Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

Preliminary communication

Reactivity of the metal coordinated allyl ligand
I. A simple route to the preparation of tris(triphenylphosphine)- and tris(triphenylphosphite)palladium(0)

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(Received May 1st, 1972; in revised form May 25th, 1972)

The attack of nucleophilic agents containing OH and NH groups on an allylic carbon atom of π-allyl complexes is thought to play an important role in the telomerization reactions of 1,3-dienes catalyzed by palladium complexes[1].

As a part of a research program on the mechanistic aspect of these reactions, we are currently investigating the nucleophilic attack at the allylic carbon atoms of some phosphine- and phosphite-containing π-allyl–palladium complexes. In the course of our investigation we have found that the action of nucleophiles on the cationic species $[\pi\text{-allyl-Pd}(PR_3)_2]^+$ ($PR_3 = P(C_6H_5)_3$, $P(OC_6H_5)_3$) constitutes an easy route to the preparation of the otherwise not easily accessible $Pd[P(C_6H_5)_3]_3$** and $Pd[P(OC_6H_5)_3]_3$. A typical preparation of these zerovalent palladium complexes is as follows.

The phosphorous ligand (2 moles) was added to a methylene chloride solution of $(\pi\text{-methallyl-PdCl})_2$ (0.5 moles), benzylamine (1.5–2 moles) was then added to the mixture. After a few minutes benzylamine chlorohydrate (2/3 of mole) separated out, the methylene chloride was evaporated, the residue washed with heptane and finally extracted with toluene.

The heptane solution was found to contain *N*-methallyl- and *N,N*-dimethallylbenzylamine. $Pd[P(C_6H_5)_3]_3$ and $Pd[P(OC_6H_5)_3]_3$ crystallized respectively as yellow and very pale yellow, almost white, crystals from the toluene solution. The yields based on palladium used were 40–50%. Both complexes are air sensitive especially in solution. The analytical data are shown in Table 1.

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**$Pd[P(C_6H_5)_3]_3$ has been isolated by Smutny and Chung from the Pd system which catalyses the degradation of phenoxyoctadiene to phenol and octatriene[2]. The complexes $[(p\text{-}XC_6H_4)_3P]_3Pd$ ($X = CH_3$, Cl) have been reported by Malatesta and Angoletta[3].

TABLE 1

ANALYTICAL DATA

	Analysis found (calcd.) %				*Mol. wt. found*[a] *(calcd.)*	*M.p.*[b] *(°C)*
	C	*H*	*P*	*Pd*		
$Pd[P(C_6H_5)_3]_3$	72.23 (72.61)	5.25 (5.08)	9.83 (10.40)	11.86 (11.91)	783 (893)	190–203 (dec)
$Pd[P(OC_6H_5)_3]_3$	61.78 (62.53)	4.51 (4.37)	8.34 (8.96)	11.22 (10.26)	921 (1037)	118–129 (dec)

[a] Cryoscopic determination in benzene under argon on samples crystallized from benzene–heptane (samples crystallized from toluene have given lower values of the molecular weights for trapping of the solvent in the crystals).

[b] Under argon. The m.p. is only approximate, depending on the rate of heating.

The molecular weights of $Pd[P(C_6H_5)_3]_3$ and $Pd[P(OC_6H_5)_3]_3$ have been determined by cryoscopy in benzene under argon. The results suggest that, within the experimental error, both complexes show little dissociation in solution, thus $Pd[P(C_6H_5)_3]_3$ must appear to behave in solution as does $Pt[P(C_6H_5)_3]_3$, for which only slight dissociation to $Pt[P(C_6H_5)_3]_2$ has been found[4]. The extension of the above mentioned reaction to the preparation of other phosphine–palladium(0) complexes is being investigated.

REFERENCES

1 W. Keim, *π-Allyl System in Catalysis* in G.N. Schrauzer (Ed.), *Transition Metals in Homogeneous Catalysis*, Marcel Dekker, New York, N.Y., 1971, p. 59.
2 E.J. Smutny and H. Chung, *Amer. Chem. Soc., Div. Petrol. Chem., Prepr.*, 14 (1969) B112.
3 L. Malatesta and M. Angoletta, *J. Chem. Soc.*, (1957) 1186.
4 J.P. Birk, J. Halpern and A.L. Pickard, *Inorg. Chem.*, 7 (1968) 2672.