Metallacyclic Complexes. Synthesis of Metallathietane-3,3-dioxide (Metallacyclosulphone) Complexes of Platinum(II), Palladium(II), and Nickel(II); Crystal Structure of *trans*-2,4-Diphenyl-1,1-bis(triphenylarsine)platinathietane-3,3-dioxide†

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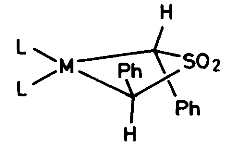
The reactions of the complexes [MCl_2L_2] with the dianion [$PhCHS(O)_2CHPh$]$^{2-}$ afford, in high yield, the metallathietane-3,3-dioxide complexes [$M\{CHPhS(O)_2CHPh\}L_2$] (M = Pt, L = $AsPh_3$, PPh_3, or SEt_2; M = Pd, L = PPh_3, PMe_3, or PEt_3; M = Ni, L = PMe_3, L_2 = $Ph_2PCH_2CH_2PPh_2$). Treatment of [$Pt\{CHPhS(O)_2CHPh\}(SEt_2)_2$] with carbon monoxide, 2,2′-bipyridyl (bipy), or cycloocta-1,5-diene (cod) results in displacement of one diethyl sulphide ligand per platinum to afford the complexes [$Pt\{CHPhS(O)_2CHPh\}(CO)(SEt_2)$], [$\{Pt[CHPhS(O)_2CHPh](SEt_2)\}_2(\mu\text{-bipy})$], and [$\{Pt[CHPhS(O)_2CHPh](SEt_2)\}_2(\mu\text{-cod})$] respectively. A single-crystal *X*-ray diffraction study has been carried out on [$Pt\{CHPhS(O)_2CHPh\}(AsPh_3)_2$]·$CH_2Cl_2$·$2H_2O$ (**1a**). The crystals are orthorhombic, space group *Pbca*, *Z* = 8, in a unit cell with *a* = 18.29(2), *b* = 24.65(2), and *c* = 22.07(5) Å. The structure has been refined to *R* 0.0725 (*R′* 0.0725) for 3 734 independent reflections with $I \geqslant 2.5\sigma(I)$. The platinathietane-3,3-dioxide ring is slightly puckered (fold angle = 24.5°) with no substantial Pt···S transannular interaction.

In view of the importance of cross ring interactions in carbon skeletal rearrangements of metallacyclobutanes[1] we are investigating the chemistry and structures of four-membered metallacycles. In previous studies we have reported a variety of highly puckered metallacyclobutan-3-one M–C–C(O)–C rings of platinum(II) and palladium(II) which contain an important Pt···C(O) bonding interaction in the four-membered ring system.[2] In this paper we describe the first examples of metallacycles which contain the M–C–S(O)$_2$–C (M = Ni, Pd, or Pt) ring system, as reported in a preliminary communication.[3]

Results and Discussion

Treatment of the complexes *cis*- or *trans*-[MCl_2L_2] (M = Pt, L = $AsPh_3$, PPh_3, or SEt_2; M = Pd, L = PPh_3, PMe_3, or PEt_3; M = Ni, L = PMe_3 or L_2 = $Ph_2PCH_2CH_2PPh_2$) with the organolithium dianion Li_2[$PhCHS(O)_2CHPh$][4] in tetrahydrofuran (thf) at low temperature affords, in moderate to good yields, microcrystalline complexes formulated as the metallathietane-3,3-dioxide species (**1a**)—(**1h**) on the basis of their microanalytical data and spectroscopic properties. Similarly, treatment of *cis*-[$PtCl_2(AsPh_3)_2$] or *trans*-[$PdCl_2(PPh_3)_2$] with K_2[$PhCHS(O)_2CHPh$][5] under identical conditions affords comparable yields of (**1a**) and (**1d**) respectively. The reaction of palladium(II) acetate with trimethylphosphine and Li_2[$PhCHS(O)_2CHPh$] also affords (**1e**) in moderate yield. The platinum and palladium complexes are isolated as white to pale yellow, air-stable solids, whereas the nickel complexes are isolated as orange to red-orange air-sensitive solids.



	M	L or L_2
(**1a**)	Pt	$AsPh_3$
(**1b**)	Pt	PPh_3
(**1c**)	Pt	SEt_2
(**1d**)	Pd	PPh_3
(**1e**)	Pd	PMe_3
(**1f**)	Pd	PEt_3
(**1g**)	Ni	PMe_3
(**1h**)	Ni	$Ph_2PCH_2CH_2PPh_2$

In order to determine the molecular structure of a platinathietane-3,3-dioxide complex, a single-crystal *X*-ray diffraction study was carried out on the complex [$Pt\{CHPhS(O)_2CHPh\}(AsPh_3)_2$]·$CH_2Cl_2$·$2H_2O$ (**1a**). The results of the *X*-ray work are summarised in Table 1. The molecular structure is shown in Figure 1, the geometry of the platinacyclosulphone ring being illustrated more clearly in Figure 2. Complex (**1a**) crystallises with one molecule of dichloromethane and two molecules of water per molecule of complex. There are no short intermolecular contacts between these solvent molecules and the platinum complex.

The principal feature of interest in the structure of (**1a**) concerns the geometry of the platinacyclosulphone ring (Figure 2). The ring is folded about the line C(1)–C(2) by 24.5°, the angle of pucker being within the range of 9—31° found for thietane-1,1-dioxide C–C–C–S(O)$_2$ rings,[6,7] and 12—30° found for platinacyclobutanes.[1] The effect of this slight bend in (**1a**) results in an increase in angle strain but a decrease in eclipsing strain until a minimum-energy balance between the two opposing effects is achieved. The 1,3-dithietane oxides

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† (2,2-Dioxo-1,3-diphenyl-2-thiapropane-1,3-diyl)bis(triphenylarsine)platinum(II).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii—xix.

Table 1. Selected interatomic bond distances (Å) and interatomic angles (°) for $[Pt\{CHPhS(O)_2CHPh\}(AsPh_3)_2]\cdot CH_2Cl_2\cdot 2H_2O$

As(1)–Pt	2.422(2)	As(2)–Pt	2.403(2)
C(1)–Pt	2.063(21)	C(2)–Pt	2.082(21)
C(15)–As(1)	1.940(12)	C(21)–As(1)	1.957(11)
C(27)–As(1)	1.940(11)	C(33)–As(2)	1.936(12)
C(39)–As(2)	1.910(15)	C(45)–As(2)	1.939(11)
O(1)–S	1.439(19)	O(2)–S	1.436(17)
C(1)–S	1.725(23)	C(2)–S	1.758(20)
C(3)–C(1)	1.583(23)	C(9)–C(2)	1.518(21)
As(2)–Pt–As(1)	98.1(1)	S–Pt–As(1)	127.5(2)
S–Pt–As(2)	132.7(2)	C(1)–Pt–As(1)	165.5(6)
C(1)–Pt–As(2)	95.8(6)	C(1)–Pt–S	38.0(6)
C(2)–Pt–As(1)	92.0(6)	C(2)–Pt–As(2)	169.0(6)
C(2)–Pt–S	39.0(6)	C(2)–Pt–C(1)	74.3(8)
C(15)–As(1)–Pt	113.5(5)	C(21)–As(1)–Pt	123.1(5)
C(21)–As(1)–C(15)	101.0(6)	C(27)–As(1)–Pt	110.0(4)
C(27)–As(1)–C(15)	107.1(7)	C(27)–As(1)–C(21)	100.5(6)
C(33)–As(2)–Pt	117.9(5)	C(39)–As(2)–Pt	114.9(5)
C(39)–As(2)–C(33)	103.6(8)	C(45)–As(2)–Pt	110.9(3)
C(45)–As(2)–C(33)	105.4(6)	C(45)–As(2)–C(39)	102.8(6)
O(1)–S–Pt	140.5(8)	O(2)–S–Pt	103.3(7)
O(2)–S–O(1)	116.2(11)	C(1)–S–Pt	47.4(7)
C(1)–S–O(1)	112.2(12)	C(1)–S–O(2)	110.7(10)
C(2)–S–Pt	48.1(7)	C(2)–S–O(1)	115.8(11)
C(2)–S–O(2)	107.4(11)	C(2)–S–C(1)	92.0(10)
S–C(1)–Pt	94.6(10)	H(1)–C(1)–Pt	112.7(6)
H(1)–C(1)–S	122.4(8)	C(3)–C(1)–Pt	122.7(13)
C(3)–C(1)–S	113.0(13)	C(3)–C(1)–H(1)	93.9(10)
S–C(2)–Pt	92.9(10)	H(2)–C(2)–Pt	118.2(6)
H(2)–C(2)–S	118.6(7)	C(9)–C(2)–Pt	117.2(12)
C(9)–C(2)–S	116.6(13)	C(9)–C(2)–H(2)	95.3(11)

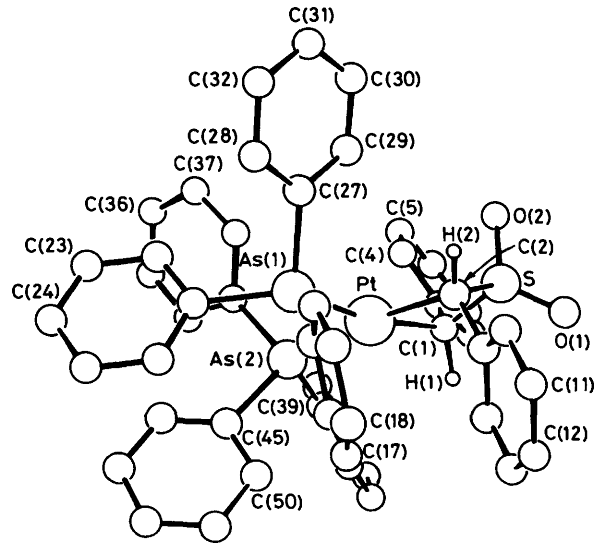


Figure 1. Molecular structure of complex (**1a**) showing the atom numbering scheme. Atoms are drawn as circles with arbitrary radii. Phenyl hydrogen atoms have been excluded

Table 2. Equations of some least-squares planes in the form $Ax + By + Cz = D$, where x, y, and z, are fractional co-ordinates: distances (Å) of relevant atoms from these planes are given in square brackets

Plane (1): Pt, As(1), As(2), C(1), C(2)
$-15.4476x + 10.8388y - 6.7397z = -2.4527$
[Pt 0.001, As(1) 0.70, As(2) − 0.068, C(1) 0.099, C(2) − 0.102]

Plane (2): Pt, As(1), As(2)
$15.6290x - 10.9498y + 5.9395z = 2.0229$

Plane (3): Pt, C(1), C(2)
$14.9696x - 10.6035y + 8.4050z = 3.3261$

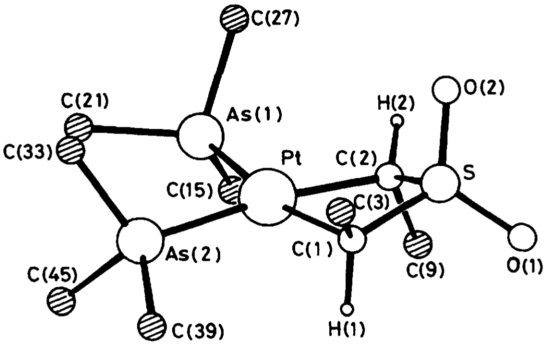


Figure 2. Molecular structure of complex (**1a**) with phenyl rings excluded

$CCl_2SCCl_2S(O)_2$[8] and $CX_2S(O)_2CX_2S(O)_2$ (X = H, F, Cl, or Br)[8,9] have been shown to contain planar rings. The Pt···S distance in (**1a**) is 2.792(5) Å but since the S–O distances are normal (S–O distances in thietane-1,1-dioxides are commonly in the range 1.42—1.46 Å)[7–9] it seems unlikely that there is any substantial bonding between the platinum and the sulphur in (**1a**). The Pt–C bond lengths are normal and are in the range found in platinacyclobutane rings,[1] but the C–S bonds are shorter than the range of 1.79—1.88 Å found in six other thietane-1,1-dioxides.[7–9] It is noteworthy that the S–CH bond distance of 1.641(5) Å in the monolithium derivative $[\{LiPhCHS(O)_2Ph\cdot Me_2NCH_2CH_2NMe_2\}_2]$ is also short and is comparable with the C=S bond length of 1.6108 Å in thioformaldehyde.[10] A short S–C bond distance has also been observed in $[\{LiCH_2S(O)_2Ph\cdot Me_2NCH_2CH_2NMe_2\}_2]$.[11] The co-ordination about the platinum is essentially square planar (Table 2), the twist angle between the AsPtAs and CPtC planes being 6.8°. The Pt–As bond distances are normal.

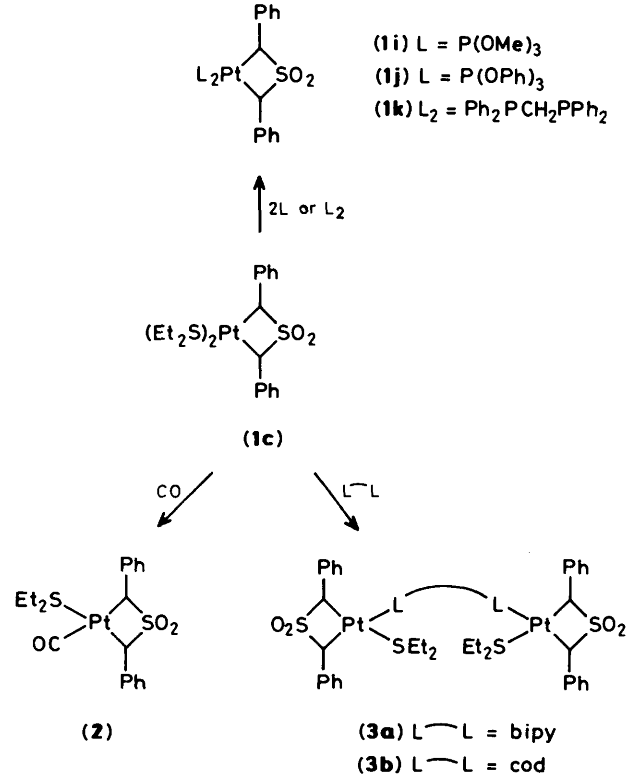
Overall the geometry of the platinathietane-3,3-dioxide ring bears a strong resemblance to platinacyclobutane complexes.[1] It is also interesting that (**1a**) is the *trans*-diphenyl-substituted isomer, with one of the phenyl groups and one S=O group in pseudo-axial environments. Pseudo-axial–equatorial 2,4-substitution has also been found to occur in puckered metallacyclobutan-3-one complexes.[2] Recent calculations on the metallacyclic species $[M(CHR^1CHR^2CHR^3)Cl_4]$ (M = Cr or W; R^1 = Me; R^2 = H or Me; R^3 = H, Me, or Et) indicate that a diequatorial substitution is the favoured conformation for a 2,4-substituted (octahedrally co-ordinated) metallacycle.[12] Isomerisation studies on 2,4-diphenylthietane dioxides also established that the phenyl groups in the more stable molecule occupy pseudo-equatorial environments, and are therefore *cis* to each other.[6] In the four-co-ordinate system (**1a**) it seems likely that torsional effects between equatorial substituents and *cis*-arsine ligands will destabilise the diequatorial isomer causing the observed equatorial–axial isomer to be favoured [the torsion angles As(2)–Pt–C(1)–C(3) and As(1)–Pt–C(2)–C(9) are 46.3 and 81.1° respectively]. Treatment of complex (**1a**) with sodium hydride followed by addition of D_2O did not lead to replacement of either axial or equatorial ring hydrogens by deuterium. Thus, at present it is not possible to say whether the formation of a *trans*-2,4-diphenyl isomer is a consequence of thermodynamic or kinetic control.

The observation that 2,4-diphenylthietane dioxides appear more acidic than the platinathietane-3,3-dioxide ring in (**1a**) is probably an indication of the enhancement of acidity by ring-strain effects.[9] Thus, since C–C bonds are shorter than Pt–C bonds, the ring strain in thietane dioxides is expected to be more than that in platinathietane-3,3-dioxides.

The room-temperature ^{1}H and ^{13}C-{^{1}H-decoupled} n.m.r. spectra of compounds (**1a**)—(**1h**) may be interpreted in terms of a planar, or rapidly inverting metallacycle. Thus, the ring CH signals in the ^{1}H n.m.r. spectrum of the triphenylphosphine-platinum complex (**1b**) appear as the A part of an AA′XX′ spin system (X = ^{31}P), to give a strong inner doublet and a weaker outer doublet, with corresponding ^{195}Pt satellites. However, in the palladium complexes (**1e**) and (**1f**) these ring CH signals are unresolved. The barrier to ring inversion of these metallathietane-3,3-dioxides must be small since non-equivalence of axial and equatorial hydrogens on the ring cannot be detected at −90 °C. The room-temperature ^{13}C-{^{1}H-decoupled} n.m.r. spectra of the bis(phosphine)metallathietane-3,3-dioxide complexes exhibit second-order ring carbon signals and appear as the A part of an AXX′ spin system (X = ^{31}P), with the platinum complex (**1b**) showing ^{195}Pt satellite features.

The i.r. spectra of complexes (**1a**)—(**1h**) exhibit a strong, sharp band in the region 1 090—1 118 cm^{-1}, assigned to the symmetric stretching mode of the S(O)$_2$ functionality. The antisymmetric stretch is observed as a notably weaker band in the region 1 258—1 278 cm^{-1}.

The lability of the diethyl sulphide ligands of complex (**1c**) provides a route to a range of platinathietane-3,3-dioxide complexes, as illustrated in the Scheme. Thus treatment of (**1c**) with 2 mol of the phosphites $P(OMe)_3$ or $P(OPh)_3$, or with 1 mol of bis(diphenylphosphino)methane (dppm) affords the platinathietane-3,3-dioxide complexes (**1i**)—(**1k**) in good yield. Complex (**1k**) was found to contain chelating dppm by comparison of the ^{1}H n.m.r. chemical shift of the dppm CH_2 protons with that of the related platinacyclopentane complex $[Pt(CH_2CH_2CH_2CH_2)(dppm)]$.[13] Treatment of (**1c**) with 1 atm (101 325 Pa) of carbon monoxide in dichloromethane for 1 h resulted in the displacement of one diethyl sulphide ligand, to afford the monocarbonyl complex (**2**). The i.r. spectrum of (**2**) displays a single, strong C≡O stretching mode at 2 070 cm^{-1} in addition to strong ν(SO$_2$) bands at 1 274 and 1 116 cm^{-1}. The ^{1}H n.m.r. spectrum of (**2**) shows ring CH resonances at δ 4.20 [s, 1 H, ^{2}J(PtH) 102] and 4.15 [s, 1 H, ^{2}J(PtH) 88 Hz]. There is no evidence for insertion of carbon monoxide into a platinum–carbon bond of (**1c**) under these conditions. In contrast, treatment of the related platinacyclobutane complexes $[Pt(CH_2CH_2CH_2)(bipy)]$ (bipy = 2,2′-bipyridyl) with carbon monoxide has been shown to afford the insertion product $[Pt(CH_2CH_2CH_2CO)(bipy)]$.[14] Since C–S bonds are longer than C–C bonds, ring strain in the sulphone system will be less than that in the platinacyclobutane complex and these differences may influence the ability of rings to undergo ring expansion with carbon monoxide. Similarly, while we find that complex (**1b**) does not react with sulphur dioxide; treatment of $[Pt(CH_2CH_2CH_2)(PMe_3)_2]$ with sulphur dioxide has been shown to yield $[Pt\{CH_2CH_2CH_2S(O)_2\}(PMe_3)_2]$.[14]



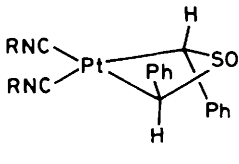
(**1i**) L = $P(OMe)_3$
(**1j**) L = $P(OPh)_3$
(**1k**) $L_2 = Ph_2PCH_2PPh_2$

(**1c**)

(**2**)

(**3a**) L⌒L = bipy
(**3b**) L⌒L = cod

Scheme.



(**4a**) R = Bu^t
(**4b**) R = Bu^n

Interestingly, treatment of (**1c**) with an excess of 2,2′-bipyridyl or cyclo-octa-1,5-diene (cod) in refluxing dichloromethane also results in the displacement of one diethyl sulphide ligand per platinum atom to afford the binuclear complexes (**3a**) and (**3b**) respectively (Scheme). The ^{1}H and ^{13}C-{^{1}H decoupled} n.m.r. spectra of complexes (**3a**) and (**3b**) exhibit two inequivalent ring CH signals (*cis* and *trans* to diethyl sulphide), both showing large couplings to ^{195}Pt. Thus the ^{1}H n.m.r. spectrum of (**3a**) shows ring CH signals at δ 4.94 [s, 2 H, ^{2}J(PtH) 104.0] and 4.36 [s, 2 H, ^{2}J(PtH) 98.0 Hz] in addition to aromatic CH and diethyl sulphide signals. The ^{13}C-{^{1}H-decoupled} n.m.r. spectrum of (**3a**) shows ring CH signals at δ 48.27 [s, ^{1}J(PtC) 624] and 40.71 [s, ^{1}J(PtC) 614 Hz]. The olefinic carbons of the cyclo-octa-1,5-diene ligand of (**3b**) appear as two resonances in the ^{13}C-{^{1}H-decoupled} n.m.r. spectrum as a result of the stereochemistry of the four-membered ring. Complexes containing bridging cyclo-octa-1,5-diene ligands have been noted before, $[\{PtX(S_2CNEt_2)\}_2(\mu\text{-cod})]$ (X = Cl or Me).[15]

Treatment of (**1a**) with an excess of either t-butyl or n-butyl isocyanide in refluxing dichloromethane affords the bis(isocyanide) complexes (**4a**) and (**4b**) respectively, in analogous fashion to the platinacyclobutane complex $[Pt(CH_2CH_2CH_2)(bipy)]$.[14] The i.r. spectrum of (**4a**) shows two terminal isocyanide bands at 2 214 and 2 188 cm^{-1}, characteristic of a *cis* product, with no evidence of insertion into the platinacycle as has been observed for metallacyclobutan-3-one complexes.[16]

Experimental

Melting points (Table 3) were measured in air (unless otherwise stated) on a Reichert hot-stage apparatus and are uncorrected. Infrared spectra were recorded as KBr discs (unless otherwise stated) on a Perkin-Elmer 580 spectrophotometer. Hydrogen-1 n.m.r. spectra were recorded on a Varian EM 390 spectrometer at 90 MHz, on a Bruker AM 300 spectrometer at 300.13 MHz, and on a Bruker Spectrospin WH 400 spectrometer at 400.13

Table 3. Yields, melting points, and analytical[a] and selected i.r.[b] data

Complex	Yield (%)	M.p./°C	Analysis (%)		$\nu(SO_2)$/cm^{-1}	
			C	H	ν_{asym}	ν_{sym}
(1a)·PhMe	94[c]	245—248[d]	59.4 (59.8)	4.5 (4.4)	1 278m	1 118vs
(1a)·$CH_2Cl_2\cdot 2H_2O$	80[e]	245—248[d]			1 278m	1 118vs
(1b)·0.5PhMe	81	259—262[d]	63.8 (63.6)	4.6 (4.6)	1 269s	1 109vs
(1c)	60	190—208[f]	41.9 (42.5)	4.9 (5.2)	1 272s	1 112vs
(1d)	56[c], 52[e]	178—182[d]	68.5 (68.6)	5.0 (4.8)	1 275m	1 111s
(1e)	57[g], 69[h]	195—197[d]	47.8 (47.8)	6.0 (6.0)	1 264s	1 097vs
(1f)·CH_2Cl_2	51	176—178[d]	48.7 (48.3)	6.7 (6.6)	1 270s	1 102vs
(1g)	23	87[d,i]	52.8 (52.5)	7.3 (7.1)	1 258s	1 090vs[j]
(1h)	28	213—217[d,i]	69.1 (68.5)	5.4 (5.2)	1 264m	1 101vs[j]
(1i)	83	140—142	35.1 (34.9)	4.4 (4.4)	1 273s	1 108vs
(1j)	75	204—206	56.1 (56.6)	4.0 (4.0)	1 279m	1 117vs
(1k)		> 220[f]	*k*	*k*	1 270m	1 102vs
(2)	94	> 170[f]	41.1 (40.9)	4.1 (4.0)	1 274s	1 116vs[l]
(3a)	92	230—240[d]	46.4 (45.5)	4.0 (4.3)[m]	1 268m	1 109vs
(3b)	74	200—220[d]	44.8 (45.3)	4.7 (4.8)	1 273m	1 113vs
(4a)	68	> 300[n]	47.8 (47.6)	4.9 (5.0)[o]	1 277m	1 114vs[p]
(4b)	72	196—197	47.9 (47.6)	4.7 (5.0)[q]	1 277m	1 111vs[r]

[a] Calculated values given in parentheses. [b] Recorded as KBr discs unless otherwise stated. [c] Using $K_2[PhCHS(O)_2CHPh]$. [d] With decomposition. [e] Using $Li_2[PhCHS(O)_2CHPh]$. [f] Decomposition to black solid, with no observed melting. [g] From palladium(II) acetate. [h] From $[PdCl_2(PMe_3)_2]$. [i] Under dinitrogen atmosphere. [j] Powder film between NaCl plates. [k] Complex crystallised with dichloromethane and light petroleum, as has been observed in dppm platinacyclopentane complexes;[13] no analytical data recorded. [l] $\nu(CO)$ at 2 070 cm^{-1}. [m] N, 2.7 (2.3%). [n] Decomposition > 200 °C to orange solid. [o] N, 4.5 (4.6%). [p] $\nu(CN)$ at 2 214vs and 2 188vs cm^{-1}. [q] N, 4.5 (4.6%). [r] $\nu(CN)$ at 2 248s and 2 232s cm^{-1}.

MHz with $SiMe_4$ (0.0 p.p.m.) as internal reference, positive values being to high frequency (low field), in $[^2H_1]$chloroform unless otherwise stated. Carbon-13, hydrogen-1 decoupled, n.m.r. spectra were recorded on a Bruker AM 300 spectrometer at 75.47 MHz and on a Bruker Spectrospin WH 400 spectrometer at 100.62 MHz with $SiMe_4$ (0.0 p.p.m.) as internal reference, in $[^2H_1]$chloroform unless otherwise stated. Phosphorus-31, hydrogen-1 decoupled, n.m.r. spectra were recorded in $[^2H_1]$chloroform (unless otherwise stated) on a JEOL JNM-FX60 spectrometer at 24.15 MHz with $[P(OH)_4]^+$ in $[^2H_2]$water (0.0 p.p.m.) as external reference, and on a Bruker Spectrospin WH 400 spectrometer at 162 MHz with H_3PO_4 as external reference.

Experiments were carried out under a dry, oxygen-free, nitrogen atmosphere using solvents which were dried and distilled under nitrogen prior to use. Light petroleum refers to the fraction of b.p. 40—60 °C. The platinum and palladium complexes were recrystallised in air. The compounds *cis*-$[PtCl_2(AsPh_3)_2]$,[17] *cis*-$[PtCl_2(PPh_3)_2]$,[18] *cis*-$[PtCl_2(SEt_2)_2]$,[19] $[PdCl_2(PPh_3)_2]$,[20] PMe_3,[21] $[PdCl_2(PMe_3)_2]$,[22] $[\{Pd(O_2CMe)_2\}_3]$,[23] $[PdCl_2(NCPh)_2]$,[24] $[NiCl_2(PMe_3)_2]$,[25] $[NiCl_2(Ph_2PCH_2CH_2PPh_2)]$,[26] and Bu^{n}NC[27] were prepared as described in the literature. The salt $K_2[PhCHS(O)_2CHPh]$ was prepared in liquid ammonia solution as described in the literature.[5] The ammonia was allowed to boil away, and the resulting solid dissolved in thf to give a solution of approximately 0.2 mol dm^{-3}, which was estimated for total base content by hydrolysis of a 5.0-cm^3 aliquot in water (*ca.* 20 cm^3), followed by titration of the liberated hydroxide with hydrochloric acid, using phenolphthalein indicator. The salt $Li_2[PhCHS(O)_2CHPh]$ was prepared as described previously,[4] except that thf was used as solvent, and a stoicheiometric quantity of n-butyl-lithium was employed. The solution was standardised as for $K_2[PhCHS(O)_2CHPh]$.

Analytical and i.r. data, melting points, and yields for the new complexes are given in Table 3.

Preparation of trans-*2,4-Diphenyl-1,1-bis(ligand)metallathietane-3,3-dioxide Complexes using* $[PhCHS(O)_2CHPh]^{2-}$.—*General method.* One molar equivalent of $M'_2[PhCHS(O)_2CHPh]$ (M' = Li or K) was added to a stirred suspension, or solution of *cis*- or *trans*-$[MCl_2L_2]$ or $[Pd(O_2CMe)_2(PMe_3)_2]$ in thf (*ca.* 50 cm^3) at −78 °C. The mixture was stirred for 10 min at −78 °C, and for a further 4 h at room temperature to give a clear solution. Evaporation to dryness under reduced pressure gave an oil which was washed with light petroleum (30 cm^3). The residual solid was extracted into dichloromethane (30 cm^3) and the solution filtered. The volume of the filtrate was reduced to *ca.* 15 cm^3, and light petroleum added to the cloud point. Cooling to −20 °C for 24 h gave a microcrystalline solid which was recrystallised and dried *in vacuo* [*ca.* 0.4 mmHg (53.6 Pa)] at 40 °C.

$[Pt\{CHPhS(O)_2CHPh\}(AsPh_3)_2]\cdot PhMe$. The compound *cis*-$[PtCl_2(AsPh_3)_2]$ (1.60 g, 1.82 mmol) and $K_2[PhCHS(O)_2CHPh]$ gave, on recrystallisation from dichloromethane–toluene, white microcrystals of compound **(1a)** with one molecule of toluene of solvation (1.929 g). N.m.r. spectra: ^1H (400 MHz), δ 7.3—6.9 (m, 45 H, Ph), 4.24 [s, 2 H, ring CH, $^2J(PtH)$ 84.9, $J(CH)$ 143.5 (d from ^{13}C spectrum)], and 2.36 (s, 3 H, Me, PhMe); ^{13}C-$\{^1H\}$ (100 MHz), δ 138.68—125.14 (m, Ph), 51.95 [s, ring CH, $^1J(PtC)$ 566.1 Hz], and 19.5 p.p.m. (s, Me, PhMe). Reaction of *cis*-$[PtCl_2(AsPh_3)_2]$ (0.40 g, 0.46 mmol) with $Li_2[PhCHS(O)_2CHPh]$ gave, on recrystallisation from dichloromethane–light petroleum, white microcrystals of compound **(1a)** with one CH_2Cl_2 and two H_2O solvent molecules (0.429 g).

$[Pt\{CHPhS(O)_2CHPh\}(PPh_3)_2]\cdot 0.5PhMe$. The compound *cis*-$[PtCl_2(PPh_3)_2]$ (0.80 g, 1.01 mmol) and $Li_2[PhCHS(O)_2CHPh]$ gave, on recrystallisation from dichloromethane–toluene, white microcrystals of compound **(1b)** with half a molecule of toluene of solvation (0.82 g). N.m.r. spectra: ^1H (400 MHz), δ 7.5—6.8 (m, 42.5 H, Ph), 3.99 [d, second order, 2 H, ring CH, $|^3J(PH)_{trans} + {}^3J(PH)_{cis}|$ 11.6, $^2J(PtH)$ 70.0], and 2.35 (s, 1.5 H, Me, PhMe); ^{13}C-$\{^1H\}$ (100 MHz), δ 138.27—125.11 (m, Ph), 56.27 [dd, second order, ring CH, $|^2J(PC)_{trans} + {}^2J(PC)_{cis}|$ 90.43, $^1J(PtC)$ 505.7], and 18.9 (s, Me, PhMe); ^{31}P-$\{^1H\}$ (162 MHz), δ 16.26 p.p.m. [s, $^1J(PtP)$ 2 532 Hz].

$[Pt\{CHPhS(O)_2CHPh\}(SEt_2)_2]$. The compound *cis*-$[PtCl_2(SEt_2)_2]$ (1.00 g, 2.24 mmol) and $Li_2[PhCHS(O)_2CHPh]$ gave, on recrystallisation from dichloromethane–light petroleum, white microcrystals of compound (**1c**) (0.83 g). N.m.r. spectra: ^1H (400 MHz), δ 7.5—7.1 (m, 10 H, Ph), 4.40 [s, 2 H, ring CH, ^2J(PtH) 98.9], 2.43—2.15 [m, 8 H, $(CH_3C\mathit{H}_2)_2S$], and 1.16 [t, 12 H, $(C\mathit{H}_3CH_2)_2S$, ^3J(HH) 7.4]; ^{13}C-$\{^1H\}$ (100 MHz), δ 140.0—125.7 (m, Ph), 47.85 [s, ring CH, ^1J(PtC) 609.3 Hz], 29.55 [s, $(CH_3\mathit{C}H_2)_2S$], and 13.05 p.p.m. [s, $(\mathit{C}H_3CH_2)_2S$].

$[Pd\{CHPhS(O)_2CHPh\}(PPh_3)_2]$. The compound $[PdCl_2(PPh_3)_2]$ (0.50 g, 0.71 mmol) and $Li_2[PhCHS(O)_2CHPh]$ gave, on recrystallisation from dichloromethane–light petroleum, pale yellow microcrystals of compound (**1d**) (0.32 g). N.m.r. spectra: ^1H (400 MHz), δ 7.5—6.8 (m, 40 H, Ph) and 3.57 [d, second order, 2 H, ring CH, $|^3J(PH)_{trans} + {}^3J(PH)_{cis}|$ 9.0]; ^{13}C-$\{^1H\}$ (100 MHz), δ 137.8—124.8 (m, Ph) and 53.10 [dd, second order, ring CH, $|^2J(PC)_{trans} + {}^2J(PC)_{cis}|$ 141.09 Hz]; ^{31}P-$\{^1H\}$ (24 MHz), δ 21.58 p.p.m. (s). Reaction of $[PdCl_2(PPh_3)_2]$ (0.30 g, 0.43 mmol) with $K_2[PhCHS(O)_2CHPh]$ gave, on recrystallisation from dichloromethane–light petroleum, compound (**1d**) (0.21 g).

$[Pd\{CHPhS(O)_2CHPh\}(PMe_3)_2]$. The compound $[Pd(O_2CMe)_2(PMe_3)_2]$, prepared *in situ* from $[\{Pd(O_2CMe)_2\}_3]$ (0.275 g, 0.409 mmol) and trimethylphosphine (0.3 cm^3, 3 mmol), and $Li_2[PhCHS(O)_2CHPh]$ gave, on recrystallisation from dichloromethane–light petroleum, white microcrystals of compound (**1e**) (0.35 g). N.m.r. spectra: ^1H (400 MHz), δ 7.36—7.04 (m, 10 H, Ph), 3.62 [d, second order, 2 H, ring CH, $|^3J(PH)_{trans} + {}^3J(PH)_{cis}|$ not discernible] and 1.06 [d, second order, 18 H, CH_3, PMe_3, $|^2J(PH) + {}^4J(PH)|$ 8.07]; ^{13}C-$\{^1H\}$ (100 MHz), δ 139.53—124.98 (m, Ph), 49.55 [dd, second order, ring CH, $|^2J(PC)_{trans} + {}^2J(PC)_{cis}|$ 112.09], and 15.93 [t, second order, CH_3, PMe_3, $|^1J(PC) + {}^3J(PC)|$ 12.86 Hz]; ^{31}P-$\{^1H\}$ (24 MHz), δ −21.38 p.p.m. (s). Reaction of $[PdCl_2(PMe_3)_2]$ (0.10 g, 0.30 mmol) with $Li_2[PhCHS(O)_2CHPh]$ gave, on recrystallisation from dichloromethane–light petroleum, compound (**1e**) (0.106 g).

$[Pd\{CHPhS(O)_2CHPh\}(PEt_3)_2]{\cdot}CH_2Cl_2$. Triethylphosphine (0.5 cm^3, 3.4 mmol) was added to a stirred suspension of $[PdCl_2(NCPh)_2]$ (0.412 g, 1.07 mmol) in toluene (20 cm^3), the resulting pale yellow solution stirred for 1 h, and evaporated to dryness under reduced pressure. The resulting solid, and $Li_2[PhCHS(O)_2CHPh]$ gave, on recrystallisation from dichloromethane–light petroleum, white microcrystals of compound (**1f**) with one molecule of CH_2Cl_2 of solvation (0.37 g). N.m.r. spectra: ^1H (400 MHz), δ 7.46—7.11 (m, 10 H, Ph), 5.35 (s, 2 H, CH_2Cl_2), 3.55 [d, second order, 2 H, ring CH, $|^3J(PH)_{trans} + {}^3J(PH)_{cis}|$ not discernible], 1.40 (m, 12 H, CH_2), and 0.97 (m, 18 H, CH_3); ^1H (400 MHz, [$^2H_2$]dichloromethane, −90 °C), identical to room temperature spectrum; ^{13}C-$\{^1H\}$ (100 MHz), δ 140.36—125.18 (m, Ph), 50.19 [d, d, second order, ring CH, $|^2J(PC)_{trans} + {}^2J(PC)_{cis}|$ 106.4 Hz], 15.94 (m, second order, CH_2), and 8.19 (s, CH_3); ^{31}P-$\{^1H\}$ (162 MHz), δ 11.38 p.p.m. (s).

$[Ni\{CHPhS(O)_2CHPh\}(PMe_3)_2]$. The compound $[NiCl_2(PMe_3)_2]$ (0.30 g, 1.06 mmol) and $Li_2[PhCHS(O)_2CHPh]$ gave, on recrystallisation from dichloromethane–toluene at −20 °C, red-orange microcrystals of compound (**1g**) (0.11 g). N.m.r. spectra: ^1H (90 MHz), δ 7.6—7.0 (m, 10 H, Ph), 3.36 [d, filled in, second order, 2 H, ring CH, $|^3J(PH)_{trans} + {}^3J(PH)_{cis}|$ 10], and 1.02 [d, second order, 18 H, PMe_3, $|^2J(PH) + {}^4J(PH)|$ 8]; ^{13}C-$\{^1H\}$ (75.5 MHz), δ 138.73—125.02 (m, Ph), 49.28 [dd, second order, ring CH, $|^2J(PC)_{trans} + {}^2J(PC)_{cis}|$ 72.94], and 15.87 [t, second order, CH_3, PMe_3, $|^1J(PC) + {}^3J(PC)|$ 13.56 Hz]; ^{31}P-$\{^1H\}$ (24 MHz), δ −12.91 p.p.m. (s).

$[Ni\{CHPhS(O)_2CHPh\}(Ph_2PCH_2CH_2PPh_2)]$. The compound $[NiCl_2(Ph_2PCH_2CH_2PPh_2)]$ (0.35 g, 0.66 mmol) and $Li_2[PhCHS(O)_2CHPh]$ gave, on recrystallisation from dichloromethane–light petroleum, orange microcrystals of compound (**1h**) (0.21 g). N.m.r. spectrum: ^1H (90 MHz), δ 7.8—6.7 (m, 30 H, Ph), 4.0 [d, d, 2 H, ring CH, $^3J(P_{cis}H)$ 5, $^3J(P_{trans}H)$ 8 Hz], and 2.2—1.7 (m, 4 H, CH_2).

Reactions of $[Pt\{CHPhS(O)_2CHPh\}(SEt_2)_2]$ (**1c**). (*a*) *With trimethyl phosphite.* A solution of complex (**1c**) (0.09 g, 0.14 mmol) in dichloromethane (20 cm^3) with trimethyl phosphite (0.2 cm^3, 1.8 mmol) was refluxed for 1 h. The mixture was evaporated to dryness under reduced pressure, and the residue recrystallised from dichloromethane–light petroleum and dried *in vacuo* to give white microcrystals of compound (**1i**) (0.083 g). N.m.r. spectra: ^1H (400 MHz), δ 7.33—7.04 (m, 10 H, Ph), 4.31 [d, second order, 2 H, ring CH, $|^3J(PH)_{trans} + {}^3J(PH)_{cis}|$ not discernible, ^2J(PtH) 68.1], and 3.40 [d, second order,[28] 18 H, Me, $P(OMe)_3$, ^3J(PH) 12.05]; ^{13}C-$\{^1H\}$ (100 MHz), δ 139.71—125.24 (m, Ph), 54.95 [dd, second order, ring CH, $|^2J(PC)_{trans} + {}^2J(PC)_{cis}|$ 148.6, ^1J(PtC) 433.4], and 51.94 (s, CH_3); ^{31}P-$\{^1H\}$ (162 MHz), δ 117.68 p.p.m. [s, ^1J(PtP) 4 099 Hz].

(*b*) *With triphenyl phosphite.* A solution of complex (**1c**) (0.15 g, 0.24 mmol) in dichloromethane (20 cm^3) with triphenyl phosphite (0.2 cm^3, 0.76 mmol) was refluxed for 2 h. Work-up as for (**1i**) gave white microcrystals of compound (**1j**) (0.19 g). N.m.r. spectra: ^1H (400 MHz), δ 7.19—6.67 (m, 40 H, Ph), and 4.29 [d, second order, 2 H, ring CH, $|^3J(PH)_{trans} + {}^3J(PH)_{cis}|$ not discernible, ^2J(PtH) 71.82]; ^{13}C-$\{^1H\}$ (100 MHz), δ 150.68—120.06 (m, Ph) and 54.62 [dd, second order, ring CH, $|^2J(PC)_{trans} + {}^2J(PC)_{cis}|$ 145.6, ^1J(PtC) not discernible]; ^{31}P-$\{^1H\}$ (162 MHz), δ 100.55 p.p.m. [s, ^1J(PtP) 4 119 Hz].

(*c*) *With dppm.* A solution of complex (**1c**) (0.10 g, 0.16 mmol) in dichloromethane (20 cm^3) with dppm (0.065 g, 0.17 mmol) was refluxed for 2 h. Work-up as for (**1i**) gave white microcrystals of (**1k**) (0.11 g). N.m.r. spectra: ^1H (300 MHz), δ 7.8—6.7 (m, 30 H, Ph), 4.91 [d, second order, 2 H, ring CH, $|^3J(PH)_{trans} + {}^3J(PH)_{cis}|$ not discernible, ^2J(PtH) 85.0], and 4.39 [t, 2 H, CH_2, dppm, ^2J(PH) 9.9, ^3J(PtH) not discernible]; ^{13}C-$\{^1H\}$ (75.5 MHz), δ 140.24—124.65 (m, Ph), 56.12 [dd, second order, ring CH, $|^2J(PC)_{trans} + {}^2J(PC)_{cis}|$ 91.8, ^1J(PtC) 461.9], and 47.05 p.p.m. [t, CH_2, dppm, ^1J(PC) 28.3 Hz, ^2J(PtC) not discernible].

(*d*) *With carbon monoxide.* Carbon monoxide was slowly bubbled through a solution of complex (**1c**) (0.10 g, 0.16 mmol) in dichloromethane (10 cm^3) for 1 h. The solution was reduced in volume to *ca.* 0.5 cm^3, and addition of light petroleum (*ca.* 50 cm^3) gave a white solid which was filtered off and dried *in vacuo* to give compound (**2**) (0.085 g). N.m.r. spectrum: ^1H (90 MHz), δ 7.5—6.8 (m, 10 H, Ph), 4.20 [s, 1 H, ring CH, ^2J(PtH) 102], 4.15 [s, 1 H, ring CH, ^2J(PtH) 88], 2.5—1.8 [m, 4 H, $(CH_3C\mathit{H}_2)_2S$], and 0.95 p.p.m. [t, 6 H, $(C\mathit{H}_3CH_2)_2S$, ^3J(HH) 7.5 Hz]. ν(CO) at 2 070 cm^{-1}.

(*e*) *With bipy.* A solution of complex (**1c**) (0.10 g, 0.16 mmol) in dichloromethane (20 cm^3) with 2,2′-bipyridyl (0.031 g, 0.20 mmol) was refluxed for 3 h. The solution was evaporated to dryness under reduced pressure and the residue recrystallised from dichloromethane–diethyl ether, and dried *in vacuo* to give yellow microcrystals of compound (**3a**) (0.09 g). N.m.r. spectra ([$^2H_2$]dichloromethane): ^1H (400 MHz), δ 8.46—7.18 (m, 28 H, aromatic CH), 4.94 [s, 2 H, ring CH, ^2J(PtH) 104.0], 4.36 [s, 2 H, ring CH, ^2J(PtH) 98.0], 2.49 [m, 4 H, $(CH_3C\mathit{H}_2)_2S$], 2.29 [m, 4 H, $(CH_3C\mathit{H}_2)_2S$], and 1.20 [t, 12 H, $(C\mathit{H}_3CH_2)_2S$, ^3J(HH) 7.4]; ^{13}C-$\{^1H\}$ (100 MHz), δ 150.99—122.72 (m, aromatic C), 48.27 [s, ring CH, ^1J(PtC) 624.0], 40.71 [s, ring CH, ^1J(PtC) 614.0 Hz], 30.02 [s, $(CH_3\mathit{C}H_2)_2S$], and 13.29 p.p.m. [s, $(\mathit{C}H_3CH_2)_2S$].

(*f*) *With cyclo-octa-*1,5*-diene.* A solution of complex (**1c**) (0.10 g, 0.16 mmol) in dichloromethane (20 cm^3) with cyclo-octa-1,5-diene (0.5 cm^3, 4.1 mmol) was refluxed for 12 h. The mixture was

Table 4. Fractional atomic co-ordinates for $[\overline{\mathrm{Pt}\{\mathrm{CHPhS(O)_2}}\mathrm{CHPh}\}(\mathrm{AsPh_3})_2]\cdot\mathrm{CH_2Cl_2}\cdot2\mathrm{H_2O}$

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Pt	0.198 35(4)	0.384 57(3)	0.527 63(4)	C(26)	0.259 7(8)	0.551 2(5)	0.464 4(7)
As(1)	0.262 82(11)	0.434 14(8)	0.449 37(11)	C(27)	0.197 4(7)	0.449 5(6)	0.382 3(6)
As(2)	0.212 82(11)	0.449 03(9)	0.608 39(12)	C(28)	0.222 1(7)	0.479 8(6)	0.333 0(6)
S	0.107 8(3)	0.294 30(22)	0.513 0(4)	C(29)	0.126 0(7)	0.429 7(6)	0.383 1(6)
O(1)	0.106 7(10)	0.236 9(8)	0.525 0(9)	C(30)	0.079 2(7)	0.440 2(6)	0.334 6(6)
O(2)	0.043 1(9)	0.316 7(7)	0.486 1(8)	C(31)	0.103 8(7)	0.470 5(6)	0.285 3(6)
C(1)	0.133 6(11)	0.331 3(8)	0.575 8(10)	C(32)	0.175 3(7)	0.490 3(6)	0.284 5(6)
C(2)	0.183 0(10)	0.318 0(8)	0.471 0(10)	C(33)	0.156 6(8)	0.515 4(5)	0.604 4(8)
C(3)	0.066 3(7)	0.350 6(6)	0.615 4(7)	C(34)	0.161 7(8)	0.554 0(5)	0.650 5(8)
C(4)	0.026 1(7)	0.395 7(6)	0.596 6(7)	C(35)	0.123 9(8)	0.602 9(5)	0.645 6(8)
C(5)	−0.034 8(7)	0.412 4(6)	0.629 7(7)	C(36)	0.080 9(8)	0.613 3(5)	0.594 7(8)
C(6)	−0.055 6(7)	0.384 1(6)	0.681 7(7)	C(37)	0.075 7(8)	0.574 7(5)	0.548 7(8)
C(7)	−0.015 4(7)	0.339 0(6)	0.700 5(7)	C(38)	0.113 5(8)	0.525 8(5)	0.553 5(8)
C(8)	0.045 5(7)	0.322 3(6)	0.667 4(7)	C(39)	0.191 9(10)	0.421 5(7)	0.687 4(7)
C(9)	0.246 8(7)	0.279 2(5)	0.463 7(8)	C(40)	0.135 0(10)	0.441 7(7)	0.723 0(7)
C(10)	0.285 4(7)	0.262 9(5)	0.515 1(8)	C(41)	0.124 2(10)	0.421 6(7)	0.781 5(7)
C(11)	0.345 7(7)	0.228 7(5)	0.509 4(8)	C(42)	0.170 2(10)	0.381 4(7)	0.804 2(7)
C(12)	0.367 5(7)	0.210 8(5)	0.452 2(8)	C(43)	0.227 1(10)	0.361 2(7)	0.768 6(7)
C(13)	0.328 9(7)	0.227 0(5)	0.400 8(8)	C(44)	0.237 9(10)	0.381 3(7)	0.710 2(7)
C(14)	0.268 5(7)	0.261 2(5)	0.406 6(8)	C(45)	0.313 9(6)	0.471 9(4)	0.615 5(5)
C(15)	0.346 0(7)	0.395 1(6)	0.416 5(7)	C(46)	0.334 2(6)	0.526 3(4)	0.619 5(5)
C(16)	0.392 3(7)	0.368 5(6)	0.457 0(7)	C(47)	0.407 6(6)	0.540 2(4)	0.626 5(5)
C(17)	0.451 7(7)	0.338 8(6)	0.435 3(7)	C(48)	0.460 8(6)	0.499 8(4)	0.629 5(5)
C(18)	0.464 8(7)	0.335 7(6)	0.373 1(7)	C(49)	0.440 5(6)	0.445 4(4)	0.625 5(5)
C(19)	0.418 5(7)	0.362 3(6)	0.332 7(7)	C(50)	0.367 1(6)	0.431 4(4)	0.618 5(5)
C(20)	0.359 1(7)	0.392 0(6)	0.354 3(7)	O(3)	0.053 6(6)	0.277 1(4)	0.319 9(5)
C(21)	0.305 5(8)	0.506 0(5)	0.462 4(7)	Cl(1)	0.181 0(6)	0.350 9(4)	0.215 1(5)
C(22)	0.380 6(8)	0.512 1(5)	0.471 0(7)	O(4)	0.044 6(6)	0.698 7(4)	0.124 3(5)
C(23)	0.409 9(8)	0.563 5(5)	0.481 6(7)	Cl(2)	0.223 1(6)	0.764 8(4)	0.189 4(5)
C(24)	0.364 1(8)	0.608 7(5)	0.483 7(7)	C(51)	0.193 7(6)	0.317 0(4)	0.154 9(5)
C(25)	0.289 0(8)	0.602 6(5)	0.475 0(7)				

evaporated to dryness under reduced pressure, and the residue recrystallised from dichloromethane–light petroleum and dried *in vacuo* to give white microcrystals of compound (**3b**) (0.07 g). N.m.r. spectra: ^{1}H (400 MHz), δ 7.56—6.96 (m, 20 H, Ph), 5.21 [m, 4 H, C=CH, *J*(PtH) 19.1], 4.50 [s, 2 H, ring CH, ^2J(PtH) 104.0], 4.40 [s, 2 H, ring CH, ^2J(PtH) 100.0], 2.44 [m, 4 H, $(\mathrm{CH_3C}H_2)_2$S], 2.21 (m, 8 H, $\mathrm{CH_2}$, cod), 2.11 [m, 4 H, $(\mathrm{CH_3C}H_2)_2$S], and 1.16 [t, 12 H, $(\mathrm{C}H_3\mathrm{CH_2})_2$S, ^3J(HH) 7.4]; ^{13}C-{^{1}H} (100 MHz), δ 138.92—125.77 (m, Ph), 103.39 [s, C=C, *J*(PtC) 84.76], 101.38 [s, C=C, *J*(PtC) 70.51], 57.28 [s, ring CH, ^1J(PtC) 586.1], 47.81 [s, ring CH, ^1J(PtC) 604.3 Hz], 30.28 (s, $\mathrm{CH_2}$, cod), 29.57 [s, $(\mathrm{CH_3}C\mathrm{H_2})_2$S], 28.12 (s, $\mathrm{CH_2}$, cod), and 13.07 p.p.m. [s, $(C\mathrm{H_3CH_2})_2$S].

Reactions of Complex (**1a**) *with Isocyanides.*—(*a*) *With t-butyl isocyanide.* A solution of complex (**1a**) (0.18 g, 0.158 mmol) in dichloromethane (20 cm^3) with t-butyl isocyanide was refluxed for 4 h. The mixture was evaporated to dryness under reduced pressure, and the solid recrystallised from dichloromethane–light petroleum and dried *in vacuo* to give white microcrystals of compound (**4a**) (0.065 g). N.m.r. spectra: ^{1}H (400 MHz), δ 7.36—7.05 (m, 10 H, Ph), 4.39 [s, 2 H, ring CH, ^2J(PtH) 79.9], and 1.19 (s, 18 H, Bu^t); ^{13}C-{^{1}H} (100 MHz), δ 139.90—124.48 (m, Ph), 57.58 (s, C, Bu^t), 50.01 [s, ring CH, ^1J(PtC) 475.7 Hz], and 29.64 p.p.m. (s, Me, Bu^t). ν(CN) at 2 214vs and 2 188vs cm^{-1}.

(*b*) *With n-butyl isocyanide.* A solution of complex (**1a**) (0.10 g, 0.087 mmol) in dichloromethane (20 cm^3) with n-butyl isocyanide (0.1 cm^3, 0.89 mmol) was refluxed for 2 h. Work-up as for (**4a**) gave white microcrystals of compound (**4b**) (0.038 g). N.m.r. spectra: ^{1}H (400 MHz), δ 7.36—6.98 (m, 10 H, Ph), 4.40 [s, 2 H, ring CH, ^2J(PtH) 79.6], 3.32 [t, 4 H, $\mathrm{CH_2}$, Bu^n, ^3J(HH) 6.6], 1.37 (qnt, 4 H, $\mathrm{CH_2}$, Bu^n, $|^3J(\mathrm{HH})|$ 6.8], 1.13 [sxt, 4 H, $\mathrm{CH_2}$, Bu^n, $|^3J(\mathrm{HH})|$ 7.4], and 0.80 [t, 6 H, $\mathrm{CH_3}$, Bu^n, ^3J(HH) 7.3]; ^{13}C-{^{1}H} (100 MHz), δ 139.78—120.78 (m, Ph), 49.93 [s, ring CH, ^1J(PtC) 481.4 Hz], 43.52 (s, $\mathrm{CH_2}$, Bu^n), 30.12 (s, $\mathrm{CH_2}$, Bu^n), 19.14 (s, $\mathrm{CH_2}$, Bu^n), and 12.91 p.p.m. (s, $\mathrm{CH_3}$, Bu^n). ν(CN) at 2 248s and 2 232s cm^{-1}.

Reaction of Complex (**1b**) *with Sulphur Dioxide.*—Sulphur dioxide was passed through a solution of complex (**1b**) (0.10 g) in dichloromethane (10 cm^3) for 2 h. Evaporation to dryness under reduced pressure afforded a white solid which was identified as starting material from its ^{31}P-{^{1}H} n.m.r. spectrum.

Crystal Structure Determination.—Crystals of complex (**1a**) were grown from dichloromethane–light petroleum. A crystal of dimensions *ca.* 0.35 × 0.32 × 0.28 mm was mounted in air. The cell dimensions were determined from an oscillation photograph about the *c* axis of the crystal and by least-squares refinement of diffractometer measurements of zero and upper layer reflections. The intensities of 9 075 reflections with $7 < 2\theta < 54°$ were measured on a Stöe STADI Weissenberg diffractometer with graphite-monochromated Mo-K_α radiation using an ω-scan technique. The data were corrected for Lorentz and polarisation effects to yield 3 734 reflections with $I \geqslant 2.5\sigma(I)$. The structure was solved using the Patterson option of SHELX 84.[29] All subsequent calculations were carried out using the computer program SHELX.[30]

Crystal data. $\mathrm{C_{50}H_{42}As_2O_2PtS\cdot CH_2Cl_2\cdot 2H_2O}$, M = 1 172.8, orthorhombic, a = 18.29(2), b = 24.65(2), c = 22.07(5) Å, U = 9.951.3 Å^3, Z = 8, D_c = 1.57 g cm^{-3}, $F(000)$ = 4 417.4, space group *Pbca*, no. 61, Mo-K_α radiation, λ = 0.710 69 Å, μ(Mo-K_α) = 42.4 cm^{-1}.

The structure was solved by conventional Patterson and difference Fourier techniques. Scattering factors were taken from ref. 31. In the final stages of full-matrix least-squares refinement only Pt, As, and S atoms were given anisotropic thermal parameters due to limitations set by the computer program. All the phenyl rings were treated as rigid bodies with D_{6h} symmetry and C–C distances of 1.395(5) Å. The hydrogen atoms were included at calculated positions [C–H 1.08(5) Å]. Final cycles of refinement included a poorly defined molecule of dichloromethane and the oxygen atoms of two molecules of water and involved 154 variables. The remaining difference Fourier map showed peaks of $<2e$, approximately 1 Å from the platinum atom. An analysis of the weighting scheme over $|F_o|$ and $(\sin \theta)/\lambda$ was satisfactory. The final cycle of refinement employed a weighting factor $w = 1\ (\sigma^2 F_o + gF_o^2)$ where, $g = 0.000\ 88$. Final $R\ [= \Sigma(|F_o| - |F_c|)/\Sigma|F_o|]$ and $R'\ \{= [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}\}$ values were 0.0725 and 0.0725 respectively. The atomic co-ordinates for the structure are given in Table 4.

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