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Preparation of sulfur ylide complexes of platinum by phase transfer catalysis

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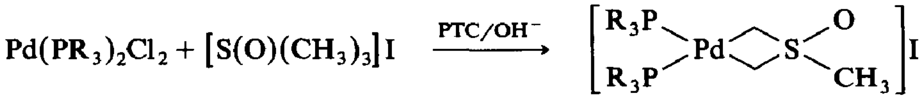
Abstract

Various sulfur ylide complexes of platinum have been prepared by the phase transfer catalysis (PTC). Thus, reaction of $Pt(PR_3)_2Cl_2$ (R = methyl or phenyl) in CH_2Cl_2 with $[S(O)(CH_3)_3]I$ under PTC/OH^- conditions, give complexes $\{Pt(PR_3)_2[(CH_2)_2S(O)(CH_3)]\}I$, which contain a bidentate double sulfur ylide. With $Pt(dppe)\ Cl_2$ (dppe = $Ph_2P(CH_2)_2PPh_2$) as starting material, a similar product was obtained. But when $Pt(dppm)Cl_2$ (dppm = $Ph_2PCH_2PPh_2$) was treated with $[S(O)(CH_3)_3]Cl$ under PTC/OH^- conditions, an unexpected product $\{Pt(PPh_2CH_3)(PPh_2OH)[(CH_2)_2S(O)(CH_3)]\}Cl$ was obtained. This compound contains a bidentate double sulfur ylide and two unsymmetrical phosphines resulting from the base hydrolysis of dppm. Compound $\{Pt(PPh_3)_2[(CH_2)_2S(O)(CH_3)]\}I$, was subjected to an X-ray diffraction study. The compound crystallized in the orthorhombic space group $Pna2_1$ with cell parameters *a* 19.332(4), *b* 11.101(5) and *c* 16.936(5) Å, $Z = 4$.

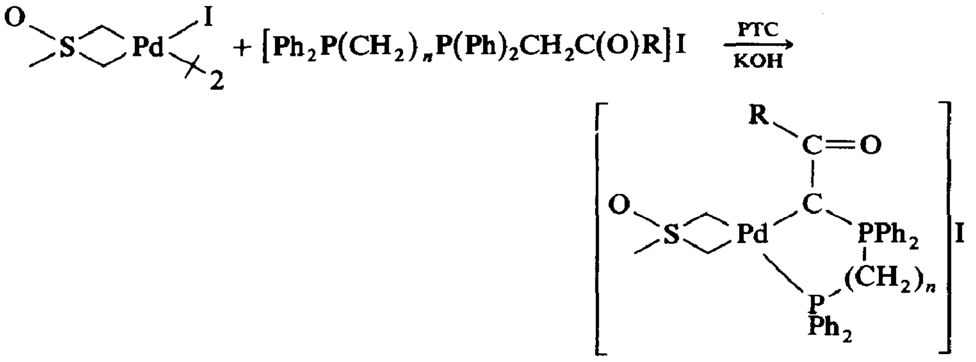
Phase transfer catalysis (PTC) is one of the most useful techniques of recently developed organic syntheses. Numerous reports have been published in this field [1–4]. Recently, the application of the PTC technique to organometallic synthesis has increased [5–14]. In our previous work, we have shown that sulfur ylide complexes of palladium can be readily prepared by PTC (eq. 1) [12,14]. This reaction is unusual in view of the known instability of sulfur ylide in anhydrous



(1)

[†] Deceased January 29th, 1987.

solvents at room temperature. This technique has many advantages, mainly because it is simple. We have extended this technique to phosphorus ylide, and found that it is also applicable to *P*,*C*-chelated phosphorus ylide (eq. 2) [15].



(2)

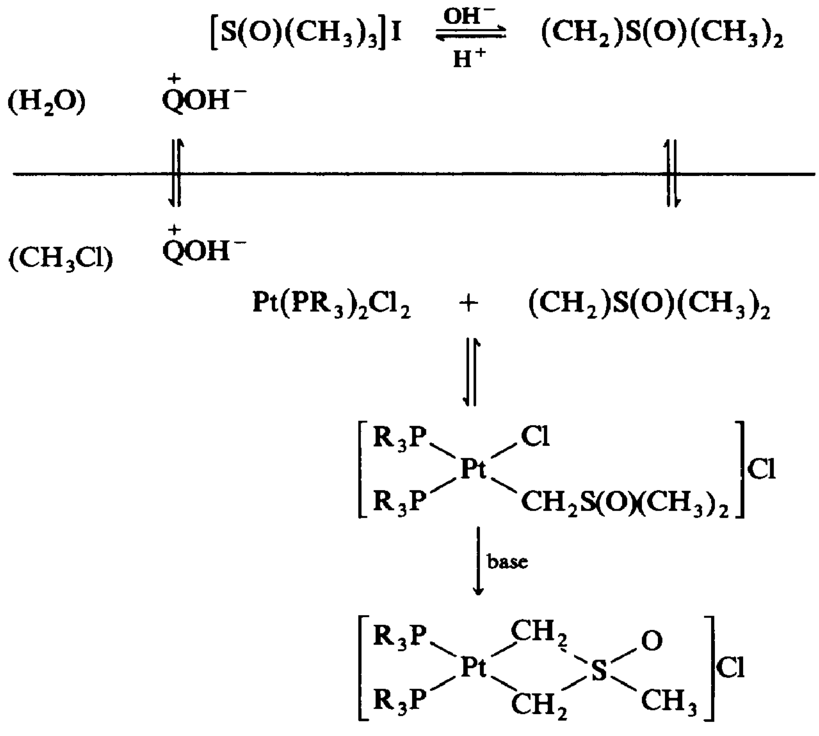
(R = alkyl or aryl; *n* = 1 or 2)

We were interested in the application of this technique to other transition metals. In this paper we report on the synthesis of sulfur ylide complexes of platinum by the PTC technique and also to illustrate the crystal structure of the complex $\{Pt(PPh_3)_2[(CH_2)_2S(O)(CH_3)]\}I$.

Results and discussion

In general, the preparation of sulfur ylide complexes of platinum is similar to that of the analogous palladium compounds [12,14]. Thus the reaction of $Pt(PPh_3)_2Cl_2$ with $[S(O)(CH_3)_3]I$ under PTC/OH$^-$ conditions resulted in the ionic compound $\{Pt(PPh_3)_2[(CH_2)_2S(O)(CH_3)]\}I$ (**1**). This ionic compound is not converted into the neutral compound, $Pt(PPh_3)(I)[(CH_2)_2S(O)(CH_3)]$ like its palladium analogue. This could be explained in terms of the slightly larger size of the Pt^{II} ion compared with that of Pd^{II}. Other bisphosphine complexes $Pt(PR_3)_2Cl_2$ (R = aryl or alkyl) work equally well. However, with the starting material, $Pt(bipy)Cl_2$, no sulfur ylide complex was obtained. During the reaction, the platinum compound was taken up by the aqueous layer and could not be isolated. We have also noted that in the preparation of palladium sulfur ylide complex under PTC/OH$^-$ conditions, the presence of iodide anion is crucial [14]; it prevents decomposition of the palladium compounds. However, for the platinum complexes, no decomposition occurs even in the absence of iodide anion. This seems to suggest that platinum compounds are more stable than the palladium compounds under PTC/OH$^-$ conditions. Pt^{II} is probably a softer acid than Pd^{II}, and it is more inert toward the hard OH$^-$. This argument also seems applicable to Ni^{II} ion. So far we have not been able to isolate any sulfur ylide complexes of nickel(II) by the PTC/OH$^-$ technique.

The methyl group on the sulfur ylide always shows a broad 1:4:1 triplet. This 1:4:1 triplet is due to the long range coupling between the methyl proton and platinum metal (^{195}Pt, $I = 1/2$, 33% natural abundance). The broadness of each signal is due to the unresolved long-range coupling between the methyl proton and methylene proton on the sulfur ylide.



Scheme 1

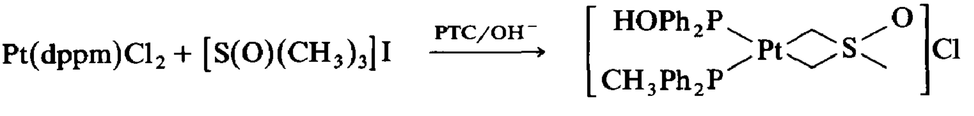
The two methyl groups on the dimethylphenylphosphine of compound **3** are nonequivalent and the ^1H NMR spectrum exhibits two sets of methyl signals in a 1:1:4:4:1:1 pattern in $CDCl_3$. This pattern is due to the coupling of methyl protons to both ^{31}P and ^{195}Pt [16]. The chemical shift difference of the two methyl signals is solvent dependent. Of the four solvents used, $CDCl_3$ gives the largest chemical shift difference (0.07 ppm), CD_2Cl_2 gives a smaller chemical shift difference (0.05 ppm), while DMSO-d_6 and acetone-d_6 do not result in any chemical shift difference. The nature of this solvent effect is not clear. It is noteworthy however, that DMSO-d_6 and acetone-d_6 both contain an oxygen atom.

Using bidentate phosphine compound $Pt(dppe)Cl_2$ (dppe = $Ph_2P(CH_2)_2PPh_2$) as a starting material, yields a corresponding sulfur ylide compound $\{Pt(dppe)[(CH_2)_2S(O)(CH_3)]\}Cl$ (**5**). This compound is not very stable in DMSO. Prolonged standing in DMSO gives the rectangular crystals of $Pt(dppe)Cl_2$. The corresponding PF_6^- salt is stable and can be obtained in crystalline materials.

The formation of sulfur-ylide complexes of platinum under PTC/OH^- conditions is best explained by Scheme 1. In an aqueous layer, sulfoxonium salt is in equilibrium with sulfur ylide. The equilibrium favors the sulfonium salt. The sulfur ylide once formed, will diffuse to the organic layer and react with $Pt(PR_3)_2Cl_2$ to afford a monodentate platinum-sulfur ylide compound $\{Pt(PR_3)_2[(CH_2)S(O)(CH_3)_2]Cl\}Cl$, which upon deprotonation of a methyl proton by a free sulfur ylide or by the OH^- in the organic layer will produce the bidentate double sulfur ylide complex, $\{Pt(PR_3)_2[(CH_2)_2S(O)(CH_3)]\}Cl$.

$Pt(dppm)Cl_2$ (dppm = $Ph_2PCH_2PPh_2$) reacting with $[S(O)(CH_3)_3]Cl$ under PTC/OH^- conditions resulted in an unexpected sulfur ylide platinum compound

$\{Pt[PPh_2(OH)](PPh_2CH_3)[(CH_2)_2S(O)(CH_3)]\}Cl$ (**6**). (eq. 3). A bidentate sulfur double ylide was formed in this reaction, and a bidentate dppm ligand was hydrolyzed to produce a $PPh_2(OH)$ and PPh_2CH_3 ligand [17]. This compound is soluble in ethanol and other polar organic solvents. The ^{31}P NMR spectrum of this compound shows that the two phosphines are nonequivalent, and the small $^{31}P-^{31}P$ coupling constant (24.4 Hz) is consistent with a *cis* configuration. The ^1H NMR spectrum shows the presence of a PPh_2CH_3 (1 : 1 : 4 : 4 : 1 : 1 multiplet at $\delta = 1.89$ ppm) and a chelated double sulfur ylide. Its molar conductivity (15 $\Omega^{-1}cm^2mol^{-1}$) is lower than the values expected for a 1 : 1 electrolyte. In ethanol, this compound can be converted to its PF_6^- salt. The PF_6^- salt and Cl^- salt show substantial differences in ^{31}P NMR chemical shift and molar conductance. These differences could possibly be due to the strong association of chloride anion with the acidic P–OH in the cation. This novel dppm hydrolysis reaction is common with other platinum compounds. Recently base hydrolysis of $Pt(dppm)Cl_2$ in DMSO and MeCN has also been found to produce *cis*- and *trans*-$[Pt(\mu\text{-}OH)(PPh_2O)(PPh_2Me)]_2$ [18]. Thus this general method is used to convert a symmetrical bidentate phosphine ligand to two unsymmetrical phosphine ligands. The preliminary result of this hydrolysis reaction was published [17] and the details will be reported later.



(3)

Surprisingly, K_2PdCl_4 reacts with $[S(O)(CH_3)_3]I$ in a basic aqueous solution to produce $\{Pd(\mu\text{-}I)[(CH_2)_2S(O)(CH_3)]\}_2$ as a yellow precipitate, no analogous platinum compound can be obtained using this method. Under similar conditions, the orange-red K_2PtCl_4 turned yellow in the aqueous solution, but the water soluble yellow compound can not be isolated and identified. Similarly, no ylide complexes of rhodium can be isolated by treating $RhCl_3$ with $[S(O)(CH_3)_3]I$ in a basic aqueous solvent. We have also attempted to synthesize sulfur ylide complexes of rhodium by the PTC/OH^- technique. When treating $Rh(PPh_3)_3Cl$ in CH_2Cl_2 with $[S(O)(CH_3)_3]I$ in water under PTC/OH^- conditions, yielded only a very small amount of ylide complex (by ^1H NMR spectroscopy), which was difficult to separate. In conclusion, for the synthesis of sulfur ylide complexes, while Pd^{II} is thus far the easiest to obtain by using both the PTC/OH^- technique and a basic aqueous solution, Pt^{II} works only by the PTC/OH^- technique, and rhodium does not work in either method.

A single crystal X-ray diffraction study has been carried out on compound **1**. The results are shown in Fig. 1. The geometry around the platinum metal is similar to its palladium analogy [14], having two *cis* triphenylphosphines, and a chelated sulfur ylide anion. The four-membered Pt–C–S–C ring is folded, and the sulfur atom is slightly out of the PtL_4 plane. As was observed previously in the palladium complexes [13,14], the methyl group is at the axial position and the oxygen atom is at the equatorial position. The bond lengths of Pt–C (1.882, 2.084 Å) and Pt–P (2.299, 2.343 Å) are comparable to other platinum complexes (1.93–2.10, 2.27–2.41 Å) [19]. The two Pt–P bond distances of **1** differ significantly, so the two Pt–C bonds are *trans* to it. The alternating bond lengths in this compound are more apparent in this than in the other two platinum-thietane-3-oxide compounds [20,21]. The S–C(1) and S–C(2) distances (1.650 and 1.637 Å) are comparable to the

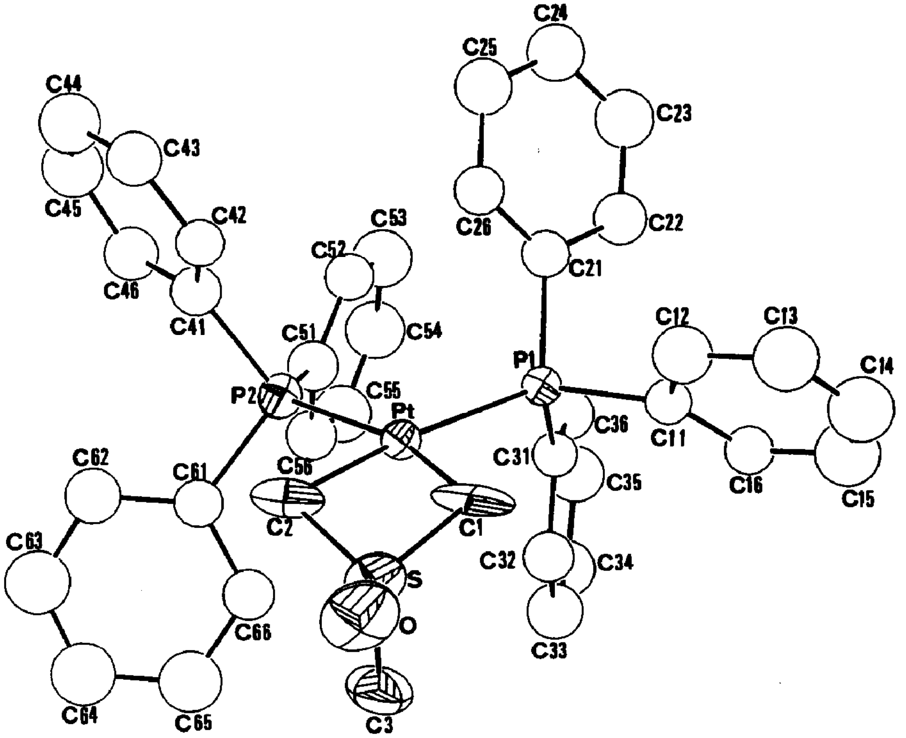


Fig. 1. ORTEP drawing of compound 1 with 50% probability ellipsoids. Blank circles represent isotropic thermal motion.

palladium analogy but are much shorter than the S–C(3) bond (1.761 Å) and those found in thietane oxide compounds (1.76–1.79 Å). The short ylidic S–C bond lengths suggest that the ylidic character is partially retained upon complexation.

Experimental

Infrared spectra were recorded on Analect-RFX-600 spectrometer in KBr pellets. ^1H NMR spectra were recorded on a Varian EM-360 spectrometer operated at 60 MHz and on a Bruker AM-300WB. Chemical shifts were recorded downfield relative to internal TMS standard. ^{31}P NMR spectra were recorded on a Bruker AM-300WB, and chemical shifts were reported with 85% H_3PO_4 as an external reference. Conductivities were measured with a WPA CMD 400 digital conductivity meter. Elemental analyses were done by Taipei or Tainan Instrumentation Center, Taiwan.

All monophosphines used in this work were purchased from Strem Chemicals. Bis(diphenylphosphino)methane, bis(diphenylphosphino)ethane and all phase transfer catalysts were purchased from Aldrich. $Pt(PPh_3)_2Cl_2$, $Pt(PPh_2CH_3)_2Cl_2$, $Pt[PPh(CH_3)_2]_2Cl_2$, $Pt(dppm)Cl_2$, and $Pt(dppe)Cl_2$ were prepared using known methods. $Pt[P(C_6H_4CH_3)_3]_2Cl_2$ was prepared by the preparation method of $Pt(PPh_3)_2Cl_2$.

$\{Pt(PPh_3)_2[(CH_2)_2S(O)(CH_3)]\}I$ *(1)*

$Pt(PPh_3)_2Cl_2$ (0.2 g, 0.25 mmol) in CH_2Cl_2 (10 ml) was mixed with trimethylsulfoxonium iodide (0.167 g, 0.76 mmol) in H_2O (5 ml, 1.8 *N* NaOH), followed by the phase transfer catalyst $^nBu_4NI$ (0.005 g, 0.013 mmol). The resultant solution was stirred at room temperature. The original colorless solution turned yellow then pale yellow, and the reaction was stopped (~ 6 h). To this pale yellow solution, 10 ml of CH_2Cl_2 was added to facilitate separation. The organic layer was separated, washed with water (three times, 20 ml each) dried with $MgSO_4$ and filtered. The solution was concentrated to 3 ml and was precipitated using ether. The crude product was obtained in 70% yield. Recrystallization from CH_2Cl_2/n-hexane gave a pale yellow crystalline compound. M.p. 215–217°C Anal. Found: C, 49.9; H, 3.9. $C_{39}H_{37}IOP_2PtS$ calcd.: C, 48.4; H, 3.9%. IR ν(SO): 1196 cm^{-1}. ^1H NMR ($CDCl_3$): 7.7–7.1 (m, 30 H, phenyl protons), 5.41 (S, 1 H, CH_2Cl_2), 3.62 (t, ^4J(PtH) 9.0 Hz, 3 H, SCH_3), 3.1–2.1 (m, 4 H, SCH_2) ppm. Molar conductivity (acetone, 3.6×10^{-3} *M*) 123 Ω^{-1} cm^2 mol^{-1}.

Compounds **2** and **3** were prepared same as compound **1**

{$Pt[P(C_6H_4CH_3)_3]_2[(CH_2)_2S(O)(CH_3)]$}I (2)

Anal. Found: C, 52.4; H, 4.8. $C_{45}H_{49}IOP_2PtS$ calcd.: C, 52.9; H, 4.8%. IR ν(SO): 1197 cm^{-1}. ^1H NMR ($CDCl_3$): 7.5–7.1 (m, 30 H, phenyl protons), 3.54 (t, ^4J(PtH) 9.0 Hz, 3 H, SCH_3), 2.6–2.0 (m, 4 H, SCH_2), 2.3 (S, 18 H, $C_6H_4CH_3$) ppm. Molar conductivity (acetone, 2.0×10^{-4} *M*) 109 Ω^{-1} cm^2 mol^{-1}.

{$Pt[PPh(CH_3)_2]_2[(CH_2)_2S(O)(CH_3)]$}I (3)

Anal. Found: C, 32.2; H, 4.1. $C_{19}H_{29}IOP_2PtS$ calcd.: C, 33.1; H, 4.2%. IR ν(SO): 1186 cm^{-1}. ^1H NMR ($CDCl_3$): 7.6–7.1 (m, 10 H, phenyl protons), 3.70 (t of t, ^4J(HH) 1.8 Hz, ^4J(PtH) 9.0 Hz, 3 H, SCH_3), 3.6–2.2 (m, 4 H, SCH_2), 1.77 and 1.70 (2 sets of 1:1:4:4:1:1, ^3J(PtH) 36.0 Hz, ^2J((P, H) 12.0 Hz, 6 H, PCH_3) ppm. Molar conductivity (acetone, 4.1×10^{-3} *M*) 128.2 Ω^{-1} cm^2 mol^{-1}.

{$Pt(PPh_2CH_3)_2[(CH_2)_2S(O)(CH_3)]$}$PF_6$ (4)

Using the same stoichiometry as in the preparation of **1**, treating $Pt(PPh_2CH_3)_2Cl_2$ with $[S(O)Me_3]Cl$ under NaOH in the presence of $^nBu_4NCl$ resulted in a pale yellow sticky compound in 80% yield. ^1H NMR and IR spectroscopic studies suggest the presence of {$Pt(PPh_2CH_3)_2[(CH_2)_2S(O)(CH_3)]$}Cl. However, it is difficult to isolate this compound in pure. Therefore 0.15 g of this crude product in 2 ml CH_2Cl_2 was added with 0.12 g of NH_4PF_6 in 5 ml of 95% ethanol, and a white precipitate was obtained immediately. After isolation and recrystallization from CH_2Cl_2/EtOH resulted in white crystals in 60% yield. Anal. Found: C, 41.2; H, 4.1. $C_{29}H_{33}F_6OP_3PtS$ calcd.: C, 41.9; H, 4.0%. IR ν(SO): 1188 cm^{-1}. ^1H NMR ($CDCl_3$) 7.6–7.1 (m, 20 H, phenyl protons), 3.27 (t, ^4J(PtH) 9.0 Hz, 3 H, SCH_3), 3.0–2.0 (m, 4 H, SCH_2), 1.8 (1:1:4:4:1:1, ^3J(PtH) 36.0 Hz, ^2J(PH) 12.0 Hz, 3 H, PCH_3) ppm. Molar conductance (acetone, ~ 10^{-3} *M*) 209 Ω^{-1} cm^2 mol^{-1}.

{$Pt(dppe)[(CH_2)_2S(O)(CH_3)]$}$PF_6$ (5)

$[S(O)(CH_3)_3]Cl$ (0.12g, 0.9 mmol) dissolved in 5 ml of 1.8 *N* KOH solution, was added to a 10 ml CH_2Cl_2 solution of $Pt(dppe)Cl_2$ (0.2g, 0.3 mmol) followed by $^nBu_4NCl$ (0.015 mmol). There was no apparent color change. After stirring for 12 h, the organic layer was separated and then washed 4 times with water. The organic layer was dried with $MgSO_4$, filtered and was evaporated by a vacuum rotary evaporator. The crude residue was washed with ether (20 ml) and 0.17 g of the product was obtained. This product became sticky after standing in the air. To 0.17 g of this product (in 1 ml of CH_2Cl_2), NH_4PF_6 (0.15 g in 3 ml of 95% EtOH) was added and a white solid was slowly precipitated from the mixture. The white solid was then filtered, washed with a small amount of alcohol, and then with ether. The final product was obtained in 60% yield. M.p. 205 °C (decompose). Anal. Found: C, 41.0; H, 3.7. $C_{29}H_{31}F_6OP_3PtS$ calcd.: C, 42.0; H, 3.7%. IR ν(SO) 1201 cm^{-1}. ^1H NMR ($CDCl_3$): 7.6–7.3 (m, 20 H, phenyl protons), 3.50 (t, ^4J(PtH) 9.0 Hz, 3 H, SCH_3), 3.70–2.55 (m, 4 H, SCH_2), 2.51 (m, 4 H, PCH_2) ppm. Molar conductivity (acetone, ~ 10^{-3} *M*) 192 Ω^{-1} cm^2 mol^{-1}.

$\{Pt(PPh_2CH_3)[PPh_2(OH)][(CH_2)_2S(O)(CH_3)]\}Cl$ (6)

Pt(dppm)Cl_2 (0.65 g, 1.0 mmol) in CH_2Cl_2 (10 ml) was treated with $[S(O)(CH_3)_3]Cl$ (0.39 g, 3.0 mmol) in an aqueous NaOH solution (5 ml, 1.8 *N*), and then $^nBu_4NCl$ (0.05 mmol) was added. The original pale green color solution changed to greenish-yellow and then pale yellow. The reaction was stopped after 4 h. The organic layer was washed 4 times with water, dried with $MgSO_4$, concentrated to 3 ml, and ether (20 ml) was added. The powder compound was collected and dried in the air. The yield was 85%. Anal. M.p. 157–159 °C; IR (KBr): ν(OH) 3380, ν(SO) 1180 cm^{-1}. Λ_M ($CHCl_3$, ~ 10^{-4} *M*) 15 Ω^{-1} cm^2 mol^{-1}; ^1H NMR ($CDCl_3$): 7.2–7.7 (m), 3.09 (t, *J*(HH) 1.8 Hz, 2.1–2.4 (m), 1.89 (m, *J*(PH) 10 Hz, *J*(PtH) 25.7 Hz) ppm; ^{31}P NMR ($CDCl_3$): 51.5 (m, *J*(PP) 24.4 Hz, *J*(PtP) 3215.5 Hz, 2.4 (m, *J*(PP) 24.4 Hz, *J*(PtP) 2948.5 Hz) ppm, downfield relative to

Table 1

Crystal data for $[Pt(PPh_3)_2(CH_2)_2S(O)(CH_3)]I$ (1)

Formula	$[Pt(PPh_3)_2(CH_2)_2S(O)(CH_3)]I$
Crystal size (mm)	0.8×0.6×0.5
Specific gravity	$Pna2_1$
a (Å)	19.332(4)
b (Å)	11.101(5)
c (Å)	16.936(5)
V (Å^3)	3634.57
Cell parameter determination (°)	$11.5 < \theta < 20.3$
Reflections	25
Z	4
F(000)	1824
Temperature	300 K
D_m, D_{calc} (g/cm^3)	1.6, 1.65
μ (mm^{-1})	4.91
Transmission coefficient	0.51–0.98
$2\theta_{max}$ (°)	50
h, *k*, *l*	0–22, 0–13, 0–20
λ (Å)	0.7107
No. of reflections, ($I > 3\sigma(I)$)	3301, 2756
No. of variables	226
R(*F*), R_w(*F*)	0.039, 0.029
S	2.965

85% H_3PO_4. Anal. Found: C, 46.3; H, 4.5. $C_{28}H_{31}ClO_2P_2PtS$ calcd.: C, 46.4; H, 4.3%.

{Pt(PPh$_2$CH$_3$)[PPh$_2$(OH)][(CH$_2$)$_2$S(O)(CH$_3$)]}PF$_6$ (7)

Compound **6** in a minimum amount of 95% EtOH, was added with a 4 molar ratio of NH_4PF_6. The white solid thus formed was filtered and washed with a small

Table 2
Atomic parameters for compound 1. (E.S.Ds. refer to the last digit)

	x	y	z	B_{iso}
Pt	0.107911(22)	0.29090(4)	0.00713	2.263(19)
I	0.31932(6)	0.35476(2)	0.08956(8)	7.06(7)
P(1)	0.12686(16)	0.1143(3)	−0.06036(22)	2.54(15)
P(2)	0.08647(16)	0.4109(3)	−0.10404(22)	2.78(16)
S	0.07393(19)	0.3388(3)	0.15884(22)	3.83(18)
O	0.0861(5)	0.3724(9)	0.2391(5)	5.9(6)
C(1)	0.1135(6)	0.2296(12)	0.1105(8)	5.0(7)
C(2)	0.0958(6)	0.4312(12)	0.0878(7)	3.6(7)
C(3)	−0.0151(7)	0.3115(13)	0.1457(10)	5.9(9)
C(11)	0.1484(5)	−0.0143(9)	0.0036(11)	2.98(23)
C(12)	0.2051(7)	0.0001(12)	0.0533(8)	4.6(4)
C(13)	0.2277(7)	−0.0975(13)	0.1030(9)	5.3(4)
C(14)	0.1911(7)	−0.1993(13)	0.0941(9)	5.7(4)
C(15)	0.1352(7)	−0.2201(13)	0.0424(8)	5.8(4)
C(16)	0.1144(5)	−0.1228(9)	0.0003(11)	3.38(25)
C(21)	0.2008(6)	0.1140(11)	−0.1258(8)	3.3(3)
C(22)	0.2134(6)	0.0140(12)	−0.1744(8)	4.0(3)
C(23)	0.2712(7)	0.0126(13)	−0.2225(9)	5.0(4)
C(24)	0.3154(7)	0.1087(13)	−0.2238(9)	4.8(4)
C(25)	0.3033(7)	0.2048(13)	−0.1731(8)	4.6(3)
C(26)	0.2453(6)	0.2062(12)	−0.1233(8)	3.5(3)
C(31)	0.0508(6)	0.0649(11)	−0.1136(8)	3.0(3)
C(32)	−0.0109(7)	0.0664(11)	−0.0709(8)	3.8(3)
C(33)	−0.0714(7)	0.0341(13)	−0.1052(9)	4.9(4)
C(34)	−0.0734(7)	−0.0003(13)	−0.1840(9)	5.3(4)
C(35)	−0.0146(8)	−0.0067(16)	−0.2268(10)	5.2(4)
C(36)	0.0498(7)	0.0295(12)	−0.1908(8)	4.1(3)
C(41)	0.1540(6)	0.5216(11)	−0.1247(8)	3.5(3)
C(42)	0.2108(6)	0.5341(11)	−0.0717(8)	3.1(3)
C(43)	0.2631(6)	0.6169(12)	−0.0853(8)	3.9(3)
C(44)	0.2608(7)	0.6850(13)	−0.1516(9)	5.0(4)
C(45)	0.2089(7)	0.6697(13)	−0.2054(9)	5.3(4)
C(46)	0.1516(7)	0.5913(13)	−0.1929(9)	4.3(3)
C(51)	0.0703(7)	0.3528(12)	−0.2017(8)	4.0(3)
C(52)	0.1232(6)	0.3115(11)	−0.2503(8)	3.6(3)
C(53)	0.1118(7)	0.2553(12)	−0.3213(9)	5.5(4)
C(54)	0.0414(7)	0.2430(13)	−0.3497(9)	5.8(4)
C(55)	−0.0106(8)	0.2822(13)	−0.3025(9)	5.6(4)
C(56)	0.0022(7)	0.3360(12)	−0.2289(8)	4.1(3)
C(61)	0.0085(7)	0.4951(12)	−0.0828(8)	3.4(3)
C(62)	0.0053(7)	0.6196(12)	−0.0911(9)	4.5(3)
C(63)	−0.0553(7)	0.6764(13)	−0.0704(10)	6.0(4)
C(64)	−0.1120(7)	0.6143(13)	−0.0404(9)	6.0(4)
C(65)	−0.1086(7)	0.4876(13)	−0.0312(8)	5.6(4)
C(66)	−0.0462(6)	0.4280(12)	−0.0519(8)	3.8(3)

Table 3
Selected bond lengths (Å) and angles (°) for compound 1

Pt–P(1)	2.299(3)	S–O	1.429(10)
Pt–P(2)	2.343(4)	S–C(1)	1.650(12)
Pt–C(1)	1.882(15)	S–C(2)	1.637(14)
Pt–C(2)	2.084(12)	S–C(3)	1.761(14)
P(1)–Pt–P(2)	96.51(13)	O–S–C(2)	119.6(6)
P(1)–Pt–C(1)	98.4(4)	O–S–C(3)	109.0(7)
P(2)–Pt–C(2)	94.7(4)	C(1)–S–C(2)	88.6(7)
C(1)–Pt–C(2)	70.5(5)	Pt–C(1)–S	99.8(7)
O–S–C(1)	126.0(7)	Pt–C(2)–S	92.4(6)

amount of 60% EtOH. The compound was obtained in a yield of 94%. Anal. M.p. 120 °C (decomposed); IR (KBr): ν(OH) 3380 cm^{-1}, ν(SO) 1180 cm^{-1}; A_M (CHCl$_3$, $\sim 10^{-4}$ M) 67 Ω^{-1} cm^2 mol^{-1}; ^{1}H NMR (CDCl$_3$): 7.2–7.7 (m), 3.1 (t, J(HH) 1.8 Hz), 2.1–2.4 (m), 1.85 (m, J(PH) 10 Hz, J(PtH) 25.7 Hz) ppm; ^{31}P NMR (CDCl$_3$) 67.9 (m, J(PP) 24.9 Hz, J(PtP) 3245.1 Hz, 2.3 (m, J(PP) 24.9 Hz, J(PtP) 2853.6 Hz), −143 (septet, J(PF) 706.2 Hz) ppm; Anal. Found: C, 40.3; H, 3.5. $C_{28}H_{31}F_6O_2P_3PtS$ calcd.: C, 40.4; H, 3.7%.

Structure determination and refinement of {Pt(PPh$_3$)$_2$[(CH$_2$)$_2$S(O)CH$_3$]}I

The diffraction data were collected on a CAD-4 diffractometer, and details of the experiment are given in Table 1. The structure was obtained by the heavy atom method with Pt and I atoms located in a Patterson map. All the other atoms were located in the subsequent Fourier synthesis. The usual full matrix least squares process was used to refine all the atomic positional and thermal parameters based on *F*. Because of the large number of variables, all the phenyl carbon atoms are considered to be isotropic. The agreement indices are also given in Table 1. The final atomic coordinates and equivalent isotropic thermal parameters are given in Table 2. The atomic scattering factors and anormalous dispersion coefficients were taken from International Tables for X-Ray Crystallography [22]. The selected bond lengths and angles are listed in Table 3. The molecular structure with atomic labelling of the complex **1** is shown in Fig. 1. The computer programs used are from NRCVAX [23].

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