

# Synthesis of platinum complexes with $\eta^4$ -C<sub>5</sub>Me<sub>4</sub>(CF<sub>3</sub>)H ligand. X-ray structure of [Pt( $\eta^4$ -C<sub>5</sub>Me<sub>4</sub>H<sub>2</sub>)Cl<sub>2</sub>] and [Pt{ $\eta^4$ -C<sub>5</sub>Me<sub>4</sub>(CF<sub>3</sub>)H}( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)]PF<sub>6</sub>

Oleg V. Gusev\*, Tat'yana A. Peganova, Mikhail A. Ievlev, Anna G. Kropotova,  
 Konstantin A. Lyssenko, Pavel V. Petrovskii, Yuri F. Oprunenko,  
 Nikolai A. Ustynyuk

*A.N. Nesmeyanov Institute of Organoelement Compounds, Academy of Sciences of Russia, 28 Vavilov Street,  
 117813 Moscow, Russian Federation*

Received 2 October 2000; received in revised form 26 November 2000; accepted 26 November 2000

## Abstract

Reaction of isomeric mixture of 1,2,3,4-tetramethyl-5-(trifluoromethyl)cyclopentadiene with Zeise's salt dimer gave the only isomer [Pt{ $\eta^4$ -C<sub>5</sub>Me<sub>4</sub>(CF<sub>3</sub>)H}Cl<sub>2</sub>] (**1**) bearing CF<sub>3</sub> group *exo* to sp<sup>3</sup> carbon atom in a high yield. An attempt to prepare **1** by reaction of K<sub>2</sub>PtCl<sub>4</sub> with C<sub>5</sub>Me<sub>4</sub>(CF<sub>3</sub>)H using hydrochloric solution of tin dichloride as a catalyst unexpectedly resulted in a formation of [Pt( $\eta^4$ -C<sub>5</sub>Me<sub>4</sub>H<sub>2</sub>)Cl<sub>2</sub>] (**2**). The X-ray structure of compound **2** is presented. Reactions of **1** with AgBF<sub>4</sub> in the presence of three different cyclopentadienes C<sub>5</sub>R<sub>4</sub>(R<sup>2</sup>)H (R<sup>1</sup> = R<sup>2</sup> = H; R<sup>1</sup> = R<sup>2</sup> = Me; R<sup>1</sup> = Me, R<sup>2</sup> = CF<sub>3</sub>) were studied. Crystal structure of complex [Pt{ $\eta^4$ -C<sub>5</sub>Me<sub>4</sub>(CF<sub>3</sub>)H}( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)]PF<sub>6</sub> (**3**) resulted from the reaction with cyclopentadiene was determined. When C<sub>5</sub>Me<sub>4</sub>(CF<sub>3</sub>)H is used the reaction yields [Pt{ $\eta^4$ -C<sub>5</sub>Me<sub>4</sub>(CF<sub>3</sub>)H}{ $\eta^5$ -C<sub>5</sub>Me<sub>4</sub>(CF<sub>3</sub>)}]]BF<sub>4</sub> (**4**) unstable in solutions. Reaction with pentamethylcyclopentadiene led to complex [Pt( $\eta^4$ -C<sub>5</sub>Me<sub>5</sub>H)( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)]BF<sub>4</sub> (**5**) and no complexes with CF<sub>3</sub> containing ligands were obtained. © 2001 Published by Elsevier Science B.V. All rights reserved.

**Keywords:** Synthesis; Platinum; Tetramethyl(trifluoromethyl)cyclopentadiene complexes; X-ray structures

## 1. Introduction

Cyclopentadienyl complexes are the most common in the organometallic chemistry of transition metals. Complexes with the 1,2,3,4-tetramethyl-5-(trifluoromethyl)-cyclopentadienyl ligand [1] are currently under active study. The source of the interest is the fact that the  $\eta^5$ -C<sub>5</sub>Me<sub>4</sub>(CF<sub>3</sub>) ligand is very similar to cyclopentadienyl in its electronic influence and very close to the  $\eta^5$ -C<sub>5</sub>Me<sub>5</sub> ligand in its steric requirements [2]. This combination of properties could allow discrimination between the influence of steric and electronic factors on chemical processes. A representative series of Group VIII metal d<sup>6</sup> complexes with the  $\eta^5$ -C<sub>5</sub>Me<sub>4</sub>(CF<sub>3</sub>) ligand [2–7] has been synthesized along with  $\eta^4$ -diene iron

complex [Fe{ $\eta^4$ -C<sub>5</sub>Me<sub>4</sub>(CF<sub>3</sub>)H}(CO)<sub>3</sub>] [4]. However the platinum d<sup>8</sup> compounds with these ligands are still unknown. We report here the synthesis of platinum d<sup>8</sup> diene complexes with the  $\eta^4$ -C<sub>5</sub>Me<sub>4</sub>(CF<sub>3</sub>)H ligand.

## 2. Results and discussion

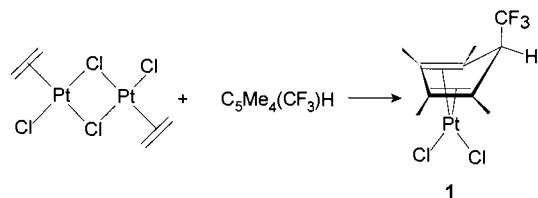
### 2.1. Synthesis of Pt{ $\eta^4$ -C<sub>5</sub>Me<sub>4</sub>(CF<sub>3</sub>)H}Cl<sub>2</sub> (**1**) and [Pt( $\eta^4$ -C<sub>5</sub>Me<sub>4</sub>H<sub>2</sub>)Cl<sub>2</sub>] (**2**) from C<sub>5</sub>Me<sub>4</sub>(CF<sub>3</sub>)H

The Zeise's salt dimer reacts with the isomeric mixture of 1,2,3,4-tetramethyl-5-(trifluoromethyl)cyclopentadiene to give the complex Pt{ $\eta^4$ -C<sub>5</sub>Me<sub>4</sub>(CF<sub>3</sub>)H}Cl<sub>2</sub> (**1**) as a crystalline product in a high yield (Scheme 1).

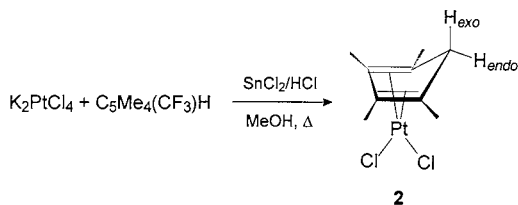
The complex **1** is the first stable d<sup>8</sup> complex with an  $\eta^4$ -C<sub>5</sub>Me<sub>4</sub>(CF<sub>3</sub>)H ligand. The signals of the CF<sub>3</sub> group are observed at  $\delta$  119.2 and –68.61 in <sup>13</sup>C{H}- and

\* Corresponding author. Tel.: +7-95-1359337; fax: +7-95-1355085.

E-mail address: gusev@ineos.ac.ru (O.V. Gusev).



Scheme 1.



Scheme 2.

$^{19}\text{F}\{\text{H}\}$ -NMR spectra of **1**, respectively. Equivalent pairs of the methyl groups appear at  $\delta$  1.53 and 2.26 in the  $^1\text{H}$ -NMR spectrum and at  $\delta$  11.6 and 15.3 in the  $^{13}\text{C}\{\text{H}\}$ -NMR spectrum. Thus, the NMR data allow the elucidation of the structure of **1** where the  $\text{CF}_3$  group is bound to the  $\text{sp}^3$  carbon atom of the  $\eta^4$ -ligand. In general the  $^1\text{H}$ -,  $^{13}\text{C}\{\text{H}\}$ - and  $^{19}\text{F}\{\text{H}\}$ -NMR spectra of complex **1** resemble those of the iron compound  $[\text{Fe}\{\eta^4\text{-C}_5\text{Me}_4(\text{CF}_3)\text{H}\}(\text{CO})_3]$  [4]. The most essential distinction is the 29-ppm downfield shift of resonances from C(2) and C(5) atoms in the 16-electron complex **1** with respect to analogous signals for the iron compound. This is probably caused by weaker back bonding in **1** [8]. Similar changes were observed earlier for the complex  $[\text{Pt}(\eta^4\text{-C}_5\text{Me}_5\text{H})\text{Cl}_2]$  [9].

The reasons why complex **1** is obtained as a single product from a mixture of three isomers of  $\text{C}_5\text{Me}_4(\text{CF}_3)\text{H}$  under mild conditions are not quite clear. It is probable that the stability of isomeric complexes having a  $\text{CF}_3$  group bound to coordinated carbons is lower in comparison to the stability of **1** so that they undergo conversion into the complex **1** in the presence of an excess of diene. Carrying out the reaction with an equimolar ratio between Zeise's salt dimer and  $\text{C}_5\text{Me}_4(\text{CF}_3)\text{H}$  results in a considerable decrease of the yield of **1**.

An attempt was also made to prepare complex **1** by reaction of  $\text{K}_2\text{PtCl}_4$  with  $\text{C}_5\text{Me}_4(\text{CF}_3)\text{H}$  in the presence of hydrochloric solution of tin dichloride as a catalyst by analogy to the preparation of  $[\text{Pt}(\eta^4\text{-C}_5\text{Me}_5\text{H})\text{Cl}_2]$  [10]. Unexpectedly  $\eta^4$ -tetramethylcyclopentadiene complex  $[\text{Pt}(\eta^4\text{-C}_5\text{Me}_4\text{H}_2)\text{Cl}_2]$  (**2**) was obtained as the only product (Scheme 2).

Complex **2** is a crystalline substance hardly soluble in common solvents. It was characterized by microanalysis

Table 1

Bond lengths (Å) and bond angles ( $^\circ$ ) in  $[\text{Pt}(\eta^4\text{-C}_5\text{Me}_4\text{H}_2)\text{Cl}_2]$  (**2**) and two crystallographically independent molecules **3'** and **3''** of  $[\text{Pt}\{\eta^4\text{-C}_5\text{Me}_4(\text{CF}_3)\text{H}\}(\eta^5\text{-C}_5\text{H}_5)]\text{PF}_6$  (**3** +  $\text{PF}_6^-$ )

	<b>2</b>	<b>3'</b>	<b>3''</b>
<i>Bond lengths</i>			
Pt(1)–C(2)	2.189(5)	2.166(4)	2.160(4)
Pt(1)–C(3)	2.134(4)	2.132(4)	2.139(4)
Pt(1)–C(4)	2.147(4)	2.132(4)	2.140(4)
Pt(1)–C(5)	2.186(5)	2.155(4)	2.161(4)
C(1)–C(2)	1.502(7)	1.546(6)	1.531(6)
C(1)–C(5)	1.509(6)	1.520(5)	1.533(5)
C(2)–C(3)	1.401(6)	1.430(5)	1.444(5)
C(3)–C(4)	1.471(6)	1.443(6)	1.450(5)
C(4)–C(5)	1.410(7)	1.440(5)	1.436(5)
Pt–Cp <sup>diene</sup> <sup>a</sup>	1.821	1.798	1.796
Pt–Cp <sup>b</sup>		1.907	1.905
$\Delta$ <sup>c</sup>	0.47	0.57	0.57
Pt–C(Cp)		2.221(4)–2.329(4)	2.219(4)–2.324(4)
C–C(Cp)		1.386(7)–1.437(8)	1.393(7)–1.455(6)
Pt(1)–Cl(1)	2.314(1)		
Pt(1)–Cl(2)	2.309(1)		
<i>Bond angles</i>			
Cl(2)–Pt(1)	91.55(5)		
–Cl(1)			
C(2)–C(1)–C(5)	97.9(4)	95.9(3)	96.4(3)
C(3)–C(2)–C(1)	110.6(4)	108.1(3)	107.8(3)
C(2)–C(3)–C(4)	106.1(4)	107.2(3)	107.2(3)
C(5)–C(4)–C(3)	107.0(4)	106.5(3)	106.4(3)
C(4)–C(5)–C(1)	109.0(4)	108.8(3)	108.8(3)
Twist angle <sup>d</sup>		36.0	20.8

<sup>a</sup> Cp<sup>diene</sup>, centre of the diene molecule, calculated with the exception of the C(1) atom.

<sup>b</sup> Cp, centre of the Cp-ring.

<sup>c</sup>  $\Delta$ , deviation of the C(1) atom from mean-square plane of the diene [C(2),C(3),C(4),C(5) atoms].

<sup>d</sup> Twist angle, pseudotorsion angle C(1)Cp<sup>diene</sup>CpC(12).

and  $^1\text{H}$ -NMR spectroscopy. Two singlets from two pairs of equivalent methyl groups are observed at  $\delta$  1.45 and 2.24 in  $^1\text{H}$ -NMR spectrum. Methylene protons exhibit AB spectrum at  $\delta$  2.45 and 3.30,  $J_{\text{AB}} = 17.4$  Hz. The fact that the upfield resonance shows a coupling constant of  $J_{\text{H-Pt}} = 14.1$  Hz and the downfield one  $-J_{\text{H-Pt}} = 26.0$  Hz leads one to expect that they are *endo*-H and *exo*-H atoms respectively.

In order to confirm the structure of complex **2** an X-ray investigation was carried out (Tables 1 and 2). It revealed that the platinum atom is coordinated with the  $\eta^4\text{-C}_5\text{Me}_4\text{H}_2$  diene ligand as well as two terminal chlorine atoms (Fig. 1a). The principal geometry in **2** is close to the structure of  $[\text{Pt}(\eta^4\text{-C}_5\text{Me}_5\{i\text{-Pr}\})\text{Cl}_2]$  [11]. The diene cycle in **2** is characterized by the envelope conformation with the deviation of the  $\text{sp}^3$  hybridized C(1) atom from C(2)–C(3)–C(4)–C(5) plane by 0.47 Å. In the crystal, complex **2** has an approximate  $C_s$  sym-

metry with the coplanar arrangement of the Pt(1), Cl(1), Cl(2) atoms and midpoints of the C(2)–C(3) and C(4)–C(5) bonds of the diene ligand (the mean deviation is 0.003 Å) (Fig. 1b). The distances Pt–C are alternated and are equal to approximately 2.187 Å for Pt(1)–C(2) and Pt(1)–C(5) bonds and to 2.140 Å for Pt(1)–C(3) and Pt(1)–C(4). The C–C bonds in the diene moiety are also essentially alternated.

The mechanism of generation of complex **2** has not been ascertained. Obviously scission of the CF<sub>3</sub> group occurs in the non-coordinated diene since complex **1** being exposed to hydrochloric solution of SnCl<sub>2</sub> gives no trace of **2**. It was shown earlier that under similar conditions the cleavage of the C–C bond in 5-(1-methoxyethyl) - 1,2,3,4,5 - pentamethylcyclopenta - 1,3-

diene took place [12]. Nevertheless the mechanism proposed by the authors fails to explain the loss of the CF<sub>3</sub> group in C<sub>5</sub>Me<sub>4</sub>(CF<sub>3</sub>)H. Probably an acidic hydrolysis of the CF<sub>3</sub> group [13] followed by decarboxylation results in a formation of C<sub>5</sub>Me<sub>4</sub>H<sub>2</sub> (Scheme 3).

It was demonstrated by GLC that on heating C<sub>5</sub>Me<sub>4</sub>(CF<sub>3</sub>)H in methanol hydrochloric solution of SnCl<sub>2</sub> in the absence of Zeise's salt dimer only a gradual disappearance of the diene takes place but the tetramethylcyclopentadiene is not formed. It can be proposed that C<sub>5</sub>Me<sub>4</sub>H<sub>2</sub> being unstable under these conditions is stabilized by coordination to Pt(II) centre in the presence of Zeise's salt dimer.

## 2.2. Reactions of [Pt{η<sup>4</sup>-C<sub>5</sub>Me<sub>4</sub>(CF<sub>3</sub>)H}Cl<sub>2</sub>] (**1**) with AgBF<sub>4</sub> in the presence of C<sub>5</sub>R<sub>4</sub><sup>1</sup>(R<sup>2</sup>)H (R<sup>1</sup> = R<sup>2</sup> = H; R<sup>1</sup> = R<sup>2</sup> = Me; R<sup>1</sup> = Me, R<sup>2</sup> = CF<sub>3</sub>)

It was shown previously that pentamethylcyclopentadiene complexes [M(η<sup>4</sup>-C<sub>5</sub>Me<sub>5</sub>H)Cl<sub>2</sub>] (M = Pd, Pt) treated with silver salts in the presence of different dienes form bis-diene complexes [M(η<sup>4</sup>-C<sub>5</sub>Me<sub>5</sub>H)(η<sup>4</sup>-diene)]<sup>2+</sup>, the latter ones being spontaneously deprotonated (Scheme 4). [10,14].

The deprotonation proceeds selectively and the propensity to deprotonation increases in a series 1,3-cyclohexadiene ca. 1,5-cyclooctadiene < *endo*-H-pentamethylcyclopentadiene < *exo*-H-pentamethylcyclopentadiene < cyclopentadiene [10]. With the aim of comparing properties of the complexes with η<sup>4</sup>-C<sub>5</sub>Me<sub>5</sub>H and η<sup>4</sup>-C<sub>5</sub>Me<sub>4</sub>(CF<sub>3</sub>)H ligands we carried out the analogous reactions with complex **1**.

Stable d<sup>8</sup> complex [Pt{η<sup>4</sup>-C<sub>5</sub>Me<sub>4</sub>(CF<sub>3</sub>)H}(η<sup>5</sup>-C<sub>5</sub>He<sub>5</sub>)]-BF<sub>4</sub> (**3**) was obtained in a high yield from the reaction of **1** with AgBF<sub>4</sub> and cyclopentadiene (Scheme 5).

Signals of CF<sub>3</sub> group are observed at δ 131.4 and –68.61 in <sup>13</sup>C{H}- and <sup>19</sup>F{H}-NMR spectra, respectively. Cyclopentadienyl ligand exhibits singlets at δ 6.33 in <sup>1</sup>H-NMR and 96.4 in <sup>13</sup>C{H}-NMR spectra. Other signals of C<sub>5</sub>Me<sub>4</sub>(CF<sub>3</sub>)H ligand are close to analogous ones for complex **1** except for the chemical shifts of the diene carbon atoms α to sp<sup>3</sup> carbon. The latter appear to be more upfield shifted than was observed for complex **1** and close to the chemical shifts for [Fe{η<sup>4</sup>-C<sub>5</sub>Me<sub>4</sub>(CF<sub>3</sub>)H}(CO)<sub>3</sub>] [4].

Single crystal X-ray structure determination was carried out for complex [Pt{η<sup>4</sup>-C<sub>5</sub>Me<sub>4</sub>(CF<sub>3</sub>)H}(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)]PF<sub>6</sub> (**3**<sup>+</sup>PF<sub>6</sub><sup>-</sup>) prepared from **3** by counterion metathesis. The crystallographic unit of **3**<sup>+</sup>PF<sub>6</sub><sup>-</sup> contains two independent molecules **3'** and **3''** (Tables 1 and 2) which differ from each other by values of the pseudotorsion angles C(1)Cp<sub>diene</sub>CpC(12) (Cp<sub>diene</sub>-centre of the diene molecule, calculated with the exception of C(1) atom; Cp-centre of the Cp-ring). This distinction between the cyclopentadienyl and diene ligands' orientation in **3'** and **3''** is probably caused by the

Table 2

Crystallographic data for [Pt(η<sup>4</sup>-C<sub>5</sub>Me<sub>4</sub>H<sub>2</sub>)Cl<sub>2</sub>] (**2**) and [Pt{η<sup>4</sup>-C<sub>5</sub>Me<sub>4</sub>(CF<sub>3</sub>)H}(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)]PF<sub>6</sub> (**3**<sup>+</sup>PF<sub>6</sub><sup>-</sup>)

Compound	<b>2</b>	<b>3</b> <sup>+</sup> PF <sub>6</sub> <sup>-</sup>
Molecular formula	C <sub>9</sub> H <sub>14</sub> Cl <sub>2</sub> Pt	C <sub>15</sub> H <sub>18</sub> F <sub>3</sub> Pt P <sub>1</sub> F <sub>6</sub>
Formula weight	388.19	595.35
Color, shape	Yellow, plate	Yellow, plate
Dimensions (mm)	0.3 × 0.2 × 0.05	0.4 × 0.1 × 0.1
Diffractometer	Siemens P3	Smart 1K CCD
Temperature (K)	298	110
Crystal system	Monoclinic	Triclinic
Space group	P2 <sub>1</sub> /c	P $\bar{1}$
a (Å)	8.858(2)	8.6939(5)
b (Å)	13.633(3)	14.2620(9)
c (Å)	9.698(4)	15.4791(9)
α (°)		69.888(1)
β (°)	108.71(2)	85.866(1)
γ (°)		88.918(1)
V (Å <sup>3</sup> )	1109.3(6)	1797.5(2)
Z	4	4
F(000)	720	1128
ρ <sub>calc</sub> (g cm <sup>-3</sup> )	2.324	2.20
Radiation, λ (Mo-K <sub>α</sub> ) (Å)	0.71072	0.71072
Linear absorption, μ (cm <sup>-1</sup> )	130.78	79.79
Absorption correction	Phi-scan	Semi-empirical from equivalents (SADABS program)
T <sub>min</sub> /T <sub>max</sub>	0.66/0.18	0.98/0.52
Scan type	θ/2θ	ω (0.3° step in ω and 10 s exposure per frame)
θ range (°)	2.67–33.08	1.52–30.04
Measured	3912 (R <sub>int</sub> = 0.0304)	19084 (R <sub>int</sub> = 0.0303)
Unique	3740	10198
With [I > 2σ(I)]	2398	8729
Parameters	166	613
Final R(F <sub>hkl</sub> ): R <sub>1</sub>	0.0273	0.0312
wR <sub>2</sub>	0.0548	0.0829
GOF	0.826	1.013
ρ <sub>max</sub> /ρ <sub>min</sub> (e Å <sup>-3</sup> )	0.729/–0.789	1.893/–3.906

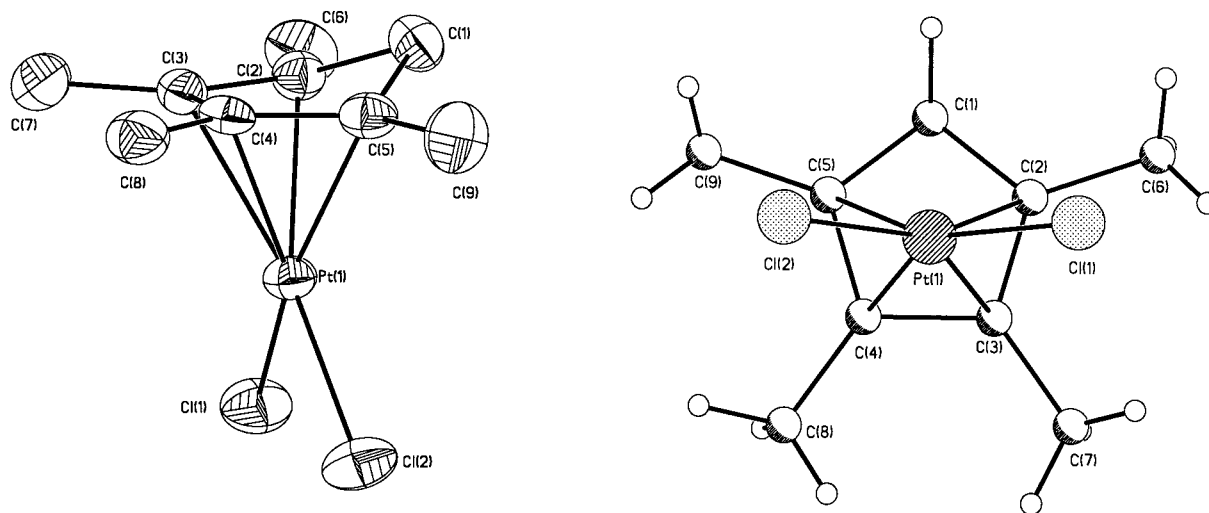


Fig. 1. Molecular structure of complex  $[\text{Pt}(\eta^4\text{-C}_5\text{Me}_4\text{H}_2)\text{Cl}_2]$  (**2**), (a) general view in presentation of atoms by 50% probability ellipsoids of thermal motion and (b) a view in projection on tetramethylcyclopentadiene ring.

presence of the shortened intermolecular  $\text{C-H}\cdots\text{F}$  contact between the  $(\eta^5\text{-C}_5\text{H}_5)$  ligand and  $\text{PF}_6^-$  anion which is observed only in the case of **3'** ( $\text{H}(13)\cdots\text{F}(6')$  2.31 Å,  $\text{C}(13)\text{H}(13)\text{F}(6')$  161°). The conformation of the diene ligand in  $3^+\text{PF}_6^-$  (Fig. 2) is close to that in **2** with the  $\text{CF}_3$  group *exo* to  $\text{sp}^3$  carbon atom. The distances  $\text{C}(2)\text{--}\text{C}(3)$ ,  $\text{C}(3)\text{--}\text{C}(4)$  and  $\text{C}(4)\text{--}\text{C}(5)$  in the diene moiety are less alternated and  $\text{Pt}\text{--}\text{C}$  distances are shortened in comparison with the data obtained for **2** (Table 1). Probably the shortening of  $\text{Pt}\text{--}\text{C}$  bonds may be explained by stronger back bonding in  $3^+\text{PF}_6^-$ , which can lead to an upfield shift of carbon atoms  $\alpha$  to  $\text{sp}^3$  carbon of the diene in the  $^{13}\text{C}\{\text{H}\}$ -NMR spectrum.

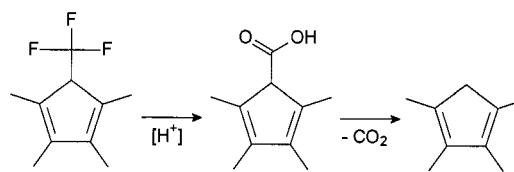
Complex **3** can be prepared in the reaction of **1** with  $\text{CpTi}$  and  $\text{TlBF}_4$  as well.

The cationic complex  $[\text{Pt}\{\eta^4\text{-C}_5\text{Me}_4(\text{CF}_3)\text{H}\}\{\eta^5\text{-C}_5\text{Me}_4(\text{CF}_3)\}]^+$  (**4**) was obtained from reaction of **1** with  $\text{AgBF}_4$  and 1,2,3,4-tetramethyl-5-(trifluoromethyl)-cyclopentadiene (Scheme 6).

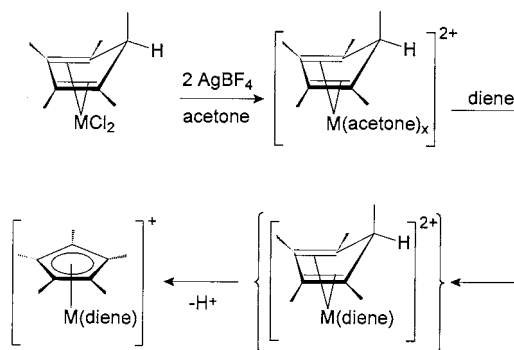
The  $^1\text{H}$ -NMR spectrum of complex **4** shows four signals arising from equivalent pairs of methyl groups at  $\delta$  1.88, 2.14, 2.27 and 2.51 along with a quartet at  $\delta$  4.75 ( $J_{\text{H-F}} = 6.4$  Hz) attributed to a hydrogen at  $\text{sp}^3$  carbon. Signals of  $\text{CF}_3$  groups belonged to  $\eta^5\text{-C}_5\text{Me}_4(\text{CF}_3)$  and  $\eta^4\text{-C}_5\text{Me}_4(\text{CF}_3)\text{H}$  ligands are observed in  $^{19}\text{F}\{\text{H}\}$ -NMR spectrum at  $\delta$  -52.97 and -69.79 correspondingly. The NMR data confirm the supposed structure of **4** where one of  $\text{CF}_3$  groups is bound with  $\text{sp}^3$  carbon atom of the diene ligand.

The complex **4** is unstable in solutions and attempts to register its  $^{13}\text{C}\{\text{H}\}$ -NMR spectrum failed. The reasons for such differing stability of the  $\text{d}^8$  complexes **3** and **4** are not quite clear. As was shown earlier, substitution of  $\text{C}_5\text{H}_5$  for  $\text{C}_5\text{Me}_4(\text{CF}_3)$  ligand leads to an increase in the stability of  $\text{d}^7$  complexes [7]. It is unlikely that methyl groups of  $\eta^5\text{-C}_5\text{Me}_4(\text{CF}_3)$  in **4** are

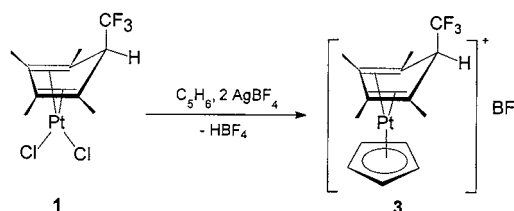
responsible for the instability of this compound, since the  $\text{d}^8$  complex  $[\text{Pt}(\eta^4\text{-C}_5\text{Me}_5\text{H})(\eta^5\text{-C}_5\text{Me}_5)]^+$  with pentamethylcyclopentadienyl ligand is quite stable [10]. On the other hand, the ability of trifluoromethyl substi-



Scheme 3.



Scheme 4.



Scheme 5.

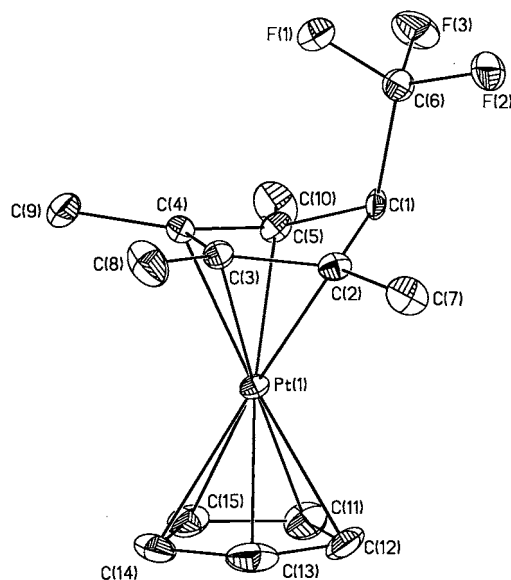
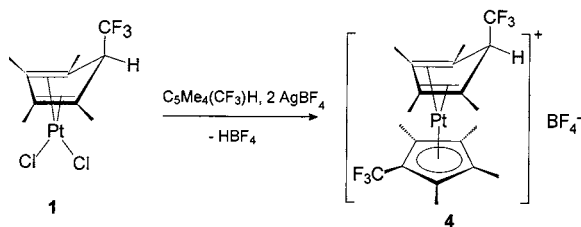
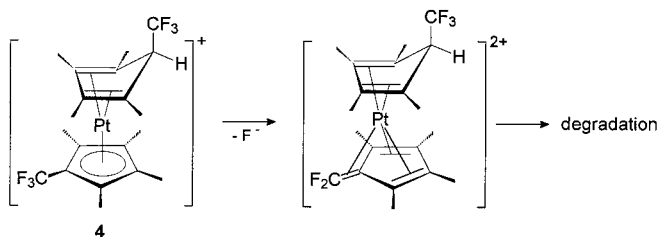


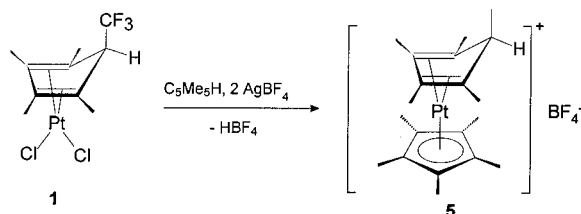
Fig. 2. Molecular structure of complex  $[\text{Pt}\{\eta^4\text{-C}_5\text{Me}_4(\text{CF}_3)\text{H}\}(\eta^5\text{-C}_5\text{H}_5)]\text{PF}_6$  ( $3^+\text{PF}_6^-$ ), general view in presentation for one ( $3'$ ) of the two independent atoms by 50% probability ellipsoids of thermal motion.



Scheme 6.



Scheme 7.



Scheme 8.

tuted cyclopentadienyl anions to eliminate fluoride ion is known [15]. For instance, anion  $(\text{C}_5\text{H}_4\text{CF}_3)^-$  con-

verts into 6,6-difluorofulvene [15], thallium trifluoromethylcyclopentadienides being also thermally unstable [16]. Attempts to prepare lithium and thallium tetramethyl(trifluoromethyl)cyclopentadienides proved unsuccessful as well [2]. The strong electron donor properties of the  $d^8$  moiety  $\{\text{Pt}\{\eta^4\text{-C}_5\text{Me}_4(\text{CF}_3)\text{H}\}$  weakening the C–F bond are the probable reason for the destabilization of complex **4**. It can be proposed that elimination of fluoride ion from **4** to give dicationic  $\eta^6\text{-1,2,3,4-tetramethyl-6,6-difluorofulvene}$  complex is followed by nucleophilic attack of  $\text{F}^-$  ion towards the metal atom and degradation of intermediate complexes (Scheme 7). The similar decomposition was found earlier for complex  $[\text{Pt}(\eta^4\text{-C}_5\text{Me}_5\text{H})(\eta^5\text{-C}_5\text{Me}_5)]\text{Cl}$  containing chloride ion [9].

Reaction of **1** with pentamethylcyclopentadiene and  $\text{AgBF}_4$  gave no trifluoromethyl containing compounds. The only compound isolated from this reaction was the known [10] complex  $[\text{Pt}(\eta^4\text{-C}_5\text{Me}_5\text{H})(\eta^5\text{-C}_5\text{Me}_5)]^+$  (**5**) (Scheme 8).

It is not clear in which step of the reaction the replacement of  $\text{C}_5\text{Me}_4(\text{CF}_3)\text{H}$  by  $\text{C}_5\text{Me}_5\text{H}$  takes place. One could unambiguously state that the substitution does not occur in the starting complex **1** because no trace of the complex  $[\text{Pt}(\eta^4\text{-C}_5\text{Me}_5\text{H})\text{Cl}_2]$  was observed when a solution of **1** and a considerable excess of pentamethylcyclopentadiene was kept at room temperature for several hours. It is likely that  $\text{C}_5\text{Me}_4(\text{CF}_3)\text{H}$  is substituted for the more electron donating pentamethylcyclopentadiene in dicationic compounds  $[\text{Pt}\{\eta^4\text{-C}_5\text{Me}_4(\text{CF}_3)\text{H}\}(\text{acetone})_x]^{2+}$  or  $[\text{Pt}\{\eta^4\text{-C}_5\text{Me}_4(\text{CF}_3)\text{H}\}(\eta^4\text{-C}_5\text{Me}_5\text{H})]^{2+}$  and subsequent deprotonation of a dication  $[\text{Pt}(\eta^4\text{-C}_5\text{Me}_5\text{H})_2]^{2+}$  results in formation of **5**.

An alternative reaction path leading to **5** is the deprotonation of complex  $[\text{Pt}\{\eta^4\text{-C}_5\text{Me}_4(\text{CF}_3)\text{H}\}(\eta^4\text{-C}_5\text{Me}_5\text{H})]^{2+}$  that must occur in this case at  $\text{C}_5\text{Me}_4(\text{CF}_3)\text{H}$  ligand containing more acidic hydrogen atom to yield  $[\text{Pt}\{\eta^5\text{-C}_5\text{Me}_4(\text{CF}_3)\}(\eta^4\text{-C}_5\text{Me}_5\text{H})]^+$  (Scheme 9). Degradation of the latter cation may proceed similar to **4**, the process being faster due to the more donating ability of  $[\text{Pt}(\eta^4\text{-C}_5\text{Me}_5\text{H})]^+$  moiety.

Thus, the platinum does not form stable  $d^8$  complexes with  $\eta^5\text{-1,2,3,4-tetramethyl-5-(trifluoromethyl)cyclopentadienyl}$  ligand while the diene  $\eta^4\text{-C}_5\text{Me}_4(\text{CF}_3)\text{H}$  complexes are stable.

### 3. Experimental

#### 3.1. General procedures

All experiments were performed under argon in solvents purified by standard methods.  $^1\text{H}$ -,  $^{19}\text{F}\{\text{H}\}$ - and  $^{13}\text{C}\{\text{H}\}$ -NMR spectra were obtained with a Bruker-WP-200-SY and Varian VXR-400 spectrometers.

Chemical shifts are reported in ppm ( $\delta$ ); proton and carbon chemical shifts are relative to  $\text{Me}_4\text{Si}$ , fluorine chemical shifts are relative to  $\text{CFCl}_3$ . Microanalyses were performed by Laboratory of Microanalysis of Institute of Organoelement Compounds.

### 3.2. Crystallography

Single crystals of **2** were obtained by crystallization from concentrated chloroform solution at room temperature (r.t.). Complex  $3^+\text{PF}_6^-$  prepared from **3** by metathesis reaction with  $\text{NH}_4\text{PF}_6$  in an acetone–water mixture formed crystals under slow diffusion of DME into diluted dichloromethane solution. Crystallographic data for complexes **2** and  $3^+\text{PF}_6^-$  are presented in Table 2. Both structures were solved by direct method and refined by full-matrix least squares against  $F^2$  in the anisotropic (H-atoms isotropic) approximation using the SHELXTL-97 package. All hydrogen atoms were located from the electron density difference synthesis and were included in the refinement in isotropic approximation.

### 3.3. Synthesis of [1,2,3,4,-tetramethyl-5-(trifluoromethyl)cyclopentadiene]platinum dichloride (**1**)

To a solution of Zeise's salt dimer (0.47 g, 1.60 mmol) in benzene (100 ml) 1,2,3,4,-tetramethyl-5-(trifluoromethyl)cyclopentadiene (0.97 g, 5.10 mmol) was added. After the reaction mixture was stirred for 24 h at r.t. the solvent was removed in vacuo. Residue was washed with hexane and dried. Yield: 0.69 g (95%) of **1**. Found: H, 3.16; C, 26.62. Calc. for  $\text{C}_{10}\text{H}_{13}\text{Cl}_2\text{F}_3\text{Pt}$ : H, 2.87; C, 26.33%.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ): 1.53 (s, 6H, 2Me,  $J_{\text{H-Pt}} = 11.0$  Hz); 2.26 (s, 6H, 2Me,  $J_{\text{H-Pt}} = 35.5$  Hz); 3.93 (q, 1H,  $J_{\text{H-F}} = 6.2$ ;  $J_{\text{H-Pt}} = 28.4$  Hz).  $^{19}\text{F}\{\text{H}\}\text{-NMR}$  ( $\text{CDCl}_3$ ):  $-68.61$  (d,  $\text{CF}_3$ ,  $J_{\text{F-H}} = 6.2$ ;  $J_{\text{F-Pt}} = 11.0$  Hz).  $^{13}\text{C}\{\text{H}\}\text{-NMR}$  ( $\text{CDCl}_3$ ): 9.8 (s, 2Me,  $J_{\text{Pt-C}} = 17.2$  Hz); 13.8 (s, 2Me,  $J_{\text{Pt-C}} = 6.3$  Hz); 62.8 (q,  $\text{CHCF}_3$ ,  $J_{\text{Pt-C}} = 54.5$ ,  $J_{\text{C-F}} = 28.7$  Hz); 89.8 (s, CMe,  $J_{\text{Pt-C}} = 129.4$  Hz);

112.8 (s, CMe,  $J_{\text{Pt-C}} = 106.6$  Hz); 119.2 (s,  $\text{CF}_3$ ,  $J_{\text{C-F}} = 414.3$ ,  $J_{\text{Pt-C}} = 43.1$  Hz).

### 3.4. Reaction of **1** with $\text{AgBF}_4$ in the presence of cyclopentadiene

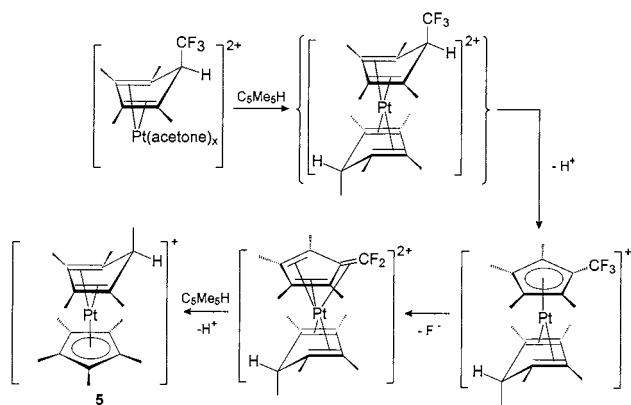
An acetone solution (20 ml) of **1** (0.15 g, 0.32 mmol) and cyclopentadiene (0.04 g, 0.64 mmol) in a two-necked 50 ml flask was chilled to  $-78^\circ\text{C}$ . 0.12 g (0.64 mmol) of  $\text{AgBF}_4$  was then added, the reaction mixture was allowed to warm to r.t. and then stirred for 1 h.  $\text{AgCl}$  was filtered off, the filtrate was concentrated to 5 ml and 20 ml of diethyl ether was added. The resulting precipitate was filtered off, washed with diethyl ether and dried in vacuo. Yield: 0.12 g (70%) of **3**. Found: H, 3.21; C, 33.49. Calc. for  $\text{C}_{15}\text{H}_{18}\text{BF}_7\text{Pt}$ : H, 3.37; C, 33.54%.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ): 2.04 (s, 6H, 2Me,  $J_{\text{H-F}} = 1.0$ ,  $J_{\text{H-Pt}} = 36.9$  Hz); 2.75 (s, 6H, 2 Me,  $J_{\text{H-Pt}} = 26.2$  Hz); 4.93 (q, 1 H,  $J_{\text{H-F}} = 7.2$ ,  $J_{\text{H-Pt}} = 65.1$  Hz); 6.33 (s, 5H,  $\text{C}_5\text{H}_5$ ,  $J_{\text{H-Pt}} = 25.6$  Hz).  $^{19}\text{F}\{\text{H}\}\text{-NMR}$  ( $\text{CDCl}_3$ ):  $-70.17$  (s  $\text{CF}_3$ ,  $J_{\text{F-Pt}} = 7.8$  Hz);  $-149.08$ ;  $-149.13$  ( $\text{BF}_4$ ).  $^{13}\text{C}\{\text{H}\}\text{-NMR}$  (acetone- $d_6$ ): 10.1 (s, 2Me,  $J_{\text{C-Pt}} = 20.7$  Hz); 15.8 (s, 2Me,  $J_{\text{C-Pt}} = 22.0$  Hz); 65.8 (q, Me,  $J_{\text{C-F}} = 26.1$ ;  $J_{\text{C-Pt}} = 125.4$  Hz); 71.3 (s, 2CMe,  $J_{\text{C-Pt}} = 221.1$  Hz); 96.4 (s,  $\text{C}_5\text{H}_5$ ,  $J_{\text{C-Pt}} = 45.0$  Hz); 108.1 (s, 2CMe,  $J_{\text{C-Pt}} = 63.3$  Hz); 131.4 (q,  $\text{CF}_3$ ,  $J_{\text{C-F}} = 416.0$  Hz).

### 3.5. Reaction of **1** with $\text{C}_5\text{H}_5\text{Tl}$

To a suspension of **1** (0.29 g, 0.50 mmol) in acetone  $\text{C}_5\text{H}_5\text{Tl}$  (0.14 g, 0.51 mmol) and  $\text{TlBF}_4$  (0.15 g, 0.51 mmol) were added. The reaction mixture was stirred for 24 h at r.t. and a precipitate of  $\text{TlCl}$  filtered off. The filtrate was concentrated to 5 ml and 20 ml of diethyl ether was added. The resulting precipitate was filtered off, washed with diethyl ether and dried in vacuo. Yield: 0.25 g (93%) of **3**. NMR data for the product are the same as previous.

### 3.6. Synthesis of ( $\eta^4$ -tetramethylcyclopentadiene)-platinum dichloride (**2**)

To a suspension of  $\text{K}_2\text{PtCl}_4$  (0.67 g, 1.60 mmol) in 40 ml of methanol 0.80g (4.2 mmol) of  $\text{C}_5\text{Me}_4(\text{CF}_3)\text{H}$  and a solution of  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  (0.25 g, 1.60 mmol) in concentrated hydrochloric acid (10 ml) were added. After the mixture was heated under reflux for 12 h the solvent was removed in vacuo. The residue was extracted with dichloromethane (300 ml). The extract was filtered and the solvent removed in vacuo. The residue was washed with diethyl ether and dried. Yield: 0.18 g (29%) of **2**. Found: H, 3.29; C, 27.70; Cl, 18.45; Pt, 50.38. Calc. for  $\text{C}_9\text{H}_{14}\text{Cl}_2\text{Pt}$ : H, 3.63; C, 27.80; Cl, 18.24; Pt, 50.33%.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ): 1.45 (s, 6H, 2Me,  $J_{\text{H-Pt}} = 9.2$  Hz); 2.24 (s, 6H, 2Me,  $J_{\text{H-Pt}} = 35.5$  Hz); 2.45 (d, 1H,  $J =$



Scheme 9.

17.4;  $J_{\text{H-Pt}} = 14.1$  Hz); 3.30 (d, 1H,  $J = 17.4$ ;  $J_{\text{H-Pt}} = 26.0$  Hz).

### 3.7. Reaction of **1** with $\text{AgBF}_4$ in the presence of $\text{C}_5\text{Me}_4(\text{CF}_3)\text{H}$

To a solution of  $[\text{Pt}\{\eta^4\text{-C}_5\text{Me}_4(\text{CF}_3)\text{H}\}\text{Cl}_2]$  (0.13 g, 0.28 mmol) and  $\text{C}_5\text{Me}_4(\text{CF}_3)\text{H}$  (0.09 g, 0.47 mmol) in acetone (20 ml) at  $0^\circ\text{C}$   $\text{AgBF}_4$  (0.11 g, 0.56 mmol) was added. The resulting mixture was allowed warm to r.t. and stirred for an additional 2 h.  $\text{AgCl}$  was filtered off, the solution was concentrated to 3 ml and 25 ml of diethyl ether was added. The resulting precipitate was filtered off, washed with diethyl ether and dried in vacuo. Yield: 0.08 g (43%) of **4**.  $^1\text{H-NMR}$  (acetone- $d_6$ ): 1.88 (s, 6H, 2Me,  $J_{\text{H-Pt}} = 37.5$  Hz); 2.14 (s, 6H, 2Me,  $J_{\text{H-Pt}} = 20.3$  Hz); 2.27 (s, 6H, 2Me,  $J_{\text{H-F}} = 0.9$ ,  $J_{\text{H-Pt}} = 11.9$  Hz); 2.51 (s, 6H, 2Me,  $J_{\text{H-Pt}} = 24.0$  Hz); 4.75 (q, 1H,  $J_{\text{H-F}} = 6.4$ ;  $J_{\text{H-Pt}} = 67.9$  Hz).  $^{19}\text{F}\{\text{H}\}$ -NMR (acetone- $d_6$ ):  $-52.97$  ( $\eta^5\text{-C}_5\text{Me}_4\text{CF}_3$ ,  $J_{\text{F-Pt}} = 35.9$  Hz);  $-69.74$  ( $\eta^4\text{-C}_5\text{Me}_4(\text{CF}_3)\text{H}$ ,  $J_{\text{F-Pt}} = 8.4$  Hz);  $-149.08$ ;  $-149.13$  ( $\text{BF}_4^-$ ).

### 3.8. Reaction of **1** with $\text{AgBF}_4$ in the presence of $\text{C}_5\text{Me}_5\text{H}$

To a solution of  $[\text{Pt}\{\eta^4\text{-C}_5\text{Me}_4(\text{CF}_3)\text{H}\}\text{Cl}_2]$  (0.14 g, 0.30 mmol) and  $\text{C}_5\text{Me}_5\text{H}$  (0.05 g, 0.36 mmol) in acetone (20 ml) at  $0^\circ\text{C}$   $\text{AgBF}_4$  (0.12 g, 0.64 mmol) was added. The resulting mixture was allowed warm to r.t. and stirred for an additional 2 h.  $\text{AgCl}$  was filtered off, the solution was concentrated to 3 ml and 25 ml of diethyl ether was added. The resulting precipitate was filtered off, washed with diethyl ether and dried in vacuo. Yield: 0.02 g (12%) of **5**.  $^1\text{H-NMR}$  (acetone- $d_6$ ): 0.68 (d, 3H, Me,  $J = 6.4$  Hz); 1.58 (s, 6H, 2Me,  $J_{\text{H-Pt}} = 30.5$  Hz); 1.99 (s, 15H,  $\text{C}_5\text{Me}_5$ ,  $J_{\text{H-Pt}} = 19.8$  Hz); 2.33 (s, 6H, 2Me,  $J_{\text{H-Pt}} = 23.6$  Hz); 3.59 (q, 1H,  $J = 6.4$ ;  $J_{\text{H-Pt}} = 54.8$  Hz).

## 4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 149 900 for complex **2** and

CCDC no. 149 901 for complex **3** $^+\text{PF}_6^-$ . Copies of this information may be obtained from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1233-336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

## Acknowledgements

The authors thank the Russian Foundation for Basic Research (grant nos. 99-03-33060a, 00-03-32855a and 00-03-32807a) for support.

## References

- [1] P.G. Gassman, J.W. Mickelson, J.R. Sowa, *Inorg. Synth.* 31 (1997) 232.
- [2] P.G. Gassman, J.W. Mickelson, J.R. Sowa, Jr, *J. Am. Chem. Soc.* 114 (1992) 6942.
- [3] P.G. Gassman, J.R. Sowa, M.G. Hill, K.R. Mann, *Organometallics* 14 (1995) 4879.
- [4] L.P. Barthel-Rosa, J.R. Sowa, P.G. Gassman, J. Fischer, B.M. McCarty, S.L. Gibson, J.H. Nelson, *Organometallics* 16 (1997) 1595.
- [5] L.P. Barthel-Rosa, V.J. Catalano, K. Maitra, J.H. Nelson, *Organometallics* 15 (1996) 3924.
- [6] O.V. Gusev, M.A. Ievlev, K.A. Lyssenko, P.V. Petrovskii, N.A. Ustynyuk, P.M. Maitlis, *Inorg. Chim. Acta* 280 (1998) 249.
- [7] O.V. Gusev, M.A. Ievlev, T.A. Peganova, M.G. Peterleitner, P.V. Petrovskii, Yu.F. Oprunenko, N.A. Ustynyuk, *J. Organomet. Chem.* 551 (1998) 93.
- [8] L.P. Szajek, J.R. Shapley, *Organometallics* 10 (1991) 2512 and references therein.
- [9] (a) O.V. Gusev, L.N. Morozova, T.A. Peganova, P.V. Petrovskii, N.A. Ustynyuk, *Izv. Acad. Nauk Ser. Khim.* (1994) 514. (b) O.V. Gusev, L.N. Morozova, T.A. Peganova, P.V. Petrovskii, N.A. Ustynyuk, *Russ. Chem. Bull.* 43 (1994) 474.
- [10] O.V. Gusev, L.N. Morozova, T.A. Peganova, P.V. Petrovskii, N.A. Ustynyuk, P.M. Maitlis, *J. Organomet. Chem.* 472 (1994) 359.
- [11] A.L. Rheingold, K.A. Jacobson, *Acta Crystallogr. Sect. C* 740 (1992) C48.
- [12] (a) P.V. Balakrishnan, P.M. Maitlis, *J. Chem. Soc. A* (1971) 1715. (b) P.V. Balakrishnan, P.M. Maitlis, *J. Chem. Soc. A* (1971) 1721.
- [13] J.H. Simons, R.E. McArthur, *Ind. Eng. Chem.* 39 (1947) 364.
- [14] O.V. Gusev, T.A. Peganova, M.G. Peterleitner, S.M. Peregodova, L.I. Denisovich, N.A. Ustynyuk, P.M. Maitlis, *J. Organomet. Chem.* 480 (1994) C16.
- [15] T. Olsson, O. Wennerstroem, *Acta Chem. Scand. B* 32 (1978) 293.
- [16] P.G. Gassman, C.H. Winter, *J. Am. Chem. Soc.* 108 (1986) 4228.