

Summary

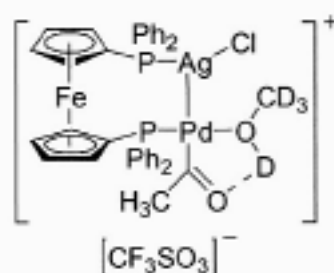
The versatility of palladium compounds containing phosphine ligands in homogeneous catalysis is well known. Therefore, stoichiometric and catalytic reactions of organopalladium(II) complexes have been studied thoroughly. The research described in this thesis involves a study of ionic palladium(II) complexes containing a palladium-carbon bond and a diphosphine ligand. We concentrated on solvolytic reactions of alkylpalladium and acylpalladium compounds. Throughout this thesis the alternating copolymerization reaction of carbon monoxide and ethene is a very important theme.

In order to understand the kinetics and mechanisms of the solvolysis reactions the first step is to define the structures of the complexes that are investigated. The structure of methylpalladium(II) complexes in the solid state and in solution is described in chapter 2. The new complexes containing ligands of the Xantphos series show that palladium oxygen interactions are very important. These ligands can act as terdentate ligands containing a palladium oxygen bond and the phosphorus atoms coordinated in a *trans*-fashion (ionic complexes), *cis*-chelating bidentate (ionic and neutral complexes) and *trans*-coordinating bidentate ligands (neutral complexes). In some cases the latter two ligand conformations were shown to interconvert in solution at room temperature. 1,1'-Bis(dialkylphosphino)ferrocene ligands showed a very versatile coordination behavior as well. A dimeric complex containing a phosphine ligand bridging between two palladium atoms (1,1'-bis(diethylphosphino)ferrocene), a *cis*-chelating ligand (1,1'-bis(diisopropylphosphino)ferrocene) and a terdentate ligand which enforces an iron-palladium interaction (1,1'-bis(di-*tert*-butylphosphino)ferrocene) were observed. A rearrangement of the dimeric complex $[(1,1'\text{-bis(diethylphosphino)ferrocene})\text{Pd}(\text{CH}_3)\text{Cl}]_2$ to the more stable monomeric complex $(1,1'\text{-bis(diethylphosphino)ferrocene})\text{Pd}(\text{CH}_3)\text{Cl}$ was observed.

The protonolysis of alkylpalladium(II) complexes is described in chapter 3. Neutral dimethylpalladium(II) complexes generally react instantaneously with a strong acid at room temperature. In contrast to ionic early transition metal complexes containing alkyl ligands, the rate of reaction of the metal-carbon bond in ionic methylpalladium(II) complexes with a strong acid was shown to be surprisingly low. However, this is in contrast with the observation of diketo end groups in the palladium catalyzed alternating CO and ethene

addition of triphenylphosphine to the acylpalladium complexes. The terdentate ligands becomes bidentate and triphenylphosphine coordinates to the palladium center.

The *cis*-chelating diphosphine ligands are more difficult to study. The fast decarbonylation reaction of the ionic acylpalladium complexes in the absence of carbon monoxide prevents a mechanistic study of the alcoholysis in most cases. The rate of methanolysis of $[(1,3\text{-bis(diphenylphosphino)propane)PdC(O)CH}_3(\text{CO})]^+ [\text{CF}_3\text{SO}_3]^-$ was determined under a CO atmosphere and depends on the acidity of the reaction medium. An increase of the acidity of the methanol solvent gave a higher rate of methanolysis, but the effect ceases at a higher acid concentration. The synthesis of methanol coordinated instead of CO coordinated acylpalladium complexes was not trivial. The use of silver triflate in methanol at low temperatures ($< -60\text{ }^\circ\text{C}$) can result in a silver-palladium complex (4) instead of the desired methanol coordinated complex.



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The reaction of $[(\text{syn-Calix[6]arene diphosphite})\text{PdC(O)CH}_3(\text{Cl})]$ and thallium(I) triflate in methanol solution gave the methanol coordinated complex $[(\text{syn-Calix[6]arene diphosphite})\text{PdC(O)CH}_3(\text{CD}_3\text{OD})]^+ [\text{CF}_3\text{SO}_3]^-$ at $-60\text{ }^\circ\text{C}$. The complex $[(\text{syn-Calix[6]arene diphosphite})\text{PdC(O)CH}_3(\text{CD}_3\text{OD})]^+ [\text{CF}_3\text{SO}_3]^-$ showed a fast methanolysis reaction and, unlike the other tested complexes, did not undergo decarbonylation under the conditions the kinetic experiments were performed. A very high positive entropy of activation was found. These data indicate that reductive elimination is the rate limiting step in the methanolysis of complexes containing a *cis*-chelating bidentate diphosphine ligand.