Coordination Chemistry Reviews 350 (2017) 84–104

Contents lists available at ScienceDirect

Coordination Chemistry Reviews

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

Review

More hydra than Janus – Non-classical coordination modes in complexes of oligopyridine ligands

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ARTICLE INFO

Article history:
Received 20 May 2017
Accepted 11 June 2017
Available online 15 June 2017

This review is dedicated to our friend and colleague, Pierre Braunstein and celebrates his contributions to organometallic and coordination chemistry as well as to the scientific culture of our region.

Keywords:
Ligand
2,2′-Bipyridine
1,10-Phenanthroline
2,2′:6′,2″-Terpyridine
Oligopyridine
Cyclometallation
Hypodentate
Reactivity

ABSTRACT

Oligopyridine ligands and the related compound 1,10-phenanthroline have played a critical role in the development of coordination chemistry. This class of ligands probably constitutes the most commonly adopted metal-binding scaffold used in supramolecular and nanoscale chemistry. The adoption of the oligopyridine metal-binding domain in such areas is often predicated upon the assumption that the ligands will adopt chelating polydentate bonding modes. This review highlights the fact that these ligands are a great deal more versatile than this assumption would suggest. In addition to the chelation, cyclometallated and hypodentate bonding modes are also commonly observed.

Contents

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http://dx.doi.org/10.1016/j.ccr.2017.06.006
0010-8545/

1. Introduction

2,2′-Bipyridine (bpy, **1**) is the parent compound of a series of classical chelating polydentate nitrogen donor ligands including 1,10-phenanthroline (phen, **2**) and 2,2′:6′,2″-terpyridine (tpy, **3**) (Scheme 1). These ligands define a paradigm of classical coordination chemistry and ever since the first description of bpy by Fritz Blau in 1888 [1], the tacit assumption is that they behave as multidentate N-donor species in which all of the available donor atoms coordinate to a metal centre [2–9]. In recent years, exceptions to this behavior have defined new bonding modalities with important consequences for the structural and reaction chemistry of these compounds. As the title of this article[1] indicates, these ligands have not just one or even two but a multiplicity of coordination modes. This review attempts to present a coherent overview of this multiplicity, including hypodentate coordination and cyclometallated binding in addition to the chelating mode. Excluded from the review are divergent oligopyridines which cannot present a polydentate chelating donor set to a metal centre; these have been partially reviewed elsewhere [10,11]. All searches of the Cambridge Structural Database (CSD) made for this review used the CSD version 5.38 with updates November 2016 and February 2017 [12] and Conquest v. 1.19 [13].

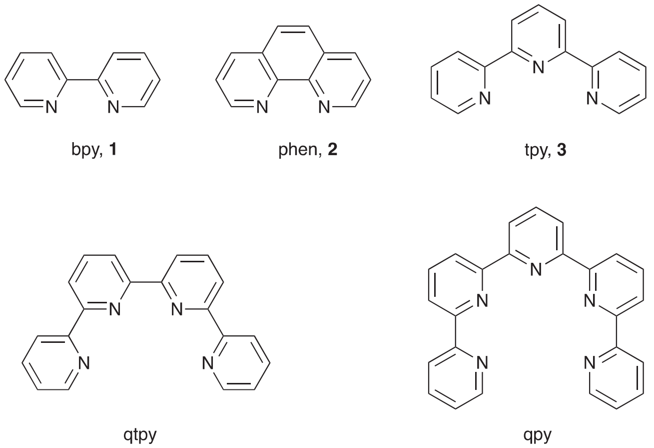
2. Hypodentate coordination

2.1. What is hypodentate coordination?

One of us introduced the term hypodentate a number of years ago to describe complexes of tpy in which one of the nitrogen atoms was not coordinated, resulting in a bidentate N,N′-bonding mode [14]. The term is now generic for coordinated ligands in which fewer than the maximum possible number of chelating donors are bound to a metal centre. Hypodentate bonding modes are emerging both as interesting and important isolated species and as postulated intermediates in the formation and dissociation of chelate complexes of these ligands as well as in novel dynamic processes. Although originally formulated for oligopyridines, the hypodentate concept has found broader acceptance, especially in the study of polydentate amines [15–35]. The description hypodentate has been used to refer both to the ligand and to the complexes incorporating such ligands. This section will consider hypodentate complexes containing oligopyridine and related ligands, especially monodentate bpy and phen ligands, mono- and bidentate tpy ligands, mono-, bi- and tridentate quaterpy ligands, mono-, bi-, tri- and tetradentate qpy ligands, and mono-, bi-, tri-, tetra- and pentadentate qpy ligands. Excluded are compounds in which the full complement of donor atoms is distributed between multiple metal centres in a bridging mode.

2.2. Design strategies for complexes containing hypodentate ligands

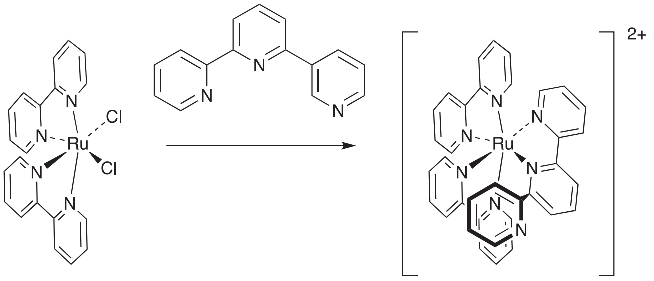
It is useful to consider design strategies for the synthesis of complexes containing hypodentate ligands. A number of approaches have been identified and implemented with various degrees of success. The first approach is to utilize a kinetically inert metal centre (typically possessing a d^3, d^6 or d^8 electron configura-



Scheme 1. The commonest oligopyridine ligands and the abbreviations used throughout this review. The IUPAC names are given in the table of ligand abbreviations (Table 1).

Table 1
Ligand abbreviations including typical examples to illustrate how substituted ligands are presented in a shortened form in the body of the text.

bpy	2,2′-bipyridine
3,3′-(HO)$_2$bpy	2,2′-bipyridine-3,3′-diol
Hhfacac	1,1,1,5,5,5-hexafluoropentane-2,4-dione
3,3′-Me$_2$bpy	3,3′-dimethyl-2,2′-bipyridine
N-Mebpy	N-methyl 2,2′-bipyridinium
N-Metpy	N-methyl 2,2′:6′,2″-terpyridinium
6,6′-Ph$_2$tpy	6,6′-diphenyl-2,2′:6′,2″-terpyridine
phen	1,10-phenanthroline
qpy	2,2′:6′,2″:6″,2‴:6‴,2⁗-quinquepyridine
qtpy	2,2′:6′,2″:6″,2‴-quaterpyridine
septipy	2,2′:6′,2″:6″,2‴:6‴,2⁗:6⁗,2⁗′:6⁗′,2⁗″-septipyridine
spy	2,2′:6′,2″:6″,2‴:6‴,2⁗:6⁗,2⁗′-sexipyridine
tpy	2,2′:6′,2″-terpyridine



Scheme 2. The kinetically inert d^6 six-coordinate complex [Ru(bpy)$_2$Cl$_2$] has two chlorido ligands which can be replaced by incoming donors. Upon reaction with tpy, only two of the three nitrogen donors of the tpy ligand can bind, giving the six-coordinate complex [Ru(bpy)$_2$(tpy-*N,N′*]$^{2+}$ containing a hypodentate (bidentate) tpy ligand [36].

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[1] The Lernaean Hydra was a multi-headed water monster of Greek mythology. In contrast, the Roman God Janus is usually depicted as having (only) two faces. The image in the graphical abstract is taken from the watercolour "Janus" by Tony Grist and made available under the Creative Commons CC0 1.0 Universal Public Domain Dedication (https://commons.wikimedia.org/wiki/File:Janus_.jpg)