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# Tetrakis and Bis Platinum(II) Iodide Complexes with Pyridine and Substituted-Pyridine Ligands

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Complexes of the type $PtL_4I_2$ where L = pyridine (py), 3-picoline (3-Me(py)), 4-picoline (4-Me(py)), 4-ethylpyridine (4-Et(py)), and 3,5-lutidine (3,5-$Me_2$py) have been synthesized. Pyrolysis of these complexes has been shown to provide a convenient route to the otherwise difficultly obtainable *trans*-$PtL_2I_2$ species.

A recent investigation[1] of the reduction of complexes of the type $PtLL'_2X_2$ (where L and L′ are bi- and monodentate, respectively) with potassium in liquid ammonia to produce additional examples[1] of paramagnetic complexes of platinum has prompted us to synthesize and examine the properties of certain complexes involving only monodentate and σ-bonding ligands. The present discussion is concerned only with pyridine and alkyl-substituted pyridines as ligands. Some of these were of interest also in connection with deprotonation studies that will be described elsewhere.[2]

Although complexes of the type $PtL_4X_2$ where L is a ligand such as primary alkylamines, urea, thiourea, etc. are well known,[3–5] relatively little is known of cases in which L is a heterocyclic ligand.[6,7] It has been reported[8] that $Pt(py)_4Cl_2 \cdot 3H_2O$ decomposes in one step to *trans*-$Pt(py)_2Cl_2$ while $[Pt(py)_4](PtCl_4)_2$ yields a mixture of isomers. Studies on the thermal decomposition of *cis*-$[Pt(NH_3)_2L_2]Cl_2$ where L is *o*-anisidine, aniline, *p*-toluidine, or a chloroaniline ligand[9,10] show that *trans*-$[Pt(NH_3)LCl_2]$ and *cis*-$[Pt(NH_3)_2Cl_2]$ are formed.

## Experimental Section

**Syntheses.**—All complexes were prepared in essentially quantitative yield by refluxing $K_2PtCl_4$[11] and the ligand (reagent grade, used without further purification) in 1:4 mole ratio in the minimum volume of distilled water until a clear solution resulted. The solutions were cooled to 25° and added to concentrated aqueous solutions of KI in water, whereupon white or cream-colored solids separated immediately. These were filtered, washed with water and 1:1 ethanol–ether mixture, and dried under reduced pressure at 25° for 24 hr. The products were characterized by analysis and X-ray diffraction data (Table I).

**Infrared Spectra.**—Samples were prepared as Nujol and hexachlorobutadiene mulls between NaCl plates (4000–650 $cm^{-1}$) and Nujol mulls between CsI plates (Beckman IR-7 instrument) and as Nujol mulls between polyethylene films (700–100 $cm^{-1}$) (Beckman IR-11 instrument). Owing to the complexity of the spectra, complete assignments could not be made. Accordingly, only those vibrations of particular interest, notably ν(Pt–I) and ν(Pt–N), are reported here (Discussion).

**Conversion of $PtL_4I_2$ to $PtL_2I_2$.**—Approximately 1-g samples of each of the complexes listed in Table I were heated at 100° ($10^{-2}$ mm) for 24 hr. The colors of the solids changed from white or cream colored to yellow, and a colorless liquid was evolved and condensed on the walls of the reaction vessels. Analytical data for Pt in the residual yellow solids were as follows: $Pt(py)_2I_2$: calcd, 32.2; found, 32.0. $Pt(3\text{-}Me(py))_2I_2$: calcd, 30.7; found, 30.4. $Pt(4\text{-}Me(py))_2I_2$: calcd, 30.7; found, 30.6. $Pt(4\text{-}Et(py))_2I_2$: calcd, 29.4; found, 29.4. $Pt(3,5\text{-}Me_2py)_2I_2$: calcd, 29.4; found, 29.3. In order to provide further information concerning the nature of these conversions, they were treated as follows.

**Differential Thermal Analysis (Dta).**—These data were obtained with a Stone differential thermal analyzer, Model 202, SH-11BR2 aluminum sample holder, platinel differential thermocouple, and platinum pans (use of glass pans gave substantially the same results). Undiluted 5-mg samples were heated from 25 to 425° at 5°/min in $N_2$ flowing at 1.2 $cm^3$/sec or *in vacuo* (0.5 mm) against an equal weight of reagent grade α-alumina. For each peak, the extrapolated onset, minimum, and extrapolated final temperatures were determined as described by McAdie.[12] The temperature scale of the analyzer was calibrated with $KNO_3$,[12] $KClO_4$,[12] and $NaNO_3$[13] and found to be accurate within ±1.5°; precision of the onset temperatures of a triplicate set of thermograms for a particular complex was ±1°. For estimation of heats of reaction, $BaCl_2 \cdot 2H_2O$ and $AgNO_3$ were used for calibration;[13] the heat constant was obtained from duplicate runs for each complex and agreed within 3%. For the process $PtL_4I_2(s) \rightarrow PtL_2I_2(s) + 2L(g)$ the heats of reaction found were 25.8, 26.8, 27.3, 28.1, and 29.1 kcal/mol where L is py, 3-Me(py), 5-Me(py), 4-Et(py), and 3,5-$Me_2$py, respectively. The essential dta data are given in Table II; typical curves are included in Figures 1 and 2.

**Thermogravimetric Analysis (Tga).**—The tga curves were obtained with a Stone TGA-5B thermogravimetric analyzer using a Pt sample holder in $N_2$ flowing at 1.3 $cm^3$/sec, a Pt thermocouple, and 22-mg samples heated at 5°/min from 25 to 825°. The instrument was calibrated using $CuSO_4 \cdot 5H_2O$. At 825°, oxygen was passed over the samples to ensure that only residual Pt remained. The temperatures recorded in Table III (see also Figures 1 and 2) for the initiation of each major inflection were obtained as extrapolations of the linear portions of the curves in the regions of accelerated decomposition.[14] Volatile decomposition products were collected and found to be soluble in common organic solvents; examination of the uv–visible spectra (Cary 14 instrument; 210–800 mμ) showed the presence of a preponderance of $I_2$ and lesser quantities of ligand. Thus for the case where the ligand was 3,5-$Me_2$py, the spectrum in ethanol showed iodine peaks at 442, 357, 290, and 221 mμ and a strong 3,5-$Me_2$py peak at 267 mμ.

Because the second inflection in the tga curves did not correspond quantitatively to any single dissociative process, samples of the 4-Me(py) complex were decomposed on a larger scale (170 mg) and the changes that occurred were observed in relation

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TABLE I

ANALYTICAL[a] AND X-RAY DIFFRACTION[b] DATA FOR $PtL_4I_2$

| L | % calcd |  |  |  | % found |  |  |  | X-Ray data[c] |
|---|---|---|---|---|---|---|---|---|---|
|  | Pt | C | H | N | Pt | C | H | N |  |
| py | 25.6 | 31.4 | 2.62 | 7.32 | 26.1 | 31.1 | 2.44 | 6.79 | 7.59 (1.0), 3.96 (0.9), 4.44 (0.6) |
| 3-Me(py) | 23.7 | 35.1 | 3.41 | 6.70 | 23.3 | 35.1 | 3.58 | 6.56 | 7.76 (1.0), 6.53 (0.9), 4.65 (0.8) |
| 4-Me(py) | 23.3 | 35.1 | 3.41 | 6.70 | 23.7 | 34.9 | 3.31 | 6.47 | 8.79 (1.0), 3.29 (0.9), 7.08 (0.8) |
| 4-Et(py) | 22.2 | 38.3 | 4.10 | 6.38 | 21.9 | 38.2 | 3.84 | 6.15 | 9.02 (1.0), 7.40 (0.9), 5.52 (0.9) |
| 3,5-$Me_2$py | 22.2 | 38.3 | 4.10 | 6.38 | 22.1 | 38.5 | 4.06 | 6.56 | 8.62 (1.0), 6.65 (1.0), 4.70 (0.8) |

[a] C, H, and N analyses by Chemalytics, Inc., Tempe, Ariz. [b] Cu Kα radiation; Ni filter; tube voltage 35 kV at 15 mA; exposure times 8–10 hr; relative intensities estimated visually. [c] Less intense lines not included.

TABLE II

DIFFERENTIAL THERMAL ANALYSIS OF $PtL_4I_2$[a]

| L | Atm | 1st endotherm, °C |  | 2nd endotherm, °C |  |
|---|---|---|---|---|---|
|  |  | Onset | Min | Onset | Min |
| py | $N_2$ | 140 | 166 | 244 | 267 |
|  | Vac | 138 | 165 | 231 | 253 |
| 3-Me(py) | $N_2$ | 108 | 134 | 239 | 257 |
|  | Vac | 105 | 132 | 195 | 228 |
| 4-Me(py) | $N_2$ | 126 | 156 | 246[b] | 264 |
|  | Vac | 127 | 155 | 230 | 248 |
| 4-Et(py) | $N_2$ | 131 | 138, 149[c] | 249 | 275 |
|  | Vac | 130 | 135, 151 | 239 | 260 |
| 3,5-$Me_2$py | $N_2$ | 129 | 157 | 243 | 267 |
|  | Vac | 128 | 155 | 222 | 248 |

[a] Minor deviations in the temperatures recorded here were observed at a heating rate of 1°/min; small but uninterpretable minima, not recorded here, were observed when decomposition was *in vacuo*. [b] Shoulder at 259°. [c] See Figure 2.

TABLE III

THERMOGRAVIMETRIC ANALYSIS OF $PtL_4I_2$[a]

| L | 1st inflection |  |  | 2nd inflection |  | Residual Pt, % |  |
|---|---|---|---|---|---|---|---|
|  | Temp,[b] °C | Wt loss, mg Calcd | Wt loss, mg Found | Temp,[b] °C | Wt loss,[c] mg | Calcd | Found |
| py | 155 | 5.34 | 5.02 | 264 | 10.36 | 25.6 | 25.6 |
| 3-Me(py) | 128 | 4.98 | 5.00 | 255 | 9.86[d] | 23.7 | 23.8 |
| 4-Me(py) | 146 | 5.14 | 5.26 | 266 | 8.25[d] | 23.7 | 23.8 |
| 4-Et(py) | 141 | 6.12 | 6.22 | 274 | 13.26[d] | 22.2 | 22.2 |
| 3,5-$Me_2$py | 138 | 6.30 | 6.18 | 257 | 12.98[d] | 22.2 | 22.1 |

[a] Weight losses observed at 0.03 mm were not significantly different. [b] By the method of ref 14. [c] A calculated value could not be obtained owing to concurrent and incomplete decomposition processes. [d] Total loss irrespective of minor inflections.

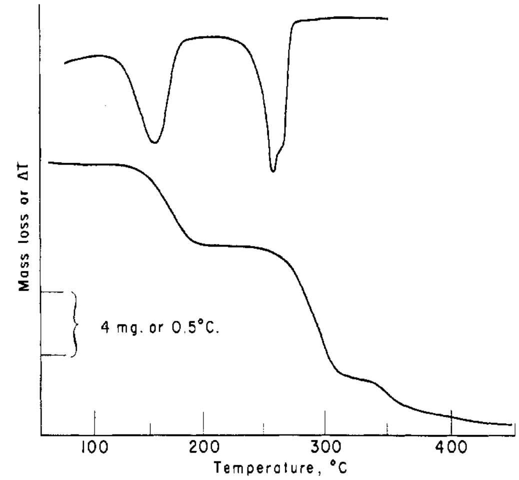

Figure 1.—Dta and tga curves for $[Pt(4\text{-}Me(py))_4]I_2$ in $N_2$.

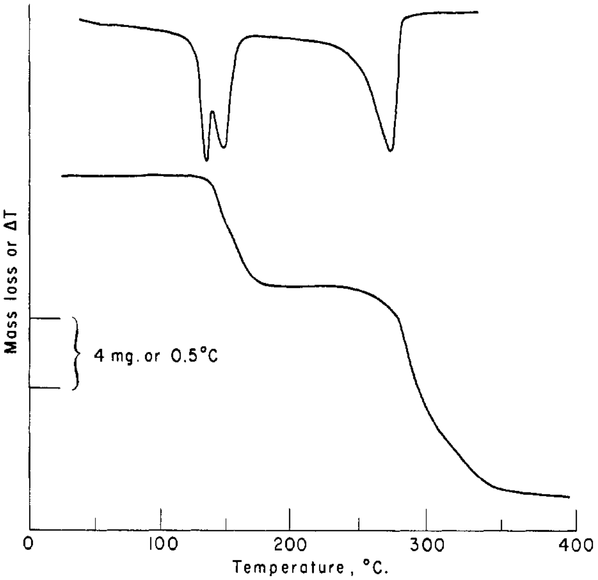

Figure 2.—Dta and tga curves for $[Pt(4\text{-}Et(py))_4]I_2$ in $N_2$.

to the tga curve. Thus, the 4-Me(py) complex in a porcelain boat was placed in a Pyrex tube and heated in a combustion furnace in flowing $N_2$ at *ca.* 4°/min. The temperature was held for 5 min at that indicated by the tga curve in order for the corresponding process to proceed to completion before resuming the temperature increase; the results were as follows: trace of $I_2$ evolution (237°), extensive $I_2$ evolution (257°), color of solid changed from yellow to brown (290°), drops of ligand condensed in cold end of tube (304°), trace of $I_2$ liberation (316°), and extensive $I_2$ liberation accompanied by yellow gas (345–350°).

In efforts to identify the species present over the temperature range corresponding to the final plateau of the tga curve, the 4-Me(py) complex was heated at 314–323° for 30 min. The platinum content of the residual black solid was of variable Pt content (56–71%). An X-ray diffraction pattern established the presence of elemental Pt, the infrared spectrum included bands characteristics of 4-Me(py), and a strong band at 178 $cm^{-1}$ ν(Pt–I) indicated the survival of some Pt–I bonds.[15]

## Discussion

The results given above show that the complexes of the type $PtL_4I_2$ are relatively unstable even at room temperature. For the case where the methyl group is in the 2 position, Ivanova[16] reported the synthesis of a tetrakis complex of Pt(II); in our experience this product was too unstable to permit further investigation.

As expected, the far-infrared spectra of $PtL_4I_2$ did not include a band attributable to ν(Pt–I). When, however, these species are thermally degraded to $PtL_2I_2$, a strong singlet absorption between 176 and 196 $cm^{-1}$ confirms the trans structure.[15] Only one infrared-active Pt–I stretching mode should be observed for the trans planar case. In the symmetry group $D_{2h}$, two stretching modes involving the metal are expected: ν(M–I) $[B_{3u}]$ and ν(M–L) $[B_{2u}]$. For the cis case ($C_{2v}$) both symmetric and antisymmetric stretching modes are expected for ν(M–I) and ν(M–L), $[A_1 +$

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$B_1$]. Since $\nu$(Pt–I) varied from 176 to 196 cm$^{-1}$, salts of the Magnus type can be excluded.

There is difference of opinion about the assignment of $\nu$(Pt–N) in both cis and trans systems of the type $PtL_2X_2$. Allen and Theophanides[17] assigned $\nu$(Pt–N) in *cis*- and *trans*-[Pt(py)$_2$Cl$_2$] to bands in the range 480–450 cm$^{-1}$. Deuteration studies however indicate[15] that these bands involve mainly ring deformational modes and it is assumed that $\nu$(Pt–N) occurs at lower frequencies. Durig and coworkers[15] assigned $\nu$(Pt–N) in the range 246–300 cm$^{-1}$, compared to the 260–300-cm$^{-1}$ range of Clark and Williams;[18] in both cases L = py. In the present work, marginal assignments (cm$^{-1}$) for this mode can be made as follows: py, 291; 3-Me(py), 261; 5-Me(py), 256; 4-Et(py), 263 and 254; 3,5-Me$_2$py, 294 and 245. These are very weak bands in all cases and are not even observed for 4-Me(py) and 4-Et(py) unless concentrated mulls are employed. Hence we conclude that from both the present and earlier work, the assignment for $\nu$(Pt–N) remains subject to question. This doubt is further accentuated by the fact that the trend in relative intensities within this series of complexes does not follow the order anticipated in relation to the nature and position of the substituents in the pyridine ring.

The first endotherm in the dta curves corresponds to the detachment of two ligands and this is confirmed by the weight losses computed from the corresponding tga curves. Only in the case of one ligand (4-Et(py)) was this endotherm resolved into a doublet, thus indicating that removal of the two ligands is a two-step process. The second endotherm corresponds to the loss of both ligand and iodine, but neither of these processes is complete over the temperature range encompassed by the second endotherms. Thereafter, both X-ray diffraction and infrared spectral data show that the decomposition product consists predominantly of elemental platinum together with some species containing Pt–I bonds and ligands. Minor but unexplainable endotherms in the dta curves and inflections in the tga curves are observed when conditions (heating rates, pressure, etc.) are changed; this suggests only that the final decomposition processes occur at different rates as the identity of the ligand is varied.

Finally, it should be noted that the heats of reaction reported above increase in the same order as the p$K_b$ values of the pyridines; hence the effect of $\pi$-back-bonding is small in comparison with that observed previously[19] for analogous complexes of cobalt(II).

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# Protonation and Solvolytic Reactions of Some Low-Valent Platinum Complexes Containing Methoxydiphenylphosphine or *n*-Butoxydiphenylphosphine as Ligands

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The complexes Pt($n$-BuOPPh$_2$)$_2$Cl$_2$, Pt($n$-BuOPPh$_2$)$_4$, and Pt(MeOPPh$_2$)$_3$ have been isolated and the reaction between protonic acids and the zerovalent complexes has been found to give labile hydrides. The attempted preparation of Pt(MeOPPh$_2$)$_3$ in ethanol gave Pt(EtOPPh$_2$)$_3$, and the attempted preparation of complexes of P(OPh)$_3$ and P(O-$p$-tolyl)$_3$ by reaction with palladium salts in methanol gave solely Pd[P(OMe)$_3$]$_2$Cl$_2$. This latter compound is stable in ethanol in the absence of P(OPh)$_3$. The complex Pt(OPPh$_2$)$_2$(HOPPh$_2$)$_2$ has been synthesized and is considered to be a platinum(II)–diphenylphosphinato complex. The substitution products of this complex with P(OPh)$_3$ and P(O-$p$-tolyl)$_3$ have the stoichiometry Pt(OPPh$_2$)$_2$[HOP(OPh)$_2$]$_2$ and Pt(OPPh$_2$)$_2$[HOP(O-$p$-tolyl)$_2$]$_2$.

## Introduction

Protonation studies of substituted phosphine[1–6] and phosphite[7–11] complexes of nickel, palladium, and platinum have recently attracted attention from several groups of workers. The protonation of Pt(PPh$_3$)$_4$ has led to the formation of stable hydrides, although until recently[6] it has been considered that the addition of HX to Pd(PPh$_3$)$_4$ would lead to the formation of Pd(PPh$_3$)$_2$X$_2$ with the evolution of hydrogen. Studies at Du Pont[7–11] have considered the isolation and catalytic properties[12] of hydrides obtained by the protonation of phosphite complexes of Ni(0), where the products are considered to be pentacoordinate nickel(II) complexes. In addition to this work $^1$H and $^{31}$P nmr studies have been made on stereochemically nonrigid hydrides of Fe,[13] Ru,[14] and Os. In view of our interest

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