

Concluding remarks

As described in *Chapter 1*, the objectives in the present thesis are: 1) the elucidation of the effect of the *o*-methoxy group introduced on the P-aryl rings of various diphosphine ligands in the palladium catalysed copolymerisation reaction of carbon monoxide and ethene and 2) the synthesis of new phosphine sulfonated ligands and their application in the less well known palladium catalysed non-alternating copolymerisation of carbon monoxide and ethene. Furthermore, the phosphine sulfonated ligands were applied in the palladium catalysed Suzuki-Miyaura cross-coupling reaction.

To reach these objectives, a large number of synthesis, studies of characterisation, catalytic reactions and high pressure NMR experiments were carried out.

In *Chapter 2*, two diphosphine ligands namely, 1,2-bis(di(2-methoxyphenyl)phosphino)ethane (*o*-MeO-dppe) and 1,3-bis(di(2-methoxyphenyl)phosphino)propane (*o*-MeO-dppp) were synthesised through a new synthetic protocol. Neutral and cationic palladium(II) complexes were synthesised and used as precatalysts in the palladium catalysed copolymerisation reaction of carbon monoxide and ethene in various reaction media. These ligands were compared with their phenyl counterparts in order to know more about the effect of the *o*-methoxy groups in the palladium catalysed CO/ethene. For this purpose, *in situ* HP-NMR experiments were carried out. It was found that irrespective of the reaction medium, the palladium(II) catalysts containing the dppp-like chelating diphosphines provide higher productivities as well as higher molecular weight polyketones as compared to the dppe-like counterparts. In 2,2,2-trifluoroethanol (TFE) was found that the *o*-methoxy oxygen atoms of either *o*-MeO-dppp or *o*-MeO-dppe ligands, produce a retardant effect on the propagation rate. This effect could be

due to the formation of an effective web of hydrogen bonding interactions with solvent molecules. As a result of the increased congestion at the metal centre, a slower diffusion of the monomers would take place. *In situ* high-pressure NMR studies have evidenced that the presence of *o*-MeO substituents on the P-aryl rings affects the kinetics of the CO/ethene copolymerisation. The rate of carbonylation of the β -keto chelates was found to be limited by the palladium(alkyl)(CO) migratory insertion, which makes the overall copolymerisation process independent of the CO pressure, at least in the range of the partial CO pressures investigated (5-30 bar).

In *chapter 3*, the synthesis of a new diphosphine ligands namely, *rac*-2,4-bis(di(2-methoxyphenyl)phosphino)pentane (*rac*-*o*-MeO-bdpp) as well as the synthesis of the corresponding palladium dichloride and palladium diacetate complexes were carried out. Since the objective of the *chapter 3* was to compare the backbone rigidity in the palladium catalysed copolymerisation reaction of carbon monoxide and ethene, this ligand was compared with the more rigid ligand 6,7-di(di-2-methoxyphenyl)phosphinyl-2,2,4,4-tetra(di-2-methoxyphenyl) $2\lambda^4,4\lambda^4$ diphosponiumbicyclo[3.1.1]heptane-bis-(PF₆) in different reaction media. It was found that the polyketone products produced with the phosphine catalysts show number-average molecular weights up to five times bigger than those obtained with the diphosponium-diphosphine catalysts. The results have been interpreted in terms of faster chain-transfer rate due to the electronic and steric properties of the diphosponium diphosphine ligand.

In *chapter 4*, new phosphine sulfonated ligands and neutral and cationic palladium(II) complexes were synthesised and characterised. These ligands were used for the non-alternating palladium catalysed copolymerization of carbon monoxide and ethene and compared with other more rigid phosphine sulfonated ligands from a mechanistic and catalytic point of view. It shows that

the complexes with the new phosphine sulfonated and more flexible ligand lead to the formation of low molecular weight copolymers, due to fast chain-transfer reactions, with an extra-ethene insertion in the growing polymer chain up to 23.2 % on addition of *p*-toluensulfonic acid, while the complexes containing the more rigid phosphine sulfonated ligand are orders of magnitude more active yielding non-alternating CO-ethene copolymers with an extra-ethene incorporation up to 27.8 %.

Operando HP-NMR experiments with both types of pre-catalyst have shown the corresponding Pd- β -chelates as resting state of the copolymerisation reaction, catalysed by neutral Pd(P-O) complexes.

In addition, due to the properties of these ligands, they were applied successfully in the Suzuki cross-coupling reaction of aryl -bromides and -chlorides under microwave conditions in neat water