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Preparation and Thermal Behaviour of Diethylenetriamine Complexes of Platinum(II)

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Abstract

Platinum(II) compounds of the type [Pt(dien)(L)]-X_2 (dien = diethylenetriamine; L = aliphatic amine, pyridine or substituted pyridine; $X^- = Cl^-, Br^-, I^-$ or ClO_4^-) have been prepared and their thermal behaviour studied by TG, DSC and FAB-MS techniques. Transformations of the title compounds into [Pt(dien)X]X + L are found to begin at temperatures which are in the order $I^- < Br^- < Cl^-$, perchlorate being not able to replace L before the related compounds explode. The starting temperature of this transformation is also dependent on L, being lower for bulkier amines. At higher temperatures [Pt(dien)-X]X compounds decompose with evolution of HX and other fragments, which leads to a black residue which on further heating decomposes into volatile products and elemental platinum.

Introduction

Thermal transformations of platinum(II) compounds of various types have been and still are widely investigated both for preparative purposes and for understanding their mechanism [1–20]. However, in spite of the great deal of work done, relatively little attention has been devoted so far to establish the part played by the reacting groups in promoting the chemical transformations.

In order to make a contribution in this field we have prepared a series of diethylenetriamine platinum(II) compounds and studied their thermal behaviour. The compounds prepared and investigated are the following: [Pt(dien)X]X (X = Cl, Br or I); [Pt(dien)(L)]$(ClO_4)_2$ [L = methylamine (NH_2Me), pyridine (py) or 4-methylpyridine (4Mepy)]; [Pt(dien)(L)]Cl_2 [L = NH_3, NH_2Me, isopropylamine (NH_2Pr^i), *sec*-butylamine (NH_2Bu^s), neopentylamine ($NH_2CH_2Bu^t$), benzylamine (NH_2CH_2Ph), cyclohexylamine ($NH_2C_6H_{11}$), dimethylamine ($NHMe_2$), 4Mepy, 2-methylpyridine (2Mepy) or 2-chloropyridine (2Clpy)] and [Pt(dien)(py)]X_2 (X = Cl, Br or I). Our purpose was to establish the sequence of the thermal transformations occurring and the extent to which they are affected by changes of coordinated or coordinating groups.

Experimental

Preparation of the Platinum(II) Compounds

Literature methods were followed to prepare [Pt(dien)Cl]Cl [21, 22], [Pt(dien)Br]Br [22] and [Pt(dien)(NH_3)]Cl_2 [22].

A general method was found particularly suitable for the preparation of the other compounds reported in this paper (Table 1). An aqueous suspension of [Pt(dien)I]I was reacted with a twice molar amount of $AgClO_4$ under stirring at 50–60 °C overnight. The suspension obtained was filtered and a portion of the filtrate was treated with a low excess of the required amine. The solution was warmed for $\frac{1}{2}$–1 h and left to stand overnight, kept dry using a rotatory evaporator. The crude material was dissolved in a small amount of acetonitrile, treated with charcoal and warmed. The solution was then filtered. Subsequent addition of an excess of ethyl ether caused the separation of diperchlorate salts of general formula [Pt(dien)(L)]$(ClO_4)_2$. These compounds were converted into chloride, bromide or iodide in a simple way. The diperchlorate was dissolved in a little acetonitrile and the resulting solution was treated with a few drops of a concentrated solution of either tetraethylammonium chloride, bromide or iodide in acetonitrile. A white material immediately separated. This was filtered, washed with acetonitrile and dried under vacuum. The elemental analysis of the products obtained is generally satisfactory (see Table 1). However, sometimes when bulky ligands are used (in particular NH_2Bu^s and 2Clpy) the analyses are only fairly satisfactory. In such cases the full conversion of [Pt(dien)(OH_2)]$^{2+}$ to [Pt(dien)(L)]$^{2+}$ could be prevented by steric restrictions. A few complexes were found to contain some water, whose amount has been measured by thermogravimetric techniques.

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TABLE 1. Elemental analyses of diethylenetriamine complexes of platinum(II)

	Complex[a]	C (%)		H (%)		N (%)	
		Calc.	Found	Calc.	Found	Calc.	Found
1	$[Pt(dien)Cl]Cl$	13.0	13.1	3.6	3.5	11.4	11.3
2	$[Pt(dien)Br]Br$	10.5	10.8	2.9	2.9	9.2	9.4
3	$[Pt(dien)I]I$	8.7	8.8	2.4	2.4	7.6	7.5
4	$[Pt(dien)(NH_2Me)](ClO_4)_2$	11.4	11.4	3.4	3.4	10.6	10.7
5	$[Pt(dien)(py)](ClO_4)_2$	18.8	18.7	3.1	3.1	9.7	9.8
6	$[Pt(dien)(4Mepy)](ClO_4)_2$	20.4	20.6	3.4	3.4	9.5	9.4
7	$[Pt(dien)(NH_3)]Cl_2$	12.4	12.5	4.2	4.3	14.5	14.4
8	$[Pt(dien)(NH_2Me)]Cl_2$	15.0	14.9	4.5	4.6	14.0	13.9
9	$[Pt(dien)(NH_2Pr^i)]Cl_2 \cdot \frac{1}{2}H_2O$	19.2	19.3	5.3	5.2	12.8	12.9
10	$[Pt(dien)(NH_2Bu^s)]Cl_2 \cdot H_2O$	20.9	20.6	5.7	5.6	12.2	12.0
11	$[Pt(dien)(NH_2CH_2Bu^t)]Cl_2$	23.7	23.6	5.7	5.7	12.3	12.0
12	$[Pt(dien)(NH_2CH_2Ph)]Cl_2$	27.7	27.1	4.7	4.8	11.8	11.6
13	$[Pt(dien)(NH_2C_6H_{11}{}^{cyclo})]Cl_2$	25.6	25.3	5.6	5.6	12.0	11.9
14	$[Pt(dien)(NHMe_2)]Cl_2 \cdot 0.7H_2O$	16.9	17.0	5.1	5.1	13.1	13.2
15	$[Pt(dien)(py)]Cl_2$	24.1	23.9	4.0	4.0	12.5	12.5
16	$[Pt(dien)(py)]Br_2$	20.1	20.1	3.4	3.4	10.4	10.4
17	$[Pt(dien)(py)]I_2$	17.1	17.0	2.9	2.8	8.9	8.9
18	$[Pt(dien)(4Mepy)]Cl_2 \cdot 0.6H_2O$	25.4	25.3	4.5	4.4	11.8	11.8
19	$[Pt(dien)(2Mepy)]Cl_2$	26.0	25.8	4.4	4.4	12.1	12.1
20	$[Pt(dien)(2Clpy)]Cl_2$	22.4	21.3	3.5	3.5	11.6	11.6

[a] When reported, the amount of water contained in the compounds is obtained from thermogravimetric measurements.

This water may simply be derived from absorption of aqueous vapour during the manipulation of the complexes.

Thermogravimetric and Differential Scanning Calorimetric Measurements

The thermal analysis were performed with a Perkin-Elmer TGS 2 thermobalance and a Perkin-Elmer DSC 4 differential scanning calorimeter. Unless otherwise stated, specimens (1–5 mg) were contained in aluminium crucibles and high purity nitrogen was used as purging gas. Heating rates ranging from 2 to 100°/min were employed, but usually a rate of 20°/min was used. The accuracy of the weights is better than 0.1% and of the enthalpies is better than 0.5%.

Mass Spectrometry Measurements

The electron impact (EI) mass spectrometric experiments were performed on a VG M16 instrument operating at 70 eV electron energy and at a source temperature of 200 °C. The samples were introduced via direct inlet probe and heated from room temperature to 300 °C at a rate of *c.* 50°/min.

The fast atom bombardment (FAB) experiments were performed on a VG ZAB 2 F instrument. The FAB gun was operated at a potential of 8 kV with a neutral beam current of xenum atoms equivalent to *c.* 15 μA. Gicerol was used as matrix.

Results and Discussion

A preliminary TG analysis showed that some $[Pt(dien)(L)]Cl_2$ complexes ($L = NH_2Pr^i$, NH_2Bu^s, $NHMe_2$, 4Mepy) undergo a weight loss at about 100 °C. If water release is responsible for this thermic event, the observed weight loss is consistent with the formulas reported in Table 1 for the named compounds and agrees with their elemental analysis. If after heating these compounds are brought to room temperature and once again submitted to TG analysis they display a behaviour which is similar to that exhibited by all the other water-free complexes of a similar formula.

The thermal behaviour in nitrogen atmosphere of $[Pt(dien)(L)]X_2$ ($X^- = Cl^-$, Br^- or I^-) is qualitatively rather similar and is suitably sketched in Fig. 1 (solid line). The relevant results referred to as points A–F of Fig. 1 are reported in Table 2.

The compounds are thermally stable up to temperature A, where a weight loss initiates (Fig. 1) and continues up to temperature B. The value of temperature A (Table 2) appears to depend on both the coordinate ligand L and the X^- anion present in $[Pt(dien)(L)]X_2$. The significant part played by X^- in promoting the transformation responsible for the observed weight loss is unambiguously recognized by comparing the thermal behaviour of $[Pt(dien)(py)]X_2$ ($X^- = Cl^-, Br^-, I^-$) (Table 2) and by observing that

TABLE 2. Results of thermal analysis measurements on the diethylenetriamine complexes of platinum(II)

Compound	TA[a]	Temperature of reference points (°C)						Heat of transition (kJ/mol)[b]		
		A	B	C	D	E	F	X	Y	Z
$\mathrm{[Pt(dien)Cl]Cl}$	TG			275	→	320	450			
	DSC	238	262	275	298			⟨0.8⟩		19.2 f
$\mathrm{[Pt(dien)Br]Br}$	TG			283	→	360				
	DSC			252	294					28.0 f
$\mathrm{[Pt(dien)I]I}$	TG			275	→	380				
	DSC			265	270					19.2 f
$\mathrm{[Pt(dien)(NH_2Me)](ClO_4)_2}$	TG			240	295	expl.				
$\mathrm{[Pt(dien)py](ClO_4)_2}$	TG			260	295	expl.				
$\mathrm{[Pt(dien)(4Mepy)](ClO_4)_2}$	TG			260	295	expl.				
$\mathrm{[Pt(dien)(NH_3)]Cl_2}$	TG	268	→	→	→	332	650			
	DSC	240	270	270	276					61.4 d
$\mathrm{[Pt(dien)(NH_2Pr\text{-}i)]Cl_2}$	TG	210	274	274	→	320				
	DSC	210	242 d					⟨28.4⟩		
$\mathrm{[Pt(dien)(NH_2Bu\text{-}s)]Cl_2}$	TG	186	270	270	→	315				
	DSC	212	253	270	290 d			12.5	54.3	
$\mathrm{[Pt(dien)(NH_2CH_2Bu\text{-}t)]Cl_2}$	TG	234	292	292	→	340				
	DSC	230	268	296	301			⟨43.9⟩		8.8 f
$\mathrm{[Pt(dien)(NH_2CH_2Ph)]Cl_2}$	TG	264	→	→	→	320				
	DSC	259	269 d					⟨47.6⟩		
$\mathrm{[Pt(dien)(NH_2C_6H_{11}\text{-}c)]Cl_2}$	TG	202	→	→	→	306	650			
	DSC	252	267 d					⟨44.3⟩		
$\mathrm{[Pt(dien)(NHMe_2)]Cl_2}$	TG	190	251	251	→	294				
	DSC	190	256	259	265			⟨43.5⟩		10.0 f
$\mathrm{[Pt(dien)py]Cl_2}$	TG	212	273	273	→	340				
	DSC	212	272	282	297			18.8	16.7	28.0 d
$\mathrm{[Pt(dien)py]Br_2}$	TG	185	266	295	→	360				
	DSC	191	261	306	321 d			14.6	11.3	
$\mathrm{[Pt(dien)py]I_2}$	TG	156	207	275	→	360				
	DSC	147	190	272	282			⟨20.1⟩		15.0 f
$\mathrm{[Pt(dien)(4Mepy)]Cl_2}$	TG	193	289	289	→	340				
	DSC	210	266	290	300 d			⟨29.3⟩		
$\mathrm{[Pt(dien)(2Mepy)]Cl_2}$	TG	225	282	282	→	320				
	DSC	226	283	284	295			⟨38.9⟩		33.4 f
$\mathrm{[Pt(dien)(2Clpy)]Cl_2}$	TG	193	275	300	→	340				
	DSC	195	230	310	317			⟨21.3⟩		15.9 f

[a] TA = Thermal analysis. [b] f = fusion, d = decomposition.

the perchlorate salts $\mathrm{[Pt(dien)(L)](ClO_4)_2}$ (L = $\mathrm{NH_2Me}$, py, 4Mepy) do not undergo substantial weight loss up to 295 °C [Table 2 and Fig. 1 (dashed line)], when they explode.

The weight loss occurring in the A–B temperature range for $X^- \neq \mathrm{ClO_4}^-$ is related to the evolution of L as shown by the typical smell exhaled by the pyridine–platinum(II) compounds heated in air as well as by the mass spectrometric measurements reported below.

At B the weight loss stops, provided that this temperature is far enough from that of the beginning of the subsequent transformation [temperature C (Fig. 1), as clearly evidentiated for L = py and X^- =

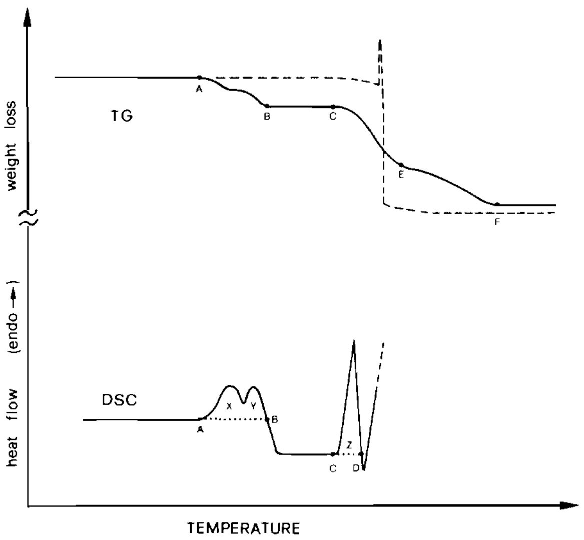


Fig. 1. Schematic general behaviour of the $[Pt(dien)L]X_2$ complexes. TG = effect of the increasing temperature on the weight loss (thermogravimetric analysis; broken line is for $X = ClO_4^-$). DSC = effect of the increasing temperature on the heat exchange (differential scanning calorimetry). The letters are the same as used in Table 2.

Br^- or I^- (Table 2)]. In such cases the weight lost is consistent with the release of 1 L. However, TG analysis for most compounds show that the A–B and C–F thermal events are not distinctly separated, and only an inflection is observed at a temperature which is taken as B = C. The weight lost at this temperature is still in fair agreement with the release of 1 L. Of course, in such cases only an approximate value of the temperatures where the first thermal event ends (temperature B) and the subsequent starts (temperature C) can be evaluated. Finally, in some cases (L = NH_3, NH_2Me, NH_2CH_2Ph, $NH_2C_6H_{11}$) the A–B and C–F thermal events are indistinguishable.

The evolution of L in the A–B temperature range does not occur in a single event, as indicated by the weight loss trend (TG; Fig. 1) as well as by the occurrence of two endothermic events (DSC, Fig. 1) during the overall loss of 1 mol of L per mol of platinum(II) complex. However, the overall A–B process suggests that at B the compounds [Pt(dien)X]X are always formed. Such a statement is strongly supported at least in the case of $[Pt(dien)(py)]Cl_2$. In fact, the IR spectrum of the product obtained at temperature B is fully superimposable to that of [Pt(dien)Cl]Cl (ν(Pt–Cl) = 338 cm^{-1}). Moreover, the loss of L has been confirmed by mass spectrometric measurements carried out on the complexes with L = py or substituted py. In fact, when these compounds are heated in the electron impact (EI) ion source they show a common behaviour characterized by the release of L in the temperature range A–B, evidentiated by the presence in the mass spectra of abundant species L^+. An attempt has been made to establish by mass spectrometric experiments the structure of the compounds formed at the temperature B, when the elimination of L is accomplished. For this purpose samples obtained by heating $[Pt(dien)(L)]X_2$ at temperature B were analyzed by fast atom bombardment (FAB) together with compounds of formula [Pt(dien)X]X ($X^- = Cl^-$, Br^-, I^-). FAB was chosen in order to reduce structural damages due both to the heating of the samples and to production of ions with high internal energies, which are implicated in the EI method. The identity of FAB mass spectra of the compounds obtained after thermal treatment (temperature B) and those of the corresponding [Pt(dien)X]X compounds confirms the identity of these species. The spectra are characterized by the absence of the molecular ions, the heaviest ionic species found being represented by $Pt(dien)X^+$ together with its fragment ions generated by losses of X and HX.

The thermal events occurring between temperatures C and F for the $[Pt(dien)(L)]X_2$ ($X^- = Cl^-$, Br^-, I^-) compounds are very similar. On the basis of the above considerations such events should be identical to those observable in the thermal behaviour of [Pt(dien)X]X. Indeed, the TG and DSC analysis of [Pt(dien)X]X is consistent with this statement (Fig. 2). In particular, it is found that such compounds are stable up to 275 °C (Table 2), which should correspond to temperature C for the thermal analysis of $[Pt(dien)(L)]X_2$. At this temperature a thermal transformation begins with a weight loss (Fig. 2) which is accompanied ($X^- = Cl^-$) or preceeded ($X^- = Br^-$, I^-) by the melting of the compounds (C–D temperature range of DSC curves). The molar enthalpies of fusion,

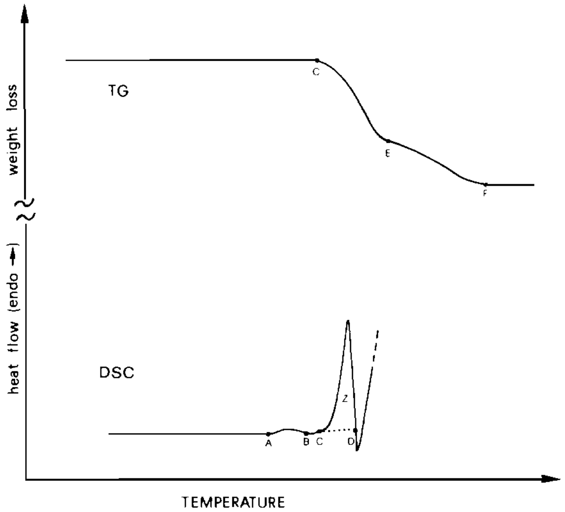


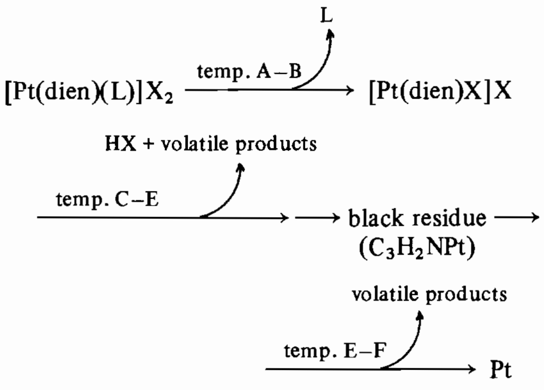
Fig. 2. Schematic general behaviour of the [Pt(dien)X]X complexes. Effect of increasing the temperature on the weight loss (TG) and on the heat exchange (DSC) of the samples. The letters are the same as used in Table 2.

at the relevant temperatures (peak Z in the figures and in Table 2, fall generally in the ranges 10–20 kJ mol^{-1}, except for a few cases where the observed endothermal event is strongly contaminated by the heat of the decomposition step C–D. The observed weight loss occurs with evolution of HX, which is also revealed in the EI mass spectra by the presence of $HX^{+\bullet}$ ions.

At temperature E (Fig. 2) the gradient of weight loss versus temperature sharply decreases. The weight left at this temperature and the elemental analysis of the black residue obtained are fairly accounted for by the formal composition C_3H_2NPt, any detectable amount of halides being absent. A further increase of the temperature in the E–F range causes a smooth weight loss, leading to platinum. Such a transformation is found to require a wider temperature interval when platinum crucibles are replaced by aluminium ones.

As expected, the thermal behaviour just described is substantially similar to that observed in the C–F temperature range for the $[Pt(dien)(L)]X_2$ compounds examined ($X^- = Cl^-$, Br^-, I^-), as evidenced by the comparison of Figs. 1 and 2 in the C–F temperature range.

On the whole, the results obtained appear to be consistent with the following sequence of events:



In an attempt to check the factors affecting the temperatures to which the more significant thermal events occur it seems profitable to take into consideration only the A–B temperature interval, where the replacement of L by X^- takes pace. The thermal events occurring at higher temperatures are related only to the decomposition of [Pt(dien)X]X and do not appear to be much affected by the nature of X^-.

Examination of the thermal behaviour up to temperature B provides evidence for the previously mentioned influence of the replacing X^- in promoting the $[Pt(dien)(L)]X_2 \rightarrow [Pt(dien)X]X + L$ transformation. The temperature where such a transformation begins (point A) follows the order $I^- < Br^- < Cl^- < ClO_4^-$. It clearly appears that the coordinating ability of X^- is implicated in the kinetics of the reactions. Accordingly, if X^- is the poor coordinating ClO_4^- neither the transformation nor release of L appear to occur. Therefore, the conclusion can be reached that the transformation under discussion operates only by the assistance of a group capable of replacing L in the platinum(II) coordination sphere. In particular it is found (L = py; Table 2) that the substitution of L starts at temperatures which increase in the order I^- (156 °C) < Br^- (185 °C) < Cl^- (212 °C). Moreover, the endothermal heat balance of the process leading to the release of L increases in the order I^- (20.1 kJ mol^{-1}) < Br^- (25.9 kJ mol^{-1}) < Cl^- (35.5 kJ mol^{-1}). All these results may well reflect, all the other factors being reasonably assumed nearly constant, the influence of a Pt–X bond-making step. The part played by X^- in the replacement of L is also stressed by FAB-MS experiments. In fact, in FAB-MS conditions the formation of the $\{Pt(dien)(py)X\}^+$ species is observed, in which X^- is likely bonded to platinum(II) before the loss of L. In an attempt to explain the fact that the overall conversion $[Pt(dien)(L)]X_2 \rightarrow [Pt(dien)X]X + L$ occurs in two different thermogravimetric and endothermal events, one could tentatively suggest the presence of two different kind of interactions in the crystals. However, FAB-MS mass spectra of a series of samples prepared by heating $[Pt(dien)(py)]Cl_2$ at different temperatures in the A–B range reveal only a progressive transformation of the starting compound in [Pt(dien)Cl]Cl.

Some information is inferred from the examination of the effect of L groups which are replaced. For L = aliphatic amines it appears that milder conditions are required to cause the thermal transformation in complexes containing bulkier L groups [i.e. NH_2Bu^s (186 °C), $NHMe_2$ (190 °C), $NH_2C_6H_{11}$ (202 °C), NH_2Pr^i (210 °C); against NH_2Me (225 °C), $NH_2CH_2Bu^s$ (234 °C), NH_2CH_2Bz (264 °C) or NH_3 (268 °C)]. Such a behaviour would suggest that the Pt–N bond is weakened by steric strain. On the other hand the heat balance of the replacement of L does not appear to substantiate unequivocably such a statement. Possibly both thermodynamic and kinetic factors are involved.

The pyridine and substituted pyridines complexes are less thermally stable than those containing aliphatic amines that are not bulky. Considering that the coordinate nitrogen of pyridines bears two carbon chains, such a behaviour could be also explained in terms of the effect caused by steric hindrance on the Pt–N bond strength. However, in these cases the low basicity of pyridines, compared to that of aliphatic amines, can itself cause a low Pt–N bond strenght. In effect, both the values of temperature A and the overall heat balance (X + Y in Table 2) increase in the order 2Clpy (194 °C, 21.3 kJ mol^{-1}) < 4Mepy (200 °C, 29.3 kJ mol^{-1}) < py (212 °C, 35.5 kJ mol^{-1}) < 2Mepy (225 °C, 38.9 kJ mol^{-1}), and may reflect a contribution of the basicity, at least as far as a comparison between 2Clpy (pK_a 0.49), py (pK_a 5.30) and 2Mepy (pK_a 5.95) complexes are concerned. A role assignable to the basicity of L in affecting its elimination is also suggested on the basis of FAB-MS experiments on [Pt(dien)(L)]Cl_2 complexes (L = py, 2Mepy, 4Mepy, 2Clpy). As noticed above, under FAB-MS conditions these compounds lead to the formation of $[Pt(dien)(L)Cl]^+$. These species are found to undergo competitive losses of L or HCl, the loss of L process being more favoured by a lower basicity of L. In fact, the ratio of loss of L over loss of HCl is 1.1 (2Clpy), 0.1 (py) and 0 (2Mepy and 4Mepy). On the other hand, in these cases some sort of steric hindrance should play a significant role in preventing the attack of X^-. In fact, it is found that the compound with L = py undergoes thermal transformation more easily than that with the bulkier 2Mepy, which in turn is similar to 2Clpy in bulkiness.

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