Acid-induced Reversal of Amine Attack at Platinum-co-ordinated Ethene *versus* Acidolysis of Platinum–Carbon σ Bonds

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The acidolysis of polynuclear platinum complexes of formula $[\{PtCl(tmen)(CH_2CH_2-)\}_nNEt_{4-n}]^+$ (tmen = *NNN'N'*-tetramethylethylenediamine, n = 1—4) to give polyalkylated ammonium ions has been carried out under different experimental conditions: (*i*) dilute perchloric acid in methanol; (*ii*) bubbling of gaseous hydrochloric acid through a chloroform solution of the complex; (*iii*) action of concentrated hydrochloric acid (37% in water) on the solid; and (*iv*) action of gaseous HCl on the solids. Overall it appears that on increasing the stability, and hence the resistance to undergo C–N bond dissociation, of the addition products, the alternative degradative path, that is cleavage of the Pt–C bond, becomes more important; the latter is also favoured by an increase in acid concentration and by a deshielding of the reaction centre. Moreover, heterogeneous conditions appear to favour Pt–C over C–N bond cleavage.

It is known that mono- and poly-alkylation of amines can be performed *via* nucleophilic addition to metal-bonded olefins and subsequent acid treatment according to the Scheme.[1,2]

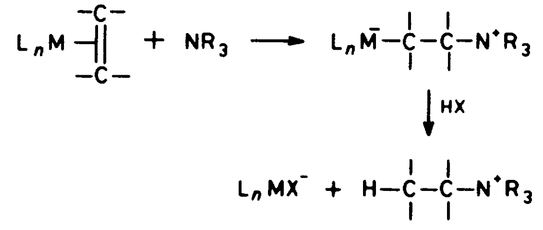
Although the intermediate species, containing σ-bonded C_2H_4, are usually rather unstable,[3-8] we recently succeeded in preparing a complete series of such species having general formula $[\{PtCl(tmen)(CH_2CH_2-)\}_nNEt_{4-n}]^+$ (tmen = *NNN'N'*-tetramethylethylenediamine, n = 1—4).[9] These were obtained using tertiary, secondary, and primary amines and ammonia as nucleophile and the cationic complex $[Pt(\eta^2\text{-}C_2H_4)Cl(tmen)]^+$ as reactive η^2-ethene substrate.

We decided to study the protolytic behaviour of these addition products and see how the reaction course could be influenced by differences in the substrates and in the protolysis conditions. In particular, we wanted to investigate the factors which influence either the platinum–carbon bond cleavage (with consequent alkylation of the amine) or the carbon–nitrogen bond dissociation (and reformation of the starting η^2-olefin complex and amine).

Experimental

Commercial reagent-grade chemicals were used without further purification. The complexes $[PtCl(tmen)(CH_2CH_2NHEt_2)][ClO_4]$ (1), $[\{PtCl(tmen)(CH_2CH_2-)\}_2NEt_2][ClO_4]$ (3), $[\{PtCl(tmen)(CH_2CH_2-)\}_3NEt][ClO_4]$ (4), and $[\{PtCl(tmen)(CH_2CH_2-\}_4N][ClO_4]$ (5) were prepared as stated in ref. 9. The compound $[PtCl(tmen)(CH_2CH_2NEt_3)][ClO_4]$ (2) was prepared using the same procedure as for compound (1). The complex $[\{PtCl(tmen)(CH_2CH_2-)\}_2(tmen)][ClO_4]_2$ (6) was prepared according to ref. 10.

Reactions.—With dilute perchloric acid. One and half times the stoicheiometric amount of acid required to cleave the Pt–C bonds was added to a solution [(1), (3), (4), or (5)] or suspension [(2) or (6)] of the substrate in methanol (5 cm^3). In all cases the amine was lost and $[Pt(\eta^2\text{-}C_2H_4)Cl(tmen)][ClO_4]$ precipitated. The yield of precipitated material was not quantitative owing to the partial solubility of this complex in methanol; however, concentration or even simple cooling of the solution yielded further quantities of product. The use of hydrochloric acid was avoided since Cl^- reacts further with $[Pt(\eta^2\text{-}C_2H_4)Cl(tmen)]^+$ displacing the ethene molecule; on the other hand, perchloric acid was a natural choice since perchlorate anion was always present in the starting substrates. The acidolysis reaction was fast in the case of mononuclear species (1) and (2) and in the case of (6), while with polynuclear species (3)—(5) the solution had to be stirred for several hours before precipitation commenced.

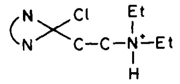
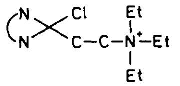
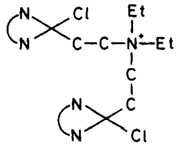
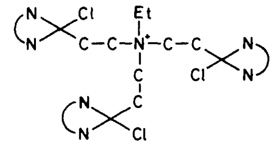
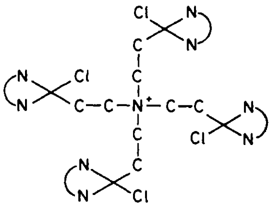
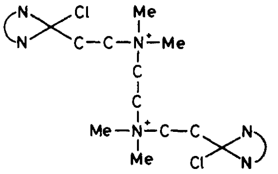


Scheme

With hydrochloric acid in chloroform. A stream of HCl [produced by dropping concentrated HCl (37% in water) into concentrated H_2SO_4 (95% in water)] was passed through a solution [(1)—(5)] or suspension [(6)] of the complex in this solvent. The yellow precipitate which formed was separated by filtration of the mother-liquor, dried *in vacuo*, and weighed. It was identified by i.r. spectroscopy as a mixture of $[PtCl_2(tmen)]$ and $[Pt(\eta^2\text{-}C_2H_4)Cl_2(Htmen)](Cl,ClO_4)$ corresponding to Pt–C and C–N bond cleavage respectively. In the case of compound (6) the precipitate contained, besides $[Pt(\eta^2\text{-}C_2H_4)Cl_2(Htmen)](Cl, ClO_4)$, also $[H_2tmen](Cl, ClO_4)_2$ which is sparingly soluble in chloroform. Washing of the precipitate with small portions of concentrated HCl (37% in water) removed all the $[Pt(\eta^2\text{-}C_2H_4)Cl_2(Htmen)](Cl, ClO_4)$ thus allowing the exact evaluation of the $[PtCl_2(tmen)]$ formed in the reaction. The chloroform solution, containing the ammonium salts together with unprecipitated $[Pt(\eta^2\text{-}C_2H_4)Cl_2(Htmen)]^+$, was left to stand for at least 24 h during which $[Pt(\eta^2\text{-}C_2H_4)Cl_2(Htmen)]^+$ reacted further to form $[PtCl_3(Htmen)]$ which separated out as orange needles. The residual solution was then evaporated to dryness and the solid residue, characterized by i.r. spectroscopy, comprised mostly salts of the ammonium ions. (The presence of very small quantities of unidentified platinum complexes did not interfere with the identification.)

With concentrated hydrochloric acid (37% *in water*). The acid (2—3 cm^3) was added to a solid sample of the complex (*ca.* 0.50 g) with stirring. If $[PtCl_2(tmen)]$ is formed in the reaction it separates from the solution and can be recovered and weighed directly, its quantity being a direct measure of

Table. Products of Pt–C and C–N bond cleavage by acid treatment. Only the primary products of acidolysis are reported [a]

Compound	Protolysis conditions $HClO_4$, MeOH	 HCl, $CHCl_3$ [b]	 HCl (37% in water or gas) [b]
(1) 	$[Pt(\eta^2\text{-}C_2H_4)Cl(tmen)]^+$, $NH_2Et_2^+$	$[PtCl_2(tmen)]$, $NHEt_3^+$	$[PtCl_2(tmen)]$, $NHEt_3^+$
(2) 	$[Pt(\eta^2\text{-}C_2H_4)Cl(tmen)]^+$, $NHEt_3^+$	$[Pt(\eta^2\text{-}C_2H_4)Cl(tmen)]^+$, $NHEt_3^+$	$[PtCl_2(tmen)]$, NEt_4^+
(3) 	$[Pt(\eta^2\text{-}C_2H_4)Cl(tmen)]^+$, $NH_2Et_2^+$	1, $NHEt_3^+$	$[PtCl_2(tmen)]$, NEt_4^+
(4) 	$[Pt(\eta^2\text{-}C_2H_4)Cl(tmen)]^+$, NH_3Et^+	2, $NHEt_3^+$	2, $NHEt_3^+$
(5) 	$[Pt(\eta^2\text{-}C_2H_4)Cl(tmen)]^+$, NH_4^+	3, $NHEt_3^+$	3, $NHEt_3^+$
(6) 	$[Pt(\eta^2\text{-}C_2H_4)Cl(tmen)]^+$, H_2tmen^{2+}	$[Pt(\eta^2\text{-}C_2H_4)Cl(tmen)]^+$, H_2tmen^{2+}	$[Pt(\eta^2\text{-}C_2H_4)Cl(tmen)]^+$, H_2tmen^{2+}

[a] The experimental yields were generally within a few per cent of the theoretical values. [b] Numbers indicate ratio of $[PtCl_2(tmen)]$ to $[Pt(\eta^2\text{-}C_2H_4)Cl(tmen)]^+$.

the Pt–C bonds cleaved in the process. The solution, containing the ammonium salt and the platinum complexes arising from C–N bond cleavage, $[Pt(\eta^2\text{-}C_2H_4)Cl_2(Htmen)]^+$ and $[PtCl_3(Htmen)]$, the latter through substitution of ethylene by Cl^- in the former, was evaporated to dryness and the solid residue treated with 10^{-3} mol dm^{-3} HCl. At this pH the complexes $[Pt(\eta^2\text{-}C_2H_4)Cl_2(Htmen)]^+$ and $[PtCl_3(Htmen)]$ transform into $[PtCl_2(tmen)]$ which precipitates, leaving an almost colourless solution.[11] The filtered solution was then evaporated to dryness and the residue, mainly ammonium salts, characterized by i.r. spectroscopy. A further purification of the ammonium salts could be carried out by crystallization from dichloromethane–diethyl ether.

Of gaseous hydrochloric acid with the solids. A sample of a complex (*ca.* 0.50 g), finely ground, was placed in a flask (150 cm^3) which was evacuated and then filled with gaseous HCl at atmospheric pressure and room temperature. After 20 min the residual HCl was pumped off and the solid characterized by i.r. spectroscopy. It comprised essentially $[PtCl_2(tmen)]$ and $[Pt(\eta^2\text{-}C_2H_4)Cl_2(Htmen)](Cl, ClO_4)$, in amounts corresponding to the extent of Pt–C and C–N bond cleavage respectively, and ammonium salt. The separation and evaluation of the individual components was performed, as described in the previous case, by treating the solid residue first with concentrated HCl (37% in water) and then with dilute HCl (10^{-3} mol dm^{-3}).

Results and Discussion

The protolysis reaction was carried out under four different conditions: (*i*) a slight excess of dilute $HClO_4$ (one and half times the stoicheiometric amount required for the acid cleavage) in methanol; (*ii*) bubbling of gaseous HCl through a chloroform solution of the complex; (*iii*) action of concentrated HCl (37% in water) directly on the solids; and (*iv*) action of gaseous HCl on the solids. The complexes examined, the reaction conditions, and the experimental results are summarized in the Table.

(*i*) In the first case the reaction was carried out by adding the dilute acid to a solution [(1), (3), (4), or (5)] or a suspension

[(2) or (6)] of the substrate in methanol. In all cases the only reaction taking place was the dissociation of the addition product to give the protonated amine and the starting η^2-ethene complex which could be recovered quantitatively from the reaction mixture. Thus no amine alkylation occurs under these conditions.

(*ii*) Bubbling gaseous HCl through a chloroform solution of the complex afforded in all cases the triethylammonium ion and the complexes [$PtCl_2$(tmen)] and [$Pt(\eta^2-C_2H_4)Cl_2$(Htmen)]$^+$, in the ratio corresponding to that of Pt–C and C–N bond cleavage respectively. The former complex precipitated and could be recovered and weighed directly. The latter compound was formed by the reaction of [$Pt(\eta^2-C_2H_4)Cl$(tmen)]$^+$ (primary product of acidolysis) with excess of HCl which caused the displacement of one end of tmen *trans* to the η^2-ethene and its replacement by a chloride ion; this complex could be either recovered, as a mixture with the ammonium salt, by evaporation to dryness of the reaction solution, or allowed to react further with chloride ion to give displacement of the olefin and formation of [$PtCl_3$(Htmen)] which separated out as red needles.[12] In the second case the ammonium salt was the only major product left in solution.

(*iii*) The direct attack of concentrated hydrochloric acid (37% in water) on the solid afforded different reaction products depending upon the nature of the substrate. Complexes (1)—(3) gave 100% Pt–C bond cleavage and formation of triethylammonium in the first case and tetraethylammonium in the last two cases. On the other hand, complexes (4)—(6) afforded salts of trialkylammonium corresponding to 66, 75, and 0% Pt–C bond cleavage respectively. The complexes [$PtCl_2$(tmen)] and [$Pt(\eta^2-C_2H_4)Cl_2$(Htmen)](Cl,ClO_4) were recovered in quantities corresponding to the extent of Pt–C and C–N bond cleavage respectively. Thus it appears that only the simpler substrates are able to form quaternary ammonium salts.

(*iv*) Direct attack of gaseous HCl on the solid afforded, in all cases, the same products as obtained by attack of concentrated HCl (37% in water). Special precautions were taken to ensure that the acidolysis reaction had gone to completion, that is longer reaction times and very fine grinding of the solids.

The above results can be better understood if we look at the ammonium salts produced in the acidolysis reaction rather than the ratio of Pt–C over C–N bond cleavage. For instance, trialkylammonium salts were always obtained when the reaction was performed in chloroform solution, although the extent of Pt–C bond cleavage was 100% in compound (1) and 0% in (2) and (6).

Thus under very mild conditions (stoicheiometric amount or slight excess of acid) there is no Pt–C bond cleavage but only C–N bond dissociation and formation of the starting $\eta^2-C_2H_4$ complex and amine. The explanation for this behaviour is that the addition products are always in equilibrium with the starting reagents (however small the extent of dissociation), therefore, if the Pt–C bond cleavage by acid is not very effective (as can be the case in dilute acid), C–N bond dissociation takes place since the free amine, being protonated, is removed from the equilibrium. This explanation is supported by the observation that if the attack by acid is carried out as in (*iii*) but using HCl of progressively reduced concentration, the extent of Pt–C bond cleavage is lowered, and, for instance, when using 1 mol dm^{-3} HCl in the case of compound (3) only the dissociation reaction takes place.

The acidolysis reaction carried out in chloroform solution represents the most significant test for comparing the reactivity of the different substrates since we operate in homogeneous, and therefore strictly analogous, conditions. As has been anticipated, we obtained in all cases the formation of trialkylammonium salts corresponding to different degrees of Pt–C bond cleavage. The data for compounds (1) and (2) clearly show that while with a monometallated trialkylammonium substrate, (1), one can get 100% Pt–C bond cleavage and formation of the corresponding trialkylammonium salt, on the contrary starting with a momometallated tetra-alkylammonium species such as (2) [the same applies also to (6)] there is no Pt–C bond cleavage at all, but instead simple C–N dissociation ending up, in both cases, with the formation of a trialkylammonium salt. On this basis it is very likely that also compounds (3)—(5) first undergo C–N bond dissociation to give a trialkylammonium salt which, afterwards, undergoes 100% Pt–C bond cleavage. The different behaviour of tri- and tetra-alkylammonium metal complexes towards acid cleavage can be related to the different thermal stabilities of the addition products of the olefin π complexes with secondary and tertiary amines, the former being far more stable than the latter.[4] Thus, it appears that on increasing the stability, and hence the resistance to dissociation, of the addition products, the alternative degradative path, that is cleavage of the Pt–C bond, becomes more important. It is also to be noted that dissociation of the addition products into the η^2-olefin complex and free amine is an intramolecular process and therefore does not depend upon the concentration of the acid or the shielding of the reaction centre, but only upon the strength of the C–N bond; on the other hand, Pt–C bond cleavage is an intermolecular process and its rate is not only dependent upon the acid concentration but also very sensitive to the shielding of the reaction centre.[13,14] Therefore in more acidic conditions [(*ii*) as compared with (*i*)] and with less hindered substrates [(1) as compared with (2)] the Pt–C bond cleavage is favoured over C–N bond dissociation. The existence of so sharp a borderline between the behaviour of tri- and tetra-alkylammonium addition products was not predictable at the beginning of this investigation.

The reactions performed under heterogeneous conditions by direct attack of concentrated HCl (37% in water) or gaseous HCl upon the solids gave rise, for the first time, to the formation of tetra-alkylammonium salts. Thus, compounds (1)—(3) undergo 100% Pt–C bond cleavage with formation of $NHEt_3^+$ in the first case and NEt_4^+ in the last two cases. On the other hand, compounds (4)—(6) give only trialkylammonium salts corresponding to a different degree of Pt–C bond cleavage. The explanation for this different behaviour is qualitatively similar to that given above. Going from (1) to (5) the molecular complexity increases causing a weakening of the C–N bond and a shielding of the Pt–C reaction centre from external reagents; both factors would favour C–N dissociation over Pt–C bond cleavage. A final point which needs comment is why compound (6) behaves similarly to (4) and (5) and not as (2) and (3). One possible explanation is that this compound is, among the other complexes of this series, the one with weakest C–N bond; in fact in this case we have two adjacent quaternary ammonium groups and it is well known that the first dissociation constant of a bis(ammonium) ion is much higher than that of a single ammonium ion.[15,16]

Overall it appears that the attack of concentrated aqueous HCl or gaseous HCl upon the solids is more effective in promoting Pt–C bond cleavage than that of gaseous HCl upon a chloroform solution. This may be due to the heterogeneous conditions which, in the former case, allow the substrates a smaller chance of undergoing C–N bond dissociation before Pt–C bond cleavage.

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