



Ruthenium(II) η^6 -arene complexes containing a dinucleating ligand based on 1,8-naphthyridine



Wei-Hung Tang, Yi-Hung Liu, Shie-Ming Peng, Shiuh-Tzung Liu*

Department of Chemistry, National Taiwan University, Taipei 106, Taiwan, ROC

ARTICLE INFO

Article history:

Received 6 September 2014

Received in revised form

16 October 2014

Accepted 21 October 2014

Available online 31 October 2014

Keywords:

Ruthenium

Naphthyridine

Quinoxaline

Oxidative coupling

Catalysis

ABSTRACT

Ruthenium arene complexes, $[(\eta^6\text{-}p\text{-cymene})_2\text{Ru}_2(\text{L})\text{Cl}_2](\text{PF}_6)_2$ [**3b**, L = 2, 7-bis(di-2-pyridinyl)-1,8-naphthyridine] and $[(\eta^6\text{-}p\text{-cymene})\text{Ru}(\text{L}')\text{Cl}](\text{PF}_6)$ [**4**, L' = tri(2-pyridinyl)amine], were synthesized and characterized by spectroscopic and analytical techniques. The molecular structure of $[(\eta^6\text{-}p\text{-cymene})_2\text{Ru}_2(\text{L})\text{Cl}_2](\text{PF}_6)_2$ (**3a**) was further determined by single-crystal X-ray analysis. The use of these ruthenium complexes as pre-catalysts for oxidative coupling of 1,2-diols/1,2-aminoalcohol with *o*-phenylenediamines leading to quinoxalines was investigated. Complex **3b** appeared to be a good catalyst for this transformation.

© 2014 Elsevier B.V. All rights reserved.

Introduction

Extensive efforts to prepare dimetallic complexes have appeared due to the interests in the study of synergistic effect between metal ions [1–22]. Thus the design of ligands for accommodation of two metal centers in close proximity plays a key role for such dimetallic species. In this regard, an incorporation of a bridging carboxylate into multidentate ligands, providing a coordination environment for the metal–metal interaction, is frequently encountered in the ligand design [23]. In order to modify the donating ability, other bridging donors are also developed. Analogous to carboxylate, the 1,8-naphthyridine moiety is considered as a “masked carboxylate”, in which the two nitrogen donors are capable to bind two metal ions in a *syn*, *syn*-coordination mode, providing a coordination environment for the metal–metal interaction (chart 1). The advantage with 1,8-naphthyridine as a bridging ligand is the feasible synthetic approaches to construct pendant arms at 2 and 7 positions of the molecule leading to the dinucleating ligands. Quite a few 1,8-naphthyridine based multidentates have been reported (Scheme 1) and the naphthyridine moiety does act a bridging ligand to assist the metal–metal interaction [24–39]. In this work, we would like to report the synthesis of the naphthyridine-based poly-pyridine **1** and its coordination

chemistry toward $[(\eta^6\text{-cymene})\text{RuCl}_2]_2$. The uniqueness of **1** is that its structure could be taken as a fused system of two molecules of tris(2-pyridyl)amine (TPN).

Results and discussion

Synthesis and characterization of Ruthenium(II) complexes

The key step of the ligand synthesis is the C–N bond formation between chloro-substituted 1,8-naphthyridine (**2**) and dipyridinylamine as shown in Scheme 2. The precursor **2** can be prepared in good yield from the condensation of 2,6-diaminopyridine with malic acid followed by diazotization, hydrolysis and chlorination, as previously reported [40]. Cross coupling of **2** with dipyridinylamine catalyzed by Pd(II) in the presence of Cs_2CO_3 proceeded smoothly to give the desired ligand **1** in 68% isolated yield.

Ligand **1** has been fully characterized by mass, ^1H and ^{13}C NMR spectroscopy (Table 1). ESI-HRMS of **1** shows m/z at 469.1893, corresponding to the composition of $\text{C}_{28}\text{H}_{21}\text{N}_8$ [M + H], which confirms the molecular formula. The ^1H NMR spectrum for **1** exhibited signals corresponding to the naphthyridine ring C–H protons which appear as two sets of doublet at δ 7.87 and 7.03 with $J = 8.8$ Hz. The pyridinyl protons showed four sets of well-resolved signals in the aromatic region (Table 1). The ^{13}C NMR spectrum showed ten signals in the range of δ 158.4–116.3, typical for sp^2 carbon shifts, consistent with the proposed structures. These NMR data support the structure of **1** with no ambiguity.

* Corresponding author. Tel.: +886 2 2366 0352; fax: +886 2 3366 8671.
E-mail address: stliu@ntu.edu.tw (S.-T. Liu).

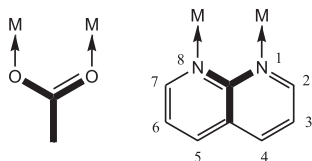
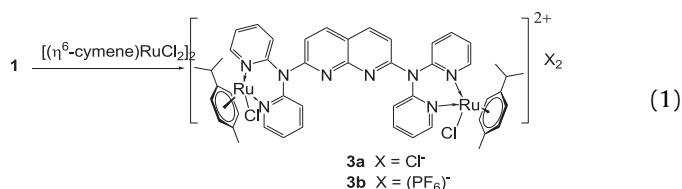


Chart 1. Coordination modes of Carboxylate and naphthyridine.

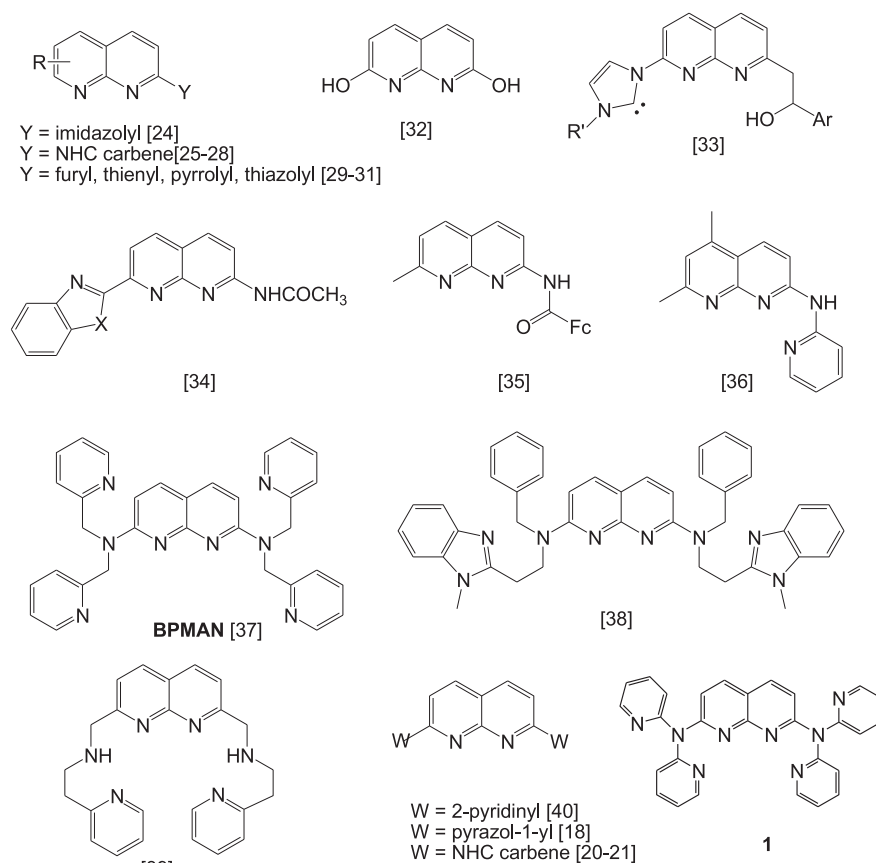
Preparation of η^6 -arene Ru(II) complexes

Complexation of **1** with arene-ruthenium(II) was investigated. Reaction of **1** with $[(\eta^6\text{-benzene})\text{RuCl}_2]_2$ in a refluxing acetonitrile solution for 12 h gave the desired complex **3a** as a dark brown solid (Eqn. (1)). Further anion metathesis of **3a** with potassium hexafluorophosphate gave **3b** as a black solid in 91% yield. The ^1H NMR resonances of naphthyridinyl and pyridinyl protons in complex **3b** appeared as two sets of doublets and four sets of signals (Table 1), indicating a symmetrical structure in **3b**. All ^1H NMR signals were de-shielded in relation to the free ligands due to the coordination

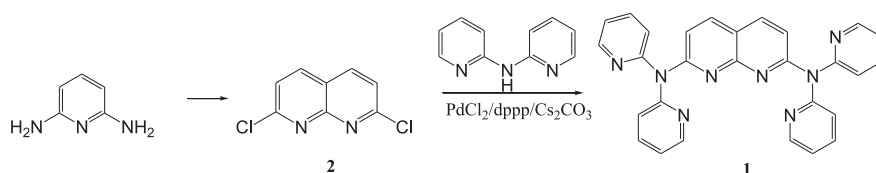
chemical shifts. Two sets of doublets at δ 5.64 and 5.22 were assigned to be the aryl protons of π -coordinating cymene, which is in agreement with the related species [41]. Crystal structure of **3a** confirms the molecular formulation of the complex.



The solubility of **3b** in organic solvents such CH_2Cl_2 or CHCl_3 is much better than that of **3a**. However, suitable crystals of **3a** (CHCl_3) ($5\text{H}_2\text{O}$) for X-ray analysis were grown by slow evaporation from a wet chloroform solution. Some key bond distances and angles are summarized in Table 2, while ORTEP plot for cationic part of **3a** is illustrated in Fig. 1. As expected from the spectroscopic analysis of **3**, both metal centers are in the same coordinated mode with the metal center being coordinated by a cymene ring, a



Scheme 1. Naphthyridine-based Multidentates.



Scheme 2. Preparation of ligand **1**.

Download English Version:

<https://daneshyari.com/en/article/1322227>

Download Persian Version:

<https://daneshyari.com/article/1322227>

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