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PREPARATION AND THERMAL STABILITY OF BIS (4-CYANOPYRIDINE) PALLADIUM (II) CHLORIDE

J. E. HOUSE, JR., AND M. E. JAMES
Department of Chemistry
Illinois State University, Normal, Illinois 61761

Recently, the complexes of several metals with 4-cyanopyridine (4-CP) (Farah and Iwamoto, 1965) and 4-cyanopyridine N-oxide (Nathan, et al., 1969; Piovesana and Selbin, 1969) have been described. The complexes with these ligands were studied to determine the mode of coordination of the ligand to the metal ion and to see if these ligands form bridged complexes. No evidence was found for nitrile coordination in complexes of 4-CP but nitrile coordination was found to occur in 2-CP and 3-CP (Farah and Iwamoto, 1965).

The solid complex of 4-CP with silver nitrate has been found to have much higher thermal stability than similar complexes containing some other pyridines which are considerably more basic (Akhavein and House, 1970); however, this complex involves coordination only through the pyridine nitrogen atom (Farah and Iwamoto, 1965; House and Akhavein, 1970). We have, therefore, been interested in the donor properties of the nitrile nitrogen in 4-CP.

We have found that heating produces stepwise decomposition of solid complexes of palladium (II) chloride which contain ligands having two donor atoms of about equal strength (House and Adams, 1970). This report describes the results of thermal studies on bis (4-cyanopyridine) palladium (II) chloride, which contains donor atoms of greatly different strengths.

EXPERIMENTAL

A solution of 4-CP was prepared containing 0.48g (5.0 m mole) in 25ml of absolute ethanol. To this solution was added 2.5 m mole of $PdCl_2$. The mixture was refluxed for several hours and yellow solid was obtained. The precipitate was separated by filtration, washed with acetone, and then air dried. Weight loss studies show that the complex contains two ligands per palladium.

Similar procedures using 4-cyanopyridine N-oxide gave dark brown ill-defined products, which were not studied further.

Thermal measurements were performed as previously described (House and Adams, 1970) using a Perkin-Elmer Differential Scanning Calorimeter, Model DSC-1B.

RESULTS AND DISCUSSION

The thermograms of $Pd(4\text{-}CP)_2Cl_2$ show only one endotherm beginning at 303°C. The samples were held at 377°C for 15 minutes after scanning to that temperature. Results obtained from several thermograms are shown in Table 1.

Table 1.—Thermal data for decomposition of $Pd(4\text{-}CP)_2Cl_2$.

Initiation Temp., °C.	% Mass loss* Calcd	Found**	△H,** kcal/mole	Ea** kcal/mole
303	54.6	53.7±2.6	19.4±2.5	60.2±1.0

*Mass loss for loss of two molecules of 4-CP per molecule of complex.

**Shown as average value ± average deviation from the mean.

Unlike the pyrazine complexes which show stepwise decomposition (House and Adams, 1970), no evidence has been found for stepwise decomposition, which would presumably involve bridging of the ligands after loss of one molecule of ligand.

When the two nitrogen atoms in 4-CP are involved in hydrogen bond formation with methyl alcohol, the nitrile nitrogen and the pyridine nitrogen cause the OH stretching band to be shifted by 61 and 212 cm^{-1} respectively from its "free" position of 3641 cm^{-1} (Cook and House, 1969). Thus, the donor properties of the nitrile nitrogen are not nearly as great as those of the pyridine nitrogen. Coordination by the nitrile group appears to be too weak to cause the 1:1 complex involving coordination by both nitrogen atoms to be stable as a decomposition product. Coordination of a nitrile group in the 4-position thus appears to be much weaker than previously believed and insignificant compared to that of the pyridine ring. This is in contrast to the behavior of 2- and 3-cyanopyridine (Farah and Iwamoto, 1965).

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