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Synthesis and characterization of platinum – selenium derivatives: X-ray structure of *trans*-Pt(PEt₃)₂(SePh)₂

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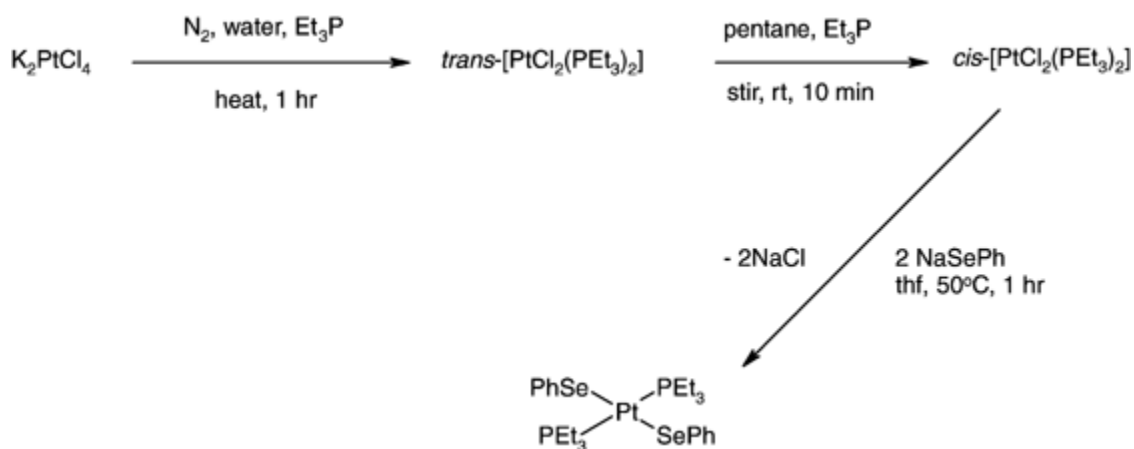
The crystal structure of *trans*-[((bis)triethylphosphine)(bis(phenylselenato))platinum (II)] has been determined by single crystal X-ray diffraction. Crystallization occurs in the triclinic space group *P*-1 (No. 2) with $a = 8.9964(2)$ Å, $b = 11.5103(2)$ Å, $c = 14.9335(3)$ Å; $\alpha = 85.8750(10)^\circ$, $\beta = 72.5350(10)^\circ$, $\gamma = 68.4450(10)^\circ$. Details of the structure and spectroscopic results are presented and discussed and comparisons are made with related square planar platinum (II) structures.

KEY WORDS:

Platinum, selenium, phosphine, square planar.

Introduction

The coordination chemistry of platinum (II) is well developed and is characterized by many interesting square planar complexes exhibiting both *cis* and *trans* geometries. In addition, there has been considerable recent interest in the chemistry of organoselenides and selenium containing ligands because of the catalytic,¹ conducting² and biomedical³ properties of their compounds. Selenides also exhibit a range of common coordination modes to transition metals such as η^1 (this work) and μ_2 (e.g. $[\text{Pt}_2(\mu\text{-Se})_2(\text{PPh}_3)_4]$).⁴ There are two straightforward synthetic preparations for mononuclear platinum complexes containing selenolato ligands: firstly, the addition of diaryl diselenides (R_2Se_2) to Pt(0) complexes results in an oxidative addition reaction, and secondly a metathesis reaction of Pt(II) halides with NaSeR. An increasingly large amount of work is being focused on the behavior of coordinated selenide with regards to its functionalization and transformation. Relatively few square planar Pt(II) complexes containing a “PtP₂Se₂” core have been synthesized and structurally characterized. Of the compounds that have been structurally characterized, only Pt(PPh₃)(SePh)₂ has been reported as a pair of geometrical isomers (*cis* and *trans*).⁵⁻⁷ In the oxidative addition process of adding Ph₂Se₂ to Pt(PPh₃)₄, the two isomers were reported to be formed at different temperatures: 80°C for the *trans* isomer and room temperature for the *cis* isomer with low temperature isolation (-5°C) needed to obtain crystals of the *cis* product. Interestingly, the usual way for observing both isomers is through the oxidative addition pathway to a Pt(0) center: a slow isomerization is seen at room temperature with a decrease in the monitored ³¹P resonances for the *cis* isomer and a corresponding increase in signal height for the *trans* isomer.⁷ It has been found, until recently, that the metathesis reaction of NaSePh with *cis*-[PtCl₂(L)₂] (L = monodentate ligand) produced only the *trans* isomer.^{5, 8} However, in a few cases Jain *et al.*⁹ reported that multinuclear NMR spectra indicated a slow *cis* to *trans* isomerization even when NaER (E = Se, Te, R = Ph, substituted Ph) reacted with mononuclear Pt complexes. In our manuscript, we report the synthesis and crystal structure of *trans*-Pt(PEt₃)₂(SePh)₂ along with some multi-nuclear NMR data and an attempted isolation of the *cis* isomer. The synthetic scheme is shown below in Eq. 1.



Equation 1. Synthesis of *trans*-Pt(PEt₃)₂(SePh)₂.

Experimental

All manipulations were carried out using conventional vacuum/Schlenk techniques under an atmosphere of argon. *Cis*-dichlorobis (triethylphosphine)platinum (II) was prepared according to a literature method.¹⁰ NMR spectra were recorded on a Bruker AMX-360 spectrometer operating at 360 MHz (¹H), 90.5 MHz (¹³C) and 145 MHz (³¹P). Elemental analysis was performed at Atlantic Microlab (Norcross, GA).

A sample of *cis*-dichlorobis (triethylphosphine)platinum (II) (0.50 g, 1.0 mmol) was dissolved in dry tetrahydrofuran (15 mL). To this solution was added a tetrahydrofuran solution of NaSePh¹¹ (0.37 g, 2.1 mmol) and the mixture was warmed to 50°C for 1 h. The solvent was removed *in vacuo* and the residue was re-dissolved in methylene chloride. It was filtered to remove insoluble NaCl and reduced to ca. 5 mL. Upon layering with n-hexane and cooling to -10°C, small yellow crystals of the title compound were obtained. Yield 0.77 g (65%).

In addition, we attempted to synthesize the *cis* isomer of Pt(PEt₃)₂(SePh)₂ in an NMR tube at low temperature and record its NMR spectrum. In a dry NMR tube containing 1 mL d₈-thf at -20°C, was added *cis*-PtCl₂(PEt₃)₂ (10 mg) followed by NaSePh (7 mg). The mixture was shaken and allowed to stand at this temperature for 1 hour. The NMR spectrum was also recorded at -20°C.

Characterization

Trans-Pt(PEt₃)₂(SePh)₂: ¹H NMR (d₈-thf): 1.00 (d of t, 18H, P-CH₂CH₃), 2.00 (d of d, P-CH₂-CH₃), 7.02 – 7.65 (10H, arom); ¹³C NMR: 8.36 (P-CH₂CH₃), 14.57 (P-CH₂CH₃), 123.46 – 139.11 (arom); ³¹P NMR: 6.4 ppm (J (PtP) = 2474 Hz). Elemental Analysis: Found C: 38.94 (Requires 38.77%); Found H: 5.39 (Requires 5.42%) *Cis*-Pt(PEt₃)₂(SePh)₂: ³¹P NMR (d₈-thf): 7.7 ppm (J(PtP) = 2740 Hz).

X-Ray

Crystal and data collection parameters for Pt(PEt₃)₂(SePh)₂ are given in Table 1. Diffracted intensities were collected on a Bruker APEX2 CCD detector using graphite monochromated Mo K α X-radiation at -150°C. Final unit cell dimensions were determined from the 6837 reflections for **1**. The data were corrected for absorption effects using a semi-empirical multi-scan method.¹²

Table 1. Crystal Data and Structure Refinement

CCDC deposit no.	602972
Color/shape	Yellow/prism
Crystal size (mm)	0.22 × 0.17 × 0.12
Empirical formula	C ₂₄ H ₄₀ P ₂ PtSe ₂
Formula weight	743.51
Temperature (K)	123(2)
Crystal system	Triclinic
Space group	<i>P</i> -1

a (Å)	8.9964(2)
b (Å)	11.5103(2)
c (Å)	14.9335(3)
α (°)	85.8750(10)
β (°)	72.5350(10)
γ (°)	68.4450(10)
V (Å) ³	1370.65(5)
Z	2
Dc (mg m ⁻³)	1.802
μ (Mo K α) (mm ⁻¹)	7.900
Theta range for collection	1.90 to 32.93
Reflections collected	8073
Independent reflections	6837 [$R_{(int)} = 0.0294$]
Data/restraints/parameters	6837 / 0 / 272
Goodness of fit on F^2	1.016
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0417$, $wR2 = 0.1034$
R indices (all data)	$R1 = 0.0538$, $wR2 = 0.1085$
Extinction coefficient	0.0069(4)
Largest difference peak/hole	2.515 / -2.264 e/Å ³

The structure was solved by direct methods which gave the location of all non-hydrogen atoms using SHELXTL ver. 6.12.¹³ Refinements were made by using a full-matrix least squares on all F^2 data using SHELXL.¹⁴ Anisotropic thermal parameters were included for all non-hydrogen atoms. All hydrogen atoms were included in calculated positions and allowed to ride on their parent carbon atom with fixed isotropic thermal parameters [$U_{iso}(H) = 1.2U_{iso}(\text{parent})$].

Results and discussion

Figure 1 shows a thermal ellipsoid plot for one of the independent molecules in the unit cell for compound **1**. An analysis of the structure reveals there are two independent molecules in the unit cell with each molecule located on a crystallographic inversion center. As expected the molecules are approximately square planar in shape [(P-Pt-Se) angles 85.85°/94.15° and 86.39°/93.61°]. Bond lengths around the central Pt atom are within the range typically found in this type of complex: Pt-P 2.3231(12) Å and 2.3252(14) Å. In a similar reported compound, a Pt-P distance of 2.304(2) Å was found in *trans*-[Pt(PEt₃)₂(4-MeSeBzo)₂]¹⁵ [(4-MeSeBzo)=4-methylbenzenecarboseleato)].

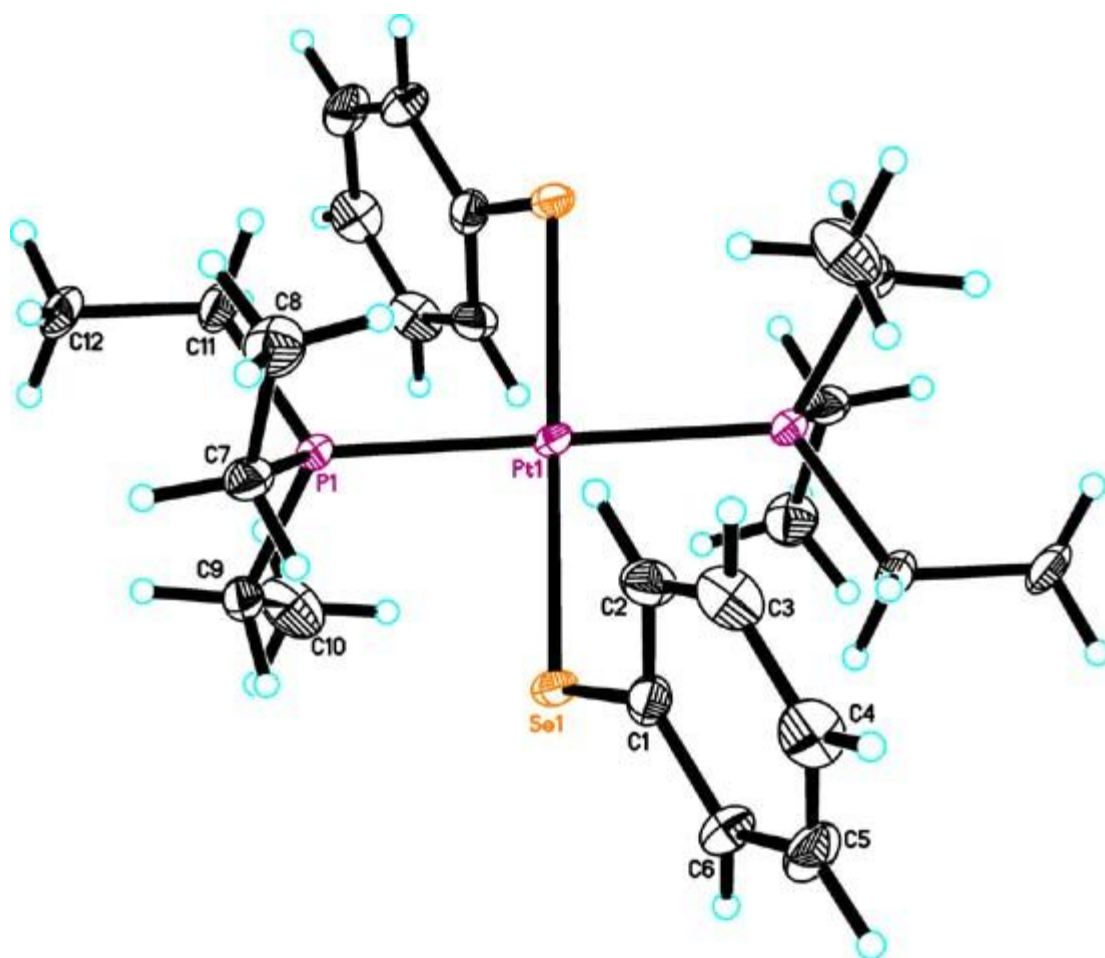


Fig. 1. Thermal ellipsoid (50% probability) plot and labeling diagram of *trans*-Pt(PET₃)₂(SePh)₂.

In this, and closely related complexes reported in their paper, Kawahara *et al.* found [$J(\text{PtP}) \approx 2450$ Hz], comparable to the value in this study and indicative of a *trans* geometry. In their synthetic method of using NaSeC(O)R' with *cis* or *trans*-[PtCl₂(PET₃)₂], their products obtained had only *trans* stereochemistry. Similarly for the Pt-Se distances, there are several related compounds available for comparison. Some of the data relating to pertinent bond distances and lengths is summarized in Table 2. The longer Pt-P bond lengths observed in the structure of **1** (compared to *cis* structural characterizations) confirm previous reports that the selenolato ligand (PhSe⁻) has a slightly stronger *trans* influence than the phosphine ligand.

Table 2. Comparison of Selected Bond Distances (Å) and Angles (°)

	[Pt(PEt ₃) ₂ (4-MeSeBzo) ₂] ¹³	[Pt(PPh ₃) ₂ (SePh) ₂] ⁶	[Pt(PPh ₃) ₂ (SePh) ₂] ⁶	[Pt(PPh ₃) ₂ (SePh) ₂] ⁵	[Pt(dppe)(SePy) ₂] ¹	[Pt(PEt ₃) ₂ (SePh) ₂] ⁵
Geometry/Notes	<i>trans</i>	<i>trans</i> /An earlier report of this structure is of limited accuracy ⁷	<i>cis</i>	<i>cis</i>	<i>cis</i> /Standard deviations not reported for all measurements	<i>trans</i> /This work – two independent molecules
Bond distance						
Pt-P	2.304(2)	2.3144(12)/2.3249(12)	2.2900(6)/2.2937(6)	2.310(2)/2.3111(9)	12.271/2.244	2.3231(12)/2.3252(14)
Pt-Se	2.452(1)	2.4525(5)/2.4548(5)	2.4885(3)/2.4506(3)	2.4604(10)/2.4970(9)	2.4335(13)/2.4980(14)	2.4692(5)/2.4744(5)
Se-C	1.913(6)	(Not reported)	(Not reported)	1.916(8)/1.937(8)		1.916(5)/1.918(5)
Bond Angle						
P(1)-Pt-Se(1)/P(2)-Pt-Se(2)	87.33(5)/92.67(5)	93.93(3)/95.21(3)	82.21(2)/85.85(2)	82.25(1)/85.75(6)	104.65/88.00	85.85(4)/86.39(3)
Pt-Se-C(1)	98.3(1)	(Not reported)	(Not reported)	106.8(2)	115.64	104.69(17)/102.59(14)

Pt(II) does not form complexes with six donor ligands, although there are instances of weak Pt-Pt interactions in square planar complexes with planar ligands; for example in the complex Pt(bipy)Cl₂, there are observed Pt-Pt separations of approx. 3.5 Å.¹⁶ In our reported structure, there are no such “short” contacts: the Pt atoms on adjacent molecules are >8.5 Å apart.

The NMR tube experiment did indeed form *cis*-PtCl₂(PEt₃)₂ at low temperatures (–20°C) but we were unable to isolate crystals from this reaction. However, the ³¹P NMR signal at 7.7 ppm [J(PtP) = 2740 Hz] is clearly indicative of the presence of the *cis* isomer. In their synthesis of Pt(SePh)₂(PPh₃)₂, Hannu *et al.*⁶ report ³¹P resonances at 19.1 and 20.8 ppm for the *cis* and *trans* isomers respectively, again with the J(PtP) value higher in the *cis* isomer. Comparable results are observed in this work.

Notes

Acknowledgments

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Supplementary materials

Crystallographic data for the structural analysis of compound **1** has been deposited at the Cambridge Crystallographic Data Center (CCDC number 602972). Copies of the information may be obtained free

of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>).

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