

# Ligand Dependent Regioselectivity in Palladium Mediated Allylic Alkylation



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2010

AKADEMISK AVHANDLING

För avläggande av filosofie doktorsexamen i kemi som, med medgivande av Institutionen för kemi, Göteborgs universitet, kommer att försvaras offentligt fredagen den 1:a oktober 2010 kl. 9.15 i sal KB, Kemigården 4, Göteborgs universitet och Chalmers tekniska högskola.

Fakultetsopponent är professor Pher G. Andersson, Institutionen för biokemi och organisk kemi, Uppsala Universitet.

## Abstract

In this thesis, different aspects on ligand dependent regioselectivity in palladium mediated allylic alkylation have been studied.

It is believed that the regioselectivity is a result of nucleophilic attack trans to phosphorous when applying ligands with different donor atoms. The regioselective memory effect (regio-retention) was studied in cationic systems utilizing a non-chiral P,N-ligand. The experimental findings showed only a small memory effect arising from the preferred attack of the nucleophile on the allylic moiety trans to phosphorous in the ligand. The reason for the low regio-retention in the reaction was shown to be due to an anion assisted apparent rotation of the  $\eta^3$ -allyl intermediate.

To minimize the dynamic processes, such as apparent rotation, pre-formed ( $\eta^3$ -allyl)Pd complexes containing a tethered ligand and an auxiliary ligand were applied in the allylic alkylation using malonate nucleophiles. The regioselectivity was shown to depend mainly on steric interactions rather than the electronic effects from the different ligands. In the complexes with less steric interactions, selectivity arising from the trans effect from the ligands could be achieved.

The structure of the tethered ( $\eta^3$ -allyl)Pd complexes in solution were determined by  $^1\text{H-NMR}$  spectroscopy, and the solid state structures were studied by X-ray diffraction spectroscopy. It has previously been reported that the longest Pd-C bond in the allylic moiety is the more reactive. Therefore, the Pd-C bond lengths in the complexes were compared with the reactivity of the different allylic positions in the alkylation reaction using sodium dimethyl malonate as nucleophile. However, no direct correlation was observed between the reactivity and the Pd-C bond lengths in the allylic moiety.

A tethered ( $\eta^3$ -allyl)Pd complex was used as a probe for the comparison of trans effects arising from different substituted pyridine derivatives. Preliminary results showed a decrease in trans effect from the pyridine ligands bearing electron donating substituents.

**Keywords:** Palladium, allylic alkylation, ( $\eta^3$ -allyl)palladium complexes, regioselectivity, PN-ligand, memory effects, dynamics, ligand effect, trans effects.

**ISBN:** 978-91-628-8161-0