

REACTIONS AND PROPERTIES OF SOME TRIMETHYLENEPLATINUM(IV) COMPLEXES

I. THERMAL DECOMPOSITION STUDIES

PETER W. HALL, RICHARD J. PUDDPHATT, KENNETH R. SEDDON and CHARLES F.H. TIPPER*

Donnan Laboratories, The University, P.O. Box 147, Liverpool L69 3BX, (Great Britain)

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Summary

The thermal decomposition of the complexes $\text{PtX}_2(\text{C}_3\text{H}_6)$, $\text{PtX}_2(\text{C}_3\text{H}_6)\text{L}_2$ and $\text{PtX}_2(\text{C}_3\text{H}_6)(\text{L}-\text{L})$ [where $\text{X} = \text{Cl}, \text{Br}$; $\text{L} = \text{pyridine}, 4\text{-methylpyridine}$; $\text{L}-\text{L} = 2,2'\text{-bipyridyl}, \text{ethylenediamine}$] has been studied by differential scanning calorimetry and thermogravimetric analysis. The first estimated Pt—C bond strength for platinum—trimethylene complexes is reported.

Introduction

Since their discovery in 1955 [1], the complexes $\text{PtX}_2(\text{C}_3\text{H}_6)$ and $\text{PtX}_2(\text{C}_3\text{H}_6)\text{L}_2$ (where $\text{X} = \text{Cl}, \text{Br}$; $\text{L} = \text{amine ligand}$) have been the subject of much discussion. Although originally formulated as cyclopropane—platinum(II) complexes, the compounds have now been established as trimethyleneplatinum(IV) compounds [2–7]. Despite extensive studies of their chemical [5, 8–10], structural [4,5] and spectroscopic [2,3,6,7] properties, there is a dearth of information about their thermal behaviour. There have only been qualitative reports that, upon heating under unspecified conditions, $[\text{PtCl}_2(\text{C}_3\text{H}_6)]_4$ evolves cyclopropane and that $\text{PtCl}_2(\text{C}_3\text{H}_6)(\text{py})_2$ gives a mixture of cyclopropane, propene and chloropropane species [2,5]. We report here the results of a study of the thermal decomposition of the complexes $\text{PtX}_2(\text{C}_3\text{H}_6)$ ($\text{X} = \text{Cl}, \text{Br}$), $\text{PtX}_2(\text{C}_3\text{H}_6)\text{L}_2$ ($\text{X} = \text{Cl}, \text{Br}$; $\text{L} = \text{pyridine (py)}, 4\text{-methylpyridine } (\gamma\text{-pic})$) and $\text{PtX}_2(\text{C}_3\text{H}_6)(\text{L}-\text{L})$ ($\text{X} = \text{Cl}, \text{Br}$; $(\text{L}-\text{L}) = 2,2'\text{-bipyridyl (bipy)}, \text{ethylenediamine (en)}$) by differential scanning calorimetry and thermogravimetric analysis, gaseous products being identified by gas chromatography and mass spectroscopy. We also report the first estimates of the mean Pt—C bond strengths in these complexes.

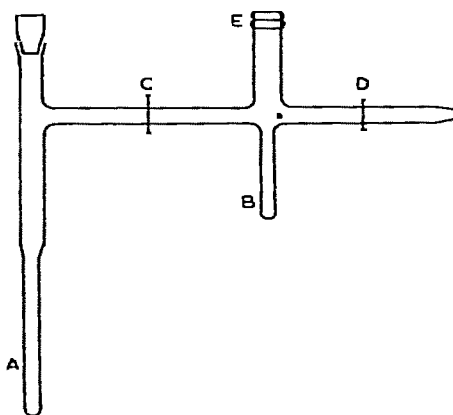


Fig. 1. Apparatus for static pyrolyses.

Results and discussion

Static pyrolyses

The apparatus used for the static pyrolyses is shown in Fig. 1, arm A (inserted into a muffled oven) containing the sample, arm B being the cold finger, C and D being greaseless taps and E being a silicone rubber septum (attached via a glass-metal seal). Each complex (ca. 0.2 g) was pyrolysed in vacuo at two different temperatures, the vapours being immediately condensed out at -196° . When each pyrolysis was complete, the condensate was isolated from the solid residue and allowed to reach equilibrium at room temperature. A minimum of five samples were removed, via the septum, by means of a locking gas syringe, and analyzed by gas chromatography. The volatile products of the pyrolyses were cyclopropane and propene. Table 1 lists the mole fraction, x , of propene in the propene/cyclopropane mixtures produced at 132 and 177° .

The maximum estimated error in the values of x was $\pm 5\%$. The temperatures were selected as being just below T_1 and just above T_1 (as determined by differential scanning calorimetry).

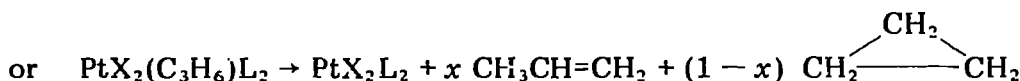
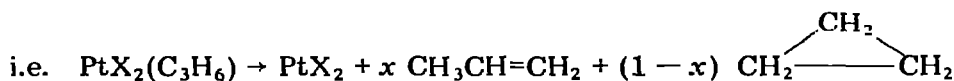
TABLE I
MOLE FRACTION (x) OF PROPENE PRODUCED BY PYROLYSIS AT TEMPERATURE T ($^{\circ}\text{C}$)

Complex	x	
	T 132 $^{\circ}$	T 177 $^{\circ}$
$[\text{PtCl}_2(\text{C}_3\text{H}_6)]_4$	0.62	0.72
$[\text{PtBr}_2(\text{C}_3\text{H}_6)]_4$	0.69	0.63
$\text{PtCl}_2(\text{C}_3\text{H}_6)(\text{py})_2$	0.81	0.78
$\text{PtBr}_2(\text{C}_3\text{H}_6)(\text{py})_2$	0.86	0.79
$\text{PtCl}_2(\text{C}_3\text{H}_6)(\gamma\text{-pic})_2$	0.90	0.88
$\text{PtBr}_2(\text{C}_3\text{H}_6)(\gamma\text{-pic})_2$	0.71	0.78
$\text{PtCl}_2(\text{C}_3\text{H}_6)(\text{en})$	0.22	0.67
$\text{PtBr}_2(\text{C}_3\text{H}_6)(\text{en})$	0.17	0.35
$\text{PtCl}_2(\text{C}_3\text{H}_6)(\text{bipy})$	0.60	0.52
$\text{PtBr}_2(\text{C}_3\text{H}_6)(\text{bipy})$	0.64	0.66

In a separate experiment, the effect of allowing the gaseous products to stand over the platinum-containing products during the pyrolysis was investigated. A slow interconversion of cyclopropane to propene was observed over a period of hours. This was not unexpected, as cyclopropane is known to isomerise to propene between 400 and 500° in the gas phase, and between 100 and 200° in the presence of a Group VIII metal [11].

Differential scanning calorimetry studies

The results of the DSC studies (T_i , T_p , T_f and ΔH_{exp}) are listed in Table 2. In all cases, except that of $\text{PtX}_2(\text{C}_3\text{H}_6)(\text{en})$, the transitions correspond to a quantitative loss of C_3H_6 (as indicated by the TGA studies):



The figures quoted in Table 2 are the mean of several experiments. The errors in the temperature values are $\pm 2^\circ$.

The DSC curves for the complexes $\text{PtX}_2(\text{C}_3\text{H}_6)(\text{bipy})$ do not indicate any reactions with a positive or negative enthalpy change until 356°. However, both TGA and static pyrolysis experiments indicated that quantitative loss of C_3H_6 occurred at about 200°. It was thus assumed that the enthalpy change for the loss of C_3H_6 from the bipyridyl complexes was zero.

The kinetics of decomposition of the complexes $\text{PtX}_2(\text{C}_3\text{H}_6)$ and $\text{PtX}_2(\text{C}_3\text{H}_6)\text{L}_2$ (where $\text{X} = \text{Cl}, \text{Br}$; $\text{L} = \text{py}, \gamma\text{-pic}$) were studied by an isothermal DSC technique. The sample was rapidly heated to ambient temperature (below T_i) for the reaction. After a time lag, decomposition commenced, the rate rising rapidly to a maximum and then falling again to zero. The time, t , between the ambient temperature being initially achieved and the maximum on the DSC curve was found to be independent of the sample size, and $1/t$ was taken as the

TABLE 2
DSC RESULTS

Complex	T_i (°C)	T_p (°C)	T_f (°C)	ΔH_{exp} (kJ mol ⁻¹)	$E(\text{Pt}-\text{C})$ (kJ mol ⁻¹)	E_a (kJ mol ⁻¹)
$[\text{PtCl}_2(\text{C}_3\text{H}_6)]_4$	148	157	169	-10.4 ± 0.2^a	119.5 ^a	158 ± 5^a
$[\text{PtBr}_2(\text{C}_3\text{H}_6)]_4$	134	139	165	-3.5 ± 0.2	121.5 ^a	146 ± 6^a
$\text{PtCl}_2(\text{C}_3\text{H}_6)(\text{py})_2$	147	155	165	-17.5 ± 0.3	117.0	226 ± 18
$\text{PtBr}_2(\text{C}_3\text{H}_6)(\text{py})_2$	142	158	167	-17.0 ± 0.1	117.4	219 ± 19
$\text{PtCl}_2(\text{C}_3\text{H}_6)(\gamma\text{-pic})_2$	152	159	178	-28.8 ± 0.6	112.9	209 ± 16
$\text{PtBr}_2(\text{C}_3\text{H}_6)(\gamma\text{-pic})_2$	144	149	177	-23.0 ± 1.2	114.2	202 ± 23
$\text{PtCl}_2(\text{C}_3\text{H}_6)(\text{en})$	148	169	176	-24.7 ± 0.7		
$\text{PtBr}_2(\text{C}_3\text{H}_6)(\text{en})$	147	161	173	-19.9 ± 0.4		
$\text{PtCl}_2(\text{C}_3\text{H}_6)(\text{bipy})$				0.0	121.4	
$\text{PtBr}_2(\text{C}_3\text{H}_6)(\text{bipy})$				0.0	123.7	

^aCalculated for the unit $\text{PtX}_2(\text{C}_3\text{H}_6)$.

rate parameter. Arrhenius plots of $\log_{10}(1/t)$ versus $10^3K/T$ were linear. Computer least squares analysis of the data gave the slopes and hence the activation energies, E_a , which are listed in Table 2.

Thermogravimetric analysis (TGA)

The results from the thermogravimetric analyses of $[\text{PtCl}_2(\text{C}_3\text{H}_6)]_4$, $[\text{PtBr}_2(\text{C}_3\text{H}_6)]_4$, $\text{PtCl}_2(\text{py})_2$ and PtCl_2 are reported in Table 3, and typical TGA/DTG curves are given in Fig. 2 for $[\text{PtCl}_2(\text{C}_3\text{H}_6)]_4$. The curves obtained for the complexes $\text{PtX}_2(\text{C}_3\text{H}_6)\text{L}_2$ (where $\text{X} = \text{Cl}, \text{Br}$; $\text{L} = \text{py}, \gamma\text{-pic}$) were all of the same general shape, showing a stable phase at about 230° . However, the weight losses found for these complexes were in all cases several percent higher than the theoretical loss for all the C_3H_6 . This was due to the partial sublimation of PtX_2L_2 prior to its decomposition. The residue from isothermal TGA experiments with the temperature locked at ca. 150° , analysed as PtX_2L_2 , and mass spectroscopic analysis of the volatile showed only cyclopropane and propene, with no trace of free amine. The decomposition pathway above 200° was that anticipated for the decomposition of PtX_2L_2 , being similar to that of $\text{PtCl}_2(\text{py})_2$ (see Table 3).

The TGA of $\text{PtX}_2(\text{C}_3\text{H}_6)(\text{en})$ [$\text{X} = \text{Cl}, \text{Br}$] showed a large initial weight loss as compared with the theoretical values for loss of C_3H_6 . When the decomposition was carried out within the direct insert probe of a mass spectrometer, at temperatures of $100\text{--}150^\circ$, the volatile decomposition products were identified as principally propene, cyclopropane, and hydrogen halide, with small amounts of ethylenediamine.

General discussion

The thermogravimetric analysis results have established that, with the exception of the ethylenediamine complexes, the ΔH_{exp} values for the thermal reactions, listed in Table 2, all correspond to the loss of C_3H_6 from the complex. Consider reaction Scheme 1.

TABLE 3
TGA RESULTS

Stable phase thermal reaction	Temperature range ($^\circ\text{C}$)	Total % wt. loss	
		Found	Calcd.
$\text{PtCl}_2(\text{C}_3\text{H}_6)$	20—205		
$\text{PtCl}_2(\text{C}_3\text{H}_6) \rightarrow \text{PtCl}_2$	205—235	11.1	13.66
$\text{PtCl}_2 \rightarrow \text{PtCl}_{0.5}$	235—300	30.6	30.92
$\text{PtCl}_{0.5} \rightarrow \text{Pt}$	300—610	35.6	36.68
$\text{PtBr}_2(\text{C}_3\text{H}_6)$	20—180		
$\text{PtBr}_2(\text{C}_3\text{H}_6) \rightarrow \text{PtBr}_2$	180—240	9.8	10.59
$\text{PtBr}_2 \rightarrow \text{Pt}$	240—670	51.0	50.87
$\text{PtCl}_2(\text{py})_2$	20—200		
$\text{PtCl}_2(\text{py})_2 \rightarrow \text{Pt}$	200—600	55.4	54.02
PtCl_2	20—300		
$\text{PtCl}_2 \rightarrow \text{Pt}$	300—530	27.6	26.68

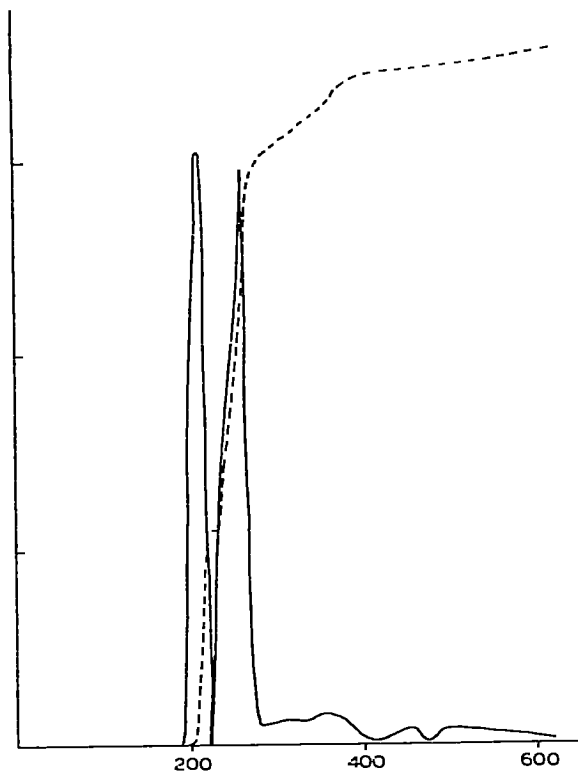
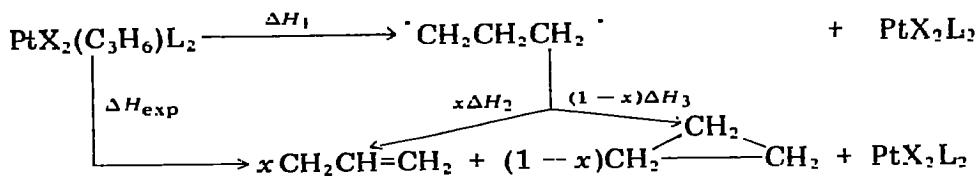
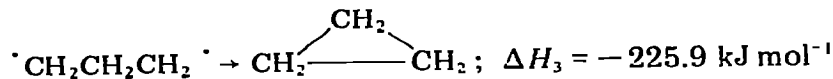


Fig. 2. TGA (broken curve) and DTG (solid curve) of $[\text{PtCl}_2(\text{C}_3\text{H}_6)]_4$. x-axis, temperature ($^{\circ}\text{C}$); y-axis, % wt. loss (to left of axis), rate of wt. loss (to right of axis) (arbitrary units).

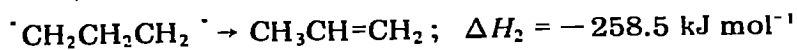
SCHEME 1



It is known that ΔH_f° for cyclopropane [12] is $53.13 \text{ kJ mol}^{-1}$ and ΔH_f° for propene [13] is $+20.5 \text{ kJ mol}^{-1}$. Also [12], for:



Thus, it can be calculated that:



Hence, ΔH_{exp} from DSC data, is given by:

$$\Delta H_{\text{exp}} = \Delta H_1 + x\Delta H_2 + (1-x)\Delta H_3$$

Assuming that the first step in the decomposition only involves the breaking of two Pt—C bonds, then the strength of these bonds, $E(\text{Pt—C})$, is given by:

$$E(\text{Pt—C}) = \frac{1}{2}[\Delta H_{\text{exp}} - x\Delta H_2 - (1-x)\Delta H_3]$$

The values of $E(\text{Pt—C})$ calculated from the experimental values of ΔH_{exp} and x (at 177°C), and the values of ΔH_2 and ΔH_3 quoted, are given in Table 2. The values of x at 177° were selected as these most closely represent the conditions of the DSC experiments. For this estimate of $E(\text{Pt—C})$, two major assumptions have been made: firstly, that there is no difference in energy between $\text{PtX}_2(\text{C}_3\text{H}_6)\text{L}_2$ and its decomposition products other than that caused by breaking Pt—C bonds, and secondly, that the enthalpy changes are temperature independent. These approximations are common in palladium and platinum thermochemistry [14–16] and it is believed that the quoted values are reasonably accurate.

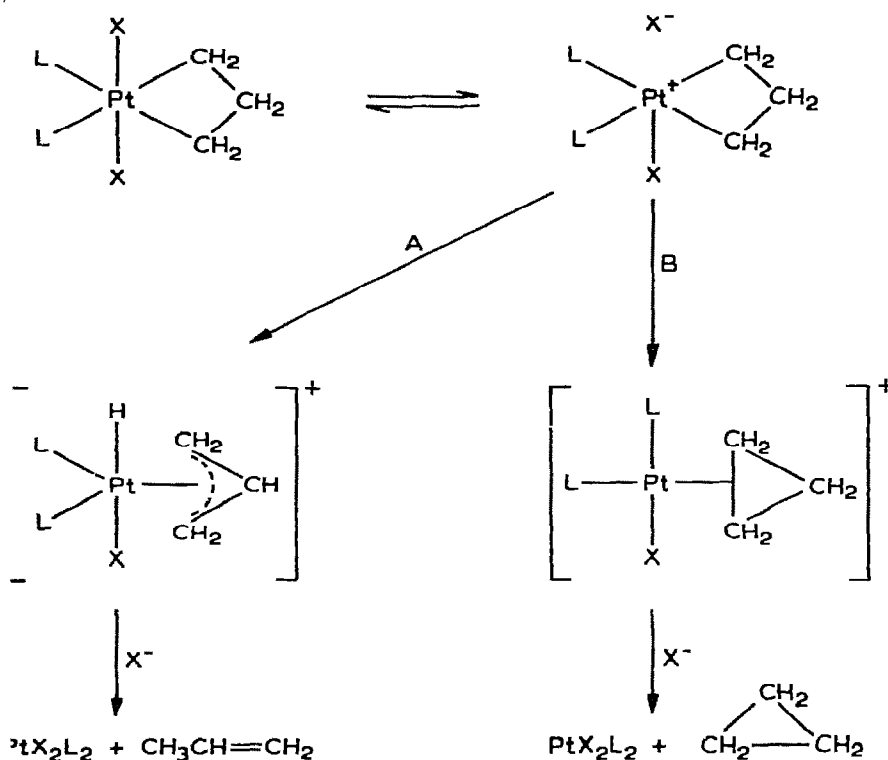
The values of $E(\text{Pt—C})$ for the trimethyleneplatinum(IV) complexes lie in the range 112–124 kJ mol⁻¹. These are significantly lower than the values of 160 kJ mol⁻¹ determined for $E(\text{Pt—CH}_3)$ in $(\text{C}_5\text{H}_5)\text{Pt}(\text{CH}_3)_3$ [17] and 144 kJ mol⁻¹ determined for $E(\text{Pt—CH}_3)$ in $\text{PtI}(\text{CH}_3)_3(\text{PMe}_2\text{Ph})_2$ [18]. The weaker bonding of the trimethylene moiety is presumably a reflection of the strain inherent in the metallocyclobutane ring. It is also interesting to compare these values with the bond energy of 270 kJ mol⁻¹ which has been determined for the platinum—acetylene linkage in $\text{PtClMe}(\text{AsMe}_3)_2(\text{CF}_3\text{C}\equiv\text{CCF}_3)$ [19], which exhibit a high degree of synergism.

The values of $E(\text{Pt—C})$ for the trimethylene complexes follow the expected trend for the *trans* influence of the ligands [20–22]. It is also of interest to note that, for pairs of complexes $\text{PtX}_2(\text{C}_3\text{H}_6)\text{L}_2$, $E(\text{Pt—C})$ is slightly higher in the bromo complexes than in the chloro complexes. If this effect is significant, it may be considered as being due to the *cis* influence [21,22] of the halide ligands, the chloride exhibiting a greater effect than the bromide.

A final point of interest is the wide range of values of x listed in Table 1. It would appear that the ligands having high *trans* influence give the highest ratio of cyclopropane/propene. Thus, of the complexes studied, those having ethylenediamine ligands gave the most cyclopropane, in accord with the observation made earlier [6] that ethylenediamine has a higher *trans* influence than pyridine or 4-methylpyridine in these complexes; and complexes containing tertiary phosphine, arsine or stibine ligands or cyanide ligands (all of which have a very high *trans* influence) evolve only cyclopropane at or below room temperature [23]. However, for the ligands of low *trans* influence, the *trans* influence series is $\gamma\text{-pic} > \text{py} > \text{Cl}, \text{Br} > \text{bipy}$ while the proportion of cyclopropane evolved on decomposition of the corresponding trimethyleneplatinum(IV) complexes follows the reverse series.

It has been shown that the thermal decomposition of trialkylplatinum(IV) complexes, R_3PtXL_2 , proceeds by dissociation of a ligand (L or X), followed by reductive elimination or β -elimination processes [15,18], and a similar mechanism can account for the products obtained from the trimethyleneplatinum(IV) complexes, which is shown in Scheme 2.

SCHEME 2



Mechanism A is favoured for ligands of low *trans* influence. It involves a β -elimination reaction to give an intermediate hydrido(π -allyl)platinum(IV) complex which then eliminates propene. Decomposition of substituted trimethyleneplatinum complexes to π -allylplatinum complexes on heating has been observed previously [8], and the mechanism is similar to that proposed for the decomposition of ethylplatinum(IV) complexes [15]. Mechanism B, which involves cleavage of the Pt—C σ bonds in one concerted step, giving an intermediate cyclopropaneplatinum(II) complex, is favoured for ligands of high *trans* influence. It is entirely analogous with the proposed mechanism of reductive elimination of ethane from trimethylplatinum(IV) complexes [18].

The decomposition of solids can be a complex process. It is probable that, for these compounds, *t* represents an induction period related to nucleation. According to the mechanism above, this initial process may depend on fission of the Pt—X bond: this hypothesis is supported by the observation that the decomposition of the tetrameric species, $[\text{PtX}_2(\text{C}_3\text{H}_6)]_4$, which contain halide bridges, had much lower activation energies than those of the monomeric $\text{PtX}_2(\text{C}_3\text{H}_6)\text{L}_2$ complexes.

Experimental

Preparation of complexes

The compounds were prepared by standard literature methods [1-3,5], and were characterised by elemental analysis, melting point, IR and NMR spectra.

Differential scanning calorimetry

The reaction enthalpies were measured on a Perkin—Elmer DSC-1B instrument, and the temperatures T_i , T_p and T_f refer to the initial, 'peak', and final temperatures of the reaction, respectively [24]. The typical sample size was 3-8 mg, the sample being contained in a 'crimped' aluminium sample pan, the holder assembly being flushed with nitrogen at ca. 17 cm³ min⁻¹. The scanning speed used was 16° min⁻¹, and the instrument was calibrated with a pure sample of indium.

Thermogravimetric analysis

The vacuum thermograms were recorded upon a Stanton Massflow Thermobalance MF-FS. The balance was operated at 10⁻⁴ mm Hg, the temperature rise being programmed at 6° min⁻¹, typical sample size being 0.15 g. The DTG curves were obtained upon a time differential of 1.25 min. The temperature range for thermal reaction was measured between successive minima (or points of inflection) upon the DTG curve. Thermograms of standard compounds under these conditions have been reported previously [25].

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