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Mono- and dinuclear ruthenium complexes of bridging ligands incorporating two di-2-pyridylamine motifs: Synthesis, spectroscopy and electrochemistry

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Abstract

Mono- and dinuclear ruthenium(II) complexes of six bridging ligands that contain a central arene (phenyl, naphthalenyl or biphenyl) core to which are attached two di-2-pyridylamine groups have been prepared. These complexes possess six-membered chelate rings. Full assignments of their ^{1}H NMR spectra are described which provides insight into the comformations of the ligands in these complexes. The extent of metal–metal communication in the dinuclear complexes was probed by electrochemical measurements and related to metal–metal distances.

Keywords: Bridging ligands; Ruthenium complexes; NMR spectroscopy; Electrochemistry; Metal–metal interactions

1. Introduction

The archetypal bidentate ligand 2,2′-bipyridine (bpy) (Fig. 1) has been used in coordination chemistry for well over a century [1], forming complexes *via* stable five-membered chelate rings with a broad range of metal centres [2]. In recent years many bridging ligands that incorporate two or more bpy type chelating motifs have been prepared [3–5]. These newer bridging ligands have been used to form multinuclear complexes with enhanced stability, and particular emphasis has been placed upon ligands that facilitate strong metal–metal interactions [6–10]. In the context of their stereochemical [11–13], electrochemical and photophysical properties [6,7,14–18], ruthenium(II) complexes of such ligands have been particularly well studied.

While ligands such as bpy, which coordinate *via* a stable five-membered chelate ring have attracted considerable attention, the class of ligands that bind to transition metals through a six-membered chelate ring have been much less studied. These ligands contain two 2-pyridyl substituents separated by a single atom spacer, X (Fig. 1) [19]. Where the spacer is a methylene group ($X = CH_2$) the compound, di-2-pyridylmethane (**dpm**), has been sparingly used as a ligand [20–22], but has recently been incorporated into a range of multidentate bridging ligands [23–27]. The sp^3 hybridised X group in **dpm** and ligands containing **dpm** has an insulating effect that limits metal–metal communication in complexes of such ligands [27]. The derivative where $X = NH$, di-2-pyridylamine (**dpa**), is a commercially available ligand that has been extensively used in coordination chemistry [28–32]. It has also been employed as a component in multidentate bridging ligands by ourselves [33–35], and others [36–39], wherein the NH group or tertiary heterocyclic amine was shown to be planar and to possess considerably more sp^2 character. This is consistent with delocalisation of the amine lone pair into the π-systems of the compound. This characteristic should facilitate

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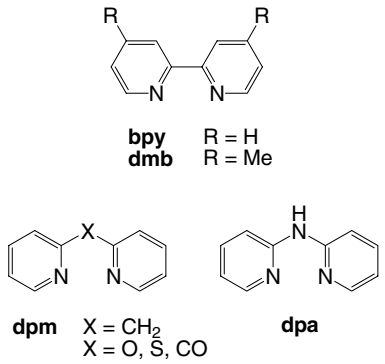
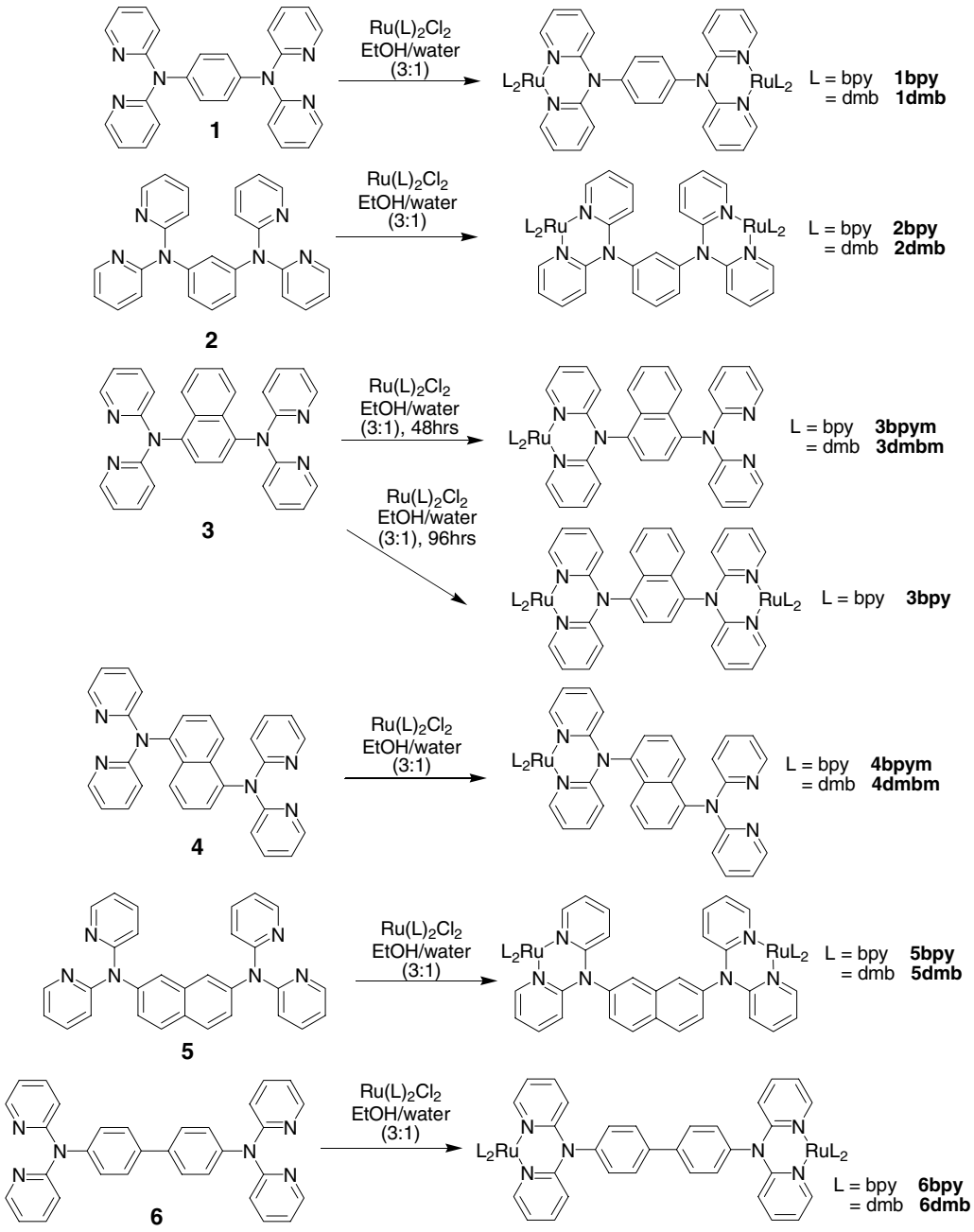


Fig. 1. Bidentate ligands that form five-membered chelate rings, **bpy** and **dmb**, and ligands that coordinate *via* six-membered chelate rings, e.g. **dpm** and **dpa**.

enhanced metal–metal interactions in complexes of bridging ligands incorporating this subunit.

In this paper we describe ruthenium complexes of six known bridging ligands **1**–**6** containing the **dpa** subunit (Scheme 1), and study the nature of the metal–ligand and metal–metal interactions within such complexes. The ligands studied are based around phenyl, naphthalenyl and biphenyl cores which have been appended with two **dpa** subunits to produce a series of potentially doubly bidentate bridging ligands. This array of ligands utilises some of the design principles outlined by us previously [4,5]; including different arene cores and substitution patterns of those cores. Ligands **1** and **6** were first studied and reported by Yang et al. [36], while we recently reported



Scheme 1.