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COORDINATION COMPOUNDS OF π -ALLYL PALLADIUM (II) WITH SUBSTITUTED OLEFINS

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ABSTRACT

The coordination compound of palladium and platinum metal are use in homogenous catalysis and developed many organometallic compound which are mainly use in the arylation of olefins and coupling reaction between substituted aromatic compound with olefins. Some researchers note that arylation was found the on a π -carbon atom of styrene and reported novel method of synthesizing stilbene derivatives by substitution of aromatic compounds for hydrogen on the double bond of the styrene-palladium chloride complex. Palladium (II) chloride can also catalyze the arylation reaction in the presence of metal acetates such as those of sodium or potassium, although palladium (II) chloride compounds have no function as an arylation catalyst without metal acetate.

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INTRODUCTION

The nobility of platinum group metals depends on their large number of valence -d- electrons which are available for tight cohesive bonding. At the present, several important processes involving platinum group- catalysed reactions with synthesis components are commercially viable ventures. The organometallic chemistry of palladium and platinum and the use of coordination compounds of these metals in homogeneous catalysis have developed tremendously since in the early 1970's. This encompasses :

- The synthesis and properties of organometallic and related coordination compounds of palladium, platinum, rhodium, osmium etc.
- Mechanistic studies of the organopalladium, platinum compounds e.g. addition, elimination reaction, insertions, substitution and isomerisations.
- Use of coordination compounds of platinum in homogeneous catalysis, ranging from mechanistic studies to models of metal surfaces to applications in organic synthesis.

The substitution reaction of platinum (II) coordination compounds have been reviewed in the past. Extensive studies on reactions of olefin in the presence of transition metal compounds have been carried out. Much less is known about arylation of olefins with transition metal coordination compounds.

Most recently, Heck described interesting arylation reactions of olefins with arylating agent such aryl mercuric halides in the presence of group VIIIth metal compounds and showed that palladium salts are the most generally useful; with rhodium and ruthenium compounds next best.

Review

Literature of surveyed during this period are summarized below- (Yuzo Fujiwara *et al.*, 1969; Heck, 1968; Heck, 1968; Moritani and Fujiwara, 1967; Moritani *et al.*, 1968) extended initial work on the reactions of the styrene- palladium (II) chloride complex with benzene derivatives to give stilbenes. Which are describe as-

It was noted that arylation was found on a π -carbon atom of styrene. The presence of a carboxylic acid such as acetic acid is essential because the reactants form a homogeneous solution and the reaction proceeds best in the solvent. Yuzo Fujiwara *et al.* reported novel method of synthesizing stilbene

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derivatives by substitution of aromatic compounds for hydrogen on the double bond of the styrene-palladium chloride complex. Palladium (II) chloride/platinum (II) chloride can also catalyze the arylation reaction in the presence of metal acetates such as those of sodium or potassium, although palladium (II)/platinum (II) chloride compounds have no function as an arylation catalyst without metal acetate. These results show that the metal acetate plays an important role in the reaction. As suggested in a preliminary publication, it may be that after the chloride anion is abstracted from the palladium (II) chloride by the metal cation (Na^+ , K^+), the palladium metal coordinates with the acetate anion which is a weaker ligand than the chloride anion, thus increasing the ability of the metal to coordinate with olefins. Therefore, it becomes possible for the olefin arylation.

Watson P.L. described the use of coordination compounds of palladium and platinum to cleave and functionalize C-H bonds is a mechanistically interesting and synthetically attractive process which has received considerable attention in recent years. An early example of a useful C-H bond cleavage by a transition metal complex is removal of an allylic hydrogen from olefin on reaction with a palladium (II) compound to provide a π -allyl palladium complex.

William H. Saunders, Jr. reported that the reactions of olefins with PdCl_2 or ionic equivalents such as $[\text{PdCl}_4]^{2-}$ to give π -allyl complex proceed via initial fast π -complexation of the olefin to palladium. The intermediate π -olefin complexes of PdCl_2 are sufficiently stable to isolate and characterize in some cases.

Olefin ^a	Palladium salt	Aromatic compd, ml	Product and yield
Styrene	$\text{Pd}(\text{OAc})_2$	Benzene,340	trans-Stilbene,90%
Styrene	PdCl_2	Benzene,120	trans-Stilbene,79%
Styrene	PdCl_2	Benzene,340	trans-Stilbene,26%
Styrene	$\text{Pd}(\text{OAc})_2$	Toluene,340	trans-p-Methylstilbene,58%; trans-o-methylstilbene,3%
Styrene	$\text{Pd}(\text{OAc})_2$	p-Xylene,340	trans-2,5-Dimethylstilbene,47%
Styrene	$\text{Pd}(\text{OAc})_2$	Ethylbenzene,185	trans-p-Ethylstilbene,52%
Styrene	PdCl_2	Ethylbenzene,483	trans-p-Ethylstilbene,22%
Styrene	$\text{Pd}(\text{OAc})_2$	Anisole,230	trans-p-Methoxystilbene,61%
Styrene	$\text{Pd}(\text{OAc})_2$	Nitrobenzene,235	trans-m-Nitrostilbene,60%
Styrene	PdCl_2	Nitrobenzene,470	trans-m-Nitrostilbene,25%

Entry	Vinylmercurial	Olefin	π -Allylpalladium compound ^a	% yield ^b
1		$\text{H}_2\text{C}=\text{CHCO}_2\text{C}_2\text{H}_5$		100 (58)
2		$\text{H}_2\text{C}=\text{CH}_2$		97 (83)
3		$\text{H}_2\text{C}=\text{CH(CH}_2)_2\text{CH}_3$		90 (82)
4		$\text{H}_2\text{C}=\text{CH}_2$		92
5a		$\text{H}_2\text{C}=\text{CH(CH}_2)_2\text{CH}_3$		67 (63) ^c
5b		$\text{H}_2\text{C}=\text{CH(CH}_2)_2\text{CH}_3$		
6		$\text{H}_2\text{C}=\text{CHCN}$		87 (71)
7		$\text{H}_2\text{C}=\text{CHCO}_2\text{C}_2\text{H}_5$		100 (67)
8		$\text{H}_2\text{C}=\text{CH}_2$		59 (37)
9		$\text{H}_2\text{C}=\text{CH(CH}_2)_2\text{CH}_3$		19 (7)

Faller *et al.* (1971), Describes steric factors and their accompanying kinetic and thermodynamic Parameters have been determined for certain 1,2,3-h³- allyl (amine) chloropalladium complexes. In which the allyl moiety is disubstituted using a combination of nmr techniques.

Stephen J. Lippard *et al.* (1972), carried out the synthesis of several monothiodibenzoylmethanato (π -allyl) palladium (II) complexes described as

- a. Di- μ -chloro-di(π -allyl)dipalladium Complexes.
- b. Monothio- β -diketone and β -Diketone Ligands.
- c. 3-Thio-1,3-diphenylprop-2-en-1-one-thallium(I), C₁₅H₁₁O₂TI.
- d. 1,3-Diphenylpropane-1,3-dionatothallium(I), C₁₅H₁₁O₂TI.
- e. π -Allylpalladium SDBM and DBM Complexes. 3-Thio-1,3-diphenylprop-f. 2-en-1-one- π -methallylpalladium(II), [(π -C₄H₇) Pd (SDBM).
- g. Thio-1,3-diphenylprop-2-en-1-one- π -allylpalladium(II), [(π -h. C₃H₅)Pd(SDBM).
- h. 3-Thio-1,3-diphenylprop-2-en-1-one- π -crotylpalladium(II), [(π -C₄H₇)Pd(SDBM).
- i. 3-Thio-1,3-diphenylprop-2-en-1-one- π -syn-1-tert-butyl-2-methallyl-palladium(II), [(π -C₈H₁₅)Pd(SDBM).
- j. 1,3-Diphenylpropane-1,3-dionato- π -methallyl palladium(II), [(π -C₄H₇)Pd(DBM).
- k. 1,3-Diphenylpropane-1,3-dionato- π -allyl palladium(II), [(π -C₃H₅)Pd(DBM).

And structural, dynamic properties of these complex in chlorobenzene solution have been studied over a wide range of temperature and concentrations using Proton nuclear magnetic resonance spectroscopy. Hughes *et al.* (1972) Larock and Brown, (1972), A mechanism is proposed in which the 1,3-diene, acting as a monodentate ligand, coordinates to the palladium through the least substituted double bond to give a σ -allylic intermediates (σ -all) (diene)Pd(x). On adopting a cis-planar orientation within this intermediate the conjugated 1,3-diene reacts with the σ -allylic ligand to give the insertion product via an electrocyclic mechanism. It is envisaged that carbon-carbon bond formation occurs outside the coordination sphere of the palladium.

Richard C. Larock, *et al.* (1976) Dieck and Heck, (1975) examine the reaction of vinylmercuric chlorides, palladium salts and simple alkenes and obtained excellent yields of π -allyl palladium compound which are given follows. Douglas R. Chrisope, *et al.* (1988).

An experimental and computational study of the formation of (π -allyl) palladium complexes from olefins and palladium (II) Salts. All involve rapid equilibrium formation of a π -olefin complex followed by, (A) insertion of the Palladium into the carbon-hydrogen bond, (B) removal of allylic hydrogen by a ligand on Palladium, or (C) removal of allylic hydrogen by an external base.

Conclusion

Orangometallic compound of (π - allyl) palladium (II) with substituted olefins is better reagent for the synthesis of many organic compound. The synthesis and structural studies of coordination compounds of palladium (II) with olefins all expected to discover and characterize new catalytic processes like arylation, addition, substitution and isomerization reactions.

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