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Preliminary communication

The reduction of allylic chlorides and $PdCl_2$ (or $PtCl_2$) to π-allyl complexes

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Various methods are known for the preparation of π-allylpalladium chloride complexes. One of these involves the reaction of allyl chloride with palladium chloride in the presence of a reducing system such as CO/H_2O[1] or $SnCl_2$[2]. It has been suggested that the reaction with CO/H_2O proceeds via an intermediate square planar palladium complex containing OH, CO, Cl and the allylic chloride as ligands with the complex subsequently decomposing to π-allylpalladium chloride and CO_2. The mechanism of the reaction with $SnCl_2$ is not known[2].

We have looked for other suitable reducing agents, and examined the use of this method for the preparation of π-allylplatinum complexes. Tests were performed with reducing agents having about the same redox potential as the system $SnCl_2 + Cl_2 \rightleftarrows SnCl_4$. The results are presented in Table 1. Although the known agents viz. CO and $SnCl_2$; give the best yields, the extreme facility of the reaction with, for example, Fe powder was remarkable. Reagents such as $FeCl_2$, $FeCl_2 \cdot 4H_2O$, CuCl, H_2S and $Na_2S_2O_3$ failed to give the desired product, mainly because of the occurrence of other reactions.

The chloride $PtCl_2$ which dissolves in acetone, tetrahydrofuran, dioxane or diglyme in the presence of LiCl gave π-allylplatinum chloride in 90% yield when $SnCl_2$ was used as the reducing agent. The CO/H_2O reducing system, on the other hand, proved

TABLE 1

SYNTHESIS OF πALLYLPALLADIUM CHLORIDE AND π-ALLYLPLATINUM CHLORIDE

Metal halide	Solvent	Reducing agent	Reaction temperature (°C)	Reaction time (min)	Yield (%)
Na_2PdCl_4	CH_3OH	$SnCl_2$ (1 equiv.)	25	90	82
Na_2PdCl_4	CH_3OH	CO	25	45	70
Na_2PdCl_4	CH_3OH	$TiCl_3$ (1 equiv.)	25	1000	51
Na_2PdCl_4	CH_3OH	Fe (3 equiv.)	25	1	39
Na_2PdCl_4	CH_3OH	Zn (3 equiv.)	25	8	24
Na_2PdCl_4	CH_3OH	Cu (3 equiv.)	25	15	24
K_2PtCl_4	LiCl/THF	$SnCl_2$ (1 equiv.)	65	60	90

ineffective: The product $[C_3H_5PtCl]_n$ has so far been made only from C_3H_5MgCl and $PtCl_2$[3].

Higher allyl chlorides failed to give π-allylplatinum complexes. Instead, disproportionation and hydrogenation occurred:

$$\text{1-chloro-2-butene} \xrightarrow[\text{THF}]{PtCl_2/SnCl_2} \text{1,3-butadiene} + \text{1-butene} + \text{2-butene}$$

(I) (II) (III) (IV)

(ratio I/II + III ≈ 1/1)

When $PtCl_2$ was omitted the 1-chloro-2-butene (I) isomerized to 3-chloro-1-butene. As no hydrogenation products were formed, it seems that the presence of $PtCl_2$ is necessary to effect the elimination of HCl from I to give II. The hydrogenolysis of organic chlorides with $HCl/SnCl_2$ is a known reaction[4].

The corresponding reaction with methallyl chloride yielded isobutene, but none of the expected methylenecyclopropane, which probably does not survive in the acid environment.

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