Addition of Hydroxide, Alkoxide, and Carboxylate Anions to Platinum-bonded Ethylene

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The cation $[\mathrm{Pt}(\eta^2\text{-}\mathrm{C_2H_4})\mathrm{Cl(tmen)}]^+$ (**1**) (tmen = *N,N,N',N'*-tetramethylethylenediamine) reacts with water and alcohol under basic conditions to give nucleophilic addition of hydroxide and alkoxide anions to ethylene and formation of $[\mathrm{Pt(CH_2CH_2OH)Cl(tmen)}]$ (**4**) and $[\mathrm{Pt(CH_2CH_2OR)Cl(tmen)}]$ [R = Me (**2**) or Et (**3**)] respectively. Compound (**4**), either in solution or in the solid, undergoes a condensation reaction with formation of $[\mathrm{(tmen)ClPt(CH_2CH_2OCH_2CH_2)PtCl(tmen)}]$ (**5**). Compound (**1**) reacts also with excess of acetate in water to give the ester complex $[\mathrm{Pt\{CH_2CH_2OC(O)Me\}Cl(tmen)}]$ (**6**). Compound (**6**), in the solid state, slowly dissociates to acetate anion and cation (**1**), redissolution in chloroform restoring the original species. Compounds (**3**)—(**6**), dissolved in methanol, are transformed into (**2**).

The addition of nucleophiles to metal-co-ordinated olefins is a topic of great interest because of its synthetic potential and mechanistic implications.[1] Theoretical studies have also been performed better to understand the factors influencing olefin reactivity,[2] the site of attack,[3] and the ease of addition of different nucleophiles.[4]

According to Hoffmann calculations,[2] the presence of a positive charge on the carbon atoms of a η^2-bonded olefin enhances its ability to undergo nucleophilic addition. Therefore cationic complexes of olefins are found to react with a wider variety of nucleophiles than neutral species of the same metal.

One of the very few reported examples of cationic compounds of platinum(II) containing olefins[5,6] is $[\mathrm{Pt}(\eta^2\text{-}\mathrm{C_2H_4})\mathrm{Cl(tmen)}]^+$ (tmen = *N,N,N',N'*-tetramethylethylenediamine) (1), synthesized by us some years ago.[7] This complex exhibits enhanced reactivity towards nucleophiles paralleling though the chemical behaviour of other cationic complexes of platinum-group metals, such as iron, ruthenium, and rhodium.[8]

The reactivity of compound (1) towards nucleophiles has been the subject of previous communications.[9] For instance, addition of the olefin takes place with inorganic anions such as $\mathrm{NO_2^-}$, $\mathrm{N_3^-}$, and $\mathrm{NCO^-}$ which in other cases give only co-ordination to the metal and displacement of the olefin.

To obtain new insight into the chemical reactivity of this complex we have performed reactions with alkoxide, acetate, and hydroxide anions. Attack of alkoxides and carboxylates upon olefinic complexes of platinum(II), leading to the formation of addition products, has been reported so far only for chelated dienes and for monoenes bearing a second co-ordinated function.[1,10] Platinum(II) complexes with singly bonded monoenes, upon reaction with alkoxides, give olefin substitution rather than addition[11] to yield unstable metal–alkoxy species.[12]

Addition of alkoxide anions to the bonded ethylene in cationic complexes of palladium(II) has already been reported to give rather stable species.[13]

Results and Discussion

The reactions of the cationic ethylene complex $[\mathrm{Pt}(\eta^2\text{-}\mathrm{C_2H_4})\mathrm{Cl(tmen)}]\mathrm{ClO_4}$ (1) with oxygen nucleophiles are shown in the Scheme.

Compound (1) reacts readily in undried methanol, containing a stoicheiometric amount of base [either potassium hydroxide or 1,8-bis(dimethylamino)naphthalene], to give in quantitative yield $[\mathrm{Pt(CH_2CH_2OMe)Cl(tmen)}]$ (2) in which a methoxide ion has added to the olefin. Using ethanol as solvent and similar reaction conditions the corresponding complex $[\mathrm{Pt(CH_2CH_2OEt)Cl(tmen)}]$ (3) is obtained.

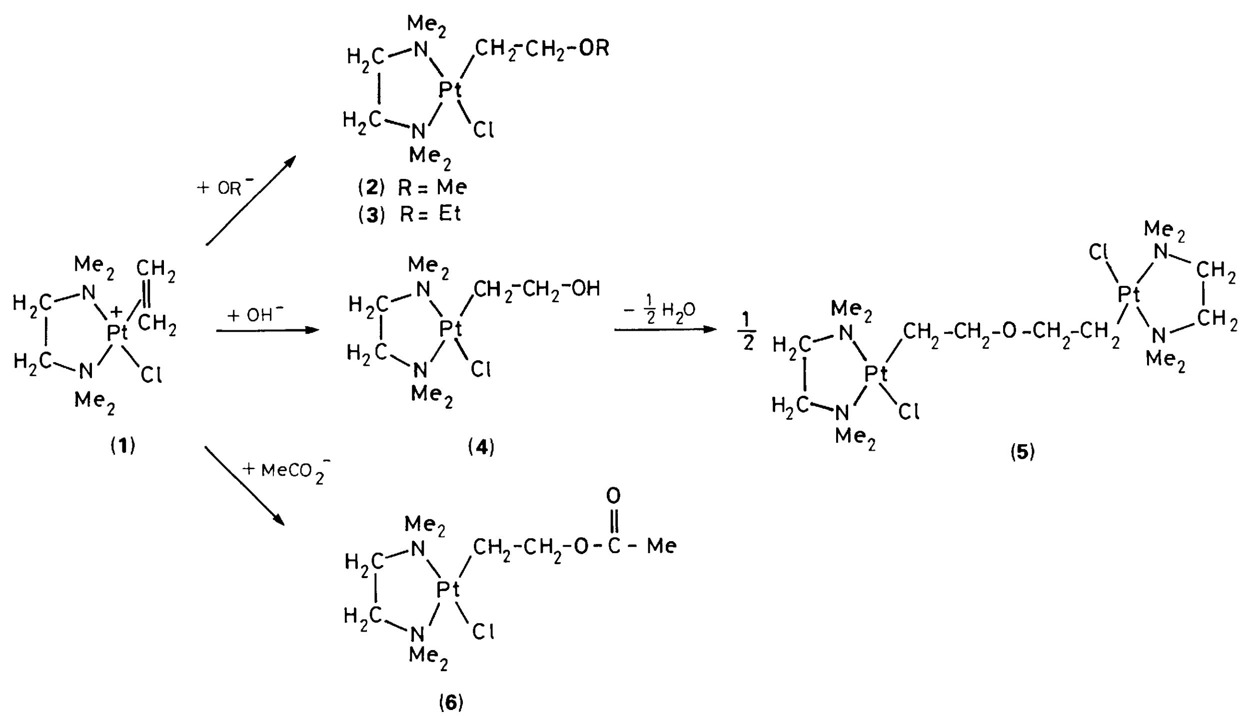
If the reaction is performed in water containing a slight excess of base, the compound $[\mathrm{Pt(CH_2CH_2OH)Cl(tmen)}]$ (4) in which $\mathrm{OH^-}$ has added to the olefin is obtained in high yield (>80%). Compound (4), however, is rather unstable and undergoes spontaneously a condensation reaction (1). This reaction is rather

$$\underset{(4)}{2[\mathrm{Pt(CH_2CH_2OH)Cl(tmen)}]} \longrightarrow$$

$$\underset{(5)}{[\mathrm{(tmen)ClPt(CH_2CH_2OCH_2CH_2)PtCl(tmen)}]} + \mathrm{H_2O} \quad (1)$$

slow, occurs both in non-aqueous solvents and in the solid state, and can be forced to the right by the presence of drying agents. For instance the i.r. spectra of samples of (4), taken at different times after their preparation, show a progressive decrease in the intensity of the signals at 3 500 and 965 $\mathrm{cm^{-1}}$ [ν(OH) and ν(CO) respectively] and simultaneous increase of signals at 1 050 [ν_{asym}(COC) of (5)] and 3 450 $\mathrm{cm^{-1}}$ [ν(OH) of free water]. The transformation can also be monitored by ^{1}H n.m.r. spectroscopy and shows that (5) is the only compound which is formed. Compound (5), once formed, is stable in aqueous solution, even in a basic medium. It can also be obtained directly from compound (1) by reaction with powdered KOH in an undried chlorinated solvent.

When compound (1) is treated in water with an excess of acetate the ester complex $[\mathrm{Pt\{CH_2CH_2OC(O)Me\}Cl(tmen)}]$ (6) is formed. This compound, however, has never been prepared in a pure form, always being contaminated by a certain amount of compound (5). It is to be noted that the reaction of (1) with acetate in methanol leads to the formation of compound (2), instead of (6), the role of acetate being that of creating a basic medium. Compound (6) is also rather unstable, and in the solid state it decomposes to acetate anion and cation (1). For instance a KBr pellet of a freshly prepared sample of (6)



Scheme.

Table. Proton chemical shifts [δ, downfield from $SiMe_4$; J(PtH) in Hz in parentheses] and characteristic i.r. bands of complexes (**1**)—(**6**)

		N.m.r.						I.r.	
					$PtC_\alpha H_2C_\beta H_2X$[a]				
Complex	Solvent	$N(CH_3)_2$	$>NCH_2CH_2N<$	η^2-C_2H_4	$C_\alpha H_2$	$C_\beta H_2$	X	ν(Pt–C)	ν(Pt–Cl)
(**1**)	CD_3OD	3.00(35)	3.08(25)	4.80(60)	—		—	458	340
		2.85(35)						368	
	CD_2Cl_2	3.02(35)	3.10[b]	4.76(60)	—		—		
		2.85(36)							
(**2**)	$CDCl_3$	2.90(52)	2.78	—	1.64(92)	3.48	3.32 (OCH_3)	485	320
		2.72(15)	2.54	—					
(**3**)	$CDCl_3$	2.90(50)	2.78	—	1.65(90)	3.54	3.50 (OCH_2)	485	320
		2.72(15)	2.55	—			1.17 ($OCCH_3$)		
(**4**)	$CDCl_3$	2.90(50)	2.78	—	1.72(90)	3.47	2.17 (OH)	490	320
		2.73(15)	2.56						
(**5**)	$CDCl_3$	2.93(50)	2.78	—	1.62(90)	3.64	—	485	315
		2.73(15)	2.56						
(**6**)	$CDCl_3$	2.95(50)	2.78	—	1.65(90)	4.22	2.00 [$OC(O)CH_3$]	485	320
		2.73(15)	2.56						

[a] These protons give well separated multiplets the mean value of which is given. [b] Broad multiplet.

shows in the i.r. spectrum two absorptions at 1 730 and 1 245 cm^{-1} assignable to the ester group. On standing at room temperature for a few days these absorptions disappear and new absorptions appear at 1 570 and 1 450 cm^{-1} which can be assigned to acetate anion. On redissolving decomposed (**6**) in chloroform the original addition product is restored.

With the exception of (**4**) which undergoes a condensation reaction, all the other complexes of the series [(**2**), (**3**), (**5**), and (**6**)] do not show any sign of decomposition after several days in solutions of chlorinated solvents. In water they withstand a moderately basic medium, while in strong alkaline solutions they tend to decompose with deposition of platinum metal; in an acidic medium the addition products revert to the starting compound (**1**).

All compounds [(**3**)—(**6**)] when dissolved in methanol are transformed completely into the species (**2**). The reaction is faster for (**4**)—(**6**) (complete in a few hours at 20 °C, in a few minutes at 60 °C) than for (**3**) (2 d at 20 °C). Moreover the formation of complex (**2**) appears to be favoured over (**3**). Compound (**3**) dissolved in a solution of ethanol–methanol (1:1 molar ratio) gives a mixture of (**2**) and (**3**) in 2:1 ratio.

Relevant i.r. and n.m.r. data are reported in the Table. All the tmen protons, in the addition products, appear at slightly higher field with respect to those of the parent cationic complex (**1**). Moreover the signals belonging to N-methyl protons of the two amine groups show remarkable differences in their coupling constant with the ^{195}Pt nucleus [^3J(PtH) = 50 and 15 Hz respectively]; the more strongly coupled signal is at lower field and is assigned to the amine group *trans* to the chlorine ligand which is expected to suffer a *trans* influence smaller than that of the amine group *trans* to the σ-bonded carbon. It is worth noting that the different *trans* influence of Cl and η^2-C_2H_4 in compound (**1**) did not cause any noticeable difference in the ^{195}Pt coupling constant of the tmen methyls all of which exhibit a ^3J(PtH) of 35 Hz. Therefore, although there is crystallographic evidence indicating that η^2-ethylene and σ-alkyl groups cause a similar lengthening of the Pt–N bond *trans* to them,[14] nevertheless the effect of the mono- and di-hapto ligands upon the ^3J(PtH) of the *trans* ligands is very much different.

Protons on the α-carbon of the Pt–CH_2CH_2–X moieties are always located at δ 1.6—1.7, while the β protons are in the expected region for the attached X group.

In conclusion the reaction with hydroxide, alkoxide, and carboxylate anions further evidentiates the different reactivity of olefins in neutral and cationic platinum complexes. In neutral complexes the site of attack is exlusively the metal centre while in the cationic species the olefin becomes the preferred reaction site. In this respect it is worth noting the reaction of compound (**1**) with phenanthroline (phen) in an alcoholic medium. This bidentate aromatic amine, unlike most of the nitrogen bases, is unable to add to the olefin but is a very good co-ordinating ligand towards platinum. On mixing the reactants one observes the immediate precipitation of $[H(phen)_2]ClO_4$[15] and dissolution of (**1**). Hence the role of phen becomes that of capturing protons while RO^- adds to the olefin. Only at much longer reaction times the phenanthroline will enter the co-ordination sphere of platinum and the very insoluble $[PtCl_2(phen)]$ complex starts to precipitate from the solution.

Experimental

Starting Materials.—Commercial reagent-grade chemicals were used without further purification, *N,N,N′,N′*-tetramethylethylenediamine was purchased from Aldrich and purified before use by distillation from potassium hydroxide, and $[Pt(\eta^2\text{-}C_2H_4)Cl(tmen)]ClO_4$ was prepared according to ref. 7.

Preparation of Complexes.—$[Pt(CH_2CH_2OMe)Cl(tmen)]$ (**2**). To a stirred solution of KOH in undried methanol (2—3 mmol in 10 cm^3 of solvent), $[Pt(\eta^2\text{-}C_2H_4)Cl(tmen)]ClO_4$ (1 mmol) was slowly added directly as a solid. While the complex dissolved a precipitate of $KClO_4$ was formed. The reaction mixture was left to stir at room temperature for *ca.* 0.5 h, then filtered and the solvent evaporated under reduced pressure. The solid residue was extracted with CH_2Cl_2, the solution was dried over Na_2SO_4 and taken to dryness by evaporation under reduced pressure, yielding pure compound (**2**), 90% referred to platinum. I.r.: ν_{asym}(COC) 1 085 cm^{-1} (Found: C, 26.9; H, 5.9; Cl, 9.0; N, 6.9. Calc. for $C_9H_{23}ClN_2OPt$: C, 26.6; H, 5.7; Cl, 8.7; N, 6.9%).

The same reaction occurs also using 1,8-bis(dimethylamino)-naphthalene (proton sponge, ps) instead of KOH as a base. However, because of the greater solubility of $[Hps]ClO_4$ as compared to $KClO_4$ in the solvents used, the isolation of pure compound (**2**) is more difficult and the yield lower.

The complex $[Pt(CH_2CH_2OEt)Cl(tmen)]$ (**3**) was prepared in a completely analogous way but using ethanol instead of methanol as the solvent. The yield was 85% referred to platinum. I.r.: ν_{asym}(C–O–C) 1 085 cm^{-1} (Found: C, 28.6; H, 5.8; Cl, 8.5; N, 6.5. Calc. for $C_{10}H_{25}ClN_2OPt$: C, 28.6; H, 6.0; Cl, 8.4; N, 6.7%).

$[Pt(CH_2CH_2OH)Cl(tmen)]$ (**4**). When the reaction of $[Pt(\eta^2\text{-}C_2H_4)Cl(tmen)]ClO_4$ (**1**) with KOH was carried out in water [1 mmol of (**1**), 2—3 mmol of KOH in 10 cm^3 of solvent] again the starting complex dissolved and $KClO_4$ was precipitated. The filtered solution was extracted with 1,2-dichloroethane and the organic phase evaporated, yielding pure compound (**4**) (80% yield). Alternatively, the water solution can be taken to dryness in a vacuum desiccator and the solid residue extracted with chlorinated solvents. The latter procedure leads to (**4**) containing a certain amount of compound (**5**) which results from condensation of two molecules of (**4**) with elimination of a molecule of water. Yield 80% referred to platinum. I.r.: ν(OH) 3 500, ν(CO) 965 cm^{-1} (Found: C, 24.8; H, 5.5; Cl, 8.7; N, 7.1. Calc. for $C_8H_{21}ClN_2OPt$: C, 24.5; H, 5.4; Cl, 9.0; N, 7.1%).

$[(tmen)ClPt(CH_2CH_2OCH_2CH_2)PtCl(tmen)]$ (**5**). The reaction between complex (**1**) and an excess of finely ground KOH performed in an undried chlorinated solvent (1,2-dichloroethane was chosen since it dissolves less water than $CHCl_3$ or CH_2Cl_2) for about 24 h led to the formation of a solution which, by evaporation of the solvent, gave compound (**5**) as unique product. Yield 80% referred to platinum. I.r.: ν(OH) absent, ν_{asym}(COC) 1 050 cm^{-1} (Found: C, 24.9; H, 5.4; Cl, 8.9; N, 7.1. Calc. for $C_{16}H_{40}Cl_2N_4OPt_2$: C, 25.1; H, 5.3; Cl, 9.3; N, 7.3%).

$[Pt\{CH_2CH_2OC(O)Me\}Cl(tmen)]$ (**6**). This compound could not be prepared in a pure form, however its formation can be observed whenever the cationic complex (**1**) is treated in water in the usual way with a 3—4 fold excess of potassium acetate. The filtered water solution, when evaporated to dryness in a vacuum desiccator, gave a solid residue which was extracted with 1,2-dichloroethane. The resulting solution, when taken to dryness by evaporation of the organic solvent, afforded a mixture of compounds (**5**) and (**6**) in *ca.* 1:1 molar ratio (from ^{1}H n.m.r. data) (Found: C, 26.2; H, 5.3; Cl, 9.2; N, 6.8. Calc. for $C_{10}H_{23}ClN_2O_2Pt$ + $C_{16}H_{40}Cl_2N_4OPt_2$: C, 26.0; H, 5.3; Cl, 8.9; N, 7.0%).

In all the reactions involving the cationic complex $[Pt(\eta^2\text{-}C_2H_4)Cl(tmen)]^+$ and occurring in a basic medium the formation of $[(tmen)ClPt\{CH_2CH_2(tmen)CH_2CH_2\}PtCl(tmen)][ClO_4]_2$ is always observed (this complex results from nucleophilic addition of a molecule of tmen to two cationic units).[7] Its yield did not exceed 5% and, being poorly soluble in all solvents used including water, it was removed from the reaction mixture at the stage of the first filtration, together with $KClO_4$.

Physical Measurements.—I.r. spectra in the range 4 000—400 cm^{-1} were recorded as KBr pellets, in the range 400—200 cm^{-1} as Polythene pellets on a Perkin-Elmer 283 spectrophotometer. Proton n.m.r. spectra were obtained with a Varian XL200 spectrometer.

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