

Review

Ruthenium pincer complexes: Ligand design and complex synthesis

Hussein A. Younus^{a,b,d}, Nazir Ahmad^{a,b}, Wei Su^{a,b}, Francis Verpoort^{a,b,c,e,*}^a Laboratory of Organometallics, Catalysis and Ordered Materials, State Key Laboratory of Advanced Technology for Materials Synthesis and Processing, Center for Chemical and Material Engineering, Wuhan University of Technology, Wuhan, China^b Department of Applied Chemistry, Faculty of Sciences, Wuhan University of Technology, Wuhan 430070, China^c Tomsk Polytechnic University, Lenin Avenue 30, 634050 Tomsk, Russian Federation^d Chemistry Department, Faculty of Science, Fayoum University, Fayoum 63514, Egypt^e Ghent University, Global Campus Songdo, 119 Songdomunhwa-Ro, Yeonsu-Gu, Incheon, South Korea

Contents

1. Introduction	113
1.1. General considerations	113
1.2. Nomenclature of pincer ligands	113
2. Synthesis of pincer ligands	114
2.1. Tuning of the pincer ligand	114
2.2. Pyridine-based pincer ligands	114
2.2.1. Phosphine-containing pincer ligands	114
2.2.2. NHC-containing pincer ligands	118
2.2.3. NNN pincer ligands	119
2.2.4. CNN pincer ligands	120
2.3. Benzene-based pincer ligands	123
2.3.1. Symmetrical pincer ligands	124
2.4. Miscellaneous pincer ligands	124
3. Synthesis of ruthenium pincer complexes	127
3.1. Direct metallation	127
3.2. C–H bond activation	133
3.3. Si–H bond activation	139
3.4. Transmetallation	139
3.5. Trans-cyclometallation	142
4. Effects of the pincer complex structure on the catalytic activity	142
4.1. Hemilability and non-innocent behavior of the pincer ligand	142
4.2. Flexibility of the pincer framework (aliphatic versus aromatic)	146
5. Conclusion and future prospects	149
Acknowledgments	149
References	149

ARTICLE INFO

Article history:

Received 6 March 2014

Received in revised form 16 June 2014

Accepted 18 June 2014

Available online 26 June 2014

Keywords:

C–H activation

Direct hydrogenation

ABSTRACT

Active transition–metal complexes based on relatively inexpensive metals are considered to be a desirable method for sustainable human industrial growth. Considering their cost efficiency, ruthenium complexes are gaining increasing attraction, instead of palladium, rhodium, and iridium. Among the ruthenium complexes, ruthenium pincer complexes (RPCs) have received much attention due to their outstanding performance. Various strategies have been developed for pincer ligand design and RPC synthesis, which indicate that ligand design is a key feature of pincer chemistry. In addition, electronic and steric effects,

* Corresponding author at: Ghent University Global Campus Songdo, 119 Songdomunhwa-Ro, Yeonsu-Gu, Incheon, South Korea.

E-mail addresses: Francis@whut.edu.cn, Francis.verpoort@ugent.be (F. Verpoort).

Direct metallation
Pincer ligand
Ruthenium pincer complex
Transfer hydrogenation
Trans-cyclometallation
Trans-metallation

hemilability, non-innocent behavior, and the flexibility of the pincer ligand have significant effects on the catalytic performance of RPCs in hydrogenation and dehydrogenation reactions.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

1.1. General considerations

In the field of homogeneous catalysis, the choice of an appropriate ligand is very important and critical for fine-tuning the catalytic activities and stereoselectivities of metal complexes. Steric and electronic properties can greatly influence the nature of the reactive species and determine the course of reactions. Pincer-based metal catalysts are exceptional in determining the balance of stability *versus* reactivity. This balance can be controlled by systematic ligand modifications and/or variation of the metal center, thereby allowing enhancement of the metal complex reactivity, stability, and reaction selectivity. Therefore, developing a tridentate pincer ligand is one of the most fruitful strategies for obtaining well-defined metal–ligand bonds.

“Pincer ligands” [1] are tridentate ligands that bind tightly to three adjacent coplanar sites of a metal center, mostly in a *meridional fashion* [2], thereby resulting in the formation of two stable cyclometallated rings. The two cyclometallated rings may be five-membered [3], six-membered [4], or hybrids of five- and six-membered rings [5]. Since the pioneering work reported by Shaw [6] and Van Koten and Noltes [7] in the 1970s using the so-called PCP and NCN type metal complexes with pincer ligands, pincer-type complexes have occupied very important roles in chemistry and chemistry-related disciplines. A wide variety of pincer structures have been designed with various transition metals as well as different ancillary ligands. Therefore, the range of pincer metal complexes is extremely broad and increasing continuously (Fig. 1) [3,8–23].

Ruthenium complexes exhibit diverse beneficial characteristics including high electron transfer ability [24], high coordination ability to hetero-atoms, low redox potentials [25], Lewis acid activity [26], and unique reactivity with metal species and intermediates, such as oxo-metals, metallacycles, carbenes, and Schiff base complexes [27–32]. Consequently, ruthenium catalysis is one of the most important catalytic tools in organic synthesis [33]. In the last year, ruthenium pincer complexes (RPCs) represented around 13% of the total research conducted in the pincer complex area (Fig. 2). Large numbers of novel and useful reactions have been developed using stoichiometric and catalytic amounts of ruthenium complexes. Compared with traditional ruthenium catalysts, pincer complexes often offer higher efficiency and selectivity, as

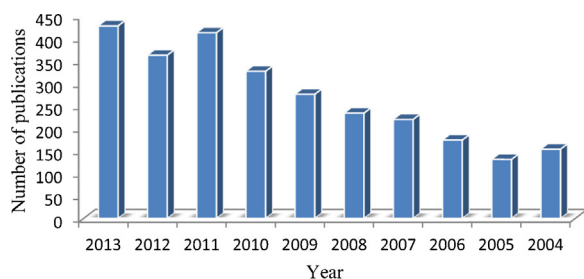


Fig. 1. Publications related to pincer complexes since 2004.

Source: Sci Finder.

well as functional group tolerance. Excellent reviews have discussed the synthesis and catalytic applications of palladium [14] and iridium [16] pincers, but only a few catalytic applications of ruthenium pincers [8,12,17,34] have been reviewed, and no previous reviews have addressed the design and synthesis of RPCs. Therefore, this review presents the different methods developed for the design and synthesis of RPCs over the last decade.

1.2. Nomenclature of pincer ligands

The nomenclature of the pincer ligand indicates the attachment points between the transition metal and the three atoms that coordinate with the metal center, the hetero/C-atoms of the side arms, and the central atom. If there are two spacers between the central moiety (pyridine, benzene, *etc.*) and the donor atoms of the side arms are C-atoms, or if there are no spacers, it will not be included in the symbol of the pincer ligand. However, if there are spacers and one or both of them are non-carbon atoms, the pincer ligand name indicates the position and type of the spacer as a superscript to the original attachment points. For example, pincer ligands of the type PNP with N/NH spacers between N and P are denoted as P^NN^NP, and as P^ON^OP in the same manner. If the pincer ligand has a CH spacer on one side and an N/NH spacer on the other side, it will be symbolized as P^NN^CP. In addition, the alkyl or the aryl group attached to the donor atom is included in the name as superscript for the donor atom, *e.g.*, PNP^{iPr} and PNP^{Ph}. When a N-heterocyclic carbene is one of the donor groups, the symbol of the pincer ligand indicates that the donor carbon atom is part of the N-heterocyclic carbene, *e.g.*, (NHC)CNN shows that the first C-atom is part of the carbene. In this review, this is indicated as a superscript for the C-atom so the symbol is C^{NHC}NN to confirm with the rules for the nomenclature of whole pincer ligands.

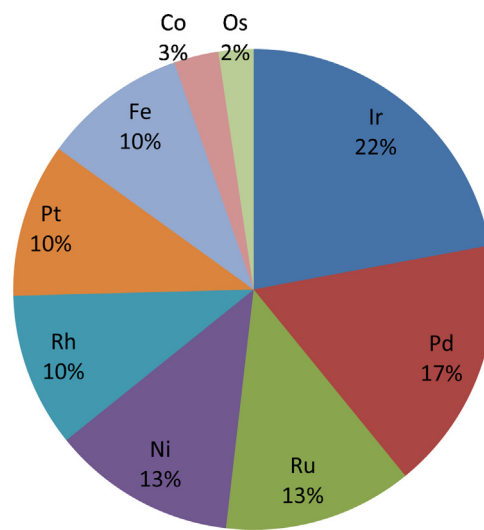


Fig. 2. Percentage of publications in 2013 related to pincer complexes with different metal ions.

Source: Sci Finder.

Download English Version:

<https://daneshyari.com/en/article/1299086>

Download Persian Version:

<https://daneshyari.com/article/1299086>

[Daneshyari.com](https://daneshyari.com)