



## Synthesis and Characterization of Ruthenium and Palladium Complexes of 2,2,6,6-Tetramethyl-3,5-heptanedione

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Ruthenium and palladium complexes of 2,2,6,6-tetramethyl-3,5-heptanedione were synthesized and characterized by elemental analyses, IR,  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR and UV. Thermal properties of these complexes were also studied by TG-DTA under air and nitrogen atmosphere.

**Key Words:** Synthesis, Palladium, Ruthenium, Complexes, 2,2,6,6-Tetramethyl-3,5-heptanedione, Thermal analysis.

### INTRODUCTION

Heterogeneous catalysts typically consist of active metals supported on porous high surface area material. Ruthenium and palladium metals play an important role as catalysts for the various hydrogenation reactions in the industrial chemistry and in the production of fine chemicals<sup>1</sup>. The methods used frequently in the preparation of heterogeneous catalysts are include co-crystallization, ion-exchange or impregnation, followed by reduction with hydrogen. In order to achieve a better dispersion of active components on the support, other loading methods have recently been explored<sup>2</sup>. For example, chemical vapour deposition is a thin film deposition technique and has been successfully applied to the preparation of certain kinds of Ru- and Pd-based hydrogenation catalysts<sup>3,4</sup>.

Volatile precursors that do not decompose during evaporation are essential for a satisfactory chemical vapour deposition process. In addition, a good precursor is required to be easy to handle and store, pure and non-toxic. Metal complexes of  $\beta$ -diketonates usually meet most of these criteria<sup>5</sup>. In this paper, we report the synthesis and thermal characteristics of  $\text{Ru}(\text{thd})_3$  and  $\text{Pd}(\text{thd})_2$ , an ideal kind of Ru and Pd precursors, which are recently being used in the preparation of hydrogenation catalysts by chemical vapour deposition.

### EXPERIMENTAL

The reagents and solvents used were of commercially available reagent quality. Chemical analyses for C and H were performed with a Carlo-Ebra Instrument, whereas metal was determined according to the conventional method. FI-IR spectra were recorded in the 4000–400  $\text{cm}^{-1}$  regions on a Perkin Elmer

880 spectrometer with KBr pellets.  $^1\text{H}$  NMR was performed on Bruker DRX-500 (500.13 MHz) and  $^{13}\text{C}$  NMR was performed on Bruker AV400 (100.62 MHz) in chloroform. Electronic spectra were scanned in EtOH or acetonitrile Shimadzu UV-2401 PC. Thermogravimetric and differential thermal analysis (TG-DTA) were carried out with a NETZSCH-STA 409 PG/PC Jupiter thermo-analysis equipment in air and nitrogen atmosphere (flux rate: 40  $\text{cm}^3 \text{min}^{-1}$ , heating rate: 10 K/min, temperature interval: 25–1000  $^\circ\text{C}$ , sample mass: 24–25 mg).

Ruthenium and palladium complexes of 2,2,6,6-tetramethyl-3,5-heptanedione (thd) were synthesized according to the previous methods with some modification and improvement<sup>6,7</sup>.

Hydrated ruthenium trichloride (1.5 g, 7 mmol), 1 g of sodium hydrogen carbonate and 10 g 2,2,6,6-tetramethyl-3,5-heptanedione were refluxed for 4 h at 140  $^\circ\text{C}$  on an oil bath and then an additional amount (2 g) of sodium hydrogen carbonate was added and the reflux was continued for another 10 h at 230  $^\circ\text{C}$ . Water and excessive 2,2,6,6-tetramethyl-3,5-heptanedione were removed by evaporating the reaction mixture under reduced pressure and the resulting residue was extracted with carbon tetrachloride, orange crystals of  $\text{Ru}(\text{thd})_3$  were obtained from carbon tetrachloride after evaporation, followed by re-crystallization in ethanol. Found : C, 61.0 %; H, 8.6 %; Ru, 15.4 %. Calculated for  $\text{C}_{33}\text{H}_{57}\text{O}_6\text{Ru}$ : C, 60.8 % H, 8.9 % Ru, 15.3 %.

Palladium chloride (1.8 g) and sodium chloride (1.18 g) were mixed in methanol (60 mL) and stirred at 40  $^\circ\text{C}$  overnight. To the mixture, 2,2,6,6-tetramethyl-3,5-heptanedione (9 mL) and sodium carbonate (1.06 g) was added and stirred. 8 h later, the resulting yellow precipitate was filtered off,

washed with water and dried under vacuum. Found : C, 55.7 %; H, 8.0 %; Pd, 22.4 %. Calculated for  $C_{22}H_{38}O_4Pd$ : C, 55.2 % H, 8.3 % Ru, 22.9 %.

## RESULTS AND DISCUSSION

The data of elemental analyses for both complexes are in good agreement with the calculated values based on the molecular formula. The IR characteristic bands of  $Ru(thd)_3$  and  $Pd(thd)_2$  are shown in Figs. 1 and 2. The binding of thd to metal atom is confirmed by vibrations at  $511\text{ cm}^{-1}$  for Ru-O and at  $516\text{ cm}^{-1}$  for Pd-O. The strong bands near  $3000\text{ cm}^{-1}$  belong to the stretching vibration of CH and  $CH_3$  and C=O is responsible for the very strong absorbance bands appearing near  $1500\text{ cm}^{-1}$  and at  $1300\text{ cm}^{-1}$ . The  $^1H$  and  $^{13}C$  NMR spectra of  $Pd(thd)_2$  are all consistent with their corresponding protons both in the chemical shifts and the number of hydrogen. The CH and  $CH_3$  protons resonated as a singlet at 1.17 and 5.56 ppm, respectively.

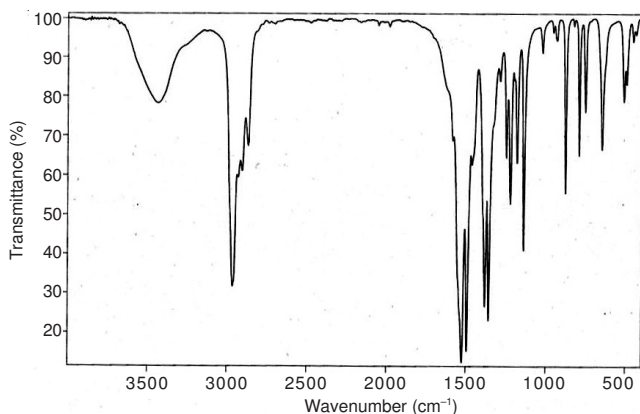


Fig. 1. IR Spectrum of  $Ru(thd)_3$  in KBr tablet

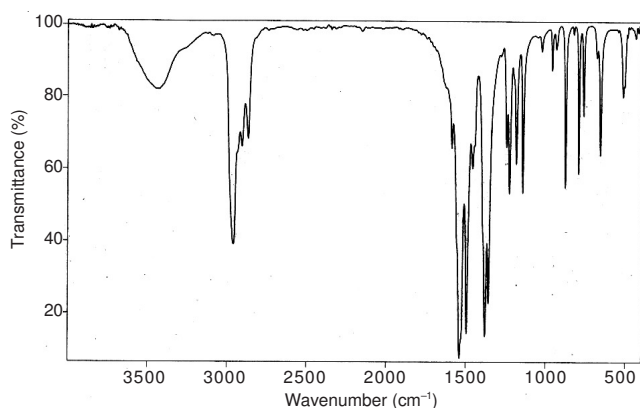


Fig. 2. IR spectrum of  $Pd(thd)_2$  in KBr tablet

The data of the chemical shifts of  $^1H$  and  $^{13}C$  NMR for both complexes are presented in Table-1.

TABLE-1  
NMR DATA FOR COMPLEXES  $Ru(thd)_3$  AND  $Pd(thd)_2$   
CHEMICAL SHIFTS ( $\delta$  ppm) REFERENCED TO  $CDCl_3$

Compound	$^1H$ NMR		$^{13}C$ NMR			
	CH	$CH_3$	C( $CH_3$ )	$CH_3$	CH	CO
$Ru(thd)_3$	1.15	2.55				
$Pd(thd)_2$	1.17	5.66	40.49	28.60	91.89	196.37

thd = 2,2,6,6-tetramethyl-3,5-heptanedione

As for  $Ru(thd)_3$ , which is paramagnetic due to  $d^5$  configuration of Ru(III), only  $^1H$  NMR exhibits the characteristics of 2,2,6,6-tetramethyl-3, 5-heptanedionate.  $^{13}C$  NMR was greatly complicated by the paramagnetism of Ru(III) and no satisfactory explanation is reported<sup>8</sup>.

In the UV spectrum,  $Ru(thd)_3$  showed two absorption peaks at 279 and 365 nm, which could be assigned to  $\pi$ - $\pi^*$  electron transition within the ligand and  $d$ - $d$  electron transition, based on the intensity and wavelengths of the absorption peaks<sup>9</sup>. In addition to the two absorption peaks similar to  $Ru(thd)_3$ , two strong absorption bands developed in the spectrum of  $Pd(thd)_2$ , probably due to M-L and L-M charge transfer transitions. The UV characteristic absorption peaks of  $Ru(thd)_3$  and  $Pd(thd)_2$  are shown in Table-2.

TABLE-2  
UV ABSORPTION SPECTRUM DATA OF  $Pd(thd)_2$  AND  $Ru(thd)_3$

Compound	$\lambda_{max}$ (nm)	Belong to
$Ru(thd)_3$	279.0	$\pi$ - $\pi^*$
	365.1	d-d
$Pd(thd)_2$	211.9	M-L
	232.1	L-M
	256.7	$\pi$ - $\pi^*$
	330.9	d-d

thd = 2,2,6,6-tetramethyl-3,5-heptanedione

Investigation on the thermal properties of  $Ru(thd)_3$  and  $Pd(thd)_2$  was made in order to provide some information for chemical vapour deposition techniques. The data obtained from TG-DTA curves are listed in Table-3. On heating the complexes underwent sublimation accompanied by decomposition both in the  $N_2$  and air atmosphere. The atmosphere had no apparent effects on starting temperatures required for sublimation and decomposition. The final decomposition product was metal in the  $N_2$  atmosphere and a mixture of metal and its oxide in the air atmosphere.

TABLE-3  
CHARACTER PARAMETERS OF TG -DTA  
CURVES OF  $Ru(thd)_3$  AND  $Pd(thd)_2$

Compound	TG		DTA	Remarks
	$T_{range}$ ( $^{\circ}C$ )	Mass loss (%)	Peaks ( $^{\circ}C$ )	
$Ru(thd)_3$ in $N_2$	165-300	96.58	282 (exo)	Sublimation decomposition
$Ru(thd)_3$ in air	164-293	93.70	290 (endo)	Sublimation decomposition
$Pd(thd)_2$ in $N_2$	190-295	75.63	238 (exo)	Sublimation decomposition
$Pd(thd)_2$ in air	185-284	78.79	283 (endo)	Sublimation decomposition

thd = 2,2,6,6-tetramethyl-3,5-heptanedione

## Conclusion

A modified method for synthesis of  $Ru(thd)_3$  and  $Pd(thd)_2$  has been developed and the complexes are well consistent with the chemical structure of  $Ru(thd)_3$  and  $Pd(thd)_2$ , as illustrated in Fig. 3. In order to obtain pure metal film, it is suggested the MOCVD process using  $Ru(thd)_3$  and  $Pd(thd)_2$  as precursors should be carried out in the  $N_2$  atmosphere.

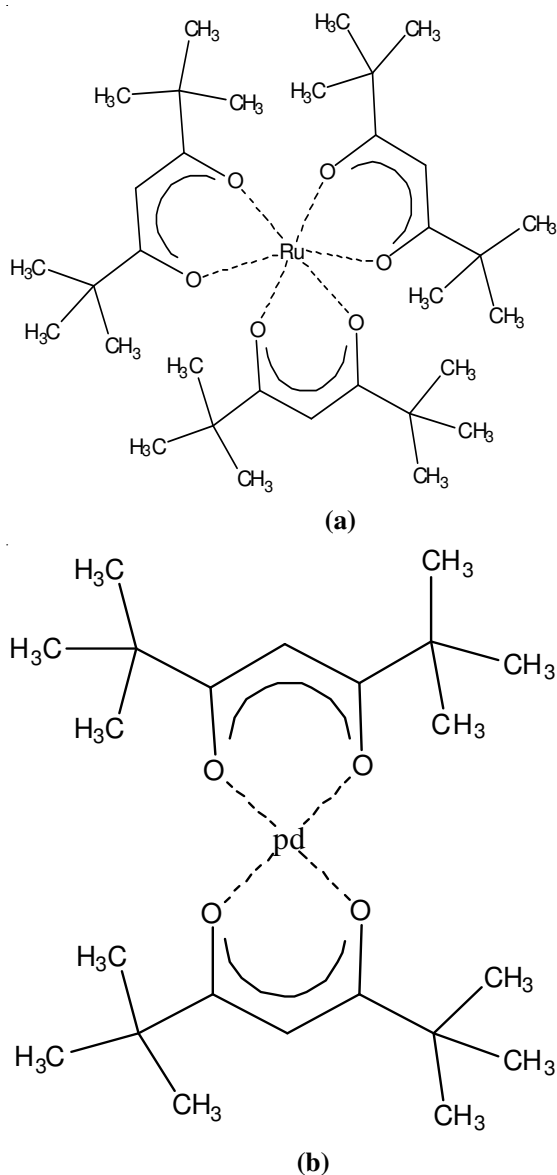


Fig. 3. Chemical structure of  $\text{Ru}(\text{thd})_3$  (a) and  $\text{Pd}(\text{thd})_2$  (b)

### ACKNOWLEDGEMENTS

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