



Bis-chelate *N*-heterocyclic tetracarbene Ru(II) complexes: Synthesis, structure, and catalytic activity toward transfer hydrogenation of ketones

Yong-Bin Lai, Chen-Shiang Lee, Wan-Jung Lin, Abbas Raja Naziruddin, Wen-Shu Hwang^{*}

Department of Chemistry, National Dong Hwa University, Hualien 974, Taiwan, ROC

ARTICLE INFO

Article history:

Received 23 October 2012

Accepted 19 January 2013

Available online 9 February 2013

Keywords:

Chelate

N-Heterocyclic carbene

Ruthenium

Catalyst

Transfer hydrogenation

ABSTRACT

Ru(II) complexes with two chelating di-*N*-heterocyclic carbenes (NHC) and two acetonitrile ligands (NHC = 1,1'-dialkyl-3,3'-methylene-diimidazol-2,2'-diylidene, and alkyl = methyl and *n*-butyl) were synthesized and structurally characterized. The crystal structures of the complexes determined by X-ray diffraction analyses show that the Ru(II) center is bound to two bidentate carbene ligands and two acetonitrile molecules, forming a distorted octahedron. The complexes prove to be an efficient catalyst having exceedingly high turnover frequencies and good reusability in transfer hydrogenation of ketones.

© 2013 Elsevier Ltd. All rights reserved.

1. Introduction

N-Heterocyclic carbene (NHCs) have emerged as an important class of ligand in organometallic chemistry and homogeneous catalysis [1]. They constitute a sterically and electronically tunable ligand set to stabilize and activate metal center and, moreover they have been identified as a competent alternatives for organophosphines [2]. So far many efficient NHC-based catalysts have been developed for wide range of organic transformations [3,4]. A majority of NHC ligands used in catalytic applications coordinate to the transition metal center in a monodentate fashion. Chelating bis-NHCs in general are of great interest since they tend to extend the range of possible NHC ligands and allow the delicate tuning of topological properties such as steric hindrance, bite angle, and fluxional behavior, which would provide a new dimension in the preparation of new catalysts with high thermal and air stabilities [4,5].

Ru(II)–NHC complexes have demonstrated good catalytic activity in hydrogen transfer reactions [6], racemization of chiral alcohols [7] and asymmetric reductions [8]. Although ruthenium–phosphine complexes displayed extremely high catalytic performance, practical difficulties such as air/moisture sensitivity, as well as possible catalytic degradation have driven chemists to use the stable metal–NHC complexes as alternative catalysts. Ruthenium complexes with *N*-functionalized chelate carbene ligands have demonstrated to be stable and effective in transfer hydrogenation of ketones [9–11]. Despite of rich catalytic activity of ruthenium complexes towards transfer hydrogenation reactions, the complexes of this

metal are mainly centered on the pyridine-bridged pincer bis carbene ligands [9]. Some ruthenium complexes with chelating bis-NHC ligands have been recently described with interesting applications in transfer hydrogenation of ketones [11]. Recently we reported that a palladium complex bearing bis-chelate tetracarbene ligands showed excellent stability and proved to be an efficient catalyst for Heck reaction [12]. To extend this work we synthesized the first ruthenium complex with bis-chelate tetracarbene ligands and two acetonitrile ligands $[\text{Ru}(\text{RCC}^{\text{meth}})_2(\text{CH}_3\text{CN})_2](\text{BF}_4)_2$, R = Me and *n*-Bu, which proved to be an excellent catalyst for transfer hydrogenation of ketones with high recyclability.

2. Results and discussion

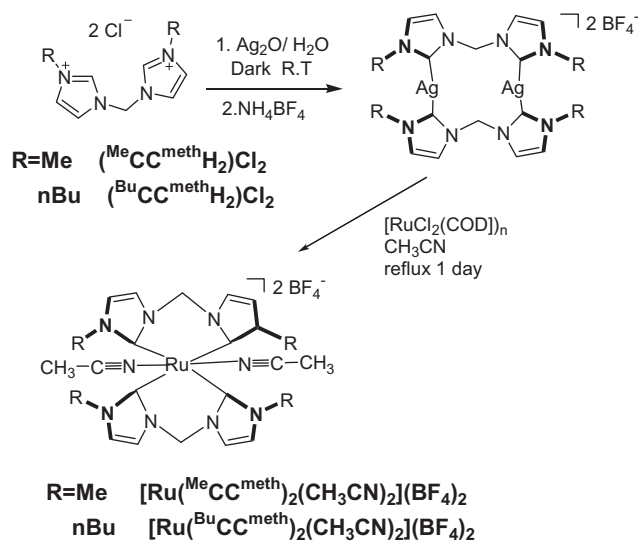
2.1. Preparation of $[\text{Ru}(\text{RCC}^{\text{R}})_2(\text{CH}_3\text{CN})_2](\text{BF}_4)_2$ complexes

Silver transfer route [13] was employed to synthesize the ruthenium(II) bis-chelate tetracarbene complex (Scheme 1). The bidentate NHC precursor 1,1'-dialkyl-3,3'-methylenediimidazolium dichloride ($\text{RCC}^{\text{meth}}\text{-H}_2\text{Cl}_2$), reacted readily with Ag_2O in an aqueous solution to yield a Ag(I)–NHC complex, which was isolated as the BF_4^- salt $[\text{Ag}_2(\text{RCC}^{\text{meth}})_2](\text{BF}_4)_2$, to avoid the interference of $\text{AgX}_2^-/\text{X}^-$ ions [12,13b]. The formation of $[\text{Ag}_2(\text{RCC}^{\text{R}})_2](\text{BF}_4)_2$ complex was confirmed by the disappearance of the imidazolium C2–H resonances in the ^1H NMR spectrum.

Further reaction of the $[\text{Ag}_2(\text{RCC}^{\text{meth}})_2](\text{BF}_4)_2$ with $[\text{RuCl}_2(\text{COD})]_n$ (COD = 1,5-cyclooctadiene) in CH_3CN yielded an air stable complex $[\text{Ru}(\text{RCC}^{\text{meth}})_2(\text{CH}_3\text{CN})_2](\text{BF}_4)_2$ in high yield. ^{13}C NMR resonances at 188.5 (R = Me) and 187.6 (R = *n*-Bu) ppm which are characteristic

^{*} Corresponding author. Tel.: +886 3 8633570; fax: +886 3 8633577.

E-mail address: hws@mail.ndhu.edu.tw (W.-S. Hwang).



Scheme 1. Synthesis of the $[\text{Ru}(\text{RCC}^{\text{meth}})_2(\text{CH}_3\text{CN})_2](\text{BF}_4)_2$.

resonances corresponding to the carbenoid C2 carbon in Ru–NHCs supports the formation of $[\text{Ru}(\text{RCC}^{\text{meth}})_2(\text{CH}_3\text{CN})_2](\text{BF}_4)_2$. The ^1H NMR spectrum of $[\text{Ru}(\text{MeCC}^{\text{meth}})_2(\text{CH}_3\text{CN})_2](\text{BF}_4)_2$ shows two sets of doublet resonances at 6.33 and 6.22 ppm with a coupling constant of $J_{\text{H-H}} = 13.1$ Hz due to the diastereotopic methylene linker that arises upon complexation due to the twisted conformation [14]. Similar resonances were also obtained in the ^1H NMR spectrum of $[\text{Ru}(\text{BuCC}^{\text{meth}})_2(\text{CH}_3\text{CN})_2](\text{BF}_4)_2$, which shows two sets of doublet at 6.61 and 6.47 ppm with a coupling constant of $J_{\text{H-H}} = 13.5$ Hz.

2.2. Crystal structures of $[\text{Ru}(\text{MeCC}^{\text{meth}})_2(\text{CH}_3\text{CN})_2](\text{BF}_4)_2$

single crystals of $[\text{Ru}(\text{MeCC}^{\text{meth}})_2(\text{CH}_3\text{CN})_2](\text{BF}_4)_2$ and $[\text{Ru}(\text{BuCC}^{\text{meth}})_2(\text{CH}_3\text{CN})_2](\text{BF}_4)_2$ suitable for X-ray diffraction studies were obtained by the slow diffusion of diethyl ether into

acetonitrile solution of the complexes. The molecular structure of $[\text{Ru}(\text{MeCC}^{\text{meth}})_2(\text{CH}_3\text{CN})_2](\text{BF}_4)_2$ is shown in Fig. 1. The complex crystallized in the monoclinic crystal system with the $P2_1/c$ space group. The structure analysis shows that it is a mononuclear Ru(II) complex with two chelating bis-carbene ligands and two mutually trans acetonitrile ligands. Each chelated bis-carbene constructed a six membered ring upon coordination and the Ru(II) center adopted an octahedral geometry with C–Ru–C bite angles of $83.04(8)^\circ$ and $83.53(8)^\circ$, which are consistent with closely related structures reported earlier [5d]. The twist angle (34.97 – 39.90°) of the heterocyclic rings related to the coordination plane defined by four coordinated carbenoid carbons indicate that the conformation adopted primarily from minimization of Me–Me nonbonding interactions, thereby leading to the chemically nonequivalent protons on the methylene linker as observed in the ^1H NMR spectrum. Two acetonitrile ligands are almost perpendicular to the NHC coordination plane $[\text{Ru}(1)–\text{C}(1)–\text{C}(10)–\text{C}(14)–\text{C}(5)]$ bearing Ru and bidentate carbene ligands. The C–Ru–N bond angles are ranges from $86.20(8)^\circ$ to $93.18(8)^\circ$ with an average of 90.0° . The bond lengths of Ru–C_{NHC} ranges from $2.086(2)$ to $2.092(2)$ Å with an average of 2.089 Å, slightly shorter than those found in typical Ru–NHC complexes [5d,9a–9c,11b,11c]. The Ru–N bond lengths were found to be Ru(1)–N(9) $2.0258(19)$ Å and Ru(1)–N(10) $2.0285(19)$ Å. A large free space in the vicinity of the two acetonitrile ligands, would probably facilitate the substitution of acetonitrile ligands by other substrates in the catalytic reaction.

The structural features around the Ru centre in $[\text{Ru}(\text{BuCC}^{\text{meth}})_2(\text{CH}_3\text{CN})_2](\text{BF}_4)_2$ are identical to those in $[\text{Ru}(\text{MeCC}^{\text{meth}})_2(\text{CH}_3\text{CN})_2](\text{BF}_4)_2$. The molecular structure of $[\text{Ru}(\text{BuCC}^{\text{meth}})_2(\text{CH}_3\text{CN})_2](\text{BF}_4)_2$ is shown in Fig. 2. The bond lengths, bond angles, and the conformation of the complex ions are similar to those of $[\text{Ru}(\text{MeCC}^{\text{meth}})_2(\text{CH}_3\text{CN})_2](\text{BF}_4)_2$. In this case the twist angle (35.99 – 45.93°) of the heterocyclic rings related to the coordination plane is greater than that of $[\text{Ru}(\text{MeCC}^{\text{Me}})_2(\text{CH}_3\text{CN})_2](\text{BF}_4)_2$ due to the Bu–Bu nonbonding interactions.

2.3. Catalytic transfer hydrogenation of ketones

The complex $[\text{Ru}(\text{MeCC}^{\text{meth}})_2(\text{CH}_3\text{CN})_2](\text{BF}_4)_2$ has been tested for its catalytic activity towards transfer hydrogenation of

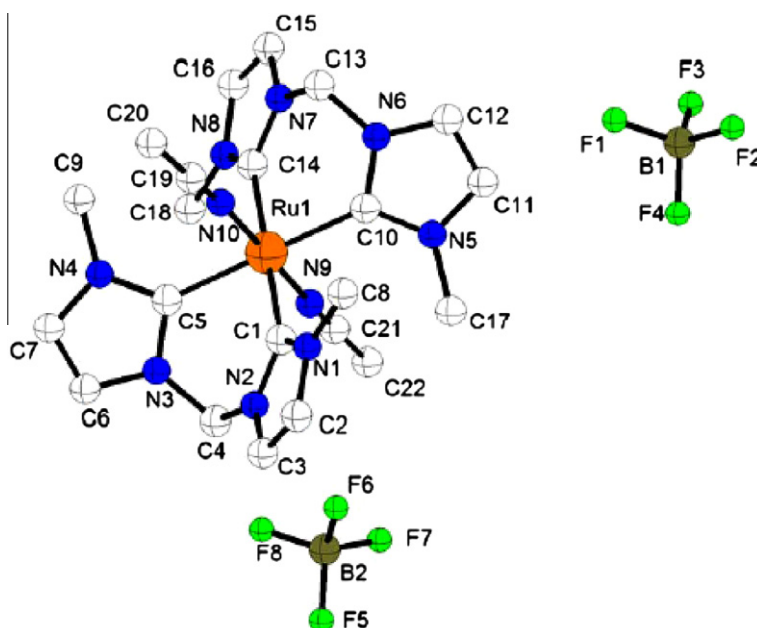


Fig. 1. The molecular structure of $[\text{Ru}(\text{MeCC}^{\text{meth}})_2(\text{CH}_3\text{CN})_2](\text{BF}_4)_2$ showing the atom labeling scheme without solvent molecules. Selected bond lengths (Å) and angles ($^\circ$): Ru1–C1, $2.087(2)$; Ru1–C5, $2.090(2)$; Ru1–C10, $2.086(2)$; Ru1–C14, $2.092(2)$; Ru1–N9, $2.0258(19)$; Ru1–N10, $2.0285(19)$; C1–Ru1–C5, $83.04(8)$; C10–Ru1–C14, $83.53(8)$; C1–Ru1–C10, 95.63 ; C5–Ru1–C14, $97.80(8)$; C1–Ru1–C14, $178.56(8)$; C5–Ru1–C10, $178.54(8)$; N9–Ru1–N10, $178.76(7)$.

Download English Version:

<https://daneshyari.com/en/article/1335820>

Download Persian Version:

<https://daneshyari.com/article/1335820>

[Daneshyari.com](https://daneshyari.com)