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THERMAL DECOMPOSITION AND ISOMERIZATION OF PLATINUM(II) PHOSPHINE DIHALIDE COMPLEXES*

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ABSTRACT

Thermal decomposition and *cis-trans* isomerization of square planar platinum(II) complexes of the type PtL_2X_2, L = organophosphorus ligand and X = halide, are reported. It is shown by thermogravimetric measurements that phenyl loss is the rate-determining step in the decomposition of arylphosphine complexes and that increased phenyl substitution in the phosphine ligand decreases the thermal stability of the complex. Thermogravimetric decomposition of such complexes in an air atmosphere is suggested as a method of platinum analysis.

INTRODUCTION

The thermal decomposition reactions of many platinum(II) complexes have been investigated in detail, especially those of complexes containing nitrogen coordinated ligands[1]. In particular it has been suggested that thermogravimetry (TG) to 900°C in an oxygen-containing atmosphere is a suitable technique for the quantitative determination of platinum in these complexes[2].

Thermal methods have also been used to study various isomerization reactions of platinum(II) complexes. Thus, it has been shown by TG/DTA that the transformation

$$[PtL_4]I_2 \rightarrow trans\text{-}PtL_2I_2$$

occurs at elevated temperatures when L is pyridine or substituted pyridine[2]. Similarly Nikolaev[3] showed by DTA that isomerization of the complex *cis*-$Pt(NH_3)_2Cl_2$ to the *trans* isomer occurred before decomposition, while Kukushkin and Postnikova[4] found that the *cis* to *trans* isomerization of complexes PtA_2I_2, where A is an amine, is a general thermal reaction. The *trans* to *cis* isomerizations of $Pt(CO)(NH_2R)Cl_2$[5] and $Pt(PMS)_2Cl_2$[6] where PMS is pentamethylenesulfide, have also been studied by DTA/TG.

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The thermal reactions of platinum(II) phosphine complexes have been much less thoroughly studied, although the catalyzed thermal isomerization of such complexes in solution has been extensively investigated[7–11]. The earliest report was by Jensen[12], who described the *cis–trans* isomerization of several phosphine complexes in the solid phase. More recently Mastin[13] and Lee and Stoufer[14] have reported on the thermal behavior, including *cis–trans* isomerization of $Pt(Ph_3P)_2X_2$ complexes while Allen et al.[15] have used DTA/TG to investigate the isomerization and volatilization of a number of palladium(II) and platinum(II) phosphines. It is the latter report which prompts us to describe the somewhat complementary results reported in the present paper.

This paper presents a study of the thermal stability and *cis–trans* isomerization of platinum(II) complexes of the type $Pt(PR_3)_2X_2$ where X = Cl, Br, or I and R = methyl, ethyl, n-butyl, n-octyl, or phenyl by TG and differential scanning calorimetry (DSC). Fifteen compounds, including six *cis–trans* isomeric pairs, were included in the study.

EXPERIMENTAL

Triethylphosphine (PEt_3) was obtained from Orgmet, Inc. Tri-n-octylphosphine (POc_3), tri-n-butylphosphine (PBu_3), dimethylphenylphosphine ($PhPMe_2$), and diphenylmethylphosphine (Ph_2PMe) were purchased from Strem Chemical Company, and triphenylphosphine (Ph_3P) from Pressure Chemical Company. The compound K_2PtCl_4 was prepared by a standard method[16].

Most of the complexes were prepared by mixing aqueous solutions of K_2PtCl_4 with phosphine in the mole ratio 1:2 according to Jensen[12], but under an N_2 atmosphere. *Cis*-$Pt(PEt_3)_2Cl_2$ was prepared by the method of Parshall[17]. The PBu_3 complexes were obtained by the method of Kauffman and Teter[18].

Cis- and *trans*-$Pt(PEt_3)_2I_2$ were prepared from the corresponding dichlorides. The *cis* isomer had to be prepared via the intermediate[12] $Pt(PEt_3)_2SO_4$; direct methathesis gave only the *trans* isomer.

Micro analyses for C and H were carried out on a Perkin-Elmer 240 elemental analyzer. All complexes (with the exception of the low-melting *cis*-$Pt(POc_3)_2Cl_2$, which was contaminated with traces of free POc_3) gave satisfactory analyses and m.p.'s.

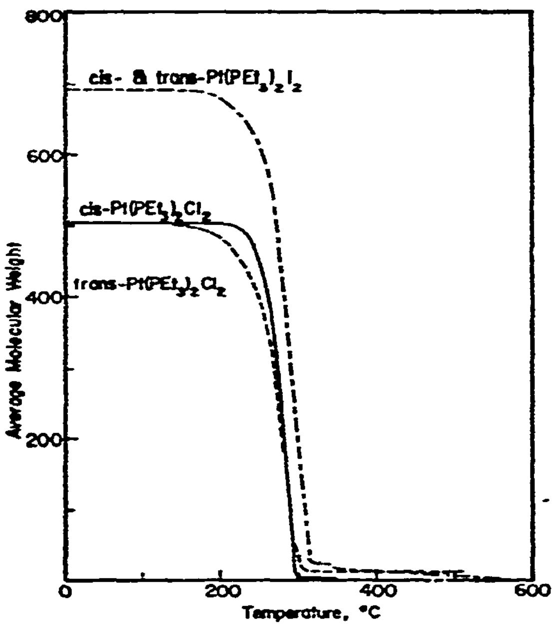
Infrared spectra were recorded on samples as Nujol mulls or KBr pellets on a Perkin-Elmer 457 spectrometer. Raman spectra of powdered solids were obtained with a Jarrell-Ash Model 25-400 spectrometer with a coherent radiation Model 52G Ar/Kr mixed gas laser operating at 514.5 or 634.1 nm as a light source.

The Perkin-Elmer TGS-1 system was used for all TG analyses. Temperature calibration was done against Curie-point standard metals supplied by the manufacturer. Sample size was 3–5 mg; platinum pans were used as sample holders. The sweep gas was either dry nitrogen or air at a flow-rate of 0.05 $ft.^3\ h^{-1}$. The heating rate was 20°C min^{-1}.

DSC curves were obtained on a Perkin-Elmer DSC-1B differential scanning calorimeter using approximately 5 mg of sample in an aluminum pan under an atmosphere of pure dry nitrogen.

RESULTS AND DISCUSSION

The TG curves for the complexes *cis*- and *trans*-$Pt(PEt_3)_2X_2$, where X = Cl or I, are shown in Fig. 1. The four compounds lose essentially all mass in a single step; the lack of residue indicates complete volatilization of these complexes without decomposition. Although the onsets of volatilization differ for the isomers when X = Cl, the volatilization curves are identical when X = I.



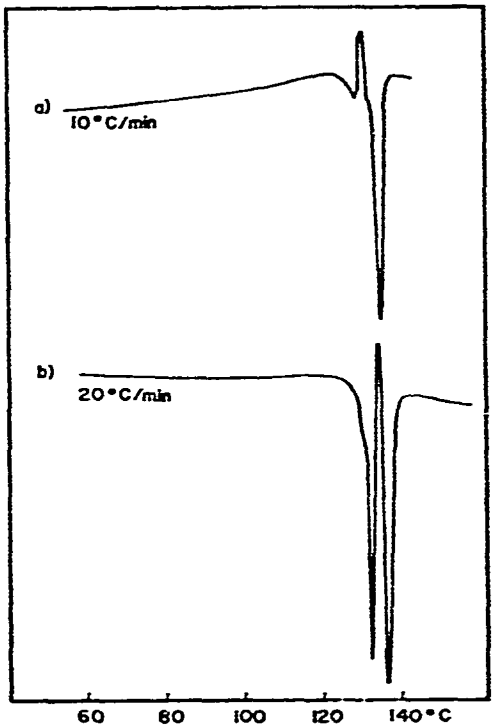


Fig. 1. TG curves of $Pt(PEt_3)_2X_2$ in an air atmosphere.

Fig. 2. DSC curve of *cis*-$Pt(PEt_3)_2I_2$. (a) at 10°C min^{-1}; (b) at 20°C min^{-1}.

Figure 2 shows the DSC trace of *cis*-$Pt(PEt_3)_2I_2$. In the scan made at 10°C min^{-1} there is evidence for a small endotherm at ca. 129°C, followed quickly by a sharp exotherm at 130°C and then a large endotherm at 135°C; the initial endotherm is much more prominent in the faster scan (20°C min^{-1}), Fig. 2b. The second endothermic peak, T_{max} = 135°C, corresponds to the m.p. of *trans*-$Pt(PEt_3)_2I_2$ (lit.[12], m.p. 136–137°C); the observation of a single Pt–I stretching band at 150 cm^{-1} in the Raman spectrum of the DSC residues confirmed the presence of the *trans* isomer. We thus ascribe the initial endotherm to partial melting of the *cis* isomer and the exothermic peak, $T_{max} = 130°C$, to the *cis–trans* isomerization process. An estimate of the heat of isomerization, $\Delta H = -3.2$ kcal mol^{-1}, was obtained from the DSC scan after analysis with a Du Pont Analog Curve Resolver, Fig. 3.

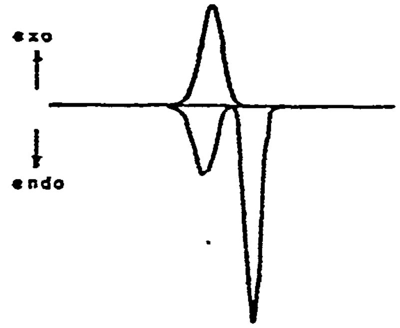


Fig. 3. Resolved DSC curve of *cis*-$Pt(PEt_3)_2I_2$.

The above observations are consistent with those reported by Allen et al.[15], in that both volatilization and isomerization of the PEt_2 complexes do occur. The *cis* iodide complex is also more labile than the *cis* chloride, in agreement with the halogen effect suggested by Allen et al.[15]. However, previous evidence from mass spectrometric studies of these complexes[19] has conclusively demonstrated that these compounds retain their geometric integrity in the vapor phase; this means that isomerization must be taking place in the solid or, more likely, in the melt. This is a very significant point in view of the mechanistic implications that would have to be drawn from a true vapor phase isomerization, i.e., that the isomerization is intramolecular, since such a process has been shown to be thermally disallowed[20,21].

Our observations on the other alkylphosphine complexes studied are also in disagreement with the results reported by Allen et al.[15]. The effect of increasing the molecular weight of the alkylphosphine on complex volatility is shown in Fig. 4. The tri-n-octyl-phosphine complex was found to be the most stable of all the compounds studied, with an extrapolated onset temperature of 338°C (356°C in nitrogen), despite the fact that it is the lowest melting of the complexes (m.p. 60°C). It should also be noted that both POc_3 and the PBu_3 complexes volatilize with decomposition. Further, the extrapolated onsets of the TG curves for *cis*- and *trans*-$Pt(PBu_3)_2Cl_2$ in nitrogen are substantially different, 245 and 282°C, respectively. The former temperature is considerably below the $T_{max} = 256°C$ DTA peak ascribed to *cis-trans* isomerization by Allen et al.[15], while the latter is below the 301°C (or 343°C) reported as the vaporization temperature of the *trans* isomer.

Results from DSC study of *cis*-$Pt(PBu_3)_2Cl_2$, shown in Fig. 5, also differed considerably from the previous report[15]. No isomerization endotherm at 256°C was noted, but there was evidence of a very slow isomerization process just above the

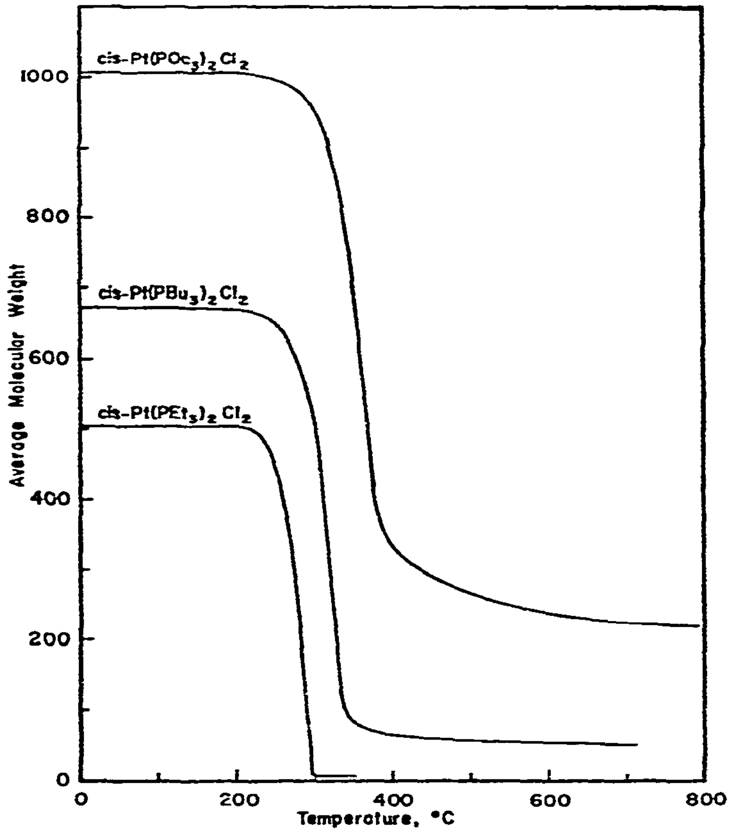


Fig. 4. TG curves of various alkylphosphine complexes of platinum(II) dichloride in an air atmosphere.

cis melting point[18], 144°C. Repetitive DSC scans of a sample of the *cis* complex, with the temperature held at 146°C after each scan, showed no change until after 20 min at the elevated temperature (scan 3); in subsequent scans the melting endotherm of the *cis* isomer broadened considerably and a new endotherm at 55°C (*trans*-$Pt(PBu_3)_2Cl_2$, m.p.[18] 65–66°C) began to grow. The far infrared of the solid after the sixth scan, when the sample had been heated to 146°C for over 60 min, showed that it contained mainly the *trans* isomer, but that some of the original *cis* compound was still present, These results are consistent with the fact that *cis*-$Pt(PBu_3)_2CL_2$ isomerizes in the melt, as has been previously demonstrated[18], and that a number of *cis* and *trans* solid solutions are formed by the isomeric mixture upon cooling.

A note of caution with regard to the comparison of thermal analysis results with those from solution studies of *cis–trans* isomerization as made by Allen et al.[15] would also seem to be in order at this point. With only two exceptions; solution studies have been of catalyzed isomerization[7–11], an associative process involving combination of complex with free phosphine in the rate-determining step, and the

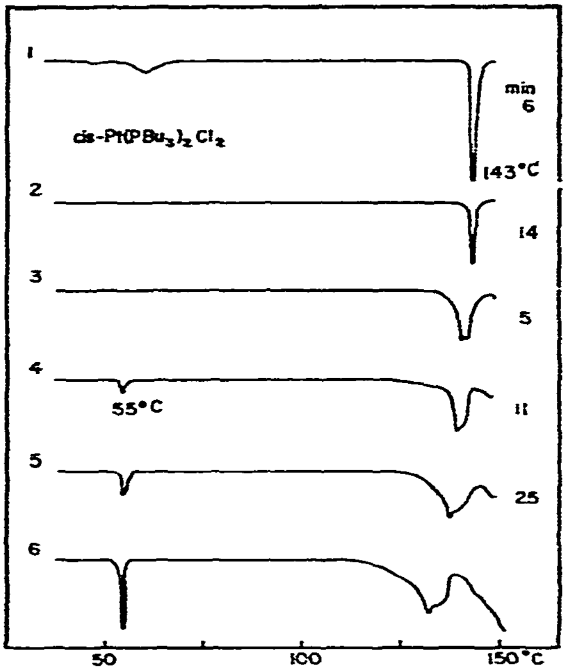


Fig. 5. Consecutive DSC scans of *cis*-Pt$(PBu_3)_2Cl_2$; sample held at 146°C for 6, 14, 5, 11, and 25 min, respectively, between scans.

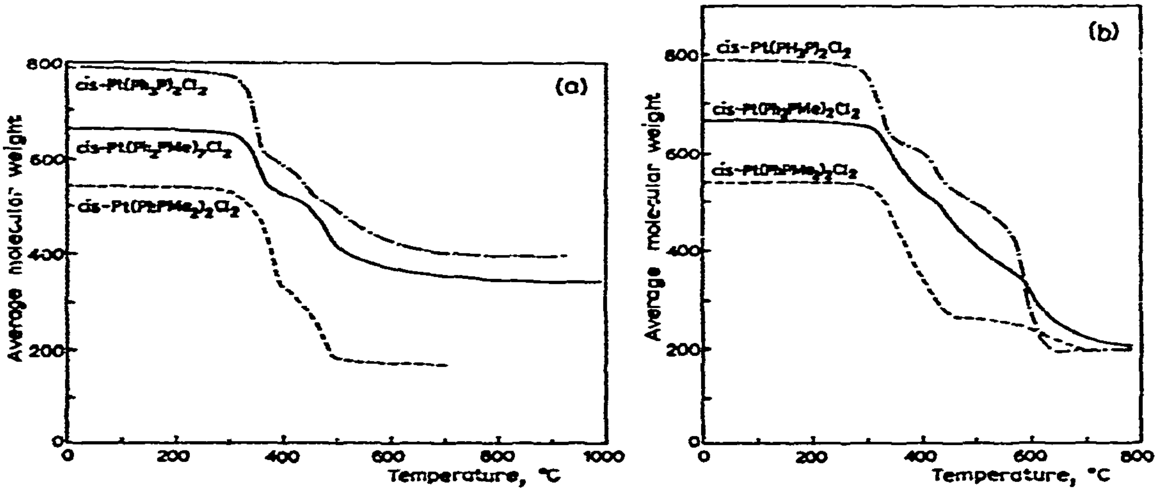


Fig. 6. TG curves of various phenyl substituted phosphine complexes of platinum(II) dichloride. (a) in nitrogen; (b) in air.

thermodynamic parameters obtained from such studies[8-11], e.g., $\Delta H^{\neq}$ or $\Delta G^{\neq}$, have been those for the activation process. The two uncatalyzed isomerizations[22,23] have been shown to occur by a dissociative mechanism and to give very different thermal parameters, e.g.[22], $\Delta G^{\neq} = 23$ kcal mol^{-1}. Therefore, even if Allen means to imply that isomerization in the melt is also a catalyzed process, a direct comparison of thermodynamic parameters obtained from DTA or DSC studies with those from solution studies is unwarranted and obviously misleading.

The final aspect of the present study concerns the factors which affect the thermal stability of phosphine complexes of platinum(II) dihalides. Accordingly, the dichloride complexes *cis*-$Pt(PR_3)_2Cl_2$ containing the phosphines $PhPMe_2$, Ph_2PMe, or Ph_3P were analyzed by TG in both nitrogen and air atmospheres (Fig. 6). The extrapolated onset temperatures for the complexes decrease in the order $PhPMe_2 > Ph_2PMe > Ph_3P$, exactly the opposite trend with increasing phenyl substitution observed previously in thermal decomposition studies of cobalt(II)[24] and nickel(II)[25] phosphine dichlorides. Since the onset temperatures are essentially the same in both gases, initial decomposition cannot be due to oxygen attack. However, the widely varying final weights shown in the nitrogen TG traces (Fig. 6a) indicate that oxygen attack is very important in the final stages of decomposition; in air all of the TG traces indicate essentially a pure platinum residue.

TG curves for the complexes *cis*- and *trans*-$Pt(Ph_3P)_2X_2$ where X = Cl, Br, or I are shown in Fig. 7. The thermograms of the six compounds are very similar, with

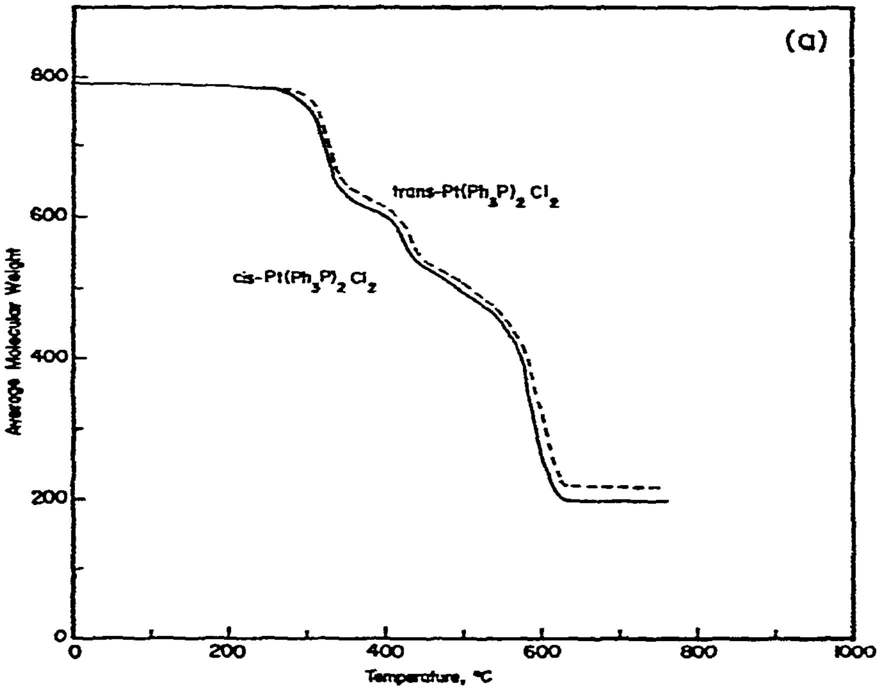


Fig. 7. TG curves of *cis*- and *trans*-$Pt(Ph_3P)_2X_2$ in an air atmosphere. (a) X = Cl; (b) X = Br; (c) X = I.

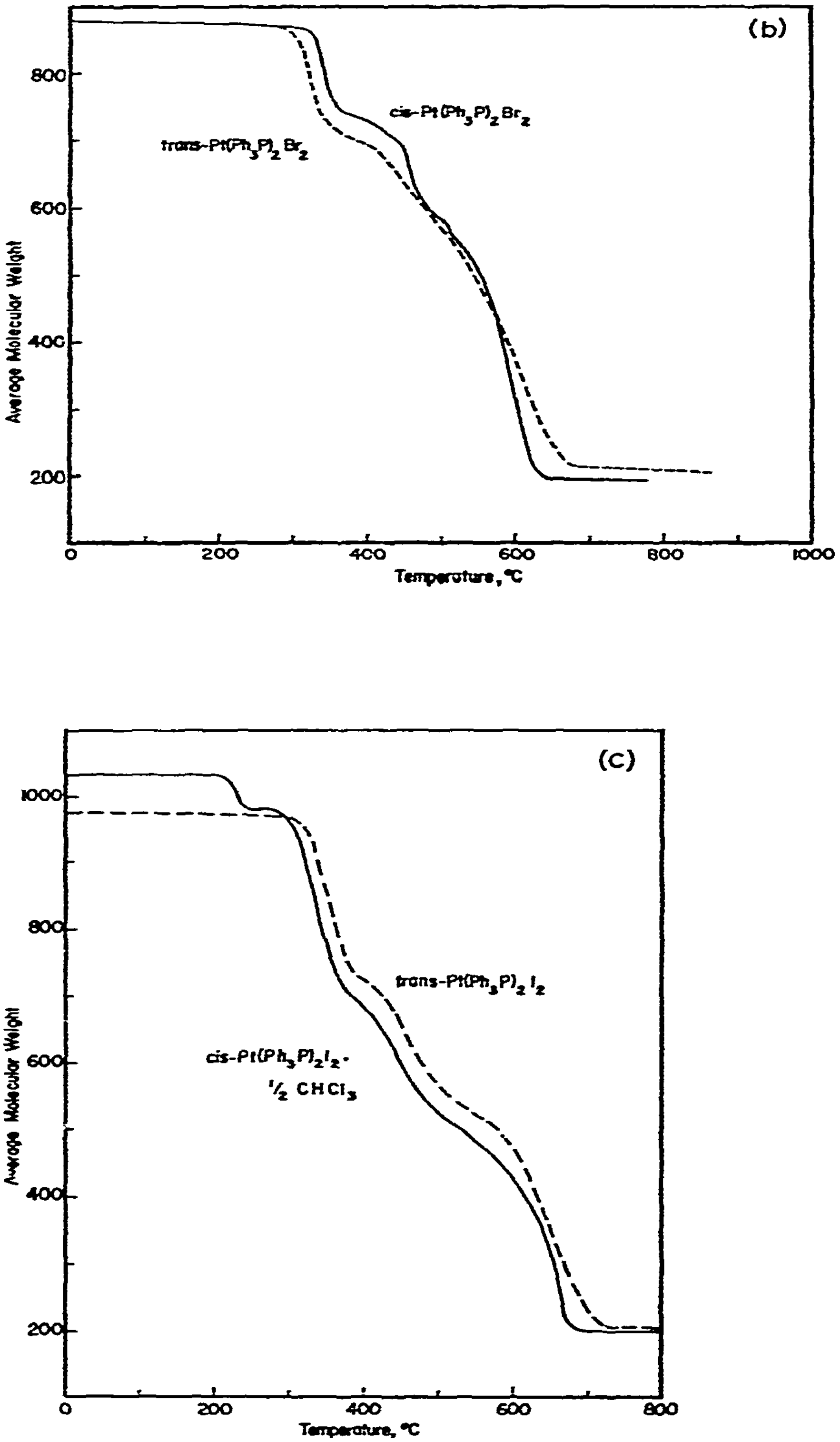


Fig. 7. (Legend see at the bottom of page 147).

all of the extrapolated onset temperatures at just above 300 °C. Even an earlier weight loss of bound chloroform[13] at ca. 200 °C from the complex cis-$Pt(Ph_3P)_2I_2 \cdot 1/2CHCl_3$ does not appear to affect this onset temperature. The thermal stability of the complexes is thus apparently independent of halide, as observed for the Ph_3P complexes of Co(II)[24], but in contrast to observations on the Ph_3P complexes of Ni(II)[25], in which stability increases in the order of $Cl<Br<I$. The residues from these analyses, done in air, again appear to be essentially pure platinum in each case. TG decomposition of a non-volatile platinum(II) phosphine complex in an air atmosphere thus appears to be a useful technique for determination of platinum content in the complex; some typical results are given in Table 1.

TABLE 1

EXAMPLES OF PLATINUM ANALYSIS BY TG

	% Pt	
	Calculated	*Found*
cis-$Pt(POc_3)_2Cl_2$	19.4	21.5
cis-$Pt(Ph_3P)_2Cl_2$	24.7	24.7
trans-$Pt(Ph_3P)_2Cl_2$	24.7	27.1
cis-$Pt(Ph_3P)_2Br_2$	22.2	22.1
trans-$Pt(Ph_3P)_2Br_2$	22.2	23.6
cis-$Pt(Ph_3P)_2I_2 \cdot 1/2CHCl_3$	18.9	19.3
trans-$Pt(Ph_3P)_2I_2$	20.0	20.9

Finally, all of the phenylphosphine complexes studied went through multiple step decomposition as shown by TG, with two or three distinct steps seen in both nitrogen and air atmosphere. This observation, the decreasing complex stability with increasing phenyl substitution in the phosphine ligand (in spite of the increasing metal–ligand bond strength which results from such substitution[26]), and the lack of a halide effect on stability indicate that phenyl loss is probably the rate-determining step in the thermal decomposition of these complexes.

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