



Review

Multidentate unsymmetrically-substituted Schiff bases and their metal complexes: Synthesis, functional materials properties, and applications to catalysis

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Dedicated to our distinguished colleague and friend Prof. Jean-Yves Saillard on the occasion of his 70th birthday.

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ABSTRACT

This review focuses on the recent developments of unsymmetrically-substituted multidentate Schiff bases whose steric and electronic characteristics are easily manipulated by selecting suitable condensing aldehydes or ketones and primary amines, and on their metal complexes. After a brief historical introduction, this manuscript is divided in three main sections. In the two first parts, the synthesis, reactivity, functions, and properties of tridentate Schiff base precursors and of quadridentate Schiff base metal complexes, respectively, are discussed through a literature survey including examples of research from the authors' groups. More specifically, the second section is formed of seven subsections with the synthesis of unsymmetrically-substituted tetradentate Schiff bases and their transition metal (V, Mn, Fe, Co, Ni, Cu, Zn, Ru, Pd, Pt) and uranyl complexes. Emphasis is given to our research work based on ferrocenyl-containing tri- and tetradentate unsymmetrically-substituted Schiff base complexes of Ni(II) and Cu(II) starting from variously substituted ferrocenyl- β -diketones. The unsymmetrically-substituted Schiff base complexes present a wide range of remarkable properties that are also summarized in this section, including structural, biocidal, magnetic, and second-order nonlinear optical properties. The third section is devoted to the catalytic activity of Schiff base metal complexes that is discussed through thirteen major organic reactions, including copper-catalyzed azide-alkyne cycloaddition (CuAAC), Henry and nitro-Mannich reactions, hydrosilylation of ketones, aldol, cyclopropanation and epoxidation reactions, among others.

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1. Introduction

The term «Schiff base» comes from the name of Hugo Schiff (1834–1915) [1,2], an Italian-naturalized chemist, German by nationality, who synthesized the first so-called Schiff base (SB) in 1864 [3,4]. Schiff bases (SBs), characterized by an imine ($>C=N-$) or azomethine ($-HC=N-$) group, are generally synthesized by condensation reactions of carbonyl functionalities (ketone or aldehyde) with primary amines. SBs have gained considerable attention due to their remarkable biological activities (such as antiapoptotic, antifungal, antibacterial, anti-inflammatory and antiviral activities) [5–7], catalytic activities [8–13], electroluminescent properties [14–16], fluorescence properties [17–19], nonlinear optical (NLO) properties [20], and applications in sensors [21] and organic photovoltaic materials [22]. Owing to the easy tunability of their stereo-electronic structures, most SBs are fascinating ligands, because they readily form stable complexes with most of the transition metals [23,24]. Consequently, during the last decades the symmetrically-substituted SB metal complexes have been intensively studied because of their specific eminent catalytic activities, and this field has been the subject of numerous reviews [25–31]. For instance, Katsuki summarized the generation of *cis*- β metallosalen and its related complexes (the term salen represents the SB obtained through the condensation of two (identical or not) salicylaldehydes with a primary diamine), and reported their structural features and their applications in asymmetric synthesis [27]. On the other hand, Soloshonok and co-workers provided a good overview of using homologation of Ni(II) unsymmetrically-substituted SB complexes to obtain asymmetric α -amino acids [30,31]. Meanwhile, more than 500 new papers on unsymmetrically-substituted SB catalysts and unsymmetrically-substituted SB metal complex systems have been reported in the last three years. Many new features have also been discovered; for instance unsymmetrically-substituted SB metal complexes are more efficient catalysts than symmetrically-substituted SB complexes for the olefin polymerization [32]. The main factors contributing to the process of unsymmetrically-substituted SB complexes are the control of their specific structures with more than two different functional SB groups [33] and their excellent electronic and steric properties that are critical in catalytic systems [34].

Since their discovery, SBs are one of the most widely used ligands due to their easy preparation and remarkable versatility, and, therefore they played a pivotal role in the development of coordination chemistry of main group elements, transition metals and lanthanides. As a consequence, this very broad research field dealing with macrocyclic and acyclic SBs and their metal com-

plexes has led to an extensive number of publications, and has been comprehensively reviewed in 1987 [35] and 2004 [36]. In 2016, Li and co-workers [37] also summarized some classical synthetic strategy of asymmetric SBs derived from diaminomaleonitrile and their Zn, Cd and Cu complexes. In this review, divided in three main parts, we will focus on the synthesis, reactivity, functions, and properties of multidentate SBs and their metal complexes, based on selected recent works. The two first part considers tridentate and unsymmetrically-substituted tetradentate SBs and their respective transition metal (V, Mn, Fe, Co, Ni, Cu, Zn, Ru, Pd, Pt) and uranyl complexes, and emphasizes our research work based on ferrocenyl-containing tri- and tetradentate unsymmetrically-substituted SB complexes of Ni(II) and Cu(II) starting from variously substituted ferrocenyl- β -diketones. Some aspects of the structural, biocidal, magnetic, and second-order nonlinear optical properties of both the multidentate SBs and complexes are also outlined in this section. The third part of the review highlights the application to catalysis of various multidentate SB complexes in a panoramic view of thirteen major organic reactions, including copper-catalyzed azide–alkyne cycloaddition (CuAAC), Henry and nitro–Mannich reactions, hydrosilylation of ketones, aldol, cyclopropanation and epoxidation reactions, among others.

2. Tridentate Schiff base ligands and their metal complexes

In general, ONN-tridentate SB ligands are formed upon mono-condensation reactions of a β -diketone with one end of a primary diamine [38–58]. Such singly condensed compounds having a free amino group are commonly referred as “half units” [38–40] as they are potential precursors in the preparation of unsymmetrically-substituted tetradentate SBs (see Section 3). The tridentate SBs can exist in solution as a tautomeric mixture of keto-amine (enamine, $-(O=C(R)-CH=C(R')-NH-)$, and keto-imine (iminone, $-(O=C(R)-CH_2-C(R')=N-)$, forms [59]. In some instances, depending on the nature of the substituents of the β -diketone and/or the presence of transition metal ions in solution, either deacetylation of the starting β -diketone [60] or formation of 1,4- and/or 1,5-diazepine can occur [61,62]. In some instances, tridentate SBs can be isolated from condensation of salicylaldehyde and diamines such as 1,2-phenylenediamine or 1,2-diaminocyclohexane [63–66], but in the cases of 1,2-ethanediamine and 1,3-propanediamine, the half-units must be trapped as metal(II) half-unit complexes (M = Ni, Cu) in order to avoid the formation of the double-condensation products [67–70].

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