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IONIC π-ALLYLIC PALLADIUM (II) COMPLEXES.

by

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Structural and chemical evidence have confirmed that the π-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 π-allylic palladium anion.

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

The general reaction is :

$$(\text{R-enyl Pd Cl})_2 + 2\text{B} = 2\ \underset{(\text{A})}{(\text{R-enyl Pd B})\text{Cl}} \qquad 1)$$

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 PF_6^- are less soluble.

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

Analysis and molecular weights from cryoscopic measurements in water confirm the assignated 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 α-α'-dipyridyl to a benzene solution of (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 :

(R-enyl Pd dip)(R-enyl Pd Cl_2).X-Ray data gave for (VII): $a=11.63 \pm 0.02$ Å; $b=10.18 \pm 0.02$ Å; $c=8.26 \pm 0.02$ Å;$\gamma = 94° \pm 30'$;

d_{exp} 1.85 g/cm^3; d_{roentg} 1.86 g/cm^3.

-TABLE I-

	COMPOUNDS	DECOMP. °C
I	$[C_3H_5Pd(dip)]^+ Cl^-$	∼ 160°
II	$[C_3H_5Pd(en)]^+ Cl^-$	110°
III	$[C_3H_5Pd(dip)]^+ PF_6^-$	260°-262°
IV	$[C_3H_5Pd(dip)]^+ [C_3H_5PdCl_2]^-$	198°
V	$[C_4H_7Pd(en)]^+ Cl^-$	140°
VI	$[C_4H_7Pd(dip)]^+ Cl^-$	140°
VII	$[C_4H_7Pd(dip)]^+ [C_4H_7PdCl_2]^-$	140°-141°
VIII	$[C_4H_7Pd(dip)]^+ PF_6^-$	250°
IX	$C_4H_7PdCl\ P\ (C_6H_5)_3$	174°

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

X-Ray data for (IX) gave :

$a=11.08\pm0.02$ Å ; $b=10.20\pm0.02$ Å ; $c\sin\beta=17.85\pm0.02$ Å ; space group $P2_{1/c}$; d_{exp} 1.52 g/cm^3 ; d_{roentg} 1.52 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.

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