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Solvolysis of Palladium-Carbon Bonds in Palladium(II) Complexes containing Diphosphine Ligands.

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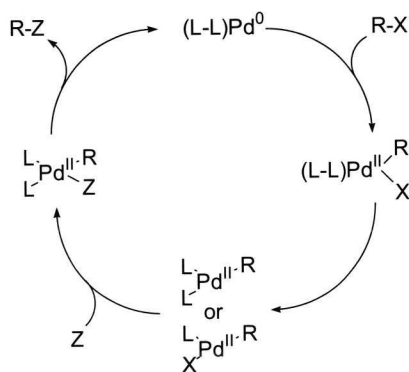
Chapter 1

General Introduction

1.1 Introduction

Palladium is the most versatile transition metal in the transition metal series. This statement is supported by the large number of palladium catalyzed reactions including oligo- and polymerization of alkenes, carbonylation of alkenes and organic halides, Wacker oxidation of alkenes, the Heck reaction, allylic alkylation, the Suzuki reaction, C-H activation, polyamide synthesis¹ and cross-coupling reactions.^{2,3} Many of these palladium catalyzed reactions proceed through a catalytic cycle that includes palladium(0) and palladium(II) intermediates. Oxidative addition, trans-metallation and reductive elimination reactions are key steps in such reactions. A general scheme is presented in scheme 1.

Scheme 1



A reaction that is thought to proceed through Pd(II) intermediates only is, except for the initiation and chain-transfer mechanisms, the coordination polymerization of unsaturated substrates. The CO and alkene copolymerization reaction is an example of such a reaction, which will be introduced in more detail.

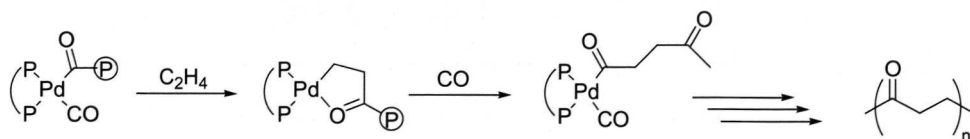
1.2 The copolymerization of CO and alkenes

An extensive review article has been written about the palladium(II) catalyzed copolymerization of CO and alkenes by Drent and Budzelaar.⁴ A brief summary of important features of this reaction will be given here and more recent advances will be highlighted.

In the palladium catalyzed hydroxy- and alkoxy-carbonylation reaction, alkenes are converted into acids and esters *resp.* An example is the methoxycarbonylation of ethene to produce methyl propionate using palladium acetate, a monodentate phosphine ligand (*e.g.* PPh₃) and an acid.⁴ The acid is an important additive, which helps to stabilize palladium(II) and is responsible for the introduction of the appropriate anions into the system. The use of other ligands by Shell ((*t*-Bu)₂P(CH₂)₃P(*t*-Bu)₂) and very recently by ICI ((*o*-C₆H₄(CH₂P(*t*-Bu)₃)₂) has resulted in unprecedentedly active catalytic systems based on bulky alkylphosphine ligands.⁵⁻⁷

Sen *et al* showed that copolymers of CO and ethene were obtained using a catalytic system which contained non-coordinating anions ([Pd(CH₃CN)₄[BF₄]₂·n(PPh₃) (n = 1-3)).⁸ An economically feasible catalyst for the CO and ethene copolymerization reaction was discovered accidentally by Drent *et al.* during research on the methyl propionate synthesis. The substitution of the monodentate phosphine for a bidentate diphosphine ligand (*e.g.* 1,3-bis(diphenylphosphino)propane, dppp) yielded a high molecular weight copolymer with a selectivity of more than 99.9 % at high rates (6000 g (g of Pd)⁻¹ h⁻¹).⁹ The copolymerization reaction gives the highest yields in methanol solvent. The copolymer obtained was a perfectly alternating copolymer of CO and ethene containing ester and keto end groups (scheme 2).

Scheme 2



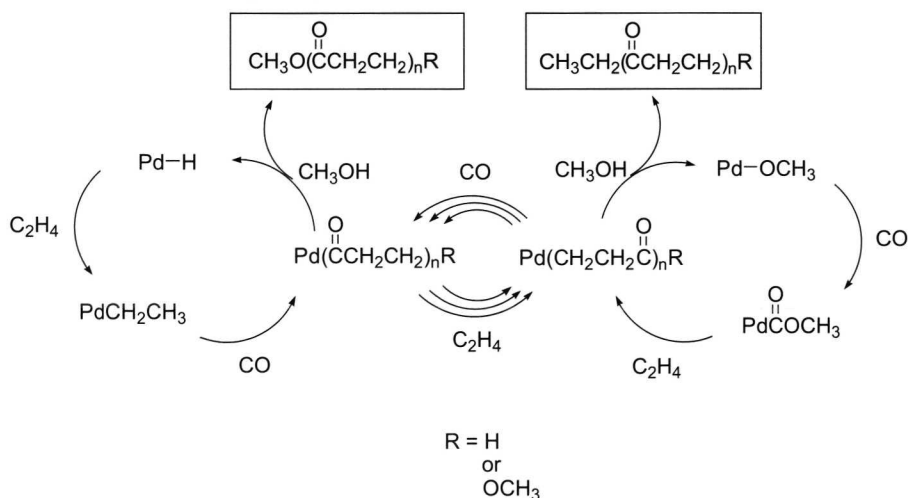
The copolymer shows neither double CO insertion errors, nor double ethene insertion errors. The insertion of CO into the acylpalladium bond is thermodynamically unfavorable. The absence of double ethene insertion errors is more surprising, since palladium is capable of

dimerizing ethene to butene at high rates. Ethene insertion does not occur under the reaction conditions due to the presence of the strongly binding CO comonomer, and the chelating alkylpalladium intermediate. Therefore, the ethene insertion into the alkylpalladium bond is kinetically unfavorable.

Many experimental studies have been devoted to the insertion reactions in recent years.¹⁰⁻¹⁵ The copolymerization reaction is classified as a homogeneously catalyzed process, but the copolymer is insoluble in methanol which means that during the polymer growth the catalyst becomes heterogeneous. Mul *et al.* studied the propagation reactions in the solid phase by IR spectroscopy and proved that ethene insertion was CO assisted.¹⁶

The end groups of the copolymer are formed in the initiation and the termination step (scheme 3). The ester end groups are either formed by the insertion of CO into the methoxypalladium bond or by the reaction of an acylpalladium bond with the methanol solvent. The keto end groups are either formed by the insertion of ethylene into the palladiumhydride bond or protonolysis of the alkylpalladium bond. Two chain-transfer mechanisms and initiation mechanisms are involved, which causes the formation of diketone and diester products.

Scheme 3



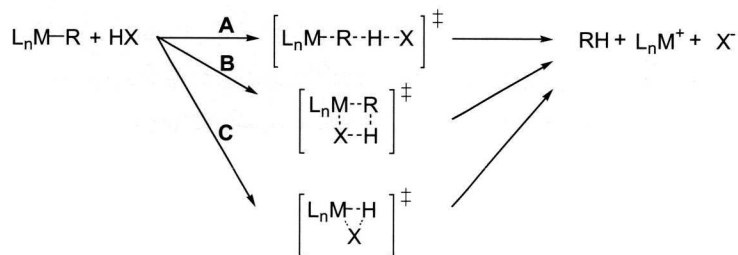
1.3 Reactivity of palladium-carbon bonds

Palladium-carbon bonds are formed in many catalytic reactions, which have already been mentioned in section 1.1, by either oxidative addition, trans-metallation, or insertion reactions. The mechanisms of the methanolysis and protonolysis reactions have not been studied thoroughly yet, in contrast to the insertion reactions (*vide supra*), and reductive elimination reaction.¹⁷⁻²⁰ However, relevant palladium chemistry and related platinum chemistry has been published and will be discussed in section 1.3.1.

1.3.1 Reactivity of alkylpalladium bonds toward electrophiles

Studies of the mechanism of protonolysis of alkylpalladium(II) bonds could not be found. In contrast, a manifold of studies were reported on the mechanism of protonolysis of alkylplatinum(II) bonds. The cleavage of non-transition metal-carbon bonds by acids has been extensively studied and its mechanism elucidated in much detail.^{21,22} The attack of the proton may take place *via* an open transition state (A, scheme 4) or a cyclic transition state (B, scheme 4).

Scheme 4

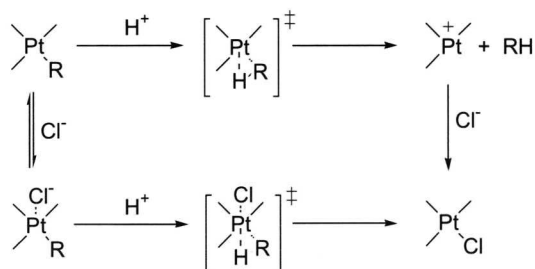


For the protonolysis of alkyl-mercury bonds in acetic acid a three-center transition state has been proposed (C, scheme 4).

In transition-metal complexes protonolysis may occur by: 1) direct attack of the proton on the metal-carbon bond (*vide supra*), or 2) oxidative addition of the acid to the metal center followed by reductive elimination of the alkane. Early protonation studies were performed by Crociani *et al* using *cis*- and *trans*-bis(aryl) and bis(alkyl)platinum(II) complexes.²³ They found that a decrease in electron density ($\text{Me} \gg \text{C}_6\text{H}_5 > \text{C}_6\text{F}_5$) on the platinum(II) center resulted in a considerably slower reaction ($k_{\text{Me}} / k_{\text{ArH}} = 10^6$). This was attributed to the stronger platinum-carbon bond in electron-poor platinum complexes. The large kinetic isotope effect ($k_{\text{H}} / k_{\text{D}} = 6$) indicated that the the transfer of the proton onto the

metal center is rate-determining. Interestingly, they showed that monoalkylplatinum(II) derivatives do not show the same kinetics. The rate law of the reaction of HCl with *trans*-[PtCl(Me)(PEt₃)₂] included, in contrast with the dialkylplatinum complexes, a chloride dependent term. The protonolysis of *cis*-[PtCl(Me)(PEt₃)₂] did not include a chloride dependent term. A pre-equilibrium can exist with a chloride coordinated intermediate (scheme 5).²⁴

Scheme 5



The absence or presence of such a pre-equilibrium governs the kinetics of the protonation reaction and whether a chloride term is present in the rate law. The oxidative addition mechanism was supported by NMR studies performed by Labinger and Puddephatt *et al.*²⁵⁻²⁸ Hydridoalkylplatinum(IV) complexes were characterized at low temperatures and gave reductive elimination of the alkane. The Pt(IV) intermediate is less likely to be formed starting from a cationic complex. Protonolysis of cationic monoalkylplatinum complexes is therefore much slower than that of neutral complexes, since no reaction of H⁺ and M⁺ occurs. Detailed mechanistic studies on the protonolysis of alkylpalladium(II) complexes have not been performed yet.

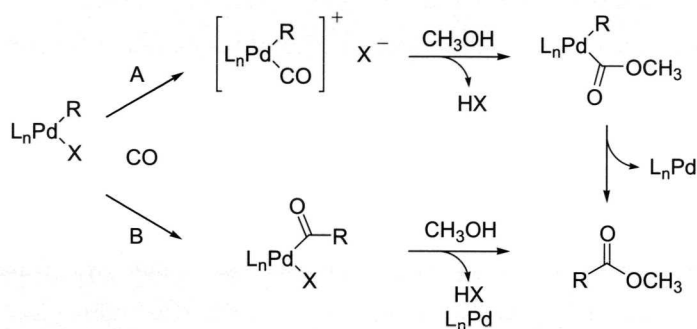
1.3.2 Reactivity of acylpalladium bonds

Acylpalladium complexes are very reactive towards a manifold of reagents. Nucleophiles such as acids,²⁹ alkoxides,³⁰ alcohols,^{6,9,31-33} and water,^{34,35} dihydrogen³⁶ and unsaturated substrates^{37,38} readily react with acylpalladium bonds to give economically valuable products.²

Solvolysis of acylpalladium(II) complexes is an important step in palladium catalyzed reactions, such as the methoxycarbonylation^{6,7} and the hydroxycarbonylation reaction.³⁴ Two possible pathways have been proposed to explain ester formation in the

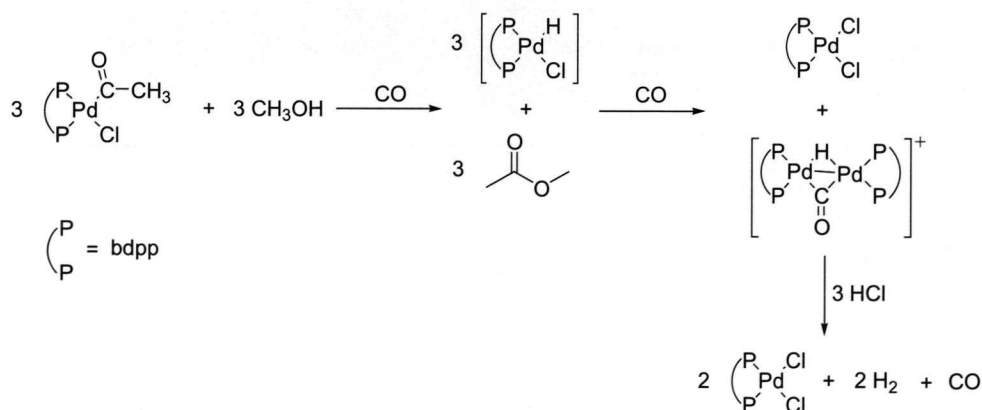
presence of CO and methanol (scheme 6).^{2,3,39} Pathway A involves a displacement of the anion by CO to give a CO-coordinated cationic organopalladium species which undergoes a nucleophilic attack. The resulting organo(acyl)palladium species releases a proton, followed by a reductive elimination which liberates the ester. Pathway B is the preferred mechanism. An acylpalladium intermediate reacts directly with the nucleophile to release the ester and the acid.

Scheme 6



The first thorough study of the reactivity of alcohols and amines towards acylpalladium bonds was published by Yamamoto *et al.*⁴⁰ They studied the reactivity of (phenylacetyl)palladium complexes containing two phosphine ligands or a bidentate diphosphine ligand. The rate of ester formation was enhanced by using less bulky and more acidic alcohols. This indicates that the coordination of the alcohol and proton transfer of the coordinated alcohol are important steps in the process of ester formation.

Scheme 7



Elsevier *et al* reported that methanolysis of $\{(2S,4S)\text{-}2,4\text{-bis(diphenylphosphino)pentane}\}\text{Pd}(\text{C}(\text{O})\text{CH}_3)\text{Cl}$ under a CO atmosphere produced a dinuclear palladium(I) hydride (scheme 7).⁴¹ This type of hydrido-bridged palladium compounds had been characterized before by Milstein *et al*.⁴² The presence of CO retards the rate of methyl acetate formation. The same effect was found when NaOMe was added to the acylpalladium chloride compound.⁴³ The CO seems to compete with the free coordination site *cis* to the acetyl group, which is available by partial dissociation of the Pd-Cl bond, thus hindering the coordination of methanol or the methoxide anion. The hydridocarbonyl complex did not show H/D exchange, but scrambling with ¹³CO was observed. The addition of HCl led to the formation of the palladiumdichloride compound (scheme 7).

1.4 Concluding Remarks

We have seen that reactions of electrophiles and nucleophiles with palladium-carbon bonds play an important role in several transition metal catalyzed processes. Mechanistic studies of such reactions, however, have been limited. Some mechanistic and kinetic studies which deal with the reactivity of acids, alcohols and amines towards neutral platinum(II) and palladium(II) complexes have been reported. Studies on the reactivity of cationic complexes have not been reported yet. In homopolymerization and copolymerization reactions much experimental and theoretical research has been devoted to insertion reactions. In contrast, the chain-transfer mechanisms are often taken for granted or even neglected in the discussion of polymerization reactions. Reactions of nucleophiles and electrophiles with palladium-carbon bonds can account for these chain-transfer mechanisms and therefore a study of such reactions is justifiable.

1.5 Scope and Contents of this Thesis

Much of the work in CO and alkene copolymerization reactions has focussed on palladium and platinum complexes containing mono- and bidentate phosphine ligands and in this thesis we deal with bidentate diphosphine ligands exclusively. The research in this thesis involves a study of the reactivity of cationic alkyl- and acylpalladium(II) complexes towards nucleophiles and electrophiles. The CO and alkene copolymerization reaction is an important reaction throughout this thesis, since the alkyl-, and acylpalladium(II) complexes which we have studied are important intermediates in this reaction.

In *Chapter 2* many of the diphosphine ligands and palladium complexes which are used in this thesis are introduced. The synthesis and characterization of methylpalladium(II) complexes containing diphosphine ligands based on the diphenyl ether, xanthene and ferrocene backbone, is described in this chapter. Some of the bidentate diphosphine ligands coordinate in a terdentate fashion.

In *Chapter 3* a new chain-transfer mechanism in the CO and ethene copolymerization reaction is presented. The rearrangement of an alkylpalladium intermediate to an enolate palladium complex is shown to be responsible for chain-transfer.

In *Chapter 4* the solvolysis reaction of acylpalladium complexes is described. The huge dependence of the rate of reaction on the ligand is shown. An unexpected silver-palladium complex is presented, which results from the reaction of silver triflate with acyl- and methylpalladium chloride complexes at low temperatures.

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