



Rhodium(III) NCN pincer complexes catalyzed transfer hydrogenation of ketones

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ABSTRACT

Air-stable monomeric rhodium(III) NCN pincer complexes were synthesized via direct C–H bond activation of 1,3-bis(2-pyridyloxy)benzene, 3,5-bis(2-pyridyloxy)toluene and 3,5-bis(2-pyridyloxy)anisole with $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ in ethanol under reflux. The synthesized complexes were characterized by elemental analysis and ^1H NMR. One of the complexes was structurally characterized by X-ray analysis. An investigation into the catalytic activity of the complex **1a** as catalyst for transfer hydrogenation of ketones to alcohols at 82 °C in the presence of *i*PrOH/KOH was undertaken with the conversions up to 99%.

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The cyclometalation reaction or intramolecular C–H bond activation, which is a major achievement of organometallic chemistry, provides access to metallacyclic derivatives of the transition metal including pincer metal complexes.^{1–7} Direct cyclometalation is one of the attractive methods for the formation of a new M–C bond, since it does not require prefunctionalization of the pincer ligand in order to achieve regioselective metalation.⁸ Direct cyclometalation of NCN pincer ligands is less common, and the topic was reviewed in 1998.⁹ Pincer-based metal complexes possess a unique balance of stability versus reactivity which can be controlled by systematic ligand modifications and/or variation of the metal centre, allowing enhancement of metal complex stability, reactivity and reaction selectivity.^{10–14}

Transfer hydrogenation of unsaturated compounds like ketones and imines using *i*PrOH/KOH as hydrogen source is a widely investigated reaction that is promoted by many transition metal complexes.¹⁵ Ru, Rh and Ir bearing nitrogen or phosphorus containing ligands are most active, which allow the easy formation of catalytically active hydride species.^{16–18} Particularly, ruthenium-based pincer complexes have proven to be highly efficient catalysts for the transfer hydrogenation of ketones.^{19–25} Albrecht and co-workers reported the use of rhodium(III) complexes containing carbenes as active catalysts for transfer hydrogenation of ketones in the presence of *i*PrOH/KOH.^{26,27} Rhodium(III) complexes with a tripodal bis(imidazolylidene) ligand was effectively used as a catalyst for transfer hydrogenation of ketones.²⁸ Further, asym-

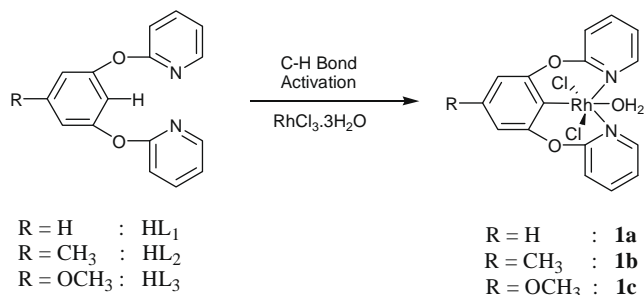
metric transfer hydrogenation of ketones was successfully carried out with a rhodium(III) arene complex.²⁹ In contrast, the rhodium(III) complexes containing NCN pincer ligand as catalyst in transfer hydrogenation of ketones has not been reported.

In recent years, we have reported the synthesis and catalytic applications of a number of ruthenium complexes.^{30–33} In view of the promising results obtained using ruthenium complexes, we focused our interest on rhodium pincer complexes for investigation. Herein, we report the synthesis of new air-stable rhodium(III) NCN pincer complexes and their catalytic application towards transfer hydrogenation of ketones.

1,3-Bis(2-pyridyloxy)benzene (HL₁), 3,5-bis(2-pyridyloxy)toluene (HL₂) and 3,5-bis(2-pyridyloxy)anisole (HL₃)^{34,35} readily reacts with $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ in refluxing ethanol in equimolar ratio for 4 h to give the rhodium pincer complexes (Scheme 1). The C–H activation at the phenyl ring of the NCN ligand led to the formation of the rhodium NCN pincer complexes composed of two six-membered metallacycles in 71–82% isolated yield. It has been observed that the pincer ligands replace two water molecules and one chloride ion from the starting precursor and the oxidation state of rhodium remains unchanged during course of cyclometalation. All the complexes are found to be air stable and are soluble in common organic solvents such as methanol, ethanol and acetonitrile. Elemental analysis (C, H and N) of the synthesized complexes were consistent with the composition proposed for all the complexes.

The rhodium pincer complexes were characterized by ^1H NMR by using $\text{DMSO}-d_6$ solvent. In ^1H NMR, all the aromatic protons in the complexes appeared as a multiplet in the region of 6.9–8.7 ppm. The central –CH proton of the phenyl ring in NCN

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1a = 1,3-bis(2-pyridyloxy)phenylaquorhodium(III) dichloride (yield = 82%); **1b** = 3,5-bis(2-pyridyloxy)tolylaquorhodium(III)dichloride (yield = 75%) and **1c** = 3,5-bis(2-pyridyloxy)anisoyl)aquorhodium(III) dichloride (yield = 71%).

Scheme 1.

ligands (6.94 ppm for HL₁, 6.66 ppm for HL₂ and 6.45 ppm for HL₃) disappeared as pincer complexes were formed, together with concomitant chemical shift changes. A singlet appeared at 2.35 and 3.73 ppm due to the presence of methyl and methoxy protons in the complexes **1b** and **1c**, respectively.

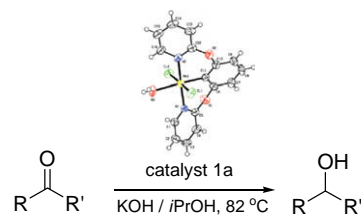
Further, the molecular structure of the pincer complex **1a** was resolved by single crystal X-ray crystallography. A chloroform/methanol solution of complex **1a** was slowly evaporated at room temperature to afford a single crystal suitable for X-ray crystallographic study. There are two crystallographically independent molecules present in the asymmetric unit cell of the complex **1a**. Both molecules have essentially identical coordination geometries, but the corresponding bond lengths and bond angles are slightly different. An ORTEP view of the complex **1a** (Fig. 1) shows clearly that the pincer ligand is coordinated to the rhodium metal via two pyridyl nitrogens and one aryl carbon in a tridentate fashion in addition to two Cl and one H₂O groups. A distorted octahedral geometry is observed as reflected in all the bond parameters around rhodium.

The bond angles for C(11)–Rh(1)–N(1) and C(11)–Rh(1)–N(2) are 88.94(16)° and 89.13(17)°, respectively, which are very close to 90°, and thus a less bond angle strain is expected around the metal than the five-membered analogues.³⁶ The two chlorine atoms are mutually *trans* to each other with almost equal distance from the metal center.

Selected bond lengths (Å): C(11)–Rh(1) 1.952(4), Cl(1)–Rh(1) 2.3362(11), Cl(2)–Rh(1) 2.3329(11), N(1)–Rh(1) 2.047(4), N(2)–Rh(1) 2.051(4), O(3)–Rh(1) 2.229(4). Selected bond angles (°): C(11)–Rh(1)–N(1) 88.94(16), C(11)–Rh(1)–N(2) 89.13(17), N(1)–Rh(1)–N(2) 178.00(17), C(11)–Rh(1)–O(3) 177.27(18), N(1)–Rh(1)–O(3) 88.37(15), N(2)–Rh(1)–O(3) 93.57(16), C(11)–Rh(1)–Cl(2) 91.42(13), N(1)–Rh(1)–Cl(2) 90.73(10), N(2)–Rh(1)–Cl(2) 89.81(10), O(3)–Rh(1)–Cl(2) 88.20(12), C(11)–Rh(1)–Cl(1) 90.76(13), N(1)–Rh(1)–Cl(1) 89.18(10), N(2)–Rh(1)–Cl(1) 90.35(10), O(3)–Rh(1)–Cl(1) 89.61(12), Cl(2)–Rh(1)–Cl(1) 177.81(5).

The synthesized rhodium(III) pincer complex **1a** catalyzes the hydrogenation of ketones via hydrogen transfer from *i*PrOH/KOH at 82 °C (Scheme 2).³⁷

Using complex **1a**, both aliphatic and aromatic ketones were efficiently reduced to their corresponding alcohols in 80–99% conversions (Table 1). The conversion of ketone to secondary alcohol in the case of acetophenone was 99% (entry 1, 24 h), which takes place at a faster rate than that for benzophenone (88%, entry 4). The presence of electron-withdrawing (Cl) or electron-donating (OCH₃) substituent on acetophenone (entries 2 and 3) has significant effect on the reduction of ketones to their corresponding alcohols. The maximum conversion of 4-methoxy acetophenone to



Scheme 2.

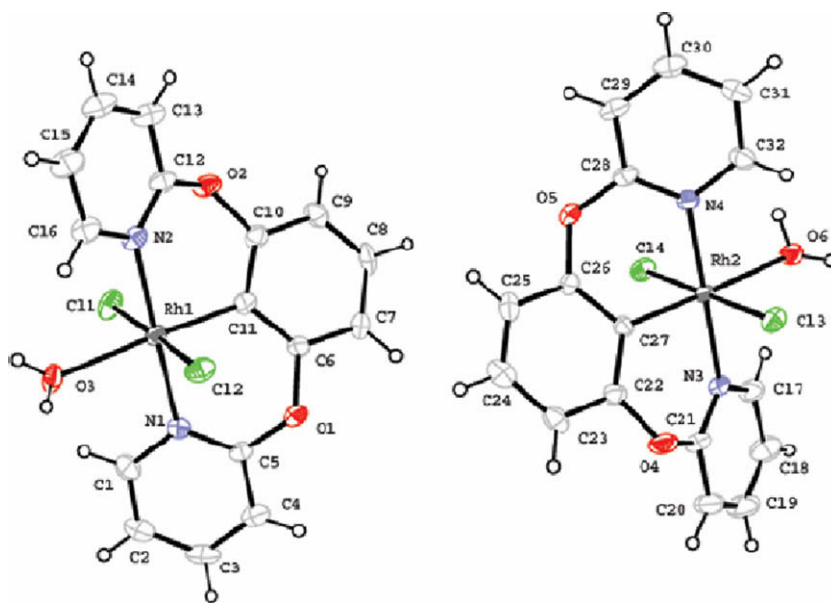
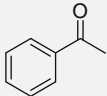
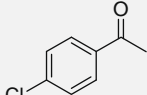
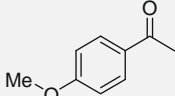
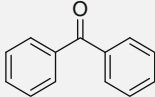


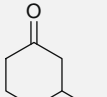

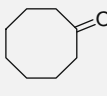
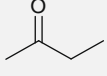
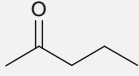
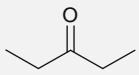


Figure 1. ORTEP diagram of the complex **1a**.

Table 1
Catalytic transfer hydrogenation of ketones using complex **1a**/iPrOH/KOH^a

Entry	Ketone	Time (h)	Conversion (%)	TON
1		10/24	94/99	188/198
2		10/24	82/98	164/196
3		10/24	69/80	138/160
4		10/24	83/88	166/176
5		10/24	72/88	144/176
6		10/24	95/99	190/198
7		10/24	93/99	186/198
8		10/24	89/98	178/196
9		10/24	88/98	176/196
10		10/24	70/88	140/176
11		10/24	73/89	146/178
12		10/24	71/88	142/176

^a Experimental conditions: reactions were carried out at 82 °C using catalyst (0.01 mmol), KOH (0.025 mmol) and ketone (2 mmol) in 5 mL of iPrOH (catalyst/ketone/KOH ratio = 1/200/2.5); conversions were determined by GC or GC–MS analysis by comparison with authentic samples; TON = mol of product/mol of catalyst.

corresponding alcohol was achieved over a period of 24 h (entry 3) and that for 4-chloro acetophenone was 98%. Similarly, 2-butanone, 2-pentanone and 3-pentanone (entries 10–12) underwent hydrogenation to afford the corresponding alcohols in 70%, 73% and 71% conversions, respectively, in 10 h and achieved maximum conversions in 24 h. Interestingly, this catalyst shows excellent activity for the conversions of six-, seven- and eight-membered cyclic ketones (entries 5–9) to their corresponding alcohols with 88% conversion in the case of cyclopentanone and conversions 98% in case of cyclohexanone, 3-methyl cyclohexanone, cycloheptanone and cyclooctanone.

In conclusion, we have demonstrated a facile and general synthetic route to rhodium(III) NCN pincer complexes via direct cyclometalation. The synthesized rhodium(III) pincer complexes are air stable and composed of two six-membered metallacycles with reduced bond angle strain around rhodium. The X-ray crystal structure of complex **1a** shows an octahedral geometry around rhodium(III) ion with little distortion. An initial foray into the utility of the complex **1a** demonstrates its ability to form active catalytic species for use in transfer hydrogenation of ketones.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2009.09.152.

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37. *Typical procedure for transfer hydrogenation of ketones:* Under an inert atmosphere, a mixture containing ketone (2 mmol), KOH (0.025 mmol), catalyst (0.01 mmol) and *i*PrOH (5.0 mL) was heated to 82 °C. At the desired reaction times, aliquots were extracted from the reaction vessel, extracted using diethyl ether, filtered through a short path of silica and the silica was washed with diethyl ether. The combined organic filtrates were evaporated and analyzed by GC or GC–MS.