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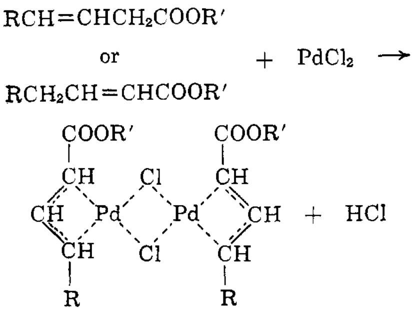
Organic Syntheses by Means of Noble Metal Compounds. IX. Preparation of a New Type of π-Allylic Palladium Chloride Complex and Its Carbonylation[1]

Sir:

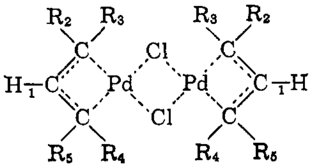
We have found that α,β- or β,γ-unsaturated carboxylic esters form a new type of π-allylic palladium chloride complexes as shown below. For example



1-carbethoxy-π-allylpalladium chloride (I) is formed from ethyl 2- or 3-butenoate. The complexes can be prepared either (1) by heating the esters in the presence of palladium chloride, (2) by addition of the esters into an alcoholic solution of sodium tetrachloropalladate, or (3) by addition of the esters into a benzene solution of bisbenzonitriledichloropalladium. The complexes are yellow crystalline substances and most of them are moderately soluble in ordinary organic solvents. The π-allylic structure was assigned to the complexes on the basis of molecular weights, elemental analyses, and n.m.r. spectra shown in Table I. The most convincing evidence was obtained from the n.m.r. spectra (in $CDCl_3$). Their τ-values and coupling constants (J) are fairly consistent with the reported values of related complexes.[2]

TABLE I

PHYSICAL PROPERTIES OF THE COMPLEXES



Starting material	Complex	R_2	R_3	R_4	R_5	M.p., °C.	Mol. wt., found (calcd.)	Analysis, %, found (calcd.) C	H	Cl	Chemical shift τ_1	τ_2	τ_3	τ_4	Coupling, c.p.s. J_{12}	J_{13}	J_{14}
Ethyl 2- and 3-butenoate	I	H	H	H	CO_2Et	141–143	497.6 (509.9)	28.44 (28.26)	3.60 (3.56)	14.08 (13.90)	3.90	5.80	6.71	6.36	7.2	12.5	11.3
Ethyl 3-pentenoate	II	H	CH_3	H	CO_2Et	140–150 dec.	527.4 (537.8)	31.35 (31.25)	4.11 (4.12)	13.21 (13.19)	4.10	5.78	...	6.56	6.9	...	10.5
Diethyl glutaconate	III	CO_2Et	H	H	CO_2Et	175–176	658.8 (654.1)	33.29 (33.05)	4.01 (4.09)	10.84 (10.89)	3.25	...	...	6.10	...	...	11.5
$CH_2{=}CHCH_2Cl$[2]		H	H	H	H						4.55	5.98	7.05	...	7.1	12.1	...

π-Allylpalladium chloride was prepared from allyl alcohol and allyl chloride.[3] In addition, different types of compounds such as mesityl oxide[4] and 2-methyl-1-pentene[5] were found to form π-allylic complexes of palladium chloride, and, in these cases, the absence of a hydrogen at a central carbon atom of the complexes was regarded as essential. Now, it has been established by the present studies that a compound having an allylic hydrogen activated by a carbonyl group can form the 1-carboxy-π-allylic complex with evolution of hydrogen chloride.

Carbonylation of π-allylpalladium chloride in ethanol to form ethyl 3-butenoate is known,[1,6,7] and it is reasonable to expect that any π-allylic complexes of palladium chloride can be carbonylated under similar conditions. Actually the complexes obtained here were found to be carbonylated to give unsaturated esters. Thus the complex I afforded ethyl glutaconate as a main product. Furthermore, having allylic hydrogens activated by the carbethoxy group, ethyl glutaconate can form the complex III. Thus, the following sequence of complex formation and carbonylation reactions has been established.

$$CH_2{=}CHCH_2Cl + PdCl_2 \longrightarrow \pi\text{-allylpalladium chloride} \xrightarrow{CO}$$

$$CH_2{=}CHCH_2COOR \xrightarrow{PdCl_2} \text{complex I} \xrightarrow{CO}$$

$$ROOCCH_2CH{=}CHCOOR \xrightarrow{PdCl_2} \text{complex III}$$

Further work is in progress on the extension of the above sequence of the reactions by carbonylating the complex III, followed by complex formation.

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