Metallacyclic Complexes. Part 2.[1] Synthesis of Metallathietane-3,3-dioxide Complexes of Platinum(II) and Palladium(II); the Crystal Structures of $[\mathrm{Pt\{CH(COPh)S(O)_2CH(COPh)\}(PPh_3)_2}]\cdot2\mathrm{CH_2Cl_2}$ and $[\mathrm{Pd\{CH(COPh)S(O)_2CH(COPh)\}(PMePh_2)_2}]\cdot\mathrm{CH_2Cl_2}\cdot\mathrm{H_2O}$†

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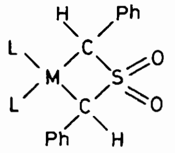
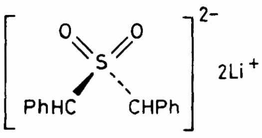
The reactions of the complexes *cis*-$[\mathrm{PtCl_2L_2}]$ or *trans*-$[\mathrm{PdCl_2L_2}]$ (L = tertiary phosphine or triphenyl phosphite) with bis(benzoylmethyl) sulphone or the dimethyl ester of 2,2′-sulphonyldiacetic acid and an excess of silver(I) oxide in refluxing dichloromethane afford, in high yields, the metallathietane-3,3-dioxide complexes $[\mathrm{M\{CH(COR)S(O)_2CH(COR)\}L_2}]$ (R = Ph, M = Pt or Pd, L = $\mathrm{PPh_3}$, $\mathrm{PMePh_2}$, $\mathrm{PMe_2Ph}$, $\mathrm{PMe_3}$, $\mathrm{PEt_3}$, or $\mathrm{PBu^n_3}$; M = Pt, L = $\mathrm{P(OPh)_3}$; R = OMe, M = Pt or Pd, L = $\mathrm{PPh_3}$). Single-crystal *X*-ray diffraction studies have been carried out on $[\mathrm{Pt\{CH(COPh)S(O)_2CH(COPh)\}(PPh_3)_2}]\cdot2\mathrm{CH_2Cl_2}$ [(**6a**)] and $[\mathrm{Pd\{CH(COPh)S(O)_2CH(COPh)\}(PMePh_2)_2}]\cdot\mathrm{CH_2Cl_2}\cdot\mathrm{H_2O}$ [(**6i**)]. Crystals of (**6a**)$\cdot2\mathrm{CH_2Cl_2}$ are triclinic, space group $P\bar{1}$, $Z = 2$, in a unit cell with lattice parameters $a = 20.835(2)$, $b = 10.628(2)$, $c = 12.577(4)$ Å, $\alpha = 109.6(1)$, $\beta = 105.8(1)$, and $\gamma = 91.4(1)^\circ$. The structure was refined to R 0.0595 (R' 0.0580) for 5 553 reflections having $7 < 2\theta < 54^\circ$ (Mo-K_α *X*-radiation) collected at room temperature. Crystals of (**6i**)$\cdot\mathrm{CH_2Cl_2}\cdot\mathrm{H_2O}$ are triclinic, space group $P\bar{1}$, $Z = 2$, in a unit cell with lattice parameters $a = 12.985(5)$, $b = 13.93(1)$, $c = 12.057(6)$ Å, $\alpha = 73.71(3)$, $\beta = 102.61(5)$, and $\gamma = 100.01(3)^\circ$. The structure was refined to R 0.0745 (R' 0.0823) for 5 536 reflections having $7 < 2\theta < 54^\circ$ collected at room temperature. Both molecules contain a puckered metallathietane-3,3-dioxide ring [fold angles 15.3(6) for (**6a**) and 30.2(2)° for (**6i**)]. The puckering of the four-membered rings, together with the presence of short C–S bonds suggests a heteroallylic contribution to the metallacyclic bonding. N.m.r. data for the metallathietane-3,3-dioxide complexes are also reported.

We have recently shown that a number of metallathietane-3,3-dioxide complexes of platinum(II) [(**1**)], palladium(II), and nickel(II) are formed on treatment of the complexes *cis*- or *trans*-$[\mathrm{MCl_2L_2}]$ (L = donor ligand) with the 1,3-dianion of dibenzyl sulphone (**2**).[1] The utility of silver(I) oxide in the synthesis of the η^3-oxodimethylenemethane–platinum complex (**3**) *via* the 1,3-disubstituted acetone (**4**)[2] led us to investigate the reactions of the related sulphones (**5**) in the synthesis of four-membered metallacycles. A preliminary account of some of this work has been reported.[3]



(**1**)
(**a**) M = Pt, L = $\mathrm{AsPh_3}$



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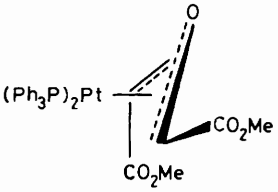
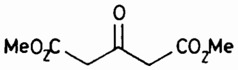


(**3**)



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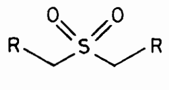

	R
(**5a**)	COPh
(**5b**)	$\mathrm{CO_2Me}$

Results and Discussion

Treatment of the complexes *cis*-$[\mathrm{PtCl_2L_2}]$ [L = $\mathrm{PPh_3}$, $\mathrm{PMePh_2}$, $\mathrm{PMe_2Ph}$, $\mathrm{PMe_3}$, $\mathrm{PEt_3}$, $\mathrm{PBu^n_3}$, or $\mathrm{P(OPh)_3}$] or *trans*-$[\mathrm{PdCl_2L_2}]$ (L = $\mathrm{PPh_3}$, $\mathrm{PMePh_2}$, $\mathrm{PMe_2Ph}$, $\mathrm{PMe_3}$, $\mathrm{PEt_3}$, or $\mathrm{PBu^n_3}$) with one equivalent of (**5a**) and an excess of silver(I) oxide in refluxing dichloromethane affords high yields of the air-stable metallathietane-3,3-dioxide complexes (**6a**)—(**6m**). Similarly, treatment of *cis*-$[\mathrm{PtCl_2(PPh_3)_2}]$ or *trans*-$[\mathrm{PdCl_2(PPh_3)_2}]$ with one equivalent of (**5b**) and an excess of silver(I) oxide affords the complexes (**6n**) and (**6o**) respectively. Interestingly, the reaction of the 1,3,5-triketone, (**7**), with *cis*-$[\mathrm{PtCl_2(PPh_3)_2}]$ in the presence of silver(I) oxide gives the known dienediolate complex (**8**).[4] This difference can be attributed to the reluctance of sulphones to take part in conjugation as compared to related ketones.

In order to compare the molecular structures of benzoyl-substituted platina- and pallada-thietane-3,3-dioxide complexes

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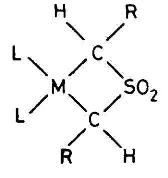
† (1,3-Dibenzoyl-2,2-dioxo-2λ^6-thiapropane-1,3-diyl)bis(triphenylphosphine)platinum(II)–dichloromethane (1/2), (1,3-dibenzoyl-2,2-dioxo-2λ^6-thiapropane-1,3-diyl)bis(methyldiphenylphosphine)palladium(II)–dichloromethane–hydrate (1/1/1).

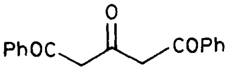
Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1989, Issue 1, pp. xvii—xx.



Complex	L	Complex	L
M = Pt; **(6a)**	PPh_3	M = Pd; **(6h)**	PPh_3
R = COPh **(6b)**	$PMePh_2$	R = COPh **(6i)**	$PMePh_2$
(6c)	PMe_2Ph	**(6j)**	PMe_2Ph
(6d)	PMe_3	**(6k)**	PMe_3
(6e)	PEt_3	**(6l)**	PEt_3
(6f)	PBu^n_3	**(6m)**	PBu^n_3
(6g)	$P(OPh)_3$		

(6n) PPh_3; M = Pt ; R = CO_2Me

(6o) PPh_3; M = Pd ; R = CO_2Me



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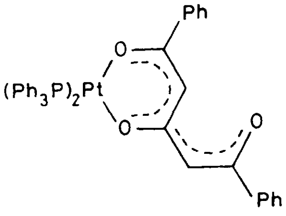


(8)

with that of the phenyl substituted platinathietane-3,3-dioxide complex[1] (**1a**), single-crystal *X*-ray diffraction studies have been carried out on the triphenylphosphine–platinum complex (**6a**)$\cdot 2CH_2Cl_2$ and the methyldiphenylphosphine–palladium complex (**6i**)$\cdot CH_2Cl_2\cdot H_2O$. The results of the *X*-ray work are summarised in Tables 1 and 2. The molecular structures of (**6a**) and (**6i**) are illustrated in Figures 1 and 2 respectively. Complex (**6a**) crystallises with two molecules of dichloromethane per molecule of complex, and complex (**6i**) crystallises with one molecule of dichloromethane plus one molecule of water per molecule of complex. There are no short intermolecular contacts between the complexes and the solvent molecules.

Table 1. Selected interatomic bond distances (Å) for $[Pt\{CH(COPh)S(O)_2CH(COPh)\}(PPh_3)_2]\cdot 2CH_2Cl_2$ [(**6a**)] and $[Pd\{CH(COPh)S(O)_2CH(COPh)\}(PMePh_2)_2]\cdot CH_2Cl_2\cdot H_2O$ [(**6i**)] with estimated standard deviations (e.s.d.s) in parentheses

	(**6a**), M = Pt	(**6i**), M = Pd
M–P(1)	2.327(3)	2.295(1)
M–P(2)	2.285(3)	2.311(2)
M–C(1)	2.106(10)	2.148(6)
M–C(2)	2.125(11)	2.122(6)
M ⋯ S	2.840(5)	2.770(2)
$CH(COPh)S(O)_2CH(COPh)$ ligands		
C(1)–S	1.762(11)	1.749(5)
C(2)–S	1.755(11)	1.738(5)
S–O(1)	1.439(9)	1.433(5)
S–O(2)	1.445(8)	1.435(4)
C(1)–C(3)	1.526(16)	1.493(6)
C(2)–C(4)	1.521(15)	1.472(7)
C(3)–O(3)	1.218(14)	1.223(6)
C(4)–O(4)	1.205(12)	1.229(6)
C(3)–C(81)	1.499(14)	1.485(6)
C(4)–C(71)	1.516(12)	1.502(6)
C(1)–H(1)	0.97(7)	
C(2)–H(2)	0.96(8)	

Triphenylphosphine ligands (**6a**)		Methyldiphenylphosphine ligands (**6i**)	
P(2)–C(11)	1.813(6)	P(1)–C(5)	1.842(6)
P(2)–C(21)	1.830(6)	P(1)–C(11)	1.814(3)
P(2)–C(31)	1.832(6)	P(1)–C(21)	1.796(3)
P(1)–C(41)	1.829(6)	P(2)–C(6)	1.830(6)
P(1)–C(51)	1.840(6)	P(2)–C(31)	1.815(4)
P(1)–C(61)	1.830(6)	P(2)–C(41)	1.814(5)

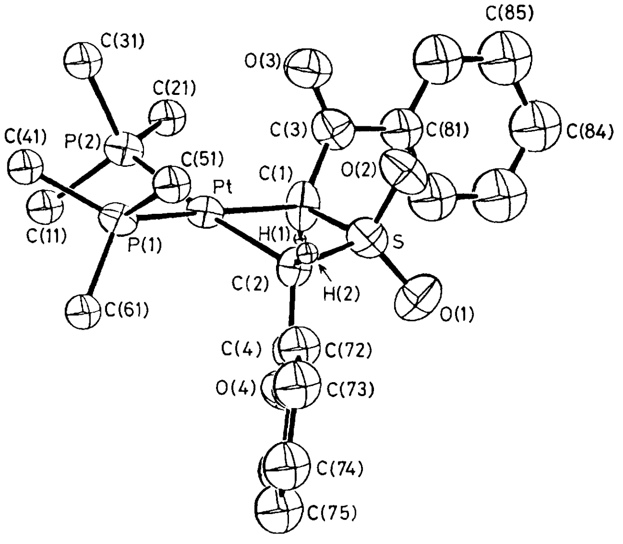


Figure 1. Molecular structure of $[Pt\{CH(COPh)S(O)_2CH(COPh)\}(PPh_3)_2]$ (**6a**), showing the atom numbering scheme. Atoms are shown as 50% thermal ellipsoids. Triphenylphosphine carbon atoms other than those bonded to phosphorus, and hydrogen atoms of phenyl rings are omitted

The structures of (**6a**) and (**6i**) are very similar to the structure of the related phenyl-substituted platinathietane-3,3-dioxide complex (**1a**).[1] The co-ordination about the platinum and palladium atoms in (**6a**) and (**6i**) is effectively square planar, with the twist angles between the P(1)–M–P(2) and C(1)–M–C(2) planes being 6.48(36) for (**6a**) and 3.47(13)° for (**6i**). The four-membered metallathietane-3,3-dioxide rings in (**6a**) and (**6i**) are non-planar, the fold angles between the C(1)–M–C(2) and C(1)–S–C(2) planes being 15.3(6) and 30.2(2)° in (**6a**) and (**6i**) respectively, as compared to 24.6° in the phenyl-substituted complex (**1a**).[1] The fold angles for these metallathietane-3,3-dioxide ring systems lie within the range of 9—35° found for thietane-1,1-dioxide, $C–C–C–S(O)_2$ ring systems.[5] Studies on platinacyclobutane ring systems have established that fold angles in these complexes lie in the range 0—30°,[6,7] whereas metallacyclobutan-3-one complexes of

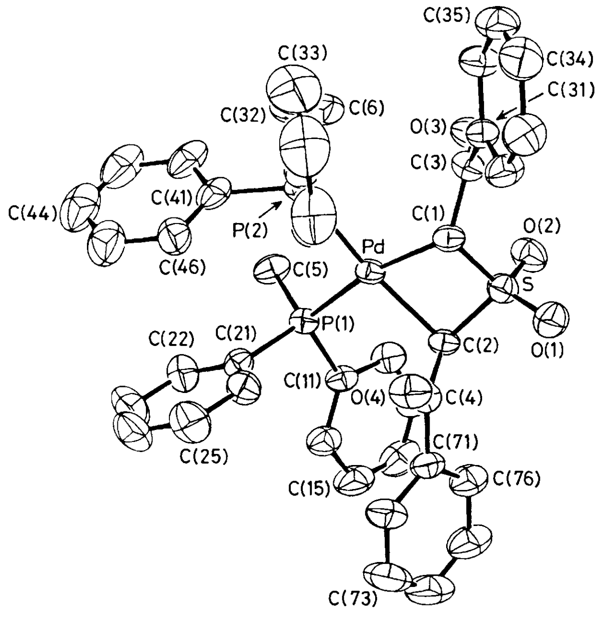
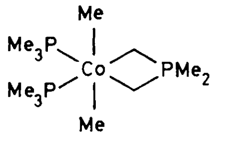


Figure 2. Molecular structure of $[\mathrm{Pt\{CH(COPh)S(O)_2CH(COPh)\}(PMePh_2)_2}]$ (**6i**), showing the atom numbering scheme. Atoms are shown as 50% thermal ellipsoids, and all hydrogen atoms are omitted

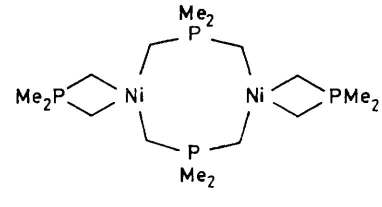
Table 2. Selected bond angles (°) for $[\mathrm{Pt\{CH(COPh)S(O)_2CH(COPh)\}(PPh_3)_2]\cdot 2CH_2Cl_2}$ [(**6a**)] and $[\mathrm{Pd\{CH(COPh)S(O)_2CH(COPh)\}(PMePh_2)_2]\cdot CH_2Cl_2\cdot H_2O}$ [(**6i**)], with e.s.d.s in parentheses

	(**6a**), M = Pt	(**6i**), M = Pd
P(1)-M-P(2)	98.5(1)	97.7(1)
P(1)-M-C(2)	91.9(3)	94.0(2)
P(2)-M-C(1)	94.2(3)	93.6(1)
C(1)-M-C(2)	75.4(4)	74.7(2)
$\mathrm{CH(COPh)S(O)_2CH(COPh)}$ ligands		
M-C(1)-S	94.0(4)	90.0(2)
M-C(2)-S	93.6(5)	91.2(2)
M-C(1)-C(3)	121.8(9)	121.2(4)
M-C(2)-C(4)	116.5(7)	106.2(4)
C(1)-S-C(2)	94.8(5)	95.9(3)
C(1)-S-O(1)	113.7(6)	110.9(3)
C(1)-S-O(2)	108.7(6)	112.2(2)
C(2)-S-O(1)	114.1(5)	112.8(3)
C(2)-S-O(2)	106.6(5)	107.9(2)
O(1)-S-O(2)	116.6(6)	115.4(3)
C(1)-C(3)-O(3)	122.1(11)	122.2(5)
C(1)-C(3)-C(81)	119.0(11)	118.1(4)
C(2)-C(4)-O(4)	121.0(10)	122.2(4)
C(2)-C(4)-C(71)	118.3(9)	119.0(4)

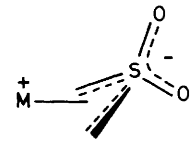
Triphenylphosphine ligands (**6a**)		Methyldiphenylphosphine ligands (**6i**)	
M-P(1)-C(41)	122.6(3)	M-P(1)-C(5)	114.6(2)
M-P(1)-C(51)	106.2(3)	M-P(1)-C(11)	115.5(2)
M-P(1)-C(61)	117.0(3)	M-P(1)-C(21)	112.9(1)
M-P(2)-C(11)	114.3(3)	M-P(2)-C(6)	113.2(2)
M-P(2)-C(21)	117.6(3)	M-P(2)-C(31)	109.6(2)
M-P(2)-C(31)	112.8(3)	M-P(2)-C(41)	121.0(1)
C(41)-P(1)-C(51)	103.4(4)	C(5)-P(1)-C(11)	101.6(2)
C(41)-P(1)-C(61)	99.8(3)	C(5)-P(1)-C(21)	106.9(2)
C(51)-P(1)-C(61)	106.1(4)	C(11)-P(1)-C(21)	104.2(2)
C(11)-P(2)-C(21)	98.9(4)	C(6)-P(2)-C(31)	105.7(2)
C(11)-P(2)-C(31)	108.4(4)	C(6)-P(2)-C(41)	103.9(3)
C(21)-P(2)-C(31)	103.4(4)	C(31)-P(2)-C(41)	101.9(2)



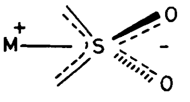
(**9**)



(**10**)



(**11**)



(**12**)

platinum(II) and palladium(II) have been shown to contain highly puckered four-membered rings, which may also be described in terms of an η^3-allylic arrangement.[2,4,8] Puckering in four-membered rings results in a decrease in eclipsing strain, concomitant with an increase in angle strain, until a minimum energy balance between the two opposing effects is achieved.

A comparison of the *X*-ray data of the metallathietane-3,3-dioxide complexes (**6a**), (**6i**), and (**1a**) with those for thietane-1,1-dioxide systems[5] reveals that the metallacycles contain shorter C–S bond distances and larger C–S–C bond angles. Hence, for thietane-1,1-dioxides the C–S bond distances lie in the range 1.79—1.88 Å, and the C–S–C bond angles lie in the range 77.6—82.2°, whereas the corresponding values for the metallathietane-3,3-dioxide complexes (**6a**), (**6i**), and (**1a**) lie in the ranges 1.72—1.76 Å and 92.0—95.9°. These data may be interpreted in terms of a reduction in ring strain of the four-membered ring system on replacement of carbon by a substantially larger platinum or palladium atom. The presence of ring strain in a cyclic organic molecule often results in lengthening of the ring bonds, as observed for example in cyclobutanes.[9] The C–S–C bond angle for dimethyl sulphone, which possesses no ring strain, is 103.0°.[10]

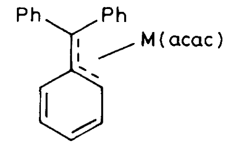
A number of chelating phosphorus and sulphur ylide complexes containing the $\mathrm{MCH_2PMe_2CH_2}$ or $\mathrm{MCH_2S(O)(Me)CH_2}$ ring systems have been found to contain notably shortened metallacyclic C–P and C–S bonds.[11,12] Thus, for example, in the octahedrally co-ordinated cobalt complex (**9**),[11] which contains a planar ylide ring, the metallacyclic C–P bond distances average 1.726(9) Å, as compared with average C–P distances in the $\mathrm{PMe_2}$ group and trimethylphosphine ligands of 1.793(8) and 1.799(9) Å respectively. This has been interpreted in terms of a contribution from a planar heteroallylic bonding representation constructed using a phosphorus $d_{x^2-y^2}$ orbital. However, square-planar cyclic ylide complexes of nickel, palladium, and platinum characteristically contain highly puckered four-membered rings,[11,12] for example, the fold angles in the dimeric complex (**10**) are 43.9°, and a contribution to the bonding from an η^3-allylic representation has been proposed to account for this non-planarity.[11] These non-planar cyclic ylide complexes thus bear a resemblance to the oxodimethylenemethane complexes, described by us,[2,4,8] which we also consider to contain a large degree of η^3-allylic character. Thus the apparent shortening of the C–S bonds of the metallathietane-3,3-dioxide complexes (**6a**), (**6i**), and (**1a**) may also be attributed to a contribution from a heteroallylic-type bonding representation as shown in (**11**) or (**12**).

Interestingly, structural studies on the lithiated sulphones $[PhS(O)_2CHRLi{\cdot}L]_2$ [(**13a**), R = H, L = tmen,[13] (**13b**), R = Ph, L = tmen,[14] and (**13c**), R = $CH{=}CH_2$, L = diglyme (tmen = tetramethylethylenediamine)][15] reveal that these compounds contain very short S–CH bonds, but the corresponding lengthening of the S=O bonds for (**13a**) and (**13b**) is of a much smaller magnitude and is undetectable in the case of (**13c**). Thus, for example, the S–CH bond distance for (**13a**) of 1.608(3) Å is much shorter than the S–CH bond distance of the parent methyl phenyl sulphone (S–CH = 1.761 Å),[13] and is comparable with the C=S bond distance for thioformaldehyde of 1.6108(9) Å.[16] However, the S=O bond distances of (**13a**) [average 1.460(2) Å] are comparable with those of methyl phenyl sulphone [average 1.459 Å].[13,17] In the metallathietane-3,3-dioxide complexes (**6a**), (**6i**), and (**1a**) which show a small degree of S–C bond shortening, the S=O bond distances appear normal. Thus, the S=O bond distances for (**6a**) and (**6i**) lie within the range 1.411—1.456 Å observed for a number of thietane-1,1-dioxide ring systems.[5]

The platinum–carbon bond distances for (**6a**) are similar to those in phosphine-containing platinacyclobutanes, for example, the average Pt–C bond distances in complexes $[Pt\{C(CN)_2CHPhC(CN)_2\}(PPh_3)_2]$[18] and $[Pt(CH_2CMe_2CH_2)(PEt_3)_2]$[7] are 2.148 and 2.083 Å respectively. Thus, as a result of the relatively large range of platinum–carbon bond distances in platinacyclobutanes, together with an absence of suitable examples for comparison, it is difficult conclusively to assign any lengthening of the platinum–carbon bonds in the platinathietane-3,3-dioxide complexes, which would result from a heteroallylic contribution to the bonding. A recent study of the σ-alkyl complexes *cis*-$[MMe_2(PMePh_2)_2]$ (M = Pd or Pt) indicates a shortening of the metal–carbon bond (with a concomitant lengthening of the metal–phosphorus bond) when the metal is changed from platinum to palladium[19] and a similar trend might be expected in the metallathietane-3,3-dioxides (**6i**) and (**6a**). However, the average Pd–C bond length in (**6i**) is not significantly different to the average Pt–C bond length in (**6a**). We note that in the η^3-benzylic complexes (**14**) the Pd–C bond distances are greater than Pt–C bond distances.[20] A similar trend is observed in η^3-oxodimethylenemethane complexes of palladium and platinum,[2,4,8] the data indicating a greater degree of allylic bonding in palladium as compared to the platinum complexes.

The rings in complexes (**6a**) and (**6i**) are formed as the '*trans*' disubstituted isomers, with one benzoyl substituent in a pseudo axial environment, and the other in a pseudo equatorial environment, as observed in the phenyl substituted complex (**1a**).[1] It is worth nothing that as a result of the *trans* substitution of the metallathietane-3,3-dioxide systems, these molecules are chiral, and an examination of the unit-cell contents for (**6a**) reveals that one molecule of both enantiomers co-crystallise from solution in a centrosymmetric unit cell.

The room-temperature ^1H and ^{13}C-{^1H-decoupled} n.m.r. spectra of (**6a**)—(**6o**) are similar to those of the related phenyl-substituted metallathietane-3,3-dioxide complexes (**1**),[1] and may be interpreted in terms of either a planar, or a rapidly inverting metallacycle. The ^1H n.m.r. spectra of all the platinum–phosphine or –phosphite complexes appear as the A part of an AA′MXX′ spin system (M = ^{195}Pt, X = ^{31}P),[21] to give a complex resonance consisting of an intense inner doublet, a



(**14**), M = Pt or Pd, acac = acetylacetonate

weaker outer doublet, together with two very weak outer doublets some distance from the centre of the resonance. This second-order spectrum is due to the presence of chemically equivalent but magnetically non-equivalent phosphorus-31 nuclei. Corresponding satellite features due to coupling to platinum-195 are observed, with values of $^2J(PtH)$ being typically around 60 Hz. The palladathietane-3,3-dioxide complexes containing phosphine ligands yield similar Pd–CH ^1H n.m.r. spectral features, although these signals are commonly poorly resolved, giving a broad single resonance from which it was not possible to measure a value of $J(PH)$. Since the carbon atoms of the metallacycle are chiral, and two methyl groups bonded to each phosphorus in the dimethylphenylphosphine complexes (**6c**) and (**6j**) are chemically non-equivalent (diastereotopic). This feature has also been observed in 1,3-disubstituted oxodimethylenemethane complexes of platinum and palladium.[2,8]

The room-temperature ^{13}C-{^1H-decoupled} n.m.r. spectra of the metallathietane-3,3-dioxide complexes (**6a**)—(**6o**) exhibit second-order ring carbon signals and appear as the A part of an AXX′ spin system (X = ^{31}P),[22] giving a doublet of doublets with a small central feature, with the platinum complexes showing the expected coupling to platinum-195, with values of $^1J(PtC)$ ranging from 354 to 446.2 Hz on changing the phosphine from trimethylphosphine through to triphenylphosphine. The values of $^1J(PtC)$ and $|^2J(PC)_{trans} + {}^2J(PC)_{cis}|$ are comparable with those of platinacyclobutanes, for example, the complex $[Pt(CH_2CH_2CH_2)(PPh_3)_2]$ shows $^1J(PtC)$ = 400 Hz and $^2J(PC)$ = 80 Hz.[6] The carbonyl carbon atoms of the benzoyl substituents of (**6a**) and (**6c**) show a coupling to platinum-195, with $^2J(PtC)$ being 35 and 32 Hz respectively, although no three-bond phosphorus coupling was discernible. The ^{13}C-{^1H} n.m.r. spectra of the complexes (**6c**) and (**6j**) containing the dimethylphenylphosphine ligand again demonstrate the chiral nature of the ring carbons, with two sets of methyl resonances being observed.

The room-temperature ^{31}P-{^1H} n.m.r. spectra for all the metallathietane-3,3-dioxide complexes containing phosphine or triphenyl phosphite ligands consist of a single resonance, with the platinum complexes showing the expected coupling to platinum-195, values of $^1J(PtP)$ being in the range 2 705—2 817 Hz for the benzoyl and methoxycarbonyl substituted complexes. The triphenyl phosphite–platinum complex (**6g**) shows a large value for $^1J(PtP)$ of 4 976 Hz.

The i.r. spectra of complexes (**6a**)—(**6o**) exhibit very strong sulphone stretching bands in the ranges 1 110—1 126 cm^{-1} and 1 290—1 310 cm^{-1}.

Experimental

Melting points (Table 3) 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. Proton n.m.r. spectra were recorded on a Varian EM390 spectrometer at 90 MHz, on a Bruker AM300 spectrometer at 300.13 MHz, and on a Bruker Spectrospin WH400 spectrometer at 400.13 MHz with $SiMe_4$ (0.0 p.p.m.) as internal reference, positive values being to high frequency (low-field), in $CDCl_3$ unless otherwise stated. ^{13}C-{^1H} N.m.r. spectra were recorded on a Bruker AM300 spectrometer at 75.47 MHz with

Table 3. Yields, m.p.s, analytical,[a] and selected i.r. data for benzoyl and methoxycarbonyl substituted metallathietane-3,3-dioxide complexes

Complex	Yield (%)	M.p. (°C)	Analysis (%) C	H	$\nu(\mathrm{SO_2})$ ($\mathrm{cm^{-1}}$)[b]
(6a)$\cdot\mathrm{CH_2Cl_2}\cdot0.5\mathrm{H_2O}$	77	185—190[c]	56.9 (57.2)	4.1 (4.1)	1 295, 1 118
(6b)$\cdot\mathrm{CH_2Cl_2}\cdot0.5\mathrm{H_2O}$	76	153—161[d]	51.7 (52.2)	4.1 (4.2)	1 295, 1 115
(6c)$\cdot\mathrm{CH_2Cl_2}$	71	111—116[d]	45.8 (46.3)	4.2 (4.2)	1 292, 1 112
(6d)	71	>230[e]	41.1 (40.8)	4.7 (4.7)	1 292, 1 111
(6e)$\cdot0.5\mathrm{CH_2Cl_2}$	81	218—222[f]	44.4 (44.2)	5.7 (5.6)	1 295, 1 118
(6f)	77	171—172	53.1 (53.6)	7.4 (7.6)	1 294, 1 117
(6g)	36	74—82	55.4 (56.0)	3.85 (3.8)	1 310, 1 126
(6h)$\cdot\mathrm{CH_2Cl_2}\cdot\mathrm{H_2O}$	94	220—222[f]	61.2 (61.5)	4.6 (4.5)	1 300, 1 112
(6i)	88	222—224[g]	62.1 (62.5)	4.6 (4.8)	1 296, 1 112
(6j)$\cdot\mathrm{CH_2Cl_2}$	94	103—106[d]	51.7 (51.6)	4.8 (4.8)	1 297, 1 115
(6k)	92	222—225[f]	46.8 (47.3)	5.4 (5.4)	1 293, 1 110
(6l)	77	211—213[f]	51.5 (52.3)	6.5 (6.6)	1 295, 1 116
(6m)	76	158—160	59.3 (59.2)	8.3 (8.2)	1 297, 1 116
(6n)$\cdot\mathrm{CH_2Cl_2}$	70	>230[e]	51.7 (51.0)	4.1 (4.0)	1 290, 1 120
(6o)$\cdot\mathrm{CH_2Cl_2}$	68	217—219[f]	56.4 (55.9)	4.5 (4.4)	1 310, 1 120

[a] Calculated values given in parentheses. [b] All bands vs (very strong). [c] Partial melting 155—165 °C with gas evolution. [d] With gas evolution. [e] Decomposition above 230 °C. [f] With decomposition. [g] Partial melting from 151 to 160 °C.

$\mathrm{SiMe_4}$ (0.0 p.p.m.) as internal reference, in $\mathrm{CDCl_3}$. ^{31}P-{^{1}H} N.m.r. spectra were recorded in dichloromethane on a JEOL-FX60 spectrometer at 24.15 MHz with $[\mathrm{P(OH)_4}]^{+}$ [23] in $\mathrm{D_2O}$ (0.0 p.p.m.) as external reference. J values in Hz.

Experiments were carried out under a dry, oxygen-free, dinitrogen 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 metallathietane-3,3-dioxide complexes **(6a)**—**(6o)** were recrystallised in air. The compounds $[\mathrm{PtCl_2(cod)}]$ (cod = cyclo-octa-1,5-diene),[24] $[\mathrm{PdCl_2(cod)}]$,[25] trimethylphosphine,[26] bis(benzoylmethyl) sulphone **(5a)**,[27] 2,2′-sulphonyldiacetic acid dimethyl ester **(5b)**,[28] and 1,5-diphenylpentane-1,3,5-trione **(7)**[29] were prepared as described in the literature.

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

*Preparation of Metallathietane-*3,3*-dioxide Complexes using Silver*(I) *Oxide; General Method.*—Two equivalents of tertiary phosphine or triphenyl phosphite, followed by one equivalent of bis(benzoylmethyl) sulphone **(5a)** or 2,2′-sulphonyldiacetic acid dimethyl ester **(5b)**, and an excess of silver(I) oxide were added in succession to a stirred solution of $[\mathrm{MCl_2(cod)}]$ (M = Pt or Pd) in dichloromethane (*ca.* 30 $\mathrm{cm^3}$), and the mixture was refluxed for 4 h. The mixture was filtered and the filtrate evaporated to dryness under reduced pressure to afford a colourless to yellowish brown oil. Dissolution of the oil in dichloromethane (*ca.* 5 $\mathrm{cm^3}$) followed by addition of light petroleum afforded, on standing, a white to pale yellow *microcrystalline* solid, which was recrystallised from dichloromethane–light petroleum, and dried *in vacuo*.

(i) $[\mathrm{Pt\{CH(COPh)S(O)_2CH(COPh)\}(PPh_3)_2}]\cdot\mathrm{CH_2Cl_2}\cdot0.5\mathrm{H_2O}$; **(6a)**$\cdot\mathrm{CH_2Cl_2}\cdot0.5\mathrm{H_2O}$. The complex $[\mathrm{PtCl_2(cod)}]$ (0.10 g, 0.27 mmol) with triphenylphosphine (0.15 g, 0.57 mmol) and **(5a)** (0.082 g, 0.27 mmol) gave white *microcrystals* of **(6a)**$\cdot\mathrm{CH_2Cl_2}\cdot0.5\mathrm{H_2O}$ (0.23 g). N.m.r. spectra: ^{1}H (300 MHz), δ 7.5—6.9 (m, 40 H, Ph), 5.31 (s, 2 H, $\mathrm{CH_2Cl_2}$), 4.86 [d, second-order, 2 H, Pt–CH, |^{3}J(PH)*trans* + ^{3}J(PH)*cis*| 9.20, ^{2}J(PtH) 61.79], and 1.81 p.p.m. (s, br, 1 H, $\mathrm{H_2O}$); ^{13}C-{^{1}H} (75.5 MHz), δ 196.30 [s, CO, ^{2}J(PtC) 35.0], 54.58 [dd, second-order, Pt–CH, |^{2}J(PC)*trans* + ^{2}J(PC)*cis*| 87.08, ^{1}J(PtC) 446.2], and 53.4 p.p.m. (s, $\mathrm{CH_2Cl_2}$); ^{31}P-{^{1}H} (24 MHz), δ 13.31 p.p.m. [s, ^{1}J(PtP) 2 817]. *X*-Ray quality *crystals* of **(6a)**$\cdot2\mathrm{CH_2Cl_2}$ were grown slowly from dichloromethane–light petroleum, in air.

(ii) $[\mathrm{Pt\{CH(COPh)S(O)_2CH(COPh)\}(PMePh_2)_2}]\cdot\mathrm{CH_2Cl_2}\cdot0.5\mathrm{H_2O}$; **(6b)**$\cdot\mathrm{CH_2Cl_2}\cdot0.5\mathrm{H_2O}$. The complex $[\mathrm{PtCl_2(cod)}]$ (0.12 g, 0.32 mmol) with methyldiphenylphosphine (0.13 g, 0.65 mmol) and **(5a)** (0.098 g, 0.33 mmol) gave white *microcrystals* of **(6b)**$\cdot\mathrm{CH_2Cl_2}\cdot0.5\mathrm{H_2O}$ (0.241 g). N.m.r. spectra: ^{1}H (300 MHz), δ 7.80—7.00 (m, 30 H, Ph), 5.30 (s, 2 H, $\mathrm{CH_2Cl_2}$), 4.80 [d, second-order, 2 H, Pt–CH, |^{3}J(PH)*trans* + ^{3}J(PH)*cis*| 9.0, ^{2}J(PtH) 59.9], 2.08 p.p.m. (s, br, 1 H, $\mathrm{H_2O}$), and 1.62 p.p.m. [d, second-order, 6 H, Me, $\mathrm{PMePh_2}$, |^{2}J(PH) + ^{4}J(PH)| 8.55, ^{3}J(PtH) 29.3]; ^{1}H (300 MHz, $\mathrm{CD_2Cl_2}$, −90 °C) identical to room temperature spectrum; ^{13}C-{^{1}H} (75.5 MHz), δ 196.20 [s, CO, ^{2}J(PtC) not discernible], 55.45 [dd, second-order, Pt–CH, |^{2}J(PC)*trans* + ^{2}J(PC)*cis*| 84.96, ^{1}J(PtC) 412.5], 53.4 (s, $\mathrm{CH_2Cl_2}$), and 13.54 p.p.m. [dd, second-order, Me, $\mathrm{PMePh_2}$, |^{1}J(PC) + ^{3}J(PC)| 46.3, ^{2}J(PtC) not discernible]; ^{31}P-{^{1}H} (24 MHz), δ −4.24 p.p.m. [s, ^{1}J(PtP) 2 759].

(iii) $[\mathrm{Pt\{CH(COPh)S(O)_2CH(COPh)\}(PMe_2Ph_2)}]\cdot\mathrm{CH_2Cl_2}$; **(6c)**$\cdot\mathrm{CH_2Cl_2}$. The complex $[\mathrm{PtCl_2(cod)}]$ (0.25 g, 0.67 mmol) with dimethylphenylphosphine (0.19 g, 1.37 mmol) and **(5a)** (0.20 g, 0.67 mmol) gave white *microcrystals* of **(6c)**$\cdot\mathrm{CH_2Cl_2}$ (0.41 g). N.m.r. spectra: ^{1}H (300 MHz), δ 8.06—7.27 (m, 20 H, Ph), 5.34 (s, 2 H, $\mathrm{CH_2Cl_2}$), 4.89 [d, second-order, 2 H, Pt–CH, |^{3}J(PH)*trans* + ^{3}J(PH)*cis*| *ca.* 9, ^{2}J(PtH) 60.06], 1.48 [d, second-order, 6 H, Me, $\mathrm{PMe_2Ph}$, |^{2}J(PH) + ^{4}J(PH)| 9.34, ^{3}J(PH) 30.2], and 1.26 p.p.m. [d, second-order, 6 H, Me, $\mathrm{PMe_2Ph}$, |^{2}J(PH) + ^{4}J(PH)| 9.41, ^{3}J(PtH) 28.7]; ^{13}C-{^{1}H} (75.5 MHz), δ 197.23 [s, CO, ^{2}J(PtC) 32.0], 55.31 [dd, second-order, Pt–CH, |^{2}J(PC)*trans* + ^{2}J(PC)*cis*| 84.39, ^{1}J(PtC) 384.5], 15.92 [dd, second-order, Me, $\mathrm{PMe_2Ph}$, |^{1}J(PC) + ^{3}J(PC)| 48.0, ^{2}J(PtC) not discernible], and 14.34 p.p.m. [dd, second-order, Me, $\mathrm{PMe_2Ph}$, |^{1}J(PC) + ^{3}J(PC)| 46.75, ^{2}J(PtC) not discernible]; ^{31}P-{^{1}H} (24 MHz), δ −17.95 p.p.m. [s, ^{1}J(PtP) 2 734].

(iv) $[\mathrm{Pt\{CH(COPh)S(O)_2CH(COPh)\}(PMe_3)_2}]$; **(6d)**. The complex $[\mathrm{PtCl_2(cod)}]$ (0.15 g, 0.401 mmol) with trimethylphosphine (0.1 $\mathrm{cm^3}$, 1.0 mmol) and **(5a)** (0.121 g, 0.401 mmol) gave white *microcrystals* of **(6d)** (0.184 g). N.m.r. spectra: ^{1}H (400 MHz), δ 8.12—7.37 (m, 10 H, Ph), 4.80 [d, second-order, 2 H, Pt–CH, |^{3}J(PH)*trans* + ^{3}J(PH)*cis*| 9.57, ^{2}J(PtH) 58.06], and 1.41 p.p.m. [d, second-order, 18 H, Me, $\mathrm{PMe_3}$, |^{2}J(PH) + ^{4}J(PH)| 9.44, ^{3}J(PtH) 29.55]; ^{13}C-{^{1}H} (75.5 MHz), δ 197.52 [s, CO, ^{2}J(PtC) not discernible], 55.10 [dd, second-order, Pt–CH, |^{2}J(PC)*trans* + ^{2}J(PC)*cis*| 84.59, ^{1}J(PtC) *ca.* 354], and 16.97 p.p.m. [dd, second-order, Me, $\mathrm{PMe_3}$, |^{1}J(PC) + ^{3}J(PC)| 47.6, ^{2}J(PtC) not discernible]; ^{31}P-{^{1}H} (24 MHz), δ −28.84 p.p.m. [s, ^{1}J(PtP) 2 705].

(v) $[\mathrm{Pt\{CH(COPh)S(O)_2CH(COPh)\}(PEt_3)_2}]\cdot0.5\mathrm{CH_2Cl_2}$; **(6e)**$\cdot0.5\mathrm{CH_2Cl_2}$. The complex $[\mathrm{PtCl_2(cod)}]$ (0.21 g, 0.56 mmol) with triethylphosphine (0.14 g, 1.18 mmol) and **(5a)** (0.17 g, 0.57 mmol) gave white *microcrystals* of **(6e)**$\cdot0.5\mathrm{CH_2Cl_2}$ (0.35 g).

N.m.r. spectra: ^{1}H (300 MHz), δ 8.20—7.35 (m, 10 H, Ph), 5.25 (s, 1 H, CH_2Cl_2), 4.62 [d, second-order, 2 H, Pt–CH, |^3J(PH)*trans* + ^3J(PH)*cis*| 9.0, ^2J(PtH) 69.2], 1.71 (m, 12 H, CH_2, PEt_3), and 0.99 p.p.m. (m, 18 H, CH_3, PEt_3); ^{31}P-{^{1}H} (24 MHz), δ 2.42 p.p.m. [s, ^1J(PtP) 2 739].

(vi) [Pt{CH(COPh)S(O)$_2$CH(COPh)}(PBu$^n{}_3$)$_2$]; (**6f**). The complex [PtCl$_2$(cod)] (0.20 g, 0.535 mmol) with PBu$^n{}_3$ (0.22 g, 1.09 mmol) and (**5a**) (0.162 g, 0.536 mmol) gave white *microcrystals* of (**6f**) (0.37 g). N.m.r. spectra: ^{1}H (400 MHz), δ 8.33—7.31 (m, 10 H, Ph), 4.58 [d, second-order, 2 H, Pt–CH, |^3J(PH)*trans* + ^3J(PH)*cis*| *ca.* 9, ^2J(PtH) 59.0], 1.80—1.09 (m, 36 H, CH_2, PBu$^n{}_3$), and 0.81 p.p.m. [t, 18 H, CH_3, PBu$^n{}_3$, ^3J(HH) 7.14]; ^{31}P-{^{1}H} (24 MHz), δ −6.25 p.p.m. [s, ^1J(PtP) 2 725].

(vii) [Pt{CH(COPh)S(O)$_2$CH(COPh)}{P(OPh)$_3$}$_2$]; (**6g**). The complex [PtCl$_2$(cod)] (0.225 g, 0.60 mmol) with triphenyl phosphite (0.38 g, 1.22 mmol) and (**5a**) (0.181 g, 0.60 mmol) gave white *microcrystals* of (**6g**) (0.24). N.m.r. spectra: ^{1}H (300 MHz), δ 8.02—6.83 (m, 40 H, Ph), and 4.60 p.p.m. [d, second-order, 2 H, Pt–CH, |^3J(PH)*trans* + ^3J(PH)*cis*| *ca.* 10, ^2J(PtH) 70.1]; ^{31}P-{^{1}H} (24 MHz), δ 95.20 p.p.m. [s, ^1J(PtP) 4 976].

(viii) [Pd{CH(COPh)S(O)$_2$CH(COPh)}(PPh$_3$)$_2$]·CH_2Cl_2·H_2O; (**6h**)·CH_2Cl_2·H_2O. The complex [PdCl$_2$(cod)] (0.20 g, 0.70 mmol) with triphenylphosphine (0.367 g, 1.40 mmol) and (**5a**) (0.211 g, 0.70 mmol) gave pale yellow *microcrystals* of (**6h**)·CH_2Cl_2·H_2O (0.68 g). N.m.r. spectra: ^{1}H (400 MHz), δ 7.68—6.97 (m, 40 H, Ph), 5.25 (s, 2 H, CH_2Cl_2), 4.86 [d, second-order, 2 H, Pd–CH, |^3J(PH)*trans* + ^3J(PH)*cis*| 9.83], and 1.90 (s, br 2 H, H_2O); ^{13}C-{^{1}H} (75.5 MHz), δ 196.13 (s, CO) and 52.15 p.p.m. [dd, second-order, Pd–CH, |^2J(PC)*trans* + ^2J(PC)*cis*| 100.61]; ^{31}P-{^{1}H} (24 MHz), δ 22.79 p.p.m. (s).

(ix) [Pd{CH(COPh)S(O)$_2$CH(COPh)}(PMePh$_2$)$_2$]; (**6i**). The complex [PdCl$_2$(cod)] (0.10 g, 0.35 mmol) with methyldiphenylphosphine (0.15 g, 0.75 mmol) and (**5a**) (0.105 g. 0.35 mmol) gave pale yellow *microcrystals* of (**6i**) (0.247 g). N.m.r. spectra: ^{1}H (400 MHz), δ 7.58—6.98 (m, 30 H, Ph), 4.39 [d, second-order, unresolved, 2 H, Pd–CH, |^3J(PH)*trans* + ^3J(PH)*cis*| not discernible], and 1.43 p.p.m. [d, second-order, 6 H, Me, PMePh$_2$, |^2J(PH) + ^4J(PH)| 7.7]; ^{13}C-{^{1}H} (100 MHz), δ 195.43 (s, CO), 52.45 [dd, second-order, Pd–CH, |^2J(PC)*trans* + ^2J(PC)*cis*| 104.08], and 12.00 p.p.m. [t, Me, PMePh$_2$, |^1J(PC) + ^3J(PC)| 27.2]; ^{31}P-{^{1}H} (24 MHz, $CDCl_3$), δ 4.64 p.p.m. (s). *X*-Ray quality *crystals* of (**6i**)·CH_2Cl_2·H_2O were grown slowly from dichloromethane–light petroleum, in air.

(x) [Pd{CH(COPh)S(O)$_2$CH(COPh)}(PMe$_2$Ph)$_2$]·CH_2Cl_2; (**6j**)·CH_2Cl_2. The complex [PdCl$_2$(cod)] (0.15 g, 0.525 mmol) with dimethylphenylphosphine (0.19 g, 1.37 mmol) and (**5a**) (0.158 g, 0.527 mmol) gave white *microcrystals* of (**6i**)·CH_2Cl_2 (0.38 g). N.m.r. spectra: ^{1}H (300 MHz), δ 8.20—7.18 (m, 20 H, Ph), 5.29 (s, 2 H, CH_2Cl_2), 4.47 [d, second-order, unresolved, 2 H, Pd–CH, |^3J(PH)*trans* + ^3J(PH)*cis*| not discernible], 1.34 [d, second-order, 6 H, Me, PMe$_2$Ph, |^2J(PH) + ^4J(PH)| 9.05], and 1.05 p.p.m. [d, second-order, 6 H, Me, PMe$_2$Ph, |^2J(PH) + ^4J(PH)| 8.88]; ^{31}P-{^{1}H} (24 MHz), δ −7.87 p.p.m. (s).

(xi) [Pd{CH(COPh)S(O)$_2$CH(COPh)}(PMe$_3$)$_2$]; (**6k**). The complex [PdCl$_2$(cod)] (0.10 g, 0.35 mmol) with trimethylphosphine (0.1 cm^3, 1.0 mmol) and (**5a**) (0.106 g, 0.351 mmol) gave white *microcrystals* of (**6k**) (0.18 g). N.m.r. spectra: ^{1}H (300 MHz), δ 8.06—7.37 (m, 10 H, Ph), 4.33 [d, second-order, unresolved, 2 H, Pd–CH, |^3J(PH)*trans* + ^3J(PH)*cis*| not discernible], and 1.23 p.p.m. [d, second-order, 18 H, Me, PMe$_3$, |^2J(PH) + ^4J(PH)| 8.9]; ^{31}P-{^{1}H} (24 MHz), δ −18.35 p.p.m. (s).

(xii) [Pd{CH(COPh)S(O)$_2$CH(COPh)}(PEt$_3$)$_2$]; (**6l**). The complex [PdCl$_2$(cod)] (0.20 g, 0.70 mmol) with triethylphosphine (0.20 g, 1.69 mmol) and (**5a**) (0.21 g, 0.7 mmol) gave white *microcrystals* of (**6l**) (0.34 g). N.m.r. spectra: ^{1}H (400 MHz), δ 8.15—7.43 (m, 10 H, Ph), 4.19 [d, second-order, 2 H, Pd–CH, |^3J(PH)*trans* + ^3J(PH)*cis*| *ca.* 8.6], 1.77—1.54 (m, 12 H, CH_2, PEt_3), and 1.05 p.p.m. (m, 18 H, CH_3, PEt_3); ^{31}P-{^{1}H} (24 MHz, $CDCl_3$), δ 13.92 (s).

(xiii) [Pd{CH(COPh)S(O)$_2$CH(COPh)}(PBu$^n{}_3$)$_2$]; (**6m**). The complex [PdCl$_2$(cod)] (0.10 g, 0.35 mmol) with PBu$^n{}_3$ (0.22 g, 1.09 mmol) and (**5a**) (0.106 g, 0.351 mmol) gave white *microcrystals* of (**6m**) (0.26 g). N.m.r. spectrum: ^{31}P-{^{1}H} (24 MHz), δ 5.45 p.p.m. (s).

(xiv) [Pt{CH(CO$_2$Me)S(O)$_2$CH(CO$_2$Me)}(PPh$_3$)$_2$]·CH_2Cl_2; (**6n**)·CH_2Cl_2. The complex [PtCl$_2$(cod)] (0.10 g, 0.27 mmol) with triphenylphosphine (0.15 g, 0.57 mmol) and (**5b**) (0.056 g, 0.27 mmol) gave white *microcrystals* of (**6n**)·CH_2Cl_2 (0.19 g). N.m.r. spectra: ^{1}H (90 MHz), δ 7.8—7.5 (m, 30 H, Ph), 5.3 (s, 2 H, CH_2Cl_2), 3.8 [d, second-order, 2 H, Pt–CH, |^3J(PH)*trans* + ^3J(PH)*cis*| *ca.* 9.5, ^2J(PtH) 65], and 3.1 p.p.m. (s, 6 H, Me); ^{31}P-{^{1}H} (24 MHz), δ 14.52 p.p.m. [s, ^1J(PtP) 2 798].

(xv) [Pd{CH(CO$_2$Me)S(O)$_2$CH(CO$_2$Me)}(PPh$_3$)$_2$]·CH_2Cl_2; (**6o**)·CH_2Cl_2. The complex [PdCl$_2$(cod)] (0.10 g, 0.35 mmol) with triphenylphosphine (0.184 g, 0.70 mmol) and (**5b**) (0.065 g, 0.35 mmol) gave white *microcrystals* of (**6o**)·CH_2Cl_2 (0.22 g). N.m.r. spectrum: ^{31}P-{^{1}H} (24 MHz), δ 25.01 p.p.m. (s).

Reaction of cis-[PtCl$_2$(PPh$_3$)$_2$] *with* (**7**) *and Silver*(I) *Oxide.*—Triphenylphosphine (0.150 g, 0.573 mmol), 1,5-diphenylpentan-1,3,5-trione (0.070 g, 0.267 mmol), and silver(I) oxide (0.4 g, 1.73 mmol) were added in succession to a stirred solution of [PtCl$_2$(cod)] (0.10 g, 0.267 mmol) in dichloromethane (25 cm^3), and the mixture was refluxed for 1 h. The insoluble silver salts were removed by filtration to give a bright yellow solution which was reduced in volume to *ca.* 3 cm^3. Addition of light petroleum (60 cm^3) gave a yellow solid which was filtered off and dried *in vacuo* to give the complex [Pt{OC(CHCOPh)CHC(Ph)O}(PPh$_3$)$_2$] (**8**) (0.216 g, 83%), identified by comparison of its ^{1}H and ^{31}P-{^{1}H} n.m.r. spectra with those of an authentic sample.[4] ^{31}P-{^{1}H} N.m.r. data (24 MHz), second-order AB spin-system, δ 14.22 [d, ^1J(PtP) 3 799, ^2J(PP) 29.3] and 8.27 p.p.m. [d, ^1J(PtP) 3 701, ^2J(PP) 29.3].

X-*Ray Crystal Structures.*—(*a*) [Pt{CH(COPh)S(O)$_2$CH(COPh)}(PPh$_3$)$_2$]·2CH_2Cl_2, (**6a**)·2CH_2Cl_2. The crystal was mounted in air. The unit-cell dimensions of the crystal were determined from oscillation photographs about the *c* axis and from its optimised counter angles for zero- and upper-layer reflections on a Weissenberg diffractomer. Intensity data were collected at room temperature on a Stoe Stadi-2 Weissenberg diffractometer using an ω-scan technique in the range $7 < 2\theta < 54°$. The 5 553 unique reflections, collected from Weissenberg layers *hk*(0—12), having $I \geqslant 3\sigma(I)$, were corrected for Lorentz and polarisation effects. An absorption correction was also applied to the data, the maximum and minimum transmission factors being 0.8094 and 0.6391 respectively. All subsequent computations were carried out using the computer program SHELX.[30]

Crystal data. $C_{52}H_{42}O_4P_2PtS\cdot 2CH_2Cl_2$, M = 1 189.8, triclinic, space group $P\bar{1}$, a = 20.835(2), b = 10.628(2), c = 12.577(4) Å, α = 109.6(1), β = 105.8(1), γ = 91.4(1)°, U = 2 501.97 Å^3, Z = 2, D_c = 1.36 g cm^{-3}, F(000) = 1 155.9, Mo-K_α *X*-radiation, λ = 0.710 69 Å, μ(Mo-K_α) = 30.16 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 block-matrix least-squares refinement all non-hydrogen atoms, with the exception of the

Table 4. Atomic positional parameters (fractional co-ordinates) for $[\overline{\text{Pt}\{\text{CH(COPh)S(O)}_2\text{C}}\text{H(COPh)}\}(\text{PPh}_3)_2]\cdot2\text{CH}_2\text{Cl}_2$ (**6a**) with e.s.d.s in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Pt	0.239 99(2)	0.089 19(5)	0.412 87(4)	C(42)	0.139 6(4)	0.222 4(7)	0.106 0(6)
P(1)	0.155 70(14)	0.046 82(28)	0.235 63(26)	C(43)	0.146 9(4)	0.261 6(7)	0.014 2(6)
P(2)	0.326 88(14)	0.167 54(28)	0.365 27(27)	C(44)	0.180 8(4)	0.186 8(7)	−0.062 4(6)
S(1)	0.225 53(15)	0.096 6(3)	0.633 35(28)	C(45)	0.207 5(4)	0.072 8(7)	−0.047 1(6)
O(1)	0.235 4(4)	0.008 4(9)	0.700 1(8)	C(46)	0.200 2(4)	0.033 6(7)	0.044 7(6)
O(2)	0.201 9(4)	0.222 8(8)	0.684 9(8)	C(51)	0.084 3(3)	0.127 6(7)	0.275 5(7)
O(3)	0.213 0(5)	0.368 5(9)	0.641 5(8)	C(52)	0.017 4(3)	0.068 7(7)	0.222 6(7)
O(4)	0.201 0(4)	−0.198 3(8)	0.467 6(8)	C(53)	−0.033 4(3)	0.134 6(7)	0.261 7(7)
C(1)	0.296 1(5)	0.129 6(13)	0.590 7(9)	C(54)	−0.017 3(3)	0.259 4(7)	0.353 9(7)
C(2)	0.171 9(5)	0.021 7(12)	0.488 0(10)	C(55)	0.049 6(3)	0.318 2(7)	0.406 8(7)
C(3)	0330 0(6)	0.271 3(13)	0.671 9(11)	C(56)	0.100 4(3)	0.252 4(7)	0.367 7(7)
C(4)	0.156 4(6)	−0.129 7(11)	0.454 3(10)	C(61)	0.122 5(3)	−0.129 2(5)	0.145 0(6)
C(5)	0.653 9(9)	0.247 6(22)	0.352 3(17)	C(62)	0.072 0(3)	−0.160 3(5)	0.037 5(6)
C(6)	0.776 4(11)	0.447 2(21)	0.246 5(22)	C(63)	0.046 6(3)	−0.294 4(5)	−0.031 7(6)
C(11)	0.356 3(4)	0.040 9(6)	0.257 9(6)	C(64)	0.071 6(3)	−0.397 4(5)	0.006 5(6)
C(12)	0.323 5(4)	−0.090 7(6)	0.206 7(6)	C(65)	0.122 1(3)	−0.366 3(5)	0.113 9(6)
C(13)	0.347 5(4)	−0.189 4(6)	0.127 1(6)	C(66)	0.147 6(3)	−0.232 2(5)	0.183 2(6)
C(14)	0.404 2(4)	−0.156 4(6)	0.098 6(6)	C(71)	0.083 4(3)	−0.192 3(8)	0.403 4(8)
C(15)	0.437 1(4)	−0.024 7(6)	0.149 8(6)	C(72)	0.030 0(3)	−0.116 5(8)	0.390 2(8)
C(16)	0.413 1(4)	0.074 0(6)	0.229 4(6)	C(73)	−0.036 0(3)	−0.180 7(8)	0.338 8(8)
C(21)	0.407 0(3)	0.233 9(7)	0.482 3(6)	C(74)	−0.048 7(8)	−0.320 7(8)	0.330 5(8)
C(22)	0.439 0(3)	0.142 8(7)	0.530 0(6)	C(75)	0.004 6(3)	−0.396 6(8)	0.313 7(8)
C(23)	0.499 8(3)	0.185 8(7)	0.620 7(6)	C(76)	0.070 7(3)	−0.332 3(8)	0.365 1(8)
C(24)	0.528 7(3)	0.319 8(7)	0.663 7(6)	C(81)	0.371 6(4)	0.293 4(9)	0.796 0(6)
C(25)	0.496 7(3)	0.411 0(7)	0.615 9(6)	C(82)	0.385 3(4)	0.185 5(9)	0.834 6(6)
C(26)	0.435 9(3)	0.368 0(7)	0.525 2(6)	C(83)	0.419 6(4)	0.209 5(9)	0.953 0(6)
C(31)	0.307 3(4)	0.307 0(6)	0.312 1(6)	C(84)	0.440 2(4)	0.341 5(9)	1.032 8(6)
C(32)	0.321 4(4)	0.317 4(6)	0.212 9(6)	C(85)	0.426 6(4)	0.449 3(9)	0.994 2(6)
C(33)	0.307 8(4)	0.430 8(6)	0.182 5(6)	C(86)	0.392 3(4)	0.425 3(9)	0.875 8(6)
C(34)	0.280 2(4)	0.533 8(6)	0.251 3(6)	Cl(1)	0.597 83(29)	0.210 8(7)	0.415 2(6)
C(35)	0.266 2(4)	0.523 4(6)	0.350 5(6)	Cl(2)	0.615 6(4)	0.202 2(7)	0.197 5(6)
C(36)	0.279 7(4)	0.410 0(6)	0.380 9(6)	Cl(3)	0.810 4(3)	0.391 4(8)	0.366 2(8)
C(41)	0.166 3(4)	0.108 4(7)	0.121 3(6)	Cl(4)	0.807 8(4)	0.382 4(9)	0.132 2(8)

Table 5. Atomic positional parameters (fractional co-ordinates) for $[\overline{\text{Pd}\{\text{CH(COPh)S(O)}_2\text{C}}\text{H(COPh)}\}(\text{PMePh}_2)_2]\cdot\text{CH}_2\text{Cl}_2\cdot\text{H}_2\text{O}$ (**6c**) with e.s.d.s in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Pd	0.500 41(3)	0.207 38(3)	0.314 23(3)	C(26)	0.458 9(3)	0.320 93(24)	0.008 21(25)
S	0.411 65(11)	0.252 16(11)	0.480 13(12)	C(31)	0.757 66(29)	0.309 94(26)	0.329 0(4)
P(1)	0.421 23(10)	0.136 29(9)	0.161 59(11)	C(32)	0.863 09(29)	0.309 98(26)	0.387 1(4)
P(2)	0.674 68(11)	0.194 28(11)	0.311 04(13)	C(33)	0.924 21(29)	0.400 47(26)	0.399 4(4)
O(1)	0.379 5(3)	0.334 7(3)	0.508 0(4)	C(34)	0.879 89(29)	0.490 89(26)	0.353 6(4)
O(2)	0.392 5(3)	0.155 4(3)	0.559 7(3)	C(35)	0.774 45(29)	0.490 84(26)	0.295 6(4)
O(3)	0.625 7(3)	0.151 83(29)	0.610 2(4)	C(36)	0.713 34(29)	0.400 38(26)	0.283 3(4)
O(4)	0.400 9(3)	0.410 65(29)	0.237 7(4)	C(41)	0.711 67(29)	0.176 6(3)	0.182 1(3)
O(5)	0.500 00(0)	0.000 00(0)	0.500 00(0)	C(42)	0.738 85(29)	0.084 4(3)	0.180 9(3)
C(1)	0.543 0(4)	0.279 1(4)	0.456 7(5)	C(43)	0.763 86(29)	0.072 1(3)	0.079 2(3)
C(2)	0.355 2(4)	0.241 6(4)	0.338 7(4)	C(44)	0.761 66(29)	0.152 0(3)	−0.021 1(3)
C(3)	0.624 4(4)	0.241 5(4)	0.561 8(5)	C(45)	0.734 49(29)	0.244 3(3)	−0.019 9(3)
C(4)	0.333 3(4)	0.336 8(4)	0.251 3(5)	C(46)	0.709 49(29)	0.256 6(3)	0.081 7(3)
C(5)	0.464 8(4)	0.014 6(4)	0.171 8(6)	C(71)	0.224 42(23)	0.344 51(29)	0.177 4(3)
C(6)	0.731 1(5)	0.093 8(5)	0.431 1(6)	C(72)	0.215 17(23)	0.412 53(29)	0.067 0(3)
C(7)	0.171 7(9)	0.204 4(9)	0.610 2(14)	C(73)	0.115 22(23)	0.424 64(29)	−0.003 2(3)
C(11)	0.278 25(19)	0.104 11(26)	0.146 2(3)	C(74)	0.024 53(23)	0.368 77(29)	0.036 9(3)
C(12)	0.239 70(19)	0.032 64(26)	0.239 3(3)	C(75)	0.033 79(23)	0.300 74(29)	0.147 3(3)
C(13)	0.130 54(19)	0.004 45(26)	0.233 1(3)	C(76)	0.133 74(23)	0.288 63(29)	0.217 6(3)
C(14)	0.059 91(19)	0.047 71(26)	0.133 8(3)	C(81)	0.705 43(24)	0.316 83(24)	0.608 0(3)
C(15)	0.098 46(19)	0.119 17(26)	0.040 7(3)	C(82)	0.688 16(24)	0.416 51(24)	0.590 4(3)
C(16)	0.207 61(19)	0.147 36(26)	0.046 9(3)	C(83)	0.764 04(24)	0.481 61(24)	0.643 7(3)
C(21)	0.440 7(3)	0.217 06(24)	0.020 91(25)	C(84)	0.857 23(24)	0.447 03(24)	0.714 5(3)
C(22)	0.439 4(3)	0.177 97(24)	−0.074 05(25)	C(85)	0.874 50(24)	0.347 35(24)	0.732 1(3)
C(23)	0.456 2(3)	0.242 77(24)	−0.181 76(25)	C(86)	0.798 62(24)	0.282 25(24)	0.678 8(3)
C(24)	0.474 4(3)	0.346 65(24)	−0.194 46(25)	Cl(1)	0.089 44(28)	0.120 95(28)	0.532 5(3)
C(25)	0.475 7(3)	0.385 72(24)	−0.099 47(25)	Cl(2)	0.116 2(3)	0.214 53(29)	0.723 5(3)

phenyl carbon atoms, were given anisotropic thermal parameters. All the phenyl rings (including hydrogen atoms) were treated as rigid bodies with D_{6h} symmetry (C–C 1.395, C–H 1.08 Å). The hydrogen atom positions for H(1) and H(2) were located from a difference Fourier map and were refined with isotropic thermal parameters. Final cycles employed a weighting factor $w = 1/(\sigma^2F + gF^2)$ ($g = 0.001\,117$) and gave the final residual indices $R\{= \Sigma(|F_o| - |F_c|)/\Sigma|F_o|\}$ 0.0595 and $R'\{= [\Sigma w(|F_o| - |F_c|)^2/\Sigma|F_c|^2]^{\frac{1}{2}}\}$ 0.0580. The atomic co-ordinates for the structure are given in Table 4.

(*b*) $[\overline{\mathrm{Pd\{CH(COPh)S(O)_2C}}\mathrm{H(COPh)\}(PMePh_2)_2]\cdot CH_2Cl_2\cdot H_2O}$, (**6i**)$\cdot$$CH_2Cl_2\cdot H_2O$. Conditions were as for (**6a**), except: 5 536 reflections from Weissenberg layers *hk*(0—13) having $I > 3\sigma(I)$; weighting parameter $g = 0.000\,820$. Final R and R' values were 0.0745 and 0.0823. No absorption correction was applied.

Crystal data. $C_{42}H_{38}O_4P_2PdS\cdot CH_2Cl_2\cdot H_2O$, $M = 908.17$, triclinic, space group $P\bar{1}$, $a = 12.985(5)$, $b = 13.93(1)$, $c = 12.057(6)$ Å, $\alpha = 73.71(3)$, $\beta = 102.61(5)$, $\gamma = 100.01(3)°$, $U = 2\,028.11$ Å^3, $Z = 2$, $D_c = 1.49$ g cm^{-3}, $F(000) = 1\,028.0$, $\mu(\text{Mo-}K_\alpha) = 6.86$ cm^{-1}. The atomic co-ordinates for the structure are given in Table 5.

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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