DOI: 10.1002/chem.200500446

Platinum Complexes of Dibenzo[1,2]Dithiin, Dibenzo[1,2]Dithiin Oxides and Related Polyaromatic Hydrocarbon Ligands

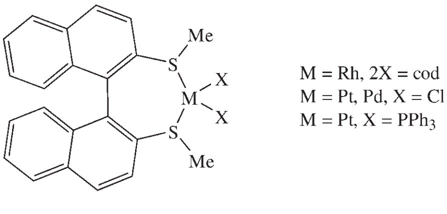
Stephen M. Aucott, Petr Kilian, Stuart D. Robertson, Alexandra M. Z. Slawin, and J. Derek Woollins*[a]

Abstract: The synthesis of platinum bisphosphine complexes of biphenyl-2,2′-dichalcogenates and the oxides of dibenzo[1,2]dithiin and related ligand systems by oxidative addition to [Pt-$(PPh_3)_4$] is reported. We also describe the synthesis of a new compound, dibenzothiophen-4-yldiselenide and its simple platinum complex (obtained by oxidative addition). All complexes have been fully characterised, principally by using multinuclear NMR spectroscopy and in six cases by means of single-crystal X-ray diffraction studies. The majority are simple S/S or Se/Se complexes, however the addition of dibenzo[1,2]dithiin trioxide to [Pt-$(PPh_3)_4$] gives a bimetallic system, [Pt-{2-[S(O)],2′-[S$(O)_2$]-biphen}(PPh_3)]$_2$, containing a central $Pt_2S_2O_2$ core in which the ligand behaves as a tridentate S,S,O donor.

Keywords: coordination · oxygen · platinum · sulfur · X-ray diffraction

Introduction

The coordination chemistry of dibenzo[1,2]dithiin and its structurally related compounds has been largely overlooked. A number of complexes containing the structurally related ligand 1,1′-binaphthalene-2,2′-dithiol have been prepared but in each case these have been formed in straightforward metathesis reactions. In many of these reactions, the purpose has been to develop complexes for catalytic polymerisation reactions such as the regioselective hydroformylation of styrene,[1] for example, by reaction of the dithiol with [Rh(μ-OMe)(cod)]$_2$ (cod = 1,5-cyclooctadiene) to give a rhodium dimer with a bridging disulfide ligand. Complexes containing the ligand 4,4-biphenanthrene-3,3′-dithiol have also been shown to react with carbon monoxide[2,3] to give interesting dinuclear tetracarbonyl complexes and with PR_3 (R = Ph, C_6H_{11}, $OC_6H_4(o\text{-}t\text{Bu})$) to give mixed-ligand di- and tetranuclear complexes. Monomeric complexes[4,5] that are formed from the related thio ether ligand are known.



Ruiz et al. also produced an interesting palladium dimer complex by using the mixed thiol thio ether derivative[6] which was shown to convert to a monomer on addition of triphenylphosphine [Eq. (1)].

Although these examples contain structurally similar ligands, a limited number of complexes containing the biphenyl dithiolate ligand are known. A derivatised version of dibenzo[1,2]dithiin has been bound to copper[7] and a molybdenum complex[8] containing two biphenyl dithiolate ligands in a distorted-square-planar-like complex with a molybdenum oxygen triple bond are also known. Mono- and dinuclear nickel complexes have also been reported.[9]

Rauchfuss et al.[10] reported the synthesis of titanocene 2,2′-dithiolatobiphenyl by ring opening of dibenzothiophene with lithium metal followed by addition of sulfur and titanocene dichloride giving the final product from a salt-elimination reaction. Recently, our group has shown[11] that this complex can also be produced by oxidative addition of dibenzo[1,2]dithiin with titanocene dicarbonyl (Ti^{II}). We have also shown[12] that the structurally similar compound naphtho[1,8-*cd*][1,2]dithiole can be added oxidatively to Pt^0 to give the Pt^{II} complex [Pt$(S_2C_{10}H_6)(PPh_3)_2$].

While the literature pertaining to complexes of dibenzo[1,2]dithiin and related complexes is sparse, there are no ex-

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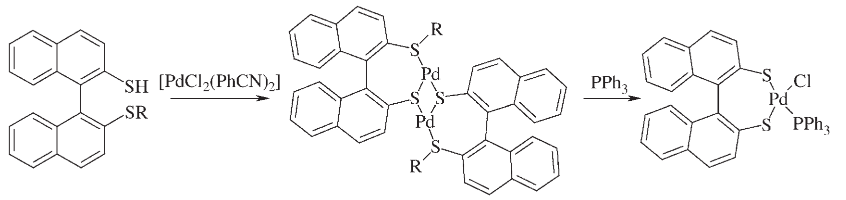
[a] Dr. S. M. Aucott, Dr. P. Kilian, S. D. Robertson,
Prof. A. M. Z. Slawin, Prof. J. D. Woollins
Department of Chemistry, University of St Andrews
Fife, Scotland KY16 9ST (UK)
Fax: (+44) 1334-463-384
E-mail: jdw3@st-andrews.ac.uk



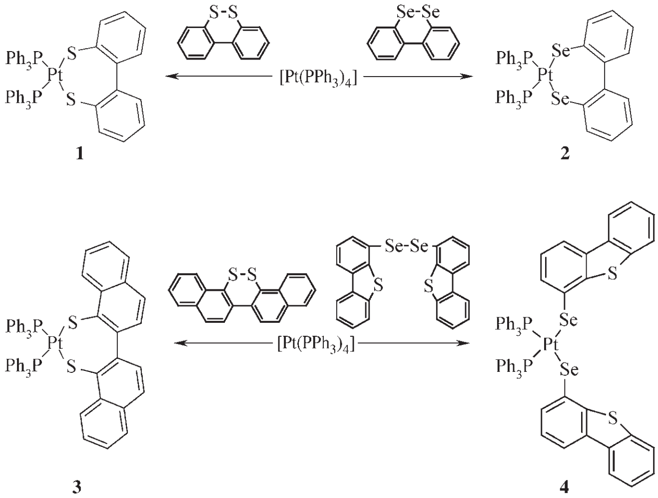
amples of biphenyl-2,2′-thiolato–sulfenato (-S−M−S(=O)-), thiolato–sulfinato (-S−M−S(=O)$_2$-) or disulfinato (-(O=)$_2$S−M−S(=O)$_2$-) metal complexes. Compared to the number of known thiolate complexes in the literature, there are very few known transition-metal complexes of sulfenato (-S(=O)R) or sulfinato (-S(=O)$_2$R).[13] Thiolato–sulfenato complexes have been obtained from oxidative addition reactions of cyclic thiosulfinates with Pt^0 precursors[14–20] and dithiirane 1-oxides[21] or by the mono-oxidation of the corresponding dithiolate complex, for example, the dinuclear iron complexes [{(OC)$_3$Fe}$_2$SCH$_2$CH$_2$S(=O)] and [{(OC)$_3$Fe}$_2$SC$_6$H$_{10}$S(=O)] which contain the bridging 1,2-ethanesulfenatothiolato and 1,2-cyclohexylsulfenatothiolato ligands, respectively.[22,23] Darensbourg et al. have used this oxidation method to prepare a series of thiolato–sulfenato, disulfenato, thiolato–sulfinato, sulfenato–sulfinato and disulfinato complexes of Ni^{II} and Pd^{II} from bis(2-mercaptoethyl-1,5-diazacyclooctane–M^{II} (M = Ni, Pd) and *N*,*N*′-bis(2-methyl-2-mercaptopropyl)-1,5-diazacyclooctane–Ni^{II}.[24–28] Other examples of these types of complexes formed by oxidation of the corresponding thiolate complexes are also known.[29–34] We have recently shown[12] that oxidative addition of the S–S bridged mono-, di- and trioxides of naphtho[1,8-*cd*][1,2]dithiole to [Pt(PPh$_3$)$_4$] takes place with relative ease and that the phosphine group *trans* to either the thiolato, sulfenato or sulfinato group gives a very distinctive and diagnostic coupling constant in the ^{31}P NMR spectra.

This paper describes the synthesis of platinum bisphosphine complexes of biphenyl-2,2′-dichalcogenates and the oxides of dibenzo[1,2]dithiin and related ligand systems by oxidative addition. We also describe the synthesis of a new compound, dibenzothiophen-4-yldiselenide. All complexes have been fully characterised, principally by using multinuclear NMR spectroscopy and in selected cases by means of single-crystal X-ray diffraction studies.

Results and Discussion

Platinum complexes of dibenzo[1,2]dithiin and related complexes: Oxidative addition reactions of dibenzo[1,2]dithiin, dibenzo[1,2]diselenin, dinaphtho[1,2-*c*:2′,1′-*e*][1,2]dithiin and dibenzothiophen-4-yldiselenide with [Pt(PPh$_3$)$_4$] all proceeded smoothly to give, in reasonable to excellent yield (55–92 %), [Pt(2,2′-S$_2$-biphen)(PPh$_3$)$_2$] (**1**; biphen = biphenyl), [Pt(2,2′-Se$_2$-biphen)(PPh$_3$)$_2$] (**2**), [Pt(2,2′-S$_2$-binap)(PPh$_3$)$_2$] (**3**; binap = binaphthalene) and [Pt(4-Se-dbt)$_2$(PPh$_3$)$_2$] (**4**; dbt = dibenzothiophene), respectively (Scheme 1).

The purification and isolation of these compounds was straightforwardly carried out by filtration through a shallow pad of silica gel and elution with dichloromethane followed by evaporation of the filtrate and precipitation of the product with diethyl ether or hexane. The ^{31}P{^{1}H} NMR spectra (CD$_2$Cl$_2$) of complexes **1**–**4** display the anticipated single resonances with platinum satellites at δ(P) = 23.1 ($^1J(^{31}P,^{195}Pt) = 2956$ Hz), 18.7 ($^1J(^{31}P,^{195}Pt) = 2990$ Hz), 23.0 ($^1J(^{31}P,^{195}Pt) = 2971$ Hz) and 19.7 ppm ($^1J(^{31}P,^{195}Pt) = 3046$ Hz), respectively, with additional ^{77}Se satellites ($^2J(^{31}P,^{77}Se) = 49$ Hz) observed in the spectrum of **2**. The expected selenium satellites in **4** are not observed, due to the poor solubility of this sample in dichloromethane causing a weaker spectrum. The ^{195}Pt NMR spectra (CD$_2$Cl$_2$) show triplets at δ(Pt) = −4553, −4785, −4530 and −4843 ppm for **1**–**4**, respectively (Table 1). We were unable to obtain ^{77}Se NMR due to the low solubility of the selenium-containing complexes.



Scheme 1. Oxidative addition reactions to prepare complexes **1**, **2**, **3** and **4**.

Satisfactory elemental analyses (Table 2) were obtained for these complexes and FAB$^+$ or electrospray(+) mass spectrometry showed *m*/*z* corresponding to [*M*+H]$^+$ and [*M*+Na]$^+$, respectively.

Platinum complexes of dibenzo[1,2]dithiin oxides: Complexes **5**, **6** and **7** were also prepared by oxidative addition of the S–S bridged mono-, di- and trioxides of dibenzo[1,2]dithiin, respectively, to [Pt(PPh$_3$)$_4$] in toluene at room temperature (Scheme 2).

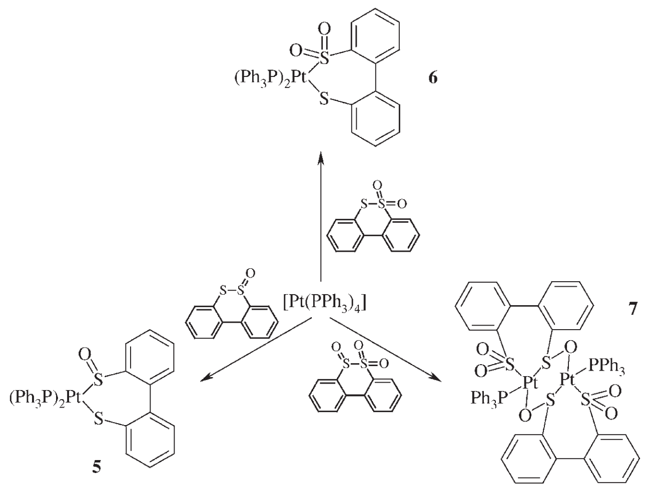
The formation of binuclear **7** is in marked contrast to the reaction with the analogous naphthalene compound which gave a simple bidentate S/S complex.[12] In the naphthalene case, the rigid backbone restrains the oxygen atoms from

Table 1. $^{31}P\{^1H\}$ and ^{195}Pt NMR data for complexes **1** to **7**.

	Chemical shifts [ppm]			Coupling constants [Hz]		
	$\delta(^{31}P_A)$	$\delta(^{31}P_X)$	$\delta(^{195}Pt)$	$^1J(P_A,Pt)$	$^1J(P_X,Pt)$	$^1J(P_A,P_X)$
1	23.1	–	−4553	2956	–	–
2	18.7	–	−4785	2990	–	–
3	23.0	–	−4530	2971	–	–
4	19.7	–	−4843	3046	–	–
5	19.2	23.7	−4234	2295	3542	26
6	14.2	20.5	−4374	2436	3130	22
7	23.3	–	−5515	3303	–	–

Table 2. Microanalytical data for complexes **1** to **7** (calculated values in parentheses).

	C	H	S
$[Pt(2,2'-S_2-biphen)(PPh_3)_2]$ (**1**)	61.45 (61.60)	4.05 (4.09)	6.90 (6.85)
$[Pt(2,2'-Se_2-biphen)(PPh_3)_2]$ (**2**)	56.12 (55.99)	3.77 (3.72)	–
$[Pt(2,2'-S_2-binap)(PPh_3)_2]$ (**3**)	65.20 (64.91)	4.04 (4.09)	6.33 (6.18)
$[Pt(4-Se-dbt)_2(PPh_3)_2]$ (**4**)	57.49 (57.93)	3.60 (3.56)	5.03 (5.15)
$[Pt\{1-S,1-[S(O)]-biphen\}(PPh_3)_2]$ (**5**)	60.23 (60.56)	3.85 (4.02)	6.61 (6.74)
$[Pt\{1-S,1-[S(O)_2]-biphen\}(PPh_3)_2]$ (**6**)	60.01 (59.56)	4.01 (3.96)	6.43 (6.63)
$[Pt\{1-[S(O)],1-[S(O)_2]-biphen\}(PPh_3)]_2$ (**7**)	50.16 (49.93)	3.28 (3.21)	8.76 (8.88)



Scheme 2. Oxidative addition reactions to prepare complexes **5**, **6** and **7**.

twisting to enable coordination whereas the biphenyl backbone allows S-O-Pt bridging to occur.

Solids **5**–**7** were obtained in good yield (78–89%). The $^{31}P\{^1H\}$ NMR (CD_2Cl_2) data for **5** and **6** are both of the AX type with corresponding platinum satellites. The phosphorus resonances and $^1J(^{31}P,^{195}Pt)$ coupling constants of complex **5**, $\delta(P_A) = 19.2$ (2295 Hz) and $\delta(P_X) = 23.7$ ppm (3542 Hz), are assigned to the phosphine groups *trans* to the sulfenato (-S(O)R) and the thiolato (-SR) groups, respectively, in accordance with previously published work on platinum phosphine complexes containing a mixture of thiolato, sulfenato or sulfinato ligands *trans* to the phosphine groups.[12] For complex **6**, the phosphorus resonances and $^1J(^{31}P,^{195}Pt)$ coupling constants, $\delta(P_A) = 14.2$ (2436 Hz) and $\delta(P_X) = 20.5$ ppm (3130 Hz), are assigned to the phosphine groups *trans* to the sulfinato ($-S(O)_2R$) and the thiolato (-SR) groups, respectively. The dimeric compound **7** shows only one resonance in the phosphorus NMR with phosphorus satellites at $\delta(P_A) = 23.3$ ppm ($^1J(^{31}P, ^{195}Pt) = 3303$ Hz). The $^{31}P\{^1H\}$ NMR spectra of **5** and **6** also show the characteristic $^2J(^{31}P_A,^{31}P_X)$ couplings of 26 and 22 Hz, respectively, which are consistent with unsymmetrically substituted platinum *cis*-diphosphine complexes. The ^{195}Pt NMR data (CD_2Cl_2) are all consistent with the proposed structures of **5**, **6** and **7**. The spectra of **5** and **6** both exhibit a doublet of doublets with the appropriate coupling constants centred at $\delta = -4234$ and -4374 ppm, respectively, while the spectrum of **7** shows a doublet centred at $\delta = 5515$ ppm (3300 Hz). IR (KBr disc) data for complexes **5**–**7** were consistent with the structural assignments showing $\tilde{\nu}(S{=}O)$ bands for complex **5** at approximately 1100 cm^{-1} and $\tilde{\nu}(S\{{=}O\}_2)$ bands for **6** at approximately 1200 and 1060 cm^{-1}. Complex **7** displys a slightly different infrared spectrum. The $\tilde{\nu}(S\{{=}O\}_2)$ bands are still present at 1208 and 1071 cm^{-1} but there is no evidence of the S=O bond. Instead, this complex contains an S−O−Pt bond and therefore the band at 843 cm^{-1} is assigned to this stretching vibration.

Satisfactory elemental analyses (Table 2) were obtained for these complexes and FAB^+ or electrospray(+) mass spectrometry showed *m*/*z* corresponding to $[M+H]^+$ and $[M+Na]^+$, respectively.

X-ray crystallography: The crystal structures of complexes **1**, **2**, **4**, **5**, **6** and **7** are shown in Figures 1 and 2 and selected bond lengths and angles are given (Tables 3 and 4). The X-ray analyses show that the platinum core of complexes **1**, **2**, **5** and **6**, like their naphthalene-backboned equivalents,[12] lie at the centre of a distorted-square-planar coordination sphere. The P(1)-Pt(1)-P(2) angles are in the range of 96–98°, in accord with previously published examples such as $[(PPh_3)_2Pt(ttn)Pt(PPh_3)_2]$ (ttn = tetrathionaphthalene).[35] The corresponding S(1)-Pt(1)-S(8) angles of **1**, **5** and **6** are in the range of 87–91°, while the Se(1)-Pt(1)-Se(8) angle of **2** is 91.47(3)°, close to idealised square-planar geometry and larger than those corresponding angles in $[Pt(S_2C_{10}H_6)(PPh_3)_2]$, $[Pt(Se_2C_{10}H_6)(PPh_3)_2]$, $[Pt(S_2OC_{10}H_6)(PPh_3)_2]$ and $[Pt(S_2O_2C_{10}H_6)(PPh_3)_2]$.[12] This can be explained by considering that this angle is part of a seven-membered PtE_2C_4 (E = S or Se) ring rather than a six-membered PtE_2C_3 ring. The presence of the extra carbon in the ring reduces strain and allows the sulfur atoms more flexibility to settle in a square-planar geometry. The C-E-Pt bond angles are found to be vastly different on each side of these complexes (102.8(4) and 115.7(4)° (**1**), 103.6(2) and 107.6(2)° (**2**), 102.3(4) and 116.3(6)° (**5**) and 112.9(2) and 106.0(2)° (**6**)). This is explained by the flexibility in the biphenyl backbone, which is also observed in the free ligand,[36] where the two

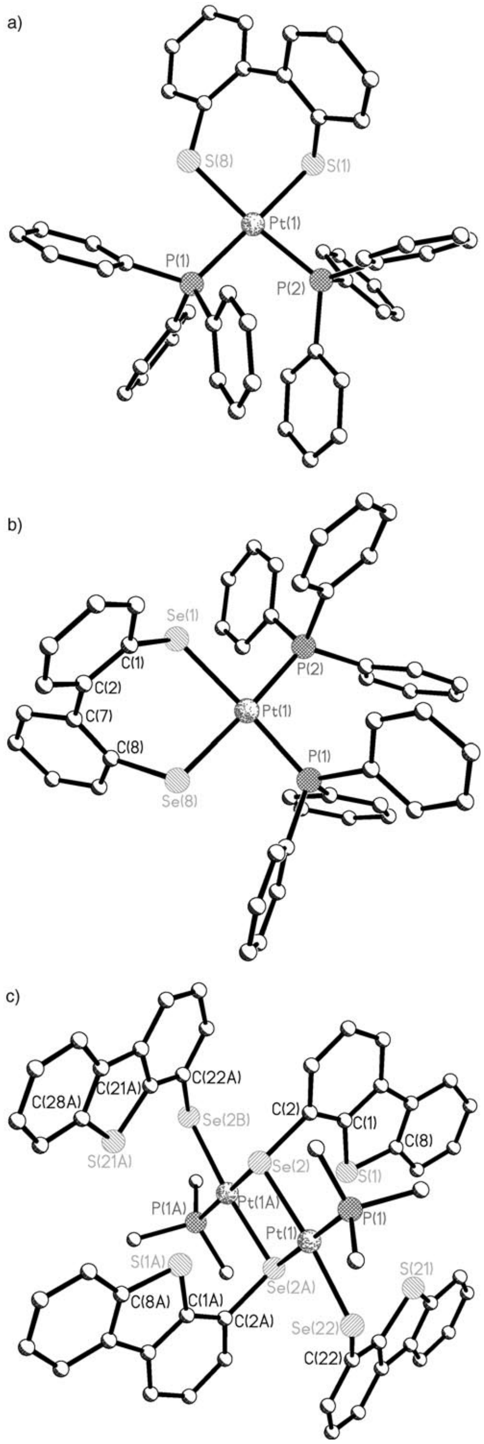


Figure 1. Crystal structures: a) [Pt(2,2′-S$_2$-biphen)(PPh$_3$)$_2$] (**1**); b) [Pt(2,2′-Se$_2$-biphen)(PPh$_3$)$_2$] (**2**); c) [Pt(4-Se-dbt)$_2$(PPh$_3$)]$_2$ obtained during efforts to recrystallise **4**.

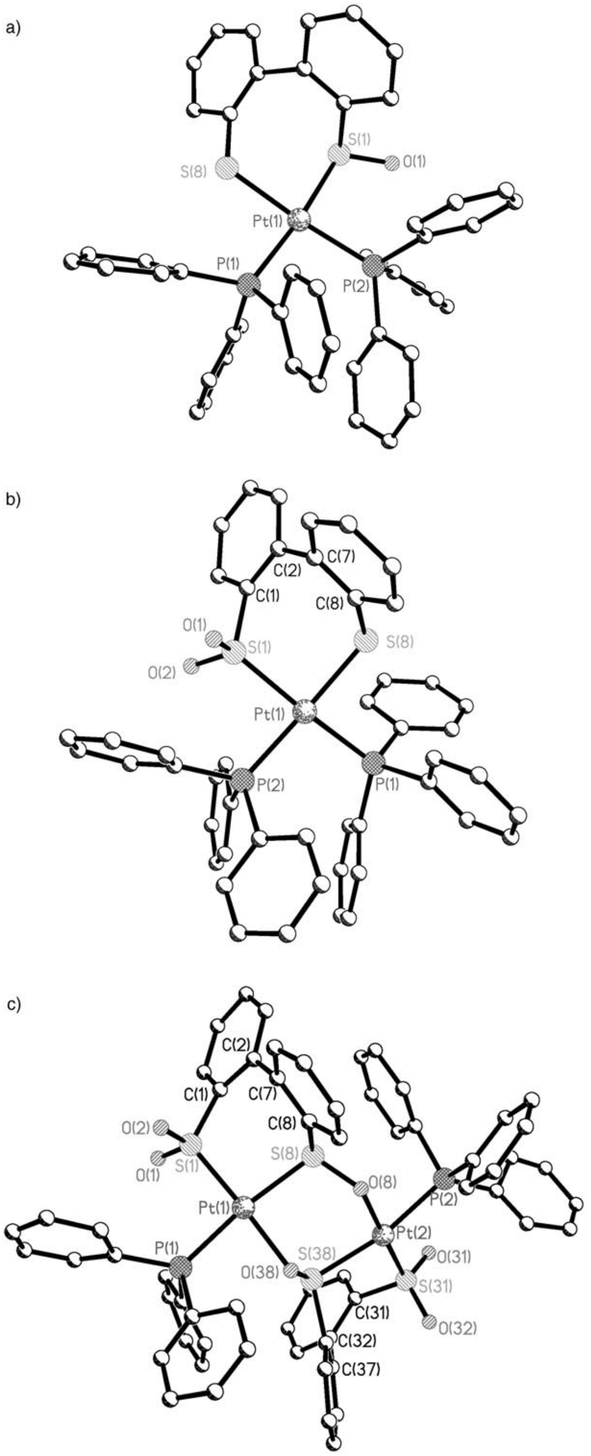


Figure 2. Crystal structure of a) [Pt{2-S,2′-[S(O)]-biphen}(PPh$_3$)$_2$] (**5**), b) [Pt{2-S,2′-[S(O)$_2$]-biphen}(PPh$_3$)$_2$] (**6**) and c) [Pt{2-[S(O)],2′-[S(O)$_2$]-biphen}(PPh$_3$)]$_2$ (**7**).

C_6 rings are not co-planar. In fact, the two C_6 rings are angled more pronouncedly than in the free ligands, with the C(1)-C(2)-C(7)-C(12) angles of **1**, **5** and **6** in the range of 54.6(7)–56.2(9)° while those of the free ligands are in the range of 28.2(3)–37.3(3)°.[36] The C(1)-C(2)-C(7)-C(12) angle of **2** is greater than that of the sulfur-containing derivatives (62.0(8)°).

The nonbonded S–S distances of 3.353(10) (**1**), 3.219(6) (**5**) and 3.334(6) Å (**6**) are much larger than those in the S–S bonded precursors,[36] and are significantly larger than the

Table 3. Selected bond lengths [Å] and angles [°] for complexes **1**, **2**, **5**, **6** and **7** (E = S or Se).

	1	**2**	**5**	**6**	**7**
Pt(1)−E(1)	2.368(6)	2.4830(8)	2.338(3)	2.3249(16)	2.212(8)
Pt(1)−E(8)	2.330(10)	2.4555(8)	2.319(3)	2.3548(15)	2.347(8)
Pt(1)−P(1)	2.283(6)	2.2775(17)	2.328(3)	2.3254(14)	2.316(8)
Pt(1)−P(2)	2.295(9)	2.2895(17)	2.306(3)	2.3181(15)	–
Pt(1)−O(38)	–	–	–	–	2.11(2)
E(1)−C(1)	1.769(10)	1.915(8)	1.834(15)	1.798(8)	1.78(3)
S(1)−O(1)	–	–	1.480(8)	1.337(7)	1.46(2)
S(1)−O(2)	–	–	–	1.580(8)	1.48(2)
C(8)−E(8)	1.797(10)	1.925(7)	1.784(17)	1.796(6)	1.79(4)
S(8)−O(8)	–	–	–	-	1.58(2)
Pt(2)−S(31)	–	–	–	–	2.214(9)
Pt(2)−S(38)	–	–	–	–	2.334(8)
Pt(2)−O(8)	–	–	–	–	2.09(2)
Pt(2)−P(2)	–	–	–	–	2.316(8)
S(31)−O(31)	–	–	–	–	1.47(2)
S(31)−O(32)	–	–	–	–	1.44(2)
S(31)−C(31)	–	–	–	–	1.82(3)
C(31)−C(32)	–	–	–	–	1.39(5)
C(32)−C(37)	–	–	–	–	1.56(4)
C(37)−C(38)	–	–	–	–	1.42(5)
C(38)−S(38)	–	–	–	–	1.81(3)
S(38)−O(38)	–	–	–	–	1.62(2)
P(1)-Pt(1)-P(2)	97.21(12)	97.28(6)	96.90(11)	96.13(5)	–
P(1)-Pt(1)-E(8)	88.11(12)	86.37(5)	87.05(12)	86.03(5)	173.0(3)
P(2)-Pt(1)-E(8)	174.51(11)	174.10(5)	175.78(12)	177.24(5)	–
P(1)-Pt(1)-E(1)	178.72(14)	177.67(5)	174.04(13)	170.75(6)	94.4(3)
P(2)-Pt(1)-E(1)	83.64(13)	84.79(5)	88.66(11)	87.26(5)	–
E(1)-Pt(1)-E(8)	91.07(13)	91.47(3)	87.46(12)	90.86(6)	92.6(3)
P(1)-Pt(1)-O(38)	–	–	–	–	82.9(6)
S(1)-Pt(1)-O(38)	–	–	–	–	176.8(6)
S(8)-Pt(1)-O(38)	–	–	–	–	90.1(6)
C(1)-E(1)-Pt(1)	102.8(4)	103.6(2)	102.3(4)	112.9(2)	113.4(11)
O(1)-S(1)-C(1)	–	–	102.1(8)	102.1(4)	105.7(14)
O(1)-S(1)-Pt(1)	–	–	115.2(4)	112.9(2)	107.4(10)
O(2)-S(1)-C(1)	–	–	–	93.4(4)	102.5(14)
O(2)-S(1)-Pt(1)	–	–	–	107.1(3)	115.7(7)
O(1)-S(1)-O(2)	–	–	–	115.8(2)	117.7(12)
C(8)-E(8)-Pt(1)	115.7(4)	107.6(2)	116.3(6)	106.0(2)	95.7(12)
C(8)-S(8)-O(8)	–	–	–	–	99.8(14)
O(8)-S(8)-Pt(1)	–	–	–	–	106.5(9)
E(1)-C(1)-C(2)	121.0(8)	122.7(6)	117.7(17)	122.1(5)	124.0(2)
C(1)-C(2)-C(7)	122.5(9)	120.1(7)	122.9(17)	124.2(6)	122.0(3)
C(2)-C(7)-C(8)	125.4(9)	123.4(7)	124.4(15)	122.2(5)	120.0(3)
C(7)-C(8)-E(8)	125.3(7)	122.8(6)	125.0(14)	122.8(5)	119.0(3)
Pt(2)-O(8)-S(8)	–	–	–	–	119.0(11)
P(2)-Pt(2)-S(31)	–	–	–	–	97.6(3)
P(2)-Pt(2)-S(38)	–	–	–	–	168.5(3)
P(2)-Pt(2)-O(8)	–	–	–	–	81.6(6)
S(31)-Pt(2)-S(38)	–	–	–	–	92.1(3)
S(31)-Pt(2)-O(8)	–	–	–	–	179.2(6)
O(8)-Pt(2)-S(38)	–	–	–	–	88.7(6)
Pt(2)-S(31)-C(31)	–	–	–	–	107.6(11)
Pt(2)-S(31)-O(31)	–	–	–	–	110.8(10)
Pt(2)-S(31)-O(32)	–	–	–	–	109.4(11)
O(31)-S(31)-O(32)	–	–	–	–	119.1(15)
O(31)-S(31)-C(31)	–	–	–	–	101.7(14)
O(32)-S(31)-C(31)	–	–	–	–	107.4(15)
S(31)-C(31)-C(32)	–	–	–	–	121.0(2)
C(38)-S(38)-Pt(2)	–	–	–	–	109.4(11)
C(38)-S(38)-O(38)	–	–	–	–	99.0(13)
O(38)-S(38)-Pt(2)	–	–	–	–	106.2(8)
C(31)-C(32)-C(37)	–	–	–	–	129.0(3)
C(32)-C(37)-C(38)	–	–	–	–	118.0(3)
C(37)-C(38)-S(38)	–	–	–	–	118.0(2)
Pt(1)-O(38)-S(38)	–	–	–	–	108.3(10)
C(1)-C(2)-C(7)-C(12)	56.2(9)	62.0(8)	56.0(8)	54.6(7)	53.0(4)
C(31)-C(32)-C(37)-C(42)	–	–	–	–	49.0(4)

corresponding distances in the naphthalene-backboned derivatives.[12] The same is noticed in the nonbonded Se–Se distance of **2**, 3.54(1) Å, which is much greater than the bond length of the free ligand (2.323(2) Å).[37] This nonbonded distance is greater than that of the complex $[Pt(Se_2C_{10}H_6)(PPh_3)_2]$[12] and is close to the van der Waals radius of selenium. The Pt−S$_{\text{(thiolato)}}$ bond lengths of **1**, **5** and **6** (2.319(2)–2.368(6) Å), the Pt−S$_{\text{(sulfenato)}}$ bond length of **5** (2.338(3) Å) and the Pt−S$_{\text{(sulfinato)}}$ bond length of **6** (2.3249(16) Å) are all very similar and close to those seen in previously reported platinum complexes.[12] Similarly, the Pt−Se bond lengths of complex **2** are very close to those of known Pt−Se containing complexes.[12,38,39]

The *trans* influence of the sulfur ligand in relation to Pt−P bond lengths has been comprehensively discussed previously.[12] Complexes **1**, **5** and **6** have Pt−P$_{(\textit{trans}\text{ to thiolato})}$ bond lengths in the range of 2.283(6)–2.3181(15) Å. The Pt−P$_{(\textit{trans}\text{ to sulfenato})}$ bond length of **5** (2.328(3) Å) and the Pt−P$_{(\textit{trans}\text{ to sulfinato})}$ bond length of **6** (2.3254(14) Å) are both longer than the Pt−P$_{(\textit{trans}\text{ to thiolato})}$ bond lengths.

The S=O bond length of **5** is 1.480(8) Å, a value very similar to those in other complexes containing a metal centre bound to a sulfenato group,[12] and also virtually identical to the same distance in the free ligand.[40] However, the two S=O bond lengths of **6** are quite different, (1.337(7) and 1.580(8) Å). These values are much smaller and greater, respectively, than the normal values seen in complexes such as **5** or the analogous complex $[Pt(S_2O_2C_{10}H_6)(PPh_3)_2]$,[12] an observation for which we have no explanation.

Table 4. Selected bond lengths [Å] and angles [°] for complex **4**.

Bond length		Angle	
Pt(1)−P(1)	2.2644(18)	P(1)-Pt(1)-Se(22)	87.43(5)
Pt(1)−Se(2)	2.4667(7)	P(1)-Pt(1)-Se(2)	96.15(5)
Pt(1)−Se(2A)	2.4595(7)	P(1)-Pt(1)-Se(2A)	175.27(5)
Pt(1)−Se(22)	2.4403(8)	Se(2)-Pt(1)-Se(22)	174.82(3)
Se(2)−C(2)	1.917(7)	Se(2)-Pt(1)-Se(2A)	82.82(2)
Se(22)−C(22)	1.916(7)	Se(2A)-Pt(1)-Se(22)	93.92(2)
		Pt(1)-Se(2)-C(2)	105.5(2)
		Pt(1)-Se(2)-Pt(1A)	97.18(2)
		C(2)-Se(2)-Pt(1A)	105.9(2)

Complex **7** exists as a platinum dimer complex containing a six-membered $Pt_2S_2O_2$ ring with two seven-membered PtS_2C_4 rings on either side. This six-membered ring is very rare, as soft platinum usually bonds preferentially to soft sulfur. Only one other example of a six-membered $Pt_2S_2O_2$ ring is known, formed by hydrolysis of $[Pt(NSO)_2(PMe_2Ph)_2]$ to give $[\{Pt(SO_3)(PMe_2Ph)_2\}_2]$.[41]

The S-Pt-O angles of **7** (90.1(6) and 88.7(6)°) are very close to idealised square-planar geometry. The S-Pt-S angles (92.6(3) and 92.1(3)°) are marginally wider than those of **1**, **5** and **6**. The other angles around platinum (S-Pt-P 94.4(3) and 97.6(3), P-Pt-O 82.9(6) and 81.6(6)°) demonstrate that the geometry is distorted square planar. Like complexes **1**, **5** and **6**, complex **7** has vastly different Pt-S-C angles (113.4(11) and 95.7(12)°) at Pt(1) whilst the same angles at Pt(2) are closer to each other (107.6(11) and 109.4(11)°). The reason for the vast difference at Pt(1) is the same as for complexes **1**, **5** and **6**: the flexibility in the biphenyl backbone (53°) causes twisting which removes any similarity between these two angles. The biphenyl backbone of the ligand bound at Pt(2) is closer to being planar (C(31)-C(32)-C(37)-C(42) = 49(4)°), giving a less drastic difference between the two Pt−S−C bond angles.

The nonbonded S–S distances (S(1)–S(8) = 3.30(1) and S(31)–S(38) = 3.28 Å) are close to those of complexes **1**, **5** and **6** and suggests that there is no bonding interaction between the two sulfur atoms. This is again due to the increased S-Pt-S angle forcing the two sulfur atoms apart.

The $Pt(1){-}S_{(sulfenato)}$ and $Pt(1){-}S_{(sulfinato)}$ bond lengths of **7** are 2.347(8) and 2.212(8) Å, respectively. The $Pt{-}S_{(sulfenato)}$ bond length is similar to the corresponding bond length in **5**, but the $Pt{-}S_{(sulfinato)}$ distance is markedly shorter than the corresponding distance in **6**. Reedijk et al.[42] have discussed Ni−S distances in a range of Ni−S and Ni−S(O) systems. The major effect is likely to be associated with the sulfur oxidation state, though there may be a *trans* influence of the opposite oxygen atom. The oxygen atom is a poor π acceptor, resulting in a shortening of the Pt−S bond length as the sulfur atom accepts the electron density of the metal d orbitals. This shortened Pt−S distance is also observed on the opposite side of the molecule (Pt(2)−S(38) = 2.334(8), Pt(2)−S(31) = 2.214(9) Å) for the same reason.

The S=O bond lengths of **7** (1.44(2)–1.48(2) Å) are very similar to those of **5** and also to those of other platinum complexes containing a mixture of thiolato, sulfenato or sulfinato groups,[12] and to that of the free ligand.[36] The S−O bond lengths (1.58(2) and 1.62(2) Å) are longer than the S=O bond lengths and are typical for sulfur–oxygen single bonds. These values are very similar to those of other known S-O-M complexes (M = Ti).[11]

By using X-ray crystallography, complex **4** was found to exist as a bimetallic platinum complex containing a four-membered Pt_2Se_2 ring. This is in contrast to the spectral data of **4** in solution; mass spectrometry and ^{31}P NMR spectroscopy suggest that it exists as a monomer with the formula $[Pt(SeC_{12}H_7S)_2(Ph_3P)_2]$. We believe that the monomeric **4** loses triphenylphosphine and dimerises during crystallisation. We have been unable to isolate crystalline monomeric **4** to date. The platinum atoms lie at the centre of a distorted-square-planar coordination sphere, consisting of three selenium atoms and one phosphorus atom. Two of the three selenium atoms are bridging between the two platinum atoms and belong to a molecule of 4-selenadibenzothiophene. The other selenium atom also belongs to a molecule of 4-selenadibenzothiophene but this ligand is terminal rather than bridging. These ligands are one half of the proligand dibenzothiophen-4-yldiselenide, showing that the platinum atom has undergone oxidative addition between the two selenium atoms. The C(2)-Se(2)-Pt(1) and C(2)-Se(2)-Pt(1A) angles are very close (105.5(2) and 105.9(2)°, respectively) showing that the C(2) atom does not sit in the plane of the four-membered ring but rather sits above the plane, with the Se−C bond almost perpendicular to the two Se−Pt bonds. The Se(2)-Pt(1)-Se(22) (174.82(3)°) and Se(2A)-Pt(1)-P(1) angles (175.27(5)°) show that the selenium atom of the terminal 4-selenadibenzothiophene and the phosphorus atom of the PPh_3 group both lie in the plane of the Pt_2Se_2 group.

The Pt−Se and Pt−P bond lengths of complex **4** are unremarkable and are found to be close to the other selenium-bound platinum complex $[Pt(Se_2C_{10}H_6)(Ph_3P)_2]$.[12]

Experimental Section

General: Unless otherwise stated, manipulations were performed under an oxygen-free nitrogen or argon atmosphere by using standard Schlenk techniques and glassware. Solvents were dried, purified and stored according to common procedures. Dibenzo[1,2]dithiin,[43] dibenzo-[1,2]diselenin,[44] 13,14-dithiapicene,[45] dibenzo[1,2]dithiin-5-oxide,[46] dibenzo[1,2]dithiin-5,5-dioxide,[47] dibenzo[1,2]dithiin-5,5,6-trioxide[47] and $[Pt(PPh_3)_4]$[48] were prepared according to literature procedures, *cis*-$[PtCl_2(PPh_3)_2]$ was synthesised by the addition of two equivalents of the appropriate phosphine ligand to $[PtCl_2(cod)]$ in dichloromethane. All other reagents were obtained commercially.

Infrared spectra were recorded as KBr pellets in the range of 4000–220 cm^{-1} on a Perkin–Elmer system 2000 Fourier transform spectrometer. $^{31}P\{^1H\}$ (109.4 MHz) and ^{195}Pt (58.1 MHz) NMR spectra were recorded on a Jeol DELTA GSX270 spectrometer with δ(P) referenced to external 85 % H_3PO_4 and δ(Pt) to external H_2PtCl_6. ^{77}Se spectra were recorded either on a Bruker AM300 or a Jeol DELTA GSX270 spectrometer operating at 57.2 and 51.5 MHz, respectively, with δ(Se) referenced to external H_2SeO_3 (δ(Se) = 1277 ppm). Elemental analyses were performed by the St. Andrews University School of Chemistry Service and positive-ion FAB mass spectra were carried out by the EPSRC National Mass Spectrometry Service, Swansea.

Precious metal salts were provided on loan by Johnson Matthey.

The final product complexes are reasonably stable to atmospheric oxygen and moisture in the solid state but were stored for longer periods under nitrogen.

Dibenzothiophen-4-yldiselenide: A solution of 2,2′-Li(LiS)$C_{12}H_8$ was prepared.[10] Selenium (1 equiv) was added and this was allowed to stir overnight. Glacial acetic acid (25 %) in tetrahydrofuran was added (30 cm^3) and this was allowed to stir in air overnight. This was then dried under pressure and purified by chromatography on silica gel using hexane/dichloromethane (50:50) as elutant. The yellow fraction was collected and recrystallised from dichloromethane/hexane to give the final product as a yellow microcrystalline solid (0.232 g, 26 %). EI MS: *m*/*z*: 526 $[M]^+$, 263 $[{}^1\!/_2M]^+$.

[Pt(2,2′-S$_2$-biphen)(PPh$_3$)$_2$] (1): [Pt(PPh$_3$)$_4$] (0.772 g, 0.620 mmol) and dibenzo[1,2]dithiin (0.134 g, 0.619 mmol) were placed under reflux in toluene (20 cm^3) for 4 h at which point a fine yellow precipitate started to appear. The mixture was put under reflux for a further 16 h and then allowed to cool. The cooled mixture was poured onto a silica gel pad in a sintered funnel and eluted with toluene (100 cm^3) which was discarded. The desired product was eluted from the silica gel with dichloromethane (300 cm^3) giving a bright yellow solution. This was dried under reduced pressure and toluene (20 cm^3) was added to give a yellow suspension. Diethyl ether (100 cm^3) was then added to the stirred suspension and the resulting solid was collected by suction filtration, washed with diethyl ether (2 × 10 cm^3) and dried in vacuo overnight. Yield: 0.533 g, 92 %; FAB$^+$ MS: *m*/*z*: 936 $[M+H]^+$, 719/720 $[M-(S_2C_{12}H_8)]^+$.

[Pt(2,2′-Se$_2$-biphen)(PPh$_3$)$_2$] (2): [Pt(PPh$_3$)$_4$] (0.676 g, 0.543 mmol) and dibenzo[1,2]diselenin (0.168 g, 0.542 mmol) were stirred in toluene (20 cm^3) at room temperature for 30 min resulting in an orange solution. The solution was poured on to a silica gel pad in a sintered funnel and the product was eluted with dichloromethane (200 cm^3). The combined toluene reaction solvent and the dichloromethane eluent were removed under pressure and the orange residue was partially suspended in toluene (10 cm^3). To the stirred toluene suspension, diethyl ether (30 cm^3) was added giving an orange microcrystalline solid. This was collected by suction filtration, washed with diethyl ether (2 × 10 cm^3) and dried in vacuo overnight. Yield: 0.480 g, 86 %; FAB$^+$ MS: *m*/*z*: 1031 $[M+H]^+$.

[Pt(2,2′-S$_2$-binap)(PPh$_3$)$_2$] (3): [Pt(PPh$_3$)$_4$] (0.295 g, 0.237 mmol) and dinaphtho[1,2-*c*:2′,1′-*e*][1,2]dithiin (0.075 g, 0.237 mmol) were stirred in toluene (20 cm^3) at room temperature for 3 h resulting in a yellow solution. The solution was poured onto a silica gel pad in a sintered funnel and eluted with dichloromethane (100 cm^3). The combined toluene reaction solvent and the dichloromethane eluent were removed under pressure and the yellow residue was dissolved in a minimum volume of dichloromethane (approximately 3 cm^3). Diethyl ether (50 cm^3) was added to precipitate the final product as a yellow solid. This was collected by suction filtration, washed with diethyl ether (2 × 10 cm^3) and dried in vacuo overnight. Yield: 0.161 g, 66 %; ES$^+$ MS: *m*/*z*: 1058 $[M+Na]^+$.

[Pt(4-Se-dbt)$_2$(PPh$_3$)$_2$] (4): [Pt(PPh$_3$)$_4$] (0.311 g, 0.250 mmol) and dibenzothiophen-4-yldiselenide (0.066 g, 0.125 mmol) were stirred in toluene (20 cm^3) for 2 h resulting in an orange solution. The solution was poured on to a silica gel pad and eluted with dichloromethane (100 cm^3). The combined toluene reaction solvent and the dichloromethane eluent were removed under pressure and the residue was re-dissolved in a minimum volume of dichloromethane (approximately 2 cm^3). Diethyl ether (25 cm^3) followed by hexane (50 cm^3) was slowly added to precipitate the final product as an orange solid. This was collected by suction filtration, washed with diethyl ether (2 × 10 cm^3) and dried in vacuo overnight. Yield: 0.135 g, 55 %; ES$^+$ MS: *m*/*z*: 1267 $[M+Na]^+$, 1006 $[(M-PPh_3)+Na]^+$.

[Pt{2-S,2′-[S(O)]-biphen}(PPh$_3$)$_2$] (5): [Pt(PPh$_3$)$_4$] (0.563 g, 0.453 mmol) and dibenzo[1,2]dithiin-5-oxide (0.105 g, 0.452 mmol) were stirred together for 18 h resulting in a golden orange solution. The solution was poured on to a silica gel pad and eluted with dichloromethane (150 cm^3) which was discarded. The desired product was eluted from the silica gel with acetone (100 cm^3). The acetone was removed under pressure and the resulting yellow/orange residue was re-dissolved in a minimum volume of dichloromethane (approximately 3 cm^3). Diethyl ether (150 cm^3) was added to precipitate the final product as a bright yellow solid. This was collected by suction filtration, washed with diethyl ether (2 × 10 cm^3) and dried in vacuo overnight. Yield: 0.369 g, 86 %; selected IR data (KBr): $\tilde{\nu} = 1098\ cm^{-1}$ (S=O); FAB$^+$ MS: *m*/*z*: 953 $[M+H]^+$, 719/720 $[M-(S_2OC_{12}H_8)]^+$.

[Pt{2-S,2′-[S(O)$_2$]-biphen}(PPh$_3$)$_2$] (6): [Pt(PPh$_3$)$_4$] (0.322 g, 0.259 mmol) and dibenzo[1,2]dithiin-5,5-dioxide (0.064 g, 0.257 mmol) were stirred together for 18 h resulting in a golden orange solution. The solution was poured on to a silica gel pad and eluted with dichloromethane (150 cm^3) which was discarded. The desired product was eluted from the silica gel with acetone (100 cm^3). The acetone was removed under pressure and the resulting yellow/orange residue was re-dissolved in a minimum volume of dichloromethane (approximately 3 cm^3). Diethyl ether (150 cm^3) was added to precipitate the final product as a bright yellow solid. This was collected by suction filtration, washed with diethyl ether (2 × 10 cm^3) and dried in vacuo overnight. Yield: 0.195 g, 78 %; selected IR data (KBr): $\tilde{\nu} = 1180,\ 1066\ cm^{-1}$ (S{=O}$_2$); FAB$^+$ MS: *m*/*z*: 969 $[M+H]^+$, 719/720 $[M-(S_2O_2C_{12}H_8)]^+$.

[Pt{2-[S(O)],2′-[S(O)$_2$]-biphen}(PPh$_3$)]$_2$ (7): [Pt(PPh$_3$)$_4$] (0.410 g, 0.329 mmol) and dibenzo[1,2]dithiin-5,5,6-trioxide (0.087 g, 0.330 mmol) were stirred together for 18 h resulting in a yellow solution. The solution

Table 5. Crystallographic data for complexes **1**, **2**, **4**, **5**, **6** and **7**.

	1	**2**	**4**	**5**	**6**	**7**
empirical formula	$C_{48}H_{38}P_2PtS_2$	$C_{49}H_{40}C_{12}P_2PtSe_2$	$C_{91}H_{66}P_2Pt_2S_4Se_4$	$C_{48}H_{38}OP_2PtS_2$	$C_{49}H_{40}Cl_2O_2P_2PtS_2$	$C_{63}H_{52}Cl_6O_6P_2Pt_2S_4$
M_r	935.93	1114.66	2055.64	951.93	1052.86	1698.11
crystal system	monoclinic	monoclinic	triclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$	$P\bar{1}$	$P2_1/c$	$P2_1/c$	$P2_1/c$
a [Å]	10.228(3)	12.994(3)	12.8759(7)	10.2583(8)	13.0888(16)	13.354(5)
b [Å]	17.319(9)	20.561(4)	13.0591(8)	17.3039(14)	20.565(3)	14.952(5)
c [Å]	22.623(5)	17.698(4)	13.2920(7)	23.0113(19)	17.767(2)	31.510(11)
α [°]	90	90	103.912(5)	90	90	90
β [°]	99.110(5)	93.326(4)	97.926(5)	100.566	92.614(4)	100.266(6)
γ [°]	90	90	112.460(4)	90	90	90
V [Å^3]	3956(25)	4720.3(17)	1938.02(19)	4015.4(6)	4777.4(10)	6191(4)
Z	4	4	1	4	4	4
ρ_{calcd} [g cm^{-3}]	1.571	1.568	1.761	1.575	1.464	1.822
μ [mm^{-1}]	3.767	4.727	5.680	3.715	3.240	5.012
reflections measured	24407	28227	10770	17285	28166	28639
independent reflections	7128	7824	6201	5727	8513	8805
final $R1$	0.0666	0.0484	0.0408	0.0497	0.0467	0.1367
final $wR2$ [$I > 2\sigma(I)$]	0.1886	0.1080	0.0811	0.0922	0.1165	0.3692

was poured on to a silica gel pad and eluted with dichloromethane (100 cm^3) which was discarded. The desired product was eluted from the silica gel with acetone (100 cm^3). The acetone was removed under pressure and the resulting yellow residue was re-dissolved in a minimum volume of dichloromethane (approximately 3 cm^3). Diethyl ether (100 cm^3) was added to precipitate the final product as a pale yellow solid. This was collected by suction filtration, washed with diethyl ether (2×10 cm^3) and dried in vacuo overnight. Yield: 0.212 g, 89%; selected IR data (KBr): $\tilde{\nu}=1208$, 1071 ($S\{=O\}_2$), 843 cm^{-1} (S-O-Pt); ES^+ MS: m/z: 1465 $[M+Na]^+$, 744 $[{}^1/_2M+Na]^+$.

Crystal structure analysis: Suitable crystals for X-ray analysis were obtained by solvent diffusion methods (CH_2Cl_2/hexane/toluene). Details of the X-ray characterisation experiments are given in Table 5. Data for **1**, **4** and **6** were collected at 93 K on a Rigaku Mercury diffractometer while data was collected for **5** at 293 K on a SMART diffractometer using $Mo_{K\alpha}$ radiation and for **7** at 93 K on a Rigaku MM007/Saturn diffractometer. All refinements were performed by using SHELXTL (Version 6.12, Bruker AXS, 2001). CCDC-268910 (**1**), -268911 (**2**), -268912 (**4**), -268913 (**5**), -268914 (**6**) and -268915 (**7**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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Received: April 20, 2005