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Stable η- and σ-Ethene Cationic Complexes of Platinum(II)

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Stable cationic complexes of platinum(II) with η- and σ-ethene have been obtained in the decomposition of five-co-ordinate $[Pt(C_2H_4)Cl_2(Me_4en)]$ *(**1**), (Me_4en = N,N,N',N'-tetramethylethylenediamine) in methanol. First a chloride ion dissociates forming the cationic intermediate* $[Pt(C_2H_4)Cl(Me_4en)]^+$*, (**3**); then two mol of (**3**) couple with a mol of diamine, via nucleophilic attack on η-ethene, to give the bis σ-ethene dimeric cation* $[(Me_4en)ClPt–C_2H_4N(CH_3)_2–C_2H_4N(CH_3)_2–C_2H_4–PtCl(Me_4en)]^{2+}$*, (**2**). Complex (**2**) can be readily isolated at 0 °C as the stable perchlorate salt, and by reaction with stoicheiometric amounts of aqueous mineral acids regenerates the parent cation (**3**), which has also been isolated and characterized.*

*The general validity of this stepwise decomposition mechanism for five-co-ordinate complexes of type (**1**), together with the reactivity of η-ethene in cationic platinum(II) complexes is discussed.*

Introduction

It is well established that in the reaction of Zeise's salt (or its dimer) with bidentate N-donor ligands, which can form with the metal five-membered chelate rings, five-co-ordinate complexes of composition $[Pt(C_2H_4)Cl_2(N–N)]$ can be isolated [1–4]; the decomposition of these species to square-planar $[PtCl_2(N–N)]$ and ethene has been studied under kinetic conditions in the bipyridyl case [5]. The reaction mechanism was solvent dependent: in chlorinated solvents (chloroform, dichloromethane, 1,2-dichloroethane) the loss of ethene occurred in a single step while in methanol, first a chloride ion dissociated with the formation of a cationic intermediate, then the latter reacted with chloride to form the final compound. None of these studies described the isolation and/or the characterization of the cationic intermediate, which was considered to be very unstable.

The isolation of a cationic ethene complex by following the decomposition reaction on a preparative scale appeared to us very attractive; it would not only give support to the proposed reaction mechanism but also would make available suitable substrates for comparing ethene reactivity going from anionic to cationic substrates. In the complexes of the latter type the ethene molecule should undergo, in principle, nucleophilic attack much more readily because of the formation of a platinum induced carbonium ion [6].

The cationic complexes of platinum(II) containing η-ethene which have been so far described are: *trans*-$[Pt(CH_3)(C_2H_4)\{P(CH_3)_2(C_6H_5)\}_2](PF_6)$ which very easily undergoes solvent displacement of the π ligand, probably because of the *trans* labilizing effect of the methyl group [7] and *trans*-$[Pt(NH_3)_2(olefin)Cl](BF_4)$ complexes which were studied only from a spectroscopic point of view [8, 9].

In this paper we report the isolation and full characterization of cationic Pt^{II} complexes containing both η- and σ-ethene obtained by controlled decomposition of five-co-ordinate $[Pt(C_2H_4)Cl_2(Me_4en)]$ (Me_4en = N,N,N',N'-tetramethylethylenediamine) in methanol.

Experimental

Starting Materials

N,N,N',N'-tetramethylethylenediamine (Me_4en) was a commercial product and was purified before use by distillation from potassium hydroxide. Zeise's salt and Zeise's dimer were prepared according to well established procedures [10, 11]. $[Pt(C_2H_4)Cl_2(Me_4en)]$ (**1**), was prepared according to ref. 4.

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Preparation of Complexes

$[(Me_4en)ClPt{-}C_2H_4N(CH_3)_2C_2H_4N(CH_3)_2{-}C_2H_4{-}PtCl(Me_4en)]^+$, (2)

This complex with $[Pt(C_2H_4)Cl_3]^-$ as counter ion was obtained warming up a solution of (1) in methanol, prepared at −10 °C. At about −3 °C a yellow compound started precipitating out. Samples of the precipitate separated when the solution had reached −3 and 0 °C, respectively, had the same composition but slightly different i.r. spectra (see text). Found: C, 20.2; H, 4.4; Cl, 18.1; N, 5.2. Calc. for (2)·$[Pt(C_2H_4)Cl_3]_2$: C, 20.5; H, 4.7; Cl, 18.1; N, 5.2%.

The perchlorate salt of (2) was prepared in two different ways:

i) A given amount of (1) (0.5 g in a typical experiment) was introduced into a solution of $Li[ClO_4]$ (a 2–3 fold excess) in MeOH and kept at 0 °C. After a few minutes' stirring a white precipitate was formed, it was collected on a sintered glass filter, washed twice with MeOH and dried. Yield 65% referred to platinum.

ii) An excess of Me_4en (2 mmol) was added under stirring to a solution of Zeise's salt (1 mmol) in MeOH containing a three-fold excess of $Li[ClO_4]$ and kept at 0 °C. After two hours' stirring the solution became colourless and a white precipitate separated out; this was collected on a sintered glass filter, washed with methanol, water, and dried. Yield 90% referred to platinum. Found: C, 24.7; H, 5.6; Cl, 13.3; N, 7.7. Calc. for (2)·$[ClO_4]_2$: C, 24.8; H, 5.3; Cl, 13.3; N, 7.9%.

$[Pt(C_2H_4)Cl(Me_4en)]^+$, (3)

The perchlorate salt of compound (3) was prepared adding the stoicheiometric amount of aqueous $HClO_4$ to a stirred suspension of (2)·$[ClO_4]_2$ (0.5 g) in MeOH (3 cm^3) at room temperature. The mixture was evaporated to dryness and extracted with small volumes of water (1 cm^3 of H_2O for three times) to separate off the perchlorate of the diammonium ion $[Me_4enH_2]^{2+}$. The residue was dried and proved to be perchlorate of (3) practically pure. The yield was only 70% since some was lost in the washing procedure. Found: C, 20.2; H, 4.3; Cl, 15.0; N, 5.9. Calc. for (3)·$[ClO_4]$: C, 20.2; H, 4.2; Cl, 15.0; N, 5.9%.

The chloride salt of (3) was prepared treating a suspension of (2) (0.5 g) in MeOH with the stoicheiometric amount of aqueous HCl. The reaction was carried out as above, however no pure product could be isolated since the increased solubility, both in methanol and water, of (3) as chloride salt made difficult its separation from the chloride of $[Me_4enH_2]^{2+}$. Furthermore (3) reacted with chloride ion to give the square-planar $[PtCl_2(Me_4en)]$, (4), which was also present in increasing quantity as the reaction time increased.

Either (2) or (3) treated with excess LiCl gave the square-planar $[PtCl_2(Me_4en)]$, (4), as yellow precipitate. In the case of (2) the solution contained also free Me_4en which was identified by isolation of the picrate salt.

The complexes *trans*-$[Pt(C_2H_4)Cl_2L]$ (L = N-methylmorpholine and 1-chloro-2-dimethylaminoethane) were prepared by the method of Schmidt and Orchin adding the appropriate amine to an aqueous solution of Zeise's salt [12]; the product is formed instantaneously and precipitates out from the solution, it was recrystallized from chloroform–pentane.

Apparatus

The i.r. spectra in the range 4000–300 cm^{-1} were recorded as KBr pellets on a Perkin-Elmer 457 spectrophotometer; the spectra in the range 500–100 cm^{-1} were recorded as polythene pellets on a Perkin-Elmer 180 instrument. The ^{1}H n.m.r. spectra were obtained with a Varian EM 390 spectrometer using deutero-methanol as solvent and tetramethylsilane as internal standard.

Results and Discussion

When a solution of $[Pt(C_2H_4)Cl_2(Me_4en)]$, (1), in methanol is allowed to warm up from −10 to 0 °C a reaction takes place whose stoicheiometry is depicted below

$$3\,[Pt(C_2H_4)Cl_2(Me_4en)] \rightarrow$$

$$[Pt_2(C_2H_4)_2Cl_2(Me_4en)_3]^{2+} + [Pt(C_2H_4)Cl_3]^- + Cl^-$$

and the complex cation $[Pt_2(C_2H_4)_2Cl_2(Me_4en)_3]$, (2), precipitates partly from the solution as the $[Pt(C_2H_4)Cl_3]^-$ salt. In the presence of added $Li[ClO_4]$, (2) precipitates quantitatively as the white diperchlorate; on the other hand Zeise's anion, which is also formed in the reaction, can be precipitated as $[Ph_4As]^+$ salt.

The perchlorate of (2) shows remarkable stability: it can be recrystallized from hot methanol and can be stored indefinitely in the solid state. When (2) has Zeise's anion as counter ion it is much more unstable, at 0 °C it undergoes a solid state transformation to a new form, (2′), having the same composition but slightly different i.r. spectrum. Both forms in contact with methanol at room temperature lead to $[PtCl_2(Me_4en)]$ as final product.

The following reactions were performed in order to establish the structure of (2) (all experiments were performed on the diperchlorate salt, in methanol, and at room temperature):

i) Reaction with excess LiCl led to the square-planar $[PtCl_2(Me_4en)]$, ethene gas, and free amine.

ii) Reaction with stoicheiometric amounts of aqueous $HClO_4$ led to a new complex of composition $[Pt(C_2H_4)Cl(Me_4en)] \cdot [ClO_4]$, (3), plus the diperchlorate of the diammonium ion $[Me_4enH_2]^{2+}$.

iii) Reaction with a stoicheiometric amount of aqueous HCl gave again the cationic species $[Pt(C_2H_4)Cl(Me_4en)]^+$, however the product was contaminated by some $[PtCl_2(Me_4en)]$ since (3) reacts with chloride ion to release ethene forming the neutral square-planar complex.

The perchlorate salt of (3) is slightly soluble in methanol and quite soluble in water from which it can be recrystallized without decomposition; the chloride salt has higher solubility but its solutions are unstable because of the reaction of the cation with chloride; the i.r. spectrum clearly indicates the presence in this compound of η-bonded ethene, therefore (3) can be unambiguously described as a diamine-chloro-η-ethene-platinum(II) cation.

The results of reactions ii) and iii) led us to think that compound (2) could be obtained from (3) in the presence of free amine, therefore we performed reaction iv) in which stoicheiometric amounts of (3) and Me_4en were allowed to react in methanol; as expected compound (2) was reobtained in quantitative yield. This observation together with the absence, in the i.r. spectrum of (2), of absorption bands assignable to the $\nu(Pt-C_2)$ moiety led us to propose for (2) the following structure: $[(Me_4en)ClPt-C_2H_4N(CH_3)_2C_2H_4N(CH_3)_2C_2H_4-PtCl(Me_4en)]^{2+}$ with a tetraalkyldiammonium ion bridging *via* metal—carbon bond two platinum atoms.

It seems very likely that in the decomposition of (1) in methanol at temperatures above −10 °C, the first event is a chloride dissociation with formation of the cationic species (3) which, in turn, undergoes nucleophilic attack by trace amounts of free amine on the η-ethene to form the σ-ethene complex (2).

I.r. and N.m.r. Data

There is no problem in locating the symmetric stretch of the $Pt-C_2$ moiety when a η-ethene is present in the compound, this always occurs near 400 cm^{-1}. On the other hand unequivocal assignments are not always possible in the region near 500 cm^{-1} where the higher $Pt-C_2$ stretching vibration or, alternatively, the $\nu(Pt-C)$ of σ-ethene occur together with the $\nu(Pt-N)$ [13, 14] and a deformation vibration of the chelate amine ring [14].

Compound (1) has a $\nu(Pt-C_2)$ at 390 cm^{-1} (mw) and shows three absorption bands at 450 (mw), 470 (ms), and 500 (m) cm^{-1}; we tentatively assign the band at 470 cm^{-1} to the asym. $\nu(Pt-C_2)$ on the ground that the *sym.* and *asym.* vibrations are usually separated by 80–100 cm^{-1} [15]. The bands at 500 and 450 cm^{-1} can be ascribed to Pt–N stretches; it is to be noted, however, that the lower stretch is not always observed in other complexes containing bidentate Me_4en.

In the cationic complex (3) the symmetric and asymmetric $\nu(Pt-C_2)$ are at 368 and 458 cm^{-1} respectively while a band at 520 cm^{-1} is assigned to $\nu(Pt-N)$ and a weaker absorption at 540 cm^{-1} can be assigned to a chelate ring-deformation mode [14].

The dimeric cation (2) does not show significant absorption below 400 cm^{-1}, except a $\nu(Pt-Cl)$ at 325 cm^{-1}, while it has medium bands at 485, 500, and 530 cm^{-1} which arise by mixing of $\nu(Pt-N)$ and $\nu(Pt-C)$ which are both present in this case.

The square-planar compound $[PtCl_2(Me_4en)]$, (4), finally, shows a $\nu(Pt-N)$ at 525 cm^{-1} and a possible ring deformation at 545 cm^{-1}.

The remaining regions of the i.r. spectrum were characterized essentially by the absorption bands of co-ordinated Me_4en, and will not be discussed in this context; however there is one observation we want to put forward. In the 700–900 cm^{-1} region of the spectrum there are absorption bands which should arise from methylene and methyl rocking vibrations together with symmetric C–N stretchings [16, 17]. In the case of complexes containing a simple chelate diamine this brought in the i.r. spectrum two absorption bands at about 810 (s) [805 in (1), 812 in (2), 812 in (3), and 815 in (4)] and 770 (ms) [775 in (1), 770 in (2), 772 in (3), and 777 in (4)] cm^{-1}. This pattern of the spectrum should reflect the *cis* geometry of the coordinated ligand. In the same region the complex (2) has, beside the two bands at 812 and 770 cm^{-1} which account for the chelate diamine, also bands at 790 and 870 cm^{-1} which should be in some way related to the bridging amine molecule. The diammonium salt, which presumably has *trans* configuration [18], has also bands at 795 and 850 cm^{-1}.

The ^1H n.m.r. spectrum of complex (3) in deuteromethanol shows the ethene resonance at 4.79 p.p.m. downfield from TMS, $J_{(PtH)} = 61$ Hz. Comparison with values observed in neutral complexes of composition *trans*-$[Pt(C_2H_4)Cl_2L]$ (L = monodentate aliphatic amine) indicates that the η-ethene absorption in the cationic complex occurs at slightly lower field with respect to the neutral case.

Significant i.r. and n.m.r. data are summarized in Table I. It is generally assumed that both σ and $d\pi \rightarrow \pi^*$ interactions make important contributions to the chemical bond, and in the cationic complex (3) the positive charge on platinum would reduce the $d\pi \rightarrow \pi^*$ interaction making the bond with ethene less tight. According to this the $\nu(Pt-C_2)$ bands, in the i.r. spectrum of (3), move to lower frequencies, the difference being significant when referred to neutral complexes of the type *trans*-$[Pt(C_2H_4)Cl_2L]$. Similarly the ethene signal, in the ^1H n.m.r. spectrum of (3), appears at lower field than that of the neutral

TABLE I. I.r.[a] and ^{1}H N.m.r.[b] Data for Some Cationic, Neutral, and Anionic η-Ethene Complexes of Platinum(II).

Compound	ν(Pt–C$_2$)		δ(C$_2$H$_4$)	J$_{(PtH)}$
	asym.	*sym.*		
$[Pt(C_2H_4)Cl(Me_4en)]^+[ClO_4]^-$	458	368	4.79	61.0
trans-$[Pt(C_2H_4)Cl_2(Me\overline{NCH_2CH_2OCH_2C}H_2)]$	490	392	4.63	63.0
trans-$[Pt(C_2H_4)Cl_2(Me_2NCH_2CH_2Cl)]$	488	392	4.58	63.4
$K^+[Pt(C_2H_4)Cl_3]^-$	492[c]	404[c]	4.39	65.1

[a] Infrared values ±3 cm^{-1}. [b] All spectra were recorded in methanol-d$_4$ solutions; chemical shifts (δ) are in p.p.m. from internal reference TMS; coupling constants (J) in Hz. [c] Reference 15.

trans-[Pt(C$_2$H$_4$)Cl$_2$L] complexes; the J$_{(PtH)}$ (see Table I), seems to decrease steadily going from anionic through neutral to cationic complexes which, again, should indicate a weakening of the bond in the same direction.

Conclusions

The investigation we have performed confirms that the decomposition in methanol of five-co-ordinate η-ethene complexes of the type [Pt(C$_2$H$_4$)Cl$_2$(N–N)] [5] to [PtCl$_2$(N–N)] and ethene occurs through a stepwise mechanism, the dissociation of a chloride ion and formation of the cationic [Pt(C$_2$H$_4$)Cl(N–N)]$^+$ species being the first event. However the cationic complex, whose stability is comparable to that of analogous complexes with acetylene [19], is very reactive towards nucleophilic reagents.

Nucleophilic attack by an aliphatic or aromatic amine on a η-bonded ethene is a well established and widely studied process [12, 20–25]. However it was not predictable that a cationic species such as (3) would be so reactive to trap an aminic function already co-ordinated to a metal atom and, furthermore, to react with a second end of a diamine molecule when the first end of this is already quaternized. This result gives support to the stepwise mechanism suggested by one of us for the reaction of *cis*-[Pt(C$_2$H$_4$)Cl$_2$L] with two mol of L to give *cis*-[Pt(C$_2$H$_4$L)ClL$_2$]Cl which should involve first substitution of the Cl *trans* to C$_2$H$_4$ by a molecule of L and formation of a cationic complex analogous to (3), then nucleophilic attack on the η-ethene of a second molecule of L (L = aliphatic or aromatic amine) [25]. Also in that case the absence of any formal charge on the Pt atom in the final σ-ethene complex should contribute to its stability.

The acid hydrolysis of (2) did not promote the cleavage of the Pt–C σ-bond, as found in other compounds formed by analogous reactions [20–22], but it regenerated the parent cation (3). The reason why the C–N bond in our case is cleaved in preference to the Pt–C bond is not clear. A possible explanation might be that compound (2) exists in equilibrium with the parent monomeric cation (3) and free amine (the existence of such an equilibrium in solution of analogous species has been already proved) [12, 24, 26] and that in acidic medium, because of protonation of the free amine, this equilibrium is shifted towards the monomeric η-ethene species before cleavage of the Pt–C bond can occur.

We are presently investigating the reaction pattern of acid hydrolysis in the case of σ-ethene complexes obtained by nucleophilic addition of secondary and primary amines to compound (3).

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