Journal of Organometallic Chemistry 765 (2014) 1–7

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

Synthesis, characterization and catalytic activity of dinuclear half-sandwich Ru(II), Rh(III) and Ir(III) complexes

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ARTICLE INFO

Article history:
Received 17 February 2014
Received in revised form
15 April 2014
Accepted 23 April 2014

Keywords:
Dinuclear complexes
Chelating ligand
Half-sandwich complexes
Amidation reaction
Beckmann rearrangement
Catalysis

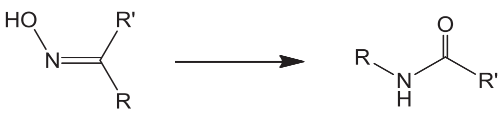
ABSTRACT

The reaction in dichloromethane between the chloro-bridged complexes $[(\eta^6\text{-}p\text{-}^i\text{PrC}_6\text{H}_4\text{Me})_2\text{Ru}_2(\mu\text{-Cl})_2\text{Cl}_2]$, $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{Rh}_2(\mu\text{-Cl})_2\text{Cl}_2]$ and $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{Ir}_2(\mu\text{-Cl})_2\text{Cl}_2]$, and the ligand precursor, 3,3′-[(1*E*,1′*E*)-{(methylenebis(4,1-phenylene))bis(azanylylidene)}bis(ethan-1-yl-1-ylidene)]bis(4-hydroxy-6-methyl-2H-pyran-2-one) (LH_2), has yielded the corresponding neutral dinuclear Ru(II), Rh(III) and Ir(III) complexes of the formula $[\{(\eta^6\text{-}p\text{-}^i\text{PrC}_6\text{H}_4\text{Me})\text{RuCl}\}_2\text{L}]$ (**1**), $[\{(\eta^5\text{-C}_5\text{Me}_5)\text{RhCl}\}_2\text{L}]$ (**2**) and $[\{(\eta^5\text{-C}_5\text{Me}_5)\text{IrCl}\}_2\text{L}]$ (**3**). The complexes were characterized by elemental analysis, infrared, ^{1}H NMR, ^{13}C NMR, ESI mass spectrometry, and complexes **2** and **3** by single-crystal X-ray structure analysis. All complexes were used as catalysts under different reaction conditions for the formation of amides from aldehydes in the presence of $\text{NH}_2\text{OH}\cdot\text{HCl}$ and NaHCO_3. All complexes show good conversion with catalytic turnover numbers up to 500.

Introduction

The amide bond formation is one of the most important reactions in organic chemistry. The formation of an amide bond is often seen as a contemporary challenge due to the occurrence of amide functions in chemicals of biological and industrial importance [1–3]. Several synthetic strategies have been developed to generate amide functions; the coupling of carboxylic acids or carboxylic acid derivatives with amines [4], the reaction of azides with water [5], the reaction of aromatic halides with an amino carbonyle [6], the reaction of alcohols with amines [7], the reaction of alcohols with a hydroxylamine hydrochloride [8], the Schmidt reaction [9], the Beckmann rearrangement [10], the conversion of aldoximes to amides [11], and the oxidative amidation of aldehydes [12]. Transition metal complexes based on manganese [13], iron [14], nickel [15], copper [16], zinc [17], zirconium [18], ruthenium [19], rhodium [20], palladium [21], silver/gold [22], and iridium [8] have been also used to synthesize amides catalytically. Mostly, these catalytic reactions require large amount of catalysts and are generally performed at high temperature.

The Beckmann rearrangement remains a traditional strategy for the preparation of amides from ketoximes in the presence of a Lewis acid catalyst (Scheme 1). However, due to an inactive migration of the hydrogen from an aldehyde/aldoxime during the amide formation, exploiting the Beckmann rearrangement is not always ideal for the synthesis of amides [23,24]. A successful modification of the standard Beckmann rearrangement conditions has been introduced by Williams using half-sandwich complexes as catalysts in the presence of *p*-toluenesulfonic acid [25], or cesium carbonate [8]. Other groups also modified the reaction conditions to increase the Beckmann rearrangement adding aluminum oxide [26], or NaHCO_3 [12,27] to catalysts and substrates. However, despite these modifications, in most cases the catalyst loading remains high, while for others, additives and high temperatures are also required.



Scheme 1. Beckmann rearrangement of oximes to form amides [28].

Therefore, in view of optimizing the reaction conditions of the Beckmann rearrangement in the presence of half-sandwich ruthenium(II), rhodium(III) and iridium(III) catalysts, a series of dinuclear complexes has been prepared: Dinuclear catalysts being potentially beneficial over mononuclear complexes [29]. All complexes were used as efficient catalysts for the aldehyde to amide transformation

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http://dx.doi.org/10.1016/j.jorganchem.2014.04.024

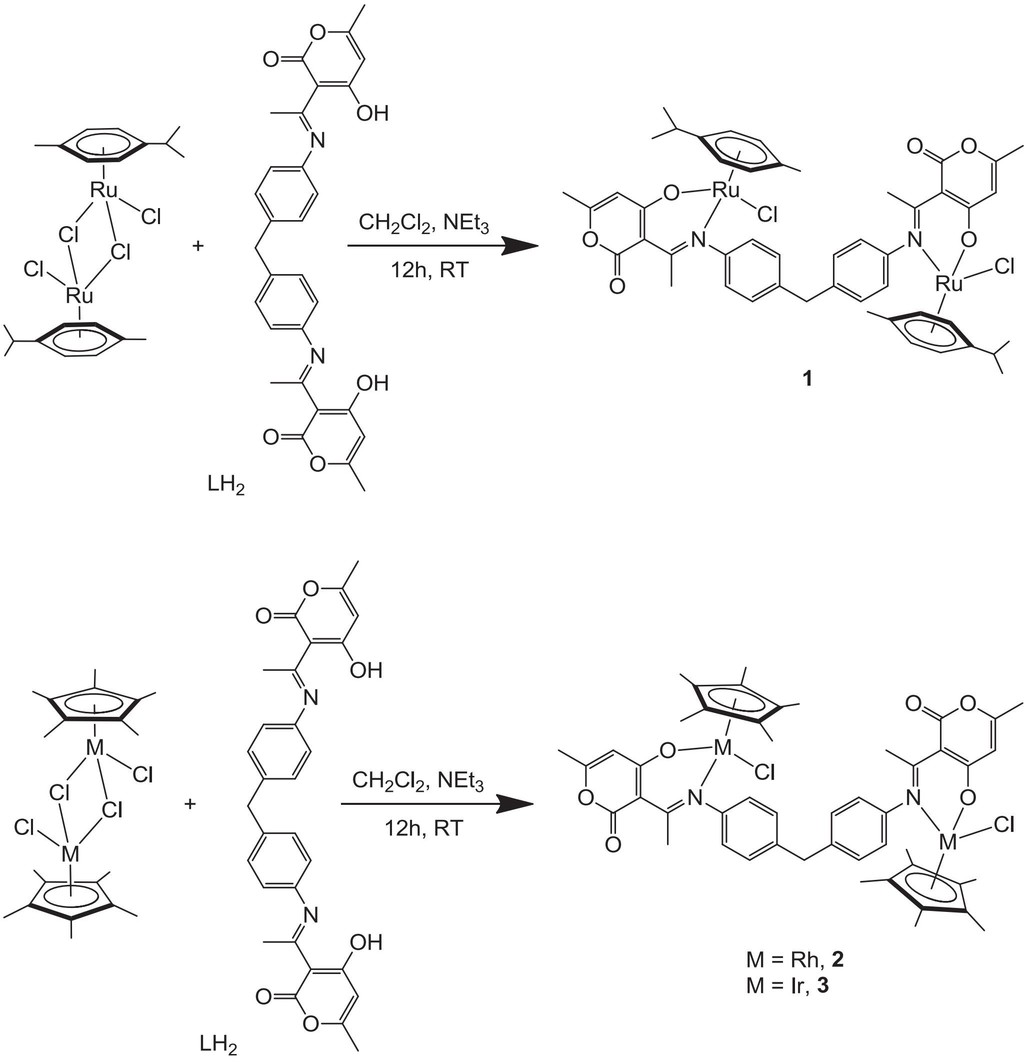
in a one pot procedure in the presence of $NaHCO_3$ and $NH_2OH\cdot HCl$. Under these conditions, the conversion from aldehyde to amide requires a low catalyst loading and gives good yields.

Results and discussion

One equivalent of the ligand precursor 3,3′-[(1*E*,1′*E*)-{(methylenebis(4,1-phenylene))bis(azanylylidene)}bis(ethan-1-yl-1-ylidene)]bis(4-hydroxy-6-methyl-2H-pyran-2-one) (LH_2) reacts with the chloro-bridged complexes $[(\eta^6\text{-}p\text{-}^iPrC_6H_4Me)_2Ru_2(\mu\text{-}Cl)_2Cl_2]$, $[(\eta^5\text{-}C_5Me_5)_2Rh_2(\mu\text{-}Cl)_2Cl_2]$ and $[(\eta^5\text{-}C_5Me_5)_2Ir_2(\mu\text{-}Cl)_2Cl_2]$ in the presence of triethylamine to afford in good yields the dinuclear half-sandwich complexes $[\{(\eta^6\text{-}p\text{-}^iPrC_6H_4Me)RuCl\}_2L]$ (**1**), $[\{(\eta^5\text{-}C_5Me_5)RhCl\}_2L]$ (**2**) and $[\{(\eta^5\text{-}C_5Me_5)IrCl\}_2L]$ (**3**), respectively (see Scheme 2). All complexes are air stable solids and they have been characterized by elemental analysis, infrared, UV–visible, ^{1}H NMR, ^{13}C NMR spectroscopy and ESI mass spectrometry (see Experimental part).

The infrared spectra of the complexes show strong stretching vibrations in the frequency range 1993–1996 cm^{-1}. The presence of this strong $\nu_{C=O}$ stretching frequency confirms that the free lactone group is not involved in the coordination of L to the metal centers. In addition, a ν_{C-O} stretching frequency, which is observed at 1329 cm^{-1} in the ligand precursor, appears shifted to higher frequency 1347–1350 cm^{-1} after the complexation, confirming the coordination of L via the enolic oxygen. Similarly, the $\nu_{C=N}$ stretching frequency in the complexes is shifted to lower frequency as compared to the ligand precursor (LH_2), indicating the coordination of the imine nitrogen towards the metals. The electronic spectra of complexes **1**–**3** show two to three absorption bands in the UV–visible region: The intense absorption observed in the range 445–488 nm is assigned to MLCT transitions, while the band around 272–296 nm corresponds to $n-\pi^*$ or $\pi-\pi^*$ transitions.

The ^{1}H NMR spectra of complexes **1**–**3** also confirm the double N∩O chelating coordination mode of L. Upon coordination, the signal associated with the azomethine protons is upfield shifted as compared to the ligand precursor by almost 1 ppm, while the two doublets associated to the equivalent aromatic protons of the phenyl groups are now split due to the diastereotopic nature of complexes **1**–**3**. Indeed, the double N∩O coordination of L to the metal centers generates two chiral-at-the-metal centers, thus giving rise to potentially three species; a pair of enantiomers (*R*,*R* and *S*,*S*) and the *meso* form (*R*,*S*). However, the ^{1}N NMR spectra show only one set of signals for all complexes, suggesting that the *racemic* or *meso* form is not obtained. The chirality of the dinuclear complexes is clearly evidenced in complex **1** in which the methyl



1

M = Rh, **2**
M = Ir, **3**

Scheme 2. Synthesis of the dinuclear half-sandwich complexes **1**–**3**.