THERMAL DECOMPOSITION OF RHODIUM(III) AND IRIDIUM(III) SATURATED METALLACYCLES

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(Received June 16th, 1980)

Summary

The thermal decomposition of the complexes $(\eta^5\text{-}C_5Me_5)\overline{M(CH_2)}_n(PPh_3)$ (M = Rh, n = 4, 5, 6; M = Ir, n = 4, 5) has been studied by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). In all cases three decomposition steps were identified, the first being the first order loss of the polymethylene moiety with formation of mixtures of the corresponding n-alkenes. The activation energy for this decomposition step ranged from 33 to 38 kcal/mol for the rhodium compounds and from 63 to 77 kcal/mol for the iridium compounds. A brief discussion of the decomposition mechanism and an estimate of the rhodium—carbon and iridium—carbon σ-bond dissociation energy are presented.

Introduction

In continuation of our studies on the chemistry of Group VIII transition metal metallacycloalkanes [1] a quantitative study was undertaken of the behaviour of the isostructural rhodium(III) and iridium(III) derivatives, I and II, upon heating in the solid state.
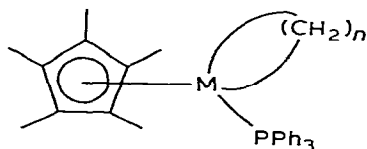
$$
\begin{aligned}
&(\text{I}a,\ M = Rh,\ n = 4;\\
&\ \text{I}b,\ M = Rh,\ n = 5;\\
&\ \text{I}c,\ M = Rh,\ n = 6;\\
&\text{II}a,\ M = Ir,\ n = 4;\\
&\text{II}b,\ M = Ir,\ n = 5)
\end{aligned}
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This is apparently the first solid-state thermolysis study of five-, six-, and seven-membered metallacycles, though some platinacyclobutane complexes have been subjected to such a study [2]. There have been studies in the past of thermolyses in the presence of a solvent [3].

The reaction kinetics were investigated by thermogravimetric analysis (TGA) and the volatile products were isolated and identified. A mechanism for the decomposition of the metallacyclic moiety is proposed and the first estimates of the mean Rh—C and Ir—C bond dissociation energies are reported.

Results and discussion

The decomposition of I and II in the solid state was studied by thermo-gravimetry (TG) and differential scanning calorimetry (DSC).

The TG and DSC curves for the rhodium compounds I are reported in the Figure 1. These compounds exhibit similar TG curves, with small differences in
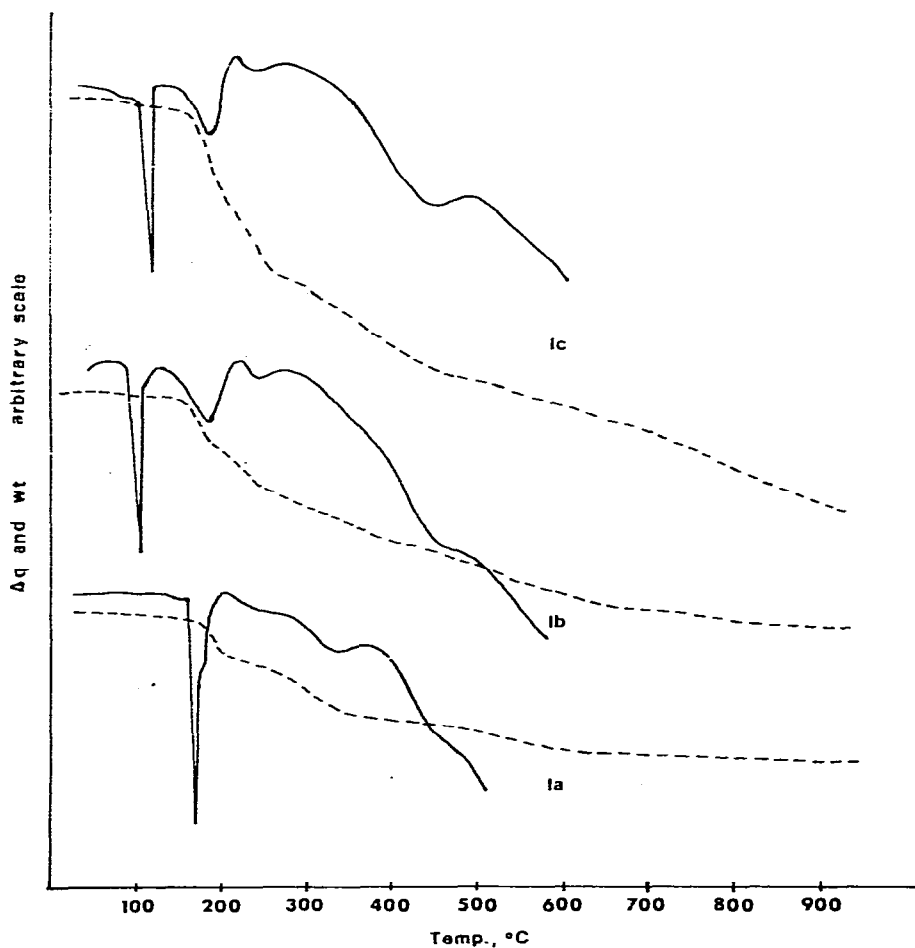

Fig. 1. TG (— — —) and DSC (————) curves for the rhodacycloalkane compounds (heating rate, 10°C/min).

the temperature ranges in which the decomposition processes take place. Three different decomposition steps have been identified. The first step, which occurs at $160-230°C$, is characterized by a weight loss consistent with the release of C_nH_{2n} and C_5Me_5 moieties. The presence of an inflexion point in the TG curves suggests the overlapping of two distinct decomposition processes. Experiments carried out at very low heating rate ($0.25°C$ min^{-1}) along with isothermal analysis at $165°C$ (e.g., Figure 2 for Ib) showed that the decomposition of all the compounds begins with release of the C_nH_{2n} moiety, followed by release of the C_5Me_5 group (isothermal analysis at $230°C$). The third step, which extends up to about $800°C$, is characterized by the release of the phenyl groups of the triphenylphosphine and this is followed by a constant mass region. The weight of the residue does not correspond to that expected for metallic rhodium, but to the sum of rhodium and phosphorus (Table 1) (the presence of phosphorus was qualitatively confirmed by X-ray scanning spectroscopy with a Jeol XD 40 instrument).

Three different decomposition steps also occur in the case of the iridium compounds II (Figure 3). The first step, at $160-240°C$, is characterized by weight loss consistent with the release of the C_nH_{2n} moiety; the second step
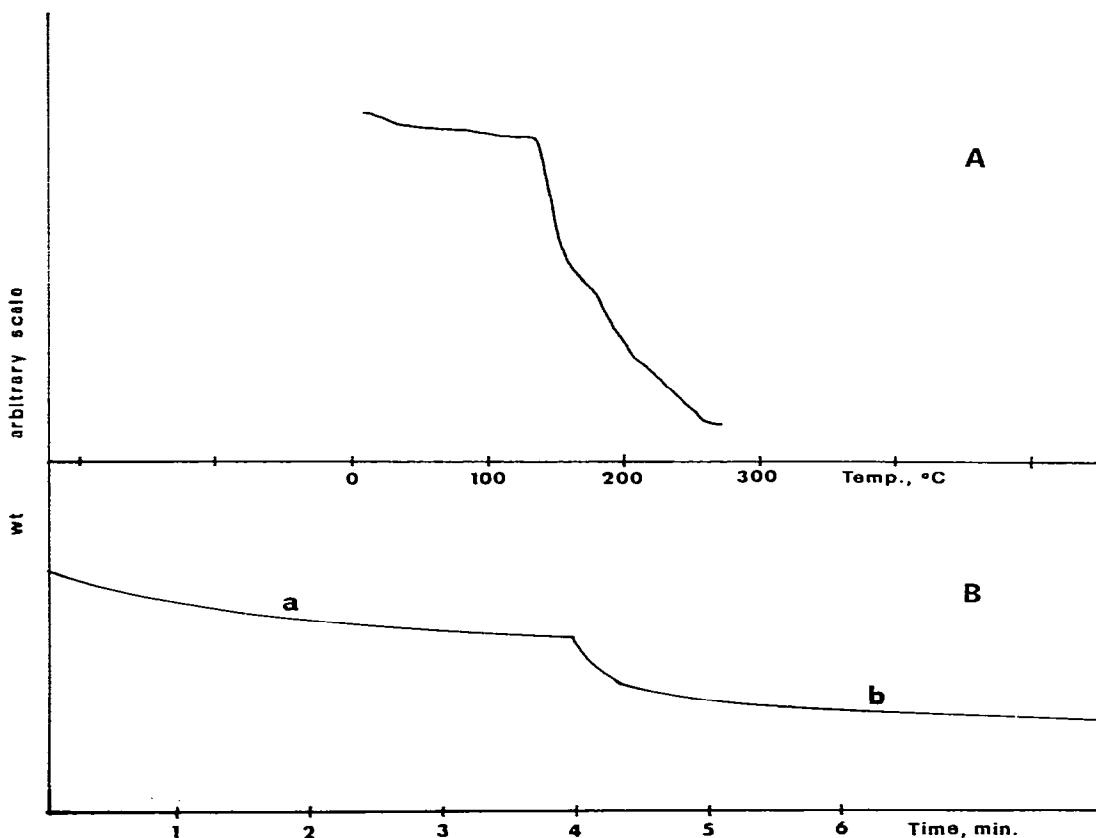

Fig. 2. TG curves for the rhodacycloalkane compound Ib. A, Heating rate, $0.25°C$/min. B, Isothermal curves; a, $165°C$; b, $230°C$.

TABLE 1

TGA DATA FOR COMPOUNDS I AND II

Compound	First step (C_nH_{2n} loss)		Second step (C_5Me_5 loss)		Residue [a]	
	Found (%) [b]	Calcd. (%)	Found (%) [b]	Calcd. (%)	Found (%) [b]	Calcd. (%)
Ia	10.3	10.07	24.3	24.27	24.4	24.06
Ib	13.8	12.27	22.0	23.68	23.7	23.47
Ic	15.5	14.37	21.2	23.10	21.9	22.90
IIa	8.8	8.67	20.7	20.90	28.2	29.76
IIb	11.0	10.61	21.7	20.45	28.9	29.13

[a] Metal plus phosphorus in the case of rhodium compounds; metal in the case of iridium compounds. [b] The values are affected by a ±0.1 uncertainty.

(240—340°C) is consistent with the release of a C_5Me_5 group, and the third (830—1000°C) with the release of PPh_3. The weight of the residue corresponds in each case to that expected for metallic iridium (Table 1).

GLC analysis of the gases leaving the thermobalance during the first step of the decomposition of I and II confirms that this step corresponds to the loss of the C_nH_{2n} moiety as the whole, giving the corresponding olefins as the
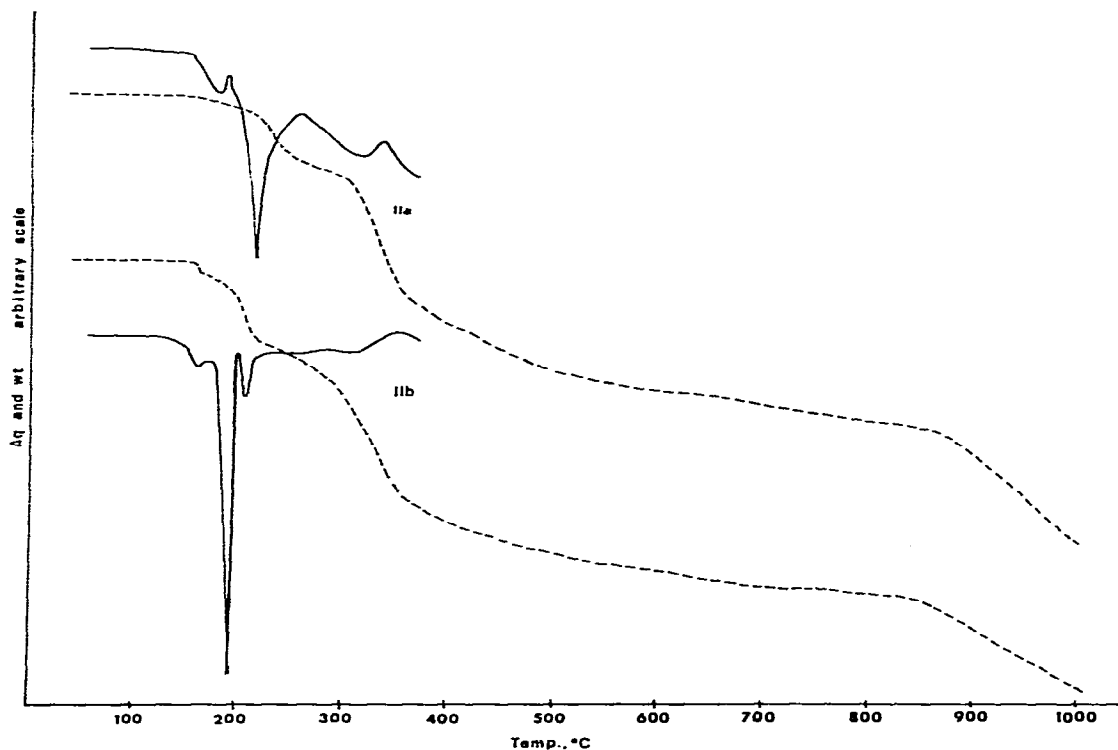

Fig. 3. TG (— — —) and DSC (———) curves for the iridiacycloalkane compounds (heating rate, 10°C/min).

TABLE 2

VOLATILE PRODUCTS LEAVING THE THERMOBALANCE IN THE FIRST STEP OF DECOMPOSITION OF THE COMPLEXES I AND II

Compound	Volatile products	Amount (%)
Ia	1-butene	49
	cis-2-butene	34
	trans-2-butene	11
	1,3-butadiene	6
Ib	1-pentene	14
	cis-2-pentene	33
	trans-2-pentene	50
	n-pentane	3
Ic	1-hexene	5
	cis-2-hexene	12
	trans-2-hexene	46
	cis-3-hexene	3
	trans-3-hexene	17
	n-hexane	10
	unidentified product	7
IIa	1-butene	13
	cis-2-butene	31
	trans-2-butene	44
	1,3-butadiene	7
	unidentified product	5
IIb	1-pentene	30
	cis-2-pentene	26
	trans-2-pentene	8
	unidentified product (high retention time)	36

greatly predominant products (Table 2). Small amounts of dienes and linear alkanes are also present in some cases. Products arising from skeletal fragmentation or from reductive elimination with bond formation between the two ring C_α atoms were not detected.

The DSC curves show that the complexes Ib and Ic melt before decomposition occurs, while Ia, IIa, and IIb melt and decompose at the same time. Melting and decomposition heats are reported in Table 3.

The activation energy (E^*) and the "reaction order" (n) for the release of the

TABLE 3

DSC DATA FOR COMPOUNDS I AND II

Compound	M.p. (°C)	Heat of fusion (kcal/ mol)	First step (C_nH_{2n} loss)			
			ΔH dec (kcal/mol)	Reaction [a] order "n"	E^{*} [b] (kcal/mol)	E^{*} [c] (kcal/mol)
Ia	—	—	10.9	1	34	33
Ib	109.7	6.1	10.9	1	38	34
Ic	107.2	5.1	10.7	1	38	34
IIa	—	—	10.5	1	63	76
IIb	—	—	9.6	1	65	77

[a] The same value was obtained by the Chatterjee method and by the Borchardt and Daniels method.
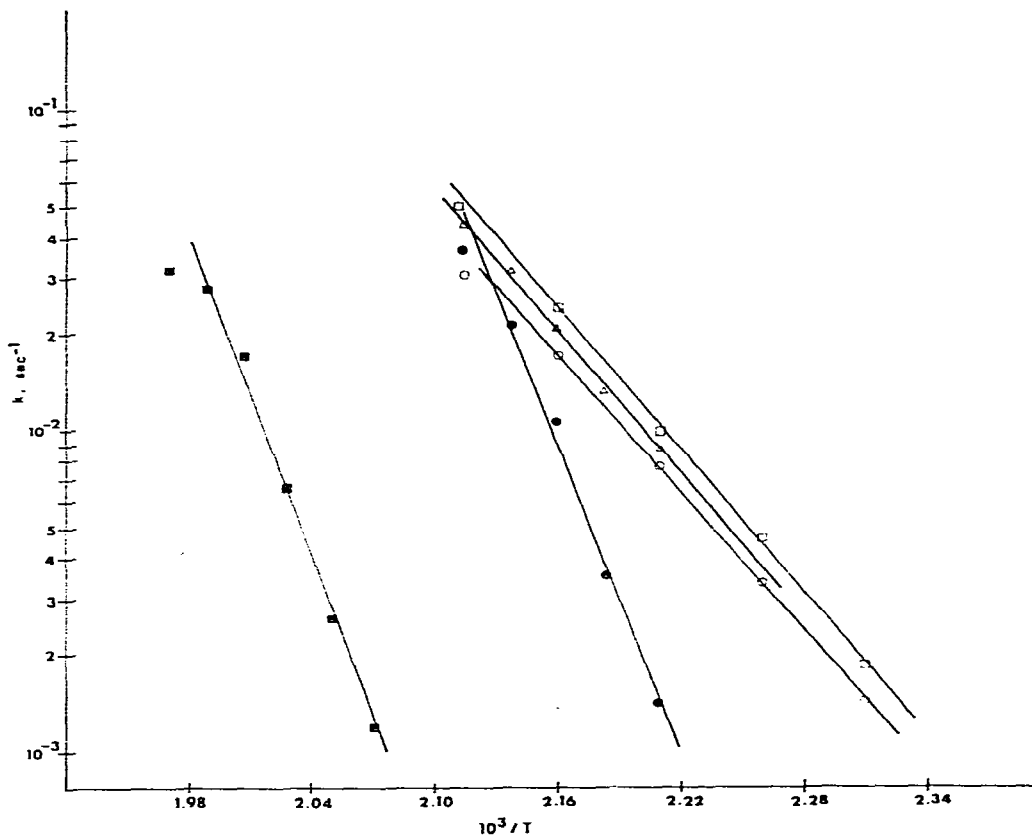[b] Calculated by the Chatterjee method. [c] Calculated by the Borchardt and Daniels method.

Fig. 4. Rate constants for the first stage of decomposition (△, Ia; ▢, Ib; ○, Ic; ■, IIa; ●, IIb).

C_nH_{2n} moiety were evaluated from TG curves by the Chatterjee method [4] and from DSC curves by the Borchardt and Daniels method [5] (Table 3). The rate constants are reported in Figure 4.

The E^* value in the case of complex Ia was found to be slightly different from those for Ib and Ic. Such a difference could be due to the fact that only in the case of Ia do the melting and decomposition take place almost at the same time; as a consequence the decomposition process, at least initially, slows down and the initial slope of the decomposition curve for Ia turns out to be slightly different from that for Ib and Ic. Because of the method used for calculating E^* and k, these quantitites could be liable to some error.

However, because all complexes I (and complexes II as well) exhibit similar activation energies, the same rate determining step (i.e., the conversion of a σ-bonded organic ligand to an active species) is probably involved. In discussing the nature of this active species it must be kept in mind that the analysis of the volatile products (Table 2) indicates that the active species cannot be a true di- or mono-radical since in that case cyclization or coupling products would predominate [6]. We are also inclined to discard β-hydride elimination as the initial process, since ring size should affect the activation energy [7]. Considering

all these facts and taking account of the views of other authors [6], we suggest that one of the two carbon—metal σ-bonds is activated with formation of a radical which remains within the coordination sphere of the metal where it undergoes reactions (e.g., intra- or inter-molecular hydrogen abstraction) with the formation of linear hydrocarbons. Thus for the mechanism suggested, the obtained E^* values (33—38 kcal/mol for rhodium, and 63—77 kcal/mol for iridium compounds) should approach the Rh—C(sp^3) and Ir—C(sp^3) σ-bonds bond dissociation energy, respectively.

Even though these figures suffer from a rather crude approach, they are of some interest since, to our knowledge, they represent the first estimates of the dissociation energies for rhodium—carbon and iridium—carbon σ-bonds.

Experimental

The compounds I and II were prepared by methods described previously [1a,b,c].

GLC analysis
The volatile products leaving the thermobalance during the first stage of the decomposition were identified by GLC analysis on a Perkin-Elmer F30 instrument by a comparison of their retention times with those of authentic samples. A 2 m $AgNO_3$ and a 2 m squalane column were used at 35—40°C.

Thermogravimetric analysis
The TG curves were obtained on a DuPont 950 thermobalance. The balance, unless otherwise noted, was operated with a dynamic atmosphere of pure argon flowing under atmospheric pressure at 100 ml min^{-1}, the temperature rise being programmed at 10°C min^{-1} and the typical sample size being 4—5 ± 0.01 mg. The sample was contained in an open platinum pan and the temperature was recorded by use of a chromel-alumel thermocouple with its sensing junction in contact with the pan.

Differential scanning calorimetry
The DSC curves were obtained on a DuPont thermal analyzer fitted with a DSC cell operating with the same experimental conditions used for TG. The typical sample size was 2.5—3.5 ± 0.05 mg and the sample was contained in an aluminum pan. The instrument was calibrated using the latent heat of fusion of gallium, indium, tin, and zinc.

Acknowledgement

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