Metallacyclic Complexes. Part 5.[1] Ligand Properties of Platinathietane-3-oxide Complexes and the Single-crystal X-Ray Structure of $[\overline{Pt\{CH(COPh)S(O)C}H(COPh)\}(PPh_3)_2\cdot RhCl(CO)]\cdot CH_2Cl_2\cdot H_2O$ †

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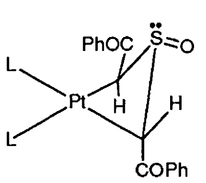
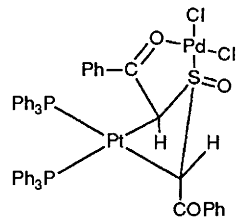
Treatment of the platinathietane-3-oxide complex $[\overline{Pt\{CH(COPh)S(O)C}H(COPh)\}(PPh_3)_2]$ **1a** with 1 mol equivalent of either $[PdCl_2(cod)]$ (cod = cycloocta-1,5-diene) or *trans*-$[PdCl_2(NCPh)_2]$ and with 0.5 mol equivalents of $[Rh_2(\mu\text{-}Cl)_2(CO)_4]$ affords the complexes $[\overline{Pt\{CH(COPh)S(O)C}H(\overline{COPh)\}}(PPh_3)_2\cdot MCl(X)]$ (M = Pd, X = Cl; M = Rh, X = CO), which contain a five-membered $\overline{M\text{–}S\text{–}C\text{–}C\text{–}O}$ ring system, formed by co-ordination of the sulphoxide sulphur and the equatorial benzoyl oxygen atom to the metal M. The absence of reaction of **1a** with the related labile platinum complexes $[PtCl_2(cod)]$ and *cis*-$[PtCl_2(NCPh)_2]$ illustrates that the sulphur atom in **1a** has relatively poor ligand properties. A single-crystal X-ray diffraction study has been carried out on $[\overline{Pt\{CH(COPh)S(O)C}H(COPh)\}(PPh_3)_2\cdot RhCl(CO)]\cdot CH_2Cl_2\cdot H_2O$, **3**. Crystals are triclinic, space group $P\bar{1}$, $Z = 2$, in a unit cell with lattice parameters $a = 11.761(17)$, $b = 20.701(18)$, $c = 13.006(16)$ Å, $\alpha = 102.8(3)$, $\beta = 124.7(3)$ and $\gamma = 88.4(2)°$. The structure was refined to R 0.0600 (R' 0.0559) for 5105 reflections having $7 < 2\theta < 54°$ collected at room temperature. It bears a strong resemblance to that of complex **1a**, but there are several differences which are discussed.

In a previous paper[1] we described the high-yield synthesis of a number of platinathietane-3-oxide complexes **1**, which contain puckered four-membered rings, with the sulphinyl oxygen adopting the expected equatorial environment. The ligand properties of sulphoxides, particularly dimethyl sulphoxide, have been well documented,[2–4] and sulphoxide groups are capable of acting as ambidentate ligands, co-ordinating to specific metal centres *via* either oxygen or sulphur according to the hardness of the metal centre. It was therefore of interest to investigate the reactions of the platinathietane-3-oxide complex **1a** with a number of metal complexes containing labile ligands. Oxygen co-ordination of 3,3-dimethylthietane 1-oxide has been previously reported in the europium complex $[Eu(dpm)_3\text{-}\{(O)\overline{SCH_2CMe_2C}H_2\}]$ (dpm = anion of dipivaloylmethane, $OCBu^tCHCBu^tO^-$).[5] Parts of this work have been reported in a preliminary communication.[6]



1a L = PPh_3
1b L = $PMePh_2$
1c L = PMe_2Ph



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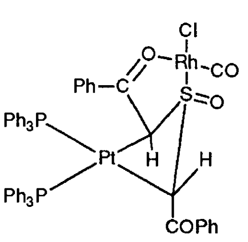

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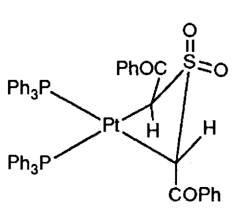

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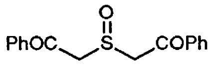

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Results and Discussion

Treatment of the platinathietane-3-oxide complex **1a** with either 1 mol equivalent of the labile palladium(II) complexes $[PdCl_2(cod)]$ (cod = cycloocta-1,5-diene) or *trans*-$[PdCl_2(NCPh)_2]$, or with 0.5 mol equivalents of tetracarbonyl-di-μ-chlorodirhodium(I), $[Rh_2(\mu\text{-}Cl)_2(CO)_4]$, in dichloromethane affords air-stable crystalline products, characterised as the chelate ligand complexes **2** and **3** respectively, on the basis of their ^1H and $^{31}P\text{-}\{^1H\}$ NMR and IR spectroscopic properties and a single-crystal X-ray diffraction study carried out on the rhodium complex **3**. The results of the X-ray work are summarised in Table 1, whilst the molecular structure is illustrated in Fig. 1, which also gives the crystallographic numbering system. The complex crystallised with one molecule of dichloromethane plus one molecule of water per molecule of complex. There are no short intermolecular contacts between the complex and the solvent molecules.

Complex **3** consists of a four-membered platinathietane-3-

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† Carbonyl-1κ*C*-chloro-1κ*Cl*-μ-(1,3,5-trioxo-1,5-diphenyl-3λ^4-thiapentane-2,4-diyl-1$\kappa^2 O^1$,*S*;2$\kappa^2 C^2$,C^4)bis(triphenylphosphine-2κ*P*)-platinumrhodium–dichloromethane–water (1/1/1).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.

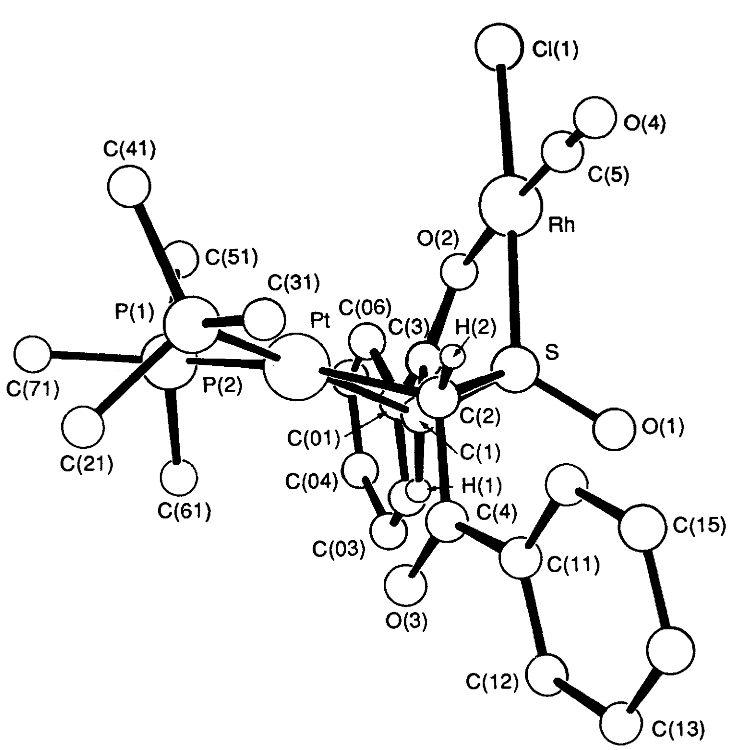


Fig. 1 Molecular structure of complex **3** with triphenylphosphine carbon atoms other than those bonded to phosphorus and hydrogen atoms of phenyl rings omitted

Table 1 Selected bond lengths (Å) and angles (°) for $[\overline{\text{Pt}\{\text{CH(COPh)S(O)C}}\text{H(COPh)}\}(\text{PPh}_3)_2\cdot\text{RhCl(CO)}]$ **3**$\cdot\text{CH}_2\text{Cl}_2\cdot\text{H}_2\text{O}$

Pt–P(1)	2.262(3)	P(1)–Pt–P(2)	98.2(1)
Pt–P(2)	2.331(3)	P(1)–Pt–C(2)	93.4(4)
Pt–C(1)	2.173(12)	P(2)–Pt–C(1)	96.4(3)
Pt–C(2)	2.122(11)	C(1)–Pt–C(2)	71.8(5)
Pt···S	2.774(4)	Pt–C(1)–S	89.1(5)
C(1)–S	1.759(13)	Pt–C(2)–S	91.7(5)
C(2)–S	1.724(14)	C(1)–S–C(2)	92.6(6)
S–O(1)	1.481(9)	C(1)–S–O(1)	114.1(6)
C(1)–C(3)	1.433(17)	C(2)–S–O(1)	113.0(6)
C(2)–C(4)	1.527(18)		
C(3)–O(2)	1.275(16)	Rh–S–C(1)	97.9(5)
C(4)–O(3)	1.201(16)	Rh–S–C(2)	113.6(4)
		Rh–S–O(1)	120.9(5)
Rh–S	2.185(4)	S–Rh–O(2)	81.9(3)
Rh–O(2)	2.124(9)	Cl(1)–Rh–O(2)	90.5(3)
Rh–C(5)	1.792(16)	Cl(1)–Rh–C(5)	92.4(5)
C(5)–O(4)	1.149(16)	Rh–C(5)–O(4)	177.6(17)
Rh–Cl(1)	2.327(4)	S–Rh–C(5)	95.1(5)
		Rh–O(2)–C(3)	117.1(8)

oxide ring system, in which the sulphur atom and the oxygen atom of the equatorial benzoyl substituent are co-ordinated to a chlorocarbonylrhodium moiety, to form a five-membered $\overline{\text{Rh–S–C–C–O}}$ chelate ring system. The structure of the platinathietane-3-oxide ring is similar to that of molecule **1a**, which we have described previously,[1] but there are several notable differences. The carbonyl group of the co-ordinated benzoyl substituent is somewhat longer [C(3)–O(2) 1.275(16) Å] than the unco-ordinated carbonyl group [C(4)–O(3) 1.201(16) Å], and is comparable with the C=O bond distance of 1.27 Å for the co-ordinated acetone ligand of the complex (acetone)-(4-hydroxy-4-methylpentan-2-one)(η^6-mesitylene)ruthenium bis(tetrafluoroborate).[7] Furthermore, the co-ordinated ketone group is somewhat distorted from coplanarity with the attached phenyl ring, as demonstrated by the O(2)–C(3)–C(01)–C(06) torsion angle of −41.68°. The unco-ordinated benzoyl group is effectively planar, since the O(3)–C(4)–C(11)–C(12) torsion angle is only 8.22°. The deviation of the co-ordinated benzoyl group from planarity is probably a consequence of steric interactions between this group and the phenyl rings of the triphenylphosphine ligands. The bond angles around the carbonyl carbon atoms of the co-ordinated and unco-ordinated benzoyl groups are fairly similar.

The geometry of the sulphoxide moiety is virtually unaffected by co-ordination to rhodium, with the C–S–O bond angles of the rhodium complex **3** being almost identical to those in complex **1a**.[1] The S=O bond length, 1.481(9) Å, is slightly shorter than the one found, 1.492(6) Å, in **1a**,[1] in which the sulphoxide group is not involved in co-ordination. A S=O bond shortening is expected when the sulphoxide group is co-ordinated *via* sulphur.[2]

The P(2)–Pt bond [2.331(3) Å], *cis* to the co-ordinated benzoyl substituent, is longer than the P(1)–Pt bond [2.262(3) Å]. The P(2)–Pt bond [2.319(2) Å] of complex **1a** is also longer than the P(1)–Pt bond [2.290(2) Å] although the difference is not as great. The co-ordination of the equatorial benzoyl substituent may have increased its effective steric bulk, causing an increased lengthening of the P(2)–Pt bond. The lengthening of platinum–phosphorus bonds *via* steric interactions with large *cis* ligands has been noted previously.[8]

The geometry about the rhodium atom is effectively square planar, with the sulphur atom *trans* to the chloride ligand, and the rhodium carbonyl *trans* to the co-ordinated benzoyl group. The twist angle between the C(5)–Rh–S and Cl(1)–Rh–O(2) planes is 3.6°. The somewhat small S–Rh–O(2) angle of 81.9(3)° is an indication of the reduced 'bite' of the chelating *S,O* ligand, which is due to the donor atoms being part of, or attached to, a rigid metallacycle. The small Rh–S–C(1) bond angle of 97.9(5)° is also an indication of the small 'bite' angle of the ligand, since the Rh–S–C(2) bond angle is 113.6(4)°. The platinum–rhodium distance is 3.529 Å, and there is subsequently no significant interaction (covalent radii: Pt 1.50; Rh 1.45 Å[9]). The remaining bond lengths and angles are unexceptional.

The ^{1}H, ^{13}C-{^{1}H} and ^{31}P-{^{1}H} NMR spectra of the co-ordinated platinathietane-3-oxide complexes **2** and **3** show the characteristic features for such a ring system. Thus, the axial and equatorial ring protons appear respectively as a doublet and a doublet of doublets, with the axial proton showing, as expected, the larger coupling to platinum-195. An interesting comparison may be made between the ring proton signals for the palladium and rhodium complexes **2** and **3**. The signals due to the axial ring protons of **2** and **3** are deshielded relative to molecule **1a**, appearing at δ 5.25 and 5.5 respectively. The axial ring proton of **1a** appears at δ 5.05. However, on examining the chemical shifts for the equatorial protons, it may be observed that in the case of the palladium complex **2** this equatorial proton appears as the lower-field ring-proton resonance at δ 5.63, and is therefore experiencing a large deshielding effect. Deshielding of the sulphoxide ring protons is consistent with co-ordination of the sulphoxide sulphur to an electron-withdrawing metal centre.[4] For the palladium complex **2** the greater deshielding of the equatorial ring proton is due to the greater proximity of this proton to the sulphur-co-ordinated $PdCl_2$ moiety. In the rhodium complex **3** only a slight deshielding of the equatorial ring proton is observed, from δ 4.65 for **1a** to δ 4.95 for **3**. This may be due in part to the rhodium(I) centre being less electron withdrawing than a palladium(II) centre. Carbonyl double bonds characteristically exhibit anisotropic shielding and deshielding effects in organic systems[10] and so it is possible that the rhodium carbonyl group, which is approximately aligned with the C(2)–H(2) bond of **3**, could be slightly shielding the equatorial proton. Metal–proton coupling is frequently observed in metal–sulphoxide systems, where the sulphoxide is sulphur-bonded, and the metal has non-zero spin.[2,3] However, no coupling of either axial or equatorial ring protons of **3** to rhodium-103 was discernible, since this coupling is likely to be very small. For example, a number of *S*-bonded dimethyl sulphoxide complexes of rhodium(I) and rhodium(III) show no discernible coupling of the methyl protons to rhodium-103.[4]

The $^{13}C\text{-}\{^1H\}$ NMR spectrum of the palladium complex **2** shows the characteristic features for the platinathietane-3-oxide ring system, with each Pt–CH ring carbon appearing as a doublet due to coupling to the *trans* phosphorus-31 nucleus, with $^2J(PC)$ values of 58.1 and 68.4 Hz being observed. No coupling of the ring carbons to their *cis* phosphines was discernible.

The $^{31}P\text{-}\{^1H\}$ NMR spectra for complexes **2** and **3** show the characteristic second-order AB spectrum for the two non-equivalent phosphines of the platinathietane-3-oxide ring system. The value of $^1J(PtP)$ for one of the triphenylphosphine ligands is much larger than the other, for example for **3**, values of $^1J(PtP)$ of 2803 and 3340 Hz are observed. The smaller value of $^1J(PtP)$ is assigned to the P(2) atom, as a result of the lengthening of the P(2)–Pt bond which is *cis* to the co-ordinated benzoyl group. The lengthening of the *cis* P(2)–Pt bond is accompanied by a shortening of the *trans* P(1)–Pt bond, with a concomitant increase in $J[P(1)Pt]$, when compared to complex **1a**.

The absence of any strong IR bands for the complexes **2** and **3** in the region 800–1030 cm^{-1} is consistent with sulphur co-ordination in these complexes.[2,4] Co-ordination of a sulphoxide ligand *via* oxygen or sulphur is known to effect a decrease or increase respectively in the S=O stretching frequency.[2,4] The S=O stretch is tentatively assigned to the strong band at 1134 cm^{-1} for **2** and 1119 cm^{-1} for **3**, these increased values of ν(S=O) being comparable with the S=O stretching frequencies in the complexes $[\{RhCl(Me_2SO\text{-}S)_2\}_2]$[4] (1100 cm^{-1}) and *trans*-$[PdCl_2(Me_2SO\text{-}S)_2]$ (1116 cm^{-1}).[11] The only other strong band in the co-ordinated sulphoxide stretching region, at around 1095 cm^{-1}, is also present in the spectrum of molecule **1a**. The palladium and rhodium complexes **2** and **3** show two strong ketone stretching bands due to the co-ordinated benzoyl substituents. The unco-ordinated benzoyl group exhibits a ν(C=O) band at 1639 cm^{-1} for **2** and 1642 cm^{-1} for **3** these values being similar to those of **1a**. The co-ordinated benzoyl groups exhibit lower values of ν(C=O), at 1490 cm^{-1} for **2** and 1510 cm^{-1} for **3**. This carbonyl bond weakening is similar to that observed in the polymeric carbonyl-bridged complex $[\{Pd[CH_2C(O)O](PPh_3)\}_n]$, for which a value of ν(C=O) of 1545 cm^{-1} is reported.[12] The rhodium carbonyl group appears as an intense band in the IR spectrum, at 1982 cm^{-1}, typical of a rhodium(I) carbonyl.[13] Weak bands at 341 and 310 cm^{-1} for **2** and 310 cm^{-1} for **3** are assigned as the metal-chloride stretching frequencies.[14]

The mechanism of formation of complexes **2** and **3** presumably involves initial co-ordination of the sulphur atom to the metal, followed by chelate-ring formation. Consistent with this, no reaction is observed between the benzoyl substituents of the platinathietane-3,3-dioxide complex **4**[15] and *trans*-$[PdCl_2(NCPh)_2]$. The reaction of *trans*$[PdCl_2(NCPh)_2]$ with 2 mol equivalents of the platinathietane-3-oxide **1a** afforded a 1:1 mixture of the chelate complex **2** and unreacted **1a**, as evidenced by $^{31}P\text{-}\{^1H\}$ NMR spectroscopy.

No reaction was observed between **1a** and either of the two labile platinum complexes $[PtCl_2(cod)]$ or *cis*-$[PtCl_2(NCPh)_2]$. Although platinum complexes are typically less labile than their palladium analogues, the absence of reaction of **1a** with labile platinum complexes indicates that its sulphoxide ligand has only poor ligand properties.[16] These poor ligand properties are further demonstrated by the absence of reaction between **1a** and $[Rh_2(\mu\text{-}Br)_2(cod)_2]$ in refluxing dichloromethane.

Interestingly, in contrast to the platinathietane-3-oxide **1a**, no reaction was observed between diphenacyl sulphoxide **5**[17] and $[PdCl_2(cod)]$. The enhanced ligand properties of the metallacycle probably arise as a result of the substitution of two hydrogen atoms of **5** by a more strongly electron-donating $Pt(PPh_3)_2$ moiety.

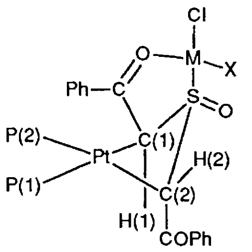
Experimental

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 NMR spectra were recorded in [$^2H_1$]chloroform on a Varian EM390 spectrometer at 90 MHz, on a Bruker AM 300 spectrometer at 300.13 MHz, and on a Bruker Spectrospin WH400 spectrometer at 400.13 MHz, with $SiMe_4$ (δ 0.0) as internal reference, positive values being to high frequency (low field). Carbon-13, hydrogen-1 decoupled, NMR spectra were recorded in [$^2H_1$]chloroform on a Bruker Spectrospin WH 400 spectrometer at 100.62 MHz with $SiMe_4$ (δ 0.0) as internal reference and the data for the aromatic region between δ 140 and 125 have been omitted. Phosphorus-31, hydrogen-1 decoupled, NMR spectra were recorded on a JEOL JNM-FX60 spectrometer at 24.15 MHz, with $[P(OH)_4]^+$ in [$^2H_2$]water (δ 0.0) as external reference.[18]

Experiments were carried out under a dry, oxygen-free, nitrogen atmosphere using solvents which were dried and distilled under nitrogen prior to use. The products were recrystallised in air. Light petroleum refers to the fraction of b.p. 40–60 °C. The platinathietane-3-oxide complex **1a**[1] and the platinathietane-3,3-dioxide complex $[Pt\{CH(COPh)S(O)_2CH(COPh)\}(PPh_3)_2]$ **4**·CH_2Cl_2·$0.5H_2O$[15] were prepared as described previously. The complexes $[PdCl_2(cod)]$,[19] *trans*-$[PdCl_2(NCPh)_2]$,[20] $[Rh_2(\mu\text{-}Cl)_2(CO)_4]$,[21] $[PtCl_2(cod)]$,[22] *cis*-$[PtCl_2(NCPh)_2]$[23] and $[Rh_2(\mu\text{-}Br)_2(cod)_2]$[24] were prepared as described in the literature.

Reactions of $[Pt\{CH(COPh)S(O)CH(COPh)\}(PPh_3)_2]$ **1a**.—(*i*) *Preparation of* $[Pt\{CH(COPh)S(O)CH(COPh)\}(PPh_3)_2\cdot PdCl_2]$ **2**·$2CH_2Cl_2$. (*a*) *From trans*-$[PdCl_2(NCPh)_2]$. A solution of *trans*-$[PdCl_2(NCPh)_2]$ (0.038 g, 0.10 mmol) in dichloromethane (10 cm^3) was added to a solution of complex **1a** (0.10 g, 0.10 mmol) in dichloromethane (25 cm^3)

to afford an orange solution, which was examined by $^{31}P-\{^1H\}$ NMR spectroscopy. This showed complete consumption of starting material, with formation of **2**. The mixture was refluxed for 1 h, and evaporation to dryness under reduced pressure afforded an orange oil. Dissolution of the oil in dichloromethane (2 cm^3) followed by addition of light petroleum (*ca.* 50 cm^3) afforded yellow *microcrystals* of complex **2**$\cdot 2CH_2Cl_2$ (0.103 g, 76%). Slow recrystallisation from dichloromethane–light petroleum afforded fine bright yellow *needles* (Found: C, 48.1; H, 3.5. $C_{52}H_{42}Cl_2O_3P_2PdPtS\cdot 2CH_2Cl_2$ requires C, 48.0; H, 3.4%), m.p. 207–210 °C (decomp.); ν(C=O) at 1639m and 1490s cm^{-1}; ν(S=O) at 1134s cm^{-1}; ν(Pd–Cl) at 341vw and 310vw cm^{-1}. NMR spectra: ^{1}H (400 MHz), δ 7.68–6.68 (m, 40 H, Ph), 5.63 {dd, 1 H, H(2), ^3J[P(1)H(2)] 9.8, ^3J[P(2)H(2)] 3.0, ^2J[PtH(2)] 44.8}, 5.25 {d, 1 H, H(1), ^3J[P(1)H(1)] 9.2, ^2J[PtH(1)] 72.0} and 5.20 (s, 4 H, CH_2Cl_2); $^{13}C-\{^1H\}$ (100 MHz), δ 211.55 [s, CO, ^2J(PtC) *ca.* 28], 196.41 [s, CO, ^2J(PtC) *ca.* 36], 64.32 {d, C(2), ^2J[P(2)C(2)] 58.1, ^1J[PtC(2)] 300.7} and 55.49 {d, C(1), ^2J[P(1)C(1)] 68.4, ^1J[PtC(1)] 429.9}; $^{31}P-\{^1H\}$ (24 MHz, [$^2H_1$]chloroform), second-order AB spin system, δ 14.72 {d, P(1), ^1J[PtP(1)] 3408, ^2J[P(2)P(1)] 19.5} and 10.08 {d, P(2), ^1J[PtP(2)] 2783, ^2J[P(1)P(2)] 19.5 Hz}.



2 M = Pd, X = Cl
3 M = Rh, X = CO

(*b*) *From* [$PdCl_2$(cod)]. A solution of [$PdCl_2$(cod)] (0.057 g, 0.20 mmol) in dichloromethane (10 cm^3) was added to a solution of complex **1a** (0.20 g, 0.20 mmol) in dichloromethane (20 cm^3) to afford an orange solution which was refluxed for 1 h. Work-up as in (*a*) above afforded fine bright yellow *needles* identified as **2**$\cdot 2CH_2Cl_2$ (0.133 g, 49%).

(*ii*) *Preparation of* [Pt{CH(COPh)S(O)CH(COPh)}$(PPh_3)_2\cdot$RhCl(CO)] **3**$\cdot CH_2Cl_2\cdot H_2O$. A solution of the complex [$Rh_2(\mu-Cl)_2(CO)_4$] (0.039 g, 0.100 mmol) in dichloromethane (5 cm^3) was added to a stirred solution of **1a** (0.20 g, 0.20 mmol) in dichloromethane (25 cm^3) to afford an orange solution which was refluxed for 30 min. Evaporation to dryness under reduced pressure afforded an orange oil. Dissolution of the oil in dichloromethane (2 cm^3) followed by addition of light petroleum afforded yellow *microcrystals* of complex **3**$\cdot CH_2Cl_2\cdot H_2O$ (0.201 g, 78%). Slow recrystallisation from dichloromethane–light petroleum afforded orange *prisms of* **3**$\cdot CH_2Cl_2\cdot H_2O$ suitable for an X-ray study (Found: C, 49.8; H, 3.9. $C_{53}H_{42}ClO_4P_2PtRhS\cdot CH_2Cl_2\cdot H_2O$ requires C, 50.9; H, 3.6%), m.p. (decomp.) >200 °C; ν[Rh(C=O)] at 1982vs cm^{-1}; ν(C=O) at 1642m and 1510m cm^{-1}; ν(S=O) at 1119s cm^{-1}; ν(Rh–Cl) at 310vw cm^{-1}. NMR spectra: ^{1}H (300 MHz), δ 8.03–6.63 (m, 40 H, Ph), 5.47 {d, 1 H, H(1), ^3J[P(1)H(1)] 9.5, ^2J[PtH(1)] 73.5}, 5.28 (s, 2 H, CH_2Cl_2), 4.95 {dd, 1 H, H(2), ^3J[P(1)H(2)] 10.05, ^3J[P(2)H(2)] 3.5, ^2J[PtH(2)] 48.0} and 2.06 (s br, 4 H, H_2O); $^{31}P-\{^1H\}$ (24 MHz), second-order AB spin system, δ 15.73 {d, P(1), ^1J[PtP(1)] 3340, ^2J[P(2)P(1)] 19.5} and 9.88 {d, P(2), ^1J[PtP(2)] 2803, ^2J[P(1)P(2)] 19.5 Hz}.

(*iii*) *With trans*-[$PdCl_2(NCPh)_2$]. A solution of *trans*-[$PdCl_2(NCPh)_2$] (0.019 g, 0.050 mmol) in dichloromethane (10 cm^3) was added to a solution of complex **1a** (0.10 g, 0.10 mmol) in dichloromethane (20 cm^3), and the mixture was refluxed for 1 h. Evaporation to dryness under reduced pressure afforded a yellow oily solid, which was shown by $^{31}P-\{^1H\}$ NMR spectroscopy to consist of a 1:1 mixture of the chelate-ring product **2** and unreacted **1a**.

(*iv*) *With* [$PtCl_2$(cod)]. A solution of [$PtCl_2$(cod)] (0.056 g, 0.149 mmol) in dichloromethane (5 cm^3) was added to a solution of complex **1a** (0.150 g, 0.149 mmol) in dichloromethane (20 cm^3), and the mixture was refluxed for 1 h. Evaporation to dryness under reduced pressure afforded an off-white solid which was shown to contain unreacted **1a** by $^{31}P-\{^1H\}$ and ^{1}H NMR spectroscopy.

(*v*) *With cis*-[$PtCl_2(NCPh)_2$]. A solution of *cis*-[$PtCl_2(NCPh)_2$] (0.070 g, 0.149 mmol) in dichloromethane (5 cm^3) was added to a solution of complex **1a** (0.150 g, 0.149 mmol) in dichloromethane (20 cm^3), and the mixture was refluxed for 12 h. Evaporation to dryness under reduced pressure afforded a pale yellow solid which was shown to contain unreacted **1a** by $^{31}P-\{^1H\}$ NMR spectroscopy.

(*vi*) *With* [$Rh_2(\mu-Br)_2(cod)_2$]. A solution of [$Rh_2(\mu-Br)_2(cod)_2$] (0.044 g, 0.059 mmol) in dichloromethane (20 cm^3) was added to a solution of complex **1a** (0.12 g, 0.12 mmol) in dichloromethane (10 cm^3), and the mixture was refluxed for 30 min. Evaporation to dryness under reduced pressure afforded an orange-yellow oil which was shown to contain unreacted **1a** by $^{31}P-\{^1H\}$ NMR spectroscopy.

Reaction of [Pt{CH(COPh)S$(O)_2$CH(COPh)}$(PPh_3)_2$] **4** *with trans*-[$PdCl_2(NCPh)_2$].—A mixture of complex **4**$\cdot CH_2Cl_2\cdot 0.5H_2O$ (0.128 g, 0.12 mmol) and *trans*-[$PdCl_2(NCPh)_2$] (0.044 g, 0.11 mmol) in dichloromethane (20 cm^3) was refluxed for 16 h. Evaporation to dryness under reduced pressure afforded a pale yellow solid which was shown to contain unreacted **4** by $^{31}P-\{^1H\}$ NMR spectroscopy.

Reaction of [$PdCl_2$(cod)] *with Diphenacyl Sulphoxide* **5**.—A solution of diphenacyl sulphoxide **5** (0.10 g, 0.35 mmol) in dichloromethane (10 cm^3) was added to a solution of [$PdCl_2$(cod)] (0.10 g, 0.35 mmol) in dichloromethane, and the mixture was refluxed for 1 h. Evaporation to dryness under reduced pressure afforded a yellow oily solid which was shown to contain unreacted **5** by ^{1}H NMR spectroscopy.

Crystal Structure Determination.—A crystal of the complex **3**$\cdot CH_2Cl_2\cdot H_2O$ was mounted in air. The intensities of 9808 reflections with $7 < 2\theta < 54°$ and $\pm h \pm k + l$ were measured on a Stöe STADI-2 Weissenberg diffractometer with graphite-monochromated Mo-Kα radiation using an ω-scan technique. The data were corrected for Lorentz and polarisation effects to yield 5105 reflections with $I \geqslant 3\sigma(I)$.

Crystal data. $C_{53}H_{42}ClO_4P_2PtRhS\cdot CH_2Cl_2\cdot H_2O$, M = 1273.32, triclinic, space group $P\bar{1}$, a = 11.761(17), b = 20.701(18), c = 13.006(16) Å, α = 102.8(3), β = 124.7(3), γ = 88.4(2)°, U = 2521.1 Å^3, Z = 2, D_c = 1.618 g cm^{-3}, λ(Mo-Kα) = 0.7107 Å, μ = 32.3 cm^{-1}.

The Pt and Rh atoms were located using the Patterson option of SHELXS 84.[25] All subsequent calculations for structure solution and refinement were carried out using the computer program SHELX.[26] Scattering factors were taken from ref. 27. Isotropic refinement of all non-hydrogen atoms gave an R factor of 0.094. An absorption correction, maximum and minimum transmission factors 0.795 and 0.711, was applied to the data. The hydrogen atoms H(1) and H(2) were placed at calculated positions then allowed to refine as normal atoms. The hydrogen atoms of the phenyl rings were refined as rigid groups with two related thermal parameters for each phenyl ring. Hydrogen atoms of a molecule of dichloromethane solvent and of a water molecule were not included in calculations. Parameter restraints would not allow all atoms to be refined with anisotropic thermal motion. All atoms other than phenyl carbon and hydrogen were refined as anisotropic and in addition the carbon atoms of two rings with highest isotropic

Table 2 Fractional atomic coordinates for complex **3**

Atom	*x*	*y*	*z*
Pt	0.325 76(5)	0.241 50(2)	0.591 57(6)
Rh	0.376 59(11)	0.235 07(5)	0.347 15(12)
P(1)	0.397 1(3)	0.158 50(15)	0.694 8(4)
P(2)	0.457 3(3)	0.331 26(15)	0.771 1(3)
S	0.180 1(3)	0.228 97(15)	0.328 2(3)
Cl(1)	0.588 0(4)	0.256 76(20)	0.377 2(5)
O(1)	0.045 6(9)	0.226 1(4)	0.202 8(9)
O(2)	0.379 8(9)	0.338 1(4)	0.419 5(9)
O(3)	−0.001 2(10)	0.217 8(6)	0.438 7(13)
O(4)	0.353 4(16)	0.091 3(5)	0.240 9(16)
C(1)	0.219 4(13)	0.300 5(6)	0.450 3(12)
H(1)	0.153 (11)	0.316(5)	0.448(11)
C(2)	0.173 1(12)	0.176 3(6)	0.410 8(13)
H(2)	0.197(11)	0.138(5)	0.376 (11)
C(3)	0.301 1(14)	0.353 4(6)	0.457 0(14)
C(4)	0.031 3(14)	0.172 2(7)	0.389 2(16)
C(5)	0.362 9(17)	0.147 7(8)	0.280 6(18)
C(01)	0.299 4(9)	0.425 0(3)	0.501 1(9)
C(02)	0.177 5(9)	0.447 9(3)	0.481 5(9)
C(03)	0.172 0(9)	0.516 2(3)	0.514 9(9)
C(04)	0.288 4(9)	0.561 5(3)	0.567 9(9)
C(05)	0.410 4(9)	0.538 6(3)	0.587 5(9)
C(06)	0.415 9(9)	0.470 3(3)	0.554 1(9)
C(11)	−0.072 3(8)	0.112 8(4)	0.296 1(10)
C(12)	−0.208 8(8)	0.117 6(4)	0.258 7(10)
C(13)	−0.312 3(8)	0.064 2(4)	0.170 9(10)
C(14)	−0.279 4(8)	0.006 0(4)	0.120 4(10)
C(15)	−0.143 0(8)	0.001 2(4)	0.157 8(10)
C(16)	−0.039 5(8)	0.054 6(4)	0.245 6(10)
C(21)	0.352 1(9)	0.168 3(4)	0.807 7(8)
C(22)	0.215 5(9)	0.180 3(4)	0.761 0(8)
C(23)	0.171 5(9)	0.188 8(4)	0.842 2(8)
C(24)	0.264 2(9)	0.185 4(4)	0.970 1(8)
C(25)	0.400 8(9)	0.173 4(4)	1.016 9(8)
C(26)	0.444 8(9)	0.164 9(4)	0.935 7(8)
C(31)	0.317 6(9)	0.074 2(3)	0.591 2(8)
C(32)	0.356 6(9)	0.047 4(3)	0.508 9(8)
C(33)	0.302 3(9)	−0.017 3(3)	0.430 2(8)
C(34)	0.208 8(9)	−0.055 1(3)	0.433 8(8)
C(35)	0.169 7(9)	−0.028 3(3)	0.516 0(8)
C(36)	0.224 1(9)	0.036 4(3)	0.594 7(8)
C(41)	0.580 9(7)	0.147 6(4)	0.773 7(9)
C(42)	0.643 3(7)	0.102 8(4)	0.851 2(9)
C(43)	0.785 1(7)	0.097 5(4)	0.911 6(9)
C(44)	0.864 4(7)	0.137 0(4)	0.894 5(9)
C(45)	0.802 0(7)	0.181 7(4)	0.817 0(9)
C(46)	0.660 3(7)	0.187 1(4)	0.756 6(9)
C(51)	0.597 9(7)	0.373 3(4)	0.781 2(9)
C(52)	0.624 0(7)	0.346 9(4)	0.689 2(9)
C(53)	0.732 5(7)	0.377 4(4)	0.695 1(9)
C(54)	0.814 8(7)	0.434 4(4)	0.792 9(9)
C(55)	0.788 7(7)	0.460 8(4)	0.885 0(9)
C(56)	0.680 2(7)	0.430 3(4)	0.879 1(9)
C(61)	0.336 6(8)	0.390 5(4)	0.763 5(9)
C(62)	0.205 7(8)	0.362 1(4)	0.719 7(9)
C(63)	0.109 9(8)	0.402 8(4)	0.721 5(9)
C(64)	0.145 2(8)	0.471 9(4)	0.767 2(9)
C(65)	0.276 1(8)	0.500 2(4)	0.811 1(9)
C(66)	0.371 9(8)	0.459 5(4)	0.809 2(9)
C(71)	0.547 6(8)	0.321 5(4)	0.932 8(6)
C(72)	0.483 0(8)	0.332 6(4)	0.996 8(6)
C(73)	0.552 0(8)	0.324 3(4)	1.121 8(6)
C(74)	0.685 6(8)	0.304 8(4)	1.182 8(6)
C(75)	0.750 2(8)	0.293 8(4)	1.118 9(6)
C(76)	0.681 1(8)	0.302 1(4)	0.993 9(6)
C(6)	0.099(5)	0.334 8(14)	1.079(3)
Cl(2)	0.056 4(7)	0.389 11(28)	1.157 7(7)
Cl(3)	0.138 0(10)	0.348 1(4)	0.985 6(10)
O(5)	0.889 0(18)	0.233 4(11)	0.597 1(18)

motion were refined anisotropically. The remaining Fourier difference map showed a residual 1e peak at 0.9 Å from Pt. An analysis of the weighting scheme over $|F_o|$ and $\sin\theta/\lambda$ was satisfactory. The final cycles of refinement employed a weighting parameter of 0.00048 where $w = 1/(\sigma^2F_o + gF_o^2)$ and gave the final residual indices $R = \Sigma(|F_o| - |F_c|)/\Sigma F_o = 0.0600$ and $R' = [\Sigma w(|F_o| - |F_c|)^2/w|F_o|^2]^{\frac{1}{2}} = 0.0559$. The atomic coordinates for the structure are given in Table 2.

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

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