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Synthesis and characterization of platinum(II)–thiolate complexes. Crystal and molecular structures of *cis*-$Pt(Ph_3P)_2(SC_6H_2\text{-}2,4,6\text{-}iPr_3)Cl$ and *cis*-$Pt(Ph_3P)_2(SC_6H_2\text{-}2,4,6\text{-}iPr_3)_2$

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Abstract

The reaction of *cis*-$Pt(Ph_3P)_2Cl_2$ with 2,4,6-triisopropylbenzenethiol (HTIPT) in benzene at 65 °C yields yellow crystals of *cis*-$[Pt(Ph_3P)_2(TIPT)Cl]$ (**1**), while the reaction of *cis*-$Pt(Ph_3P)_2Cl_2$ and HTIPT in benzene at room temperature yields *cis*-$[Pt(Ph_3P)_2(TIPT)_2]$ (**2**). In contrast to the tendency of solutions of $[Pt(R_3P)_2(SR')_2]$ complexes with sterically innocent thiolates to rearrange into a complex mixture of *cis* and *trans* complexes and polynuclear materials upon exposure to air, solutions of both **1** and **2** are stable with respect to isomerization and oligomerization. Crystal data: $C_{51}H_{50}P_2SClPt\cdot 2H_2O$ (**1**$\cdot 2H_2O$), monoclinic $P2_1/c$, $a=16.131(5)$, $b=18.294(3)$, $c=17.803(6)$ Å, $\beta=110.40(2)°$, $V=4924(2)$ Å^3, $Z=4$, $D_{calc}=1.380$ g cm^{-1}; structure solution and refinement based on 2932 reflections converged at 0.074. $C_{66}H_{76}P_2S_2Pt$ (**2**), monoclinic $P2_1/n$, $a=10.854(2)$, $b=20.639(5)$, $c=27.080(6)$ Å, $\beta=100.43(2)°$, $V=5966(4)$ Å^3, $Z=4$, $D_{calc}=1.325$ g cm^{-3}; structure solution and refinement based on 4550 reflections converged at 0.049.

Key words: Crystal structures; Platinum complexes, Thiolate complexes

Introduction

Although platinum–thiolato complexes have an extensive chemistry [1–4], the structural characteristics of mononuclear species remain unexplored. Monomeric complexes of the type $[PtL_2(SR)_2]$ where $L=PR_3$ have been extensively studied in the context of *cis–trans* isomerization [4]. The chemistry of these species is complicated by their tendency to form bridged binuclear species, as well as complex polymers which are difficult to purify and characterize. Inhibition of polymerization and an increase in the general stability of the complexes has been accomplished by introduction of chelating thiolates and/or phosphine ligands [3, 4].

In an effort to prepare mononuclear complexes of the class $[PtL_2(SR)_2]$ with monodentate ligand types, we have exploited the sterically-hindered ligand triisopropylbenzenethiol (HTIPT) whose versatility in the isolation and crystallization of mononuclear complexes is well documented [5, 6]. The reactions of HTIPT with $[Pt(Ph_3P)_2Cl_2]$ are found to proceed smoothly to give *cis*-$[Pt(Ph_3P)_2(TIPT)Cl]$ (**1**) and *cis*-$[Pt(Ph_3P)_2(TIPT)_2]$ (**2**), whose spectroscopic properties and molecular structures are described in this work. The X-ray structures of **1**$\cdot 2H_2O$ and **2** represent rare examples of structurally characterized mononuclear Pt–thiolato complexes.

Experimental

All reactions were carried out in an atmosphere of N_2. The complex *cis*-$Pt(Ph_3P)_2Cl_2$ [7] and the ligand HTIPT [5] were prepared by the published procedures. The ^{195}Pt NMR measurements were taken on a 250 MHz Bruker instrument with potassium hexachloroplatinate as an external standard. The IR spectra were measured using a 2020 Galaxy series FT-IR. UV–Vis spectra were measured on a Varian Cray 1 UV–Vis spectrophotometer. Potassium tetrachloroplatinate was a generous gift from the Johnson-Mathey precious metals loan program.

Preparation of cis-$[Pt(Ph_3P)_2(TIPT)Cl]\cdot 2H_2O$ *(*$1\cdot 2H_2O$*)*

The thiolate HTIPT (0.59 g, 2.5 mmol) was added dropwise with stirring to a solution of $Pt(Ph_3P)_2Cl_2$ (2.00 g, 2.5 mmol) in 20 ml of benzene. After stirring

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for 0.5 h, the solution was evaporated to dryness. The red residue was washed with methanol. Recrystallization from benzene/methanol yielded red–orange crystals of **1**·$2H_2O$ in 55% yield. Melting point 154 °C. *Anal.* Calc. for $C_{51}H_{54}O_2P_2SClPt$: H, 5.36; C, 61.88; P, 6.27; Cl, 3.53; S, 3.24. Found: H, 5.48; C, 62.03; P, 6.12; Cl, 3.39; S, 3.23%. IR (KBr pellet, cm^{-1}): ν(C–S), 750(s). UV–Vis [benzene, nm (ϵ in cm^{-1} M^{-1} l)]: 424 (857). ^{195}Pt NMR (ppm): −4590; *J*(Pt–P) 1367, 6631 Hz.

Preparation of cis-[Pt(Ph$_3$P)$_2$(TIPT)$_2$] (2)

The ligand HTIPT (1.18 g, 5.0 mmol) was added dropwise with stirring to a solution of $Pt(Ph_3P)_2Cl_2$ (2.00 g, 2.5 mmol) in 20 ml benzene at 65 °C. After allowing the resulting yellow solution to cool to room temperature, petroleum ether was added until turbidity was apparent. Upon standing, yellow crystals of **2** were isolated in 50% yield. Melting point 221 °C. *Anal.* Calc. for $C_{66}H_{76}P_2S_2Pt$: H, 6.43; C, 66.59; P, 5.20; S, 5.39. Found: H, 6.30; C, 66.39; P, 5.28; S, 5.36%. IR (KBr pellet, cm^{-1}): ν(C–S), 750. UV–Vis [nm, (ϵ in cm^{-1} M^{-1} l)]: 460 (959). ^{195}Pt NMR (ppm): −4420; *J*(Pt–P) 3078 Hz.

X-ray crystallographic studies

X-ray data was collected on a Rigaku AFC5S four-circle diffractometer. Table 1 summarizes the crystal parameters and details of the structure solution and refinement. Non-hydrogen atoms were refined using isotropic temperatures factors except for Pt, S, P and Cl which were refined anisotropically. All hydrogen atoms were placed at idealized positions and refined as fixed contributors. Atomic positional parameters for **1**·$2H_2O$ and **2** are presented in Tables 2 and 3, respectively. Bond lengths and angles for the structures are compared in Table 4.

TABLE 1. Summary of crystal data and experimental conditions for the X-ray studies of [Pt(Ph$_3$P)$_2$(TIPT)Cl]·$2H_2O$ (**1**·$2H_2O$) and [Pt(Ph$_3$P)$_2$(TIPT)$_2$] (**2**)

	1·$2H_2O$	**2**
Composition	$C_{51}H_{54}O_2P_2SClPt$	$C_{66}H_{76}P_2S_2Pt$
Space group	$P2_1/n$	$P2_1/n$
a (Å)	16.131(4)	10.854(2)
b (Å)	18.293(3)	20.639(5)
c (Å)	17.803(6)	27.080(6)
β (°)	110.40(2)	100.43(2)
V (Å^3)	4924(3)	5966(4)
Z	4	4
D_{calc} (g cm^{-1})	1.380	1.325
T (K)	296	296
λ (cm)	0.71073 (Mo Kα)	0.71073 (Mo Kα)
μ (cm^{-1})	30.7	25.3
No. observed reflections ($I_o \geq 3\sigma(I_o)$)	2932	4550
R	0.074	0.049
R_w	0.085	0.068
GOF	2.94	2.56

TABLE 2. Atomic positional parameters for **1**·$2H_2O$

Atom	*x*	*y*	*z*
Pt	0.88651(7)	0.17627(5)	0.54000(6)
Cl	1.0136(4)	0.1563(4)	0.6517(4)
S(1)	0.8006(5)	0.1207(4)	0.6045(4)
P(1)	0.7623(5)	0.1891(3)	0.4325(4)
P(2)	0.9787(5)	0.2349(4)	0.4871(4)
O(1)	0.5894(8)	0.1211(6)	0.6746(7)
O(2)	0.6146(8)	0.0486(7)	0.8250(7)
C(1)	0.847(2)	0.125(1)	0.711(1)
C(2)	0.866(2)	0.061(1)	0.754(1)
C(3)	0.890(2)	0.066(1)	0.838(2)
C(4)	0.894(2)	0.128(2)	0.879(2)
C(5)	0.877(2)	0.191(1)	0.835(2)
C(6)	0.853(2)	0.194(1)	0.750(2)
C(7)	0.865(2)	−0.013(1)	0.711(1)
C(8)	0.772(2)	−0.043(2)	0.696(2)
C(9)	0.932(2)	−0.064(2)	0.758(2)
C(10)	0.919(3)	0.120(2)	0.970(2)
C(11)	0.841(3)	0.135(2)	0.993(3)
C(12)	0.999(3)	0.166(2)	1.012(3)
C(13)	0.835(2)	0.263(1)	0.702(1)
C(14)	0.890(2)	0.329(2)	0.751(1)
C(15)	0.737(2)	0.283(2)	0.683(2)
C(21)	0.777(2)	0.158(1)	0.343(1)
C(22)	0.825(2)	0.096(2)	0.349(2)
C(23)	0.839(2)	0.062(2)	0.282(2)
C(24)	0.800(2)	0.096(2)	0.206(2)
C(25)	0.753(2)	0.158(2)	0.198(2)
C(26)	0.742(2)	0.189(1)	0.267(2)
C(27)	0.721(2)	0.282(1)	0.421(1)
C(28)	0.762(2)	0.333(2)	0.480(1)
C(29)	0.728(2)	0.404(2)	0.474(2)
C(30)	0.652(2)	0.423(1)	0.413(2)
C(31)	0.610(2)	0.371(2)	0.359(2)
C(32)	0.644(2)	0.303(1)	0.359(1)
C(33)	0.666(2)	0.137(1)	0.430(1)
C(34)	0.646(2)	0.070(2)	0.388(2)
C(35)	0.567(2)	0.035(2)	0.389(2)
C(36)	0.514(2)	0.060(2)	0.427(2)
C(37)	0.533(2)	0.121(2)	0.470(2)
C(38)	0.609(2)	0.160(1)	0.468(1)
C(39)	1.076(2)	0.179(1)	0.496(1)
C(40)	1.062(2)	0.105(2)	0.486(2)
C(41)	1.143(2)	0.059(2)	0.489(2)
C(42)	1.216(2)	0.090(2)	0.496(2)
C(43)	1.232(2)	0.164(2)	0.505(2)
C(44)	1.161(2)	0.209(2)	0.504(2)
C(45)	1.020(1)	0.322(1)	0.542(1)
C(46)	1.005(2)	0.337(1)	0.609(1)
C(47)	1.035(2)	0.405(2)	0.646(2)
C(48)	1.071(2)	0.455(1)	0.613(2)
C(49)	1.088(2)	0.441(2)	0.547(2)
C(50)	1.062(2)	0.374(1)	0.507(1)
C(51)	0.944(2)	0.267(1)	0.382(1)
C(52)	0.971(2)	0.231(1)	0.325(2)
C(53)	0.941(2)	0.256(2)	0.246(2)
C(54)	0.888(2)	0.316(2)	0.226(2)
C(55)	0.861(2)	0.352(2)	0.280(2)
C(56)	0.887(2)	0.329(1)	0.360(1)

TABLE 3. Atomic positional parameters for **2**

Atom	x	y	z
Pt	−0.11129(5)	0.14931(3)	0.14510(2)
S(1)	−0.1189(4)	0.2630(2)	0.1533(1)
S(2)	−0.2063(3)	0.1506(2)	0.0595(1)
P(1)	0.0066(4)	0.1522(2)	0.2252(1)
P(2)	−0.1320(4)	0.0370(2)	0.1377(1)
C(1)	−0.263(1)	0.2998(7)	0.1247(5)
C(2)	−0.258(1)	0.3572(8)	0.0960(5)
C(3)	−0.369(2)	0.3919(8)	0.0782(6)
C(4)	−0.481(2)	0.3737(8)	0.0889(6)
C(5)	−0.487(1)	0.3197(8)	0.1171(6)
C(6)	−0.379(1)	0.2813(7)	0.1361(5)
C(7)	−0.131(2)	0.3798(8)	0.0857(6)
C(8)	−0.064(2)	0.419(1)	0.1275(8)
C(9)	−0.145(2)	0.421(1)	0.0368(8)
C(10)	−0.603(2)	0.411(1)	0.0722(8)
C(11)	−0.647(2)	0.401(1)	0.0157(9)
C(12)	−0.596(3)	0.477(2)	0.086(1)
C(13)	−0.392(2)	0.2282(9)	0.1725(7)
C(14)	−0.513(2)	0.190(1)	0.1611(8)
C(15)	−0.370(2)	0.252(1)	0.2265(7)
C(16)	−0.155(1)	0.2111(7)	0.0197(5)
C(17)	−0.030(2)	0.2306(8)	0.0227(6)
C(18)	−0.000(2)	0.2737(9)	−0.0150(7)
C(19)	−0.086(2)	0.293(1)	−0.0516(8)
C(20)	−0.209(2)	0.274(1)	−0.0554(7)
C(21)	−0.246(1)	0.2316(7)	−0.0220(5)
C(22)	0.079(2)	0.2049(8)	0.0597(6)
C(23)	0.158(2)	0.257(1)	0.0920(8)
C(24)	0.166(2)	0.164(1)	0.0335(8)
C(25)	−0.052(3)	0.336(2)	−0.095(1)
C(26)	−0.038(3)	0.301(2)	−0.139(1)
C(27)	−0.018(3)	0.394(2)	−0.085(1)
C(28)	−0.381(1)	0.2100(7)	−0.0292(6)
C(29)	−0.438(2)	0.201(1)	−0.0851(7)
C(30)	−0.459(2)	0.254(1)	−0.0039(8)
C(31)	0.084(1)	0.2286(7)	0.2448(5)
C(32)	0.200(2)	0.2430(9)	0.2328(7)
C(33)	0.261(2)	0.303(1)	0.2480(8)
C(34)	0.201(2)	0.345(1)	0.2739(7)
C(35)	0.088(2)	0.3344(9)	0.2837(7)
C(36)	0.026(2)	0.2753(9)	0.2697(6)
C(37)	0.143(1)	0.0988(7)	0.2305(5)
C(38)	0.191(2)	0.0870(8)	0.1871(6)
C(39)	0.297(2)	0.047(1)	0.1885(7)
C(40)	0.353(2)	0.022(1)	0.2338(8)
C(41)	0.307(2)	0.030(1)	0.2756(8)
C(42)	0.197(2)	0.0701(9)	0.2760(7)
C(43)	−0.075(1)	0.1333(7)	0.2771(6)
C(44)	−0.193(1)	0.1114(8)	0.2667(6)
C(45)	−0.258(2)	0.095(1)	0.3059(7)
C(46)	−0.195(2)	0.102(1)	0.3558(8)
C(47)	−0.077(2)	0.125(1)	0.3651(8)
C(48)	−0.013(2)	0.1427(9)	0.3268(6)
C(49)	−0.016(1)	−0.0069(7)	0.1108(5)
C(50)	0.040(1)	0.0219(8)	0.0752(6)
C(51)	0.126(2)	−0.0110(8)	0.0517(6)
C(52)	0.151(2)	−0.0744(8)	0.0625(6)
C(53)	0.094(2)	−0.1049(9)	0.0968(6)
C(54)	0.013(1)	−0.0738(8)	0.1221(6)
C(55)	−0.141(1)	−0.0101(7)	0.1942(5)
C(56)	−0.035(2)	−0.0270(8)	0.2284(6)
C(57)	−0.043(2)	−0.0612(9)	0.2724(6)
C(58)	−0.158(2)	−0.0757(9)	0.2832(7)
C(59)	−0.263(2)	−0.060(1)	0.2512(7)
C(60)	−0.257(1)	−0.0279(8)	0.2054(6)
C(61)	−0.281(1)	0.0152(7)	0.0988(5)
C(62)	−0.386(1)	0.0499(8)	0.1028(6)
C(63)	−0.507(2)	0.0276(9)	0.0783(7)
C(64)	−0.515(2)	−0.031(1)	0.0517(7)
C(65)	−0.409(2)	−0.064(1)	0.0474(7)
C(66)	−0.293(2)	−0.0434(8)	0.0716(6)

TABLE 4. Comparison of selected bond lengths (Å) and angles (°) for **1** $2H_2O$ and **2**

	1 $2H_2O$	**2**
Pt–Cl	2.335(6)	
Pt–S1	2.320(7)	2.359(4)
Pt–S2		2.359(4)
Pt–P1	2.250(6)	2.310(4)
Pt–P2	2.286(7)	2.335(4)
S1–C1	1.78(2)	1.79(1)
S2–C16		1.80(1)
P–C	1.78(2)–1.87(2)	1.80(2)–1.83(1)
Cl–Pt–S1	90.5(2)	
Cl–Pt–P1	176.9(2)	
Cl–Pt–P2	85.4(2)	
S1–Pt–S2		93.7(1)
S1–Pt–P1	87.6(2)	84.8(1)
S1–Pt–P2	175.0(2)	172.4(1)
S2–Pt–P1		172.1(1)
S2–Pt–P2		84.8(1)
P1–Pt–P2	96.6(2)	97.7(1)
Pt–S1–C1	113.8(9)	115.2(5)
Pt–S2–C16		118.0(5)

Results and discussion

The synthesis of $[Pt(Ph_3P)_2(TIPT)Cl]$ (**1**) and $[Pt(Ph_3P)_2(TIPT)_2]$ (**2**) is accomplished by the displacement of one or two chloride ligands, respectively, from bis(triphenylphosphine) platinum dichloride under N_2, as shown in eqns. (1) and (2). The stepwise formation of the mono- and disubstituted thiolate complexes is

$$[Pt(Ph_3P)_2Cl_2] + HTIPT \xrightarrow[\text{benzene}]{N_2} cis\text{-}[Pt(Ph_3P)_2(TIPT)Cl] + HCl \quad (1)$$

$$cis\text{-}[Pt(Ph_3P)_2Cl_2] + 2HTIPT \xrightarrow[\text{benzene}]{N_2} cis\text{-}[Pt(Ph_3P)_2(TIPT)_2] + 2HCl \quad (2)$$

consistent with simple chloride ligand displacement via an S_N2 mechanism, as previously suggested [4].

However, the chemistry is quite distinct from that previously reported for the reactions of *cis*-[$Pt(Ph_3P)_2Cl_2$] with sterically-innocent thiolate ligands In these cases, the isolation of [$Pt(Ph_3P)_2(SR)_2$] complexes for R = alkyl and aryl required the presence of triethylamine, eqn. (3).

$$cis\text{-}[Pt(Ph_3P)_2Cl_2] + 2HSR + 2Et_3N \xrightarrow[\text{toluene}]{N_2} [Pt(Ph_3P)_2(SR)_2] + 2Et_3NHCl \quad (3)$$

Furthermore, arenethiols were found to give complexes of *trans* geometry exclusively, while alkenethiols gave *cis* complexes [4]. The chemistry was further complicated by the air sensitivity of the *cis* derivatives in solution, which react to give a complex mixture of species, containing both *cis* and *trans* isomers, the dimer [$(Ph_3P)(RS)Pt(\mu\text{-}SR)_2Pt(SR)(Ph_3P)$], and often larger oligomers. The failure to observe any formation of *trans* species or of oligomeric materials in solutions of **1** and **2** under anaerobic or aerobic conditions most likely reflects the resistance of the TIPT ligand toward oxidation to form disulfide species RSSR and to the steric influence of the bulky substituents. Thus, one of the air rearrangement products of *cis*-[$Pt(Ph_3P)_2(SCH_2Ph)_2$] is the disulfide $PhCH_2SSCH_2Ph$. In contrast, no disulfide is observed in solutions of **2** exposed to air, a feature consistent with greatly enhanced stability of sterically-hindered thiolates such as TIPT with respect to oxidation and disulfide formation [5]. Moreover, since reactions of square planar Pt(II) complexes proceed by S_N2 processes, the steric constraints imposed by the TIPT ligands in the presence of PPh_3 ligands should effectively block the reactivity.

The structures of **1** and **2** are illustrated in Figs. 1 and 2, respectively. The structure of **1** consists of mononuclear [$(Pt(Ph_3P)_2(TIPT)Cl$] units with the triphenylphosphine ligands adopting *cis* geometry about the square planar Pt(II) site. The major distortions from idealized geometry are consequences of the presence of three different donor atom types and of the steric constraints of the bulky substituents. Thus, the P1–Pt–P2 angle expands to 96.6(2)° from the idealized value of 90° in order to accommodate the phenyl substituents of the PPh_3 ligands. Consequently, the other valence angles about the Pt site must contract, as shown in Table 4. In order to minimize steric congestion, the phenyl ring of the TIPT ligand is oriented approximately normal to the {PtP_2SCl} plane. A noteworthy feature of the structure is the significant difference in Pt–P bond lengths of 2.250(6) and 2.286(7) Å for Pt–P1 and Pt–P2, respectively, suggesting that the structural *trans* influence of the thiolate is somewhat greater than that of the chloride.

The structure of **2** is related to that of **1** by substitution of a TIPT ligand for Cl^-. Once again, the steric requirements of the *cis*-{$Pt(PPh_3)_2$} unit determine the angular distortions from idealized geometry about the Pt(II) center, producing a P1–Pt–P2 angle of 97.7(1)°. However, the presence of two sterically-hindered thiolate ligands results in an S1–Pt–S2 angle of 93.7(1)°, compared to the S1–Pt–Cl angle of 90.5(2)° observed for **1**. The steric interaction between the TIPT ligands is apparently minimized by parallel stacking of the rings which adopt an orientation approximately normal to the {PtP_2S_2} plane. Such parallel disposition of rings effectively reduces the steric demands of the TIPT ligand relative to that of PPh_3, a feature consistent with the P1–Pt–P2 and S1–Pt–S2 bond angles. A comparison of the metrical parameters associated with **1** and **2** shows a general expansion of Pt–ligand distances

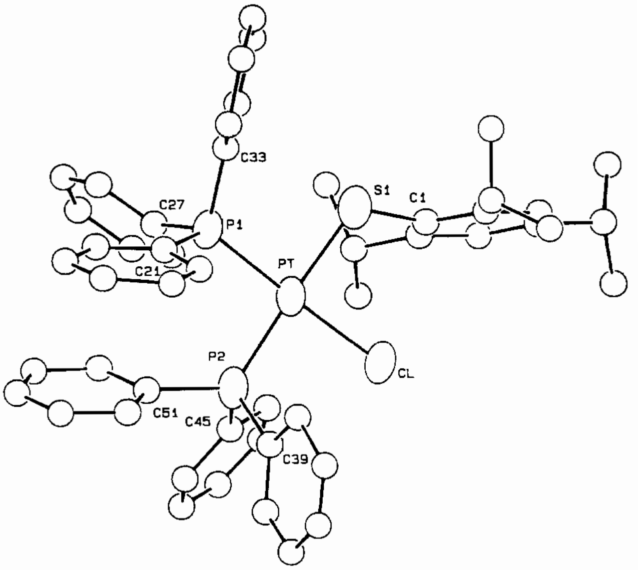

Fig 1. A view of the structure of [$Pt(Ph_3P)_2(TIPT)Cl$] (**1**), showing the atom-labeling scheme.

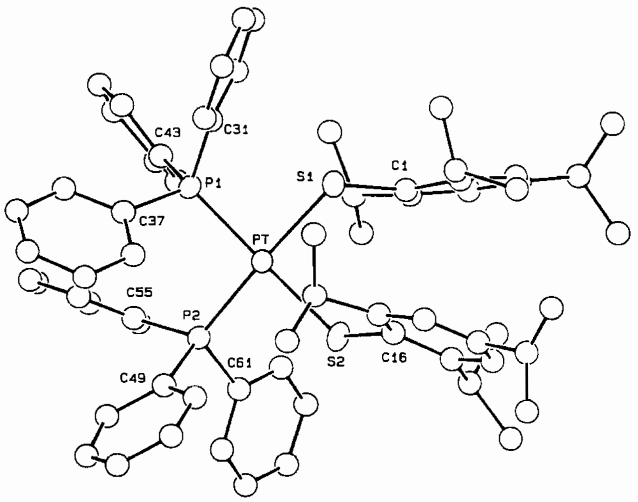

Fig. 2. An ORTEP plot of the structure of [$Pt(Ph_3P)_2(TIPT)_2$] (**2**), showing the atom-labeling scheme.

in **2**, presumably reflecting the added steric congestion and the *trans* influence of the second thiolate ligand.

It is noteworthy that while the TIPT ligand appears to exert a structural *trans* influence, this is not reflected in the reaction chemistry. The product composition of **2** most likely reflects the *trans* labilizing power of PPh_3 and the leaving group character of the chloride ligand, both of which favor the formation of the *cis*-$[Pt(PPh_3)_2(TIPT)_2]$ product.

The ^{195}Pt NMR properties of the new compounds are also consistent with the bonding characteristics of Pt(II) coordination compounds. The chemical shifts for **1** and **2** are similar to those of *cis*-$[Pt(Ph(CH_3)_2P)_2(CH_3)_2]$ and *cis*-$[Pt(Ph(CH_3)_2P)_2(CH_3)Cl]$ [8]. Since chemical shifts are correlated with reciprocal transition energies involving the d orbitals, and both RS^- and CH_3^- would have similar crystal field and *trans* directing properties, this behavior is expected [9, 10]. As expected the monosubstituted analogue **1** exhibits two different platinum–phosphorus coupling constants ('Experimental'). Since the magnitude of the coupling will be dependent on the strength of the Pt–P bond, the larger coupling for this complex (6631 Hz) is associated with the phosphine *trans* to the weak *trans* directing chloride ligand [9, 10].

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