

Short Communication

Crystal and Molecular Structure of *trans*-Chlorobis(triphenylphosphine)(2-thienyl) Platinum(II)

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The coordination chemistry of platinum and palladium complexes with selenium- and tellurium-containing ligands has seen extensive research activity.^{1,2} These complexes find potential utility in the low-temperature preparation of binary platinum and palladium selenides and tellurides. While crystal structures are known for several species, the information on their formation is rather sparse. We report here the crystal and molecular structure of *trans*-chlorobis(triphenylphosphine)(2-thienyl)platinum(II), which is formed as one of the products in the reaction of tetrakis(triphenylphosphine)platinum(0) with bis(2-thienyl) ditelluride in dichloromethane. While the preparation of the complex has previously been reported from dichloro-(η -cycloocta-1,5-diene)platinum(II) and thienyltrimethylstannane,³ and from 2-thienylmercury(II)chloride and [Pt(PPh₃)₄],⁴ no structural data have been published. The structures of several analogous compounds, however, are known as exemplified by *trans*-chlorophenylbis(triphenylphosphine)platinum(II)⁵ and dichloro(μ -2,5-thien-2,5-diyl) bis{ μ -2-1,6-bis(diphenylphosphino)hexane-*P,P'*-platinum(II)}.⁶

Experimental

Sample preparation. The synthetic work was carried out under a dry nitrogen atmosphere. Tetrakis(triphenylphosphine)platinum(0) was prepared as described by Ugo *et al.*,⁷ and bis(2-thienyl) ditelluride was prepared according to Engman and Cava.⁸

Bis(2-thienyl) ditelluride (70 mg, 0.17 mmol) was added under constant stirring into 30 cm³ of a dichloromethane solution containing 410 mg (0.33

mmol) of [Pt(PPh₃)₄]. The stirring was continued overnight. The mixture was concentrated by the partial evaporation of dichloromethane and 15 cm³ of hexane was added into the resulting solution. The precipitate was dried in vacuum and washed several times with diethylether. Upon recrystallization from dichloromethane yellow crystalline material was obtained as one of the products. These yellow crystals were picked under a microscope for elemental analysis, ³¹P NMR spectroscopic measurements, and for crystal structure determination. (Found: C 57.29; H 4.09; S 3.91. Calc. for C₄₀ClH₃₃P₂PtS: C 57.31; H 3.97; S 3.82.)

NMR spectroscopy. The ³¹P-{H} spectrum was recorded on a Bruker DPX400 operating at 162 MHz. The solvent, CDCl₃, was used as an internal ²H lock. The ³¹P chemical shifts are reported relative to 85% H₃PO₄(aq).

Crystal structure determination. A yellow crystal (0.45 × 0.30 × 0.10 mm) was used for the crystal structure determination. Diffraction data were collected on a Siemens R3m diffractometer at 293 K using graphite monochromated Mo K α radiation (λ = 0.710 73 Å). Crystal data and experimental details of the data collection are shown in Table 1. The unit cell parameters were determined by the least-squares refinement of 25 automatically centered reflections. Two reference reflections were used to monitor the stability of the crystal. Their intensities were recorded periodically after each batch of 98 data. The decay of the crystal appeared to be negligible during the data collection. The total number of 8231 reflections were collected in the 2 θ range 4–55°. The reflection data were corrected for Lorentz and polarization effects. No absorption correction was applied.

The structure was solved by direct methods using the

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Table 1. Crystal data and structure refinement for [PtCl(C₄H₃S)(PPh₃)₂].

Complex	[PtCl(C ₄ H ₃ S)(PPh ₃) ₂]
Formula weight	838.2
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	<i>P</i> $\bar{1}$
Unit cell dimensions	<i>a</i> = 12.139(2) Å α = 90.44(3)° <i>b</i> = 12.706(3) Å β = 115.00(3)° <i>c</i> = 13.335(3) Å γ = 108.81(3)°
Volume	1739.5(6) Å ³
Z	2
Density (calculated)	1.600 Mg m ⁻³
Absorption coefficient	4.290 mm ⁻¹
<i>F</i> (000)	828
Crystal size	0.45 × 0.30 × 0.10 mm
Θ -Range for data collection	2.11–27.50°
Index ranges	0 ≤ <i>h</i> ≤ 15, −16 ≤ <i>k</i> ≤ 15, −17 ≤ <i>l</i> ≤ 15
Reflections collected	8231
Independent reflections	7982 [<i>R</i> (int) = 0.0312]
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data / restraints / parameters	7982 / 0 / 407
Goodness-of-fit on <i>F</i> ²	1.022
<i>R</i> -Indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0520, <i>wR</i> ₂ = 0.1221
<i>R</i> -Indices (all data)	<i>R</i> ₁ = 0.0698, <i>wR</i> ₂ = 0.1258
Extinction coefficient	0.0000(3)
Largest diff. peak and hole	3.124 and −2.896 e Å ⁻³

Siemens SHELXTL PLUS⁹ system and refined using SHELXL-93.¹⁰ After the full-matrix least-squares refinement of the non-hydrogen atoms with anisotropic thermal parameters the hydrogen atoms were placed in calculated positions in the aromatic rings (C–H = 0.93 Å). In the final refinement the hydrogen atoms were allowed to ride on the carbon atom to which they were bonded. The isotropic thermal parameters of the hydrogen atoms were fixed at 1.2 times that of the corresponding carbon atom. The scattering factors for the neutral atoms were those incorporated with the programs. Fractional coordinates and isotropic thermal parameters are listed in Table 2. Selected bond distances and angles are shown in Table 3. The anisotropic thermal parameters, calculated hydrogen atom positions, all bond parameters and structure factor tables can be obtained from the authors upon request.

Results and discussion

The reaction of tetrakis(triphenylphosphine)platinum(0) with bis(2-thienyl)ditelluride in dichloromethane affords several products. Upon recrystallization from dichloromethane one of the products could be separated as yellow crystals. Surprisingly, the product turned out to be a tellurium-free platinum complex [PtCl(C₄H₃S)(PPh₃)₂]. The molecular structure of the complex is shown in Fig. 1. As seen in Table 3, the coordination around platinum is approximately square planar, with Pt–P, Pt–Cl and Pt–C bond lengths near to

Table 2. Atomic coordinates (× 10⁴) and equivalent isotropic displacement parameters (Å² × 10³) for [PtCl(C₄H₃S)(PPh₃)₂].

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U</i> (eq) ^a
Pt	3637(1)	2150(1)	2642(1)	32(1)
P(1)	1609(2)	1783(2)	2584(2)	32(1)
P(2)	5703(2)	2533(2)	2812(2)	34(1)
Cl	3995(2)	4103(2)	2600(2)	52(1)
S(1)	2918(3)	−475(2)	1665(2)	60(1)
C(2)	3432(7)	551(6)	2792(7)	40(2)
C(3)	3712(7)	66(7)	3785(7)	42(2)
C(4)	3465(10)	−1127(8)	3530(9)	64(3)
C(5)	3050(10)	−1495(8)	2465(10)	70(3)
C(11)	654(7)	2583(6)	1729(7)	36(2)
C(12)	883(8)	3018(7)	873(7)	46(2)
C(13)	30(10)	3504(8)	126(9)	64(3)
C(14)	−992(10)	3543(8)	251(9)	62(3)
C(15)	−1197(10)	3128(9)	1124(10)	68(3)
C(16)	−414(9)	2634(7)	1843(9)	57(2)
C(21)	435(7)	338(6)	2039(6)	33(2)
C(22)	−580(7)	64(6)	966(7)	41(2)
C(23)	−1464(9)	−1029(7)	552(8)	52(2)
C(24)	−1310(9)	−1856(7)	1192(8)	56(2)
C(25)	−302(9)	−1613(7)	2249(8)	51(2)
C(26)	586(8)	−501(7)	2689(7)	44(2)
C(31)	1764(7)	2100(6)	3988(6)	37(2)
C(32)	2880(8)	2958(7)	4768(7)	50(2)
C(33)	3000(9)	3255(8)	5810(8)	60(2)
C(34)	2025(10)	2703(8)	6097(8)	60(2)
C(35)	935(9)	1846(8)	5343(8)	57(2)
C(36)	778(8)	1553(7)	4280(7)	46(2)
C(41)	6182(7)	1364(6)	2619(7)	42(2)
C(42)	6262(9)	1085(7)	1633(8)	53(2)
C(43)	6597(11)	151(10)	1518(10)	75(3)
C(44)	6888(12)	−478(10)	2354(10)	77(3)
C(45)	6833(11)	−197(9)	3305(10)	72(3)
C(46)	6446(9)	703(7)	3449(8)	53(2)
C(51)	5996(7)	3418(6)	1827(7)	38(2)
C(52)	7084(9)	4418(7)	2177(8)	52(2)
C(53)	7295(10)	5022(8)	1380(10)	61(3)
C(54)	6500(11)	4701(9)	280(10)	65(3)
C(55)	5401(11)	3717(10)	−81(9)	69(3)
C(56)	5160(9)	3091(8)	708(8)	54(2)
C(61)	6963(7)	3271(6)	4201(7)	43(2)
C(62)	6689(9)	3798(8)	4931(8)	57(2)
C(63)	7616(12)	4341(9)	5974(9)	76(3)
C(64)	8854(12)	4379(9)	6335(10)	84(4)
C(65)	9180(10)	3905(9)	5642(9)	75(3)
C(66)	8254(8)	3336(8)	4581(9)	60(3)

^a *U*(eq) is defined as one third of the trace of the orthogonalized *U*_{*ij*} tensor.

Table 3. Selected bond lengths (in Å) and angles (in °).

Pt–C(2)	1.988(8)	C(2)–Pt–P(2)	90.9(2)
Pt–P(2)	2.304(2)	C(2)–Pt–P(1)	88.8(2)
Pt–P(1)	2.321(2)	P(2)–Pt–P(1)	176.6(1)
Pt–Cl	2.383(2)	C(2)–Pt–Cl	175.9(2)
P(1)–C(11)	1.826(8)	P(2)–Pt–Cl	87.68(8)
P(1)–C(31)	1.828(8)	P(1)–Pt–Cl	92.36(8)
P(1)–C(21)	1.830(7)		
P(2)–C(51)	1.811(8)		
P(2)–C(41)	1.813(8)		
P(2)–C(61)	1.817(8)		

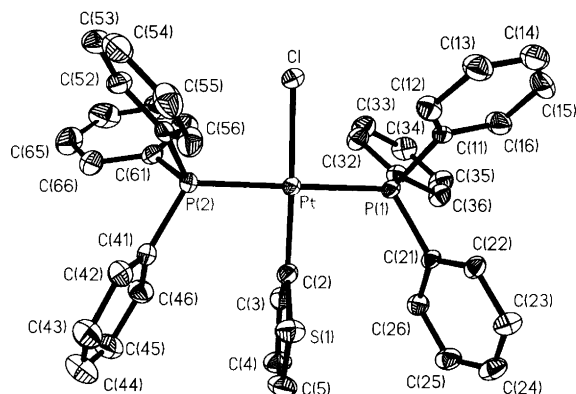


Fig. 1. Molecular structure of *trans*-[PtCl(C₄H₃S)(PPh₃)₂].

the values found in dichloro(μ -2,5-thien-2,5-diyl)bis{ μ -2-1,6-bis{(diphenylphosphino)hexane-*P,P'*}-platinum}.⁶ The two platinum environments in the latter complex are virtually identical to that observed for [PtCl(C₄H₃S)(PPh₃)₂]. The bond lengths are also consistent with the values in *trans*-chloro(phenyl)bis-(triphenylphosphine)platinum(II).⁵

The ³¹P-{H} NMR spectrum showed a resonance at 23.9 ppm, with the phosphorus-platinum coupling constant ¹J_{PtP} of 2900 Hz. The ³¹P chemical shift and the platinum phosphorus coupling agree well with the ³¹P NMR spectroscopic parameters reported previously for [PtCl(C₄H₃S)(PPh₃)₂].³ The appearance of the strong ³¹P NMR resonance at 23.9 ppm in the bulk sample indicates that the complex is indeed one of the main products in the reaction of tetrakis(triphenylphosphine)platinum(0) with bis(2-thienyl)ditelluride.

Chia and McWhinnie¹¹ have reported that a related reaction involving tetrakis(triphenylphosphine)palladium(0) and bis(2-thienyl)ditelluride produces a dinuclear complex [Pd(PPh₃)(TeC₄H₃S)(μ -TeC₄H₃S)₂-Pd(PPh₃)(TeC₄H₃S)]. Upon reinvestigation of this reaction we observed that a hexanuclear complex [Pd₆Te₆(C₄H₃S)₂(PPh₃)₆Cl₂] is one of the products. (For a preliminary report of the crystal structure determination of the complex, see Ref. 12.) It may be possible that the yet unidentified products are the platinum ana-

logues of the dinuclear or the hexanuclear complexes observed in the case of palladium. It is also possible that the formation of [PtCl(C₄H₃S)(PPh₃)₂] plays an important role in the actual reaction route. The appearance of chlorine coordinated to platinum in the present case, where the starting material contains no chlorine, has been explained in terms of the interaction between the platinum center and dichloromethane.^{13,14} This kind of interaction finds support in the preparation and structural characterization of [PdCl(CH₂Cl)(PPh₃)₂].¹³ A detailed study of the reaction pathway and the product distribution in the reactions of [M(PPh₃)₄] (M = Pd, Pt) and (C₄H₃S)₂Te₂ is currently in progress.

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