ChemPubSoc Europe
DOI: 10.1002/ejic.201900455
EurJIC European Journal of Inorganic Chemistry
Full Paper

Half-Sandwich Complexes

Chemoselective Reduction of Imines Catalyzed by Ruthenium(II) Half-Sandwich Complexes: A Mechanistic Study

Noor U. Din Reshi,[a] Lakshay Kathuria,[a] and Ashoka G. Samuelson*[a]

Abstract: Ruthenium half-sandwich complexes ligated to chiral 2-oxazolidinethiones or 2-thiozolidinethiones in the reduction of N-benzylideneaniline using silyl hydrides as reductants has been examined. The chemoselective reduction of imines takes place under mild conditions to afford the corresponding amines in nearly quantitative yield. Mechanistic studies indicate that dissociation of the ancillary ligands generate the active catalyst in all the complexes studied, which is the same species generated by $[Ru(p\text{-cymene})(Cl)_2]_2$ under the reaction conditions. This results in the formation of a single catalytic species irrespective of the starting half-sandwich complex. Detailed mechanistic studies involving trapping of intermediates, in situ studies using mass spectrometry and NMR spectroscopy were carried out using the active catalyst generated by $[Ru(p\text{-cymene})(Cl)_2]_2$. The mechanism of the reaction is dependent on the number of the hydrogen atoms in the reducing silane. The reaction proceeds via Gade-Hoffman pathway or Zheng-Chan pathway when a dihydro or trihydrosilane is the reductant. However, the use of a monohydrosilane, leads to longer reaction times presumably due to a change in the reaction pathway.

Introduction

Amines are widely used in the synthesis of agrochemicals, natural products, pharmaceuticals, as well as biologically valuable fine chemicals.[1–4] They are present in different alkaloids, amino acids, and nucleotides. Several methodologies have been developed to synthesize amines. For example, the transition-metal catalyzed C-N bond formation especially using Pd-catalyzed Buchwald–Hartwig and Cu-catalyzed Ullman reactions has emerged as a useful method in amine synthesis.[5,6] The use of stoichiometric quantities of reductants such as lithium aluminium hydride and lithium borohydride for reducing imines, amides, cyanides, and nitroarenes is an alternative route to synthesize amines. However, these reductants are sensitive to air and moisture, incompatible to various functional groups and result in the formation of metal salt by-products.[7] Although the alkylation of ammonia using alkyl halides or alcohols is a simple method for preparation of amines, alkylation is difficult to control with alkyl iodides and bromides.[8]

The transition metal catalyzed hydrogenation, transfer hydrogenation, and reductive amination are also simple methods for amine synthesis. Although hydrogen is the ideal reducing agent, it is not suitable for many substrates due to high temperatures and high pressures required, and absence of chemoselectivity.[9–12] Reductive amination of carbonyl compounds using primary amines, via sequential condensation and catalytic reduction, constitutes a basic method for producing substituted amines, but it often requires drastic reaction conditions.[13–19] Transfer hydrogenation using silanes provides an attractive alternative method of reduction through hydrosilylation.

Hydrosilylation of imines has been performed under mild conditions in the presence of various metal catalysts; however, in comparison with the asymmetric hydrosilylation of prochiral ketones, the reaction of prochiral imines has been more challenging in achieving good enantioselectivity.[20] Most of the homogeneous transition metal catalysts for hydrosilylation of imines are based on platinum, rhodium, palladium, and titanium.[21] However, catalysts based on ruthenium, iridium, iron, zinc, nickel, palladium, and rhenium are also reported.[22] Catalysts based on Ru are widely used in reduction, more so in asymmetric hydrogenation and transfer hydrogenation of imines.[23–25] On the other hand, there are not many examples of ruthenium catalyzed hydrosilylation of imines.[26–30]

Dixneuf and co-workers reported $[RuCl_2(p\text{-cymene})]_2$ (**P**) as an efficient catalyst for the hydrosilylation of imines.[31] They obtained a variety of secondary amines in 69–97 % yield from the corresponding imines using a catalyst loading of 1–2 mol-%. The reaction was done in ethanol under ambient conditions at room temperature using PMHS as reductant which is an inexpensive by-product from the silicon industry. Furthermore, this strategy offered a very good chemoselectivity for reduction of the C=N bond and functional groups like -CN, $-NO_2$, C=O, and C=C were tolerated. Furthermore, the use of ethanol eliminated the need for a desilylation step which is usually involved in the hydrosilylation reactions to generate the product from the intermediate silylamine or silyl ether. This method was also applied successfully for hydrosilylation of difficult to reduce ketimines using 2 mol-% of the catalyst at room temperature for 4–20 h.

---

[a] Department of Inorganic and Physical Chemistry,
Indian Institute of Science,
Bangalore 560012, Karnataka, India
E-mail: ashoka@iisc.ac.in
http://ipc.iisc.ac.in/~ags/

Supporting information and ORCID(s) from the author(s) for this article are available on the WWW under https://doi.org/10.1002/ejic.201900455.