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Review

Coordination chemistry of mononuclear ruthenium complexes bearing versatile 1,8-naphthyridine units: Utilization of specific reaction sites constructed by the secondary coordination sphere

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ABSTRACT

This article reviews recent work in the area of ligand-centered reactivities in mononuclear ruthenium complexes. The coordination chemistry of polypyridine-derived ligands is discussed, with particular focus on their ligand-centered redox properties originating from the attachment of redox-responsive 1,8-naphthyridine functional groups. This review provides key insights towards the incorporation of sophisticated and versatile 1,8-naphthyridine-based ligands into mononuclear ruthenium complexes.

Contents

1. Introduction

The primary coordination sphere of a metal complex controls its characteristic properties through the presence of direct covalent bonds between the metal center and the ligands. For example, compounds based on polypyridyl components that contain transition metals, such as ruthenium(II), play important roles in solar energy conversion and in the data storage of image or electronic information at the molecular level [1–4]. In addition, polypyridyl ruthenium complexes are considered prototypes in coordination chemistry due to the inertness of their metal-pyridyl bonds. In contrast, noncovalent interactions such as intramolecular hydrogen bonds and van der Waals forces between ligands establish the secondary coordination spheres of metal complexes, with an appropriate arrangement of ligands in the secondary coordination

Abbreviations: bpy, 2,2′-bipyridine; Im, imidazole; MLCT, metal-to-ligand charge transfer; NAD, nicotinamide adenine dinucleotide; NAP, naphthyridine; NHC, *N*-heterocyclic carbene; phen, 1,10-phenanthroline; pic, 4-picoline; PPh_3, triphenylphosphine; py, pyridine; TN, turnover number; tpy, 2,2′:6′,2″-terpyridine; TR-IR, time-resolved infrared.

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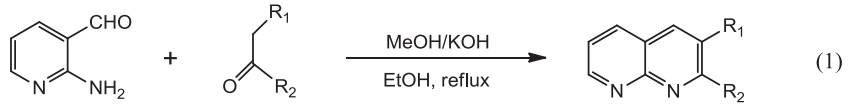
sphere also regulating the reactivity of the coordinated ligands [5–8]. As nature often utilizes the active sites of metalloproteins to create more elaborate reaction spaces and promote biochemical reactions, the ability of metalloproteins to regulate their coordination environments has been studied using numerous model compounds [9–16]. As such, nature can be considered the true pioneer of coordination chemistry involving versatile ligands. In the context of biomolecules, significant attention is currently being focused on ligand-centered reactivities in transition metal complexes [17–20].

In this context, the naphthyridines (NAPs) are a group of diazanaphthalenes that contain a single nitrogen atom in each ring but no nitrogen atom at either of the bridgehead positions [21]. Several structural isomers exist, including 1,8- and 1,5-NAP, where the 1,8-NAPs are key components of a number of antibacterial agents [22]. Thus, in addition to their obvious medicinal applications, 1,8-NAP and its derivatives have been employed in coordination chemistry as bridging ligands for the construction of molecular architectures. However, since the initial report by Tanaka and co-workers describing a detailed 1,8-NAP-based redox reaction [23], attention has also been paid to the ligand-centered reactivities of a variety of NAP ligands in the context of the nicotinamide adenine dinucleotide (NAD) coenzyme and its model compounds [24–26]. Studies into metal complexes that are covalently connected through pyridyl binding sites and versatile NAP ligands are therefore of particular interest, as they exhibit potential in the context of catalytic, energy storage and conversion, and biological applications.

Thus, we herein examine the various routes reported to date for the synthesis of ligands containing polypyridyl binding sites with 1,8-NAP frameworks that are closely related to biologically important molecules. In addition, the coordination chemistry of these ligands in mononuclear ruthenium complexes and the reactivities of the ligands in the secondary coordination sphere are also examined.

synthetic procedure towards the 1,8-NAP framework is given in Eq. (1) [29–32], where these compounds are prepared via the Friedländer condensation of 2-aminonicotinaldehyde with the corresponding acyl derivatives. In this system, the precursor 2-aminonicotinaldehyde must be freshly prepared and used immediately after isolation to avoid self-condensation side reactions. Indeed, a facile synthesis of 2-aminonicotinaldehyde was reported by Caluwe and co-workers in 1974 [31], with modifications being introduced later by Dunbar et al. [33] and Rivera et al. [34]. In addition, the preparation of various alkyl-substituted (i.e., 2- and/or 3-position) NAP ligands has also been reported [35–40], where the introduction of bonding substituents at the 2-position of the NAP ring gives rise to polydentate or bridging ligands. For example, as shown in Scheme 1, furyl (**2**), thiazolyl (**3**), pyrrolyl (**4**), thienyl (**5**), 2-hydroxyphenyl (**6**), and pyridyl (**7**) groups can be introduced covalently to the 2-position of the NAP core [33,35,37]. Indeed, the crystal structure of **7** was recently determined by X-ray crystallographic measurements [41], where it was found that C—H···N interactions and intermolecular π–π stacking generate a three-dimensional network. These effects lead to small dihedral angles between the NAP ring system and the pyridine group (Fig. 1a). Furthermore, in the context of 2-pyridyl derivatives, the extended π-conjugation system of **8** was also prepared (Scheme 1) [42–45], and its crystal structure was confirmed by our research group (Fig. 1b). Moreover, various aryl- and alkyl-disubstituted 1,8-NAPs have recently been reacted with alcohols to achieve high yielding β-alkylation transformations (Eq. (2)) [46]. Based on the confirmed molecular structure of one such derivative by X-ray crystallographic measurements, mechanistic investigations suggested that the reaction undergoes a hydrogen-transfer-mediated alkylation.



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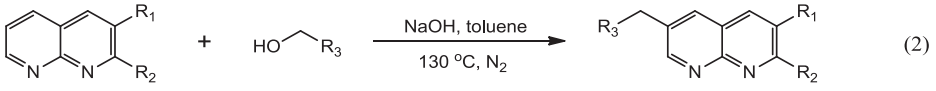

(2)

2. Preparation of 1,8-NAP-based ligands

The framework of interest in the context of this study is that of 1,8-NAP (**1**, Eq. (1)). Although 1,8-NAP is commercially available from a number of suppliers, a variety of functionalized 1,8-NAP derivatives can also be synthesized via a range of previously reported procedures. To date, two key methods for the preparation of naphthyridines have been reported, namely the Skraup reaction and the Friedländer reaction [27,28]. Thus, the general

A number of tridentate systems bearing multiple 1,8-NAP units have also been synthesized. For example, the Friedländer reaction of 2-aminonicotinaldehyde with 4-*tert*-butyl-2,6-diacetylpyridine or 2,6-diacetylpyridine in ethanolic KOH provides tridentate ligands **9** and **10**, respectively (see Fig. 2) [47–49]. A similar reaction between 6-*tert*-butyl-2-aminonicotinaldehyde and 2,6-diacetylpyridine afforded tridentate ligand **11** (Fig. 2) [50].

Furthermore, a ligand containing both the 1,8-NAP and *N*-heterocyclic carbene (NHC) moieties was reported by Bera and

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