



Doctoral Thesis

PGSE (diffusion) and 2-D NMR studies on chiral organometallic complexes application to enantioselective catalysis

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Publication Date:

2001

Permanent Link:

<https://doi.org/10.3929/ethz-a-004237402> →

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Diss. ETH No. 14323

**PGSE (Diffusion) and 2-D NMR Studies on Chiral
Organometallic Complexes. Application to
Enantioselective Catalysis.**

A dissertation submitted to the
SWISS FEDERAL INSTITUTE OF TECHNOLOGY ZURICH

For the degree of
DOCTOR OF NATURAL SCIENCE

Presented by

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Zurich 2001

Summary

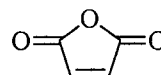
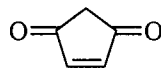
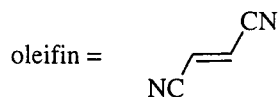
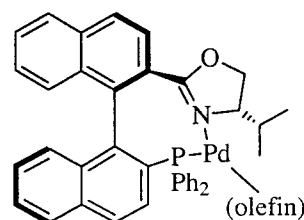
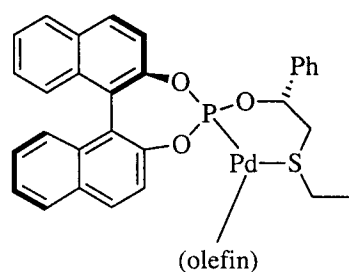
This thesis focuses on the applications of Pulsed Field Gradient Spin Echo (PGSE) NMR experiments and on multidimensional NMR techniques to the study of organometallic complexes relevant to enantioselective homogenous catalysis.

PGSE measurements on a large selection of organometallic complexes, e.g. Pd(II), Cu(I), Ru(II), etc, of differing molecular volumes, are demonstrated to provide a practical alternative to classical methods used in organometallic chemistry for estimating molecular size. This method is especially valuable where the “unknown” complex can not be isolated and/or where a side product is of particular interest, since it is possible to measure several components of a mixture simultaneously. Equally interesting, PGSE data can be used to investigate the phenomena of ion-pairing and hydrogen bonding in solution. Not only ^1H resonances are suitable for PGSE measurements, but also other nuclei can be used. Of particular interest is the use of ^{19}F signals when measuring diffusion coefficients of molecules or ions without protons, as PF_6^- , BF_4^- , OTf^- , etc. These anions are currently in use in a relatively large number of organometallic compounds in homogeneous catalysis and/or organic synthesis. ^1H and ^{19}F PGSE experiments can be used to determine diffusion coefficients for the cation and the anion separately and thus for investigating ion-pairing.

Interestingly, $[\text{Ru}(\text{Cl})(\text{PBU}_3)_2(\text{benzene})]\text{PF}_6$ shows ion-pairing as a function of the polarity of the solvent. In CDCl_3 solution the complex is present as a tight ion pair, whereas in CD_2Cl_2 the cation and the anion are moving separately.

Further, PGSE measurements can be used to study the degree of dimerization of diols, as for example 1,1'-binaphthol or TADDOL ($\alpha,\alpha,\alpha',\alpha'$ -Tetraaryl-2,2-dimethyl-1,3-dioxolan-4,5-dimethanol) derivatives.

Multidimensional NMR studies on organometallic complexes are shown to provide useful information on structure and bonding in catalysts and precursors.



For the Pd(0)(olefin) complexes shown above exchange spectroscopy and ^{13}C NMR data, reported in the tables below, provide useful information on the dynamics in solution and on the π -back bonding from the metal center to the olefin.

Exchange for the Pd(0) complexes as a function of the olefin.

olefin	P,N	P,S
fumaronitrile	no exchange	rotation
maleic anhydride	intramolecular	intermolecular
pentendione	intramolecular	intermolecular

The ^{13}C NMR data for the compounds shown above.

olefin	P,N	P,S
fumaronitrile	22.4-24.0	28.4-31.6
maleic anhydride	44.9-47.9	51.8-53.4
pentendione	65.3-70.9	72.6-73.5

The data indicate that the π -back bonding from the palladium zero valent center to the olefinic double bond is stronger for the complexes bearing the P,N ligand.