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The Kinetics and Mechanism of the Isomerisation of (Bromotrifluoroethylene)-bis(triphenylarsine)platinum(0) to Bromo(trifluorovinyl)bis(triphenylarsine)-platinum(II).

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SUMMARY

The kinetics of isomerisation of the alkene complex [$Pt(C_2F_3Br)(AsPh_3)_2$] to the alkenyl complex [$PtBr(CF{=}CF_2)(AsPh_3)_2$] have been studied in a range of solvents. The very small variation of isomerisation rate with the nature of the solvent suggests that the mechanism is intramolecular.

INTRODUCTION

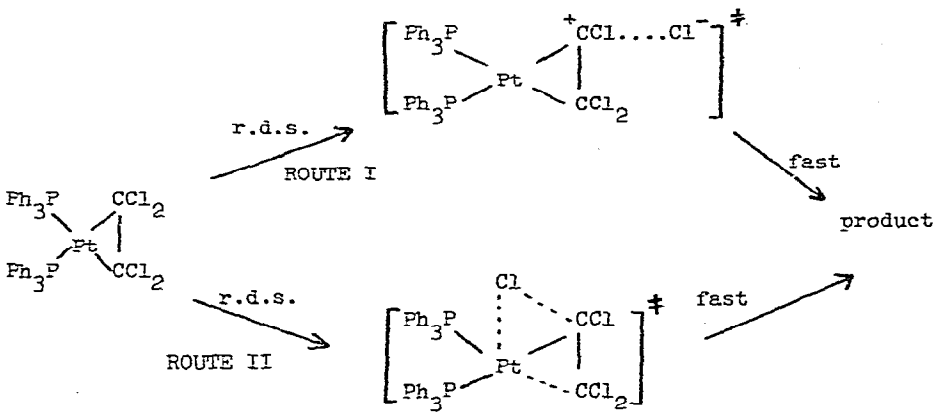
We have previously examined the kinetics of isomerisation of two chloro-alkene-bis-phosphine complexes of platinum(0):[1,2]

$$Pt(C_2Cl_4)(PPh_3)_2 \rightarrow \underline{cis}\text{-}PtCl(CCl{=}CCl_2)(PPh_3)_2$$

$$Pt(C_2HCl_3)(PPh_3)_2 \rightarrow \underline{cis}\text{-}PtCl(CH{=}CCl_2)(PPh_3)_2$$

The variation of isomerisation rates with solvent nature suggested that the mechanism of the first reaction involved rate-determining release of chloride from the chloro-alkene ligand (route I), but that the mechanism

of the latter reaction had characteristics intermediate between this effectively S_N1 mechanism and an intramolecular (effectively S_E2 with respect to the chloride) transfer of chloride from carbon to platinum (route II). Subsequent kinetic and stereochemical studies on isomerisation of analogous platinum(0) complexes of such ligands as cis- and trans-CFCl=CFCl indicated the operation of a dissociative mechanism. However observed stereochemical retention indicated that the leaving chloride could not be completely separated from the platinum at any stage, hence it was proposed that the transition state was of the form of a tight ion-pair.[3] Such an ion-pair



mechanism is a concept intermediate between a fully dissociative process and a true intramolecular process.

In view of the greater affinity of bromide than of chloride for platinum(II), we wished to examine the isomerisation of an analogous bromoalkene complex to see whether there was evidence for such a reaction occurring by an intramolecular mechanism (cf. route II). Rate constants and activation parameters for the isomerisation of $[Pt(CF_2{=}CFCl)(PMePh_2)_2]$ and of $[Pt(CF_2{=}CFBr)(PMePh_2)_2]$ in ethanol have been reported.[3] The kinetic parameters for these two isomerisations are very similar, which suggests a common mechanism, presumed to be dissociative via an ion-pair intermediate from the values of the activation entropies and the stereochemical con-

clusions from the closely related reactions mentioned above. Unfortunately the dependence of kinetic parameters on solvent was not investigated for these reactions.

The isomerisation of many bromoalkene complexes is either so rapid that one can only isolate the bromovinyl product, or so slow that accurate monitoring of rates is extremely difficult at experimentally reasonable temperatures. The isomerisation of the complex $[Pt(CF_2{=}CFBr)(AsPh_3)_2]$ to $[PtBr(CF{=}CF_2)(AsPh_3)_2]$ does take place at convenient rates, and we have therefore established the dependence of its rate of isomerisation on solvent nature.

RESULTS AND DISCUSSION

In all the solvents used, the isomerisation

$$Pt(C_2F_3Br)(AsPh_3)_2 \rightarrow Pt(Br)(CF{=}CF_2)(AsPh_3)_2$$

follows first-order kinetics. Average values for the first-order rate constants for isomerisation in several solvents are reported in Table 1. This Table also includes the empirical solvent parameters Y (Grunwald-Winstein)[4] and S (Brownstein).[5] Logarithms of isomerisation rate constants in the protic solvents are plotted against the respective solvent S values in Fig. 1. There is a reasonable correlation, as indeed there is for the analogous plot of logarithms of rate constants against solvent Y values. The kinetic results for the aprotic solvents do not fall on these correlation lines. This is not a significant result in view of the non-correlation of spectroscopic parameters for charge-transfer spectra of organometallic compounds in protic and in aprotic solvents.[8]

The slopes, R, of the graphs of logarithms of rate constants against solvent S values, for this isomerisation, the isomerisation of the similar complexes $[Pt(C_2Cl_4)(PPh_3)_2]$ and $[Pt(C_2HCl_3)(PPh_3)_2$, and the reference

TABLE 1

First-order rate constants (k_1) for the isomerisation of $[Pt(C_2F_3Br)(AsPh_3)_2]$ in a range of solvents at 35°C; solvent Y values are taken from ref. 4, S values from ref. 5.

Solvent	S	Y	$10^4 k_1/sec^{-1}$
MeOH	0.0499	-1.090	1.30
EtOH	0	-2.033	1.63
n-PrOH	-0.0158	-2.30[a]	1.01
i-PrOH	-0.0413	-2.73	0.53
n-BuOH	-0.0240		0.66
t-BuOH	-0.1047	-3.26	0.28
$CHCl_3$	-0.2000		0.77
Dioxan	-0.179		0.71

[a] Estimated via solvent Z (ref. 6) and E_T (ref. 7) values.

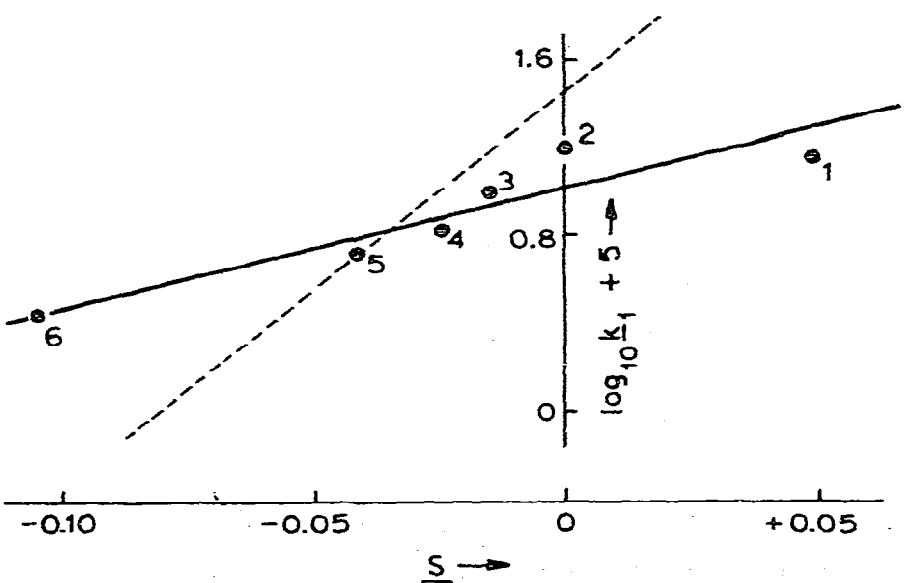


Fig. 1. The dependence of logarithms of first-order rate constants (k_1) for the isomerisation of $[Pt(C_2F_3Br)(AsPh_3)_2]$ on solvent S values; 1 MeOH, 2 EtOH, 3 n-PrOH, 4 n-BuOH, 5 i-PrOH, 6 t-BuOH. The dashed line shows the analogous dependence for isomerisation of $[Pt(C_2Cl_4)(PPh_3)_2]$ (ref. 1).

TABLE 2

Values of $\underline{R}$ and $\underline{m}$ for alkene→alkenyl complex isomerisations and for reference organic S_N1 solvolyses.

	Substrate	$\underline{R}$	$\underline{m}$	Ref.
Isomerisation:	$[Pt(C_2F_3Br)(AsPh_3)_2]$	4.9 ± 1.2	0.32 ± 0.12	This work
	$[Pt(C_2HCl_3)(PPh_3)_2]$	10.2 ± 0.5	0.54 ± 0.07	2
	$[Pt(C_2Cl_4)(PPh_3)_2]$	18.0 ± 1.0	0.86 ± 0.07	1
Solvolysis:	Me_3CCl	36	1.00	4
	Me_3CBr		0.92	9

organic S_N1 reaction are reported in Table 2. The slopes, $\underline{m}$, of the analogous $\underline{Y}$ value plots are also included in this Table, as are the standard errors of each slope. In all cases the $\underline{R}$ and $\underline{m}$ values refer to isomerisation in protic solvents only. The distribution of the $\underline{R}$ and $\underline{m}$ values in Table 2 suggests that whereas the mechanism of isomerisation of the tetrachloroethylene complex probably approximates to S_N1 carbon-chloride bond breaking, the mechanism of isomerisation of the bromotrifluoroethylene complex is closer to intramolecular. This mechanistic trend is consistent with the known affinities of platinum(II) for chloride and bromide.

The reactivity of this type of complex towards isomerisation is greatly affected by the nature of the Group V ligands and by the nature of the non-migrating atoms in the coordinated olefin. Whether these variables also have a significant effect on the isomerisation mechanism is a pertinent question which, as stated in the Introduction, chemical difficulties at present prevent us from answering. A few qualitative observations on the rearrangement of $[Pt(C_2F_3Br)(PMePh_2)_2]$ to $[PtBr(CF{=}CF_2)(PMePh_2)_2]$ under various conditions have been reported,[10] but the authors did not provide a detailed discussion of the mechanism of the bromide transfer step.

EXPERIMENTAL

The compound $[Pt(C_2F_3Br)(AsPh_3)_2]$ was prepared as described in the literature.[11] This bromotrifluoroethylene compound has λ_{max} = 230 nm; the bromotrifluoroalkenyl product has λ_{max} = 231, 253 nm. The most satisfactory wavelength for monitoring the kinetics of isomerisation was found to be 265 nm. For the kinetic runs solutions of concentration ca. 10^{-4} mol dm^{-3} $[Pt(C_2F_3Br)(AsPh_3)_2]$ were used. Runs were conducted in 10 mm silica cells in the thermostatted cell compartment of a Unicam SP800A recording spectrophotometer. Rate constants were computed (Elliott 4130) using a standard least mean squares program.

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