

2-Methoxycycloocta-1,5-dienyl platinum complexes as precursors for platinum nanoparticles

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Abstract. Thermolysis of $[\text{Pt}_2(\mu\text{-OR})_2(\text{C}_8\text{H}_{12}\text{OMe})_2]$ (R = Me or Ac) in hexadecylamine (HDA) at 210°C under argon atmosphere gave platinum nanoparticles which were characterized by XRD, EDAX and TEM analysis. Both spherical (~10 nm) and rod-like (~19 nm length with aspect ratio of 2:3) face centred cubic (*fcc*) platinum metal nanoparticles could be isolated. The thermogravimetric analyses of these complexes revealed that they undergo a single step decomposition leading to the formation of platinum metal powder.

Keywords. Platinum complexes; pyrolysis; platinum nanoparticles; XRD; TEM.

1. Introduction

Noble-metal nanoparticles have attracted considerable attention during the last 15 years or so due to their applications in catalysis, electronics and biology (Eustis and Al-Sayed 2006; Astruc 2008). Palladium and platinum nanoparticles are widely used for hydrogenation (Mandal *et al* 2002; Wilson *et al* 2006; Ganesan *et al* 2007) and C–C coupling (Gaikwad *et al* 2007; Gallon *et al* 2007; Kovala-Demertzi *et al* 2008; Yang *et al* 2008) reactions, oxidation of alcohols (Wang *et al* 2007) and hydrogen absorption (Kobayashi *et al* 2008). Platinum nanoparticles are prepared by different methods like sono-chemical (Fujimoto *et al* 2001), radiolytic (Belapurkar *et al* 2001) and predominantly by chemical reduction of either PtCl_2 or H_2PtCl_6 in the presence of a suitable capping agent. A variety of reducing agents, such as hydrogen (Yamada *et al* 2005; Wang and Toshima 1997), NaBH_4 (van Rheenen *et al* 1983; Perez *et al* 1999), hydrazine (Solla-Gullon *et al* 2000) and potassium bitartrate (Tan *et al* 2003) have been successfully employed for the preparation of platinum nanoparticles in different shapes (Ahmadi *et al* 1996; Bi and Lu 2008).

Palladium and platinum chlorides, e.g. PdCl_2 in Wacker process and H_2PtCl_6 in hydrosilylation, are widely used in organic transformations involving olefins (Speier *et al* 1957; Smidt *et al* 1962; Speier 1979). Although identity of active catalytic species in these reactions often remain elusive, a metal(0), usually metal nanoparticles species, is believed to be an active catalyst. For instance hydrosilylation of olefins by chloroplatinic acid requires induction

period during which an active catalytic species, finely divided platinum(0), forms. Arguably platinum olefin complexes may, therefore, serve as precursors for the preparation of platinum nanoparticles, although organometallic platinum complexes have been used for deposition of thin films on a variety of substrates (Hierso *et al* 1998). Thus to evaluate suitability of platinum olefin complexes for the preparation of platinum nanoparticles we have chosen two well characterized platinum complexes, $[\text{Pt}_2(\mu\text{-OR})_2(\text{C}_8\text{H}_{12}\text{OMe})_2]$ (R = Me, Ac), reported in the literature (Giordano and Vitagliano 1981; Goel *et al* 1981; Goel and Vanderveer 1984) for the present investigation. The results of this work are presented herein.

2. Experimental

2.1 Materials

The complexes, $[\text{Pt}_2(\mu\text{-OR})_2(\text{C}_8\text{H}_{12}\text{OMe})_2]$ (R = Me, Ac), were prepared according to literature methods (Giordano and Vitagliano 1981; Goel *et al* 1981; Goel and Vanderveer 1984), purified by recrystallization and characterized by elemental analysis and ^1H NMR spectral data. Solvo-thermal decomposition was carried out in a three-necked round bottom flask under an argon atmosphere.

2.2 Instruments

TG curves were obtained at a heating rate of $10^\circ\text{C min}^{-1}$ under flowing argon on a Setaram 92-16-18 instrument. EDAX and SEM were recorded on a Tescan Vega 2300T/40 instrument. Powder XRD patterns were recorded on a Philips PW1820 using Cu-K_α radiation. A JEOL-

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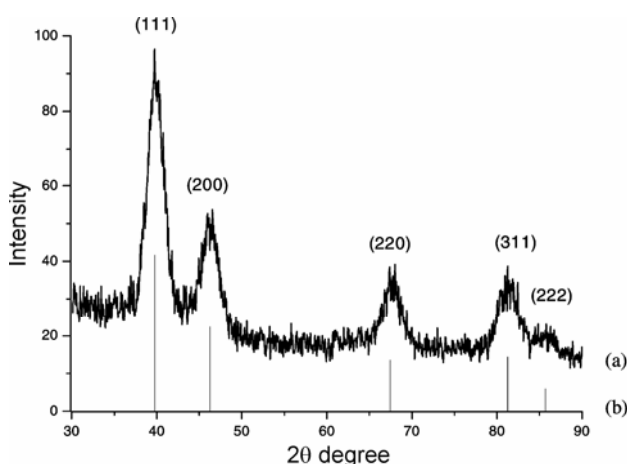
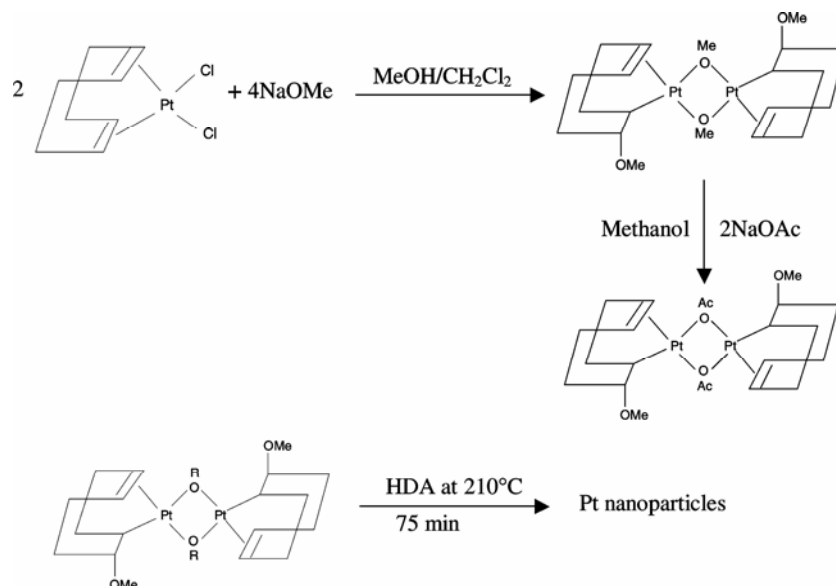


Figure 1. (a) Powder XRD pattern of the residue obtained after decomposition of $[\text{Pt}_2(\mu\text{-OMe})_2(\text{C}_8\text{H}_{12}\text{OMe})_2]$ in HDA at 210°C . (b) Powder Diffraction File No. 04-0802 compiled by JCPDS-ICDD, International Centre for Diffraction Data USA, 1990.

200FX transmission electron microscope operating at accelerating voltages up to 200 kV was used for TEM studies. The samples for TEM and SAED were prepared by placing a drop of sample dispersed in acetone on a carbon-coated copper grid.

2.3 Preparation of Pt nanoparticles

(a) A mixture of $[\text{Pt}_2(\mu\text{-OMe})_2(\text{C}_8\text{H}_{12}\text{OMe})_2]$ (59 mg, 0.08 mmol) and HDA (2.5 g) was taken in a 100 mL three-necked round-bottom flask and degassed at 90°C under vacuum and stirring for 30 min. The reaction flask

was filled with argon and the temperature was raised to 150°C and maintained for 15 min whereupon colour changed from pale yellow to yellowish-brown indicating decomposition of the precursor. The reaction temperature was further raised to 210°C and maintained for 30 min during which a black residue was formed. The reaction mixture was then cooled to 60°C and 10 cm^3 of toluene was added. A black precipitate was obtained by adding methanol which was then separated by centrifugation, washed with methanol and dried. Similarly, decomposition of $[\text{Pt}_2(\mu\text{-OAc})_2(\text{C}_8\text{H}_{12}\text{OMe})_2]$ in HDA at 210°C also yielded platinum nanoparticles.

(b) A weighed amount of $[\text{Pt}_2(\mu\text{-OMe})_2(\text{C}_8\text{H}_{12}\text{OMe})_2]$ (70 mg, 0.09 mmol) was taken in a quartz boat and heated in a furnace at 250°C for 3 h under flowing argon. The residue obtained was washed with benzene and hexane and dried under vacuum (41 mg, 58%).

3. Results and discussion

The complexes, $[\text{Pt}_2(\mu\text{-OR})_2(\text{C}_8\text{H}_{12}\text{OMe})_2]$ ($\text{R} = \text{Me}, \text{Ac}$), were prepared according to the reaction routes shown in scheme 1 and were used after recrystallization (Giordano and Vitagliano 1981; Goel *et al* 1981; Goel and Vanderveer 1984). Thermogravimetric analyses of $[\text{Pt}_2(\mu\text{-OR})_2(\text{C}_8\text{H}_{12}\text{OMe})_2]$ ($\text{R} = \text{Me}, \text{Ac}$) complexes were carried out. The TG curves of these complexes showed a single step of decomposition with an onset temperature of 149°C for $[\text{Pt}_2(\mu\text{-OMe})_2(\text{C}_8\text{H}_{12}\text{OMe})_2]$ and 144°C for $[\text{Pt}_2(\mu\text{-OAc})_2(\text{C}_8\text{H}_{12}\text{OMe})_2]$ complexes. The TG data indicates that acetato-bridged complex is more labile than the methoxy bridged derivative. The solvothermal decomposition of both the complexes in coordinating solvents

such as HDA (hexadecylamine, bp: 330°C) at 210°C led to the formation of platinum nanoparticles as inferred from powder XRD patterns (figure 1) (JCPDS file no. 04-

0802) of the residue. The complex $[\text{Pt}_2(\mu\text{-OMe})_2(\text{C}_8\text{H}_{12}\text{OMe})_2]$ on pyrolysis in a furnace at 250°C gave platinum metal powder as inferred from powder XRD patterns of the residue.

The particle sizes calculated from Scherrer formula for the samples prepared by thermolysis in HDA at 210°C were 3.6 ± 0.6 nm (from $[\text{Pt}_2(\mu\text{-OMe})_2(\text{C}_8\text{H}_{12}\text{OMe})_2]$) and 3 ± 0.6 nm (from $[\text{Pt}_2(\mu\text{-OAc})_2(\text{C}_8\text{H}_{12}\text{OMe})_2]$). The TEM images of the former (methoxy bridged complex) showed that the particles are in spherical shape with average diameter of ~ 10 nm (figure 2) while in the latter (acetate-bridged complex), they were rod-like with aspect ratio of 2.3 and average diameter of ~ 19 nm (figure 3). The mismatch between the sizes estimated by XRD and obtained by TEM is because particles size does not determine linewidth directly in XRD. The SAED patterns displaying concentric rings (inset of figure 2a) corresponding to the lattice planes (111), (200) and (220) are consistent with the *fcc* phase of the platinum nanoparticles. The size distribution of particles (from $[\text{Pt}_2(\mu\text{-OMe})_2(\text{C}_8\text{H}_{12}\text{OMe})_2]$) was measured by counting 300 particles. The average size of particles was 10.5 ± 0.5 nm, with sizes ranging from 9–12 nm (inset of figure 2b). Also the size distribution of rod-shaped particles (from $[\text{Pt}_2(\mu\text{-OAc})_2(\text{C}_8\text{H}_{12}\text{OMe})_2]$) was measured by counting 200 particles. The average size of particles was 19.5 ± 0.5 nm in length, with sizes ranging from 18–21 nm (inset of figure 3).

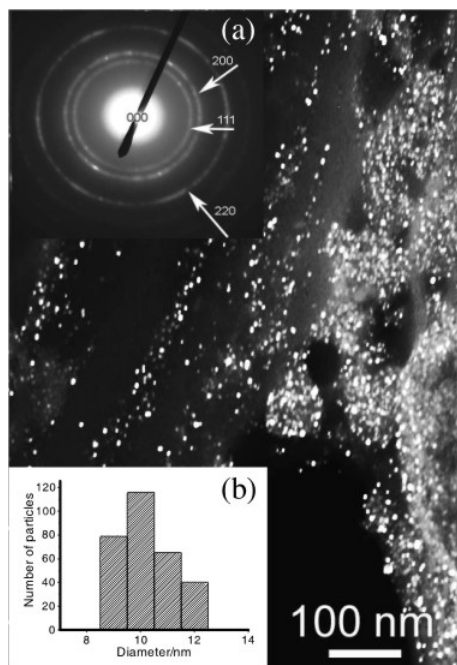


Figure 2. TEM picture of residue obtained after decomposition of $[\text{Pt}_2(\mu\text{-OMe})_2(\text{C}_8\text{H}_{12}\text{OMe})_2]$ in HDA at 210°C; insets show (a) SAED pattern and (b) size distribution.

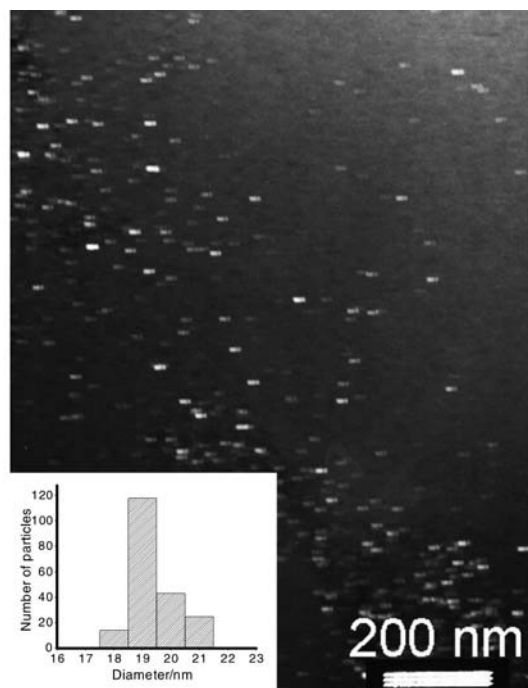


Figure 3. TEM picture of residue obtained after decomposition of $[\text{Pt}_2(\mu\text{-OAc})_2(\text{C}_8\text{H}_{12}\text{OMe})_2]$ in HDA at 210°C; inset shows size distribution.

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