

## Thermal studies on pentamethylcyclopentadienylrhodium(III) derivatives with N-donor ligands

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### Abstract

The TG, DTG and DSC study of pentamethylcyclopentadienylrhodium(III) derivatives  $[\text{Cp}^*\text{RhCl}_2\text{L}]$  ( $\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$ ;  $\text{L} = o\text{-aminophenol}$ , pyridine, 4-cyanopyridine, 4-methylpyridine, 4-chloropyridine, or 4-bromopyridine),  $[\text{Cp}^*\text{RhCl}_2(\mu\text{-ppda})\text{Cl}_2\text{RhCp}^*]$  (ppda = *p*-phenylenediamine) and  $[\text{Cp}^*\text{RhClL}_2]\text{Cl}$  ( $\text{L}_2$  (chelating bidentate) = ethylenediamine, tetramethylethylenediamine, or *o*-phenylenediamine) was carried out under a dynamic nitrogen atmosphere. From the DSC curves the heat of decomposition was calculated. The values of kinetic parameters such as activation energy  $E$ , frequency factor  $A$  and reaction order have been obtained using the Coats–Redfern and Horowitz–Metzger equations.

### INTRODUCTION

There is an increasing interest in the chemistry of  $[\text{Cp}^*\text{RhClL}_2]$ -type complexes ( $\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$ ) because of their potential use as redox catalysts [1, 2]. The chloro-bridged binuclear complex  $[\text{Cp}^*\text{ClRh}(\mu\text{-Cl})_2\text{RhClCp}^*]$  has been extensively used as a precursor in the synthesis of mononuclear complexes of the types  $[\text{Cp}^*\text{RhCl}_2\text{L}]$  and  $[\text{Cp}^*\text{RhClL}_2]^+$  [3–8].

The synthesis, structural characterization and thermogravimetric data of cationic  $[\text{Cp}^*\text{RhClL}_2]\text{Cl}$  [ $\text{L}_2$ (bidentate) = ethylenediamine (en), tetramethylethylenediamine (tmed) or *o*-phenylenediamine (opda)] and neutral  $[\text{Cp}^*\text{RhCl}_2(\text{oap})]$  (oap = *o*-aminophenol) complexes as well as the neutral binuclear complex  $[\text{Cp}^*\text{RhCl}_2]_2(\mu\text{-ppda})$  (ppda = *p*-phenylenediamine) have been reported recently [9].  $^1\text{H NMR}$  data indicated that in acetone or dimethyl sulphoxide solutions some of these complexes

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dissociate to give the precursor  $\{[\text{Cp}^*\text{RhCl}(\mu\text{-Cl})_2]\}$  and the free ligand L. Thermogravimetric data also showed the relatively great thermal stability of the chloro-bridged rhodium complex.

Here we describe the synthesis of the new complexes  $[\text{Cp}^*\text{RhCl}_2\text{L}]$  (L = 4-Mepy, 4-Clpy or 4-Brpy; py = pyridine) and the thermal behaviour of these and the above-mentioned rhodium complexes. The previously reported  $[\text{Cp}^*\text{RhCl}_2(\text{py})]$  is also included [3]. The thermal study includes the determination by non-isothermal methods (Coats–Redfern and Horowitz–Metzger) of kinetic parameters of the decomposition of the complexes.

## EXPERIMENTAL

### *Preparation of complexes*

All the operations were carried out under nitrogen and the solvents were dried by conventional methods. The neutral ligands were obtained from commercial sources. Pentamethylcyclopentadiene, bis[dichloro(pentamethylcyclopentadienyl)rhodium(III)] [3, 10] and the complexes I–III and VII–X [3, 9] were prepared by published procedures. Numbering system:  $[\text{Cp}^*\text{RhCl}_2\text{L}]$  ( $\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$ , L = *o*-aminophenol (oap) (I), pyridine (py) (II), 4-cyanopyridine (4-CNpy) (III), 4-methylpyridine (4-Mepy) (IV), 4-chloropyridine (4-Clpy) (V), 4-bromopyridine (4-Brpy) (VI));  $[\text{Cp}^*\text{RhCl}_2(\mu\text{-ppda})\text{Cl}_2\text{RhCp}^*]$  (ppda = *p*-phenylenediamine) (VII);  $[\text{Cp}^*\text{RhCl}_2\text{L}_2]\text{Cl}$  ( $\text{L}_2$  (chelating bidentate) = ethylenediamine (en) (VIII), tetramethylenediamine (tmed) (IX), *o*-phenylenediamine (opda) (X)).

Complexes IV–VI were synthesized according to the following general method. The corresponding ligand (4-Mepy, 4-Clpy · HCl or 4-Brpy · HCl respectively; 0.32 mmol) in dichloromethane (5 ml) was added to a solution of  $\{[\text{Cp}^*\text{RhCl}(\mu\text{-Cl})_2]\}$  (0.16 mmol) in dichloromethane (5 ml) (under nitrogen). After 1 h, with constant stirring, the resulting red solution was concentrated under reduced pressure; the addition of diethyl ether caused the formation of orange crystals, which were filtered off and vacuum dried.

### *Characterization*

The C, H and N analyses were performed with a Perkin-Elmer 240C microanalyser. Conductivities were measured with a Crison 525 conductimeter. The  $^1\text{H}$ NMR spectra were recorded on a Bruker AC 200E instrument. IR spectra were recorded on a Perkin-Elmer 1430 spectrophotometer using Nujol mulls between polyethylene sheets.

The IR and NMR data for the complexes I–III and VII–X were concordant with those previously reported, and the relevant data for the new complexes IV–VI are given below.

[Cp\*RhCl<sub>2</sub>(4-Mepy)]. Orange crystals, yield 80%. Analysis: found (%): C, 47.4; H, 5.8; N, 3.1; calcd.: C, 47.7; H, 5.5; N, 3.5. Non-conductor in acetone. IR (cm<sup>-1</sup>) (Nujol): 1610 m, 1025 m, 820 s (py ring), 275 s and 265 s (Rh–Cl stretch). <sup>1</sup>H NMR (δ) [solvent (CD<sub>3</sub>)<sub>2</sub>CO; reference SiMe<sub>4</sub>]: 8.78 (doublet, 2 H, 2- and 6-H of 4-Mepy, *J* 5.8 Hz), 7.32 (doublet 2 H, 3- and 5-H of 4-Mepy, *J* 5.9 Hz), 2.43 (singlet, 3 H, Me of 4-Mepy) and 1.52 (singlet, 15 H, Cp\*).

[Cp\*RhCl<sub>2</sub>(4-Clpy)]. Orange crystals, yield 70%. Analysis: found (%): C, 42.3; H, 4.5; N, 3.0; calcd.: C, 42.6; H, 4.5; N, 3.3. Non-conductor in acetone. IR (cm<sup>-1</sup>) (Nujol): 1580 s, 1550 m, 1405 s, 1025 s, 830 s (py ring), 275 s and 265 s (Rh–Cl stretch). <sup>1</sup>H NMR (δ) [solvent (CD<sub>3</sub>)<sub>2</sub>CO; reference SiMe<sub>4</sub>]: 8.93 (multiplet, 2 H, 2- and 6-H of 4-Clpy), 7.60 (multiplet, 2 H, 3- and 5-H of 4-Clpy) and 1.55 (singlet, 15 H, Cp\*).

[Cp\*RhCl<sub>2</sub>(4-Brpy)]. Orange crystals, yield 70%. Analysis: found (%): C, 38.2; H, 4.3; N, 2.8; calcd.: C, 38.5; H, 4.1; N, 3.0. Non-conductor in acetone. IR (cm<sup>-1</sup>) (Nujol): 1575 s, 1545 m, 1400 s, 1025 s, 825 s (py ring), 275 s and 260 s (Rh–Cl stretch). <sup>1</sup>H NMR (δ) [solvent (CD<sub>3</sub>)<sub>2</sub>CO; reference SiMe<sub>4</sub>]: 8.82 (multiplet, 2 H, 2- and 6-H of 4-Brpy), 7.75 (multiplet, 2 H, 3- and 5-H of 4-Brpy) and 1.55 (singlet, 15 H, Cp\*).

### Thermal analysis

Thermoanalytical data were obtained from TG, DTG, and DSC curves. These were recorded on a Mettler TA-3000 system provided with a Mettler TG-50 thermobalance and a DSC-20 differential scanning calorimeter. The atmosphere used was a pure nitrogen flow (100 ml min<sup>-1</sup>). The heating rate was 5°C min<sup>-1</sup> with a sample mass range of 3–10 mg.

## RESULTS AND DISCUSSION

### Neutral complexes

The TG curves of these complexes are presented in Fig. 1. Only the oap complex contains hydration water (0.5 mol) which is lost in the temperature range 109–124°C to give the anhydrous complex.

All the complexes decompose on heating to give the binuclear rhodium complex {[Cp\*RhCl(μ-Cl)]<sub>2</sub>} with the concomitant release of the neutral ligand L (eqn. (1)).

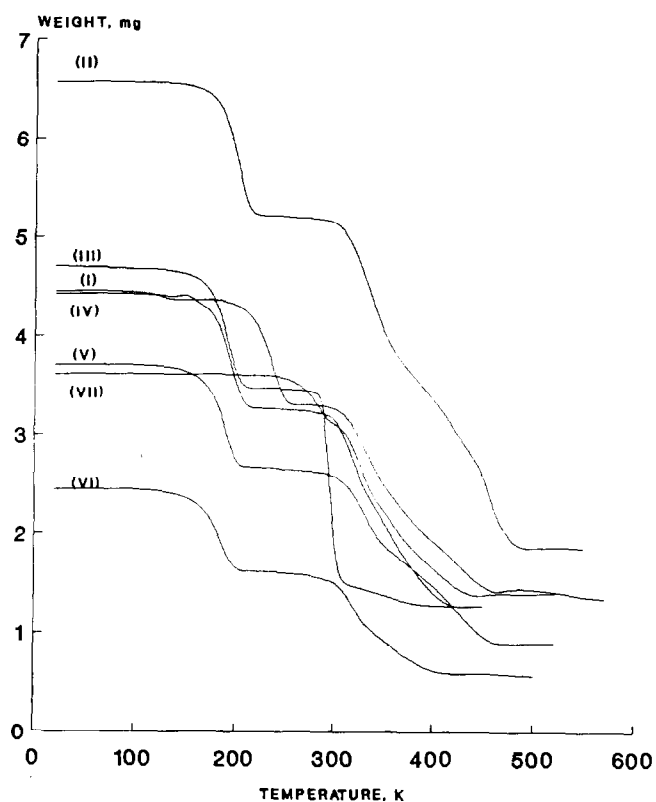
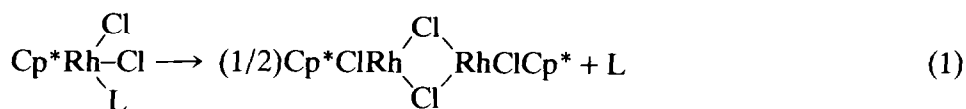


Fig. 1. TG curves of the neutral complexes I–VII.



The thermal treatment of the binuclear ppda compound also yields the chloro-bridged complex, according to eqn. (2).

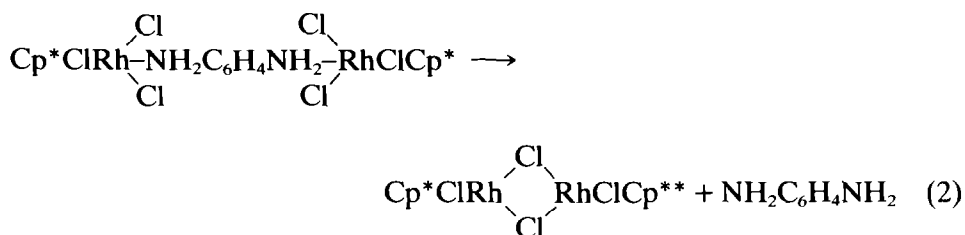


TABLE 1

TG, DTG and DSC data for the neutral rhodium complexes I–VII (under dynamic nitrogen atmosphere; heating rate 5° min<sup>-1</sup>)

Complex	Step	Temperature range (°C)	DTG <sub>max</sub> (°C)	Weight loss (%) Found (calc.)	Assignment	Enthalpy change (kJ mol <sup>-1</sup> )
(I) [Cp*RhCl <sub>2</sub> -(oap)] · 0.5 H <sub>2</sub> O	1	109–134	129	2.0 (2.1)	0.5 H <sub>2</sub> O	112.2
	2	187–248	241	24.5 (25.5)	oap	
	3	286–462	332	44.6 (48.2)	Cp* + 2 Cl	
	Residue	>700	—	28.9 (24.1)	Rh <sup>0</sup>	
(II) [Cp*RhCl <sub>2</sub> (py)]	1	144–214	206	20.2 (20.4)	py	84.7
	2	285–560	330	50.8 (53.1)	Cp* + 2 Cl	
	Residue	>700	452	—	29.0 (26.5)	
(III) [Cp*RhCl <sub>2</sub> (4-CNpy)]	1	132–206	194	25.5 (25.2)	4CNpy	87.5
	2	270–387	293	46.0 (49.9)	Cp* + 2 Cl	
	Residue	>700	—	28.5 (24.9)	Rh <sup>0</sup>	
(IV) [Cp*RhCl <sub>2</sub> (4-Mepy)]	1	137–207	198	25.0 (23.2)	4Mepy	90.8
	2	278–421	320	49.9 (51.3)	Cp* + 2 Cl	
	Residue	>700	—	25.1 (25.6)	Rh <sup>0</sup>	
(V) [Cp*RhCl <sub>2</sub> (4-Clpy)]	1	134–201	194	26.4 (26.9)	4-Clpy	87.8
	2	302–464	323	40.2 (48.8)	Cp* + 2 Cl	
	Residue	>700	—	23.4 (24.4)	Rh <sup>0</sup>	
(VI) [Cp*RhCl <sub>2</sub> (4-Brpy)]	1	143–198	191	33.8 (33.8)	4-Brpy	91.4
	2	300–517	333	46.9 (44.1)	Cp* + 2 Cl	
	Residue	>700	—	19.3 (22.0)	Rh <sup>0</sup>	
(VII) {[Cp*RhCl <sub>2</sub> ] <sub>2</sub> -(μ-ppda)}	1	238–296	289	13.5 (14.9)	ppda	122.2
	2	296–442	325	54.2 (56.8)	Cp* + 2 Cl	
	Residue	>700	—	32.3 (28.4)	Rh <sup>0</sup>	

The temperature ranges and the DTG peaks for the thermal decomposition of each complex are listed in Table 1. Subsequent decomposition of the chloro-bridged complex occurs in the temperature ranges given in Table 1, the final residue being metallic rhodium above 700°C.

The intermediate chloro-bridged binuclear complex can be isolated in every case and identified by <sup>1</sup>H NMR spectroscopy [9]. In (CD<sub>3</sub>)<sub>2</sub>SO solution its spectrum shows a unique singlet (at 1.60 ppm from SiMe<sub>4</sub>) arising from the five equivalent methyl groups of the Cp\*.

The enthalpy changes for the thermal decomposition processes represented by eqns. (1) and (2) were calculated by integration of the endothermic peaks in the corresponding DSC curves. The experimental results are collected in Table 1.

### Cationic complexes

The corresponding TG curves are found in Fig. 2 and the temperature ranges and the DTG peaks for the thermal decomposition stages of each

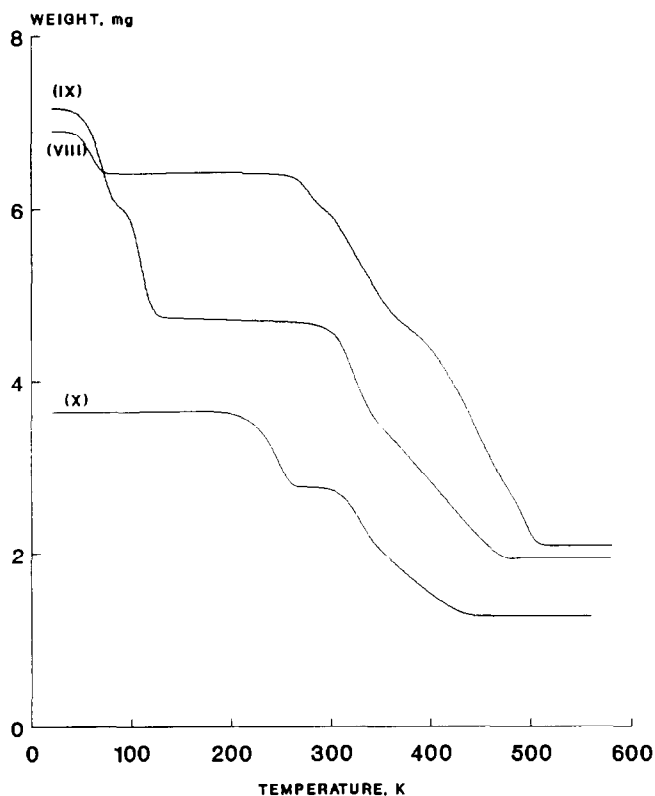


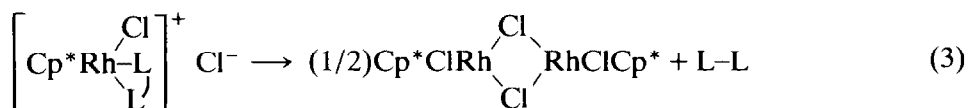
Fig. 2. TG curves of the cationic complexes VIII–X.

TABLE 2

TG, DTG and DSC data for the cationic rhodium complexes VIII–X (under dynamic nitrogen atmosphere; heating rate  $5^{\circ} \text{ min}^{-1}$ )

Complex	Step	Temperature range ( $^{\circ}\text{C}$ )	DTG <sub>max</sub> ( $^{\circ}\text{C}$ )	Weight loss (%) Found (calc.)	Assignment	Enthalpy change ( $\text{kJ mol}^{-1}$ )
(VIII) $[\text{Cp}^*\text{RhCl}(\text{en})]\text{Cl} \cdot 2\text{H}_2\text{O}$	1	40–72	62	7.2 (8.9)	2 $\text{H}_2\text{O}$	77.7
	2	250–560	313	62.7 (65.7)	en + $\text{Cp}^*$ + 2 Cl	
	Residue	>700	—	230.3 (25.4)	$\text{Rh}^0$	
(IX) $[\text{Cp}^*\text{RhCl}(\text{tmed})]\text{Cl} \cdot 2\text{H}_2\text{O}$	1	40–130	73	33.9 (33.0)	2 $\text{H}_2\text{O}$ + tmed	
	2	288–480	317	38.5 (44.7)	$\text{Cp}^*$ + 2 Cl	
	Residue	>700	—	27.6 (22.3)	$\text{Rh}^0$	
(X) $[\text{Cp}^*\text{RhCl}(\text{opda})]\text{Cl}$	1	192–259	252	23.9 (25.9)	opda	109.2
	2	289–442	328	42.5 (49.4)	$\text{Cp}^*$ + 2 Cl	
	Residue	>700	—	33.6 (24.7)	$\text{Rh}^0$	

complex are presented in Table 2. The en and tmed complexes are dihydrated whereas the opda complex is anhydrous. Although the thermal treatment of the en complex yields the anhydrous compound in the range 40–72°C, the latter gives metallic rhodium directly without formation of  $\{[\text{Cp}^*\text{RhCl}(\mu\text{-Cl})_2]\}$  as a stable intermediate species. However, the tmed complex releases the two  $\text{H}_2\text{O}$  molecules in the range 40–130°C and the anhydrous tmed and opda compounds both give the chloro-bridged binuclear rhodium complex (eqn. (3)) as a stable intermediate before the final decomposition to metallic rhodium.



Of the two coordination vacancies created by liberation of the chelating bidentate ligand on thermal treatment, one is occupied by the chloride ion which enters the coordination sphere of the metal centre whereas the other is occupied by the bridging chloride, as in the case of the neutral complexes reported above.

From the corresponding endothermic peaks of the DSC curves, the enthalpy changes for the dehydration of the en complex and the liberation of opda from the opda complex have been determined. As expected, the liberation of the chelating (opda) or bridging (ppda) ligands is a more endothermic process than the liberation of the monodentate ligands (oap, py and 4-substituted py).

#### Determination of kinetic parameters

Kinetic parameters for some of the processes studied in the preceding paragraphs were calculated from the TG curves using the two non-mechanistic methods of Coats–Redfern and Horowitz–Metzger. The following equations were used.

(a) The Coats–Redfern eqn. [11]

$$\ln \left[ \frac{1 - (1 - \alpha)^{1-n}}{T^2(1-n)} \right] = \ln \left[ \frac{AR}{\beta E} (1 - 2RT/E) \right] - \frac{E}{RT}$$

(b) The Horowitz–Metzger eqn. [12]

$$\ln \left[ \frac{1 - (1 - \alpha)^{1-n}}{1-n} \right] = \frac{E\theta}{RT_s} - \frac{E}{RT_s} + \ln \frac{ART_s^2}{\beta E}$$

where  $\alpha$  is the fraction of the sample decomposed at time  $t$ ,  $\theta = T - T_s$ ,  $T_s$  is the DTG peak temperature,  $\beta$  is the heating rate,  $E$  is the energy of

TABLE 3

Kinetic parameters and correlation coefficients ( $r$ ) calculated using the Coats–Redfern (CR) and Horowitz–Metzger (HM) equations

Compound	Method	Stage	Reaction order	$E$ (kJ mol <sup>-1</sup> )	$A$ (s <sup>-1</sup> )	$r$
(I)	CR	2	1/2	155.3	$3.9 \times 10^{13}$	0.9995
	HM	2	1/2	175.1	$4.7 \times 10^{15}$	0.9993
(II)	CR	1	1/2	138.5	$8.1 \times 10^{12}$	0.9993
	HM	1	1/2	154.9	$5.5 \times 10^{14}$	0.9999
(III)	CR	1	1/2	128.1	$1.1 \times 10^{12}$	0.9998
	HM	1	1/2	143.0	$5.6 \times 10^{13}$	0.9999
(IV)	CR	1	1/2	131.8	$2.4 \times 10^{12}$	0.9993
	HM	1	1/2	148.8	$2.1 \times 10^{14}$	0.9999
(V)	CR	1	0	96.8	$2.4 \times 10^8$	0.9999
	HM	1	0	113.8	$2.4 \times 10^{10}$	0.9997
(VI)	CR	1	0	77.6	$1.6 \times 10^6$	0.9999
	HM	1	0	93.0	$1.1 \times 10^8$	0.9997
(VII)	CR	1	1/2	168.1	$2.8 \times 10^{13}$	0.9996
	HM	1	1/2	189.3	$3.0 \times 10^{15}$	0.9996
(VIII)	CR	1	1	131.2	$4.2 \times 10^{18}$	0.9994
	HM	1	1	141.7	$1.9 \times 10^{20}$	0.9991
(X)	CR	1	1/2	131.8	$7.1 \times 10^{10}$	0.9995
	HM	1	1/2	150.4	$5.7 \times 10^{12}$	0.9999

activation,  $n$  is the order of reaction, and  $A$  is the pre-exponential factor. Values of the kinetic parameters and linear regression coefficients are listed in Table 3.

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