis Varian Spectrophotometer in the range 800–200 nm. The ^1H NMR spectra were recorded in $CDCl_3$ on Bruker (400 MHz) equipment with TMS (δ 0.00) as an internal standard. Organic compounds in catalysis were identified by gas chromatography (GC) using Bruker 436-GC using GC-FID detector equipped with a column (15 m - 0.25 mm - 0.25 mm) and high purity nitrogen as carrier gas.



Ia **Ib**

Scheme 1. Thione and thiol forms of thioamide.

2.3. Synthesis of new ruthenium(II) arene thioamide complexes

A mixture containing $[Ru(\eta^6\text{-}p\text{-cymene})Cl_2]_2$ (50 mg, 0.082 mmol), thioamide (37.4–40.8 mg, 0.164 mmol) and PPh_3 (42.8 mg, 0.164 mmol) in MeOH (20 mL) and Et_3N (1 mL) was heated to reflux for 2 h. To the hot solution was added solid $NaBPh_4$ (58.6 mg, 0.164 mmol), which caused precipitation of an orange to brown solid on cooling. The product was isolated by filtration, washed with H_2O, a little cold MeOH, diethyl ether and was subsequently dried in vacuum. The resulting complexes were recrystallized from CH_2Cl_2/Pet.ether and dried under vacuum. The purity of the complexes was checked by TLC. Yield = 78–84%.

2.4. Analytical and spectral data for the complexes

2.4.1. $[(\eta^6\text{-}p\text{-cymene})Ru[\kappa^2\text{-}S,N\text{-}C_6H_4CS{=}N\text{-}(2\text{-}MePh)(PPh_3)]^+[BPh_4]^-]$ (1)

Brown solid.Yield: 82%, M.p. 182 °C (with decomposition). Found: C, 74.80%; H, 5.78%; N, 2.63%; S, 3.09%. Calc. for $C_{65}H_{60}BN_2PRuS$: C, 74.77%; H, 5.79%; N, 2.68%; S, 3.07%. FT-IR (KBr cm^{-1}): 1586 ($\upsilon_{C=N}$); 1325 ($\upsilon_{C\text{-}S}$). UV–Vis (CH_2Cl_2; λ, nm): 425, 268, 229. NMR ($CDCl_3$): δ_H (400 MHz): 6.71–8.47 (m, 43H, Ar, PPh_3, BPh_4), 4.85–6.70 (d, 4H, cymene Ar–H), 2.3 (s, 3H, CH_3), 1.3 (s, 3H, cymene-CH_3), 0.88–0.92 (d, 6H, cymene-*i*-propyl methyl). ^{13}C NMR (100 MHz, $CDCl_3$) (δ ppm): 171.5, 168.9, 167.5, 164.1, 162.3, 161.3, 152.4, 148.1, 137.9, 135.3, 131.9, 129.6, 129.3, 128.8, 128.0, 126.7, 123.2, 117.7, 105.5, 94.5, 81.2, 29.6, 21.7, 20.9, 20.2, 17.1.

2.4.2. $[(\eta^6\text{-}p\text{-cymene})Ru[\kappa^2\text{-}S,N\text{-}C_6H_4CS{=}N\text{-}(3\text{-}MePh)(PPh_3)]^+[BPh_4]^-]$ (2)

Brown solid.Yield: 73%, M.p. 202 °C (with decomposition). Found: C, 74.81%; H, 5.81%; N, 2.61%; S, 3.07%. Calc. for $C_{65}H_{60}BN_2PRuS$: C, 74.77%; H, 5.79%; N, 2.68%; S, 3.07%. FT-IR (KBr cm^{-1}): 1591 ($\upsilon_{C=N}$); 1334 ($\upsilon_{C\text{-}S}$). UV–Vis (CH_2Cl_2; λ, nm): 430, 271, 228. NMR ($CDCl_3$): δ_H (400 MHz): 6.71–8.54 (m, 43H, Ar, PPh_3, BPh_4), 4.84–5.66 (d, 4H, cymene Ar–H), 2.34 (s, 3H, CH_3), 1.33 (s, 3H, cymene-CH_3), 1.29–2.1 (d, 6H, cymene-*i*-propyl methyl). ^{13}C NMR (100 MHz, $CDCl_3$) (δ ppm): 168.5, 166.9, 163.7, 162.1, 161.7, 161.2, 158.9, 146.2, 138.9, 136.4, 132.1, 131.8, 130.9, 129.5, 127.8, 124.8, 121.9, 116.6, 111.2, 99.1, 86.1, 32.7, 23.7, 22.3, 21.7, 19.2.

2.4.3. $[(\eta^6\text{-}p\text{-cymene})Ru[\kappa^2\text{-}S,N\text{-}C_6H_4CS = N\text{-}(4\text{-}MePh)(PPh_3)]^+[BPh_4]^-]$ (3)

Brown solid.Yield: 78%, M.p. 196 °C (with decomposition). Found: C, 74.71%; H, 5.78%; N, 2.65%; S, 3.06%. Calc. for $C_{65}H_{60}BN_2PRuS$: C, 74.77%; H, 5.79%; N, 2.68%; S, 3.07%. FT-IR (KBr cm^{-1}): 1599 ($\upsilon_{C=N}$); 1317 ($\upsilon_{C\text{-}S}$). UV–Vis (CH_2Cl_2; λ, nm): 421, 271, 231. NMR ($CDCl_3$): δ_H (400 MHz): 6.82–7.3 (m, 43H, Ar, PPh_3, BPh_4), 4.88–5.67 (d, 4H, cymene Ar–H), 2.36 (s, 3H, CH_3), 1.36 (s, 3H, cymene-CH_3), 0.91–0.96 (d, 6H, cymene-*i*-propyl methyl). ^{13}C NMR (100 MHz, $CDCl_3$) (δ ppm): 169.5, 164.9, 164.4, 163.9, 163.4, 160.2, 156.7, 147.3, 138.1, 136.4, 134.1, 133.7, 131.3, 129.5, 128.7, 125.7, 122.0, 113.9, 106.9, 95.6, 82.8, 30.7, 24.7, 21.3, 21.2, 18.2.

2.4.4. $[(\eta^6\text{-}p\text{-cymene})Ru[\kappa^2\text{-}S,N\text{-}C_6H_4CS = N\text{-}(2,3,4\text{-}TriMePh)(PPh_3)]^+[BPh_4]^-]$ **(4)**

Brown solid.Yield: 75%, M.p. 206 °C (with decomposition). Found: C, 75.10%; H, 6.05%; N, 2.59%; S, 2.89%. Calc. for $C_{67}H_{64}BN_2PRuS$: C, 75.06%; H, 6.02%; N, 2.61%; S, 2.99%. FT-IR (KBr cm^{-1}): 1594 ($\upsilon_{C=N}$); 1338 ($\upsilon_{C\text{-}S}$). UV–Vis (CH_2Cl_2; λ, nm): 425, 268, 229. NMR ($CDCl_3$): δ_H (400 MHz): 6.63–8.38 (m, 41H, Ar, PPh_3,