

Review

Asymmetric catalysis with octahedral stereogenic-at-metal complexes featuring chiral ligands

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ABSTRACT

The synthesis and the design of octahedral stereogenic-at-metal complexes featuring chiral ligands and their application as chiral catalysts in various asymmetric reactions are highlighted and discussed in the present review article. Owing to their ligand-located stereogenic elements, such complexes are conveniently accessible stereochemically-defined as Λ - and/or Δ -configured diastereomers, which can be viewed as 'pseudoenantiomers' when one primarily focuses on the stereogenic arrangement of multidentate ligands around the metal center. Their convenient synthesis poses a practical advantage over octahedral stereogenic-only-at-metal complexes, where the synthesis of the according Λ - and/or Δ -configured isomers, which are consequentially 'true enantiomers', is often somewhat cumbersome. However, octahedral stereogenic-at-metal complexes featuring chiral ligands offer the same favorable scaffold for the design of asymmetric catalysts as related octahedral stereogenic-only-at-metal complexes, namely a chiral, propeller-shaped arrangement of bidentate or tridentate ligands around a stereogenic octahedral metal center. These attractive features are the reason why we focus in the present review on the, from our perspective, highly capable and promising class of octahedral stereogenic-at-metal catalysts featuring chiral ligands. In the following paragraphs, we will discuss recent examples of such catalysts, which have so far been utilized as chiral Lewis acid catalysts, as chiral Brønsted acid catalysts, and as chiral hydrogen-bonding catalysts in various asymmetric reactions.

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1. Introduction

Asymmetric catalysis constitutes a powerful and important tool for the synthesis of chiral building blocks, which are demanded for the synthesis of pharmaceutical and agricultural chemicals. This is particularly the case for those building blocks which are not or only uneconomically accessible from the chiral pool [1,2].

Generally, two classes of chiral catalysts can be distinguished: 1) purely organic catalysts, that is to say ‘traditional’ organocatalysts [3–6], and 2) organometallic catalysts [7]. The majority of the latter contain chiral organic ligands which coordinate to a transition metal center and they activate their substrates for reaction either a) via coordination of the respective substrates to the catalyst’s Lewis acidic metal center going along with an electronic activation, also photoinduced where applicable [8–14], b) via covalent and/or non-covalent interactions of the substrates with the catalyst’s ligand sphere (e.g., via multiple hydrogen-bonding interactions) [15–25], c) or via a combination of both [26–30]. The catalyst’s stereoinformation is then either transferred in a stereogenic reaction to a prochiral substrate or the chiral catalyst discriminates between two substrate enantiomers in the case of a (dynamic) kinetic resolution [31,32].

Importantly, the spatial arrangement of achiral or chiral bi- or tridentate ligands around an octahedral metal center can render that metal center itself a stereocenter (Figs. 1 and 2) [23,24,33–45]. For such complexes the terms *chiral-at-metal* and (more accurately) *stereogenic-at-metal* have been coined [46–54]. And for those complexes which feature a stereogenic metal center as their *exclusive element of chirality*, i.e., with all the coordinating ligands being *achiral*, the more restricting terms *chiral-only-at-metal* and (more accurately) *stereogenic-only-at-metal* have been coined (Fig. 2a) [55]. In the following paragraphs, we will exclusively use the more accurate terms *stereogenic-at-metal* and *stereogenic-only-at-metal*.

The absolute configuration of the metal center of octahedral stereogenic-(only)-at-metal complexes is designated as Λ in case the chiral/achiral bidentate or tridentate ligands shape a left-handed propeller and as Δ in case they shape a right-handed propeller (Fig. 1) [48,51,56–58].

In recent years, octahedral stereogenic-only-at-metal complexes [33–39,62,63,65–74] as well as stereogenic-at-metal complexes featuring chiral ligands [40–45,59–61,64] have proven their capabilities as stereoselective catalysts in various asymmetric transformations. Many of them have been identified as highly effective and highly enantioselective (in some cases >99% ee were

found for the products) and that often at remarkably low catalyst loadings – sometimes even at parts-per-million loadings [74].

For the Lewis acidic octahedral stereogenic-at-metal catalysts featuring two adjacent coordination sites and two exchange-inert bidentate cyclometalated ligands, which have recently been introduced by Meggers and coworkers [14], their high efficiency can be traced back as follows: these catalysts selectively (photo-)activate substrates via bidentate coordination to the Lewis acidic transition metal center and the accordingly activated substrates are then surrounded by the propeller-shaped arrangement of coordinatively-inert cyclometalated ligands, which offers the opportunity to highly efficiently shield one face of the activated prochiral substrates [14].

In contrast, for completely kinetically-inert octahedral stereogenic-at-metal catalysts, where the metal center mainly fulfills a structural role as a ‘glue’ for the participating organic ligands, their high efficiency can be traced back as follows: these catalysts activate and align their substrates for reaction via well-orchestrated and custom-tailored (non-)covalent interactions, e.g., via multiple cooperative hydrogen-bonding interactions [23–25,61]. Here, the globular, chiral, and rigid propeller-shaped ligand sphere of such complexes offers a highly eligible scaffold for the rational design of such (non-)covalent interactions [23,35,39–44, 59–62,64,74].

To the best of our knowledge, the first intentional application of an octahedral stereogenic-only-at-metal complex as a chiral catalyst in an asymmetric reaction was reported by Fontecave and co-workers in 2003 [33]. The authors reported about enantiopure bis-cyclometalated stereogenic-only-at-metal Ru(II) complex Δ -1, which they employed as a chiral catalyst in the asymmetric oxidation of sulfides to chiral sulfoxides with hydrogen peroxide (Scheme 1) [33].

After Fontecave’s work, several other groups started to develop and to use octahedral stereogenic-at-metal complexes as chiral catalysts in asymmetric reactions, in particular in the second half of the last decade [23,35,40,41]. As far as that is concerned, stereogenic-only-at-metal catalysts (Fig. 2a) have recently been thoroughly summarized and discussed in several review articles [14,25,55,75].

From our point of view, octahedral stereogenic-at-metal catalysts featuring chiral ligands (Fig. 2b) have so far somewhat been neglected and only superficially been reviewed [76], even though they have also well-proven their capabilities as useful chiral catalysts and, moreover, they offer some advantages over stereogenic-only-at-metal catalysts [40–45,59–61,64,77–108]. For instance, the

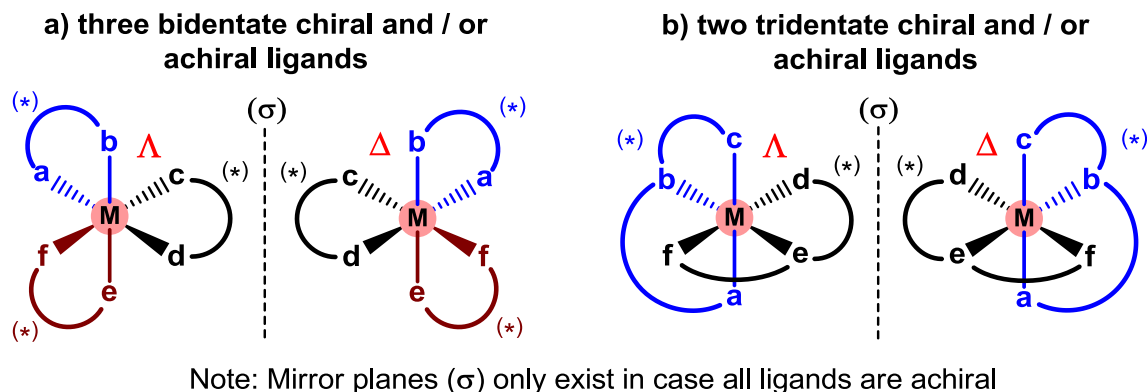


Fig. 1. Schematic representations of octahedral stereogenic-(only)-at-metal complexes featuring three bidentate (a) or two tridentate (b) chiral (*) or achiral ligands. Note that the Λ - and Δ -configured complexes are only enantiomers (\rightarrow mirror planes σ) in case they exclusively feature achiral ligands, i.e., when they are stereogenic-only-at-metal. In case they do feature one or more chiral ligand(s) they are diastereomers. Those diastereomers can be viewed as ‘pseudoenantiomers’ when one primarily focuses on the stereogenic arrangement of multidentate ligands around the metal center.

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