

Review

Chiral multifunctional molecules based on organometallic helicenes: Recent advances



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ABSTRACT

Organometallic chemistry of helicenes ligands has received great attention and can be considered as a useful tool for the development of chiral multifunctional molecules displaying optimized chiroptical properties in combination with other properties provided by metallic centers. Over the past decade, we have explored different families of transition-metal based helicenes bearing a C-M bond, namely metal-ethynyl and metal-vinyl-helicenes, cyclometallated helicenic complexes based on C^N or C^C chelates, and helicene-bipy complexes bearing either bipy C^N chelate or C-M bonds with ancillary ligands. We have studied their electronic and (chir)optical properties, together with potential applications in materials science. In this review, we will describe the recent advances achieved in our group in this field of research.

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1. Introduction

Helicenes are inherently chiral molecules bearing *ortho*-fused aromatic or heteroaromatic rings with extended π -conjugation [1–5]. A [*n*]helicene possessing more than 5 aromatic rings ($n \geq 5$) can exist as two stable enantiomers, which are denoted as *P* (right handedness) and *M* (left handedness). The inherently chiral topology in combination with extended π -conjugation in helicenes is known to result in large-magnitude optical rotations (ORs) and strong electronic circular dichroism (ECD) spectra [6–8]. Besides, helicenes display other properties, such as vibrational circular dichroism (VCD) [9,10], Raman optical activity (ROA) [11], circular polarized luminescence (CPL) [12,13], non linear optical (NLO) activity [14,15], catalytic activity [16,17], spin selectivity [18], biological activity [19], sensing [20], or self-assembly [21,22]. Recently, chiral metallohelices have attracted much interest and different types have been reported [23], on account of the following reasons. First of all, simply through basic coordination and organometallic chemistry [24], metals are able to provide powerful templates for assembling π -conjugated ligands into well-defined molecular structures [25–29]. Secondly, the introduction of metal ions into π -helical fragments may endow them with novel properties such as luminescence [30] or redox activity [29]. Finally, coordination and organometallic chemistry also provide simple strategies to tune the chiroptical, optical and electronic properties of helicenes ligands, since the topology along with the nature of the metal–ligand and ligand–ligand interactions can be modified by changing the metal center, together with coordination sphere geometry, redox state of metallic helicenes, and so on. All these properties are important features for the development of new types of chiral materials, such as chiral Organic Light-Emitting Diodes (OLEDs), chiroptical switches, conductive materials, emissive molecules for bioimaging, sensors, non linear optical materials, to name a few [31–33]. In the last decade our group has been developing the structural diversity that can be created from the combination of organic chemistry of helicenes with the chemistry of transition-metal complexes [23], either via coordination-driven self-assembly of helicenic ligands or via helicene-based organometallic species. While several reviews and books have been published on purely organic helicenes derivatives [1–5], we focus here on the organometallic helicenes reported by our group, *i.e.* organometallic helicenes bearing a C–M σ bonds [23,26].

The first helicenes were reported by Meisenheimer and Witte in 1903 [34]. In the next few decades, there has been little development on organic helicenes, until the 1950s when Newman and coworkers started to develop their synthetic and separation methods; then helicenes chemistry started to take off [35–37]. The chemistry of organometallic helicenes was pioneered by Thomas Katz in the late 1970s [23,38]. In the last decade our group has been developing a diversity of such helicene-based organometallic complexes. These can be divided into different families: 1) metal-vinyl- and metal-ethynyl-helicenes, 2) cyclometallated helicenic complexes based on C^N chelates, 3) cyclometallated helicenic complexes based on C^C chelates, and 4) helicene-bipy complexes bearing either bipy C^N chelates or C–M bonds with ancillary ligands. We will show that each class of compounds provides helicenes with different functionalities. New fundamental knowledge

in chiral complexes can be established and different future applications can be targeted.

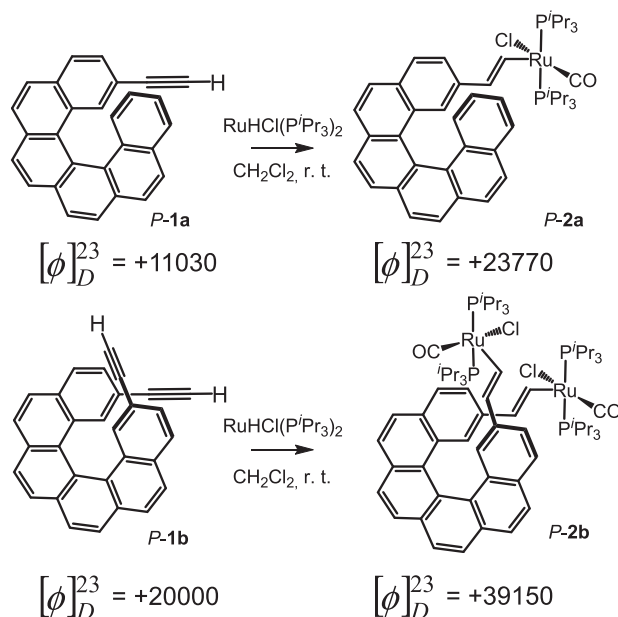
2. Metal-vinyl- and metal-ethynyl-helicenes

Metal-ethynyl and metal-vinyl-helicenes are organometallic helicenes in which a metal is grafted to a carbohelicenic unit through a π -conjugated bridge, being either a vinyl or an ethynyl linker. The grafting of metal centers such as ruthenium or osmium onto a helicenic scaffold leads to significant modification of electronic density distribution and of photophysical and spectroscopic properties [39]. Furthermore, aryl-alkynyl-metal units such as helicene-ethynyl-gold ones can be assembled in a controlled way through coordination with a multitopic ligand, typically a ditopic biphosphine [40,41].

2.1. Metal-vinyl-helicene complexes

2.1.1. Helicene-vinyl-ruthenium complexes

Several examples of metal-vinyl complexes have been described in the literature [42–44], most of them bearing a ruthenium or an osmium atom (displaying a good match between energies of their d orbitals with the π -orbitals of the unsaturated ligand) and showing good redox activity and catalytic properties [45]. In 2012, our group reported carbo[6]helicene scaffolds grafted with one or two vinyl-ruthenium moieties [46], showing fully reversible redox-triggered chiroptical switching activity [47]. These enantiopure carbo[6]helicene-vinyl-ruthenium complexes were prepared by hydorruthenation of enantiopure mono-2-ethynyl-carbo[6]helicenes *P*(+) and *M*(-)–**1a**, or bis-2,15-ethynyl-carbo[6]helicenes *P*(+) and *M*(-)–**1b** (Scheme 1). The introduction



Scheme 1. Synthesis of *P* enantiopure mono- and bis-Ru^{II}-vinyl-helicene complexes **2a,b** by hydorruthenation of *P*-mono- and bis-ethynyl-helicene ligands **1a,b**. Molar rotation values^a measured in CH₂Cl₂ at concentrations around 5 · 10^{−5} M [46].

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