

# Trifluoromethylselenato(0) and trifluoromethyltellurato(0) complexes of platinum(II)

Natalya V. Kirij<sup>a</sup>, Wieland Tyrra<sup>b,\*</sup>, Ingo Pantenburg<sup>b</sup>, Daniela Naumann<sup>b</sup>, Harald Scherer<sup>b</sup>, Dieter Naumann<sup>b,\*</sup>, Yuri L. Yagupolskii<sup>a</sup>

<sup>a</sup> Institute of Organic Chemistry, National Academy of Sciences of the Ukraine, Murmanskaya St. 5, UA-02094 Kyiv, Ukraine

<sup>b</sup> Institut für Anorganische Chemie, Universität zu Köln, Greinstrasse 6, D-50939 Köln, Germany

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## Abstract

The series of *cis/trans*-trifluoromethylselenato complexes  $[\text{Pt}(\text{SeCF}_3)_2 - x\text{Cl}_x(\text{PPh}_3)_2]$  ( $x = 0, 1$ ) was identified by NMR spectroscopic methods. While in acetonitrile solution spectra are dominated by the resonances of the *cis* derivatives, those of pure *cis*- $[\text{Pt}(\text{SeCF}_3)_2 - (\text{PPh}_3)_2]$  indicate *cis-trans*-isomerisation in  $\text{CH}_2\text{Cl}_2$  solution. In contrast, exchange reactions of *cis*- $[\text{PtCl}_2(\text{PPh}_3)_2]$  and  $[\text{NMe}_4]\text{TeCF}_3$  only gave evidence for *cis* isomers. Molecular structures of *cis*- and *trans*- $[\text{Pt}(\text{SeCF}_3)_2(\text{PPh}_3)_2]$  and *cis*- $[\text{Pt}(\text{TeCF}_3)_2(\text{PPh}_3)_2]$  are discussed in comparison with related compounds.

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**Keywords:** Trifluoromethylselenato; Trifluoromethyltellurato; Platinum; Crystal structure

## 1. Introduction

The chemistry of group 10 metal chalcogenates proves to be a field of considerable interest [1]. Applications as single-source precursors for low-temperature syntheses of metal chalcogenides make this class of compounds attractive for further investigations. The area is dominated by compounds containing the M-SR unit [2], while there has not been put much light on the heavier chalcogenates. The ease in obtaining trifluoromethylchalcogenates of sulphur [3], selenium [4], and tellurium [5], together with the poor solubility of tetramethylammonium halides in common organic solvents, encouraged us to study halide exchange reactions of these tetramethylammonium derivatives [3–5] and group 10 and 11 halides [6–8].

Most palladium and platinum chalcogenato compounds were prepared via oxidative addition of diorganodichalcogen derivatives to tetrakis(triorganophosphine)metal(0)

complexes. Experimental [9–13] and theoretical [9,14] approaches have been carried out to provide a deeper insight into the mechanism of *cis/trans* isomerization. The primary formed products were identified as *cis*- $[\text{M}(\text{ER})_2(\text{PR}'_3)_2]$  ( $\text{M} = \text{Pd}, \text{Pt}$ ;  $\text{E} = \text{S}, \text{Se}, \text{Te}$ ;  $\text{R}, \text{R}' =$  organic groups) which may dimerize by loss of one  $\text{PR}'_3$  ligand to  $[\text{M}(\text{ER})_2(\text{PR}'_3)]_2$ . Finally,  $\text{PR}'_3$  adds again to the dimer and causes the formation of the *trans* isomer, *trans*- $[\text{M}(\text{ER})_2(\text{PR}'_3)_2]$ .

While  $\text{SCF}_3$ -compounds of Pt(II) are well documented and characterized especially by NMR spectroscopic means [8,15–17] and crystallographic data [8], those containing the heavier chalcogens are unknown so far. In analogy to reactions of *cis*- $[\text{PtCl}_2(\text{PPh}_3)_2]$  and  $[\text{NMe}_4]\text{SCF}_3$  [8], we report in this paper our results with the heavier chalcogen derivatives.

## 2. Results and discussion

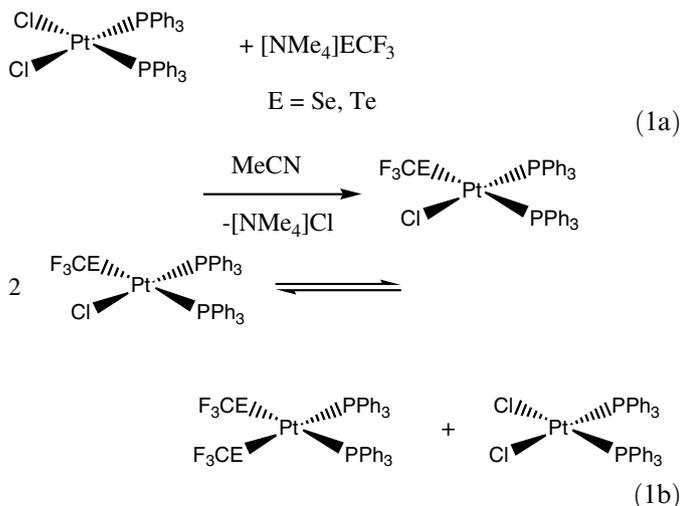
### 2.1. Exchange reactions between *cis*- $[\text{PtCl}_2(\text{PPh}_3)_2]$ and $[\text{NMe}_4]\text{ECF}_3$ ( $\text{E} = \text{Se}, \text{Te}$ )

Reactions of *cis*- $[\text{PtCl}_2(\text{PPh}_3)_2]$  and  $[\text{NMe}_4]\text{ECF}_3$  ( $\text{E} = \text{Se}, \text{Te}$ ) in stoichiometric ratios of 1:1 proceed more or less

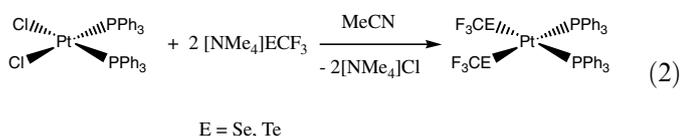
\* Corresponding authors. Tel.: +49 221 4703276; fax: +49 221 4703276/4705196.

E-mail addresses: tyrra@uni-koeln.de (W. Tyrra), d.naumann@uni-koeln.de (D. Naumann).

indiscriminately to give product mixtures of *cis*-[Pt(ECF<sub>3</sub>)Cl(PPh<sub>3</sub>)<sub>2</sub>] (Eq. (1a)), equilibrating with *cis*-[Pt(ECF<sub>3</sub>)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] and the starting material (Eq. (1b)).



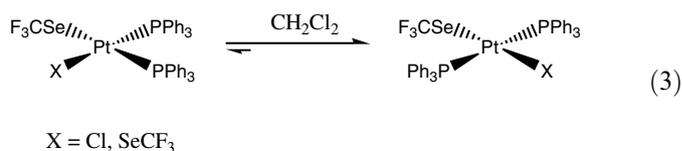
Selective reactions occur with stoichiometric ratios of *cis*-[PtCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] and [NMe<sub>4</sub>]ECF<sub>3</sub> (E = Se, Te) of 1:2. In both cases in MeCN solution, the *cis* complexes, *cis*-[Pt(ECF<sub>3</sub>)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>], are selectively formed (Eq. (2)).



Both compounds were isolated as yellow or orange crystals and their composition was elucidated by NMR spectroscopic means (Table 1) as well as XRD measurements (Table 2, Figs. 1 and 5). Elemental analyses support the compositions.

While *cis*-[Pt(TeCF<sub>3</sub>)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] does not undergo *cis*–*trans* isomerization in CH<sub>2</sub>Cl<sub>2</sub> or MeCN solutions, the sele-

nium derivatives, *cis*-[Pt(SeCF<sub>3</sub>)Cl(PPh<sub>3</sub>)<sub>2</sub>] and *cis*-[Pt(SeCF<sub>3</sub>)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>], equilibrate with the corresponding *trans* isomers (Eq. (3)). After a total reaction time of 60 h, the equilibrium is shifted completely to the right (Eq. (3)). <sup>19</sup>F and <sup>31</sup>P NMR spectra recorded after 24 and 48 h only showed the resonances of the monomeric *cis* and *trans* isomers. No spectroscopic evidence was found for a dimeric compound such as [Pt(SeCF<sub>3</sub>)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] respective for free PPh<sub>3</sub>. Possibly, the life-time of such dimers which were even isolated in other cases, e.g., [Pt(Se(2-C<sub>4</sub>H<sub>9</sub>S))<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] [11]) is too short to be detected on the NMR time-scale. Unlike in CH<sub>2</sub>Cl<sub>2</sub>, isomerization appears to be very slow in MeCN.



Re-dissolving of the crystalline material obtained after isomerization in CH<sub>2</sub>Cl<sub>2</sub> showed that the *trans* isomer does not undergo any exchange processes in MeCN. Results of the crystal structure analysis for *trans*-[Pt(SeCF<sub>3</sub>)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] are given later.

A complete set of the NMR data for all derivatives synthesized or detected is provided in Table 1 indicating good agreement with data reported for the sulphur derivatives [8,15–17] and related PtSeR, e.g., [9,10,18–20] and PtTeR compounds e.g. [19–21] as well as, with respect to the ECF<sub>3</sub> group, group 11 metallates [6,7]. In solution the existence of only one *cis*- and one *trans*-isomer is anticipated, while in the solid state [Pt(ER)<sub>2</sub>(PR'<sub>3</sub>)<sub>2</sub>] complexes could give rise to four possible isomers, *cis/anti*, *cis/syn*, *trans/anti* and *trans/syn* [9] (Scheme 1).

Table 1  
Compilation of NMR chemical shifts and couplings of PtECF<sub>3</sub> compounds (E = Se, Te; 21 °C, CD<sub>2</sub>Cl<sub>2</sub>)<sup>a</sup>

	<i>cis</i> -Pt(SeCF <sub>3</sub> )Cl(PPh <sub>3</sub> ) <sub>2</sub>	<i>trans</i> -Pt(SeCF <sub>3</sub> )Cl(PPh <sub>3</sub> ) <sub>2</sub>	<i>cis</i> -Pt(SeCF <sub>3</sub> ) <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub>	<i>trans</i> -Pt(SeCF <sub>3</sub> ) <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub>	<i>cis</i> -Pt(TeCF <sub>3</sub> )Cl(PPh <sub>3</sub> ) <sub>2</sub>	<i>cis</i> -Pt(TeCF <sub>3</sub> ) <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub>
δ ( <sup>19</sup> F)	−21.6	−23.8	−21.7	−22.9	−18.2	−19.6
<sup>3</sup> J <sub>Pt,F</sub> (Hz)	45	88	57	64	28	42
δ ( <sup>31</sup> P) <sup>b</sup>	17.8/14.6	21.7	14.1	17.2	18.5/12.5	11.1
<sup>1</sup> J <sub>Pt,P</sub> (Hz) <sup>b</sup>	2998/3703	2644	3143	2660	2790/3710	3095
<sup>4</sup> J <sub>P,F</sub> (Hz) <sup>b</sup>	10.7/0.9	1.4	Not resolved	Not resolved	9.0/1.2	≈3.9
<sup>2</sup> J <sub>P,P</sub> (Hz)	15				15	
<sup>2</sup> J <sub>Se(Te),P</sub> (Hz) <sup>b</sup>	n.o./≈70		n.o./≈140		n.o./≈120	≈90/≈110
δ ( <sup>195</sup> Pt)	−4550	−4626	−4788	−4344	−4602 <sup>d</sup>	−5122 <sup>d</sup>
δ ( <sup>77</sup> Se)	393	239	267	237		
δ ( <sup>125</sup> Te)					692 <sup>d</sup>	457 <sup>d</sup>
<sup>2</sup> J <sub>Se(Te),F</sub> (Hz)	≈30	30	33	33	99	134
					103 <sup>d</sup>	150 <sup>d</sup>
<sup>1</sup> J <sub>Pt,Se(Te)</sub> (Hz)	≈160	≈150	≈18	≈13	Broad	≈490

<sup>a</sup> <sup>13</sup>C NMR signals of ECF<sub>3</sub> groups were detected in all cases as quartets at 125 ± 2 ppm (<sup>1</sup>J<sub>F,C</sub> ≈ 330 Hz) for SeCF<sub>3</sub> groups and 93 ± 2 ppm (<sup>1</sup>J<sub>F,C</sub> ≈ 360 Hz) for TeCF<sub>3</sub> groups.

<sup>b</sup> First value: PPh<sub>3</sub> standing *trans* to ECF<sub>3</sub>; second value: PPh<sub>3</sub> standing *cis* to ECF<sub>3</sub>.

<sup>c</sup> n.o., not observed.

<sup>d</sup> Solvent, DMF-*d*<sub>7</sub>.

Table 2

Crystal data and structure refinement parameters for *cis*-Pt(SeCF<sub>3</sub>)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (**1**), *cis*-Pt(TeCF<sub>3</sub>)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (**2**) and *trans*-Pt(SeCF<sub>3</sub>)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> · 2CH<sub>2</sub>Cl<sub>2</sub> (**3**)

	1	2	3
Empirical formula	C <sub>38</sub> H <sub>30</sub> F <sub>6</sub> P <sub>2</sub> Se <sub>2</sub> Pt	C <sub>38</sub> H <sub>30</sub> F <sub>6</sub> P <sub>2</sub> Te <sub>2</sub> Pt	C <sub>40</sub> H <sub>34</sub> F <sub>6</sub> P <sub>2</sub> Cl <sub>4</sub> Se <sub>2</sub> Pt
Formula mass (g mol <sup>-1</sup> )	1015.57	1112.85	1185.42
Data collection			
Diffractometer		STOE image plate diffraction system II	
Radiation		Mo K $\alpha$ (graphite monochromator, $\lambda = 0.71073$ Å)	
Temperature (K)	150(2)	150(2)	150(2)
Index range	-12 $\leq h \leq$ 12 -25 $\leq k \leq$ 24 -13 $\leq l \leq$ 13	-26 $\leq h \leq$ 24 -15 $\leq k \leq$ 15 -19 $\leq l \leq$ 19	-13 $\leq h \leq$ 13 -15 $\leq k \leq$ 13 -15 $\leq l \leq$ 15
Rotation angle	0° $\leq \omega \leq$ 180°; $\varphi = 0^\circ$ 0° $\leq \omega \leq$ 68°; $\varphi = 90^\circ$	0° $\leq \omega \leq$ 180°; $\varphi = 0^\circ$ 0° $\leq \omega \leq$ 88°; $\varphi = 90^\circ$	0° $\leq \omega \leq$ 180°; $\varphi = 0^\circ$ 0° $\leq \omega \leq$ 180°; $\varphi = 90^\circ$
Increment	$\Delta\omega = 2^\circ$	$\Delta\omega = 1^\circ$	$\Delta\omega = 2^\circ$
No. of images	124	268	180
Exposure time (min)	7	3	3
Detector distance (mm)	120	100	120
2 $\theta$ Range	1.9–54.8	1.9–54.8	2.3–59.5
Total data collected	19 790	21 779	20 123
Unique data	7906	4153	5700
Observed data	6721	3776	5263
R <sub>merg</sub>	0.0654	0.0352	0.0340
Absorption correction		Numerical, after crystal shape optimization [42,44]	
Transmission	0.2751/0.4810	0.3049/0.5154	0.3039/0.5707
Crystallographic data			
Crystal size (mm <sup>3</sup> )	0.2 · 0.05 · 0.05	0.2 · 0.1 · 0.1	0.2 · 0.1 · 0.1
Colour, habit	Yellow, column	Yellow, prism	Yellow, prism
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	<i>P</i> 2 <sub>1</sub> (no. 4)	<i>C</i> 2/ <i>c</i> (no. 15)	<i>P</i> $\bar{1}$ (no. 2)
<i>a</i> (Å)	9.619(1)	20.395(1)	9.546(1)
<i>b</i> (Å)	20.036(2)	12.347(1)	11.012(1)
<i>c</i> (Å)	10.194(1)	15.514(1)	11.258(1)
$\alpha$ (°)			70.34(1)
$\beta$ (°)	111.04(1)	103.79(1)	68.04(1)
$\gamma$ (°)			89.51(1)
Volume (Å <sup>3</sup> )	1833.7(4)	3794.1(4)	1024.3(2)
<i>Z</i>	2	4	1
<i>D</i> <sub>calc</sub> (g cm <sup>-3</sup> )	1.839	1.948	1.922
$\mu$ (Mo K $\alpha$ , mm <sup>-1</sup> )	5.956	5.346	5.598
<i>F</i> (000)	976	2096	572
Structure analysis and refinement			
Structure determination		SIR-92 [46] and SHELXL-97 [47]	
No. of variables	444	224	253
<i>R</i> indexes [ <i>I</i> > 2 $\sigma$ ]	<i>R</i> <sub>1</sub> = 0.0367	<i>R</i> <sub>1</sub> = 0.0223	<i>R</i> <sub>1</sub> = 0.0238
<i>R</i> indexes (all data)	<i>wR</i> <sub>2</sub> = 0.0800 <i>R</i> <sub>1</sub> = 0.0482 <i>wR</i> <sub>2</sub> = 0.0858	<i>wR</i> <sub>2</sub> = 0.0553 <i>R</i> <sub>1</sub> = 0.0247 <i>wR</i> <sub>2</sub> = 0.0561	<i>wR</i> <sub>2</sub> = 0.0528 <i>R</i> <sub>1</sub> = 0.0272 <i>wR</i> <sub>2</sub> = 0.0548
Flack <i>x</i>	-0.025(8)	–	–
<i>S</i> (all data)	0.967	1.012	1.072
Hole/peak [e Å <sup>-3</sup> ]	-1.648/1.199	-1.123/0.948	-1.371/1.245
CCDC-number [48]	286231	275938	286232

$R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ ,  $wR_2 = [\sum w(|F_o|^2 - |F_c|^2)^2 / \sum w(|F_o|^2)^2]^{1/2}$ ,  $S_2 = [\sum w(|F_o|^2 - |F_c|^2)^2 / (n - p)]^{1/2}$ , with  $w = 1/[\sigma^2(F_o)^2 + (0.0475 \cdot P)^2]$  for (**1**),  $w = 1/[\sigma^2(F_o)^2 + (0.0389 \cdot P)^2]$  for (**2**) and  $w = 1/[\sigma^2(F_o)^2 + (0.0253 \cdot P)^2 + 1.310 \cdot P]$  for (**3**), where  $P = (F_o^2 + 2F_c^2)/3$ ,  $F_c^* = kF_c[1 + 0.001 \cdot |F_c|^2 \lambda^3 / \sin(2\theta)]^{-1/4}$ .

## 2.2. Molecular structures of *cis*-[Pt(SeCF<sub>3</sub>)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] (**1**), *trans*-[Pt(SeCF<sub>3</sub>)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] (**3**) and *cis*-[Pt(TeCF<sub>3</sub>)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] (**2**)

Although the number of compounds with the structural motif PtSeR (R = organic ligand) is increasing, e.g. [9,10,18,20,22–26], the molecular structures of the first alkylselenatoplatinum derivatives *cis*-[Pt(SeCF<sub>3</sub>)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>]

(**1**), *trans*-[Pt(SeCF<sub>3</sub>)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] (**3**) are best compared with the structures of *cis*-[Pt(SePh)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] [10,25] and *trans*-[Pt(SePh)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] [25,26].

Both derivatives (Table 2, Fig. 1–4) **1** (*P*2<sub>1</sub> (no. 4)) and **3** (*P* $\bar{1}$  (no. 2)) crystallise in *anti*-conformation with respect to the CF<sub>3</sub> groups [9]. Pt–Se distances are slightly longer for the *cis*-derivative, **1**, than for the *trans*-isomer, **3**. Together with Pt–P distances, these values best match data reported

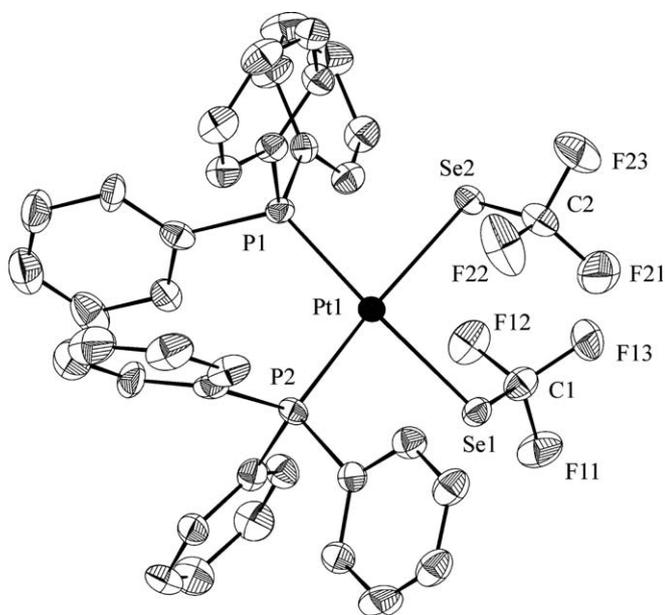
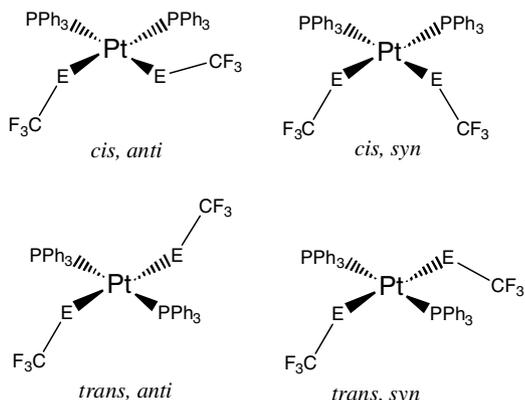


Fig. 1. The molecular structure of *cis*-Pt(SeCF<sub>3</sub>)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (**1**) (50% probability ellipsoids; H-atoms have been omitted). Interatomic distances in Å and angles in degrees (with estimated standard deviations in parantheses): Pt1–Se1 2.488(1), Pt1–Se2 2.484(1), Pt1–P1 2.283(2), Pt1–P2 2.280(2), Se1–C1 1.943(8), Se2–C2 1.942(10), C1–F 1.340(10)–1.365(10), C2–F 1.337(10)–1.345(11); and Se1–Pt1–Se2 91.98(3), P1–Pt1–P2 100.71(7), Se1–Pt1–P1 168.53(5), Se2–Pt1–P2 167.78(5), Se1–Pt1–P2 85.31(6), Se2–Pt1–P1 84.10(5).



Scheme 1. Possible isomers of [Pt(ECF<sub>3</sub>)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] (E = Se, Te) in the solid state.

for SePh derivatives. Thus, none of the molecular structures of **1** and **3** gives evidence for deviations being subscribed to different electronic characteristics of the trifluoromethyl group in comparison with aromatic substituents. A systematic approach as outlined in [9] can neither be supported nor attenuated. All data fall into the range of values obtained for related compounds, e.g. [9,10,18,20,22–26] within limits of accuracy.

While there are numerous platinum compounds with the structural element PtSeR (R = organic substituent) and phosphine ligands (see above) known, the number of tellurato-platinum compounds is limited [20,27–30]. In this series, *cis*-[Pt(TeCF<sub>3</sub>)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] represents the first example of its kind.

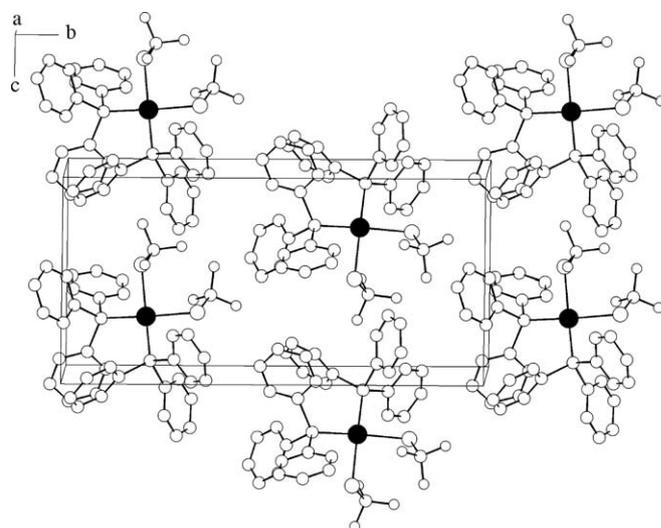


Fig. 2. Perspective view of the unit cell in the crystal structure of *cis*-Pt(SeCF<sub>3</sub>)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (**1**).

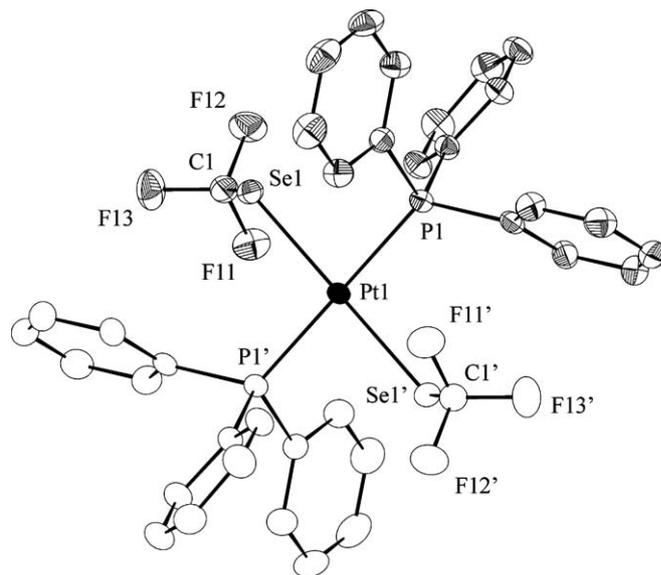


Fig. 3. The molecular structure of *trans*-Pt(SeCF<sub>3</sub>)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> · 2CH<sub>2</sub>Cl<sub>2</sub> (**3**) (50% probability ellipsoids; symmetry-related atoms are drawn as empty ellipsoids; solvent molecules and H-atoms have been omitted). Interatomic distances in Å and angles in degrees (with estimated standard deviations in parantheses): Pt1–Se1 2.461(1) 2×, Pt1–P1 2.325(1) 2×, Se1–C1 1.949(3), C1–F11 1.347(3), C1–F12 1.351(3), C1–F13 1.341(3); and Se1–Pt1–Se1' 180, P1–Pt1–P1' 180, Se1–Pt1–P1 84.39(2) 2×, Se1–Pt1–P1' 95.61(2) 2×.

*cis*-[Pt(TeCF<sub>3</sub>)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] (**2**) crystallizes in the monoclinic space group *C2/c* (no. 15) with four molecules per unit cell (Table 2; Fig. 5 and 6) as the *cis, anti* isomer. The nearly square-planar arrangement of ligands around the platinum centre is in absolute agreement with expectations for d<sup>8</sup> complexes. Bond lengths of 2.649(1) Å (2×) (Pt–Te) and 2.294(1) Å (2×) (Pt–P) differ from those values determined for 1,2-benzeneditellurato-bis(triphenylphosphine)-platinum(II) [29], to our knowledge the only example of a Pt–Te complex with the tellurium atoms in *cis* arrangement.

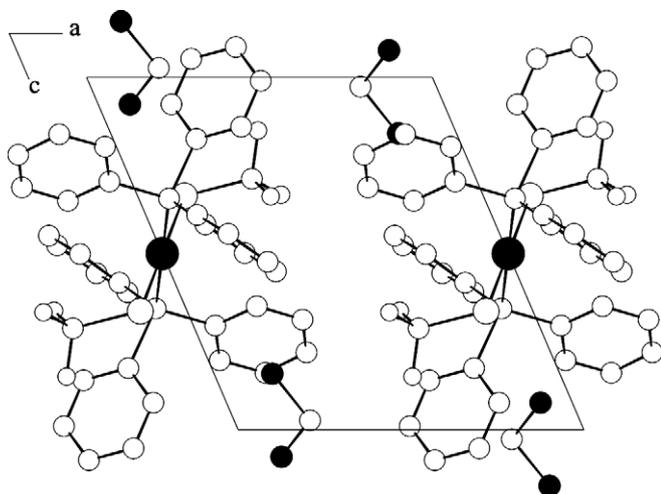


Fig. 4. The packing diagram for *trans*-Pt(SeCF<sub>3</sub>)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> · 2CH<sub>2</sub>Cl<sub>2</sub> (**3**) viewed along the crystallographic *b*-axis.

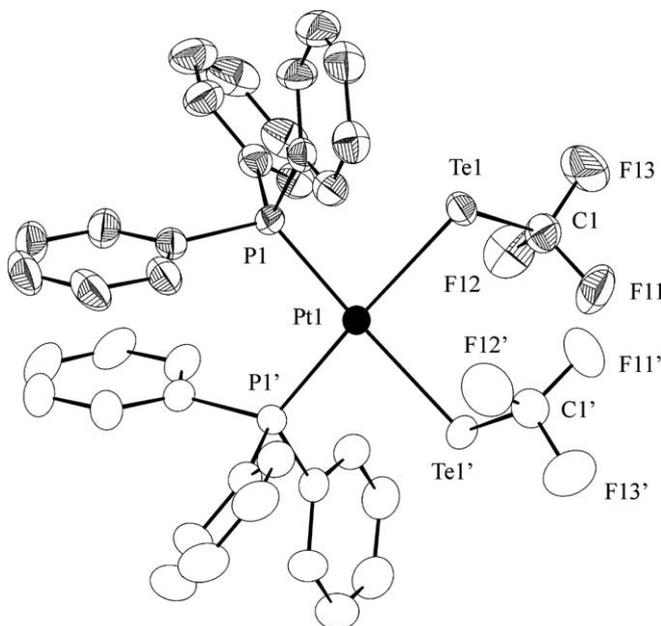


Fig. 5. The molecular structure of *cis*-Pt(TeCF<sub>3</sub>)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (**2**) (50% probability ellipsoids; symmetry-related atoms are drawn as empty ellipsoids; H-atoms have been omitted). Interatomic distances in Å and angles in degrees (with estimated standard deviations in parentheses): Pt–Te1 2.649(1) 2×, Pt–P1 2.294(1) 2×, Te1–C1 2.157(3), C1–F11 1.336(4), C1–F12 1.347(4), C1–F13 1.349(4); Te1–Pt1–P1 83.60(1), Te1–Pt1–P1' 174.13(2), Te1–Pt1–Te1' 93.57(1), P1–Pt1–P1' 99.68(3).

In this case, Pt–Te bonds are shorter (0.05–0.06 Å), while Pt–P bond lengths are slightly elongated (0.01–0.03 Å). The Pt–Te bond lengths in *cis*-[Pt(TeCF<sub>3</sub>)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] (**2**) are absolutely within the range of reported values [20,27–30]. The value of 2.649(1) Å matches that of 2.623(1) Å reported for the terminal TePh group in [Pt<sub>2</sub>(TePh)(μ-TePh)<sub>2</sub>(PEt<sub>3</sub>)<sub>2</sub>(η<sup>5</sup>-2-CB<sub>10</sub>H<sub>11</sub>)] [20]. Deviations of Pt–P bond lengths and angles measured and documented in the literature may be attributed to packing effects.

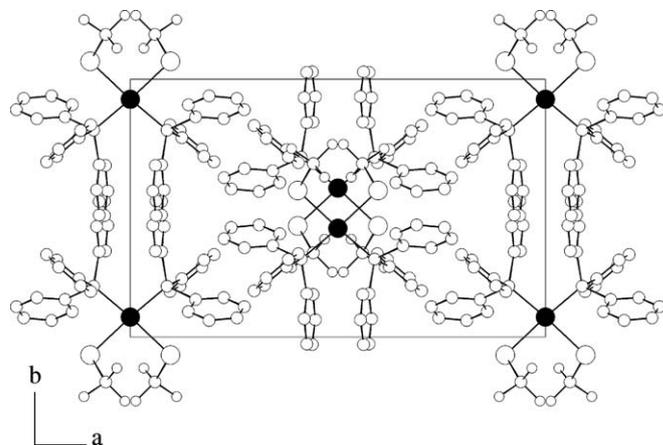


Fig. 6. The packing diagram for *cis*-Pt(TeCF<sub>3</sub>)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (**2**) viewed along the crystallographic *c*-axis.

### 2.3. A short comparison of the molecular structures of *cis*-[Pt(ECF<sub>3</sub>)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] (E = S [8], Se, Te)

All three compounds crystallize in monoclinic space groups acentric *P*2<sub>1</sub> (S, Se) or centric *C*2/*c* (Te). The inner co-ordination spheres are not influenced by this difference: Pt–P distances are of comparable lengths, Pt–E bond lengths deviate from each other in the expected manner and the angles around the platinum centre are not significantly influenced. The effect of lone electron pairs on the Pt–E–C angle as found for chalcogenato (carboxylato) compounds [31,32], is here negligibly small; all three compounds show comparable data (101.1–102.9°) for the Pt–E–C angles with the Pt–Se–C angle being most acute.

On the other hand, ECF<sub>3</sub> groups resemble the character of halides [33–35]. Consequently, a short comparison of structural data is given, i.e., in detail *cis*-[Pt(SCF<sub>3</sub>)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] resembles *cis*-[PtCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] [36], *cis*-[Pt(SeCF<sub>3</sub>)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] (**1**), resembles *cis*-[PtBr<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] and, finally, *cis*-[Pt(TeCF<sub>3</sub>)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] (**2**), looks like the iodo derivative, *cis*-[PtI<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>]. Unfortunately, no crystallographic data for the latter halo complexes are available, but a comparison with related complexes displays absolutely comparable Pt–X and Pt–ECF<sub>3</sub> interatomic distances (X = Br, E = Se [37]; X = I, E = Te) [38,39]. Especially *trans*-[Pt(SeCF<sub>3</sub>)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] · 2 CH<sub>2</sub>Cl<sub>2</sub>, **3**, is very similar to *trans*-[PtBr<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] · 2CH<sub>2</sub>Cl<sub>2</sub> [40].

## 3. Experimental

### 3.1. General

Schlenk techniques were used throughout all manipulations. *cis*-[PtCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] (ABCR) was used as received. [NMe<sub>4</sub>]SeCF<sub>3</sub> and [NMe<sub>4</sub>]TeCF<sub>3</sub> were prepared according to the literature procedures [4,5]. All solvents were dried by routine methods prior to use. NMR spectra were recorded on Bruker spectrometers AC200 and AVANCE 400 (<sup>1</sup>H, <sup>19</sup>F, <sup>13</sup>C, <sup>31</sup>P, <sup>77</sup>Se, <sup>125</sup>Te, and <sup>195</sup>Pt). External standards were used in all cases (<sup>1</sup>H, <sup>13</sup>C: Me<sub>4</sub>Si; <sup>19</sup>F: CCl<sub>3</sub>F; <sup>31</sup>P:

H<sub>3</sub>PO<sub>4</sub> (85%); <sup>77</sup>Se: Me<sub>2</sub>Se; <sup>125</sup>Te: Me<sub>2</sub>Te; <sup>195</sup>Pt: Na<sub>2</sub>PtCl<sub>6</sub>. Acetone-*d*<sub>6</sub> was used as an external lock (5 mm tube) in reaction control measurements while an original sample of the reaction mixture was measured in a 4 mm insert. HMBC technique was employed to determine the <sup>195</sup>Pt chemical shifts and to locate the ECF<sub>3</sub> (E = Se, Te) groups in the <sup>77</sup>Se and <sup>125</sup>Te NMR spectra. Coupling patterns were calculated using the program gNMR [41].

### 3.2. X-ray crystal structure determinations

Single crystals were grown from saturated acetonitrile (**1**, **2**) or dichloromethane (**3**) solutions of the crude materials at –21 °C. All compounds *cis*-Pt(SeCF<sub>3</sub>)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (**1**), *cis*-Pt(TeCF<sub>3</sub>)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (**2**), and *trans*-Pt(SeCF<sub>3</sub>)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (**3**) form yellow single crystals which were sealed in glass capillaries and the suitability was checked with the help of an IP-diffractometer (STOE IPDS II). The same device was used to collect the reflection data of the respective best specimen using graphite-monochromated Mo K $\alpha$  radiation (0.71073 Å). The data were corrected for Lorentz and polarization effects. A numerical absorption correction based on crystal-shape optimization was applied for all data [42]. The programs used are Stoe's X-Area [43], including X-RED and X-SHAPE for data reduction and absorption correction [44], and the WINGX suite of programs [45], including SIR-92 [46] and SHELXL-97 [47] for structure solution and refinement. All hydrogen atoms were placed in idealized positions and constrained to ride on their parent atom. The last cycles of refinement included atomic positions for all the atoms, anisotropic thermal parameters for all the non-hydrogen atoms and isotropic thermal parameters for all of the hydrogen atoms.

### 3.3. Synthesis of *cis*-Pt(SeCF<sub>3</sub>)Cl(PPh<sub>3</sub>)<sub>2</sub> (E = Se, Te)

To a solution of 0.79 g (1.0 mmol) *cis*-PtCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> in 10 mL CH<sub>2</sub>Cl<sub>2</sub> 0.24 g (1.1 mmol) [NMe<sub>4</sub>]SeCF<sub>3</sub> were added at room temperature. The mixture was stirred for 3 h wherein the colour changed from nearly colourless into bright yellow. [NMe<sub>4</sub>]Cl which has precipitated was filtered off and the crude material dried. Analysis by <sup>19</sup>F and <sup>31</sup>P NMR spectroscopic methods revealed a composition of 85% *cis*-Pt(SeCF<sub>3</sub>)Cl(PPh<sub>3</sub>)<sub>2</sub> and 15% *cis*-Pt(SeCF<sub>3</sub>)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>. The analogous reaction with [NMe<sub>4</sub>]TeCF<sub>3</sub> (0.30 g; 1.1 mmol) carried out in MeCN gave a product mixture of 80% *cis*-Pt(TeCF<sub>3</sub>)Cl(PPh<sub>3</sub>)<sub>2</sub>, 6% *cis*-Pt(TeCF<sub>3</sub>)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> and 14% *cis*-PtCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>.

### 3.4. Synthesis of *cis*-Pt(SeCF<sub>3</sub>)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (E = Se, Te)

In a similar manner as described above, 0.48 g (2.2 mmol) [NMe<sub>4</sub>]ECF<sub>3</sub> (E = Se, Te (0.60 g; 2.2 mmol)) were added to a suspension of 0.79 g (1.0 mmol) *cis*-PtCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> in 10 mL MeCN at room temperature. The mixtures were stirred for 60 min and became orange. [NMe<sub>4</sub>]Cl was filtered off and the crude material was dried. The com-

position of the crude material was determined (<sup>19</sup>F and <sup>31</sup>P NMR) to consist of  $\approx$ 95% *cis*-Pt(SeCF<sub>3</sub>)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> and  $\approx$ 5% *trans*-Pt(SeCF<sub>3</sub>)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> in the case of the selenium derivative and exclusively of *cis*-Pt(TeCF<sub>3</sub>)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> for the tellurium compound. In both cases, re-crystallisation from MeCN (–21 °C) gave yellow or orange crystals of the *cis* derivatives in approximately 90% yields.

*cis*-Pt(SeCF<sub>3</sub>)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>. M.p. 196–197 °C (dec.). Anal. Calc. for C<sub>38</sub>H<sub>30</sub>P<sub>2</sub>F<sub>6</sub>Se<sub>2</sub>Pt: C, 44.94; H, 2.98. Found: C, 45.38; H, 3.00%.

*cis*-Pt(TeCF<sub>3</sub>)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>. M.p. 158–159 °C (dec.). Anal. Calc. for C<sub>38</sub>H<sub>30</sub>P<sub>2</sub>F<sub>6</sub>Te<sub>2</sub>Pt: C, 41.01; H, 2.72. Found: C, 40.72; H, 2.73%.

### 3.5. Synthesis of *trans*-Pt(SeCF<sub>3</sub>)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>

Dissolution of 0.50 g (0.5 mmol) *cis*-Pt(SeCF<sub>3</sub>)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> in 10 mL CH<sub>2</sub>Cl<sub>2</sub> in an open beaker at ambient temperature afforded quantitatively yellow crystals of *trans*-Pt(SeCF<sub>3</sub>)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> · 2CH<sub>2</sub>Cl<sub>2</sub> (0.59 g; 0.5 mmol) upon crystallization at room temperature over a period of 60 h. The crystals loose CH<sub>2</sub>Cl<sub>2</sub> upon storing in ambient atmosphere for several weeks.

*trans*-Pt(SeCF<sub>3</sub>)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>. M.p. 216–218 °C (dec.). Anal. Calc. for C<sub>38</sub>H<sub>30</sub>P<sub>2</sub>F<sub>6</sub>Se<sub>2</sub>Pt: C, 44.94; H, 2.98. Found: C, 45.15; H, 3.22%.

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