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Thermal analysis of coordination compounds. Part 3. Thermal decomposition of platinum complexes containing triphenylphosphine, triphenylarsine and triphenylstibine

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Abstract

Studies by thermogravimetric analysis (TG) and differential thermal analysis (DTA) of the complexes $[PtCl_2L_2]$ (L is PPh_3, $AsPh_3$, $SbPh_3$), $[PtL_n]$ ($n=3$, L is $SbPh_3$; $n=4$, L is PPh_3, $AsPh_3$); $[(PtL_3)_2N_2]$; $[(PtL_3)_2C_2]$ and $[Pt(CO)_2L_2]$ (L is $SbPh_3$) are described. Analysis of the TG and DTA curves showed that Pt(II) complexes of the type $[PtCl_2L_2]$ have a higher thermal stability than the corresponding Pt(0) complexes of the type $[PtL_n]$, with the exception of $[Pt(SbPh_3)_3]$, which is more stable than $[PtCl_2(SbPh_3)_2]$. Thermal stabilities of each of the complexes are compared with those of the others in the series. Mechanisms of thermal decomposition of complexes of the types $[PtCl_2L_2]$ and $[PtL_n]$ are proposed. Residues of the samples were characterized by chemical tests and IR spectroscopy. The residue from the thermal decomposition of $[PtCl_2L_2]$ (L is PPh_3, $AsPh_3$) and $[Pt(PPh_3)_4]$ is metallic platinum. For $[Pt(AsPh_3)_4]$ the residue is a mixture of Pt and As, whereas for the complexes containing $SbPh_3$ the residues are mixtures of Pt and Sb. In these cases, the proportional contents of Pt and As or Pt and Sb correspond to the stoichiometry of these elements in the respective complexes. The complexes $\{[Pt(SbPh_3)_3]_2N_2\}$, $\{[Pt(SbPh_3)_3]_2C_2\}$ lose N_2 or the ethynediyl group at 130–150°C and are transformed into $[Pt(SbPh_3)_3]$.

Keywords: Platinum complexes; Thermal analysis; Thermal decomposition; Triphenylarsine; Triphenylphosphine; Triphenylstibine

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1. Introduction

Complexes of platinum, especially of the type $[PtCl_2L_2]$ [L is PPh_3 (triphenylphosphine), $AsPh_3$ (triphenylarsine) or $SbPh_3$ (triphenylstibine)] and $[PtL_n]$ ($n=3$, L is $SbPh_3$; $n=4$, L is PPh_3 or $AsPh_3$) have extensive applications in the field of homogeneous catalysis [1–4] and are widely used as precursors for the preparation of organometallic compounds generally [5–8]. However, the thermal stability and mechanisms of thermal decomposition of these compounds have not been studied. In the present paper, a thermal analysis study of the complexes $[(PtL_3)_2N_2]$, $[(PtL_3)_2C_2]$, $[Pt(CO)_2L_2]$ (L is $SbPh_3$), $[PtCl_2L_2]$ and $[PtL_n]$ is described, which was carried out using thermogravimetric analysis (TG) and differential thermal analysis (DTA) techniques.

2. Experimental

The DTA curves in the range 25–900°C were obtained using RB-12 equipment, a classical system for differential thermal analysis manufactured by BP Engenharia (Brazil), having two ovens and connected to an ECB X-T RB-102 recorder. Each of the ovens has a nickel block with three cylindrical holes to accommodate the Pt/Pt–Rh(13%) thermocouples for the block, the sample, and the reference temperature detector. α-Alumina previously calcined at 1100°C was used as standard reference material. The actual temperature was measured with an analogue pyrometer calibrated with a reference substance of standardized melting point. The equipment was used only under a static air atmosphere at ambient pressure. The samples were diluted to 25% by mass with α-alumina to ensure that both sample and reference material had constant thermal conductivity, and the resulting mixtures and reference material were tightly and homogeneously packed into the holes in the nickel block. The heating rate was $10.0\,K\,min^{-1}$.

The TG curves, also in the range 25–900°C, were obtained using a Perkin-Elmer thermogravimetric analysis system of the null balance type calibrated with a standard weight. A sample containing 4–10 mg of the material was placed in a 0.3 ml platinum crucible and heated at $10\,K\,min^{-1}$ in a dynamic atmosphere of air with flow rate $30\,ml\,min^{-1}$.

The IR spectra of the complexes in the form of CsI pellets were recorded with a Perkin-Elmer 567 apparatus in the region $4000–200\,cm^{-1}$.

Elemental analyses of carbon and hydrogen were provided by the CETEC (Fundação Centro Tecnológico de Minas Gerais: Technological Centre Foundation of Minas Gerais), Belo Horizonte, MG, Brazil and by the Instituto de Química, USP (USP Institute of Chemistry), São Paulo, SP, Brazil. The platinum content was established from the mass of the residue obtained in the TG analysis.

The uncorrected melting points were determined on an FP-2 Mettler system.

The complexes $[PtCl_2(EPh_3)_2]$ (E is P, As or Sb) were synthesized by addition of a hot ethanolic solution of EPh_3 to a cold solution of $H_2[PtCl_6]$, also in ethanol [9,10]. $[Pt(EPh_3)_4]$ (E is P or As) and $[Pt(SbPh_3)_3]$ were obtained from $[PtCl_2(EPh_3)_2]$ and an excess of EPh_3, also in ethanol medium, by reduction with $NaBH_4$ or N_2H_4 under an inert atmosphere [9,11,12]. When gaseous nitrogen, acetylene or carbon monoxide was bubbled through an ethanolic suspension of $[PtCl_2(SbPh_3)_2]$ and an excess of $SbPh_3$ in the presence of $NaBH_4$, the complexes $\{[Pt(SbPh_3)_3]_2N_2\}$, $\{[Pt(SbPh_3)_3]_2C_2\}$ and $[Pt(CO)_2(SbPh_3)_2]$ were obtained [13].

3. Results and discussion

The results of elemental analysis for carbon, hydrogen and platinum are shown in Table 1, and confirm the proposed stoichiometry of the compounds. The melting points of the complexes are in agreement with the literature data [9–13] and are also shown in Table 1.

The complexes $[PtCl_2(EPh_3)_2]$ (E is P, As or Sb) have a square planar structure, whereas $[Pt(EPh_3)_4]$ (E is P or As) and $[Pt(CO)_2(SbPh_3)_2]$ have tetrahedral structures [9,11,13]. The compounds $\{[Pt(SbPh_3)_3]_2N_2\}$ and $\{[Pt(SbPh_3)_3]_2C_2\}$ contain dinitrogen or an ethynediyl group as a bridge, respectively [12,13] whereas $[Pt(SbPh_3)_3]$, a zerovalent formally 16-electron complex, probably has a trigonal structure; it is an unusual compound and is remarkably unreactive towards reagents which react quickly with other zerovalent phosphine compounds [13].

Figs. 1 and 2 show the DTA and the TG curves respectively of the platinum complexes and of the free ligands PPh_3, $AsPh_3$ and $SbPh_3$. Table 2 gives the temperatures related to the observed peaks on the DTA curves corresponding to the mass losses observed on the TG curves.

From an analysis of the TG and DTA curves of the bivalent Pt complexes $[PtCl_2L_2]$ (L is PPh_3, $AsPh_3$ or $SbPh_3$) and of the zerovalent Pt complexes of the type $[PtL_n]$ ($n = 3$, L is $SbPh_3$; $n = 4$, L is PPh_3 or $AsPh_3$), we conclude that the thermal stability of the Pt(II) compounds is higher than that of the corresponding Pt(0) complexes, with the exception of $[Pt(SbPh_3)_3]$, which is more stable than $[PtCl_2(SbPh_3)_2]$. The relative thermal stability is obtained by comparison of the initial and final decomposition

Table 1
Analytical data and melting points for the platinum complexes

Complexes	Melting point/°C	Found/%			Calculated/%		
		C	H	Pt	C	H	Pt
$[PtCl_2(PPh_3)_2]$	>300	54.51	3.91	24.75	54.69	3.82	24.68
$[PtCl_2(AsPh_3)_2]$	>300	49.38	3.17	22.06	49.22	3.44	22.21
$[PtCl_2(SbPh_3)_2]$	130d	44.57	3.28	20.21	44.48	3.11	20.07
$[Pt(PPh_3)_4]$	85–87	69.42	4.70	15.74	69.50	4.86	15.68
$[Pt(AsPh_3)_4]$	180–181	61.08	4.35	14.30	60.90	4.26	13.74
$[Pt(SbPh_3)_3]$	180d	51.67	3.63	15.50	51.71	3.62	15.55
$\{[Pt(SbPh_3)_3]_2N_2\}$	180d	51.32	3.76	15.31	51.14	3.58	15.38
$\{[Pt(SbPh_3)_3]_2C_2\}$	190d	52.08	3.69	15.47	52.17	3.58	15.41
$[Pt(CO)_2(SbPh_3)_2]$	130d	47.97	3.29	20.65	47.68	3.16	20.38

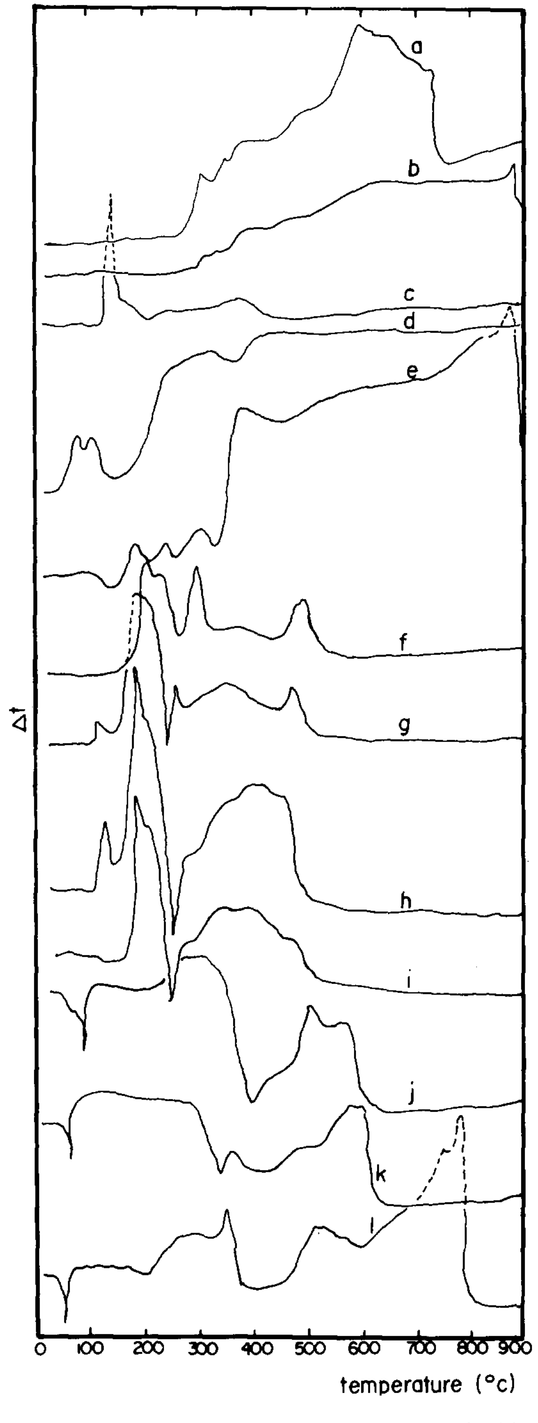

Fig. 1. DTA curves of the platinum compounds and free ligands diluted to 25% in α-alumina. Heating rate 10.0 K min^{-1}: a, $[PtCl_2(PPh_3)_2]$; b, $[PtCl_2(AsPh_3)_2]$; c, $[PtCl_2(SbPh_3)_2]$; d, $[Pt(PPh_3)_4]$; e, $[Pt(AsPh_3)_4]$; f, $[Pt(SbPh_3)_3]$; g, $\{[Pt(SbPh_3)_3]_2N_2\}$; h, $\{[Pt(SbPh_3)_3]_2C_2\}$; i, $[Pt(CO)_2(SbPh_3)_2]$; j, PPh_3; k, $AsPh_3$; l, $SbPh_3$.

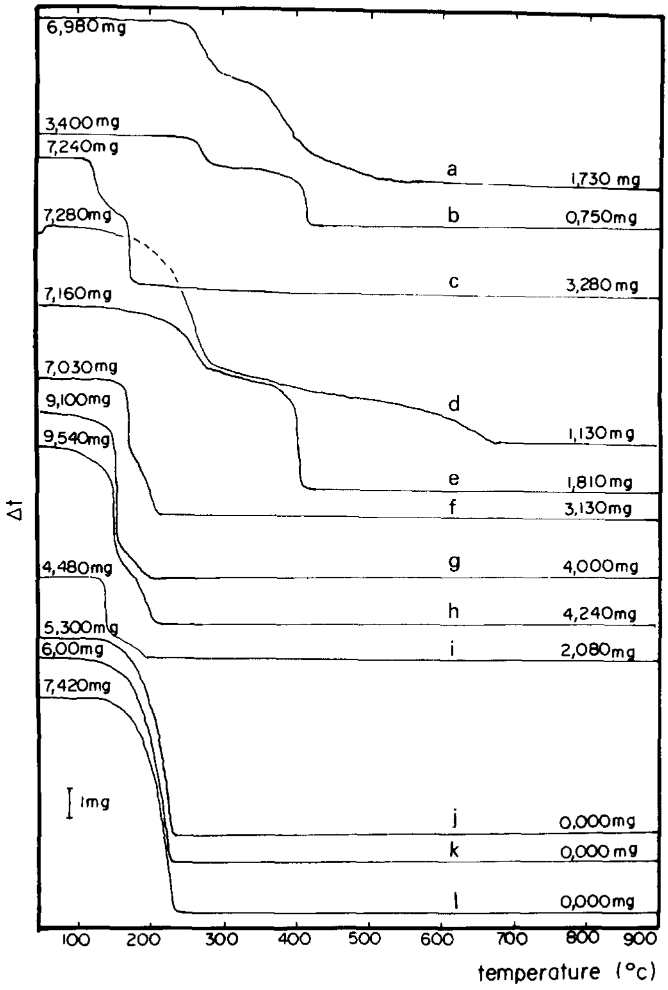

Fig. 2. TG curves of the platinum compounds and free ligands. Heating rate 10.0 K min^{-1}. For key to compounds see Fig. 1.

temperatures of the compounds, as shown in Table 3. On the basis of the thermal analysis results, the following series of thermal stability are proposed

$$[PtCl_2(PPh_3)_2] > [PtCl_2(AsPh_3)_2] > [PtCl_2(SbPh_3)_2]$$

$$[Pt(SbPh_3)_3] > [Pt(AsPh_3)_4] > [Pt(PPh_3)_4]$$

For the Pt(II) complexes the series of thermal stability follows the sequence $PPh_3 > AsPh_3 > SbPh_3$, which is the reverse of the order for the zerovalent complexes.

In a previous paper [14], we stated that the thermal stability of the analogous bivalent compounds of palladium follows the same trend as that of the platinum

Table 2
Temperatures of DTA peaks of the complexes and ligands

Complexes and ligands	Peak temperatures/°C	
	Exothermic	Endothermic
$[PtCl_2(PPh_3)_2]$	305, 350, 375, 480, 595, 725	
$[PtCl_2(AsPh_3)_2]$	880	
$[PtCl_2(SbPh_3)_2]$	145, 375	210
$[Pt(PPh_3)_4]$	85, 115, 330	
$[Pt(AsPh_3)_4]$	190, 240, 305, 380, 880	
$[Pt(SbPh_3)_3]$	205, 235, 300, 480, 500	
$\{[Pt(SbPh_3)_3]_2N_2\}$	120, 185, 200, 255, 355, 475	240
$\{[Pt(SbPh_3)_3]_2C_2\}$	130, 185, 200, 275, 345, 400, 460	260
$[Pt(CO)_2(SbPh_3)_2]$	195, 215, 275, 350, 400, 470	260
PPh_3	290, 500, 560	80, 395
$AsPh_3$	360, 480, 570, 590	60
$SbPh_3$	170, 280, 350, 510, 530, 755, 780	55

Table 3
Initial and final temperatures of thermal decomposition processes of the complexes

Complexes	Temperature/°C	
	Initial	Final
$[PtCl_2(PPh_3)_2]$	250	870
$[PtCl_2(AsPh_3)_2]$	240	430
$[PtCl_2(SbPh_3)_2]$	120	390
$[Pt(PPh_3)_4]$	100	719
$[Pt(AsPh_3)_4]$	150	420
$[Pt(SbPh_3)_3]$	180	220
$\{[Pt(SbPh_3)_3]_2N_2\}$	120	200
$\{[Pt(SbPh_3)_3]_2C_2\}$	130	210
$[Pt(CO)_2(SbPh_3)_2]$	130	190

compounds. For the zerovalent compounds of palladium, the thermal stability decreases in the order $AsPh_3 > SbPh_3 > PPh_3$.

The compound $[Pt(PPh_3)_4]$ is the most unstable of the series. The complex is chemically unstable in air, undergoing decomposition even in the solid state. In the IR spectrum of a sample of this compound maintained in air for a few hours is observed the appearance of strong bands at 1680 and 1190 cm^{-1}, corresponding to C–O and P–O, which are indicative of the formation of the CO_3^{2-} anion [15–17] and the phosphine oxide Ph_3PO [18].

The TG curves of $[Pt(PPh_3)_4]$ (curve d, Fig. 2) indicate an increase in mass at $\approx$60°C, in agreement with two exothermic peaks at 85 and 115°C shown in the corresponding DTA curve (curve d, Fig. 1). Hence the complex is unstable relative to

$[Pd(PPh_3)_4]$. This complex undergoes a similar increase in mass at 70°C and also exhibits two exothermic peaks at 100 and 120°C in the DTA curve [14].

Analysing the TG curves of the complexes $[PtCl_2L_2]$ and $[PtL_n]$, it can also be established that, in all cases, the rate of thermal decomposition of the compounds increases in the order $PPh_3 < AsPh_3 < SbPh_3$, as the slopes of the curves increase in the same order. An inverse tendency is observed for the final temperatures of the processes of thermal decomposition, as shown in Table 3.

Zerovalent compounds of palladium and platinum are usually chemically unstable. Compounds of the type $[ML_4]$ (M is Pd, L is PPh_3, $AsPh_3$ or $SbPh_3$; M is Pt, L is PPh_3 or $AsPh_3$) are very unstable and are therefore prepared and stored under an inert atmosphere. Conversely, $[Pt(SbPh_3)_3]$ can be prepared and stored in air. This exceptional stability can be attributed to the complex being tricoordinate, which, allied to the smaller cone angle of $SbPh_3$ in relation to $AsPh_3$ and PPh_3 [19], should contribute to a reduction in steric hindrance. As a consequence, the thermal stability of the compound is increased.

The high chemical stability of $[Pt(SbPh_3)_3]$, even when stored in air, can be confirmed by vibrational spectroscopy in the infrared region. The spectra obtained did not show any alteration in the composition of the compound even six months after the synthesis, as observed in the case of $[Pt(PPh_3)_4]$. However, the DTA curves of three samples of $[Pt(SbPh_3)_3]$, obtained from the freshly prepared compound, 40 days after the synthesis and 6 months after the synthesis (Fig. 3), indicated mechanisms character-

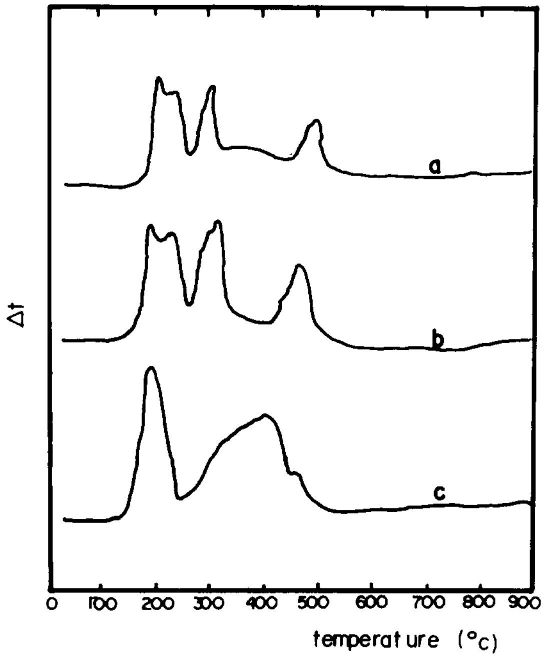

Fig. 3. DTA curves of $[Pt(SbPh_3)_3]$ diluted to 25% in α-alumina. Heating rate 10.0 K min^{-1}: a, freshly prepared; b, 40 days after synthesis; c, six months after synthesis.

istic of thermal decomposition as a function of the time elapsed since the preparation of the sample. This result does not agree with the information from the infrared spectra. The TG curves are not affected by the age of the sample and have the appearance of curve f in Fig. 2. The differences observed in the DTA curves of $[Pt(SbPh_3)_3]$ suggest that structural changes occur in the sample as a function of storage time.

During the thermal decomposition of the complexes $[PtCl_2L_2]$ and $[PtL_n]$, it was possible to identify intermediates. For the complexes containing PPh_3 or $AsPh_3$, when heated in a test tube, evolution of the free ligand was apparent. The ligand that crystallized in the upper part of the test tube was identified by its melting point and infrared spectrum. The same behaviour was observed for the analogous $[PdCl_2L_2]$ and $[PdL_n]$ compounds [14].

Despite the evidence of the evolution of free triphenylarsine during the heating of $[Pt(AsPh_3)_4]$, the final residue exhibited the presence of arsenic together with platinum. Arsenic is identified by qualitative tests with hydrogen sulphide gas and a solution of ammonium molybdate after dissolution of the residue in aqua regia [20].

Heating of the compounds $[PtCl_2(SbPh_3)_2]$ and $[Pt(SbPh_3)_3]$ did not show evolution of free triphenylstibine, and qualitative tests with hydrogen sulphide gas and water of the metallic residue of the thermal decomposition, after dissolution in aqua regia, indicated the presence of antimony [20] together with platinum.

Table 4 contains the initial masses of the investigated complexes of platinum and of the residues obtained from thermogravimetry. The residual mass from thermal decomposition of $[PtCl_2(PPh_3)_2]$, $[PtCl_2(AsPh_3)_2]$ and $[Pt(PPh_3)_4]$ indicates that the respective residues are composed exclusively of metallic platinum. The composition of the residue from $[Pt(AsPh_3)_4]$ is in agreement with the stoichiometric proportion Pt + 2As and the compositions of the residues from the compounds $[PtCl_2(SbPh_3)_2]$ and $[Pt(SbPh_3)_3]$ are in agreement with the proportions Pt + 2Sb and Pt + 3Sb, respectively.

Table 4
Thermogravimetric data for the complexes and ligands

Complexes and ligands	$m_{initial}$/mg	m_{final}/mg (% residue)	Theor./% (residue)	Pt/% (theor. %)
$[PtCl_2(PPh_3)_2]$	6.980	1.730 (24.79)	24.68 (Pt)	24.79 (24.68)
$[PtCl_2(AsPh_3)_2]$	3.400	0.750 (22.06)	22.25 (Pt)	22.06 (22.25)
$[PtCl_2(SbPh_3)_2]$	7.240	3.290 (45.44)	45.12 (Pt + 2Sb)	20.21 (20.07)
$[Pt(PPh_3)_4]$	7.180	1.130 (15.74)	15.68 (Pt)	15.74 (15.68)
$[Pt(AsPh_3)_4]$	7.160	1.810 (25.28)	24.16 (Pt + 2As)	14.30 (13.74)
$[Pt(SbPh_3)_3]$	7.030	3.130 (44.52)	44.67 (Pt + 3Sb)	15.50 (15.55)
$\{[Pt(SbPh_3)_3]_2N_2\}$	9.100	4.000 (43.96)	44.18 (Pt + 3Sb)	15.31 (15.38)
$\{[Pt(SbPh_3)_3]_2C_2\}$	9.540	4.240 (44.44)	44.25 (Pt + 3Sb)	15.47 (15.41)
$[Pt(CO)_2(SbPh_3)_2]$	4.480	2.080 (46.43)	45.82 (Pt + 2Sb)	20.65 (20.38)
PPh_3	5.300	0.000		
$AsPh_3$	6.000	0.000		
$SbPh_3$	7.420	0.000		

Based on this information and from the mass losses observed in the TG curves (curves a–f, Fig. 2), it is possible to establish tentative mechanisms of thermal decomposition for the complexes $[PtCl_2L_2]$ and $[PtL_n]$

$$[PtCl_2(PPh_3)_2] \xrightarrow{250\text{–}360^\circ C} :PtCl_2(PPh_3): \xrightarrow{360\text{–}490^\circ C} :PtCl_2: \xrightarrow{870^\circ C} Pt$$

$$[PtCl_2(AsPh_3)_2] \xrightarrow{240\text{–}290^\circ C} :PtCl_2(AsPh_3): \xrightarrow{400\text{–}430^\circ C} Pt$$

$$[PtCl_2(SbPh_3)_2] \xrightarrow{120\text{–}180^\circ C} :Pt+2Sb+C: \xrightarrow{390^\circ C} Pt+2Sb$$

$$[Pt(PPh_3)_4] \xrightarrow{100\text{–}280^\circ C} :Pt(PPh_3)_{1,5}: \xrightarrow{710^\circ C} Pt$$

$$[Pt(AsPh_3)_4] \xrightarrow{150\text{–}395^\circ C} :Pt(AsPh_3)_2: \xrightarrow{420^\circ C} Pt+2As$$

$$[Pt(SbPh_3)_3] \xrightarrow{180\text{–}220^\circ C} Pt+3Sb$$

The TG curves of the complexes $\{[Pt(SbPh_3)_3]_2N_2\}$, $\{[Pt(SbPh_3)_3]_2C_2\}$ and $[Pt(CO)_2(SbPh_3)_2]$ (curves g, h and i, Fig. 2) are similar to each other and are also similar to the TG curves of $[PtCl_2(SbPh_3)_2]$ and $[Pt(SbPh_3)_3]$ (curves c and f, Fig. 2), suggesting a mechanism of thermal decomposition in two consecutive steps. During the thermal decomposition process no evolution of free ligand was observed, and qualitative tests of the residues from these compounds permitted identification of antimony together with platinum. Analysing relationships between the final residues from the thermal decomposition process of the complexes and the initial masses of the samples, it was possible to establish the composition of the residues. Thus, $\{[Pt(SbPh_3)_3]_2N_2\}$ and $\{[Pt(SbPh_3)_3]_2C_2\}$ give residues with the stoichiometric proportion Pt + 3Sb and $[Pt(CO)_2(SbPh_3)_2]$ produces a residue with the proportion Pt + 2Sb. The thermogravimetric data are presented in Table 4.

The DTA curves of $[Pt(SbPh_3)_3]_2N_2$ show an exothermic peak at 120°C and the curves of $[Pt(SbPh_3)_3]_2C_2$ also show an exothermic peak at 130°C (curves g and h, Fig. 1), corresponding to the loss of dinitrogen or to the ethynediyl group, respectively. The TG curves of the two compounds (curves g and h, Fig. 2) also indicated a small mass loss at these temperatures corresponding to the respective ligands. Both complexes, when maintained for 2–5 min at 150°C, are transformed into $[Pt(SbPh_3)_3]$, as confirmed by elemental analysis of carbon and hydrogen and by thermogravimetric analysis. The transformation was also proved by the disappearance in the infrared spectrum of the band at 1750 cm^{-1} attributed to the stretching frequency of the dinitrogen or the ethynediyl group. The complexes $\{[Pt(SbPh_3)_3]_2N_2\}$ and $\{[Pt(SbPh_3)_3]_2C_2\}$ undergo decomposition at ambient temperature within a period of 3–6 days after preparation, yielding in both cases $[Pt(SbPh_3)_3]$ [13].

The DTA curve of $[Pt(CO)_2(SbPh_3)_2]$ (curve i, Fig. 1) is similar to the curves for the complexes $\{[Pt(SbPh_3)_3]_2N_2\}$ and $\{[Pt(SbPh_3)_3]_2C_2\}$, but no peaks were observed in the 100–150°C region.

The DTA and TG curves j, k and l (Figs. 1 and 2) correspond to the free ligands PPh_3, $AsPh_3$ and $SbPh_3$. Endothermic peaks at 80, 60 and 55°C, respectively, are observed on these DTA curves. Such peaks are related to the respective melting points of the ligands [21]. The TG curves indicate total mass loss, which is consistent with complete sublimation of the ligand.

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