

IONIC  $\pi$ -ALLYLIC PALLADIUM (II) COMPLEXES.

by

G.Paiaro and A.Musco

Laboratorio di Chimica Generale e Inorganica dell'Istituto Chimico dell'Università di Napoli - Sez.VII del Centro Nazionale di Chimica Macromolecolare del C.N.R.

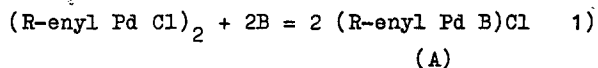
(Received 21 March 1965)

Structural and chemical evidence have confirmed that the  $\pi$ -allylic palladium (II) chloro complexes have binuclear structures with chloro-bridges (1,2,3).

These compounds are soluble in aqueous solutions of alkaline halides, but it is not possible to separate the salts having the  $\pi$ -allylic palladium anion.

We have succeeded in preparing ionic compounds stable in the solid state and polar solvents by using bidentate ligands such as ethylenediamine (en) and  $\alpha$ - $\alpha'$ -dipyridyl (dip).

The general reaction is :



where B is a bidentate base and R-enyl is an allyl or

a crotyl residue (Table I).

These white compounds are very soluble in methanol and water but the corresponding salts with  $\text{PF}_6^-$  are less soluble.

The compounds (A) are uni-univalent electrolytes in water (Molar conductance of (V) at  $25^\circ\text{C}$ :  $119 \text{ ohms}^{-1} \text{ cm}^2$  at the concentration  $1.015 \cdot 10^{-3} \text{ M}$ ).

Analysis and molecular weights from cryoscopic measurements in water confirm the assigned formulas and moreover I.R. spectra assure that the nature of C-Pd bond is not changed.

In addition we have prepared an insoluble product by adding a stoichiometric amount of  $\alpha\text{-}\alpha'$ -dipyridyl to a benzene solution of  $(\text{R-enyl Pd Cl})_2$ .

The resulting compound is stable in the solid state and is crystallizable from nitrobenzene.

The stoichiometry of the reaction and the molecular weight determined by X-Ray analysis confirm the formula :

$(\text{R-enyl Pd dip})(\text{R-enyl Pd Cl}_2)$ . X-Ray data gave for (VII):  
 $a=11.63 \pm 0.02 \text{ \AA}$ ;  $b=10.18 \pm 0.02 \text{ \AA}$ ;  $c=8.26 \pm 0.02 \text{ \AA}$ ;  $\gamma=94^\circ \pm 30'$ ;  
 $d_{\text{exp}} 1.85 \text{ g/cm}^3$ ;  $d_{\text{roentg}} 1.86 \text{ g/cm}^3$ .

-TABLE I-

	COMPOUNDS	DECOMP. °C
I	$[\text{C}_3\text{H}_5\text{Pd}(\text{dip})]^+ \text{Cl}^-$	~ 160°
II	$[\text{C}_3\text{H}_5\text{Pd}(\text{en})]^+ \text{Cl}^-$	110°
III	$[\text{C}_3\text{H}_5\text{Pd}(\text{dip})]^+ \text{PF}_6^-$	260°-262°
IV	$[\text{C}_3\text{H}_5\text{Pd}(\text{dip})]^+ [\text{C}_3\text{H}_5\text{PdCl}_2]^-$	198°
V	$[\text{C}_4\text{H}_7\text{Pd}(\text{en})]^+ \text{Cl}^-$	140°
VI	$[\text{C}_4\text{H}_7\text{Pd}(\text{dip})]^+ \text{Cl}^-$	140°
VII	$[\text{C}_4\text{H}_7\text{Pd}(\text{dip})]^+ [\text{C}_4\text{H}_7\text{PdCl}_2]^-$	140°-141°
VIII	$[\text{C}_4\text{H}_7\text{Pd}(\text{dip})]^+ \text{PF}_6^-$	250°
IX	$\text{C}_4\text{H}_7\text{PdCl P}(\text{C}_6\text{H}_5)_3$	174°

In addition by using triphenylphosphine (4) as ligand we have obtained a non ionic monomeric pale yellow complex.

X-Ray data for (IX) gave :

$a=11.08\pm 0.02 \text{ \AA}$  ;  $b=10.20\pm 0.02 \text{ \AA}$  ;  $c\sin\beta = 17.85\pm 0.02 \text{ \AA}$  ; space group  $P2_1/c$  ;  $d_{\text{exp}} 1.52 \text{ g/cm}^3$  ;  $d_{\text{roentg}} 1.52 \text{ g/cm}^3$ .

This compound is very stable and does not lose triphenylphosphine as do the corresponding compounds with monoamines.

It is crystallizable from acetone or ethyl acetate.

#### REFERENCES

- 1) R.G.Guy and B.L.Shaw - *Advanced Inorg. Chemistry and Radiochemistry* Vol.4, 117 (1962).
- 2) W.E.Oberhansli and L.F.Dahl - *J.Organometal. Chem.* 3, 43 (1965).
- 3) S.D.Robinson and B.L.Shaw - *J.Chem.Soc. (London)* 4806 (1963).
- 4) G.W.Parshall and G.Wilkinson - *Chem. and Ind. (London)* 261 (1962).