Journal of Organometallic Chemistry 829 (2017) 2–10

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

Review

N-heterocyclic silylenes as powerful steering ligands in catalysis

Saeed Raoufmoghaddam, Yu-Peng Zhou, Yuwen Wang, Matthias Driess*

Department of Chemistry, Metalorganics and Inorganic Materials, Technische Universität Berlin, Strasse des 17. Juni 135, Sekr. C2, D-10623 Berlin, Germany

ARTICLE INFO

Article history:
Received 30 June 2016
Received in revised form
20 July 2016
Accepted 20 July 2016
Available online 22 July 2016

Keywords:
Silylenes
Silicon analogues of carbenes
Homogeneous catalysis
Hydrosilylation
Pincer ligands

ABSTRACT

The present review highlights the role of N-heterocyclic silylene (NHSi) ligands, the silicon analogues of N-heterocyclic carbenes (NHCs), utilized in various catalytic organic transformations. The application of such novel ligands coordinated by different metal sites offers massive opportunities in organic synthesis. Despite significant advances in the synthesis of NHSi-based metal complexes, the use of these compounds in organic methodologies is still in its initial stages. Since NHSi ligands promote the σ donor-ability of phosphines and even that of NHCs, they can facilitate catalytic events by lowering the energy barrier of the rate limiting steps such as oxidative additions. This encourages scientists to utilize NHSi-metal complexes in exploiting catalyzed reactions and to revisit and improve various existing organic methodologies. This is demonstrated in several showcases of organic transformations including the Heck coupling, Suzuki coupling, alkyne and ketone hydrosilylation, amide reduction, cyclotrimerization of alkynes (in the absence and the presence of an organo cyanide), and Sonogashira cross-coupling reactions. The latter represents a novel and unexpected steering function of NHSi-based systems in homogeneous catalysis.

© 2016 Elsevier B.V. All rights reserved.

Contents

1. Introduction

N-heterocyclic carbenes (NHCs) metal complexes have been reported for a vast variety of transition metals and recognised to act as versatile precatalysts for the development of various types of catalytic organic transformations [1–8]. In contrast, related N-heterocyclic silylene (NHSi) systems, the heavier congeners of NHCs, have far less been subjected in related synthetic protocols. Only recently, the chemistry of transition-metal complexes bearing isolable NHSi ligands has introduced attractive and new synthetic methods with wide variety of properties that has largely influenced organic methodologies, in particular small-molecule activations, hydrosilylation reactions and C-C cross-coupling reactions (Fig. 1) [9–13].

Despite many N-heterocyclic Silylene (NHSi)-metal complexes that have been synthesized since the seminal work of Welz and Schmid in 1977 [14–17], the first utilization of a 'simple' NHSi ligand in homogenous metal-mediated catalysis was reported in 2001 [18].

In the following years, numerous mono-dentate and multi-dentate NHSi ligands as well as their corresponding catalytically active metal complexes were designed and synthesized [11,19–23].

NHSis can be considered as particularly strong σ donor ligands. Recently, our group studied the σ donor strength of a particular type of NHSi ligands [LSi(R):] in corresponding metal complexes [LSi(R):→M] bearing a ß-diketiminate backbone and different

* Corresponding author.
E-mail address: matthias.driess@tu-berlin.de (M. Driess).

http://dx.doi.org/10.1016/j.jorganchem.2016.07.014
0022-328X/© 2016 Elsevier B.V. All rights reserved.

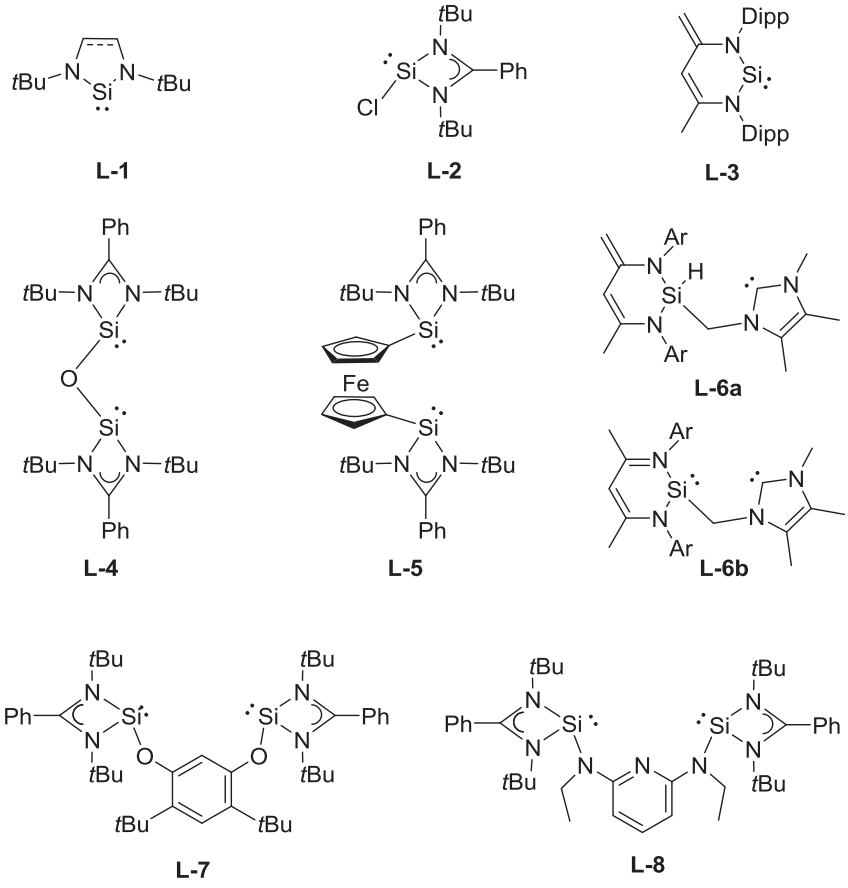


Fig. 1. Various N-heterocyclic silylene-based ligands (NHSi) used in homogeneous catalysis.

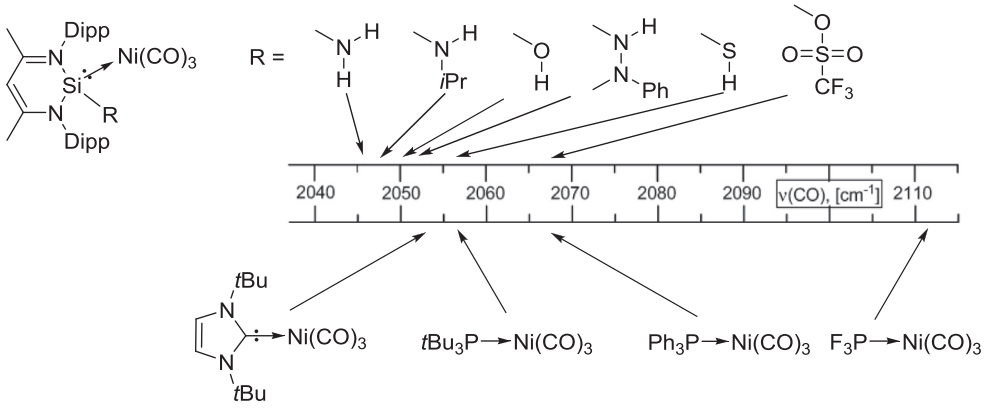
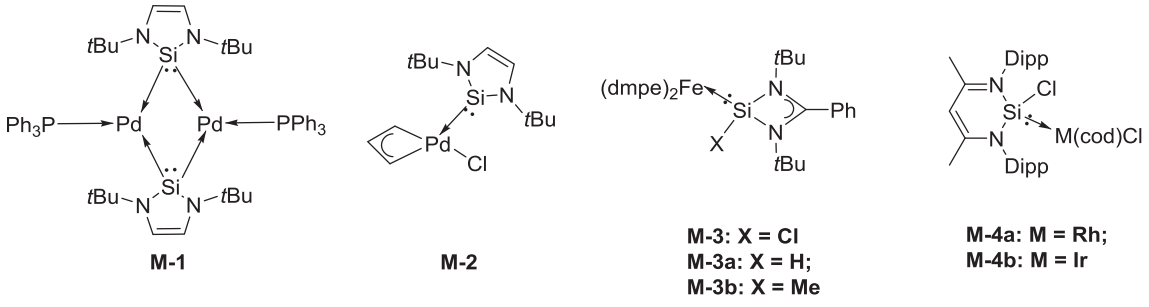


Fig. 2. Comparison of the carbonyl stretching modes (A_1) of NHSi-Ni(CO)$_3$ complexes with related phosphine and NHC analogous, reflecting the tunable donor-acceptor ability of the particular NHSi ligand [LSi(R):] in a relatively broad range.



Scheme 1. The mono-dentate NHSi complexes employed in catalysis.

Download English Version:

https://daneshyari.com/en/article/5153186

Download Persian Version:

https://daneshyari.com/article/5153186

Daneshyari.com