

Preliminary communication

The reduction of allylic chlorides and PdCl₂ (or PtCl₂) to π -allyl complexes

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(Received October 21st, 1970)

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/H₂O¹ or SnCl₂². It has been suggested that the reaction with CO/H₂O 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 CO₂. The mechanism of the reaction with SnCl₂ is not known².

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 SnCl₂ + Cl₂ \rightleftharpoons SnCl₄. The results are presented in Table 1. Although the known agents viz. CO and SnCl₂; give the best yields, the extreme facility of the reaction with, for example, Fe powder was remarkable. Reagents such as FeCl₂, FeCl₂ · 4H₂O, CuCl, H₂S and Na₂S₂O₃ failed to give the desired product, mainly because of the occurrence of other reactions.

The chloride PtCl₂ which dissolves in acetone, tetrahydrofuran, dioxane or diglyme in the presence of LiCl gave π -allylplatinum chloride in 90% yield when SnCl₂ was used as the reducing agent. The CO/H₂O reducing system, on the other hand, proved

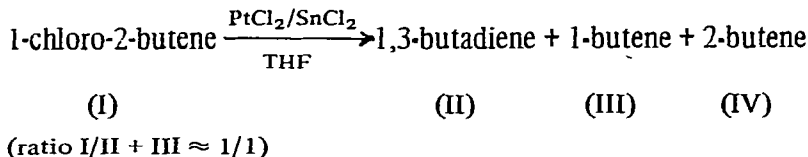
TABLE 1

SYNTHESIS OF π -ALLYLPALLADIUM CHLORIDE AND π -ALLYLPLATINUM CHLORIDE

Metal halide	Solvent	Reducing agent	Reaction temperature (°C)	Reaction time (min)	Yield (%)
Na ₂ PdCl ₄	CH ₃ OH	SnCl ₂ (1 equiv.)	25	90	82
Na ₂ PdCl ₄	CH ₃ OH	CO	25	45	70
Na ₂ PdCl ₄	CH ₃ OH	TiCl ₃ (1 equiv.)	25	1000	51
Na ₂ PdCl ₄	CH ₃ OH	Fe (3 equiv.)	25	1	39
Na ₂ PdCl ₄	CH ₃ OH	Zn (3 equiv.)	25	8	24
Na ₂ PdCl ₄	CH ₃ OH	Cu (3 equiv.)	25	15	24
K ₂ PtCl ₄	LiCl/THF	SnCl ₂ (1 equiv.)	65	60	90

ineffective: The product $[\text{C}_3\text{H}_5\text{PtCl}]_n$ has so far been made only from $\text{C}_3\text{H}_5\text{MgCl}$ and PtCl_2^3 .

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



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 reaction⁴.

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

REFERENCES

- 1 J.K. Nicholson, J. Powell and B.L. Shaw, *Chem. Commun.*, (1966) 174, and references cited therein.
- 2 M. Sakakibara, Y. Takahashi, S. Sakai and Y. Ishii, *Chem. Commun.*, (1969) 396; R. Pietropaolo, G. Dolcetti, M. Giustiniani and U. Belluco, *Inorg. Chem.*, 9 (1970) 549.
- 3 R. Raper and W.S. McDonald, *Chem. Commun.*, (1970) 655, and references cited therein.
- 4 L.F. Fieser and M. Fieser, *Reagents for organic synthesis*, Wiley, New York, 1967, p. 1113.

J. Organometal. Chem., 26 (1971) C25–C26