Polyhedron 40 (2012) 40-45

Contents lists available at SciVerse ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly

Volatile fluorinated trimethylplatinum(IV) β -diketonates: Synthesis, properties, and structure

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ARTICLE INFO

Article history: Received 11 October 2011 Accepted 27 March 2012 Available online 6 April 2012

Keywords: Organoplatinum(IV) precursors β-Diketonate Trimethylplatinum(IV) Volatility Structure

ABSTRACT

Stable volatile fluorinated trimethylplatinum(IV) β -diketonates: [(CH₃)₃Pt(CF₃-CO-CH-CO-CF₃)H₂O], (CH₃)₃Pt(hfac)H₂O (**1**); [(CH₃)₃Pt(CF₃-CO-CH-CO-CH₃)H₂O], (CH₃)₃Pt(ffac)H₂O (**2**); [(CH₃)₃Pt(CF₃-CO-CH-CO-CH₃)H₂O], (CH₃)₃Pt(ffac)H₂O (**2**); [(CH₃)₃Pt(CF₃-CO-CH-CO-C(CH₃)₃H₂O], (CH₃)₃Pt(ptac)H₂O (**3**) were synthesized with the yield of 92–95%. The obtained compounds were identified by elemental analysis, ¹H and ¹³C NMR, IR-spectroscopy. Crystal structure and thermal properties were studied. In compounds **1**, **2**, and **3**, the coordination Pt polyhedron is a slightly distorted PtC₃O₃ octahedron formed by three methyl groups, water molecule, and two oxygen atoms of the bidentate ligand. The Pt-C_{Me}, Pt-O_L, and Pt-O_W bond lengths and the chelate O-Pt-O angle values are within 1.86–2.16, 2.04–2.27, and 2.23–2.30 Å and 87.8–88.9°, respectively, in all complexes. The complexes are not sensitive to oxygen and moisture and stable for a long time upon storage.

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1. Introduction

Nanostructures and nanolayers on the basis of platinum metals are used in microelectronics, catalysis, etc. [1–3]. Metal–organic chemical vapor deposition (MOCVD) is widely used technique to produce such materials [4,5] from volatile precursors. Different Pt(II) and Pt(IV) volatile precursors are reviewed in [6]. Among known volatile Pt compounds used to produce platinum coatings by MOCVD, complexes with β -diketones, complexes of dimethyl platinum with cyclooctadiene (COD)Pt(CH₃)₂ and complexes of a trimethyl-cyclopentadienyl family are the most investigated. Besides sufficient volatility, MOCVD precursors should have good vaporization stability, moderate thermal stability and it is desirable that they are stable to moisture and oxygen, low-toxic. β -Diketonate complexes are met to these requirements; using the ligands (RC(O)CHC(O)R') with different terminal substituents allows tuning physico-chemical properties of the precursor.

Platinum forms with β -diketones both homoleptic square planar complexes Pt^{II}(β -diketonate)₂ and heteroleptic octahedral complexes R₃Pt^{IV}(β -diketonate)₂. Trialkylplatinum(IV) derivatives are used as starting compounds to obtain Pt(IV) β -diketonates, the most common choice is stable trimethylplatinum iodide, (CH₃)₃PtI, first prepared in [7]. It is known that trimethylplatinum(IV) and β -diketones form dimeric complexes of the general formula [Me₃Pt(R-CO-CH-CO-R)]₂, where R is an alkyl radical C_nH_{2n-1}, *n* = 3-5 [8-11]. In the dimeric [(CH₃)₃Pt(acac)]₂ complex, for example, acetylacetone behaves as a tridentate ligand involving the third donor, the middle ring carbon atom, along with two donor oxygen atoms to form the bridge $Pt-C_{\gamma}$ bond, thus resulting in the dimer:



However dimers are poorly volatile. The insertion of CF₃ groups into chelating ligands is known to improve volatility of the complexes [12]. We were the first to synthesize trimethylplatinum(IV) chelates based on various fluorinated β -diketones [13,14]. Fluorinated trimethylplatinum(IV) β -diketonates were revealed to be more volatile than homoleptic platinum(II) β -diketonates thoroughly studied by us earlier [15]. From the structural standpoint, fluorinated trimethylplatinum(IV) β -diketonates have not been studied: there is no data in the Cambridge Structural Database (CSDB).

This paper deals with the three volatile fluorinated trimethylplatinum(IV) β -diketonates, [(CH₃)₃Pt(CF₃-CO-CH-CO-CF₃)H₂O],



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^{0277-5387/\$ -} see front matter @ 2012 Published by Elsevier Ltd. http://dx.doi.org/10.1016/j.poly.2012.03.045

 $(CH_3)_3Pt(hfac)H_2O(1); [(CH_3)_3Pt(CF_3-CO-CH-CO-CH_3)H_2O], (CH_3)_3 Pt(tfac)H_2O(2); [(CH_3)_3Pt(CF_3-CO-CH-CO-C(CH_3)_3)H_2O], (CH_3)_3 Pt(ptac)H_2O(3), the synthesis, elemental analysis data, IR and ¹H and ¹³C NMR spectra, thermal study of the complexes, and their crystal structures.$

2. Results and discussion

2.1. Synthesis and characterization of [(CH₃)₃Pt(CF₃-CO-CH-CO-CF₃)H₂O], (**1**); [(CH₃)₃Pt(CF₃-CO-CH-CO-CH₃)H₂O], (**2**); [(CH₃)₃Pt(CF₃-CO-CH-CO-C(CH₃)₃ H₂O], (**3**)

The complexes **1–3** were synthesized according the following scheme:

 $K_2PtCl_6 \overset{+3CH_3Mgl}{\rightarrow} (CH_3)_3PtI \overset{+KL_F,H_2O}{\rightarrow} (CH_3)_3Pt(L_F)H_2O$

where HL_F – fluorinated β -diketone: 1,1,1,5,5,5-hexafluoro-2,4-pentanedione – $CF_3COCH_2COCF_3$ (Hhfac); 1,1,1-trifluoro-2,4-pentanedione – $CF_3COCH_2CO-CH_3$ (Htfac); 1,1,1-trifluoro-5,5-dimethyl-2,4hexanedione – $CF_3COCH_2CO-C(CH_3)_3$ (Hptac).

Trimethylplatinum iodide, (CH₃)₃Ptl, was used as the starting compound for the synthesis of volatile platinum(IV) β -diketonates. This compound was previously prepared from anhydrous salt K₂PtCl₆ and CH₃Mgl by the Grignard reaction according to the procedure from [16]. It should be noted we have modified this procedure and increased the yield of the complex from 55% to 75%. Potassium salts of the ligands (KL_F) previously obtained by mixing ethanol solutions of KOH and HL_F in 1:1 ratio were used for the synthesis of β -diketonates platinum(IV).

It is noteworthy that in the case of using the potassium ligand salts (KL_F) to synthesize fluorinated β -diketonates the yield of the target product was no more than 50%. We succeeded in preparing fluorinated trimethylplatinum(IV) β -diketonates with the 92–95% yield by adding silver ions in the reaction mixture. The complexes prepared are crystalline substances readily soluble in organic solvents, they are not sensitive to oxygen and moisture and stable for a long time upon storage.

Mass spectra of the reported compounds recorded under electron impact (EI) ionization (70 eV) are similar, peak at maximal mass-tocharge (m/z) ratio corresponds to [(CH₃)₃PtL_F]⁺, the most intensive platinum containing peak is [(CH₃)₃PtL_F]⁺, there no molecular ion corresponding to [(CH₃)₃PtL_FH₂O]⁺ was recorded. The last fact is obviously explained by instability of the molecular ion formed under EI. We do not use softer ionization technique since occurrence of water as a ligand in the complex was confirmed by other methods.

IR spectra of compounds **1–3** confirm the chelate type of platinum – β -diketonate bonding. The C–H and Pt–CH₃ stretching vibrations occur at 3000–2800 cm⁻¹. Characteristic C–O and C=C vibrations of the chelate ring appear at 1650–1450 cm⁻¹. The less intense bands at 500–600 cm⁻¹ are associated with the Pt–C vibrations [18]. The presence of the water in the complexes is supported by strong absorption bands of the O–H vibrations at 3607 and 3435 cm⁻¹ (**1**), one wide band at 3437 cm⁻¹ (**2**), and at 3623 and 3352 cm⁻¹ (**3**), respectively [19]. In ¹H NMR spectra of complexes **1–3** protons of the CH₃ groups linked to the platinum atoms appear as one triplet of the equivalent CH₃ groups regardless of the β -diketonate ligand composition. These and elemental analysis data confirm the successful preparation of complexes **1–3**.

While using fluorinated β -diketones for the synthesis, we expected the formation of dimeric chelates similar to trimethylplatinum acetylacetonate [(CH₃)₃Pt(acac)]₂, since the trifluoromethyl group allows no steric hindrance to produce dimers [17]. However, it was found that fluorinated β -diketones do not form dimeric complexes. An obligatory condition for the formation of a monomeric fluorinated trimethylplatinum β -diketonate is the presence of a do-

nor ligand, e.g., H₂O, in the reaction mixture. This molecule has to occupy the sixth coordination site in the monomeric trimethylplatinum β-diketonate complex. This is why we failed to obtain fluorinated trimethylplatinum β-diketonates in anhydrous solvents. On adding a small amount of water in the reaction mixture (96% ethanol is sufficient), monomeric fluorinated complexes containing the water molecule are prepared. Thus, fluorinated trimethylplatinum β -diketonates form no dimers through Pt–C_{γ} bonding, as it occurs in trimethylplatinum β-diketonates with phenyl or alkyl substituents in the ligand. Possibly, an increase in electronegativity of the terminal β-diketonate group results in an increase in the positive charge on C_{γ} atom of the β -diketonate ligand. Thus the probability for $Pt-C_{\gamma}$ bonding decreases allowing platinum to coordinate other donor ligands. Note that water molecule is bound to platinum only in fluorinated B-diketonates. It was established that water is preserved in the composition even after repeated sublimation of the complexes in vacuum.

2.2. Structural characterization of 1, 2, and 3

The single crystals for X-ray study were prepared from their solutions in hexane at 0 °C. The structures of compounds **1–3** belong to the molecular type and are composed of neutral mononuclear [(CH₃)₃Pt(L)H₂O] complexes, the structures of **1** and **2** having two crystallographically independent complexes each. Crystals of compound **2** tend to be twinned. Fig. 1a–c shows the structures of the molecules for all complexes. The coordination Pt polyhedron is the slightly distorted PtC₃O₃ octahedron formed by three methyl groups, water molecule, and two oxygen atoms of bidentately coordinated β-diketonate ligand.

The structure of **1** (Fig. 1a) has the average values of geometric characteristics of the coordination groups as follows: the Pt-CH₃, Pt-O_L, and Pt-O_W distances, 2.013, 2.194, and 2.283 Å, respectively; the deviations of the bond *cis*-angles from the ideal 90° angle on the central Pt atom is no more than 4.7°. The C₃ and O₃ planes of two triangular faces of Pt octahedra are virtually parallel; the dihedral angles do not exceed 3.8°. In the symmetric β-diketonate hfa-ligand, the average values of the O–C, C–C $_{\gamma}$, C–C_{Me}, and C– F bond lengths are 1.253, 1.378, 1.528, and 1.304 Å, respectively, the average value of the chelate O-Pt-O angles being 87.8°. The bending of the chelate rings along the 0...0 line may be as much as 15.0° and the average intramolecular $F_{\dots}H_{\gamma}$ contacts in the complexes are \sim 2.33 Å. A projection of the structure on the xyplane is shown in Fig. 2a. In the crystal, the complexes are linked by weak hydrogen bonds involving the molecule of the coordinated water of one complex and the hfa ligand oxygen atoms of the other, the O...O separation being 2.88 Å. The intermolecular F...F and F...H contacts between the terminal substituents are 2.91 and 2.59 Å, respectively. The shortest Pt...Pt separations between the centers of the complexes are 5.377-6.280 Å.

In the structure of **2** (Fig. 1b), the deviations of the bond *cis*-angles from the ideal 90° angle on the central Pt atoms reach 7.1°, the average chelate O-Pt-O angle being 88.9°. In the metal cycle, the Pt-O_L distances on the side of various substituents differ noticeably, the average value being 2.04 and 2.27 Å on the side of the fluorinated substituent and the methyl one, respectively. In the β -diketonate ligand, the difference in the O–C, C–C $_{\gamma}$, and C–C_{Me} bond lengths is 0.14, 0.10, and 0.03 Å, respectively, on the side of different substituents. The average C-F distance is 1.31 Å for CF₃ groups. The bending of the chelate rings along the 0...0 line is 13.7 Å. In the coordination environment, the average $Pt-O_W$ bond length is 2.25 Å. The scatter in the Pt-CH₃ bonds is great with the average value of 2.02 Å. The projection of the crystal structure along the y-axis is shown in Fig. 2b. The structure belongs to the layer type with the interlayer d_{200} distance of 9.25 Å. The molecules in the layer are hydrogen-bonded those involving the mole-



Fig. 1. ORTEP drawing of $[(CH_3)_3Pt(hfac)H_2O](1) - (a), [(CH_3)_3Pt(tfac)H_2O](2) - (b), [(CH_3)_3Pt(ptac)H_2O](3) - (c).$

cules of the coordinated water and oxygen atoms of β -diketonate ligands. The O...O separations for the O–H...O bonds are 2.86 Å. Four nearest Pt...Pt distances in the layer are 5.37–6.10 Å. The intermolecular F...H contacts have the minimal values of 2.60 Å.

In the structure of **3** (Fig. 1c), the deviations of the bond *cis*-angles from the ideal 90° angle on the central Pt atom do not exceed 3.0°, the chelate O–Pt–O angle being 88.2°. In the metal cycle, the Pt–O_L distances on the side of various substituents differ moderately, 0.020, with the average value of 2.165 Å. In the β -diketonate ligand, the difference in the O–C, C–C $_{\gamma}$, and C–C_{Me} bond lengths is 0.039, 0.074, and 0.012 Å, respectively, on the side of various substituents. In the CF_{3–} and C(CH₃)₃ groups, the average C–F and C–C bond lengths are 1.334 and 1.531 Å, respectively. The bending of the chelate ring along the O…O line is 13.6°, the intramolecular F(1)…H $_{\gamma}$ contact is 2.35 Å. The torsion C(2)C(1)C(4)F(1) and O(2)C(3)C(5)C(51) angles are 6.2°



Fig. 2. Projection of the crystal packing of compounds 1 - (a), 2 - (b) and 3 - (c).

and 4.8° , respectively. In the coordination environment, the Pt–O_W distance is 2.246 Å, and the Pt–CH₃ bond length is 2.006 Å in the trans-position to the water molecule, slightly shorter than two other bonds with the average value of 2.017 Å. The C₃ and O₃ planes of the triangular faces of the Pt octahedron are virtually parallel, the dihedral angle between them being 2.4°.

The projection of the crystal structure on the (100) plane is shown in Fig. 2c. The structure is of the layer type. In the layer, the molecules of the complexes are hydrogen-bonded those involving the molecule of the coordinated water. The complexes are combined by the O–H...O bonds into centrosymmetrical dimer associates with the Pt...Pt separation of 5.318 Å, while the O...O and H...O those are 2.84 and 1.87 Å, respectively. The O–H...F hydrogen bonds of 3.20 and 2.45 Å bind the complexes in the *x*-axis direction, the Pt...Pt distance being 6.037 Å. The intermolecular F...F and F...H contacts in the layer have the minimal values of 3.17 and 2.68 Å, respectively. The H atoms of the terminal But^r substituents emerge at the surface of the layers, the intermolecular H...H distances between the layers are >2.63 Å.

2.3. Thermal properties investigation of $[(CH_3)_3Pt(CF_3-CO-CH-CO-CF_3)H_2O]$ (**1**), $[(CH_3)_3Pt(CF_3-CO-CH-CO-CH_3)H_2O]$ (**2**) and $[(CH_3)_3Pt(CF_3-CO-CH-CO-C(CH_3)_3 H_2O]$ (**3**)

We performed investigation of thermal behavior of the reported compounds both in solid phase by thermogravimetry TG, and in vapor phase using special mass spectrometry (MS) based technique.



Fig. 3. TGA profiles for: $(CH_3)_3Pt(hfac)H_2O(1)$; $(CH_3)_3Pt(tfac)H_2O(2)$; $(CH_3)_3Pt(ptac)-H_2O(3)$ and $[(CH_3)_3Pt(acac)]_2(4)$.

TG analysis was performed up to 250 °C in helium flow. The TG profiles of complexes **1–3** are shown in Fig. 3. The curve for the dimeric complex of trimethylplatinum with acetylacetone – $[(CH_3)_3Pt(acac)]_2$, obtained in the same conditions is given to compare thermal properties of monomeric and dimeric trimethylplatinum β -diketonates. Upon heating in the helium flow, trimethylplatinum(IV) β -diketonates behave alike depending on ligand nature and the chelate complex structure. An analysis of the TG profiles revealed that the sublimation of compounds **1–3** begins at 80–90 °C, suggesting their significant volatility as compared to the dimeric $[(CH_3)_3Pt(acac)]_2$ complex, which begins to sublimate only at 160 °C. Upon further increasing the temperature, the sublimation process proceeds with a partial decomposition in all cases but to a variable extent. Fluorinated substituents in the

Table 1

Crystal data and structure refinement for 1, 2 and 3.

β-diketonate ligand are known to provide greater volatility of the complexes [12,16]. Among the platinum(IV) complexes under study, complex **1** involving two CF₃ groups is the most volatile. The mass loss of complex **1** under heating was ~95% because of the quick sublimation. For complexes **2** and **3** this value is 64.5% and 62.2%, respectively, owing to decreasing the thermal stability. Compared to monomeric complexes, the dimeric [(CH₃)₃Pt(acac)]₂ complex (Fig. 3, curve **4**) has a rather high thermal stability. It decomposes with melting in one stage at 195–200 °C. On heating the mass loss, however, was 49.4% because of the low volatility of the dimeric complex. Thus, our TG study has evidenced that the reduced thermal stability of fluorinated monomeric trimethylplatinum adducts **1–3** is compensated for by their high volatility unlike the dimeric trimethylplatinum(IV) acetylacetonate with an inverse dependence between these properties.

It should be mentioned that the dimeric complex $[(CH_3)_3Pt(a-cac)]_2$ which is less suitable as a precursor for CVD processes because of its lower volatility was used for platinum coatings deposition so far [20]. In our opinion, among the compounds **1–3** the complex $(CH_3)_3Pt(hfac)H_2O(1)$ can be recommended as a promising CVD precursor due to its high volatility.

To test availability of the synthesized compounds as CVD precursors we have performed preliminary MS experiments ensured tracking changes of gas phase composition during the programmed heating of the precursor in a miniature hot wall CVD reactor built in the time-of-flight mass analyzer at high vacuum conditions without any sampling effect. This technique is described elsewhere [21]. It was used to evaluate compound's vaporization stability and to investigate gaseous decomposition products. Evaporation temperatures were 50, 85 and 80 for compounds **1**, **2** and **3**, respectively. After experiments with compounds **2** and **3** black residue was found in the evaporator indicating relatively poor vaporisation stability. That is in accordance with TGA results. From temperature dependences of intensity of ion peaks, onset of precursors'

Empirical formula	$C_8H_{12}F_6O_3Pt(1)$	$C_8H_{15}F_3O_3Pt(2)$	$C_{11}H_{21}F_3 O_3Pt(3)$
Formula weight	465.27	411.29	453.37
<i>T</i> (K)	296(2)	296(2)	240(2)
Crystal system	triclinic	orthorhombic	triclinic
Space group	ΡĪ	Pca2 ₁	PĪ
Unit cell dimensions			
a (Å)	9.4964(8)	18.505(2)	6.0370(2)
b (Å)	11.4669(10)	8.2154(9)	9.7089(3)
c (Å)	11.8904(10)	15.7735(15)	12.8183(4)
α (°)	85.667(5)	90	81.486(2)
β (°)	83.460(5)	90	84.557(2)
γ (°)	83.209(5)	90	81.703(2)
$V(Å^3)$	1274.81(19)	2398.0(4)	733.18(4)
Ζ	4	4	2
D_{calc} (g/cm ³)	2.424	2.278	2.054
Absorption coefficient (mm ⁻¹)	11.078	11.728	9.600
F(000)	864	1536	432
Crystal size (mm)	$0.24 \times 0.01 \times 0.01$	$0.22 \times 0.08 \times 0.01$	$0.02 \times 0.06 \times 0.02$
θ range for data collection	2.66-25.68	2.58-27.50	1.61-30.05
Index ranges	$-11 \leqslant h \leqslant 11$, $-13 \leqslant k \leqslant 13$,	$-24\leqslant h\leqslant 24$, $-10\leqslant k\leqslant 10$,	$-8\leqslant h\leqslant $ 8, $-12\leqslant k\leqslant 1$ 3,
	$-14 \leqslant l \leqslant 14$	$-20 \leqslant l \leqslant 20$	$-16 \leqslant l \leqslant 18$
Reflections collected	19099	33543	15128
Independent reflections (R _{int})	4819 (0.0403)	5472 (0.1446)	4229 (0.0405)
Completeness to $\theta = 25.00^{\circ}$ (%)	99.4	99.7	100.0
Maximum and minimum transmission	0.8973/0.1763	0.8917/0.1823	0.8312/0.2266
Refinement method	Full-matrix least-squares on F ²	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	4819/6/331	5472/112/255	4229/0/193
Goodness-of-fit on F^2	1.071	0.857	1.061
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0436, wR_2 = 0.1166$	$R_1 = 0.0650, wR_2 = 0.1434$	$R_1 = 0.0289, wR_2 = 0.0582$
R indices (all data)	$R_1 = 0.0639, wR_2 = 0.1244$	$R_1 = 0.1568, wR_2 = 0.1637$	$R_1 = 0.0367, wR_2 = 0.0601$
Difference map (maximum, minimum,	5.733/-1.223	5.786/-2.098	1.657/-1.391
e Å ⁻³)			

 Table 2

 Bond lengths and angles in complexes 1, 2 and 3 (the mean values are in parentheses).

Bond	<i>d</i> (A)			
	1	2	3	
Pt−CH ₃	1.999-2.027 (2.013)	1.86-2.16 (2.02)	2.006-2.020 (2.013)	
Pt-O _L	2.184-2.208 (2.194)	$\langle 2.27 \rangle$ (CH ₃)	2.155 (Bu ^t)	
		$\langle 2.04 \rangle$ (CF ₃)	2.175 (CF ₃)	
Pt-O _W	(2.283)	(2.225)	2.246	
0-C	1.240-1.281 (1.253)	(1.18) (CH ₃)	1.252 (Bu ^t)	
		$\langle 1.32 \rangle$ (CF ₃)	1.291 (CF ₃)	
C–Cγ	1.337-1.408 (1.378)	$\langle 1.30 \rangle$ (CH ₃)	1.434 (Bu ^t)	
		$\langle 1.40 \rangle$ (CF ₃)	1.366 (CF ₃)	
C-C _{Me}	1.521-1.535 (1.528)	$\langle 1.54 \rangle$ (CH ₃)	(1.524)	
		$\langle 1.57 \rangle$ (CF ₃)		
C–F	1.233–1.324 (1.304)	(1.31)	(1.334)	
C–C			(1.531)	
Angle	ω (°)			
O-Pt-O	$\langle 87.8 \rangle$	$\langle 88.9 \rangle$	88.25	

heterogeneous decomposition was revealed: 110 ± 10 °C, 115 ± 10 °C and 105 ± 10 °C for compounds **1**, **2** and **3** respectively. Maximal decomposition degree (appeared in mass spectrum by intensity of the initial compound peaks close to background value) is reached in the temperature range 150–160 °C depend on compound. As detailed investigation of decomposition mechanism will be subject of forthcoming paper so we just note that HL_F, C1–C3 hydrocarbons were recorded among gaseous products.

3. Concluding remarks

Three volatile complex of trimethylplatinum(IV) with fluorinated β -diketonate and water ligands have been synthesized with high yield, they are not sensitive to oxygen and moisture and stable for a long time upon storage. The complexes are of monomeric molecular type and have octahedral structure where β -diketonate is bidentately coordinated through the two oxygen atoms and water ligand is in the axial position. It was found that water is preserved in the composition even after repeated sublimation of the complexes in vacuum.

Investigation of thermal behavior of the reported compounds both in solid phase by thermogravimetry TG, and in vapor phase using special mass spectrometry (MS) based technique has been performed. Complex **1** containing hexafluoroacetylacetonate ligand showed the best vaporization stability and volatility among the reported compound. Revealed thermal properties together with high storage and handling stability makes it more attractive precursor for Pt films chemical vapor deposition.

4. Experimental

4.1. General considerations

The starting complex, trimethylplatinum(IV) iodide – $(CH_3)_3$ Ptl, was prepared from K₂PtCl₆, synthesized in its turn from chloroplatinic acid hexahydrate, H₂PtCl₆·H₂O, (Pt 99.9%). Compounds $(CH_3)_3$ Pt(hfac)H₂O (**1**), $(CH_3)_3$ Pt(tfac)H₂O (**2**), and $(CH_3)_3$ Pt(ptac)H₂O (**3**) have been purified by vacuum sublimation in a gradient tube oven ($P \sim 10^{-2}$ Torr, T = 50-150 °C). Elemental analysis was performed with Carlo-Erba 1106 (Italy) device. Infrared spectra were measured in KBr pellets, with use of a Scimitar FTS2000 spectrometer. ¹H NMR and ¹³C NMR spectra were recorded on a Bruker MSL300 spectrometer (300 MHz, 25 °C) and Bruker Avance-500 (125 MHz, 25 °C) respectively, CDCl₃ was used as a solvent in both cases.

TG measurements were carried out on a Netzsch TG 209 F1 thermal analyzer under a helium flow (40 ml/min) with the heat-

ing rate of $10 \,^{\circ}$ C min⁻¹. The temperature range was $20-250 \,^{\circ}$ C, the open crucibles were standard, and the sample mass was taken to be ca. 10-13 mg. Melting points were determined by a Kofler M.p. apparatus.

MS experiments were preformed using setup imitating a miniature MOCVD equipment consisting of an evaporator and a temperature-controlled reactor connected to a time-of-flight mass spectrometer through an effusive orifice. Full range mass spectra were recorded each 10° during the reactor heating. Data collection and processing were performed using National Instruments Corp. hardware and software.

X-ray intensity data were collected on a SMART APEX II CCD (Bruker (AXS) diffractometer using standard technique (ω - and φ -scans of narrow frames) and corrected for absorption effects (sADABS). The structures were solved by direct methods and refined by full-matrix least-squares on F^2 using the shell 97 program set (Bruker AXS Inc., 2004) [22]. Crystallographic data and details of single-crystal diffraction experiments for compounds **1–3** are given in Table 1. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms H_{γ} were located from a difference map and were included in the refinement. The hydrogen atoms of the CH₃ groups were calculated by geometrical methods. Selected bond lengths and angles are in Table 2.

4.2. Synthesis of complex (CH₃)₃PtI

The Grignard reagent CH₃MgI was prepared from magnesium powder (1.32 g, 55.0 mmol) and iodine methyl (7.81 g, 55.0 mmol) in 50 ml of absolute diethyl ether, with further addition of 60 ml benzene, and then the solution was cooled to -20 °C. Dried Na₂PtCl₆ salt (1.00 g, 11.0 mmol) was dispersed in the cooled solution under an argon flow with vigorous stirring. The reaction mixture was stirred under an inert atmosphere at -10 °C for 2 h, gradually taking the dark brown color, and then the temperature was allowed to 0 °C. The complex was isolated from the reaction mixture with water slightly acidified by HCl with ice. The organic layer was separated and the water layer was extracted with benzene three times. The prepared compound was isolated by solvent evaporation with no heating. Yield: 0.61 g (75%). The (CH₃)₃PtI complex is a crystalline orange substance, insoluble in water but readily soluble in organic solvents.

4.3. Synthesis of [(CH₃)₃Pt(CF₃-CO-CH-CO-CF₃)H₂O] (**1**), [(CH₃)₃Pt(CH₃-CO-CH-CO-CF₃)H₂O] (**2**) and [(CH₃)₃Pt(CF₃-CO-CH-CO-CF₃)H₂O] (**2**)

Fluorinated trimethylplatinum(IV) β -diketonates were synthesized by a similar technique. The (CH₃)₃PtI complex (1 g, 2.7 mmol) was dissolved in 50 ml of benzene. Then 5.4 mmol of potassium salt of the appropriate ligand were added to the obtained orange solution and AgF salt (0.34 g, 2.7 mmol) was dispersed. The reaction mixture was stirred at 45–50 °C until the solution became colorless and the AgI and KF salts were precipitated. The residue was filtered off and the solution was fully evaporated. The dry residue was extracted with hexane. The isolated product was purified by sublimation under a reduced pressure.

Complex **1**: Yield 1.18 g (94%), yellow crystals. M.p.: 120–122 °C. *Anal.* Calc. for $C_8H_{12}F_6O_3Pt$: C, 20.64; H, 2.58; F, 24.51. Found; C, 21.02; H, 2.81; F, 24.73%. ¹H NMR (ppm): 1.24 [s, 9H, Pt–CH₃, ²*J*_(Pt–H) = 79 Hz]; 2.66 [m, 2H, H₂O]; 5.98 [m, 1H, CH]. ¹³C NMR (ppm): -10.63 [(Pt–(CH₃)₃, ³*J*_(C-Pt) = 785 Hz]; 90.82[(–CH=), ³*J*_(C-Pt) = 27 Hz]; 118.28 [(–CF₃), *J*_(C-F) = 285 Hz, ³*J*_(C-Pt) = 12 Hz]; 174.3 [(O=<u>C</u>–CF₃), ²*J*_(C-F) = 33 Hz, ³*J*_(C-Pt) = 13 Hz]. IR (cm⁻¹): 3607 (s), 3435 (s, br), 2980 (m), 2911 (m), 2818 (m), 1638 (vs), 1608 (s), 1559 (s), 1530 (s), 1462 (vs), 1335 (m), 1256 (vs), 1205 (vs), 1152 (vs), 1085 (s), 880 (w), 804 (s), 744 (w), 680 (s), 584 (m), 497 (w), 402 (w). *Complex* **2**: Yield 0.94 g (85%), white crystals. M.p.: 85–87 °C. *Anal.* Calc. for $C_8H_{15}F_3O_3Pt$: C, 23.36; H, 3.65; F, 13.87. Found; C, 23.54; H, 3.43; F, 14.11%. ¹H NMR (ppm): 1.11 [s, 9H, Pt–CH₃, ²*J*_(Pt–H) = 78 Hz]; 2.08 [m, 3H, CH₃–CO]; 2.69 [m, 2H, H₂O]; 5.62 [m, 1H, CH]. ¹³C NMR (ppm): -11.95 [(Pt–CH₃, ³*J*_(C–Pt) = 785.5 Hz]; 29.93 [(–CH₃), ³*J*_(C–Pt) = 7.9 Hz]; 96.3 [(–CH=), ³*J*_(C–Pt) = 25 Hz]; 118.95 [(–CF₃), *J*_(C–F) = 284.6 Hz, ²*J*_(C–Pt) = 13.7 Hz]; 166.67 [(O=<u>C</u>–CF₃), ²*J*_(C–F) = 31.4 Hz, ²*J*_(C–Pt) = 9 Hz]; 194.67 [(O=<u>C</u>–CH₃), ²*J*_(C–Pt) = 11.5 Hz. IR (cm⁻¹): 3436 (s, br) 2974 (m) 2906 (m), 2818 (m), 1618 (vs), 1527 (s), 1450 (s), 1427 (s), 1286 (vs), 1233 (s), 1198 (s), 1140 (vs), 1092 (w), 934 (w), 865 (m), 790 (m), 734 (m), 621 (m), 581 (m), 430 (m).

Complex **3**: Yield 1.06 g (87%), yellow crystals. M.p.: 107–108 °C. *Anal.* Calc. for $C_{11}H_{21}F_3O_3Pt: C, 29.14$; H, 4.63; F, 12.58. Found; C, 29.45; H, 4.76; F, 13.04%. ¹H NMR (ppm): 1.13 [s, 9H, Pt–CH₃, ²*J*_(Pt–H) = 78 Hz]; 1.17 [s, 9H, C(CH₃)₃–CO]; 2.00 [m, 2H, H₂O]; 5.79 [m, 1H, CH]. ¹³C NMR (ppm): -11.78 [(Pt–CH₃, ³*J*_(C–Pt) = 784 Hz]; 27.58 [(–C(<u>CH₃</u>)₃]; 42.76 [(–<u>C</u>(CH₃)₃]; 92 [(–CH=), ³*J*_(C–Pt) = 26 Hz]; 119.3 [(–CF₃), *J*_(C–F) = 285 Hz]; 166.4 [(O=<u>C</u>–CF₃), *J*_(C–F) = 30.5 Hz]; 203.9 [(O=<u>C</u>–C(CH₃)₃]. IR (cm⁻¹): 3623 (s), 3352 (s, br), 2963 (vs), 2932 (s), 2899 (vs), 2814 (m), 1624 (vs), 1612 (vs), 1516 (s), 1462 (s), 1393 (m), 1294 (vs), 1258 (s), 1202 (vs), 1133 (vs), 1029 (s), 938 (w), 851 (m), 807 (m), 703 (m), 582 (w), 480 (w), 428 (w).

Acknowledgment

The authors thank Mrs. Tamara Yudanova for her help in translation of the paper from Russian.

Appendix A. Supplementary data

CCDC 846092, 846549, and 846303 contains the supplementary crystallographic data for **1**, **2**, and **3**, respectively. These data can be

obtained free of charge via http://www.ccdc.cam.ac.uk/conts/ retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk

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