DIFFERENTIAL SCANNING CALORIMETRY STUDY OF β-HYDRIDE ELIMINATION FROM *cis*- AND *trans*-CHLORO-(n-ALKYL)BIS(TRIETHYLPHOSPHINE)PLATINUM(II) COMPLEXES

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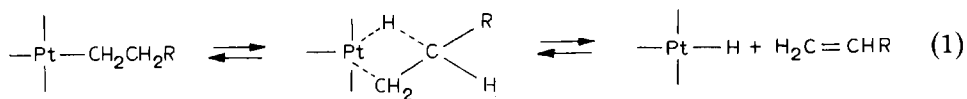
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Summary

The enthalpies and activation energies of β-hydride elimination from the complexes *cis*- and *trans*-[Pt(PEt$_3$)$_2$(n-alkyl)Cl] (n-alkyl = Et, Pr, Bu) leading to *trans*-[Pt(PEt$_3$)$_2$(H)Cl] and olefins are reported. A tentative value of 573 kJ mol^{-1} has been derived for the bond energy, E(Pt–H), in *trans*-[Pt(PEt$_3$)$_2$(H)Cl].

The relative ease with which σ bonds between carbon and a transition metal can be made or broken is of fundamental importance in a variety of organometallic, biological and catalytic systems [1]. The relatively low thermal stability of many transition-metal alkyl complexes has been associated with the availability of decomposition pathways having low activation energies denied to their Main-Group analogues. One such decomposition route is β-elimination, which can be represented by eq. 1.

$$\text{—Pt—CH}_2\text{CH}_2\text{R} \rightleftharpoons \text{—Pt} \begin{array}{c} \text{H} \\ \diagup \\ \text{CH}_2 \end{array} \text{C} \begin{array}{c} \text{R} \\ \diagdown \\ \text{H} \end{array} \rightleftharpoons \text{—Pt—H} + \text{H}_2\text{C}=\text{CHR} \qquad (1)$$

We have already shown [2] that complexes of the type *cis*-[Pt(PEt$_3$)$_2$(n-alkyl)Cl], in contrast to the relative inertness of their *trans* analogs, undergo in solution a facile and irreversible β-hydride elimination whose rate is almost unaffected by the length of the aliphatic chain. This fact, together with the paucity of thermochemical data on complexes of platinum with phosphine or alkyl ligands [3], prompted us to carry out a DSC study of the thermal decomposition of a series of structurally related complexes *cis*- and *trans*-[Pt(PEt$_3$)$_2$(R)Cl] (R = ethyl, n-propyl and n-butyl).

TABLE 1

PRODUCTS AND CONDITIONS IN THE β-HYDRIDE ELIMINATION OF SOME ALKYLPLATINUM(II) COMPLEXES

Complex	Reaction temperature (K)	Hydride (%)	Alkenes (%)						others
			Ethene	Propene	But-1-ene	cis-But-2-ene	trans-But-2-ene		
(1) cis-[Pt(PEt$_3$)$_2$(Et)Cl]	423	80	97						3
(2) trans-[Pt(PEt$_3$)$_2$(Et)Cl]	463	85	97						3
(3) cis-[Pt(PEt$_3$)$_2$(n-Pr)Cl]	373	71		99					1
(4) trans-[Pt(PEt$_3$)$_2$(n-Pr)Cl]	423	86		97					3
(5) cis-[Pt(PEt$_3$)$_2$(n-Bu)Cl]	373	75			83	9	6		2
(6) trans-[Pt(PEt$_3$)$_2$(n-Bu)Cl]	418	100			76	9	12		3

TABLE 2

DSC ENTHALPY AND ACTIVATION ENERGY DATA FOR THERMAL β-HYDRIDE ELIMINATION FROM SOME PLATINUM(II) COMPLEXES

Complex	M.p. (K)	$\Delta H_{m.p.}$ (kJ mol^{-1})	Temperature range (K)	$\Delta H_{reaction(1)}$ (kJ mol^{-1})	$E_{a(1)}$ (kJ mol^{-1})	log A (s^{-1})
(1) cis-[Pt(PEt$_3$)$_2$(Et)Cl]	337	20	418–453	−86±4	41±4	3.7 ±0.5
(2) trans-[Pt(PEt$_3$)$_2$(Et)Cl]	330	30	463–498	−66±3	20±2	0.94±0.2
(3) cis-[Pt(PEt$_3$)$_2$(n-Pr)Cl]	350	17	358–388	−129±8	23±1	2.3 ±0.2
(4) trans-[Pt(PEt$_3$)$_2$(n-Pr)Cl]	325	16	418–433	−69±3	32±7	3.3 ±0.9
(5) cis-[Pt(PEt$_3$)$_2$(n-Bu)Cl]	341	21	353–393	−133±8	33±1	3.7 ±0.1
(6) trans-[Pt(PEt$_3$)$_2$(n-Bu)Cl]	316	17	398–423	−63±4	15±0.5	1.2 ±0.06
(7) trans-[Pt(PEt$_3$)$_2$(H)Cl]	355	18				

Experimental

The synthesis of the platinum complexes has been reported elsewhere [4]. Samples were characterized by elemental analysis, melting points, UV, IR, and ^{1}H and ^{31}P NMR spectra.

Differential scanning calorimetry (DSC) studies were carried out on a Perkin–Elmer DSC-2 instrument equipped with a computer data-station 3600 Perkin–Elmer and a TADS program. The instrument was preset at 308 K and the weighed sample (1–3 mg), sealed in aluminium pans with a perforated cap, was either heated at 5° min^{-1} (dynamic tests) or rapidly brought to a predetermined temperature (isothermal tests). All experiments were carried out under nitrogen. The values of the enthalpies of reaction obtained by the two methods were comparable, and are reported in Table 2 as the statistical mean of at least five experiments.

The energies of activation were calculated from isothermal measurements carried out at various temperatures. The weight loss was obtained using a Perkin–Elmer TGS-2 thermoanalyzer under the conditions used for the DSC experiments. The yield of the reaction was also determined by comparing the area of the melting peak of the hydride product with that of the unchanged starting material in the mixture recovered from the isothermal experiments.

The volatile products were analyzed using a Fractovap GV Carlo Erba gas chromatograph with a 80–100 Carbopack/0.15% picric acid column. Products were identified by comparison of their retention times with those of authentic samples.

Results and discussion

The complexes decompose above their melting points to give *trans*-[Pt(PEt$_3$)$_2$(H)Cl] and volatile products (see Table 1). In the case of the ethyl and n-propyl derivatives the only volatile products were ethene and 1-propene respectively, while for the n-butyl derivative 1-butene, *cis*-2-butene and *trans*-2-butene were detected. Under the experimental conditions described above, the only reaction which went to completion was the thermal decomposition of *trans*-[Pt(PEt$_3$)$_2$(n-Bu)Cl] which gave a quantitative yield of hydrido product. Lower yields and unchanged alkyl complex were found in all the other cases, irrespective of whether the starting material was a *cis* or a *trans* isomer. This seems unlikely to be due to a reversible equilibrium, since it is well known that insertion of olefins into the Pt–H bond of *trans*-[Pt(PEt$_3$)$_2$(H)Cl], at least in solution and under pressure, always leads to a *trans* geometry for the corresponding alkyl complex [5]. If it is the presence of olefins in the melt that prevents the thermal decomposition of the total amount of alkyl complex, their effect must be felt in the early stages of the process.

The measured enthalpies of reactions as shown in eq. 2, corrected for the unreacted material and reported in Table 2, indicate that β-hydride elimination is a

$$cis/trans\text{-}\left[Pt(PEt_3)_2(n\text{-alkyl})Cl\right] \rightarrow trans\text{-}\left[Pt(PEt_3)_2(H)Cl\right] + olefins \qquad (2)$$
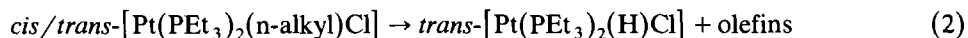
thermodynamically favorable process. If we assume that these enthalpies of decomposition can be regarded as being at the same temperature and that the differences between the enthalpies of evaporation of the reactant [Pt(PEt$_3$)$_2$(n-alkyl)Cl] and of the product *trans*-[Pt(PEt$_3$)$_2$(H)Cl] are reasonably constant and small for various alkyls and for isomers, then the measured enthalpies of decomposition should be

close to those in the gas phase. Similar reasoning was used by Mortimer et al. [6] in deriving bond dissociation enthalpies for the attachment of various ligands to platinum. Bearing in mind that any particular reaction involves C–H and Pt–C bond breaking and C=C and Pt–H bond formation, it appears that the measured enthalpies in Table 2 are determined by the greater dissociation enthalpy of the metal–hydride bond compared with that of the metal–alkyl bond. Using the values $E(C-C)$ 358.46 kJ mol^{-1}, $E(C-H)_s$ 407.40 kJ mol^{-1} and $E(C=C)$ 556.50 kJ mol^{-1} it is possible to derive a value for the difference in bond dissociation enthalpies $D(Pt-H) - D(Pt-C)$ of 274 ± 3 kJ mol^{-1} for the *trans* compounds and of 324 ± 25 kJ mol^{-1} for the *cis* isomers. This difference may well reflect a minor bond-enthalpy contribution by the alkyl group *trans* to the strong activating phosphine ligand with respect to that *trans* to chloride, while steric crowding may be a contributory factor. A detailed study by Skinner et al. of the thermal decomposition of platinum complexes containing phosphine ligands has given a value of 249 kJ mol^{-1} for the bond enthalpy contribution of Pt–CH$_3$ in *cis*-[Pt(PEt$_3$)$_2$MeCl] [7]. This value can be used to derive a tentative value of 573 kJ mol^{-1} for the Pt–H bond enthalpy contribution in *trans*-[Pt(PEt$_3$)$_2$(H)Cl].

Reproducible regular DSC curves were obtained from the reactions carried out isothermally at various temperatures, and the activation energy was calculated using Barton's equation [8]:

$$\ln r_\alpha = \ln A\, f(\alpha) - E/RT$$

The salient feature of the results shown in Table 2 is that the activation energies are low, and in all cases much lower than the enthalpies of decomposition. This is a further confirmation of the well known kinetic lability of n-alkyl derivatives [8] and that β-hydride elimination is a favorable pathway for thermal decomposition.

Intimate mixtures of *trans*-[Pt(PEt$_3$)$_2$(Et)Cl] and free PPh$_3$ were thermolysed as previously described for the pure compound. The added phosphine melts and considerably inhibits the β-hydride elimination, suggesting that, if solvent effects are not involved, a dissociative loss of phosphine is a pre-requisite for the occurrence of the process, as is the case for the decomposition of dialkyl and dicycloalkylbis(phosphine)platinum(II) complexes in non polar solvents [9]. In the case of *cis*-[Pt(PPh$_3$)$_2$(Bu)$_2$] [10] dissociation of a phosphine ligand produces a vacant coordination site, then 1-butene is eliminated and the resulting transient n-butyl(hydrido)platinum(II) intermediate undergoes intramolecular elimination to give n-butane and platinum(0) products. As shown in this work, the thermal decomposition of the corresponding chloroalkyl complexes leads to a stable metal hydrido product, and only olefins are formed.

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