Synthesis, PGSE diffusion and multidimensional NMR studies on transition metal organometallic species applications in coordination chemistry and homogeneous catalysis

Author(s): Nama, Devendra Babu
Publication Date: 2007

Permanent Link: https://doi.org/10.3929/ethz-a-005421415

Rights / License: In Copyright - Non-Commercial Use Permitted
Dissertation ETH Nr. 17177

**Synthesis, PGSE Diffusion and Multidimensional NMR Studies on Transition Metal Organometallic Species: Applications in Coordination Chemistry and Homogeneous Catalysis**

A Dissertation submitted to the

SWISS FEDERAL INSTITUTE OF TECHNOLOGY ZURICH

For the degree of

Doctor of Sciences

Presented by

Devendra Babu Nama
M.Sc., Bangalore University, India
Born October 05th 1977
Citizen of India

Accepted on the recommendation of
Prof. Dr. P. S. Pregosin, Examiner
Prof. Dr. W. H. Koppenol, Co-examiner

Zurich, 2007
Summary

The applications of Pulsed Gradient Spin Echo (PGSE) diffusion, exchange and multidimensional NMR techniques to the study of organometallic complexes relevant to coordination and homogeneous catalysis are described in this thesis.

Chapter 1 describes the basic principles of NMR spectroscopy, and specifically, PGSE NMR and its applications to organometallic/coordination chemistry.

Chapter 2 focuses on diffusion studies on a modest number of mono and dicationic Pd(II) complexes and neutral Pt(II) complexes, plus $^{195}\text{Pt}$ as a diffusion probe for PGSE diffusion measurements. Thus, studies are related to molecular volumes, solvent and/or anion effects on ion pairing, hydrogen bonding and aggregation effects.

A series of mono-cationic palladium BINAP complexes, $[\text{Pd}(\text{rac-BINAP})(\text{an acetylacetonate anion})][X]$, ($X = \text{a}, \text{CF}_3\text{SO}_3^-, \text{b}, \text{BF}_4^-$), have been synthesized and characterized. These salts are believed to be intermediates in catalytic hydroamination or Michael reaction.

Chapter 3 deals with structure, exchange and dynamics (restricted rotation) of Ru(II) and Rh(I) N-heterocyclic carbene complexes.
The phosphine (PPh₃) exchange and dissociation have been studied via variable temperature and 2D NMR methods. Restricted rotation of the bulky carbene ligand in Ru(II) and Rh(I) carbene complexes is discussed based on line shape and exchange NMR studies.
Zusammenfassung

Diese Dissertation beschreibt die Anwendung von Pulsed Gradient Spin Echo (PGSE) Diffusionen, Austausch und multidimensionalen NMR Methoden zur Untersuchung von organometallischen Komplexen in Bezug auf die Koordination und die Anwendung in homogener Katalyse.

Kapitel 1 beschreibt die Grundprinzipien der NMR-Spektroskopie, speziell die PGSE NMR-Methode und ihre Anwendung in der Koordinations-Chemie.


Es wurde eine Serie von mono-kationischen Palladium-BINAP-Komplexen, $[\text{Pd}(\text{rac-BINAP})(\text{Acetylacetonat-Anion})][X]$, $(X = \text{a, CF}_3\text{SO}_3^-, \text{b, BF}_4^-)$, synthetisiert und charakterisiert. Man glaubt dass diese Salze Intermediate in katalysierten Hydroaminierungen und Michale Reaktionen sind.
Kapitel 3 handelt von Strukturen, Austausch und dynamischen Prozessen (eingeschränkte Rotationen) von Ru(II) und Rh(I) N-heterocyclischen Carben-Komplexen.