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REACTIONS AND PROPERTIES OF SOME TRIMETHYLENEPLATINUM(IV) COMPLEXES

II. REACTIONS WITH ADDED LIGANDS

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Summary

The ligands L in the compounds $PtX_2(C_3H_6)L_2$ (X = Cl, Br) are found to be replaced in the order, tetrahydrofuran, pyridine, 4-methylpyridine, ethylenediamine, without displacement of the trimethylene moiety. A dimethylformamide derivative of trimethyleneplatinum(IV) was also prepared, but dimethyl sulphoxide and olefins (ethylene, cyclooctadiene) displace the C_3H_6 under some conditions.

No reaction with triphenylphosphine, arsine and stibine in DMSO and DMF occurs if L_2 = ethylenediamine or 2,2'-bipyridine, but when L = C_5H_5N or $4\text{-}CH_3C_5H_4N$, reductive elimination occurs with evolution of cyclopropane. The yield of gas depends, however, on the nature of L, X and the entering ligand, due to the parallel formation of coloured products, in which the platinum trimethylene ring is intact, under some conditions. The kinetics of the cyclopropane displacement have been studied and a mechanism involving ionic intermediates is proposed.

Introduction

In part I the results of a study of the thermal decomposition of a number of trimethyleneplatinum(IV) complexes, $[PtX_2(C_3H_6)]_4$ and $PtX_2(C_3H_6)L_2$ (where X = Cl, Br; L = nitrogen ligand), were reported [1]. The elimination of the C_3H_6 moiety appears to be the first step and estimates of the mean Pt—C bond strengths were obtained.

The trimethylene moiety can also be displaced quantitatively as cyclopropane by reaction with ligands of high *trans*-effect, such as CN^-, I^- and PPh_3 [2], and (under certain conditions) with olefins, e.g. propene [3], propenylbenzene [4], but such processes have not been studied in any detail. We have investigated the stoichiometry and kinetics of the reactions of the monomeric platinum complexes $PtX_2(C_3H_6)L_2$ with triphenylphosphine, arsine and stibine, and obtained further information on the replacement of L and of the C_3H_6 moiety by other ligands.

Results and discussion

The reactions of trimethyleneplatinum(IV) complexes with added ligands fall into two classes: (*i*) processes in which the tetramer is converted into a monomer by addition of an appropriate ligand, or L is replaced by another ligand, but in which the trimethyleneplatinum ring remains intact, and (*ii*) processes in which reductive elimination of the C_3H_6 moiety as cyclopropane occurs. With certain ligands, e.g. $SbPh_3$, both types of process may take place simultaneously (see below).

Most of the work has been concerned with the reactions with triphenylphosphine, arsine and stibine, but some data on reactions with other ligands are reported first.

Reactions with oxygen, nitrogen and sulphur compounds

The tetramers, $[PtX_2(C_3H_6)]_4$ (X = Cl, Br), are sparingly soluble in tetrahydrofuran (THF), and can be recovered unchanged by allowing the solvent to evaporate. Addition of a slight excess of pyridine (if necessary followed by water) precipitates $PtX_2(C_3H_6)(C_5H_5N)_2$. Addition of a slight excess of 4-methylpyridine (γ-picoline) to a solution of $PtCl_2(C_3H_6)(C_5H_5N)_2$ in $CDCl_3$ gives the corresponding picoline compound (as shown by ^1H NMR). The normal method of preparation of the ethylenediamine compound (L = ½ $NH_2CH_2CH_2NH_2$) is from the corresponding pyridine or picoline compound by displacement [5]. Thus, assuming that the THF solution contains monomeric $PtX_2(C_3H_6)(THF)_2$, THF being a very weak ligand (cf. dioxan [6]), the order of Pt—L bond strengths is: $THF < C_5H_5N < 4\text{-}CH_3C_5H_4N < NH_2CH_2CH_2NH_2$.

Dichlorotrimethyleneplatinum(IV) tetramer also dissolves in dimethylformamide and a compound having the apparent formula $(DMF)_{1.5}PtCl_2(C_3H_6)$ can be obtianed from the solution. Possibly one DMF molecule acts as a bridging ligand between two $(DMF)PtCl_2(C_3H_6)$ moieties.

The tetramers dissolve in dimethyl sulphoxide (DMSO), or a solution in THF reacts with DMSO, eliminating cyclopropane rapidly (as shown by ^1H NMR) and giving $PtX_2(DMSO)_2$. The ethylenediamine compounds $PtX_2(C_3H_6)(en)$ do not eliminate cyclopropane at 35° when dissolved in DMSO-d_6 (as shown by ^1H NMR), whereas the pyridine and picoline complexes decompose slowly. After 4.5 h the % C_3H_6 evolved is: (I) $PtCl_2(C_3H_6)(C_5H_5N)_2$, 27; (II) $PtBr_2(C_3H_6)(C_5H_5N)_2$ 47.5; $PtCl_2(C_3H_6)(4\text{-}CH_3C_5H_4N)_2$, 45. Addition of 1.5 mole DMF per mole Pt compound to the solution reduces the rate of decomposition, viz. (I), 15% and (II), 30% in 4.5 h. Obviously DMSO replaces even the unidentate nitrogen ligands with difficulty but, when attached to the platinum, has a high *trans*-effect giving rapid elimination of cyclopropane.

Reactions with olefins

Ethylene does not react with $PtCl_2(C_3H_6)(C_5H_5N)_2$ in benzene solution (as shown by ^{1}H NMR), but on passing the gas through a solution of dichlorotrimethyleneplatinum(IV) tetramer in THF, Zeise's dimer $[PtCl_2(C_2H_4)]_2$ is formed. On passing cyclopropane through a THF solution of the dimer, the trimethylene compound is reformed (cf. preparation of substituted trimethyleneplatinum(IV) compounds from Zeise's dimer [4]). Also Brown [3] has found that the reaction:

$$4\,\overline{\mathrm{CH_2CH_2CH_2}} + 2(\mathrm{PtCl_2CH_3CH{=}CH_2})_2 \rightleftharpoons [\mathrm{PtCl_2(CH_2)_3}]_4 + 4\,\mathrm{CH_3CH{=}CH_2}$$

is reversible.

Other olefins, e.g. cyclohexene, cyclooctadiene (COD), also eliminate the trimethylene moiety (as shown by ^{1}H NMR). When COD is added to a solution of $[PtCl_2(C_3H_6)]_4$ in DMF a compound containing both COD and DMF, and having the probable formula $(PtCl_2 \cdot DMF)_2COD$, is produced. It would appear that the COD is bridging two $PtCl_2 \cdot DMF$ moieties. No dichlorotrimethyleneplatinum(IV) tetramer is precipitated, however, on passing cyclopropane through a solution of $PtCl_2 \cdot COD$ in methylene chloride, whereas Brown [3] found that the tetramer is formed if $(PtCl_2 \cdot CH_3CH{=}CH_2)_2$ is used (see above).

Obviously, an olefin can replace a weak ligand attached to the trimethyleneplatinum(IV) moiety and may then cause elimination of cyclopropane if this is removed so as to displace the equilibrium. The initial step in the reverse reaction appears to involve coordination of cyclopropane to a vacant site on the Pt^{II} with the dimers which are slightly dissociated in solution, but with $PtCl_2 \cdot COD$, cyclopropane cannot displace the chelate olefin.

Reactions with triphenylphosphine, arsine and stibine (M)

The extent of reaction (A) in solution, as measured by the yield of cyclo-

$$\mathrm{PtX_2 \cdot (CH_2)_3L_2} + 2\,\mathrm{M} \rightarrow \mathrm{PtX_2M_2} + 2\,\mathrm{L} + \overline{\mathrm{CH_2CH_2CH_2}} \qquad (\mathrm{A})$$

propane evolved, varied from 0 — 100% depending on the nature of L, X and M and on the solvent and temperature. For example, with the ethylenediamine and 2,2'-bipyridine compounds ($L_2 = NH_2CH_2CH_2NH_2$, $C_{10}H_8N_2$; X = Cl, Br) no reaction occurs even with triphenylphosphine [although all the cyclopropane is evolved with CN^- and $PtCl_2(C_3H_6)(en)$], whereas $PtCl_2(C_3H_6)(C_5H_5N)_2$ and $SbPh_3$ give 100% cyclopropane at room temperature.

The reactions between $AsPh_3$ and $SbPh_3$ and the trimethylene compounds (L = C_5H_5N or 4-$CH_3C_5H_4N$ and X = Cl or Br) were followed in a closed system by measuring the volume of gas evolved as a function of time using a gas burette (see experimental section). The choice of solvents was limited, since the reactants and products had to be soluble and it had to be possible to saturate the reactant solution with cyclopropane (before mixing) without too much difficulty. It was found that DMSO and DMF were the most suitable. The main kinetic (and stoichiometric) data are summarised in Table 1; some typical first and second order plots are shown in Fig. 1. The reactions of triphenylphosphine with all four platinum compounds in both solvents, and of triphenylstibine with the dichloro- and dibromo-trimethyleneplatinum(IV) tetramers in DMF, proceed too rapidly for rate measurements and appear to evolve 100% cyclopropane.

At any temperature, the rate constants, and even the reaction order, depend

TABLE 1

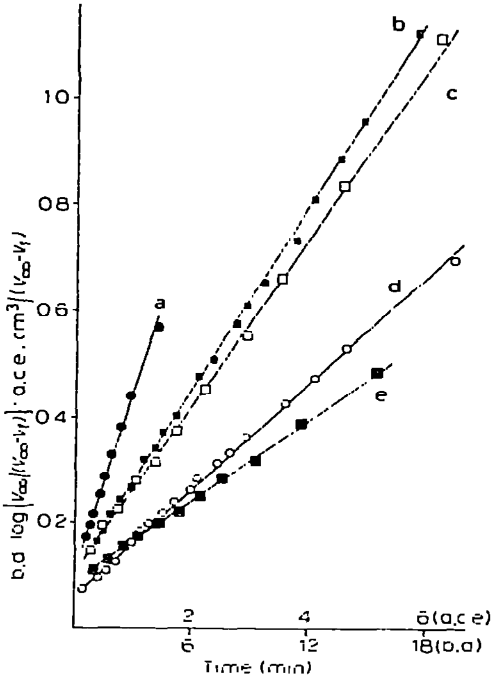
DATA ON THE REACTIONS OF TRIMETHYLENEPLATINUM(IV) COMPOUNDS AND TRIPHENYLARSINE AND STIBINE

MPh_3[a]	Solvent	Temp. (°C)	% reaction[b]	Order	Rate constant[c]
$PtCl_2(C_3H_6)(C_5H_5N)_2$					
$SbPh_3$	DMSO	25.2	> 90	2	0.16 ± 0.01
	DMSO	30.2	> 90	2	0.28
	0.062 *M*(py) in DMSO[d]	30.2	> 90	1	3.6×10^{-3}
	0.093 *M*(py) in DMSO	30.2	80	1	1.6×10^{-3}
	0.155 *M*(py) in DMSO	30.2	60	1	1.4×10^{-3}
	DMF	25.05	> 90	2	0.11 ± 0.01
	DMF	30.2	> 90	2	0.285 ± 0.04
	0.062 *M*(py) in DMF	30.2	> 90	1	1.3×10^{-3}
	DMF	35.1	> 90	2	0.435 ± 0.02
$AsPh_3$	DMSO	30.2	> 90	2	1.4
	0.062 *M*(py) in DMSO	30.2	> 90	1	4.1×10^{-3}
	DMF	30.2	> 90	2	0.585 ± 0.015
	0.062 *M*(py) in DMF	30.2	> 90	1	2.9×10^{-3}
$PtCl_2(C_3H_6)(4\text{-}CH_3C_5H_4N)_2$					
$SbPh_3$	DMSO	25.2	85	2	0.168 ± 0.025
	DMSO	30.2	75	2	0.32 ± 0.03
	DMF	25.2	> 90	1	$(1.35 \pm 0.01) \times 10^{-3}$
	DMF	30.2	> 90	1	$(2.14 \pm 0.06) \times 10^{-3}$
	DMF	35.1	> 90	1	$(3.0 \pm 0.1) \times 10^{-3}$
$AsPh_3$	DMF	30.2	> 90	1	4.85×10^{-3}
$PtBr_2(C_3H_6)(C_5H_5N)_2$					
$SbPh_3$	DMF	30.2	65	2	0.13 ± 0.01
$AsPh_3$	DMF	30.2	60	2	0.20 ± 0.02
$PtBr_2(C_3H_6)(4\text{-}CH_3C_5H_4N)_2$					
$SbPh_3$	DMF	30.2	60	2	0.30 ± 0.01

[a] The stoichiometric ratio of the reactants according to (A) was used, the concentration of the platinum compound being 0.022 *M*. [b] The percentage of the theoretical volume of cyclopropane actually evolved. > 90% indicates that probably all the cyclopropane is evolved within experimental error. [c] The units *k* are s^{-1} and $dm^3 mol^{-1} s^{-1}$ for the first and second order processes, respectively. The error ranges are only attached when replicate experiments were performed. [d] (py) = pyridine.

on the nature of L, M and the solvent. The reactions are second order, *k* increasing on replacement of pyridine by 4-methylpyridine or of Br by Cl, except for $PtCl_2(C_3H_6)(4\text{-}CH_3C_5H_4N)_2$ in DMF (first order). The rate of evolution of cyclopropane increases in the order $PPh_3 \gg AsPh_3 > SbPh_3$. Added pyridine reduces the rate of reaction and the order changes from two to one. The temperature range for the rate measurements was restricted because (*i*) at temperatures below 25° it was not possible to saturate the reactant solutions with cyclopropane satisfactorily, (*ii*) at 35° the platinum compounds tended to decompose in DMSO while the solutions were being saturated (see above), and (*iii*) the reactions in DMF were too rapid to follow above 35°. However, for triphenylstibine plus dichlorobis(pyridine)trimethyleneplatinum(IV) or the 4-methylpyridine analogue in DMF rate constants were obtained at three temperatures, and Arrhenius plots (Fig. 2) gave overall activation energies of (82 ± 14) and (46 ± 3) kJ mol^{-1} respectively.

Some reaction mixtures evolved too little cyclopropane for the kinetics to



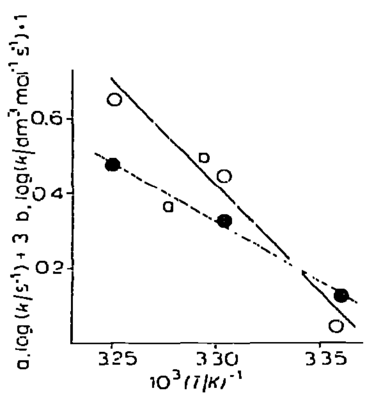


Fig. 1. Typical first and second order plots for the evolution of cyclopropane at 30.2°. a, $PtCl_2(C_3H_6)(C_5H_5N)_2$ + 2 $AsPh_3$ in DMSO (second order): b, $PtCl_2(C_3H_6)(4\text{-}CH_3C_5H_4N)_2$ + 2 $SbPh_3$ in DMF (first order): c, $PtCl_2(C_3H_6)(C_5H_5N)_2$ + 2 $AsPh_3$ in DMF (second order). d, $PtCl_2(C_3H_6)(C_5H_5N)_2$ + 2 $SbPh_3$ + 0.062 M C_5H_5N in DMF (first order): e, $PtCl_2(C_3H_6)(C_5H_5N)_2$ + 2 $SbPh_3$ in DMSO (second order). Initial concentration of platinum compound, 0.022M.

Zero time is indefinite due to the experimental technique.

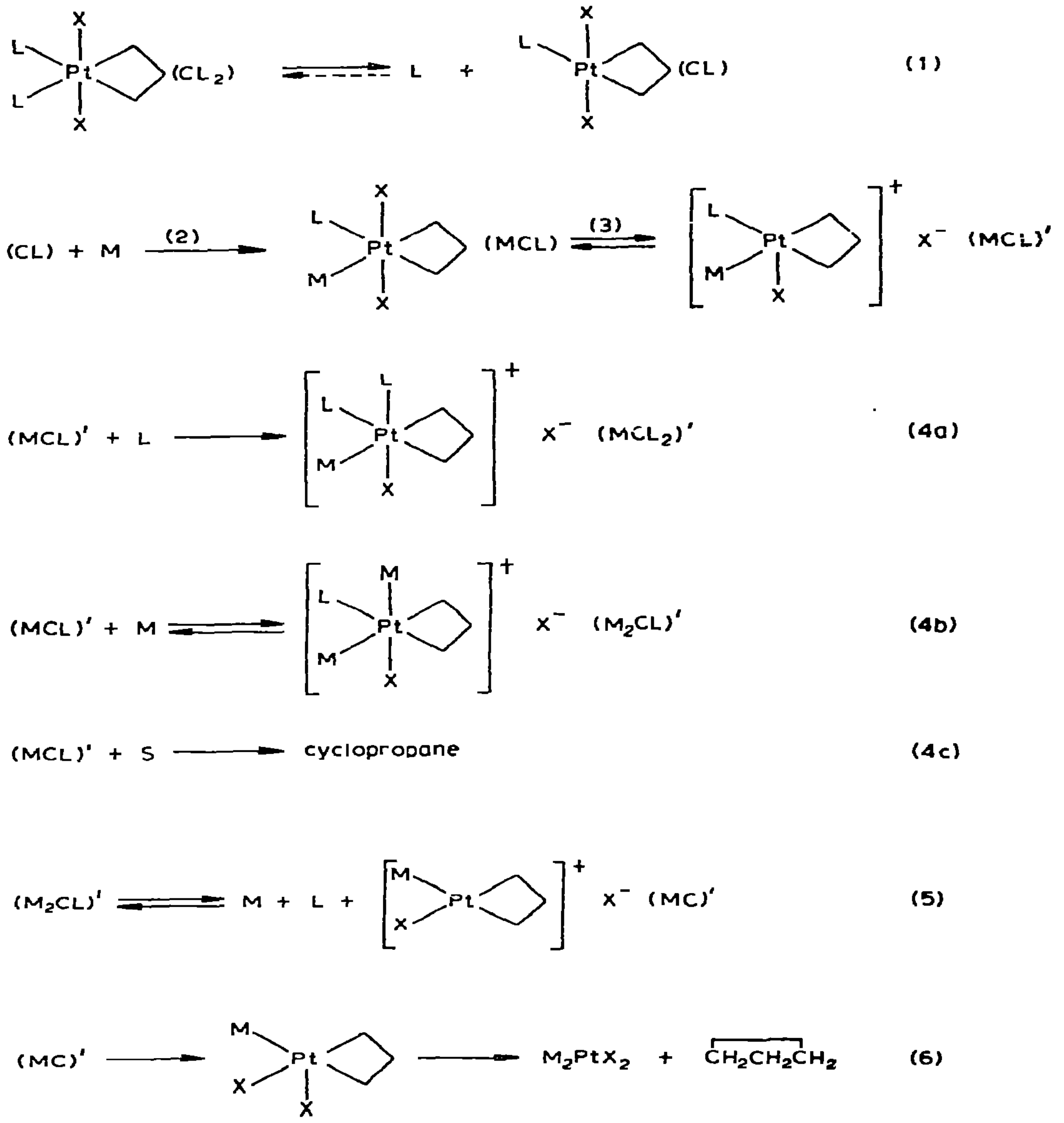
Fig. 2. Variation of the rate constants for the evolution of cyclopropane with temperature. a, $PtCl_2(C_3H_6)$-$(4\text{-}CH_3C_5H_4N)_2$ + 2 $SbPh_3$ in DMF (first order): b, $PtCl_2(C_3H_6)(C_5H_5N)_2$ + 2 $SbPh_3$ in DMF (second order). Initial concentration of platinum compound, 0.022M.

be obtained. For instance, only 20, 15 and 45% of the theoretical amount of cyclopropane based on (A) was evolved with 2 $SbPh_3$ + $PtBr_2(C_3H_6)(C_5H_5N)_2$, 2 $SbPh_3$ + $PtBr_2(C_3H_6)(4\text{-}CH_3C_5H_4N)_2$ and 2 $AsPh_3$ + $PtBr_2(C_3H_6)(C_5H_5N)_2$, respectively. Also addition of pyridine (or 4-methylpyridine or ethylenediamine) reduced the yield of cyclopropane (see Table 1); and no reaction occurred with $PtCl_2(C_3H_6)(C_5H_5N)_2$ and triphenylstibine in pyridine solution (as shown by ^1H NMR). Since reaction (A) is not reversible, presumably products containing a $Pt(C_3H_6)$ moiety and $AsPh_3$ or $SbPh_3$ are formed under certain conditions. It was possible to show the formation of red and peach coloured products, which were stable in solution but difficult to isolate and handle because they reacted very rapidly with water to evolve cyclopropane. These products, in which the trimethyleneplatinum ring appears to be intact, probably account for the reduced yield of cyclopropane with some systems.

The mechanism of Scheme 1, although some of the steps are undoubtedly somewhat speculative, appears to provide a reasonable explanation of the experimental data.

The initial dissociation (1) explains why reaction does not occur with the ethylenediamine and bipyridine compounds, and is also indicated by the observa-

SCHEME 1



tion that added C_5D_5N replaces C_5H_5N in $PtCl_2(C_3H_6)(C_5H_5N)_2$ in benzene solution [7]. Reaction (2) is presumably very much faster than (−1) except when the concentration of added L is very high. DMSO and DMF have high relative permittivities (dielectric constants) and will promote the isomerisation of MCL to ionic species in solution*. Similar ionic species have been suggested as intermediates in the decomposition of trimethyleneplatinum(IV) compounds [1], and in the reductive elimination of iodobenzene from $PtI_2Ph_2(PEt_3)_2$ in methanol solution [8]. Also the reaction of $(CH_3)_3PtIQ_2$ (Q = PMe_2Ph) with $AgPF_6$ and neutral

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* The species (MCL)', $(M_2CL)'$ and (MC)' are assumed to be intimate ion pairs.

ligands (L) gives $[(CH_3)_3PtQ_2L]^+PF_6^-$ when L = C_5H_5N, $SbMe_3$ but C_2H_6 + $[CH_3PtQ_2L]^+PF_6^-$ if L = PPh_3, $AsPh_3$ or $SbPh_3$ [9]. The species $(MCL_2)'$ represents the coloured products responsible for the variation in stoichiometry; addition of water removes L and reverses reaction (4a) sothat (4b) followed by (5) and (6) occurs. Addition of excess L to the initial reaction mixture increases the rate of (4a) with respect to that of (4b) reducing the yield of cyclopropane.

The rate of gas evolution is given by

$$d[C_3H_6]/dt = k_6[(MC)'] + k_{4c}[(MCL)'][S]$$

Assuming a stationary concentration for $(MC)'$ and that CL_2 is converted to MCL almost immediately on mixing, the rate expression becomes

$$\frac{d[C_3H_6]}{dt} = \frac{k_5k_6K_3K_{4b}[CL_2][M]}{k_{-5}[M][L] + k_6} + k_{4c}K_3[CL_2][S]$$

If with $PtCl_2(C_3H_6)(4\text{-}CH_3C_5H_4N)_2$ in DMF the second term is predominant then, since the solvent concentration is constant, the reaction will be first order as found experimentally. $AsPh_3$ will be more efficient in displacing the chloride than will $SbPh_3$ and so K_3, and thus the rate is greater with the former. Reaction (4c) presumably takes place in several steps, the first being the attachment of a DMF molecule at the vacant site on the platinum. The overall activation energy is $E_{4c} + \Delta H_3$, neither of which are, of course, known.

Assuming that, with the other systems, the second term in the rate expression is negligible and, in the absence of added L, $k_6 \gg k_{-5}[M][L]$, the rate is given by;

$$d[C_3H_6]/dt = k_5K_3K_{4b}[CL_2][M]$$

and the evolution of cyclopropane is second order. For any one platinum compound, K_3 and K_{4b} (and thus the rate) will both increase in the order $SbPh_3 < AsPh_3 \ll PPh_3$. The rate will also depend on the nature of X and L through K_3 and K_{4b} and on the solvent through K_3. The overall activation energy is given by $E_5 + \Delta H_3 + \Delta H_{4b}$ and again cannot be associated with any elementary step.

In the presence of a high enough concentration of added ligand L, $k_6 \ll k_{-5}[M][L]$ and

$$\frac{d[C_3H_6]}{dt} = \frac{k_5k_6K_3K_{4b}[CL_2]}{k_{-5}[L]}$$

and the process becomes first order in the platinum compound, the rate decreasing as [L] is increased.

Conclusions

The trimethyleneplatinum(IV) complexes $PtX_2(C_3H_6)L_2$ are stable when X = Cl or Br and L is an oxygen or nitrogen-donor ligand. We showed previously [1] that these compounds decompose probably through an ionic intermediate and we were able to estimate the Pt—C bond strength to be in the region 113—124 kJ mol^{-1}. However if ligands such as alkenes, cyanide, or sulphur, phosphorus, arsenic or antimony donor ligands are coordinated to platinum then cyclopropane is eliminated rapidly at room temperature. In order to explain fully the chemical and kinetic data it has been necessary to propose a somewhat complex mechanism, but the essential feature is that if a ligand of high *trans*-effect can coordinate to platinum then cyclopropane is eliminated readily. Hence the stronger ligands such as tertiary phosphines eliminate cyclopropane more rapidly than the weaker ligands such as alkenes due largely to this greater ability to replace other ligands on platinum, and the trimethyleneplatinum(IV) complexes with the chelate ligands ethylenediamine or 2,2'-bipyridine are not readily decomposed even by tertiary phosphines. Since alkenes, which have a high *trans*-effect but a low *trans*-influence, will cause loss of cyclopropane from the trimethyleneplatinum(IV) complexes, it seems that the ready elimination of cyclopropane is not due primarily to a weakening of the Pt—C bonds in the ground state of the trimethyleneplatinum(IV) complexes but to a lowering of the activation energy for loss of cyclopropane (i.e. it is a kinetic rather than a thermodynamic effect). This can be understood if the trimethyleneplatinum(IV) is considered as being formed by overlap of filled Walsh orbitals of cyclopropane with a vacant σ-orbital on platinum with strong backbonding from filled *d*-orbitals of π-symmetry on platinum to vacant Walsh orbitals of cyclopropane [4,10]. Coordination of a competing π-acceptor ligand, such as ethylene or triphenylstibine, to platinum will facilitate the formation of the presumed intermediate cyclopropaneplatinum(II) complex (which then eliminates cyclopropane) by withdrawing π-electron density from platinum. Although, due to the complex mechanism with triphenylarsine and stibine, the activation energy for the final step (6), which leads to the elimination of cyclopropane, is not known, it must be very much less than the Pt—C bond strength in the trimethyleneplatinum(IV) moiety, and a concerted elimination step is indicated.

Experimental

Preparation and characterisation of known compounds

The trimethyleneplatinum(IV) complexes and $PtCl_2(COD)$ were prepared by standard methods [2,5,6,11] and, together with the compounds $PtX_2(DMSO)_2$ and $PtX_2 \cdot M_2$ (M = PPh_3, AsPh, $SbPh_3$; X = Cl, Br), were characterised by elemental analysis, melting point, IR and NMR spectra.

For the kinetic experiments, triphenylstibine was recrystallised first from n-propanol/water and then from acetaldehyde, triphenylarsine from acetaldehyde and triphenylphosphine from ethanol. DMSO and DMF from freshly opened bottles contained no impurities, or water, which could be detected by ^{1}H NMR, and were generally used directly, since the rate coefficients (and yields of cyclopropane) were the same within experimental error as when these solvents were purified by fractional distillation under reduced pressure.

Reactions with DMF

Dichlorotrimethyleneplatinum(IV) tetramer dissolved in DMF to give a yellow solution. On removing the solvent under vacuum a brown crystalline solid was obtained, melting range 75—82°, which darkened and decomposed after about 8 days. The IR spectra showed mainly bands due to DMF, but on adding $SbPh_3$ to a solution of the compound in $CDCl_3$ the ^1H NMR spectrum showed that cyclopropane was evolved. The ether washed solid analysed as: found: C, 21.4; H, 4.2; N, 4.9; Pt, 47.0. $C_{15}H_{33}Cl_4N_3O_3Pt_2$ calcd.: C, 21.6; H, 4.0; N, 5.0; Pt, 46.7%.

Reactions with olefins

Ethylene was passed through a solution of $[PtCl_2 \cdot C_3H_6]_4$ in THF for several hours. Removal of the solvent under vacuum gave an orange-brown solid, the IR spectrum of which showed bands at 1425 and 1022 cm^{-1} characteristic of ethylene. The ^1H NMR spectrum in acetone-d_6 showed a singlet at δ 4.75 ppm with satellites having $^2J(Pt-H)$ = 56Hz and an area of approximately half that of the central peak. No data on the NMR spectrum of Zeise's compound under the same conditions appears to be available, but for a solution of 1,3-dichloro-2-ethylene-4-pyridineplatinum(II) in $CDCl_3$ the chemical shift for the ethylenic hydrogens is δ 4.87 ppm and $^2J(Pt-H)$ = 60.6Hz [12]. It seems certain that the orange-brown product is $[PtCl_2(C_2H_4)]_2$.

Addition of COD to a DMF solution of dichlorotrimethyleneplatinum(IV) tetramer gave a yellow solution. Removal of the solvent under vacuum left a yellow crystalline solid, melting range 122—130° (dec.) which was quite stable. The solid was insoluble in acetone-d_6, but, on addition of triphenylphosphine, ^1H NMR showed the presence of free COD. The crystals analysed as: found: C, 23.0; H, 3.4; N, 2.9; Pt, 48.3. $C_{13}H_{26}Cl_4N_2O_2Pt_2$ calcd.: C, 21.4; H, 3.3; N, 3.6; Pt, 49.6%; probably they contain some $PtCl_2 \cdot COD$.

Reactions with PPh_3, $AsPh_3$ and $SbPh_3$

The evolution of cyclopropane was followed using the reaction vessel shown in Fig. 3. 10 cm^3 of the solution of platinum compound was put in bulb A and

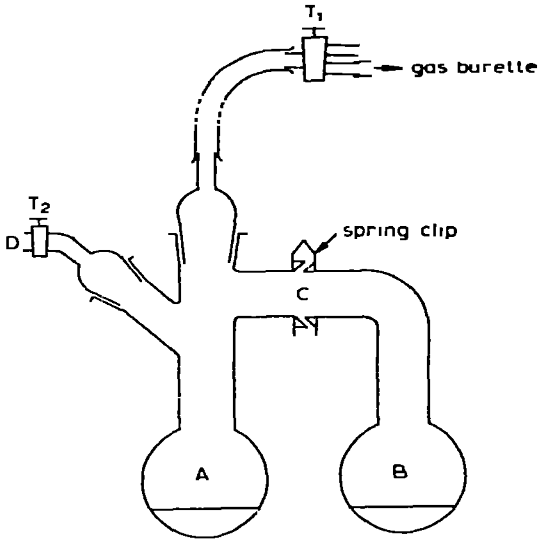

Fig. 3. Reaction vessel for kinetic experiments.

10 cm^3 of a solution of the phosphine (plus added pyridine, if appropriate) in bulb B. The two bulbs were joined by the ball and socket joint C, the reaction vessel attached to a holder in a thermostat and connected to a thermostatted gas burette (containing water) through the two-way tap T1. The vessel and gas burette were flushed out with cyclopropane from a cylinder attached at D through tap T2 and the solutions shaken to saturate them with the gas which could take several hours, but no mixing of the contents of bulbs A and B was found to occur. When saturation was complete, the shaker was stopped, the solutions mixed by rotating bulb B through 180°, and after returning B to its original position, shaking was restarted and the rate of evolution of gas followed. Increasing the rate of shaking did not alter the rate constants within experimental error. The final volume of cyclopropane produced (V_∞) was reduced to 0° and 1 atm pressure and compared with the theoretical volume calculated from the initial amount of platinum compound, assuming the gas behaves ideally.

0.2 g dibromobis(pyridine)trimethyleneplatinum(IV) and 0.3 g $SbPh_3$ (approximately a 1/2 mol ratio) were dissolved in the minimum amount of DMSO and allowed to react at room temperature in vacuo until gas evolution ceased. The degassed solution was frozen to —196° and became wine red. Degassed water was distilled onto the frozen solid and the whole allowed to warm up slowly. As soon as the mixture began to melt the red colour disappeared and a yellow solid was formed accompanied by the evolution of gas. This was collected and the IR spectrum showed it to be cyclopropane. The yellow solid was filtered off and found to be $PtBr_2(SbPh_3)_2$. The reaction was repeated using chloroform as solvent and cooling the solution. A red solid precipitated and removal of the $CHCl_3$ in vacuo gave red crystals, which turned yellow on exposure to the atmosphere.

Using dibromobis(4-methylpyridine)trimethyleneplatinum(IV) and $SbPh_3$ in $CHCl_3$, a red solid was again obtained. On warming the solid or reacting it with water in vacuo, cyclopropane was evolved as shown by the IR spectrum. Even under vacuum or on handling in a dry-box the solid tended to become yellow. Addition of $CDCl_3$ gave a red-orange solution (with undissolved yellow solid) and the ^1H NMR spectrum showed (as well as phenyl resonances) two apparent singlets at δ 0.2 and 2.28 ppm (area ratio, 1/2), the resonance at δ 0.2 ppm decreasing in intensity with time.

Using $PtCl_2(C_3H_6)(4\text{-}CH_3C_5H_4N)_2$ and $SbPh_3$ in $CHCl_3$, a peach-coloured solid was obtained, which turned yellowish as the chloroform was removed. It was handled in a dry-box; the IR spectrum in Nujol showed mainly bands corresponding to $PtCl_2(SbPh_3)_2$ but with a strong absorption at 800 cm^{-1}.

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