VOLATILE β-DIKETONATO COMPLEXES OF RUTHENIUM, PALLADIUM AND PLATINUM
Preparation and thermal characterization

M. Lashdaf[1], *T. Hatanpää*[2] *and M. Tiitta*[3]

[1]Volatec Oy, Linnankoskenkatu 34, FIN-06100 Porvoo, Finland
[2]Department of Chemistry, University of Helsinki, Laboratory of Inorganic Chemistry,
P. O. Box 6, FIN-00014 Helsinki, Finland
[3]Fortum Oil and Gas, Oil Research, P.O. Box 310, 06101 Porvoo, Finland

Abstract

Ruthenium, palladium and platinum complexes of 2,2,6,6-tetramethyl-3,5-heptanedione (thd) and ruthenium tris acetylacetonate (acac) were synthetized and studied with TG, DTA, DSC and MS methods. Thermal properties of ruthenocene were also studied. The platinum thd complex has the highest volatility despite the second highest molecular mass of the complex. All the complexes sublimed under reduced pressure. Ru(acac)$_3$ decomposed during sublimation under atmospheric pressure of nitrogen whereas the other compounds studied sublimed also under these conditions. Pd(thd)$_2$ reduced under atmospheric pressure of H$_2$/N$_2$ (5% H$_2$) whereas the ruthenium complexes were not reduced. The field desorption mass spectra of complexes showed only the molecular peaks and no fragmentation occurred.

Keywords: atomic layer epitaxy, catalyst precursor, chemical vapor deposition, decomposition, diketonate, platinum, palladium, reduction, ruthenium, ruthenocene, sublimation

Introduction

Heterogeneous catalysts typically consist of active metals supported on porous high surface area material. The Ru, Pd and Pt metals on supports play an important role as catalysts for the various hydrogenation reactions in the industrial chemistry and in the production of fine chemicals [1]. Typically, Ru, Pd and Pt containing catalysts are prepared by precipitation or by deposition methods such as impregnation [2] or ion exchange [3].

Chemical vapor deposition (CVD) and atomic layer epitaxy (ALE) are thin film deposition methods that have also been used for the preparation of different hydrogenation catalysts [4, 5]. For a comprehensive review of the adsorption-controlled preparation of heterogeneous catalysts, see the article by Haukka *et al.* [6]. Essential for both the CVD and ALE depositions are volatile precursors that do not decompose during vaporisation. In addition, precursors should be non-pyrophoric, easy to handle and store, pure and non-toxic. Metal β-diketonates meet most of these criteria [7]. In

this paper, we present the preparation and thermal characteristics of Ru, Pd and Pt β-diketonate complexes that can be used as source materials for the CVD or ALE preparation of catalysts for hydrogenation reactions.

2,4-Pentanedione (acac) is a common ligand, forming chelates with almost all transition metals [8]. Another widely utilised ligand is 2,2,6,6-tetramethyl-3,5-heptanedione (thd). Fluorine substitution of the β-diketonates enhances the volatility but as a drawback small amounts of fluorine originating from the β-diketonate ligand can, however, contaminate the catalysts [9]. Thus, we focused our studies to the 2,4-pentanedione and 2,2,6,6-tetramethyl-3,5-heptanedione complexes containing only carbon, oxygen and hydrogen that can easily be removed. For comparison, a volatile precursor ruthenocene was included to the thermal studies.

The blue product of catalytic hydrogen reduction of hydrated ruthenium(III) chloride in methanol has been used as a convenient method to produce a starting material for the synthesis of a number of ruthenium(III) and ruthenium(II) complexes [10, 11]. The so-called blue solution used to prepare tris(β-diketonato)ruthenium complexes can readily be obtained by reducing the ruthenium(III) compound with an ethanol–hydrochloric acid mixture or just with ethanol [12–15].

Bis(2,4-pentanedionato)platinum(II) was first prepared by Werner [16], but the yield of the synthesis reported later by Gringberg and Chapurskii [17] was only 35%. Platinum(II) and palladium(II) β-diketonates with other ligands have been prepared by reaction of $[M(H_2O)_4]^{2+}$ with a sodium or potassium salt of the β-diketone compound [18, 19]. The complex $[Pt(H_2O)_4]^{2+}$ is synthetized by adding mercury(II) perchlorate and/or silver(I) perchlorate to aqueous solution of $Na_2[PtCl_4]$ or potassium tetrachloroplatinate(II), $K_2[PtCl_4]$. The kinetics for halide anation reactions to form $Pt[H_2O]_4^{2+}$ ion ($K_2[PtCl_4] \rightarrow [Pt(H_2O)_4]^{2+}$) have been studied in detail by Elding [20, 21].

β-Diketonates of Pd have been prepared by adding a methanol solution of sodium hexachlorodipalladate(II), $Na_2[Pd_2Cl_6]$, to more than two equivalents of free ligand followed by an appropriate amount of sodium carbonate [22]. Another way to prepare Pd β-diketonates described in the literature is the synthesis over palladium aqua complex [18]. The synthesis is similar to synthesis of platinum β-diketonates described above. The only square-planar tetra-aqua complex described in the literature so far is $[Pd(H_2O)_4]^{2+}$ [19, 22–25].

Experimental

Preparation of the complexes

All the β-diketonate complexes studied were synthetized by us while ruthenocene, studied for comparison to the β-diketonate based ruthenium compounds, was purchased from Aldrich. β-Diketonate ligands 2,4-pentanedione (99%) and 2,2,6,6-tetramethyl-3,5-heptanedione (>97%) needed for the complex preparations were bought from Merck. Other chemicals required for complex preparations were hydrated ruthenium trichloride (Strem Chemicals Inc.) and potassium hydrogen carbonate (99.5%,

Merck) for ruthenium complexes, potassium tetrachloroplatinate(II) (99.9%, Strem), mercury(II) oxide yellow 99% (Strem), perchloric acid (70%, Riedel- de Haen), silver perchlorate monohydrate (>99%, Fluka) for platinum complexes and anhydrous palladium(II) chloride (60% Pd, Fluka), sodium carbonate (99.8%, Riedel-de Haen) and methanol (99.8% Riedel de Haen) for the synthesis of palladium complexes.

Tris (2,4-pentanedionato)ruthenium(III) and
tris(2,2,6,6-tetramethyl-3,5-heptanedionato)ruthenium(III)

Ruthenium complexes were prepared after a modified method of Rose *et al.* [10, 11]. Hydrated ruthenium trichloride (10 g) was dissolved in a mixture of 250 mL dist. water and 250 mL ethanol. The reddish brown solution was refluxed for 2 days. The colour of the solution turned dark green and then deep blue. In order to prevent the reaction from stopping, 100 mL distilled water was added after 5 h from the start of the reaction. The ligand (45 mL) was added fast into the ruthenium solution, and the mixture was refluxed until its blue colour turned to red (about one h). The mixture was cooled and 15.21 g of potassium hydrogen carbonate was added to neutralise the liberated protons. Then the reaction mixture was refluxed again for 4 h. After the reaction was completed, reaction mixture was left to cool over night under stirring. The resulting precipitate was collected by filtration and dried under a vacuum. The product was purified by sublimation at 160°C in 0.01 Hgmm pressure. Tris(2,4-pentanedionato)ruthenium was prepared in a similar manner.

Bis(2,2,6,6-tetramethyl-3,5-heptanedionato)platinum(II)

Bis(2,2,6,6-tetramethyl-3,5-heptanedionato)platinum(II) (Pt(thd)$_2$) was prepared in three different ways. In all methods platinum aqua complex was the reactive platinum species. No Pt(thd)$_2$ was formed when the synthesis methods found to be successful for the Ru or Pd β-diketonates were employed. The methods used can be described as follows:

Preparation using mercury(II) and silver(I). The synthesis is adopted from the recipe of Pt(acac)$_2$ presented by Werner [16]

Pulverized K$_2$[PtCl$_4$] (2.08 g, 0.005 mol) was dissolved in 1 M HClO$_4$ (141 mL) and the mixture was stirred for about one h. This produced a red solution. The formed KClO$_4$ precipitate was filtered. Yellow mercury(II) oxide (3.26 g, 0.015 mol) was dissolved in 1 M HClO$_4$ (40 mL), and the resulting solution was added slowly (1–2 drop sec^{-1}) to the Pt(II) solution under stirring. After that a solution of silver perchlorate (1.04 g, 0.005 mol) in 1 M HClO$_4$ (10 mL) was added into the reaction mixture. The precipitate was filtered promptly, and the filtrate was made up to 200 mL by adding 1 M HClO$_4$. The ligand 2,2,6,6-tetramethyl-3,5-heptanedione (3.3 g, 0.018 mol) dissolved in a 2.5 M aqueous NaOH solution (8 mL) was added dropwise to the Pt(II) solution (70 mL) with a pipette so that each drop of the ligand solution contacted the metal solution. After the ligand solution was added, pH of the mixture

was adjusted to 4.5 with 10 M NaOH solution (about 22 mL). Stirring was continued for additional 20 h. The creamy-yellow precipitate was filtered, washed three times with water and dried over silica gel in vacuum. The product was purified by sublimation.

Preparation using stepwise addition of the ligand into the Pt solution

In order to prevent the formation of Hg(thd)$_2$ which has been built in the synthesis A, a mixture of NaOH and ligand was added stepwise into the Pt solution prepared like in the synthesis A. The NaOH–Hthd mixture was divided into four fractions. After addition of each fraction the precipitate was filtered, dried and sublimed separately.

Preparation using only silver(I)

3.5 g (0.008 mol) of K$_2$[PtCl$_4$] was added to 400 mL 1 M perchloric acid in a 1000 mL flask with glass stopper. The mixture was flushed with nitrogen to prevent oxidation, placed in a dark air-thermostat at about 70°C and stirred for 90 min until all the K$_2$[PtCl$_4$] was dissolved. A 0.2 M silver perchlorate solution (400 mL) was added slowly over a period of 7 h with continuous stirring in order to prevent the formation of a sparingly soluble Ag$_2$[PtCl$_4$] precipitate. The mixture was then stirred for 6 days in the dark under nitrogen at 70°C. The resulting platinum(II) perchlorate solution was filtered. The ligand 2,2,6,6-tetramethyl-3,5-heptanedione (3.13 g, 0.018 mol) dissolved in a 2.5 M NaOH (0.7 g, 0.0018 mol) was added slowly to the platinum(II) perchlorate solution. The yellow precipitate was filtered, dried in vacuum and purified by sublimation.

Bis(2,2,6,6-tetramethyl-3,5-heptanedionato)palladium

Bis(2,2,6,6-tetramethyl-3,5-heptanedionato)palladium (Pd(thd)$_2$) was prepared after a modified recipe of White [22]. Palladium chloride (1.8 g, 0.01 mol) and sodium chloride (0.59 g, 0.01 mol) were dissolved in methanol (50 mL) and stirred at room temperature overnight. The solution was filtered in a 100 mL volumetric flask and diluted with methanol to give 0.1 M palladium(II) concentration. A mixture of this solution (100 mL), the ligand 2,2,6,6-tetramethyl-3,5-dione (9 mL), and sodium carbonate (1.06 g, 0.01 mol) was stirred overnight. The resulting yellow precipitate was filtered off, dried in vacuum and sublimed.

Analysis

The thermal behaviour of the prepared metal complexes was studied by thermogravimetry (TG), single differential thermal analysis (SDTA) and differential scanning calorimetry (DSC). TG and SDTA measurements were made in flowing inert nitrogen and reductive hydrogen/nitrogen (5% H$_2$) atmosphere. The TG/SDTA measurements were carried out with a Mettler-Toledo TA8000 system equipped with a TGA 850 thermobalance. DSC measurements were made with a Mettler-Toledo Star

DSC equipment. The sample size in the TG/SDTA measurements was about 10 mg and in the DSC measurements 5 mg. The heating rate was 10°C min^{-1} in all the measurements.

The molecular formulas of the volatilized species were determined by the field ionization/desorption technique with a mass spectrometer VG ProSpec. The mass spectrometric measurement by field ionization/desorption is a technique where the fragmentation of the compounds is limited [26].

^{1}H and ^{13}C NMR spectra of the studied ruthenium and palladium complexes were recorded with a Varian Gemini 2000 spectrometer at ambient temperature. Chemical shifts were referenced to tetramethylsilane and are given in ppm.

Results and discussion

Synthesis

All the complexes could be prepared after the recipes described in the experimental section. The products were purified by vacuum sublimation. Sublimation temperatures, melting points, sublimation yields and the colour of the complexes are given in Table 1. The preparation method B (stepwise addition of ligand into the Pt solution) resulted the purest $Pt(thd)_2$ with the highest yield of synthesis.

Table 1 Sublimation temperature in pressure 0.01 Hgmm, melting point and the colour of the complexes

Compound	Sublimation temperature/°C	Melting point/ °C	Sublimation yield/%	Colour
$Ru(thd)_3$	160–195	216[1]	100.0	red
$Ru(Cp)_2$		195	99.5	white
$Ru(acac)_3$	210–240	232	65.0	brown
$Pd(thd)_2$	155–160	239	99.8	yellow
$Pt(thd)_2$	90–95	255	100.0	yellow
$Hg(thd)_2$	190–200			white

[*]The melting points were measured by DSC technique, [1]also visually observed

Mass spectra

Mass spectrometric analysis and NMR spectra were used for the identification of synthesised complexes. Since the field ionization technique was used in the mass spectrometric measurements, no fragmentation of the complexes occurred but only the isotope distribution of the desired complexes is seen in the mass spectra.

In the mass spectrum of $Ru(thd)_3$ the molecular ions are observed at 645–654 *m/z* and in the mass spectrum of $Ru(acac)_3$ at 393–402 *m/z* with the corresponding isotope distribution. Species originating from $Ru(thd)_2$ or $Ru(acac)_2$ were not detected though the ethanolic solution used in the preparation could cause partial

reduction of Ru^{3+} to Ru^{2+}. Small amount of water was removed from $Ru(acac)_3$ sample in the beginning of the mass spectrometric measurement.
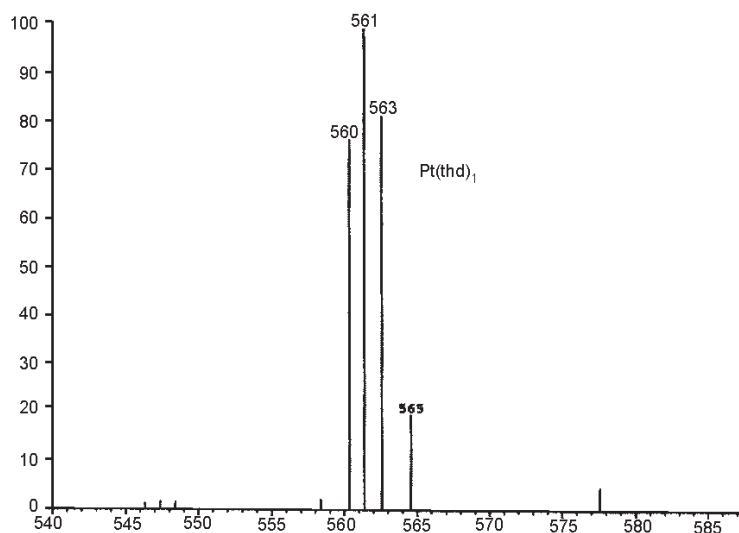

Fig. 1 The mass spectrum of $Pt(thd)_2$

For $Pd(thd)_2$ the molecular ion is observed at 473 *m/z*. Figure 1 shows the mass spectrum of pure $Pt(thd)_2$. The molecular ion is seen at 561 *m/z*. Mass spectrometric analysis showed that the synthesis of $Pt(thd)_2$ after the recipe of Werner [16] resulted in a mixture of $Pt(thd)_2$, $Hg(thd)_2$ and K_2HgCl_4 but the components of the mixture could be separated via careful sublimation. No quantitative amount of $Pt(thd)_2$ was formed when only silver salt was used in the synthesis. This indicates that $Pt(thd)_2$ is also formed via exchange reaction of $Hg(thd)_2$ with $Pt(H_2O)_4^{2+}$.

NMR spectra

^{1}H NMR spectra were measured for all the ruthenium and palladium complexes studied. Results are reported in Table 2. Because the ruthenium(III) complexes are paramagnetic, the spectra are different compared to the spectra of the other metal complexes. The signals appear at unusual positions and in some cases their interpretation is difficult. For example, the signals of the methine protons of the β-diketonate ligands appear at very high field. ^{13}C NMR spectra were not measured for ruthenium complexes because of the paramagnetism.

Table 2 NMR data for complexes Ru(acac)$_3$, Ru(thd)$_3$, RuCp$_2$ and Pd(thd)$_2$.
Chemical shifts (δ) referenced to TMS

Compound	^{1}H NMR		^{13}C NMR				
	CH	CH$_3$	C(CH$_3$)	CH$_3$	(C(CH$_3$))	CH	CO
Ru(acac)$_3$	−30.02	−5.58					
Ru(thd)$_3$	−32.76		2.50				
RuCp$_2$	2.70						
Pd(thd)$_2$	5.67		1.14	28.60	40.52	91.96	196.46

Thermal analyses

Since the complexes are used as precursors for catalysts that are prepared by impregnation or by CVD or ALE techniques, knowledge about their reduction and thermal behaviour is required. Thus we made TG/SDTA analysis both in the flowing nitrogen and reductive H$_2$/N$_2$ (5% H$_2$) atmospheres. The summary of the results is presented in Table 3.

Table 3 Temperatures and masses measured by TG and SDTA in N$_2$ and N$_2$/H$_2$ (5% H$_2$) atmospheres

Compound	TG in N$_2$		TG in H$_2$		SDTA	
	T/°C	mass remaining/%	T/°C	mass remaining/%	in N$_2$ T/°C	in H$_2$ T/°C
Ru(acac)$_3$	146, 263, 344, 600	90.90, 79.14, 68.18, 62.44	140, 252, 362, 600	91.79, 80.71, 66.80, 60.96	107, 238, 310	106, 235, 310
Ru(Cp)$_2$	215	0.27	211	0.00	123, 204	120, 202
Ru(thd)$_3$	284	0.13	283	0.00	164, 179, 190, 216, 275	164, 179, 189, 215, 274
Pt(thd)$_2$	263, 415, 600	39.52, 17.53, 3.32	250, 408, 600	49.31, 18.89, 3.31	–	–
Pd(thd)$_2$	291	1.66	153	22.63	243, 278	129(ex), 151

For metal complex to be volatile, it is generally desirable that the molecular mass and interactions between molecules are minimized – monomeric complexes with low molecular mass are preferred. Tendency of metal ion to form oligomeric complexes and tendency to interact with surroundings increases with increasing preferred coordination number, ion size and size-to-charge ratio. Known crystal structures of Ru(acac)$_3$ [27], RuCp$_2$ [28], and Pd(thd)$_2$ [29] show that these complexes are monomeric in solid phase. Structures Ru(thd)$_3$, and Pt(thd)$_2$ have not been reported, but it is obvious that these complexes are monomeric too. Complex Pt(thd)$_2$ has the highest volatility despite the second highest molecular mass of the complex. Molecu-

lar masses of the complexes decrease in order Ru(thd)$_3$>Pt(thd)$_2$>Pd(thd)$_2$>Ru(acac)$_3$ >RuCp$_2$. However, the size of Pt^{2+} ion (0.60 Å) is smaller than Ru^{3+} and Pd^{2+} ions (0.68 and 0.64 Å, respectively) [30], and this can explain the better volatility of the Pt(thd)$_2$ complex.
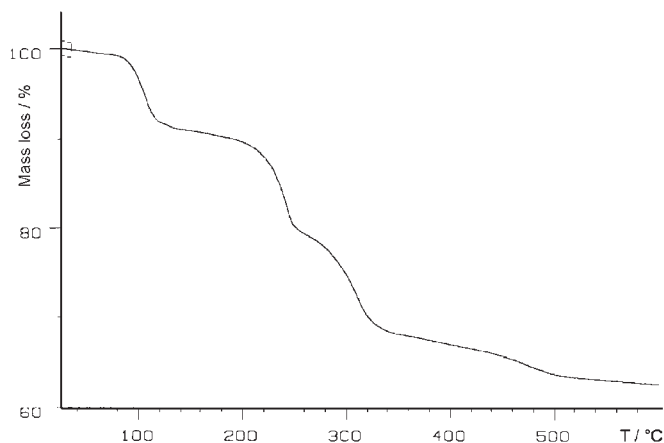
Fig. 2 TG curve of Ru(acac)$_3$ in N$_2$ atmosphere

Ru(acac)$_3$ behaved similarly in both nitrogen and hydrogen containing nitrogen atmospheres and decomposed in the TG measurements (Fig. 2). However, under reduced pressure it could be sublimed (Table 1). In the TG curve it is possible to separate 4 different steps of mass loss. In nitrogen flow the steps are located at ($T_{1/2}$) 40–146, 146–263, 263–344, and 344–600°C and the corresponding mass losses are 8.96, 11.76, 10.96, 5.74 and the residue at 600°C is 62.44%. The first step could be due to loss of coordinated water, which is also seen, in the mass spectrum of the complex. If the first mass loss (8.96%) corresponds water release one water molecule is bounded with one Ru(acac)$_3$ complex. Other three steps are associated to thermal decomposition. The TG curve measured in the hydrogen containing atmosphere is very similar, but the residue is 60.96% that is 1.51% smaller than the residue in pure nitrogen atmosphere.

Other ruthenium complexes, Ru(thd)$_3$ and Ru(Cp)$_2$, sublimed almost entirely under both nitrogen and hydrogen containing atmosphere. Figures 3 and 4 present the TG and SDTA curves for Ru(thd)$_3$ and Ru(Cp)$_2$ measured in H$_2$/N$_2$ (5% H$_2$) flow. Both complexes evaporated at 2–4°C higher temperature in pure nitrogen flow but otherwise the curves were identical with the curves measured in 5% hydrogen flow. For Ru(thd)$_3$ the residues were smaller than 0.14% which indicates that decomposition is negligible. The residues for Ru(Cp)$_2$ were 0.28 and 0.00% in the nitrogen and hydrogen containing atmospheres, respectively. SDTA analysis showed two endothermic signals due to melting and evaporation of Ru(Cp)$_2$ while 5 endotherms are seen in the SDTA of Ru(thd)$_3$ (Table 3). The first three endotherms are believed to be

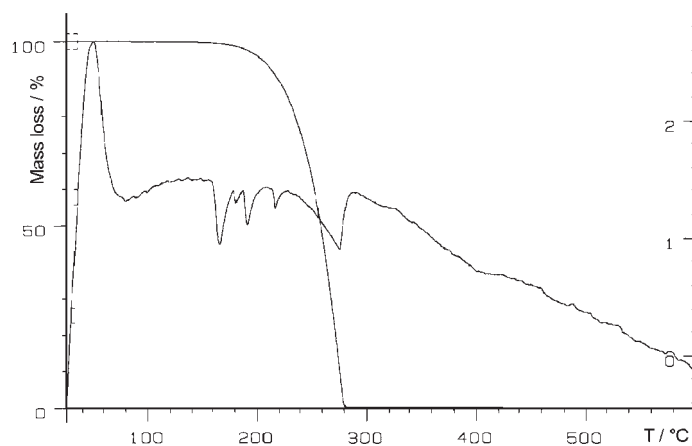**Fig. 3** TG and SDTA curves of Ru(thd)$_3$ in H$_2$/N$_2$ (5% H$_2$) atmosphere
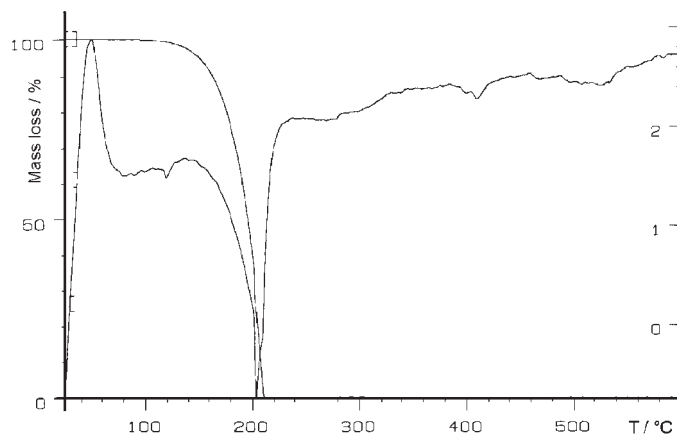
Fig. 4 TG and SDTA curves of Ru(Cp)$_3$ in H$_2$/N$_2$ (5% H$_2$) atmosphere

due to phase changes while the fourth is assigned for melting. DSC measurement of Ru(thd)$_3$ shows four endotherms (Fig. 5).

Morozova *et al.* [31] earlier reported TG and DTA data for Ru(acac)$_3$ and Ru(thd)$_2$. Their sample of Ru(acac)$_3$ decomposed under helium atmosphere in one step, starting at 285°C, leaving less than 20% residue. For Ru(thd)$_3$ they report TG and DTA characteristics under helium similar to our findings under nitrogen. Morozova *et al.* also report that under hydrogen atmosphere ruthenium complexes are reduced to metallic ruthenium. Here our findings are in slight disagreement. However, they have probably used pure H$_2$ atmosphere while we used 5% hydrogen–nitrogen mixture. Morozova *et al.* have assigned the DTA endotherm at 162°C to melting of Ru(thd)$_3$ but we observed that the complex melts at 216°C where an endotherm (DSC, SDTA) is also observed.
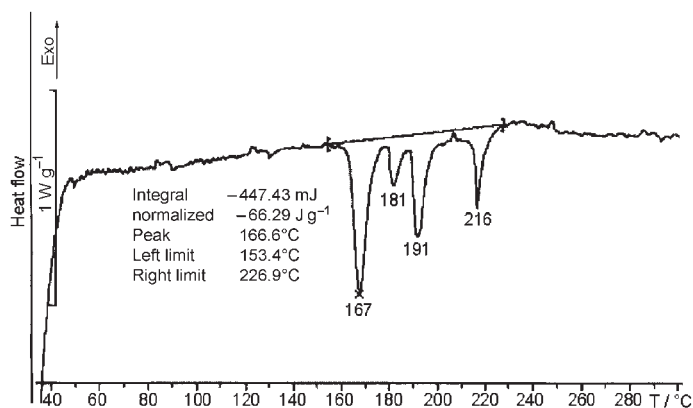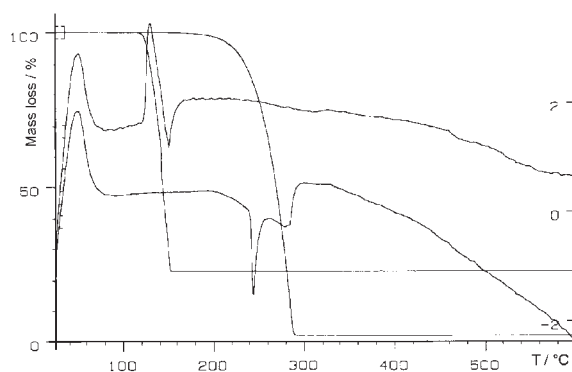
Fig. 5 DSC curve of Ru(thd)$_3$

Fig. 6 TG and SDTA curves of Pd(thd)$_2$ in N$_2$ and H$_2$/N$_2$ (5% H$_2$) atmosphere

Figure 6 shows the TG and SDTA curves of Pd(thd)$_2$ in nitrogen and in hydrogen containing atmosphere, respectively. Pd(thd)$_2$ sublimed under the nitrogen atmosphere. Some decomposition took place since the residue of the TG-measurement was 1.66%. Under hydrogen atmosphere Pd(thd)$_2$ was reduced to metallic palladium in one step. Theoretical residue for Pd is 22.50 and the measured residue was 22.63%. SDTA in 5% H$_2$ containing atmosphere showed exothermic change caused by the reduction process. DSC analysis of Pd(thd)$_2$ similar to that of Pt(thd)$_2$ gave one single signal that is most probably due to melting (Fig. 7).

Figure 8 shows the TG and DTG curves of Pt(thd)$_2$ in nitrogen atmosphere. The evaporation of the complex seems to happen in three different phases. Similar curve is observed under H$_2$/N$_2$ (5% H$_2$) atmosphere. However, the sample size in these experiments was only about 2 mg. The mass spectrometric analyses showed only Pt(thd)$_2$ with its isotope distribution (Fig. 1). The reason for three different phases in the evaporation can thus not be the impurities of the complex but some thermal changes of Pt(thd)$_2$ complex.
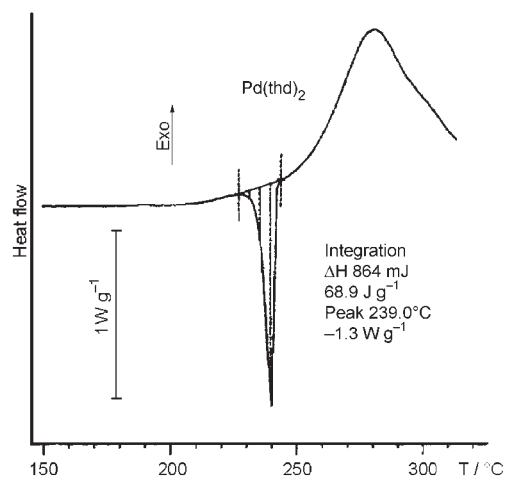
Fig. 7 DSC curve of Pd(thd)$_2$
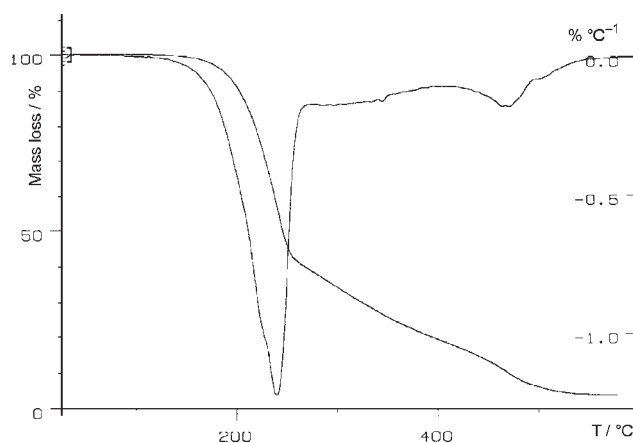
Fig. 8 TG and DTG curves of Pt(thd)$_2$ in N$_2$ atmosphere. Sample size: about 2 mg

Conclusions

All the studied complexes are suitable precursors for the ALE and CVD preparations on basis of their thermal behaviour. Sublimation in reduced pressure, TG and SDTA analysis showed that Ru(thd)$_3$, Ru(Cp)$_2$, Pd(thd)$_2$ and Pt(thd)$_2$ evaporated easily in the inert atmosphere. Ru(acac)$_3$ decomposed in the atmospheric pressure but could be sublimed under reduced pressure. Pd(thd)$_2$ was reduced to metallic Pd under hydrogen flow. Ru(thd)$_3$ and Ru(Cp)$_2$ evaporated both under hydrogen and nitrogen. The results indicate that the ligands of complexes should probably be removed before the reduction of metal precursors to the metal in the catalyst preparation. Pd(thd)$_2$ does not seem to require ligand removal before the reduction.

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