Metallacyclic Complexes. Part 4.[1] Synthesis of Platinathietane-3-oxide Complexes, and the Single-crystal *X*-Ray Structure of $[\mathrm{Pt\{CH(COPh)S(O)CH(COPh)\}(PPh_3)_2}]\cdot 2\mathrm{CH_2Cl_2}$ †

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Treatment of the complexes *cis*-$[\mathrm{PtCl_2L_2}]$ with diphenacyl sulphoxide, $(\mathrm{PhCOCH_2})_2\mathrm{SO}$, and an excess of silver(I) oxide in refluxing dichloromethane affords high yields of the platinathietane-3-oxide complexes $[\mathrm{Pt\{CH(COPh)S(O)CH(COPh)\}L_2}]$ (L = $\mathrm{PPh_3}$, $\mathrm{PMePh_2}$, or $\mathrm{PMe_2Ph}$). A single-crystal *X*-ray diffraction study has been carried out on $[\mathrm{Pt\{CH(COPh)S(O)CH(COPh)\}(PPh_3)_2}]$ (**6a**)·$2\mathrm{CH_2Cl_2}$. The crystals are triclinic, space group $P\bar{1}$, $Z = 2$, in a unit cell with $a = 13.824(1)$, $b = 12.953(2)$, $c = 19.248(6)$ Å, $\alpha = 118.0(2)$, $\beta = 52.4(2)$, and $\gamma = 113.56(5)°$. The structure has been refined to R 0.0487 (R' 0.0512) for 7 864 reflections with $(I) \geqslant 3\sigma(I)$. The complex contains a puckered platinathietane-3-oxide ring [fold angle 36.65(46)°] with the sulphinyl oxygen in the expected equatorial environment. The presence of short carbon–sulphur bonds is interpreted in terms of a contribution from a heteroallylic bonding representation. Room-temperature ^{1}H n.m.r. spectra for the platinathietane-3-oxide complexes indicate that the four-membered rings are puckered and non-fluxional in solution. The magnitude of the platinum-195 coupling to the axial and equatorial ring hydrogens of the platinathietane-3-oxide ring is dependent upon the orientation of the CH bonds with respect to the square-planar platinum function and the magnitudes of ^3J(*cis*-PPtCH) are dihedral angle controlled. The reaction of $[\mathrm{Pt_2Br_4(PEt_3)_2}]$ with 1 equivalent of triphenylarsine and diphenacyl sulphoxide per platinum and an excess of silver(I) oxide in refluxing dichloromethane affords the mixed-ligand complex $[\mathrm{Pt\{CH(COPh)S(O)CH(COPh)\}(AsPh_3)(PEt_3)}]$, which exists as a mixture of two isomers, the major (76%) isomer having the triphenylarsine ligand *trans* to an axial COPh substituent.

The utility of silver(I) oxide in the synthesis of the metallathietane-3,3-dioxide complexes (**1**),[2] and the oxodimethylenemethane complex (**2**)[3] *via* the 1,3-disubstituted dimethyl sulphones (**3**) and the dimethyl ester of 3-oxopentane-3,5-dioic acid (**4**) respectively, led us to investigate reactions of the diphenacyl sulphoxide (**5**) in the synthesis of platinathietane-3-oxide complexes. In previous studies on metallacyclobutan-3-ones of $\mathrm{Pt^{II}}$ and $\mathrm{Pd^{II}}$ the presence of highly puckered metallacyclic rings and transannular M···CO interactions has been established and it is apparent that these systems can also be regarded as oxodimethylenemethane metal complexes.[3,4] The availability of platinathietane-3-oxide complexes would afford the opportunity to investigate the conformation of this new ring system and to determine the competing conformational requirements of an oxygen atom and a non-bonding sulphur electron pair in a metallathietane-3-oxide (metallacyclosulphoxide). Some of the results have appeared in a preliminary communication.[5]

Results and Discussion

Treatment of the complexes *cis*-$[\mathrm{PtCl_2L_2}]$ (L = $\mathrm{PPh_3}$, $\mathrm{PMePh_2}$, or $\mathrm{PMe_2Ph}$) with diphenacyl sulphoxide (**5**) and an excess of silver(I) oxide in refluxing dichloromethane affords, in high yields, the platinathietane-3-oxide complexes $[\mathrm{Pt\{CH(COPh)S(O)CH(COPh)\}L_2}]$ (**6a**)—(**6c**) as air-stable white to pale yellow microcrystalline solids.

In order to determine the molecular structure of a platinathietane-3-oxide complex, a single-crystal *X*-ray diffraction study was carried out on the complex $[\mathrm{Pt\{CH(COPh)S(O)CH(COPh)\}(PPh_3)_2}]$ (**6a**)·$2\mathrm{CH_2Cl_2}$. The results of the *X*-ray work are summarised in Table 1. The molecular structure is shown in Figure 1. Complex (**6a**) crystallises with two molecules of dichloromethane per molecule of complex. There are no short intermolecular contacts between the solvent molecules and the platinum complex.

A principal feature of interest in the structure of (**6a**) concerns the geometry of the platinacyclosulphoxide ring. The ring is folded about the line C(1)–C(2) by 36.7(5)°, with the sulphinyl oxygen in an equatorial environment. The presence of an axial lone pair on sulphur will therefore reduce steric strain between this axial environment and the bis(triphenylphosphine)platinum group since lone pairs occupy less space and are more deformable than oxygen atoms.[6] Furthermore, with the sulphur lone pair in an axial environment more ring folding can occur as compared with the related metallacyclic sulphone $[\mathrm{Pt\{CH(COPh)S(O)_2CH(COPh)\}(PPh_3)_2}]$, (**1a**) (fold angle = 15.3°).[2] Similar differences between the fold angles of thietane-1-oxides (range 27—41.9°)[7] and thietane-1,1-dioxides (range 9—31°)[8] have also been observed. In platinacyclobutanes fold angles typically lie in the range 0—30 °.[9–11] It is also noteworthy that the sulphur ylide complexes (**7**)—(**9**) have been shown to contain puckered rings with equatorial sulphinyl oxygens.[12–14]

The C–S ring bonds in compound (**6a**) are shorter than those expected from studies on thietane-1-oxides (range 1.79—1.89 Å).[7] This C–S bond shortening appears to be characteristic of M–C–S(O)$_2$–C rings (M = Pt[2,15] or Pd[2]) and of the cyclic

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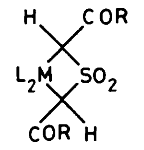
† (1,3-Dibenzoyl-2-oxo-2λ^4-thiapropane-1,3-diyl)bis(triphenylphosphine)platinum(II)–dichloromethane (1/2).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.



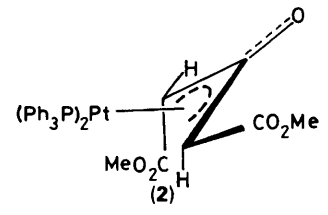
(1)

M = Pt or Pd

L = Tertiary phosphine or P(OPh)$_3$

R = Ph or OMe

(1a) M = Pt, L = PPh$_3$, R = Ph



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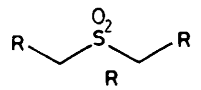
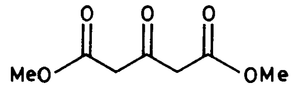


(3a) COPh

(3b) CO$_2$Me



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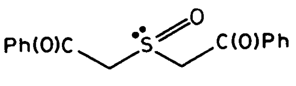

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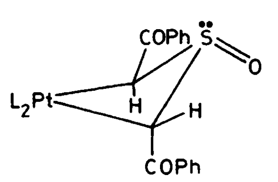


L

(6a) PPh$_3$

(6b) PMePh$_2$

(6c) PMe$_2$Ph

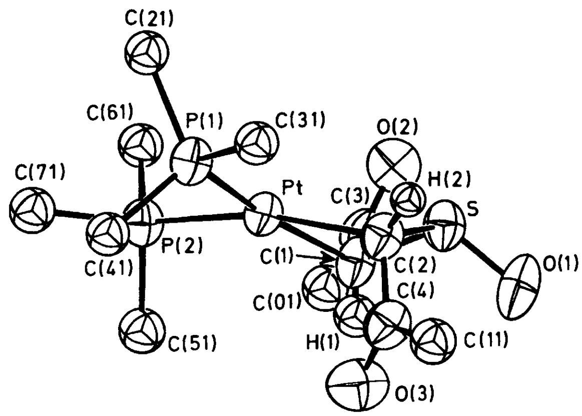
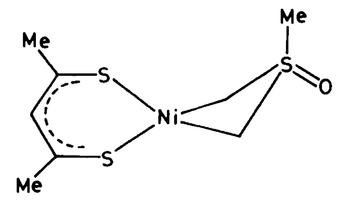


Figure 1. Molecular structure of [Pt{CH(COPh)S(O)CH(COPh)}(PPh$_3$)$_2$] (**6a**), with only the attached carbon atoms of phenyl rings illustrated

Table 1. Selected intramolecular bond lengths (Å) and angles (°) for [Pt{CH(COPh)S(O)CH(COPh)}(PPh$_3$)$_2$] (**6a**)·2CH$_2$Cl$_2$, with estimated standard deviations in parentheses

Pt–P(1)	2.290(2)	P(1)–Pt–P(2)	97.7(1)
Pt–P(2)	2.319(2)	P(1)–Pt–C(2)	94.8(2)
Pt–C(1)	2.163(7)	P(2)–Pt–C(1)	95.1(2)
Pt–C(2)	2.122(6)	C(1)–Pt–C(2)	72.6(2)
Pt···S	2.840(5)	Pt–C(1)–S	91.7(3)
		Pt–C(2)–S	92.5(3)
CH(COPh)S(O)CH(COPh) ligand			
C(1)–S	1.779(7)	C(1)–S–C(2)	90.4(3)
C(2)–S	1.797(7)	C(1)–S–O(1)	111.0(4)
S–O(1)	1.492(6)	C(2)–S–O(1)	113.0(3)
C(1)–C(3)	1.476(10)	C(3)–C(1)–S	111.4(6)
C(2)–C(4)	1.487(11)	C(4)–C(2)–S	112.5(5)
C(3)–O(2)	1.221(9)	C(1)–C(3)–C(01)	120.0(7)
C(4)–O(3)	1.218(9)	C(1)–C(3)–O(2)	121.9(7)
C(3)–C(01)	1.497(8)	C(2)–C(4)–C(11)	120.2(6)
C(4)–C(11)	1.496(8)	C(2)–C(4)–O(3)	121.0(6)
C(1)–H(1)	0.83(8)		
C(2)–H(2)	0.94(6)		
Triphenylphosphine ligands			
P(1)–C(21)	1.813(4)	C(21)–P(1)–C(31)	98.4(2)
P(1)–C(31)	1.831(4)	C(21)–P(1)–C(41)	110.1(2)
P(1)–C(41)	1.806(4)	C(31)–P(1)–C(41)	102.9(2)
P(2)–C(51)	1.829(4)	C(51)–P(2)–C(61)	108.5(2)
P(2)–C(61)	1.824(4)	C(51)–P(2)–C(71)	102.5(2)
P(2)–C(71)	1.832(4)	C(61)–P(2)–C(71)	99.9(2)



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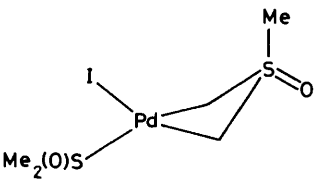

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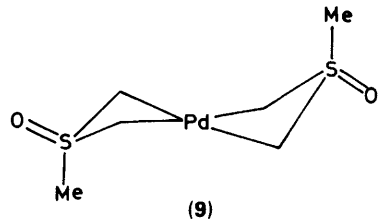

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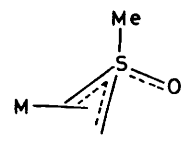

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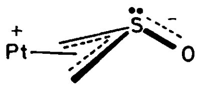


(11)

ylide complexes (**7**)—(**9**).[12–14] In the cyclic ylide complexes it has been interpreted to a partial retention of ylidic character, with a contribution to the metallacyclic bonding from a heteroallylic representation such as (**10**).[12–14] A contribution to the bonding in (**6a**) from the heteroallylic representation (**11**) could account for the C–S bond shortening in (**6a**). The shorter Pt–C and C–S bonds found in the metallacyclic sulphone (**1a**) as compared to the metallacyclic sulphoxide (**6a**) is presumably due to the greater electronegativity of sulphur(VI) as compared to sulphur(IV). However, despite different fold angles and Pt–C and C–S bond distances in (**1a**) and (**6a**), the Pt···S distances are equal [2.840(5) Å]. The S–O distance of 1.492(6) Å in compound (**6a**) is in the range of 1.52—1.70 Å commonly found for thietane-1-oxides and there is thus no significant transannular Pt···S interaction in (**6a**). Similarly no Pt···S interactions have been observed in platina- or pallada-cyclosulphones.[2,15]

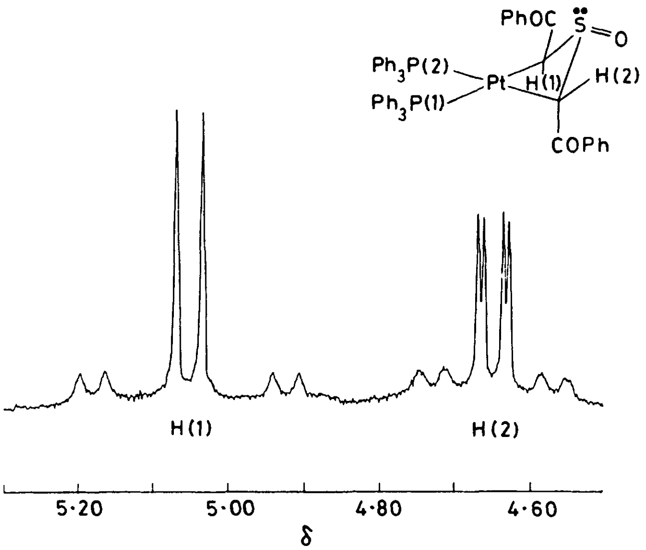


Figure 2. Room-temperature ^1H n.m.r. spectrum for Pt–CH ring protons of compound (**6a**)

The geometry about the platinum atom in compound (**6a**) is essentially square planar, with a small twist angle of 9.16° between the P(1)–Pt–P(2) and C(1)–Pt–C(3) planes. We also note that (**6a**) exists as the *trans*-disubstituted isomer, with one benzoyl substituent in a pseudo-axial environment, and the other in a pseudo-equatorial environment, a mode of substitution which has been shown to be favoured in 2,4-disubstituted metallathietane-3,3-dioxide complexes[2,15] and a range of 2,4-disubstituted metallacyclobutan-3-ones.[3,4]

The room-temperature ^1H n.m.r. spectra for the platinathietane-3-oxide complexes (**6a**)—(**6c**) are consistent with the puckered static structure, depicted in Figure 1. Two distinct resonances are observed for the axial and equatorial ring hydrogens H(1) and H(2) respectively, as illustrated for complex (**6a**) in Figure 2. The magnitude of the coupling of H(1) and H(2) to their *cis* and *trans* phosphorus-31 nuclei indicate that the three-bond *cis*-P–Pt–C–H couplings are under dihedral angle control, as in the well known Karplus relationships for vicinal H–C–C–H couplings in organic molecules.[16] Thus, the lower frequency resonance due to the equatorial hydrogen H(2) shows coupling to both the *cis* phosphorus atom [the P(1)–Pt–C(2)–H(2) torsion angle is −42.39°] and the *trans* phosphorus atom, to give a doublet of doublets. The higher frequency resonance due to the axial ring hydrogen H(1) shows coupling to its *trans* phosphorus atom only, to give a doublet.

No coupling of H(1) to its *cis* phosphorus P(2) is observed, since the P(2)–Pt–C(1)–H(1) torsion angle is −88.25°.

The ^{31}P-$\{^1H\}$ n.m.r. spectra for (**6a**)—(**6c**) show the presence of two non-equivalent ^{31}P nuclei, and second-order AB spectra are observed, to give a doublet of doublets with corresponding platinum-195 satellites. For example, for complex (**6a**), resonances at δ 17.31 [d, P(1), $^1J(PtP)$ 2 920, $^2J(PP)$ 19.5 Hz] and 12.58 p.p.m. [d, P(2), $^1J(PtP)$ 2 783, $^2J(PP)$ 19.5 Hz] are observed.

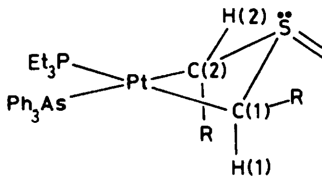
The ^1H-$\{^{31}P\}$ broad-band decoupled n.m.r. spectrum of (**6a**), measured at 360 MHz, consists of two single resonances at δ 5.03 [s, H(1), $^2J(PtH)$ 77.3 Hz] and 4.63 p.p.m. [s, H(2), $^2J(PtH)$ 48.8 Hz]. This indicates that there is no long-range proton–proton coupling between H(1) and H(2). Irradiation of the P(2) resonance leaves the H(1) resonance as a doublet, and collapses the H(2) resonance to a doublet. However, there is a reduction in the magnitude of the observed phosphorus–proton splittings $J[P(1)H(1)]$ and $J[P(1)H(2)]$ on irradiation of P(2). This may be due to some off-resonance decoupling of the P(1) nucleus occurring on irradiation of P(2), or due to the use of too much decoupling power.[17] Irradiation of the P(1) resonance collapses the H(1) resonance to a singlet, consistent with the *trans* assignment of P(1) and H(1), and collapses the H(2) resonance to a doublet, but again with a somewhat reduced splitting. The magnitude of the coupling of H(2) to P(1) is greater than to P(2), the coupling constants being 10.05 and 2.06 Hz respectively.

The ^1H n.m.r. spectrum of compound (**6a**) also reveals that the coupling of the axial proton H(1) to the platinum-195 nucleus is greater than for the equatorial proton H(2), with $^2J[PtH(1)]$ 77.3 Hz and $^2J[PtH(2)]$ 48.8 Hz. The value of $^2J(PH)$ in cyclic organophosphorus compounds has been observed to be greatest when the coupled proton lies close to the phosphorus lone pair.[18] Similar effects have also been observed in imines, hydrazones, oximes, and aziridines, the magnitude of $^2J(^{15}NH)$ being enhanced if the nitrogen lone pair approaches the coupled hydrogen.[19] The C(1)–H(1) vector in (**6a**), as determined from the *X*-ray study, is aligned with the vector on platinum (defined as the *z* direction) which is perpendicular to the C(1)–Pt–C(3) plane, whereas the equatorial C(2)–H(2) vector is not. Thus, the angles between the C(1)–H(1) and C(2)–H(2) vectors, and the vector on platinum perpendicular to the C(1)–Pt ··· C(3) plane, are 17.75 and 124.68° respectively. The axial hydrogen H(1) is subsequently closer to the platinum centre, as indicated by the *X*-ray data [Pt ··· H(1) 2.528, Pt ··· H(2) 2.774 Å]. It would therefore seem reasonable that the axial hydrogen H(1) experiences a greater coupling to the platinum-195 nucleus since it lies closer to non-bonding electron density on the platinum. This effect is also transmitted to the *trans* phosphine ligands, since the values of $^3J[P(1)H(1)]$ are greater than the values of $^3J[P(2)H(2)]$, for a given complex. Similarly in η^3-allyl complexes of platinum(II), coupling of platinum-195 is greater to the *anti* than to the *syn* hydrogens,[20,21] these *anti* and *syn* hydrogens being analogous to the axial and equatorial hydrogens respectively of a platinathietane-3-oxide complex. Platinum oxodimethylenemethane complexes similarly display a larger $J(PtH)$ coupling to the axial hydrogens than to the equatorial hydrogens.[3,4] The values of $^3J(PH)$ in η^3-allyl and oxodimethylenemethane complexes of platinum and palladium are also greater for the *anti* (axial) protons.[3,4,21,22]

The ^1H n.m.r. spectrum of compound (**6a**) is independent of temperature in the range −90 to +60 °C and it seems likely that the platinathietane-3-oxides (**6**) are rigid in solution. We also note that sulphoxides characteristically retain their stereochemical integrity at room temperature.[23]

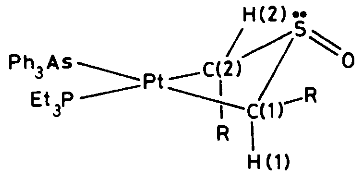
The chiral nature of the α-carbon atoms of the platinathietane-3-oxide ring may be demonstrated by the ^1H n.m.r. spectrum of the dimethylphenylphosphine complex (**6c**), in which all four methyl groups are non-equivalent (two pairs of diastereotopic methyl groups). This property has been described previously for the dimethylphenylphosphine-containing metallathietane-3,3-dioxide complexes.[2]

The ^{13}C-$\{^1H\}$ n.m.r. spectra for the platinathietane-3-oxide complexes (**6a**)—(**6c**) show two distinct resonances for the Pt–CH ring carbons. Thus, for the methyldiphenylphosphine complex (**6b**), resonances due to ring carbons C(1) and C(2) are observed at δ 44.76 and 49.98 p.p.m., each showing a large coupling to the *trans* phosphorus-31 atom $\{^2J[P(1)C(1)]$ 63.8 and $^2J[P(2)C(2)]$ 71.2 Hz$\}$ as well as to the platinum-195 atom $\{^1J[PtC(1)]$ 391 and $^1J[PtC(2)]$ 398 Hz$\}$. These ring carbons also show a small coupling to the *cis* phosphorus-31 atom $\{^2J[P(2)C(1)]$ 2.7 and $^2J[P(1)C(2)]$ 2.25 Hz$\}$. The assignment of these carbon atoms is tentatively made by a consideration of the above coupling constants, together with the *X*-ray data for the triphenyl phosphine complex. Thus, carbon atom C(1), which has the longer platinum–carbon bond when compared to C(2), may be expected to display smaller couplings



(12a)

R=COPh



(12b)

to platinum-195 and *trans*-phosphorus-31 atoms, as is observed. Furthermore, C(1) is *trans* to the phosphorus atom P(1), which has a shorter platinum–phosphorus bond, and has a larger value of ^1J(PtP) than does the phosphorus P(2).

The carbonyl carbon atoms of the benzoyl substituents appear as two weak signals in the ranges δ 202.35—203.51 and 196.06—199.15 p.p.m., with those of the PMe$_2$Ph complex (**6c**) being sufficiently resolved to show coupling to both the platinum-195 atom [^2J(PtC) 30.2 and 38.5 Hz], and the *trans* phosphorus-31 atom [^3J(PC) 3.9 and 5.2 Hz]. Hence one of these carbonyl carbon atoms displays a greater coupling to platinum-195 and phosphorus-31 than the other, again consistent with the presence of a static, puckered metallacycle in solution. The axial carbonyl group C(4)–O(3) is closer to the platinum centre and thus experiences a greater coupling to the platinum-195 and phosphorus-31 nuclei than does the equatorial carbonyl group C(3)–O(2) [the distances Pt···C(4) and Pt···C(3) are 3.009 and 3.236 Å respectively]. This is similar to the greater phosphorus and platinum couplings displayed by an axial ring proton, as described previously.

Treatment of the bromide-bridged dimeric complex [Pt$_2$Br$_4$(PEt$_3$)$_2$] with 1 equivalent of triphenylarsine and 1 equivalent of (**5**) in the presence of excess of silver(I) oxide afforded the mixed-ligand platinathietane-3-oxide complex [Pt{CH(COPh)S(O)CH(COPh)}(AsPh$_3$)(PEt$_3$)] (**12**) in good yield.

The ^{31}P-{^{1}H} n.m.r. spectrum of the initially isolated product of the mixed-ligand complex (**12**) reveals the presence of two complexes, each displaying platinum-195 coupling on the single phosphorus resonance, with ^1J(PtP) values of 2 793 and 2 759 Hz being observed for the major (76%) and minor (24%) isomers, (**12a**) and (**12b**) respectively. By means of ^{1}H n.m.r. spectroscopy, relative configurations for these complexes may be assigned, on the basis of the magnitudes of the phosphorus-ring hydrogen coupling constants, which are under dihedral angle control, as described previously for the bis(phosphine) complex (**6a**). The major isomer (**12a**) has the triphenylarsine ligand *trans* to the carbon bearing an axial benzoyl substituent, and the minor isomer (**12b**) has the triphenylarsine ligand *trans* to the carbon bearing an equatorial benzoyl substituent. Thus, for complex (**12a**) the axial and equatorial ring protons both appear as doublets due to phosphorus coupling. However, the axial ring proton signal for the minor isomer (**12b**) appears as a singlet, since the *cis*-P–Pt–C–H torsion angle is expected to be around 90°, and therefore no phosphorus coupling would be expected. The magnitudes of platinum coupling on these ring protons are also consistent with their assignment as axial or equatorial, with the lower-field axial protons showing the expected greater coupling to platinum-195. Thus, for example, the axial proton of (**12a**) shows a large *trans* phosphorus coupling (10.0 Hz), together with a large platinum coupling (66.8 Hz), whereas the axial proton of (**12b**) shows a large platinum coupling of 86.3 Hz, but no phosphorus coupling. The equatorial proton of (**12b**) shows the expected smaller coupling to phosphorus of 3.0 Hz, together with a relatively small platinum coupling of 51.8 Hz.

Steric effects of the triphenylarsine and triethylphosphine ligands may influence the isomer distribution. The major isomer (**12a**) has the equatorial benzoyl substituent *cis* to the triphenylarsine ligand, which would be expected to have a longer platinum–ligand bond. The torsional strain between an equatorial benzoyl group and a *cis* ligand might therefore be smaller for triphenylarsine than triethylphosphine, and this would account for the preferential formation of isomer (**12a**). Slow recrystallisation of the mixture of isomers of (**12**) from dichloromethane–light petroleum afforded pale yellow crystals of the major isomer (**12a**), but (**12b**) could not be obtained pure.

The i.r. spectrum of the dimethylphenylphosphine complex (**6c**) has an intense band in the sulphoxide stretching region, at 1 016 cm^{-1}, assigned to ν(S=O). However, the i.r. spectra of the triphenylphoshine and methyldiphenylphosphine complexes (**6a**) and (**6b**) respectively contain several bands in the sulphoxide stretching region; those at 1 023 cm^{-1} for (**6a**) and 1 016 cm^{-1} for (**6b**) may be tentatively assigned to ν(S=O). On going from diphenacyl sulphoxide (**5**) to the platinathietane-3-oxide (**6a**) there is a decrease in ν(S=O) of 9 cm^{-1}, and a similar, but larger decrease in ν(S=O) is observed on going from diphenacyl sulphone[24] to the platinathietane-3,3-dioxide complex (**1a**) of *ca.* 30 cm^{-1}. The benzoyl carbonyl groups appear as strong, somewhat broad bands around 1 620 and 1 630 cm^{-1}.

It is finally worth noting that a platinathietane-3-oxide was not obtained on treatment of thi-irane-*S*-oxide with [Pt(η^2-C$_2$H$_4$)(PPh$_3$)$_2$].[25] Ring opening reactions of cyclopropanes by low-valent metal complexes have been shown to be a useful synthetic route to platinacyclobutane complexes but platinum(0) will only ring-open three-membered rings bearing electron-withdrawing substituents.[9]

Experimental

Melting points were measured in air on a Reichert hot-stage apparatus and are uncorrected. Infrared spectra were recorded as KBr discs on a Perkin-Elmer 580 spectrophotometer. Hydrogen-1 n.m.r. spectra were recorded on a Bruker AM300 spectrometer at 300.13 MHz or on a Bruker Spectrospin WH400 spectrometer at 400.13 MHz, and hydrogen-1, phosphorus-31 decoupled, spectra on a Bruker WH360 spectrometer operating at 360.13 MHz, in [^{2}H$_1$]chloroform, with SiMe$_4$ (0.0 p.p.m.) as internal reference, positive values being to high frequency (low field). Hydrogen-1 phosphorus-31 splittings were reduced from the true coupling constant in the ^{1}H-{^{31}P} n.m.r. spectra,[16] but are reported as the coupling constant in order to illustrate the relative hydrogen-1 phosphorus-31 couplings in the platinathietane-3-oxide ring systems. Carbon-13, hydrogen-1 decoupled n.m.r. spectra were recorded in [^{2}H$_1$]chloroform on a Bruker AM300 spectrometer at 75.47 MHz with SiMe$_4$ (0.0 p.p.m.) as internal reference, and the data for the aromatic region between δ 140 and 125 p.p.m. have been omitted. Phosphorus-31, hydrogen-1 decoupled n.m.r. spectra were recorded on a JEOL JNM-FX60 spectrometer at 24.15 MHz with [P(OH)$_4$]$^+$ in [^{2}H$_2$]water (0.0 p.p.m.) as external reference.[26]

Experiments were carried out under a dry, oxygen-free, nitrogen atmosphere using solvents which were dried and distilled under nitrogen prior to use. The platinathietane-3-oxide complexes were recrystallised in air. Light petroleum refers to the fraction of b.p. 40—60 °C. The compounds diphenacyl sulphoxide (**5**),[27] [$PtCl_2$(cod)] (cod = cyclo-octa-1,5-diene),[28] and [{$PtBr_2(PEt_3)$}$_2$][29] were prepared as described in the literature.

Preparation of Platinathietane-3-oxide Complexes.—(i) [Pt{CH(COPh)S(O)CH(COPh)}$(PPh_3)_2$] (**6a**). Triphenylphosphine (0.28 g, 1.07 mmol), diphenacyl sulphoxide (0.153 g, 0.53 mmol), and silver(I) oxide (0.4 g, 1.7 mmol) were added in succession to a stirred solution of [$PtCl_2$(cod)] (0.20 g, 0.53 mmol) in dichloromethane (25 cm^3), and the mixture was refluxed for 2 h. Filtration through 1 cm of Celite gave a pale yellow solution which was evaporated to dryness under reduced pressure to afford a pale yellow oil. Dissolution of the oil in dichloromethane (*ca.* 2 cm^3) followed by addition of light petroleum (*ca.* 50 cm^3) gave, on standing for 12 h, a pale yellow microcrystalline *solid* which was filtered off and dried *in vacuo* to give the required complex (**6a**) (0.518 g, 97%) (Found: C, 62.5; H, 4.2. $C_{52}H_{42}O_3P_2PtS$ requires C, 62.2; H, 4.2%), m.p. softens 168—180 °C, resolidifies 180—190 °C, and decomp. >190 °C; ν(C=O) at 1 631vs (br), ν(S=O) at 1 023 s cm^{-1}. N.m.r. spectra: ^{1}H (300 MHz), δ 7.52—6.79 (m, 40 H, Ph), 5.05 {d, 1 H, H(1), ^3J[P(1)H(1)] 10.31, ^2J[PtH(1)] 77.3}, and 4.65 {dd, 1 H, H(2), ^3J[P(1)H(2)] 10.05, ^3J[P(2)H(2)] 2.06, ^2J[PtH(2)] 48.8}; (400 MHz, −90 °C, [$^2H_2$]dichloromethane or +60 °C, [$^2H_8$]-toluene), identical to room temperature spectrum; ^{1}H-{^{31}P} (360 MHz, broad-band irradiation), δ 5.03 {s, 1 H, H(1), ^2J[PtH(1)] 77.3} and 4.63 p.p.m. {s, 1 H, H(2), ^2J[PtH(2)] 48.8}; [360 MHz, irradiated at 145.787 405 MHz {P(1)}], δ 5.03 {s, 1 H, H(1), ^2J[PtH(1)] 77.3} and 4.63 p.p.m. {d, 1 H, H(2), ^3J[P(2)H(2)] 2.06, ^2J[PtH(2)] 48.8}; [360 MHz, irradiated at 145.786 752 MHz {P(2)}], δ 5.03 {d, 1 H, H(1), ^3J[P(1)H(1)] 10.31, ^2J[PtH(1)] 77.3} and 4.63 p.p.m. {d, 1 H, H(2), ^3J[P(1)H(2)] 10.05, ^2J[PtH(2)] 48.8}; ^{13}C-{^{1}H} (100 MHz), δ 202.35 [d, CO, ^3J(PC) 4.03, ^2J(PtC) not discernible], 199.15 [d, CO, ^3J(PC) 5.02, ^2J(PtC) not discernible], 48.00 {d, C(2), ^2J[P(2)C(2)] 71.48, ^2J[P(1)C(2)] not discernible, ^1J[PtC(2)] *ca.* 402}, and 45.05 p.p.m. {d, C(1), ^2J[P(1)C(1)] 67.20, ^2J[P(2)C(1)] not discernible, ^1J[PtC(1)] *ca.* 410}; ^{31}P-{^{1}H} (24 MHz), second-order AB spin system, δ 17.31 {d, P(1), ^1J[PtP(1)] 2 920, ^2J[P(2)P(1)] 19.5} and 12.58 p.p.m. {d, P(2), ^1J[PtP(2)] 2 783, ^2J[P(1)P(2)] 19.5 Hz}. See Figure 2. *X*-Ray quality *crystals* of (**6a**)·$2CH_2Cl_2$ were grown slowly from dichloromethane–light petroleum, in air.

(ii) [Pt{CH(COPh)S(O)CH(COPh)}$(PMePh_2)_2$] (**6b**)·H_2O. Methyldiphenylphosphine (0.07 cm^3, 0.38 mmol), diphenacyl sulphoxide (0.077 g, 0.27 mmol), and silver(I) oxide (0.3 g, 1.3 mmol) were added in succession to a stirred solution of [$PtCl_2$(cod)] (0.10 g, 0.27 mmol) in dichloromethane (25 cm^3), and the mixture was refluxed for 2 h. Work-up as in (i) above afforded pale yellow *microcrystals* of the required complex (**6b**)·H_2O (0.203 g, 85%) (Found: C, 55.2; H, 4.5. $C_{42}H_{38}O_3P_2PtS·H_2O$ requires C, 56.2; H, 4.5%), m.p. 196—198 °C (decomp.); ν(C=O) at 1 631vs and 1 620vs, ν(S=O) at 1 016vs (br) cm^{-1}. N.m.r. spectra: ^{1}H (300 MHz), δ 7.60—6.95 (m, 30 H, Ph), 5.36 {d, 1 H, H(1), ^3J[P(1)H(1)] 9.90, ^2J[PtH(1)] 70.5}, 4.79 {dd, 1 H, H(2), ^3J[P(1)H(2)] 9.64, ^3J[P(2)H(2)] 4.02, ^2J[PtH(2)] 54.03}, 2.09 (s, br, 2 H, H_2O), 1.78 [d, 3 H, Me, $PMePh_2$, |^2J(PH) + ^4J(PH)| 9.06, ^3J(PtH) 28.5], and 1.39 [d, 3 H, Me, $PMePh_2$, |^2J(PH) + ^4J(PH)| 8.98, ^3J(PtH) 28.4]; ^{13}C-{^{1}H} (75.5 MHz), δ 203.0 [d, CO, ^3J(PC) *ca.* 4, ^2J(PtC) not discernible], 196.8 [d, CO, ^3J(PC) *ca.* 5, ^2J(PtC) not discernible], 49.98 {dd, C(2), ^2J[P(2)C(2)] 71.2, ^2J[P(1)C(2)] 2.3, ^1J[PtC(2)] *ca.* 398}, 44.76 {dd, C(1), ^2J[P(1)C(1)] 63.8, ^2J[P(2)C(1)] 2.7, ^1J[PtC(1)] *ca.* 391}, 13.46 [d, Me, $PMePh_2$, |^1J(PC) + ^3J(PC)| 19.7, ^2J(PtC) not discernible], and 13.00 [d, Me, $PMePh_2$, |^1J(PC) + ^3J(PC)| 19.6, ^2J(PtC) not discernible]; ^{31}P-{^{1}H} (24 MHz), second-order AB spin system, δ −1.55 {d, P(2), ^1J[PtP(2)] 2 739, ^2J[P(1)P(2)] 14.7} and − 3.69 p.p.m. {d, P(1), ^1J[PtP(1)] 2 822, ^2J[P(2)P(1)] 14.7 Hz}. See Figure 2.

(iii) [Pt{CH(COPh)S(O)CH(COPh)}$(PMe_2Ph)_2$] (**6c**)·0.5CH_2Cl_2. Dimethylphenylphosphine (0.15 g, 1.08 mmol), diphenacyl sulphoxide (0.153 g, 0.535 mmol), and silver(I) oxide (0.4 g, 1.7 mmol) were added in succession to a stirred solution of [$PtCl_2$(cod)] (0.20 g, 0.53 mmol) in dichloromethane (25 cm^3), and the mixture was refluxed for 1.5 h. Work-up as in (i) above afforded pale yellow *microcrystals* of the required complex (**6c**)·0.5CH_2Cl_2 (0.173 g, 40%) (Found: C, 48.7; H, 4.5. $C_{32}H_{34}O_3P_2PtS·0.5CH_2Cl_2$ requires C, 48.9; H, 4.3%), m.p. 109—112 °C; ν(C=O) at 1 636s and 1 627s, ν(S=O) at 1 016s cm^{-1}. N.m.r. spectra: ^{1}H (300 MHz), δ 8.00—7.16 (m, 20 H, Ph), 5.31 (s, 1 H, CH_2Cl_2), 5.26 {d, 1 H, H (1), ^3J[P(1)H(1)] 10.0, ^2J[PtH(1)] 68.4}, 5.21 {dd, 1 H, H(2), ^3J[P(1)H(2)] 8.7, ^3J[P(2)H(2)] 4.7, ^2J[PtH(2)] 55.2}, 1.45 [d, 3 H, Me, PMe_2Ph, |^2J(PH) + ^4J(PH)| 9.6, ^3J(PtH) *ca.* 30], 1.37 [d, 3 H, Me, PMe_2Ph, |^2J(PH) + ^4J(PH)| 9.5, ^3J(PtH) *ca.* 30], 1.22 [d, 3 H, Me, PMe_2Ph, |^2J(PH) + ^4J(PH)| 9.6, ^3J(PtH) *ca.* 30], and 1.16 [d, 3 H, Me, PMe_2Ph, |^2J(PH) + ^4J(PH)| 9.5, ^3J(PtH) *ca.* 30]; ^{13}C-{^{1}H} (75.5 MHz), δ 203.51 [d, CO, ^3J(PC) 3.9, ^2J(PtC) 30.2], 196.06 [d, CO, ^3J(PC) 5.2, ^2J(PtC) 38.5], 50.38 {dd, C(2), ^2J[P(2)C(2)] 68.9, ^2J[P(1)C(2)] 2.2, ^1J[PtC(2)] 378.7}, 43.44 {dd, C(1), ^2J[P(1)C(1)] 62.1, ^2J[P(2)C(1)] 2.6, ^1J[PtC(1)] 355.3}, 15.79 [d, Me, PMe_2Ph, |^1J(PC) + ^3J(PC)| 17.3, ^2J(PtC) not discernible], 15.33 [d, Me, PMe_2Ph, |^1J(PC) + ^3J(PC)| 17.4, ^2J(PtC) not discernible], 15.20 [d, Me, PMe_2Ph, |^1J(PC) + ^3J(PC)| 12.8, ^2J(PtC) not discernible], and 14.75 p.p.m. [d, Me, PMe_2Ph, |^1J(PC) + ^3J(PC)| 11.8, ^2J(PtC) not discernible]; ^{31}P-{^{1}H} (24 MHz), second-order AB spin system, δ −16.26 {d, P(2), ^1J[PtP(2)] 2 734, ^2J[P(1)P(2)] 19.5} and −17.42 p.p.m. {d, P(1), ^1J[PtP(1)] 2 788, ^2J[P(2)P(1)] 19.5 Hz}. See Figure 2.

(iv) [Pt{CH(COPh)S(O)CH(COPh)}$(AsPh_3)(PEt_3)$] (**12**). Triphenylarsine (0.065 g, 0.212 mmol), diphenacyl sulphoxide (0.062 g, 0.216 mmol), and silver(I) oxide (0.3 g, 1.3 mmol) were added in succession to a stirred solution of the complex [{$PtBr_2(PEt_3)$}$_2$] (0.10 g, 0.106 mmol) in dichloromethane (25 cm^3). The mixture was refluxed for 15 h, filtered, and the filtrate evaporated to dryness under reduced pressure to afford a pale yellow oil, which was shown by ^{31}P-{^{1}H} and ^{1}H n.m.r. spectroscopy to consist of a mixture of isomers (**12a**) (76%) and (**12b**) (24%). Dissolution of the oil in dichloromethane (*ca.* 3 cm^3) followed by addition of light petroleum (*ca.* 70 cm^3) afforded an off-white solid (0.319 g, 84%) which contained the same ratio of isomers (**12a**) and (**12b**) as the oil. Slow recrystallisation from dichloromethane–light petroleum afforded pale yellow *microcrystals* of pure isomer (**12a**) (0.046 g, 12%).

Isomer (**12a**). (Found: C, 53.6; H, 4.6. $C_{40}H_{42}AsO_3PPtS$ requires C, 53.2; H, 4.7%), m.p. 187—193 °C (decomp.); ν(C=O) at 1 638vs and 1 630vs, ν(S=O) at 1 030vs cm^{-1}. N.m.r. spectra: ^{1}H (300 MHz), δ 8.13—6.72 (m, 25 H, Ph), 5.39 {d, 1 H, H(2), ^3J[PH(2)] 8.45, ^2J[PtH(2)] 58.5}, 4.99 {d, 1 H, H(1), ^3J[PH(1)] 10.0, ^2J[PtH(1)] 66.8}, 1.40—1.08 (m, 6 H, CH_2, PEt_3), and 0.77 (m, 9 H, CH_3, PEt_3); ^{13}C-{^{1}H} (75.5 MHz), δ 201.19 [s, br, CO, ^2J(PtC) *ca.* 32], 196.73 [s, CO, ^2J(PtC) *ca.* 47], 49.04 [d, C(1), ^2J(PC) 65.7, ^1J(PtC) 345.2], 38.30 [s, br, C(2), ^1J(PtC) 490.4], 16.20 [CH_2, PEt_3, ^1J(PC) 31.4, ^2J(PtC) 8.8], and 7.97 p.p.m. [s, br, CH_3, PEt_3, *J*(PC) not discernible]; ^{31}P-{^{1}H} (24 MHz), δ 5.65 p.p.m. [s, ^1J(PtP) 2 793 Hz].

Isomer (**12b**). N.m.r. spectra: ^{1}H (300 MHz), platinathietane-3-oxide ring resonances at δ 5.29 [s, 1 H, H(1), ^2J(PtH) 86.3] and 4.43 [d, 1 H, H(2), ^3J(PH) 3.0, ^2J(PtH) 51.8]; ^{31}P-{^{1}H} (24 MHz), δ 1.21 p.p.m. [s, ^1J(PtP) 2 759 Hz].

Table 2. Fractional atomic co-ordinates

Atom	*x*	*y*	*z*
Pt	0.466 03(2)	0.496 84(2)	0.280 52(2)
P(1)	0.472 88(14)	0.687 72(15)	0.376 07(12)
P(2)	0.669 97(15)	0.505 08(15)	0.188 32(12)
S	0.270 30(15)	0.303 06(16)	0.299 23(13)
O(1)	0.180 6(5)	0.228 2(5)	0.266 4(4)
O(2)	0.451 5(5)	0.170 7(5)	0.231 6(4)
O(3)	0.300 9(5)	0.469 5(6)	0.204 5(4)
C(1)	0.417 0(6)	0.314 0(6)	0.208 8(5)
C(2)	0.277 8(6)	0.459 8(6)	0.332 6(5)
C(3)	0.473 9(6)	0.215 9(6)	0.179 7(5)
C(4)	0.242 1(6)	0.488 2(6)	0.284 6(5)
C(5)	0.175 7(13)	0.211 5(13)	0.102 7(10)
C(6)	0.201 3(25)	−0.024 1(25)	0.317 5(19)
C(01)	0.561 7(4)	0.169 0(4)	0.083 98(26)
C(02)	0.654 6(4)	0.124 8(4)	0.064 00(26)
C(03)	0.730 6(4)	0.069 1(4)	−0.024 36(26)
C(04)	0.713 7(4)	0.057 6(4)	−0.092 76(26)
C(05)	0.620 9(4)	0.101 8(4)	−0.072 77(26)
C(06)	0.544 9(4)	0.157 5(4)	0.015 59(26)
C(11)	0.129 5(4)	0.535 3(4)	0.333 8(3)
C(12)	0.076 4(4)	0.592 6(4)	0.425 6(3)
C(13)	−0.024 9(4)	0.640 6(4)	0.467 2(3)
C(14)	−0.073 0(4)	0.631 4(4)	0.417 0(3)
C(15)	−0.019 9(4)	0.574 1(4)	0.325 2(3)
C(16)	0.081 4(4)	0.526 0(4)	0.283 6(3)
C(21)	0.541 2(4)	0.720 0(4)	0.443 02(29)
C(22)	0.573 1(4)	0.625 9(4)	0.437 49(29)
C(23)	0.613 3(4)	0.643 1(4)	0.494 93(29)
C(24)	0.621 6(4)	0.754 4(4)	0.557 89(29)
C(25)	0.589 7(4)	0.848 5(4)	0.563 43(29)
C(26)	0.549 5(4)	0.831 3(4)	0.506 00(29)
C(31)	0.330 8(3)	0.735 4(4)	0.466 30(28)
C(32)	0.259 1(3)	0.677 3(4)	0.530 07(28)
C(33)	0.152 1(3)	0.713 1(4)	0.602 12(28)
C(34)	0.116 7(3)	0.806 9(4)	0.610 41(28)
C(35)	0.188 3(3)	0.865 0(4)	0.546 64(28)
C(36)	0.295 4(3)	0.829 2(4)	0.474 59(28)
C(41)	0.543 1(4)	0.795 5(4)	0.318 6(3)
C(42)	0.627 8(4)	0.896 8(4)	0.331 3(3)
C(43)	0.671 4(4)	0.976 5(4)	0.285 8(3)
C(44)	0.630 3(4)	0.954 8(4)	0.227 8(3)
C(45)	0.545 6(4)	0.853 5(4)	0.215 2(3)
C(46)	0.502 1(4)	0.773 8(4)	0.260 6(3)
C(51)	0.695 5(5)	0.450 9(5)	0.073 71(27)
C(52)	0.791 3(5)	0.395 6(5)	0.000 73(27)
C(53)	0.808 4(5)	0.362 0(5)	−0.085 22(27)
C(54)	0.729 5(5)	0.383 7(5)	−0.098 17(27)
C(55)	0.633 7(5)	0.439 0(5)	−0.025 18(27)
C(56)	0.616 7(5)	0.472 6(5)	0.060 77(27)
C(61)	0.737 6(4)	0.418 6(4)	0.196 6(3)
C(62)	0.858 8(4)	0.412 6(4)	0.143 7(3)
C(63)	0.906 0(4)	0.343 9(4)	0.151 7(3)
C(64)	0.832 0(4)	0.281 2(4)	0.212 5(3)
C(65)	0.710 8(4)	0.287 2(4)	0.265 3(3)
C(66)	0.663 6(4)	0.355 9(4)	0.257 3(3)
C(71)	0.776 5(4)	0.646 0(4)	0.193 5(3)
C(72)	0.816 5(4)	0.693 2(4)	0.256 6(3)
C(73)	0.897 9(4)	0.800 2(4)	0.260 8(3)
C(74)	0.939 4(4)	0.860 0(4)	0.201 9(3)
C(75)	0.899 5(4)	0.812 8(4)	0.138 8(3)
C(76)	0.818 0(4)	0.705 8(4)	0.134 6(3)
Cl(1)	0.055 7(5)	0.104 1(4)	0.091 3(6)
Cl(2)	0.273 6(8)	0.248 5(8)	0.014 9(5)
Cl(3)	0.217 9(7)	−0.131 4(6)	0.326 4(6)
Cl(4)	0.088 3(7)	0.038 4(7)	0.390 9(8)
H(1)	0.411(6)	0.316(6)	0.169(5)
H(2)	0.222(5)	0.482(5)	0.393(4)

Crystal Structure Determination.—Crystals of complex (**6a**)·$2CH_2Cl_2$ were obtained by crystallisation from dichloromethane–light petroleum. A pale yellow irregular crystal of approximate dimensions 0.13 × 0.14 × 0.25 mm was mounted in a thin-walled glass capillary under a nitrogen atmosphere saturated with dichloromethane–light petroleum. The cell dimensions were determined from oscillation photographs for the rotation axis (*c*) and from optimised counter angles for zero- and upper-layer reflections. Data were collected on a Stöe STADI-2 Weissenberg diffractometer using an ω-scan technique in the range $7 \leqslant 2\theta \leqslant 54°$; the 7 864 unique reflections collected from Weissenberg layers *h k* (0—22) having $(I) \geqslant 3\sigma(I)$ were corrected for Lorentz and polarisation effects. Subsequent calculations were carried out using the computer program SHELX.[30]

Crystal data. $C_{52}H_{42}O_3P_2PtS{\cdot}2CH_2Cl_2$, $M = 1\,173.77$, triclinic, space group $P\bar{1}$, $a = 13.824(1)$, $b = 12.953(2)$, $c = 19.248(6)$ Å, $\alpha = 118.0(2)$, $\beta = 52.4(2)$, $\gamma = 113.56(5)°$, $U = 2\,464.7$ Å^3, $Z = 2$, $D_c = 1.48$ g cm^{-3}, $F(000) = 1\,171.9$, Mo-K_α radiation, $\lambda = 0.710\,69$ Å, μ(Mo-K_α) = 30.60 cm^{-1}.

The transformation matrix $0 - 1\,0{:}-1\,0\,0{:}1\,0 - 1{:}$ gives a conventional reduced cell 12.953, 13.824, 15.391 Å, 97.77, 103.19, 113.56°. The non-standard cell was used throughout the analysis.

The molecular structure was solved by conventional Patterson and difference Fourier techniques. Scattering factors were taken from ref. 31. An absorption correction was applied to the data, the maximum and minimum transmission factors being 0.5410 and 0.4636 respectively. In the final stages of blocked-matrix least-squares refinements all non-hydrogen atoms with the exception of the phenyl carbon atoms and the carbon atoms of the solvent dichloromethane molecules were given antisotropic thermal parameters. All phenyl rings were treated as rigid bodies with D_{6h} symmetry and carbon–carbon distances of 1.395(5) Å. The phenyl hydrogen atoms were included at calculated positions [C–H 1.08(5) Å]. The H(1) and H(2) atoms were located and refined as free atoms. Two molecules of dichloromethane solvent were included in the final cycles of refinement. Final cycles employed a weighting factor *w*, calculated from $w = k/(\sigma^2F + gF^2)$ where $k = 1.9971$ and $g = 0.000\,718$. 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 are 0.0487 and 0.0512 respectively. The atomic co-ordinates for the structure are given in Table 2.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

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