

# Convenient synthesis of cationic allylplatinum(II) complexes with tertiary phosphines by oxidative allyl transfer from ammonium cations to platinum(0) substrates. Crystal and molecular structures of $\eta^3$ -propenyl- and $\eta^3$ -2-methylpropenyl-bis-(triphenylphosphine)platinum(II)perchlorates

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## Abstract

A large variety of cationic  $\eta^3$ -allylplatinum(II) complexes of the type  $[\text{Pt}(\eta^3\text{-CH}_2\text{C(R)C(R')C(R'')})\text{(PPh}_3)_2]^+$  (**1a–f**) are prepared in high yield by oxidative allyl transfer from the ammonium cations  $[\text{NEt}_3\text{CH}_2\text{C(R)=C(R')}]^+$  to  $[\text{Pt}(\eta^2\text{-C}_2\text{H}_4)\text{(PPh}_3)_2]$ . A similar reaction of  $[\text{NEt}_3\text{CH}_2\text{C(R)=C(R')}]^+$  with  $[\text{Pt}(\text{cod})_2]$  yields the related complexes  $[\text{Pt}(\eta^3\text{-CH}_2\text{C(R)C(R')})_2(\text{cod})]^+$  (**2a–c**), indicating a rather general feasibility of such synthetic route. The 1,5-cyclooctadiene ligand of complexes **2a,c** can be easily displaced by mono- and bidentate tertiary phosphines. The solution behaviour of the cationic  $\eta^3$ -allyl platinum(II) complexes has been studied by multinuclear NMR spectroscopy. The solid state structures of the complexes  $[\text{Pt}(\eta^3\text{-CH}_2\text{CHCH}_2)\text{(PPh}_3)_2]^+$  (**1a**) and  $[\text{Pt}(\eta^3\text{-CH}_2\text{C(Me)CH}_2)\text{(PPh}_3)_2]^+$  (**1b**) have been determined by X-ray analyses. In **1b**, the 2-methylpropenyl ligand is symmetrically  $\eta^3$ -bound to platinum and assumes a unique orientation relative to the average coordination plane. In **1a**, however, the propenyl ligand is disordered in two opposite orientations with occupation factors of 0.65 and 0.35. In the orientation with 0.65 occupation factor, the allyl ligand is symmetrically  $\eta^3$ -bound to the metal, whereas, in the opposite orientation the C–C bond distances within the allyl group are considerably different [1.46(4) and 1.23(4) Å] with the three allyl carbon atoms being at roughly equal distances from platinum. Even though the  $\text{C}_3\text{H}_5$  group is affected by large anisotropic thermal motion, the observed asymmetry may also arise from a prevailing  $\eta^1$ ,  $\eta^2$  coordination of the ligand in the solid. © 2000 Elsevier Science S.A. All rights reserved.

**Keywords:** Synthesis; Platinum; Allyl complexes; X-ray structures

## 1. Introduction

The cationic complexes  $[\text{Pt}(\eta^3\text{-all})\text{L}_2]^+$  [all = allylic ligand; L = PPh<sub>3</sub>; L<sub>2</sub> = 1,5-cyclooctadiene (cod)] have generally been prepared through oxidative addition of allyl halides[1] or acetates[2] to  $[\text{Pt}(\text{PPh}_3)_3]$  or  $[\text{Pt}(\text{cod})_2]$ ,

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followed by exchange of the halide or acetate with the poorly coordinating  $\text{BF}_4^-$  or  $\text{ClO}_4^-$  anions.

In an early report, it was shown that the platinum(0) substrates, such as  $[\text{Pt}(\text{PPh}_3)_3]$  and  $[\text{Pt}(\eta^2\text{-C}_2\text{H}_4)(\text{PPh}_3)_2]$ , yield the derivatives  $[\text{Pt}(\eta^3\text{-all})\text{L}_2]^+$  upon treatment with allyl ammonium cations [3]. Such a reaction, involving an oxidative allyl transfer, has also been used to prepare cationic  $\eta^3$ -allylpalladium(II) complexes containing monodentate phosphine and phosphite ligands [4] or bidentate ligands, such as 1,2-bis(diphenylphosphino)ethane [5] or  $\alpha$ -diimines [6]. Furthermore, the same type of reaction has been exploited for selective desallylation of allyl amines catalyzed by palladium(0) compounds [7]. On the other hand,  $\eta^3$ -allylplatinum(II) complexes have also been obtained in redox transmetalation reactions involving an allyl group transfer from palladium(II) to platinum(0) compounds [8].

The principal object of the present work was to extend this synthetic approach using variously substituted allyl ammonium cations to show the general feasibility of this method. In addition, starting from  $[\text{Pt}(\text{cod})_2]$ , the allyl transfer reaction affords an easy route for the preparation of  $\eta^3$ -allylplatinum(II) complexes containing mono- and bidentate ancillary ligands, through displacement of the weakly bound 1,5-cyclooctadiene.

## 2. Experimental

**Safety note.** Caution! Perchlorate salts are potentially explosive. Only small amounts of these materials should be prepared, and they should be handled with great caution.

### 2.1. General

$^1\text{H}$ -,  $^{13}\text{C}$ -, and  $^{31}\text{P}$ -NMR spectra were recorded at 200.133, 50.323, and 81.015 MHz, respectively, in  $\text{CDCl}_3$ , with a Bruker AC 200 spectrometer. Infrared spectra were recorded on a Perkin–Elmer 983 spectrometer. Melting points were measured on samples in unsealed capillary tubes and are uncorrected. Elemental analyses were carried out by the department of Analytical Chemistry of the University of Padua.

THF, diethyl ether and toluene were dried over sodium, in the presence of benzophenone, and distilled under nitrogen.  $\text{CH}_2\text{Cl}_2$  was dried over calcium hydride and freshly distilled under nitrogen. All other reagents were purchased from commercial suppliers and used as received. All manipulations were carried out under dry nitrogen atmosphere using standard Schlenk techniques.

$[\text{Pt}(\text{PPh}_3)_2(\text{C}_2\text{H}_4)]$  [9] and  $[\text{Pt}(\text{cod})_2]$  [10] were synthesized according to a previously described procedures.

### 2.2. Synthesis of triethylallylammonium salts (a–f)

To a solution of  $\text{NaClO}_4$  (6.11 g, 50.0 mmol) or  $\text{NaBF}_4$  (5.49 g, 50.0 mmol) in acetone (50 ml) were added  $\text{NEt}_3$  (1.70 ml, 12.0 mmol) and then the allylbromide (11.0 mmol). The reaction mixture was stirred at room temperature (r.t.) overnight and then concentrated to dryness in vacuo.  $\text{CH}_2\text{Cl}_2$  (25 ml) was added to the solid and, after filtration, the solution was concentrated at reduced pressure. Addition of  $\text{Et}_2\text{O}$  gave the salt as a white solid, or pale yellow oil (**d**), which was filtered and dried under vacuum. This procedure was used to prepare the compounds described below.

#### 2.2.1. $[\text{NEt}_3\text{CH}_2\text{CH}=\text{CH}_2]\text{ClO}_4$ (**a**)

Yield: 96%.  $^1\text{H}$ -NMR: 5.95–5.66 (m, 3H), 3.89 (d,  $J_{\text{HH}} = 6.6$  Hz, 2H), 3.33 (q,  $J_{\text{HH}} = 7.3$  Hz, 6H), 1.35 (t,  $J_{\text{HH}} = 7.3$  Hz, 9H); m.p. 235°C (dec.). Anal. Calc. for  $\text{C}_9\text{H}_{20}\text{ClNO}_4$ : C, 44.72; H, 8.34; N, 5.79. Found: C, 45.1; H, 8.5; N, 5.5%.

#### 2.2.2. $[\text{NEt}_3\text{CH}_2\text{C}(\text{Me})=\text{CH}_2]\text{ClO}_4$ (**b**)

Yield: 96%.  $^1\text{H}$ -NMR: 5.52 (bs, 1H), 5.36 (s, 1H), 3.83 (bs, 2H), 3.34 (q,  $J_{\text{HH}} = 7.3$  Hz, 6H), 2.00 (bs, 3H), 1.38 (t,  $J_{\text{HH}} = 7.3$ , 9H); m.p. 67–69°C. Anal. Calc. for  $\text{C}_{10}\text{H}_{22}\text{ClNO}_4$ : C, 46.96; H, 8.67; N, 5.48. Found: C, 47.1; H, 8.3; N, 5.3%.

#### 2.2.3. $[\text{NEt}_3\text{CH}_2\text{CH}=\text{CMe}_2]\text{ClO}_4$ (**c**)

Yield: 94%.  $^1\text{H}$ -NMR: 5.21 (bt,  $J_{\text{HH}} = 7.7$  Hz, 1H), 3.77 (d,  $J_{\text{HH}} = 7.7$  Hz, 2H), 3.26 (q,  $J_{\text{HH}} = 7.3$  Hz, 6H), 1.84 (s, 3H), 1.77 (bs, 3H), 1.32 (t,  $J_{\text{HH}} = 7.3$  Hz, 9H); m.p. 111–113°C. Anal. Calc. for  $\text{C}_{11}\text{H}_{24}\text{ClNO}_4$ : C, 48.98; H, 8.97; N, 5.19. Found: C, 50.2; H, 9.3; N, 5.0%.

#### 2.2.4. *trans*- $[\text{NEt}_3\text{CH}_2\text{CH}=\text{CHMe}]\text{BF}_4$ (**d**)

Yield: 98%.  $^1\text{H}$ -NMR: 6.13 (dq,  $J_{\text{HH}} = 15.2, 6.5$  Hz, 1H), 5.46 (dtq,  $J_{\text{HH}} = 15.2, 7.5, 1.7$  Hz, 1H), 3.76 (d,  $J_{\text{HH}} = 7.5$  Hz, 2H), 3.24 (q,  $J_{\text{HH}} = 7.3$  Hz, 6H), 1.78 (dd,  $J_{\text{HH}} = 6.5, 1.7$  Hz, 3H), 1.30 (t,  $J_{\text{HH}} = 7.3$  Hz, 9H); m.p. 83–86°C. Anal. Calc. for  $\text{C}_{10}\text{H}_{22}\text{BF}_4\text{N}$ : C, 49.41; H, 9.12; N, 5.76. Found: C, 50.2; H, 9.4; N, 5.9%.

#### 2.2.5. *trans*- $[\text{NEt}_3\text{CH}_2\text{CH}=\text{CHEt}]\text{BF}_4$ (**e**)

This compound is a pale yellow viscous oil obtained in 88% yield.  $^1\text{H}$ -NMR: 6.02 (dt,  $J_{\text{HH}} = 11.0, 7.6$  Hz, 1H), 5.42 (dt,  $J_{\text{HH}} = 11.0, 7.5, 1.5$  Hz, 1H), 3.88 (d,  $J_{\text{HH}} = 7.5$  Hz, 2H), 3.33 (q,  $J_{\text{HH}} = 7.2$  Hz, 6H), 2.19 (dq,  $J_{\text{HH}} = 7.6, 7.6, 1.5$  Hz, 2H), 1.35 (t,  $J_{\text{HH}} = 7.2$  Hz, 9H), 1.03 (t,  $J_{\text{HH}} = 7.6$  Hz, 3H). Anal. Calc. for  $\text{C}_{11}\text{H}_{24}\text{BF}_4\text{N}$ : C, 51.38; H, 9.41; N, 5.45. Found: C, 50.3; H, 9.1; N, 5.2%.

### 2.2.6. *trans*-[NEt<sub>3</sub>CH<sub>2</sub>CH=CHPh]BF<sub>4</sub> (**f**)

Yield: 96%. <sup>1</sup>H-NMR: 6.99 (d, *J*<sub>HH</sub> = 15.7 Hz, 1H), 6.16 (dt, *J*<sub>HH</sub> = 15.7, 7.5 Hz, 1H), 4.07 (d, *J*<sub>HH</sub> = 7.5 Hz, 2H), 3.33 (q, *J*<sub>HH</sub> = 7.2 Hz, 6H), 1.36 (t, *J*<sub>HH</sub> = 7.2 Hz, 9H); m.p. 103–105°C. Anal. Calc. for C<sub>15</sub>H<sub>24</sub>BF<sub>4</sub>N: C, 59.04; H, 7.93; N, 4.59. Found: C, 57.6; H, 7.5; N, 4.2%.

### 2.3. Synthesis of the cationic complexes

#### [Pt(η<sup>3</sup>-CH<sub>2</sub>C(R)C(R')(R''))(PPh<sub>3</sub>)<sub>2</sub>]<sup>+</sup> (**1a–f**)

Unless otherwise mentioned, the allylplatinum complexes **1a–f(X)** (X<sup>−</sup> = ClO<sub>4</sub><sup>−</sup>, BF<sub>4</sub><sup>−</sup>) were prepared according to the procedure outlined below for **1a(ClO<sub>4</sub>)**.

To a solution of [Pt(PPh<sub>3</sub>)<sub>2</sub>(C<sub>2</sub>H<sub>4</sub>)] (0.187 g, 0.25 mmol) in THF (30 ml), solid [NEt<sub>3</sub>CH<sub>2</sub>=CHCH<sub>2</sub>]<sup>+</sup>ClO<sub>4</sub><sup>−</sup> (0.060 g, 0.25 mmol) was added in one portion, and the reaction mixture stirred at r.t. for 4 h. The white solid formed was filtered off, washed with THF and dried under vacuum. Yield: 0.122 g, 57%. A second fraction was obtained by reducing the mother liquor to a small volume, and adding Et<sub>2</sub>O. Total yield 82%; m.p. 247°C (dec.). Anal. Calc. for C<sub>39</sub>H<sub>35</sub>ClO<sub>4</sub>P<sub>2</sub>Pt: C, 54.46; H, 4.10. Found: C, 53.7; H, 4.0%.

#### 2.3.1. **1b(ClO<sub>4</sub>)**

Yield 97%; m.p. 267–269°C (dec.). Anal. Calc. for C<sub>40</sub>H<sub>37</sub>ClO<sub>4</sub>P<sub>2</sub>Pt: C, 54.96; H, 4.27. Found: C, 53.3; H, 4.1%.

#### 2.3.2. **1c(ClO<sub>4</sub>)**

The reaction mixture was stirred for 24 h; yield: 87%; m.p. 199–201°C (dec.). Anal. Calc. for C<sub>41</sub>H<sub>39</sub>ClO<sub>4</sub>P<sub>2</sub>Pt: C, 55.44; H, 4.43. Found: C, 55.0; H, 4.2%. This complex was also prepared by adding PPh<sub>3</sub> (0.106 g, 0.40 mmol) to a solution of complex **2c(ClO<sub>4</sub>)** (0.095 g, 0.20 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (20 ml). The resulting solution was stirred for 6 h and then concentrated at reduced pressure. Addition of diethyl ether gave a white solid which was filtered, washed with Et<sub>2</sub>O and dried under vacuum. Yield: 0.149 g, 84%.

#### 2.3.3. **1d(BF<sub>4</sub>)**

Yield 88%; m.p. 241–243°C (dec.). Anal. Calc. for C<sub>40</sub>H<sub>37</sub>BF<sub>4</sub>P<sub>2</sub>Pt: C, 55.77; H, 4.33. Found: C, 55.1; H, 4.0%.

#### 2.3.4. **1e(BF<sub>4</sub>)**

The reaction mixture was refluxed at 66°C for 24 h; yield: 90%; m.p. 242–243°C (dec.). Anal. Calc. for C<sub>41</sub>H<sub>39</sub>BF<sub>4</sub>P<sub>2</sub>Pt: C, 56.25; H, 4.49. Found: C, 55.2; H, 4.2%.

#### 2.3.5. **1f(BF<sub>4</sub>)**

The reaction mixture was stirred for 24 h; yield: 88%; m.p. 194–196°C (dec.). Anal. Calc. for C<sub>45</sub>H<sub>39</sub>BF<sub>4</sub>P<sub>2</sub>Pt: C, 58.52; H, 4.26. Found: C, 57.6; H, 4.0%.

Selected <sup>1</sup>H-, <sup>31</sup>P-{<sup>1</sup>H}- and <sup>13</sup>C-{<sup>1</sup>H}-NMR data of complexes **1a–f(X)** are reported in Tables 1 and 2.

### 2.4. Synthesis of the cationic complexes

#### [Pt(η<sup>3</sup>-CH<sub>2</sub>C(R)C(R')<sub>2</sub>)(cod)]<sup>+</sup> (**2a–c**)

Complexes **2a–c(ClO<sub>4</sub>)** were prepared according to the procedure described below for **2a(ClO<sub>4</sub>)**. To a stirred suspension of allylammonium salt [NEt<sub>3</sub>CH<sub>2</sub>CH=CH<sub>2</sub>]<sup>+</sup>ClO<sub>4</sub><sup>−</sup> (0.121 g, 0.50 mmol) in THF (50 ml), solid Pt(cod)<sub>2</sub> (0.206 g, 0.50 mmol) was added in one portion, and after a few minutes an off-white solid began to precipitate. The reaction mixture was kept aside for 2 h, and then reduced to small volume. The product was filtered off, washed with THF (3 × 3 ml) and dried under vacuum. Yield: 0.187 g, 84%; m.p. 172–175°C (dec.). Anal. Calc. for C<sub>11</sub>H<sub>17</sub>ClO<sub>4</sub>Pt: C, 29.77; H, 3.86. Found: C, 28.4; H, 3.6%.

#### 2.4.1. **2b(ClO<sub>4</sub>)**

Yield 80%; m.p. 209–212°C. Anal. Calc. for C<sub>12</sub>H<sub>19</sub>ClO<sub>4</sub>Pt: C, 31.48; H, 4.18. Found: C, 30.2; H, 4.0%.

#### 2.4.2. **2c(ClO<sub>4</sub>)**

Yield 79%; m.p. 185–189°C (dec.). Anal. Calc. for C<sub>13</sub>H<sub>21</sub>ClO<sub>4</sub>Pt: C, 33.09; H, 4.49. Found: C, 32.5; H, 4.2%.

Selected <sup>1</sup>H- and <sup>13</sup>C-{<sup>1</sup>H}-NMR data of complexes **2a–c(ClO<sub>4</sub>)** are reported in Tables 1 and 2.

### 2.5. Synthesis of the cationic complexes

#### [Pt(η<sup>3</sup>-CH<sub>2</sub>CHC(R)<sub>2</sub>)(L)<sub>2</sub>]<sup>+</sup> (**3a and 3c**)

Complexes **3a(ClO<sub>4</sub>)** and **3c(ClO<sub>4</sub>)** were prepared by cod displacement from the parent compounds **2a(ClO<sub>4</sub>)** and **2c(ClO<sub>4</sub>)** according to the following procedure. To a stirred suspension of [Pt(η<sup>3</sup>-CH<sub>2</sub>CHC(R)<sub>2</sub>)(cod)]ClO<sub>4</sub> (0.25 mmol) in THF (25 ml), a solution of diphos [1,2-bis(diphenylphosphino)ethane] (0.100 g, 0.25 mmol) in THF (10 ml) was added dropwise at r.t. The resulting solution was further stirred for 1 h and then concentrated. Addition of *n*-pentane gave an oily product which was decanted and dried under vacuum. Repetition of operations succeeded in obtaining the solid complexes **3a(ClO<sub>4</sub>)** and **3c(ClO<sub>4</sub>)**.

#### 2.5.1. **3a(ClO<sub>4</sub>)**

Yield: 71%. Anal. Calc. for C<sub>29</sub>H<sub>29</sub>ClO<sub>4</sub>P<sub>2</sub>Pt: C, 47.45; H, 3.98. Found: C, 46.8; H, 3.7%.

#### 2.5.2. **3c(ClO<sub>4</sub>)**

Yield: 87%. Anal. Calc. for C<sub>31</sub>H<sub>33</sub>ClO<sub>4</sub>P<sub>2</sub>Pt: C, 48.86; H, 4.36. Found: C, 48.1; H, 4.2%.

Selected <sup>1</sup>H-, <sup>31</sup>P-{<sup>1</sup>H}- and <sup>13</sup>C-{<sup>1</sup>H}-NMR data of complexes **3a(ClO<sub>4</sub>)** and **3c(ClO<sub>4</sub>)** are reported in Tables 1 and 2.

Table 1  
Selected  $^1\text{H-NMR}$  data <sup>a</sup>

Compound	Allyl protons					Others	
	H <sub>3s</sub>	H <sub>3a</sub>	R	R' <sub>syn</sub>	R'' <sub>anti</sub>		
<b>1a</b> (ClO <sub>4</sub> )	3.73 d, (5.8) <sup>b</sup>	3.01 dd, (12.6) <sup>b</sup> , (7.8) <sup>c</sup> , (38.6) <sup>d</sup>	5.52 m	3.73 d, (5.8) <sup>b</sup>	3.01 dd, (12.6) <sup>b</sup> , (7.8) <sup>c</sup> , (38.6) <sup>d</sup>		
<b>1b</b> (ClO <sub>4</sub> )	3.41 s	3.24 d, (8.3) <sup>c</sup> , (38.4) <sup>d</sup>	2.00 s, (63.8) <sup>d</sup>	3.41 s	3.24 d, (8.3) <sup>c</sup> , (38.4) <sup>d</sup>		
<b>1c</b> (ClO <sub>4</sub> )	3.47 m	2.36 m	5.37 m	1.32 dd, (7.9) <sup>c</sup> , (3.4) <sup>d</sup>	1.18 dd, (4.6) <sup>c</sup> , (1.8) <sup>d</sup>		
<b>1d</b> (BF <sub>4</sub> )							
<i>syn</i>	3.26 m	2.92 m	5.31 m	1.23 m	3.86 m		
<i>anti</i>	4.00 m	2.59 m	5.54 m	4.44 m	1.03 m		
<b>1e</b> (BF <sub>4</sub> )							
<i>syn</i>	3.29 br	2.92 m, (37.5) <sup>d</sup>	5.28 m	1.16 br; 0.76 t, (7.2) <sup>c</sup>	3.75 m, (50.0) <sup>d</sup>		
<i>anti</i>	4.00 br	2.49 m, (41.0) <sup>d</sup>	5.58 m	4.30 br	1.36 br; 0.64 t, (7.2) <sup>c</sup>		
<b>1f</b> (BF <sub>4</sub> )	3.40 <sup>f</sup> m	3.36 <sup>f</sup> m	5.92 m	6.90–6.67 m	4.86 dd, (13.2) <sup>b</sup> , (9.4) <sup>c</sup> , (37.2) <sup>d</sup>		
						1,5-cyclopentadiene protons	
						CH	
<b>2a</b> (ClO <sub>4</sub> )	4.89 br	3.43 br	5.94 qt, (10.2) <sup>b</sup> , (75.7) <sup>d</sup>	4.89 br	3.43 br	6.13 m br, (71.7) <sup>d</sup>	CH <sub>2</sub> 2.55 m br
<b>2b</b> (ClO <sub>4</sub> )	4.66 br	3.31 br, (29.3) <sup>d</sup>	2.01 s, (90.3) <sup>d</sup>	4.66 br	3.31 br, (29.3) <sup>d</sup>	6.11 m br, (68.5) <sup>d</sup>	2.62 m br
<b>2c</b> (ClO <sub>4</sub> )	4.46 br	3.34 br	5.60 t, (10.7) <sup>b</sup> , (75.7) <sup>d</sup>	2.23 s, (7.1) <sup>d</sup>	1.55 s, (5.4) <sup>d</sup>	6.24 m br, (73.1) <sup>d</sup> ; 5.41 m br, (67.0) <sup>d</sup>	2.52 m br
						diphos CH <sub>2</sub> protons	
<b>3a</b> (ClO <sub>4</sub> )	4.72 m	2.98 dd, (13.9) <sup>b</sup> , (8.7) <sup>c</sup> , (44.6) <sup>d</sup>	5.30 m, (48.3) <sup>d</sup>	4.72 m	2.98 dd, (13.9) <sup>b</sup> , (8.7) <sup>c</sup> , (44.6) <sup>d</sup>	2.93–2.49 m	
<b>3c</b> (ClO <sub>4</sub> )	4.09 m	mk <sup>g</sup>	5.15 m, (50.7) <sup>d</sup>	2.06 dd, (6.7) <sup>c</sup> , (4.6) <sup>c</sup> , (9.3) <sup>d</sup>	0.94 s, (7.0) <sup>d</sup>	3.20–2.53 m	

<sup>a</sup> In CDCl<sub>3</sub>, CHCl<sub>3</sub> ( $\delta = 7.26$ ) as internal standard; coupling constant in Hz; d, doublet; dd, doublet of doublets; t, triplet; qt, quintet; m, multiplet; br, broad; mk, masked. The proton numbering scheme is reported in Eqs. (1)–(3).

<sup>b</sup>  $J(\text{HR})$ .

<sup>c</sup>  $J(\text{HP})$ .

<sup>d</sup>  $J(\text{HPt})$ .

<sup>e</sup>  $J(\text{HH})$ .

<sup>f</sup> Partially overlapped resonances.

<sup>g</sup> Masked by diphos CH<sub>2</sub> resonances.

Table 2  
Selected  $^{13}\text{C}$ - and  $^{31}\text{P}$ -NMR data <sup>a</sup>

Compound	Allyl carbons						Others	$^{31}\text{P}$ -NMR	
	C <sub>1</sub>	C <sub>2</sub>	C <sub>3</sub>	R	R'	R''			
<b>1a</b> (ClO <sub>4</sub> )	70.67 m <sup>b</sup>	119.85 t, (18.1) <sup>d</sup> , (2.6) <sup>e</sup>	70.67 m					16.14 s, (3987.0) <sup>f</sup>	
<b>1b</b> (ClO <sub>4</sub> )	70.08 m <sup>c</sup>	130.71 s, (32.8) <sup>d</sup>	70.08 m	24.98 s, (33.0) <sup>d</sup>				17.80 s, (3862.1) <sup>f</sup>	
<b>1c</b> (ClO <sub>4</sub> )	105.98 d, (50.4) <sup>d</sup> , (25.3) <sup>e</sup>	110.72 t, (20.9) <sup>d</sup> , (3.0) <sup>e</sup>	59.03 d, (120.5) <sup>d</sup> , (30.1) <sup>e</sup>		25.02 d, (2.5) <sup>e</sup>	21.87 d, (32.5) <sup>d</sup> , (4.8) <sup>e</sup>		19.80 d (3952.8) <sup>f</sup> , (8.7) <sup>g</sup>	16.33 d, (4074.3) <sup>f</sup> , (8.7) <sup>g</sup>
<b>1d</b> (BF <sub>4</sub> ) <i>syn</i>	88.56 d, (42.3) <sup>d</sup> , (26.8) <sup>e</sup>	118.93 t, (24.2) <sup>d</sup> , (3.1) <sup>e</sup>	65.77 d, (107.9) <sup>d</sup> , (28.5) <sup>e</sup>		16.57 d, (4.8) <sup>d</sup> , (2.4) <sup>e</sup>			20.73 d, (3939.0) <sup>f</sup> , (9.0) <sup>g</sup>	17.37 d, (4157.8) <sup>f</sup> , (9.0) <sup>g</sup>
<i>anti</i>	88.98 d, (31.4) <sup>d</sup> , (27.0) <sup>e</sup>	113.43 t, (29.2) <sup>d</sup> , (2.8) <sup>e</sup>	62.36 d, (95.1) <sup>d</sup> , (29.6) <sup>e</sup>			15.34 d, (32.3) <sup>d</sup> , (4.5) <sup>e</sup>		17.54 d, (4028.7) <sup>f</sup> , (10.7) <sup>g</sup>	16.30 d, (3851.5) <sup>f</sup> , (10.7) <sup>g</sup>
<b>1e</b> (BF <sub>4</sub> ) <i>syn</i>	94.63 d, (46.0) <sup>d</sup> , (26.7) <sup>e</sup>	118.11 t, (16.2) <sup>d</sup> , (3.2) <sup>e</sup>	66.71 d, (105.5) <sup>d</sup> , (27.7) <sup>e</sup>		25.05 d, (1.8) <sup>e</sup> ; 17.44 d, (2.5) <sup>e</sup>			20.38 d, (3955.0) <sup>f</sup> , (9.4) <sup>g</sup>	17.12 d, (4133.1) <sup>f</sup> , (9.4) <sup>g</sup>
<i>anti</i>	95.59 d, (40.8) <sup>d</sup> , (26.9) <sup>e</sup>	112.79 t, (16.2) <sup>d</sup> , (2.7) <sup>e</sup>	62.70 d, (115.5) <sup>d</sup> , (30.5) <sup>e</sup>			23.93 d, (4.0) <sup>e</sup> ; 17.30 d, (2.7) <sup>e</sup>		17.51 d, (4029.4) <sup>f</sup> , (10.7) <sup>g</sup>	16.27 d, (3845.5) <sup>f</sup> , (10.7) <sup>g</sup>

Table 2 (Continued)

Compound	Allyl carbons						Others	<sup>31</sup> P-NMR		
	C <sub>1</sub>	C <sub>2</sub>	C <sub>3</sub>	R	R'	R''				
<b>1f</b> (BF <sub>4</sub> )	91.54 d, (26.3) <sup>e</sup>	113.19 s br	66.84 d, (27.4) <sup>e</sup>					19.43 d, (4011.0) <sup>f</sup> , (11.4) <sup>g</sup>	16.27 d, (4191.7) <sup>f</sup> , (11.4) <sup>g</sup>	
							1,5-cyclooctadiene carbons			
							CH	CH <sub>2</sub>		
<b>2a</b> (ClO <sub>4</sub> )	68.71 s, (145.6) <sup>d</sup>	122.41 s, (46.7) <sup>d</sup>	68.71 s, (145.6) <sup>d</sup>				103.87 m br	30.79 s		
<b>2b</b> (ClO <sub>4</sub> )	68.29 s, (152.6) <sup>d</sup>	140.26 s, (44.7) <sup>d</sup>	68.29 s, (152.6) <sup>d</sup>	25.76 s, (43.4) <sup>d</sup>			102.75 s	30.86 s		
<b>2c</b> (ClO <sub>4</sub> )	102.04 s, (131.9) <sup>d</sup>	114.28 s, (44.7) <sup>d</sup>	58.59 s, (193.3) <sup>d</sup>		26.40 s	22.37 s, (45.0) <sup>d</sup>	109.31 m br, (126.0) <sup>d</sup> ; 104.30 m br, (105.5) <sup>d</sup>	30.67 br; 29.64 br		
							diphos carbons			
<b>3a</b> (ClO <sub>4</sub> )	64.10 d, (83.1) <sup>d</sup> , (29.1) <sup>e</sup>	119.03 s, (23.1) <sup>d</sup>	64.10 d, (83.1) <sup>d</sup> , (29.1) <sup>e</sup>				28.88 dd, (52.5) <sup>d</sup> , (40.7) <sup>e</sup> , (8.7) <sup>e</sup>		47.85 s, (3701.7) <sup>f</sup>	
<b>3c</b> (ClO <sub>4</sub> )	99.18 dd, (66.5) <sup>d</sup> , (25.3) <sup>e</sup> , (2.4) <sup>e</sup>	111.74 t, (22.0) <sup>d</sup> , (3.1) <sup>e</sup>	54.05 d, (127.3) <sup>d</sup> , (30.2) <sup>e</sup>		26.76 s	21.42 d, (34.1) <sup>d</sup> , (4.0) <sup>e</sup>	30.71 dd, (49.4) <sup>d</sup> , (38.5) <sup>e</sup> , (10.5) <sup>e</sup>	28.35 dd, (49.7) <sup>d</sup> , (38.9) <sup>e</sup> , (10.8) <sup>e</sup>	46.79 d, (3721.9) <sup>f</sup> , (10.0) <sup>g</sup>	46.35 d, (3661.3) <sup>f</sup> , (10.0) <sup>g</sup>

<sup>a</sup> In CDCl<sub>3</sub>; coupling constants in Hz; s, singlet; d, doublet; dd, doublet of doublets; t, triplet; m, multiplet; br, broad. The carbon numbering scheme is reported in Eqs. (1)–(3).

<sup>b</sup> X part of an AA'MX spin system (A, A' = <sup>31</sup>P; M = <sup>195</sup>Pt; see text);  $J(\text{CP}) = -30.7$ ,  $J(\text{CP}') = 2.8$ ,  $J(\text{PP}') = 9.0$ ,  $J(\text{CPt}) = 78.8$  Hz.

<sup>c</sup> X part of an AA'MX spin system (A, A' = <sup>31</sup>P; M = <sup>195</sup>Pt; see text);  $J(\text{CP}) = -31.0$ ,  $J(\text{CP}') = 2.8$ ,  $J(\text{PP}') = 9.0$ ,  $J(\text{CPt}) = 86.8$  Hz.

<sup>d</sup>  $J(\text{CPt})$ .

<sup>e</sup>  $J(\text{CP})$ .

<sup>f</sup>  $J(\text{PPt})$ .

<sup>g</sup>  $J(\text{PP})$ .

Table 3  
Experimental data for the crystallographic analyses

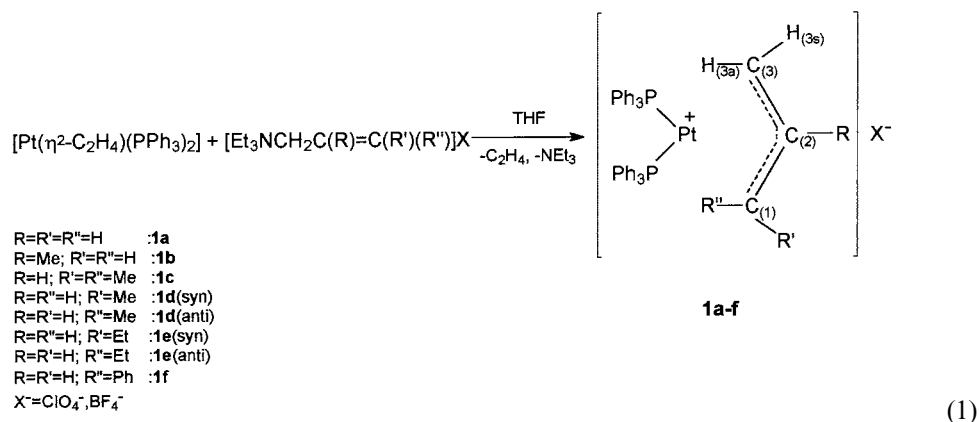
Compound	<b>1a</b> (ClO <sub>4</sub> )	<b>1b</b> (ClO <sub>4</sub> )
Formula	C <sub>30</sub> H <sub>35</sub> ClO <sub>4</sub> P <sub>2</sub> Pt	C <sub>40</sub> H <sub>37</sub> ClO <sub>4</sub> P <sub>2</sub> Pt
Molecular weight	860.2	874.2
Color	Colorless	Colorless
Crystal size (mm)	0.42 × 0.48 × 0.36	0.34 × 0.44 × 0.32
Crystal system	Monoclinic	Monoclinic
Space group	C2/c	Cc
<i>a</i> (Å)	25.525(5)	14.556(3)
<i>b</i> (Å)	17.364(3)	14.856(3)
<i>c</i> (Å)	17.931(3)	17.197(4)
β (°)	118.28(3)	94.83(3)
<i>V</i> (Å <sup>3</sup> )	6999(3)	3706(1)
<i>Z</i>	8	4
<i>D</i> <sub>calc</sub> (g cm <sup>-3</sup> )	1.632	1.567
<i>F</i> (000)	3408	1736
θ Range (°)	3–26	3–28
Radiation (λ (Å))	Mo–K <sub>α</sub> (0.71073)	Mo–K <sub>α</sub> (0.71073)
μ (cm <sup>-1</sup> )	42.2	39.8
<i>T</i> (K)	293(2)	293(2)
No. of reflections collected	9037	5993
No. of observed [ <i>I</i> ≥ 3σ( <i>I</i> )]	5097	4408
<i>R</i> = Σ  <i>F</i> <sub>o</sub>   –   <i>F</i> <sub>c</sub>  /Σ  <i>F</i> <sub>o</sub>	0.045	0.039
<i>R</i> <sub>w</sub> (on <i>F</i> <sup>2</sup> )	0.106	0.078
GoF	1.19	1.19

introduced at calculated positions in their described geometries and during refinement were allowed to ride on the attached carbon atoms with fixed isotropic thermal parameters (1.2*U*<sub>equiv</sub> of the parent carbon atom). For the **1b**(ClO<sub>4</sub>) structure the Flack parameter [14] has been refined. Calculations were performed with the SHELX-93 program [15], using the scattering factors included therein. The program for the ORTEP drawing was taken from Ref. [16].

### 3. Results and discussion

Platinum(0) complexes are known to react rapidly with allyl halides in acetone or dichloromethane solution to give the allylplatinum(II) derivatives [17]. Moreover they behave like strong nucleophiles toward the allyl group bonded to the quaternary nitrogen [3] from which a good leaving group, such as the neutral amine, is released.

To enlarge the practicability of the latter reaction for the synthesis of allylplatinum(II) complexes, the allylammonium salts **a–f** were prepared and reacted with [Pt(PPh<sub>3</sub>)<sub>2</sub>(η<sup>2</sup>-C<sub>2</sub>H<sub>4</sub>)] in THF solution to afford the cationic complexes **1a–f** according to Eq. (1).



#### 2.6. X-ray measurements and structure determination

Crystal data, collected reflections and parameters of the final refinement for [Pt(η<sup>3</sup>-CH<sub>2</sub>CHCH<sub>2</sub>)(PPh<sub>3</sub>)<sub>2</sub>]-ClO<sub>4</sub>, **1a**(ClO<sub>4</sub>), and [Pt(η<sup>3</sup>-CH<sub>2</sub>C(Me)CH<sub>2</sub>)(PPh<sub>3</sub>)<sub>2</sub>]-ClO<sub>4</sub>, **1b**(ClO<sub>4</sub>), are reported in Table 3. Reflections were collected using a Philips PW1100 diffractometer (Febo System) [11] with graphite-monochromated (Mo–K<sub>α</sub>) radiation, following the standard procedures. There were no significant fluctuations of intensities other than those expected from Poisson statistics. All intensities were corrected for Lorentz polarization and absorption [12]. The positions of the heavy atoms were obtained from Patterson syntheses [13]. All non-H atoms were located in the subsequent Fourier maps. Structures were refined by full-matrix least-squares using anisotropic temperature factors for non-hydrogen atoms. Hydrogen atoms were

The reaction time and temperature depend on the substituents of the allylic precursors (see Section 2).

Complexes **1d**(BF<sub>4</sub>) and **1e**(BF<sub>4</sub>) were obtained as mixtures of *syn* and *anti* isomers (4/1 and 3/2 molar ratios, respectively), indicating that the *syn* geometry is favoured by the less sterically demanding substituent [18], whereas the allylic phenyl group in **f** leads to the formation of the complex **1f**(BF<sub>4</sub>) as a pure *syn* isomer [18].

The <sup>1</sup>H-NMR spectra (Table 1) show the presence of static η<sup>3</sup>-allyl ligands in the cationic complexes **1a–f**, as reported for compounds [Pt(η<sup>3</sup>-allyl)(PR<sub>3</sub>)<sub>2</sub>]<sup>+</sup>X<sup>-</sup> where X<sup>-</sup> is a non-coordinating anion (such as BF<sub>4</sub><sup>-</sup>, PF<sub>6</sub><sup>-</sup>, ClO<sub>4</sub><sup>-</sup> or NO<sub>3</sub><sup>-</sup>) [17,19]. In the <sup>1</sup>H-NMR spectra, the allyl *anti* protons always appear at higher field than the *syn* protons, as they are nearer to the metal centre and hence more strongly shielded.

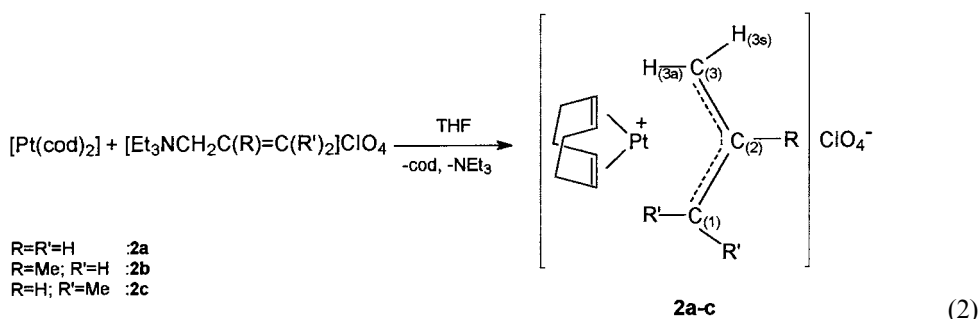
The  $^{31}\text{P}$ -NMR spectra of **1a**( $\text{ClO}_4$ ) and **1b**( $\text{ClO}_4$ ) (Table 2) are characterized by singlets, while in **1c**( $\text{ClO}_4$ ) and **1d–f**( $\text{BF}_4$ ) the asymmetric allyl group gives rise to two doublets of an AB system flanked by  $^{195}\text{Pt}$  satellites.

In Table 2, selected  $^{13}\text{C}$ -NMR data of allyl platinum complexes are also reported. For our systems the assignment of the allyl carbon resonances is rather simple: the central carbon  $\text{C}_2$  appears as a singlet (or triplet) at lower field, the unsubstituted carbon  $\text{C}_3$  is always at higher field, while the carbon  $\text{C}_1$  moves downfield by introducing one or two substituents [20]. In complexes

mium compounds with platinum(0) complexes [3]. It should be noted that the cationic complexes **1a** and **1b** were already obtained following the later procedure.

In this paper we have shown that the above reaction appears to be of general application for the synthesis of cationic Pt(II) complexes containing variously substituted allyl ligands.

Our subsequent step was to explore the oxidative allyl transfer process from ammonium cations to bis(1,5-cyclooctadiene)platinum(0). By this way we prepared complexes **2a–c**( $\text{ClO}_4$ ) according to Eq. (2).



**1a**( $\text{ClO}_4$ ) and **1b**( $\text{ClO}_4$ ), the terminal carbon resonances of the  $\eta^3$ -allyl ligand appear as a multiplet, which was analysed as the X part of an AA'MX (A, A' =  $^{31}\text{P}$ ; M =  $^{195}\text{Pt}$ ; X =  $^{13}\text{C}$ ) spin system [21]; the coupling constants (Table 2) were refined using a G-NMR 4.0 program, the simulated spectra being in a good agreement with the experimental ones.

Quite similar  $^{13}\text{C}$ -NMR patterns have been previously observed for the olefin carbons in complexes of the type  $[\text{Pt}(\eta^2\text{-ol})(\text{PPh}_3)_2]$  (ol = diethyl fumarate or maleate) [22].

The magnetic non-equivalence of the  $^{31}\text{P}$  nuclei in the *cis*-Pt( $\text{PPh}_3$ )<sub>2</sub> unit, may be ascribed to a slow rotation, on the  $^{13}\text{C}$ -NMR time scale, of the  $\text{PPh}_3$  ligands around the Pt–P bonds, caused by steric interactions as early proposed for the complex  $[\text{Pt}(\eta^3\text{-CH}_2\text{CHCH}_2\text{-}(\text{PCy}_3)_2)\text{PF}_6$  [19c].

This interpretation is also supported by the  $^{13}\text{C}$ -NMR spectrum of  $[\text{Pt}(\eta^3\text{-CH}_2\text{CHCH}_2)(\text{diphos})]^+$  (**3a**) where the terminal allyl carbons appear as a simple doublet at 64.10 ppm, flanked by  $^{195}\text{Pt}$  satellites, indicating the presence of magnetically equivalent  $^{31}\text{P}$  nuclei. In this case, only a fast conformational rearrangement of the five-membered Pt(diphos) ring can take place, which generates an averaged plane of symmetry, passing through the central allyl carbon and perpendicular to the P–Pt–P coordination plane.

Cationic allyl complexes were previously prepared by Kurosawa by reacting cationic platinum(II) hydrides with allylic alcohols, diallyl ethers [19a], or with allylic amines [23], and subsequently by reacting allylammo-

The cationic compounds **2a** and **2b** were previously prepared by halide abstraction with silver tetrafluoroborate or hexafluorophosphate either from  $\eta^1$ -allylplatinum complexes [1] or, in the case of **2b**, from the dimer  $[\text{Pt}(\eta^3\text{-CH}_2\text{C}(\text{Me})\text{CH}_2)\text{Cl}]_2$  in the presence of cod [24]. It is clear, however, that our method is more feasible and of more general applicability.

The complexes **2a–c**( $\text{ClO}_4$ ) containing the modest  $\sigma$ -donor 1,5-cyclooctadiene ligand exhibit a dynamic behaviour in solution.

Examination of the  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectra (Tables 1 and 2) shows that the allyl group undergoes an  $\eta^3$ - $\eta^1$ - $\eta^3$  interconversion at r.t. For the cationic complexes **2a** and **2b** such interconversion involves breaking of a Pt–C bond, which can occur at either the two ends of the symmetric allyl ligand, whereas in **2c** the breaking occurs selectively at the substituted carbon atom [1]. While the dynamic behaviour of the cationic complexes **2a** and **2b** have been already discussed in detail [1], we like to describe here the NMR data of **2c**.

At 253 K, in  $\text{CDCl}_3$ , the  $\eta^3$ - $\eta^1$ - $\eta^3$  process is frozen out allowing analysis of the  $^1\text{H}$ -NMR spectrum. In fact, all the allylic proton resonances appear as doublets of doublets: at 5.53 ppm ( $J_{\text{HH}} = 13.7$  and 7.6,  $J_{\text{HPt}} = 76.1\text{Hz}$ ), 4.47 ppm ( $J_{\text{HH}} = 7.6$  and 3.8 Hz), and 3.09 ppm ( $J_{\text{HH}} = 13.7$  and 3.8,  $J_{\text{HPt}} = 42.3$  Hz) for the central, *syn* and *anti* protons, respectively.

On raising the temperature, the signals of *syn* and *anti* protons progressively broaden, until at r.t. they collapse completely, and the central proton appears as a sharp triplet at 5.60 ppm ( $J_{\text{HH}} = 10.7$ ,  $J_{\text{HPt}} = 75.7$  Hz). An approximate calculation gives a  $\Delta G^\ddagger$  of ca. 15.0 kcal



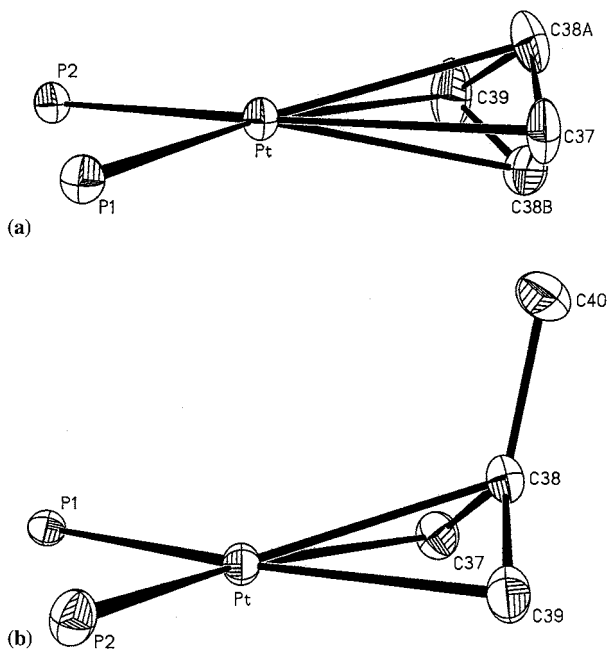


Fig. 1. (a) Perspective view of the platinum coordination plane of  $[\text{Pt}(\eta^3\text{-CH}_2\text{CHCH}_2)(\text{PPh}_3)_2]^+$  (**1a**) showing the two orientations of the allyl ligand. (b) Perspective view of the coordination plane of  $[\text{Pt}(\eta^3\text{-CH}_2\text{C}(\text{Me})\text{CH}_2)(\text{PPh}_3)_2]^+$  (**1b**).

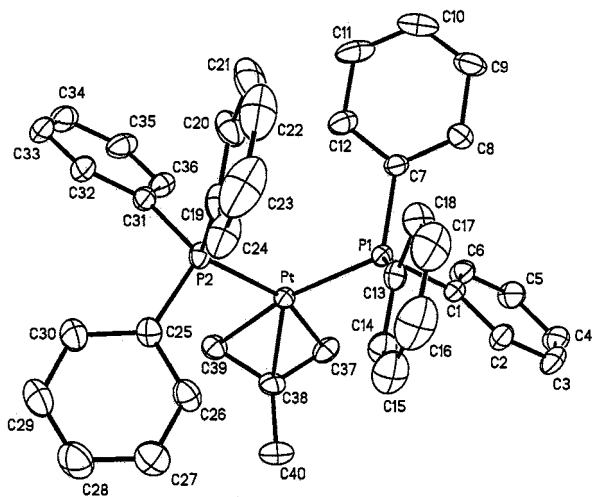
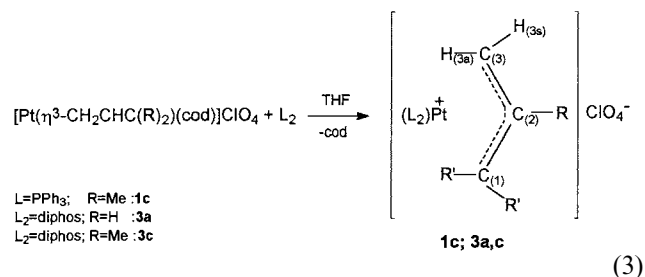


Fig. 2. ORTEP drawing of the cationic complex **1b** with the atom numbering scheme.

$\text{mol}^{-1}$  for the whole process, evaluated on the basis of the loss of the geminal HH coupling [21].

Complexes of the type  $[\text{Pt}(\text{cod})(\eta^3\text{-allyl})]^+$  are good starting materials for the synthesis of allyl compounds bearing a wide variety of ancillary ligands. For example,  $\text{PPh}_3$  or 1,2-bis(diphenylphosphino)ethane displace quantitatively 1,5-cyclooctadiene leading to compounds **1**( $\text{ClO}_4$ ) or **3**( $\text{ClO}_4$ ), respectively.



(3)

The  $^1\text{H-NMR}$  spectra of **3a,c**( $\text{ClO}_4$ ) shows that the allyl ligands are rigid in solution at r.t., and the  $^{31}\text{P-NMR}$  spectroscopy evidences a singlet for the symmetric cationic complex **3a**, and an AB system for **3c**, both with  $^{195}\text{Pt}$  satellites, as previously described for **1a** and **1c**.

It is noteworthy that complexes **3a,c**( $\text{ClO}_4$ ) could not be achieved through reaction (1) being  $[\text{Pt}(\eta^2\text{-C}_2\text{H}_4)(\text{diphos})]$  not stable [25], so that reaction (3) appears to be a new and easy approach to perform the synthesis of cationic allyl platinum complexes with diphos and, possibly, with a variety of bidentate ligands.

### 3.1. Structural characterization of complexes **1a**( $\text{ClO}_4$ ) and **1b**( $\text{ClO}_4$ )

The structures of **1a**( $\text{ClO}_4$ ) and **1b**( $\text{ClO}_4$ ) consist of discrete cations and anions. A perspective view of the platinum coordination plane is shown in Fig. 1a, b for the cationic complexes **1a** and **1b**, respectively. An ORTEP drawing of the cation  $[\text{Pt}(\eta^3\text{-CH}_2\text{C}(\text{Me})\text{CH}_2)(\text{PPh}_3)_2]^+$  is shown in Fig. 2.

Table 4

Selected bond lengths (Å) and angles (°) for  $[\text{Pt}(\text{PPh}_3)_2(\eta^3\text{-CH}_2\text{CHCH}_2)]^+$  (**1a**) and  $[\text{Pt}(\text{PPh}_3)_2(\eta^3\text{-CH}_2\text{C}(\text{CH}_3)\text{CH}_2)]^+$  (**1b**)

	<b>1a</b>	<b>1b</b>
Pt–P(1)	2.280(3)	2.293(1)
Pt–P(2)	2.287(2)	2.311(2)
Pt–C(37)	2.171(7)	2.19(1)
Pt–C(38A)	2.17(1)	2.21(1)
Pt–C(38B)	2.16(2)	–
Pt–C(39)	2.20(1)	2.21(1)
C(37)–C(38A)	1.39(2)	1.41(2)
C(37)–C(38B)	1.46(4)	–
C(38A)–C(39)	1.37(2)	1.43(2)
C(38B)–C(39)	1.24(4)	–
C(38)–C(40)	–	1.50(1)
P(1)–Pt–P(2)	100.85(8)	103.92(7)
P(1)–Pt–C(37)	95.9(3)	97.4(3)
P(1)–Pt–C(39)	163.8(3)	164.6(3)
P(2)–Pt–C(37)	163.1(2)	158.7(3)
P(2)–Pt–C(39)	94.7(3)	91.5(3)
C(37)–Pt–C(39)	68.4(4)	67.2(4)
C(37)–C(38A)–C(39)	126(1)	118(1)
C(37)–C(38B)–C(39)	131(3)	–
C(37)–C(38)–C(40)	–	120.3(9)
C(39)–C(38)–C(40)	–	120.4(9)

Table 5  
Selected bond lengths(Å) and angles (°) in the complexes  $[\text{Pt}(\eta^3\text{-CH}_2\text{CHCH}_2)(\text{L}_2)]^+$

	Pt–P	Pt–C <sub>t</sub> <sup>a</sup>	Pt–C <sub>c</sub> <sup>b</sup>	C <sub>t</sub> –C <sub>c</sub>	C <sub>t</sub> –C <sub>c</sub>	C <sub>t</sub> –C <sub>c</sub> –C <sub>t</sub>	P–Pt–P
L = PCy <sub>3</sub> <sup>c</sup>	2.327(4), 2.335(3)	2.24(2), 2.24(2)	2.19(3), 2.16(5)	1.36(4), 1.39(5)	1.47(4), 1.44(6)	126(3), 126(4)	111.2(1)
L <sub>2</sub> = biphemp <sup>d</sup>	2.277(2), 2.279(3)	2.20(1), 2.22(1)	2.18(2), 2.14(3)	1.34(3), 1.39(3)	1.45(3), 1.40(3)	–	95.4(1)
L = PPh <sub>3</sub> <sup>c</sup>	2.280(2), 2.287(2)	2.171(7), 2.20(1)	2.17(2), 2.16(2)	1.39(3), 1.46(4)	1.37(3), 1.23(4)	126(1), 131(1)	100.85(8)

<sup>a</sup> C<sub>t</sub>, terminal carbon in the allyl group.

<sup>b</sup> C<sub>c</sub>, central carbon in the allyl group.

<sup>c</sup> Ref. [26].

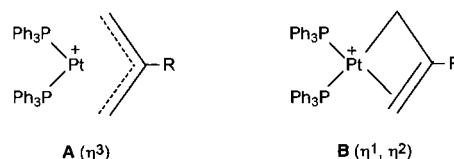
<sup>d</sup> Ref. [27].

<sup>e</sup> Present work.

Selected bond lengths and angles for both complexes are presented in Table 4.

The cationic complex **1a** exhibits a distorted square-planar configuration with C(37)–Pt–C(39) and P(1)–Pt–P(2) angles of 68.4(4)° and 100.85(8)°, respectively, and with the Pt atom lying out of 0.05 Å from the P(1), P(2), C(37), C(39) plane. The central carbon atom of the allyl ligand is disordered in two positions with an occupation factor of 0.65 for C(38A) and 0.35 for C(38B). In both orientations, the three allyl carbon atoms are bonded to platinum at roughly equal distances. In the C(37)–C(38A)–C(39) unit the C–C bond distances are of comparable values [1.39(2) and 1.37(2) Å], whereas in C(37)–C(38B)–C(39) unit the C–C bond lengths are significantly different [1.46(4) and 1.24(4) Å]. The C(37)–Pt–C(39) plane forms a dihedral angle of 62(2)° with the C(37)–C(38A)–C(39) plane, and of 58(2)° with the C(37)–C(38B)–C(39) plane. In both cases, the allyl central atom is inclined away from the metal. The coordination of the allyl moiety in two opposite orientations appears to be a common feature for cationic complexes with the unsubstituted  $\pi$ -allyl ligand of the type  $[\text{Pt}(\eta^3\text{-CH}_2\text{CHCH}_2)(\text{L}_2)]^+$ , as it has been observed for L = PCy<sub>3</sub> [26] and L<sub>2</sub> = biphemp [biphemp = (6,6'-dimethyl-1,1'-biphenyl-diyl)bis(diphenylphosphine)] [27]. A comparison of some selected bond distances and angles of the latter compounds with those of **1a** (Table 5) shows that: (i) the Pt–P bonds and P–Pt–P angle decrease on going from PCy<sub>3</sub> to the less sterically demanding phosphines PPh<sub>3</sub> and biphemp; (ii) in one of the two orientations, the C–C bond lengths of the allyl ligand are considerably different, the largest difference (ca. 0.2 Å) being observed for L = PPh<sub>3</sub> (**1a**).

A comparable difference in the two allyl bond distances [1.41(3) and 1.21(3) Å] was observed for the cationic complexes  $[\text{Pt}(\eta^3\text{-CH}_2\text{C}(\text{OH})\text{CH}_2)(\text{PPh}_3)_2]^+$ , and was ascribed to large anisotropic thermal motion of the allyl ligand [28]. Although the high estimated S.D. values make precise deductions difficult, the difference in the C–C bond lengths may alternatively arise from a different bonding mode in which the limiting  $\eta^1$ ,  $\eta^2$  structure **B** predominates:



According to this picture, the allyl ligand of the cationic complex **1a** would exist in the solid state in the orientation C(37)–C(38A)–C(39) with an  $\eta^3$ -bonding mode **A**, and in the orientation C(37)–C(38B)–C(39) with a bonding mode much closer to **B**. This view is indirectly supported by the unequal statistical distribution of the two orientations in the crystal.

The X-ray structural analysis of **1b** shows the 2-methylallyl ligand in a unique orientation relative to the rest of the molecule (Figs. 1b and 2), as it was found (to the best of our knowledge) in all the structures of the 2-substituted allyl derivatives  $[\text{Pt}(\eta^3\text{-CH}_2\text{C}(\text{R})\text{CH}_2)(\text{PPh}_3)_2]^+$  (R = NEt<sub>2</sub> [29] and OH [28]). The coordination around the central metal is distorted square-planar with C(37)–Pt–C(39) and P(1)–Pt–P(2) angles of 67.2(4)° and 103.92(7)°, respectively, and with the Pt atom lying on the P(1), P(2), C(37), C(39) plane. The 2-methylallyl moiety is  $\eta^3$ -bound to platinum, as indicated by the almost equal Pt–C(37), Pt–C(38), Pt–C(39) bond distances, and by the nearly identical C(37)–C(38) and C(38)–C(39) bond lengths [1.41(2) and 1.43(2) Å, respectively]. The C(37)–Pt–C(39) and the C(37)–C(38)–C(39) planes form a dihedral angle of 68.7(9)°, with the central carbon atom C(38) inclined away from the metal. It is worth noting that the methyl carbon atom C(40) is not coplanar with the other allyl carbon atoms, but is bent towards the metal at a distance of 0.30(1) Å from the C(37)–C(38)–C(39) plane. A similar structural feature was previously observed for palladium(II) derivatives containing the  $\eta^3$ -2-methylallyl ligand [30].

In conclusion, the introduction of a 2-methyl substituent in the allyl group stabilizes only one orientation of the ligand, which assumes an  $\eta^3$ -bonding mode with a decreased inclination of the allyl plane with respect to the C(37)–Pt–C(39) plane.

#### 4. Supplementary material

Crystallographic data (excluding structure factors) for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 139489 for compound  $[\text{Pt}(\eta^3\text{-CH}_2\text{CHCH}_2)(\text{PPh}_3)_2]\cdot\text{ClO}_4$ , and CCDC no. 139490 for compound  $[\text{Pt}(\eta^3\text{-CH}_2\text{C}(\text{Me})\text{CH}_2)(\text{PPh}_3)_2]\cdot\text{ClO}_4$ . Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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