Syntheses of the Cyclic Platinum(II) Thiolate Complexes $[\overline{Pt\{SCH_2C(O)CH_2}\}(PPh_3)_2]$ and $[\{\overline{Pt[SCH_2C(O)CH_2}](PPh_3)\}_2]$†

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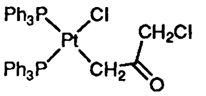
Treatment of $[Pt(\eta^2\text{-}RCH{=}CHR)(PPh_3)_2]$ (R = H or Ph) with 1,3-dichloroacetone gave the chloroacetonyl complex *cis*-$[PtCl\{CH_2C(O)CH_2Cl\}(PPh_3)_2]$ **1** which readily cyclised in high yield to the thiolate complex $[\overline{Pt\{SCH_2C(O)CH_2}\}(PPh_3)_2]$ **2** by treatment with sodium sulfide. Complexes **1** and **2** have been fully characterised by IR and NMR spectroscopies, and by elemental analysis. Ligand substitution reactions of complex **2** with an excess of isocyanide RNC (R = Bu^t, Bu^n or 2,6-xylyl), an excess of tri-*n*-butylphosphine or 1 equivalent of trimethyl phosphite in dichloromethane afforded the monosubstituted complexes $[\overline{Pt\{SCH_2C(O)CH_2}\}(PPh_3)(L)]$). These complexes were typically isolated as a mixture of isomers, with the major isomer in each case having the PPh$_3$ ligand *trans* to CH$_2$. Treatment of complex **2** with an excess of trimethyl phosphite yielded the bis(phosphite) complex $[\overline{Pt\{SCH_2C(O)CH_2}\}\{P(OMe)_3\}_2]$. Reaction of **2** with $[Rh_2(\mu\text{-}Cl)_2(CO)_4]$ afforded a mixture of products from which the thiolate-bridged dimeric complex $[\{\overline{Pt[SCH_2C(O)CH_2}](PPh_3)\}_2]$ was isolated and characterised by a single-crystal X-ray diffraction study, which confirmed the formulation of these complexes as five-membered ring thiolates.

The thiolate ligand, RS$^-$, is a fundamental class of ligand, and one which shows a very high propensity for strongly binding to soft, late transition metals, in particular, for example, platinum(II),[1-3] and gold(I).[1,4-6] Due to the occurrence of metal–thiolate complexes in biological systems,[1,7] and in inorganic pharmaceuticals,[4-6] there has been a resurgence of interest in metal–thiolate chemistry, and several reviews on the subject have been published.[1,8] One of the major routes to metal–thiolate complexes involves the nucleophilic displacement of metal-bound halide groups by the thiolate anion, and a range of complexes has been prepared using this methodology.[1,2,9]

During our studies on metallacyclobutan-3-one [dimethylene(oxo)methane complexes] of the transition metals, we prepared the chloroacetonyl complex *cis*-$[PtCl\{CH_2C(O)CH_2Cl\}(PPh_3)_2]$ **1**, and found that reductive Wurtz-type coupling on **1** using sodium amalgam leads to the formation of the platinacyclobutan-3-one ring [dimethylene(oxo)methane] complex $[\overline{Pt\{CH_2C(O)CH_2}\}(PPh_3)_2]$.[10] We subsequently reasoned that the presence of two *cis*-disposed halogens in **1** should permit, by nucleophilic displacement reactions, the synthesis of a range of novel metallacyclic complexes. In this paper we report full details on the synthesis and characterisation of **1**, together with the cyclic thiolate complex $[\overline{Pt\{SCH_2C(O)CH_2}\}(PPh_3)_2]$ **2**, prepared by reaction of **1** with sodium sulfide.



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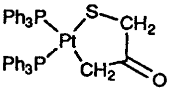

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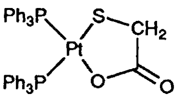

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Results and Discussion

Reaction of the zerovalent platinum complexes $[Pt(\eta^2\text{-}C_2H_4)(PPh_3)_2]$ or $[Pt(\eta^2\text{-}trans\text{-}PhCH{=}CHPh)(PPh_3)_2]$ with 1,3-dichloroacetone in diethyl ether yields the chloroacetonyl complex *cis*-$[PtCl\{CH_2C(O)CH_2Cl\}(PPh_3)_2]$ **1** as a white microcrystalline solid in almost quantitative yield. The compound has been fully characterised by elemental analysis and by NMR and IR spectroscopies. Thus, the $^{31}P\text{-}\{^1H\}$ NMR spectrum of **1** shows two inequivalent triphenylphosphine ligands as AB doublets at δ 20.6 and 18.1, showing satellites due to coupling to ^{195}Pt with $^1J(PtP)$ 2075.2 and 4257.8 Hz respectively. These values are characteristic of triphenylphosphine ligands *trans* to respectively high and low *trans* influence chloroacetonyl and chloro ligands. In comparison, values of $^1J(PtP)$ for *cis*-$[PtCl_2(PPh_3)_2]$[11] and *cis*-$[PtMe_2(PPh_3)_2]$[12] are 3676 and 1852 Hz respectively. The ^1H NMR spectrum of complex **1** showed, in addition to the expected phenyl proton resonances, a singlet at δ 4.49 due to the CH$_2$Cl group, together with a doublet of doublets centred at δ 2.63 due to the PtCH$_2$ group, showing couplings to the *cis* and *trans* phosphines of 5.3 and 10.5 Hz, and coupling to ^{195}Pt of 73.8 Hz. The $^{13}C\text{-}\{^1H\}$ NMR spectrum was also consistent with the structure. The carbonyl carbon appears as a weak resonance at δ 204.7, showing coupling to the *trans* phosphine only [$^3J(PC)$ 5.4 Hz], as well as to platinum [$^2J(PtC)$ 42.2 Hz]. The ^{13}C NMR resonances due to the methylene carbons were highly diagnostic; the CH$_2$Cl carbon appears as a singlet at δ 50.7, whereas the PtCH$_2$ carbon shows the expected coupling to both *cis* [$^2J(PC)$ 3.8 Hz] and *trans* [$^2J(PC)$ 78.6 Hz] phosphines, as well as a large one-bond coupling to ^{195}Pt of 444.3 Hz. The IR spectrum of **1** revealed a strong sharp band at 1678 cm^{-1}, attributable to the carbonyl group.

Reaction of complex **1** with an excess of sodium sulfide in refluxing acetone–methanol was found to give the cyclic

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue I, pp. xxiii–xxviii.

thiolate complex **2** as an air-stable pale yellow microcrystalline solid in high yield. The reaction of dithiols with 1,3-dichloroacetone has recently been reported[13] as a synthetic route to cyclic ketones which also contain thioether groups, in analogy with the synthesis of **2**. Overall, complex **2** bears a very strong resemblance to the cyclic mercaptoacetic acid-derived platinum thiolate complex $[\overline{Pt\{SCH_2C(O)O}\}(PPh_3)_2]$ **3** reported recently.[14] Notably, complex **2** was the only phosphorus-containing product formed in the reaction, as observed by $^{31}P-\{^1H\}$ NMR spectroscopy on the crude reaction product, which showed only signals due to **2** as two AB doublets at δ 25.8 and 21.7 with couplings to ^{195}Pt of 2434.1 and 3222.7 Hz respectively. This is illustrated in Fig. 1, with the $^{31}P-\{^1H\}$ NMR spectrum of the starting complex **1** for comparison. These resonances are assigned to triphenylphosphine ligands *trans* to alkyl and thiolato groups on platinum respectively. The ^1H NMR spectrum of **2** confirms that metallacycle formation has occurred, by the introduction of ^{31}P and ^{195}Pt couplings on the $PtSCH_2$ methylene group, when compared with the starting complex **1**, which does not show analogous couplings on the CH_2Cl carbon. Thus, in complex **2** the $PtSCH_2$ protons appear as a doublet showing ^{195}Pt coupling of 30.45 Hz, together with a weak four-bond coupling to (presumably) the *trans* phosphine of 1.67 Hz. In contrast, the spectral features of the $PtCH_2$ group are, as expected, relatively unchanged from the starting chloro complex **1**. The carbonyl group of **2** also shows couplings in the $^{13}C-\{^1H\}$ NMR spectrum to both phosphine ligands and the ^{195}Pt nucleus.

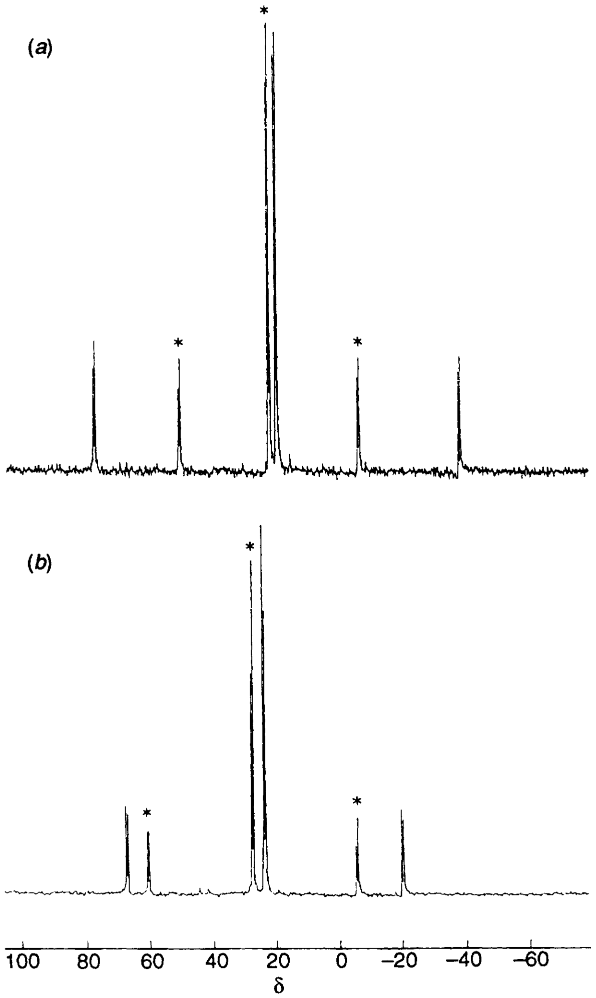
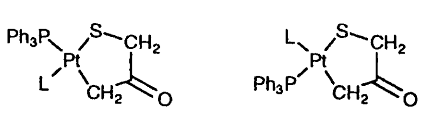


Fig. 1 $^{31}P-\{^1H\}$ NMR spectra of (*a*) *cis*-$[PtCl\{CH_2C(O)CH_2Cl\}(PPh_3)_2]$ **1** and (*b*) $[\overline{Pt\{SCH_2C(O)CH_2}\}(PPh_3)_2]$ **2**. Peaks marked * are assigned to triphenylphosphine ligands *trans* to CH_2 groups

The IR spectrum of compound **2** shows a strong band at 1650 cm^{-1}, somewhat lower than the C=O stretching frequencies of **1** (1678 cm^{-1}) and cyclopentanone (1740 cm^{-1}),[15] but identical to the C=O stretching frequency of complex **3**.[14] In a study of platinum–thiolate complexes[2] the Pt–S stretching frequency has previously been assigned in the region 317–374 cm^{-1}. The far-IR and Raman spectra of complex **2** show only two equal intensity bands in the region 300–400 cm^{-1}, at 346 and 340 cm^{-1}, one or both of which are tentatively assignable to the Pt–S stretching frequency. Evidence for the formulation of **2** as the more likely five-membered ring, as opposed to a ten-membered ring system, is provided, by its fast atom bombardment mass spectrum which shows the expected molecular ion for $[M + H]^+$ at m/z 808. In addition, there was excellent agreement between the observed and calculated isotopomer distributions for $C_{39}H_{34}OP_2PtS$.

Ligand Displacement Reactions of the Cyclic Thiolate **2**.—(*a*) *With isocyanides*. Treatment of complex **2** with either a large excess of either *tert*- or *n*-butyl isocyanide, or with a slight excess of 2,6-xylyl isocyanide, in dichloromethane, results in displacement of one PPh_3 ligand to give the mixed ligand complexes **4**–**6** respectively. The isolated complexes exist as a mixture of major (*a*) and minor (*b*) isomers, with the major isomers in all cases having the triphenylphosphine ligand *trans* to the CH_2 group. This is readily ascertained by $^{31}P-\{^1H\}$ NMR spectroscopy which shows, for the major isomers, values of $^1J(PtP)$ in the range 2143.6–2155.7 Hz, these values being characteristic for phosphine ligands *trans* to the high *trans*-influence CH_2 group, by comparison with the starting complex **2**. The presence of varying amounts of a minor isomer, having the PPh_3 ligand *trans* to S was readily inferred from the presence of extra resonances in the $^{31}P-\{^1H\}$ NMR spectra. Thus, for example, in the xylyl compound **6** the resonance shows $^1J(PtP)$ 3222.5 Hz, indicative of PPh_3 *trans* to S. The largest amount of the minor isomer, 29%, occurred for the 2,6-xylyl isocyanide complex, whereas for the *n*-butyl isocyanide, only trace amounts of the minor isomer could be detected. The difference in behaviour may arise due to steric differences between the isocyanide ligands. Further evidence for the presence of two isomers is provided by $^{13}C-\{^1H\}$ and ^1H NMR spectra of these complexes, which show additional resonances due to the minor isomer, the values of $J(PH)$, $J(PC)$, $J(PtH)$ and $J(PtC)$ being highly diagnostic. Thus, the major isomer **6a** shows a $PtCH_2$ resonance showing coupling to the *trans* phosphine [$^3J(PH)$ 9.4 Hz] and to platinum [$J(PtH)$ 63.9 Hz], these values being comparable to those in the bis(phosphine) complex **2**, where the $PtCH_2$ group has corresponding coupling constants of 8.4 and 62.5 Hz. Furthermore, the minor isomer **6b**, having the $PtCH_2$ protons *cis* to the phosphine ligand, shows a much smaller ^{31}P coupling (5.2 Hz) compared to the large *trans* coupling (9.4 Hz) in the major isomer **6a**.

Additional information can be obtained on inspection of the ^1H chemical shifts of the two CH_2 groups in the different isomers. The $PtSCH_2$ protons of both **6a** and **6b** resonate in similar positions (δ 3.08 and 3.17 respectively) compared to the starting complex **2** (δ 3.05). In contrast, however, whereas the



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4a	$CNBu^t$	**4b**
5a	$CNBu^n$	**5b**
6a	$CNC_6H_3Me_2$-2,6	**6b**
7a	$P(OMe)_3$	**7b**
8a	PBu^n_3	**8b**

$PtCH_2$ protons of the minor isomer **6b** appear at a very similar chemical shift (δ 2.44) to **2** (δ 2.49), the $PtCH_2$ protons of the major isomer **6a** are noticeably deshielded, appearing at δ 3.22. This deshielding presumably arises due to the anisotropic effect of the isocyanide triple bond in close proximity to these protons in the major isomer. It is worth noting that we observe no evidence for insertion of isocyanide into either the $PtCH_2$ or the PtS bonds. We have found previously,[16,17] in studies of isocyanide insertion into PtCHR bonds contained in four-membered rings, that the substituent R must be an electron-withdrawing group in order for isocyanide insertion to occur. The major isomers of these complexes are those formed by displacement of the PPh_3 ligand *trans* to the *lower trans*-influence thiolate group, possibly suggesting that the CH_2 and S moieties in **2** may have differing *trans* influences and *trans* effects.

(*b*) *With phosphites and tri-*n*-butylphosphine*. Treatment of the bis(triphenylphosphine) complex **2** with 1 equivalent of trimethyl phosphite in dichloromethane also results in displacement of the PPh_3 ligand *trans* to the thiolate, giving complex **7** in high yield. As for the isocyanide complexes, NMR spectroscopy was highly informative of the structure, and reveals the presence of a minor isomer **7b** (6%) having the PPh_3 ligand *trans* to the thiolate group. Thus, for the major isomer **7a**, the $^{31}P-\{^1H\}$ NMR spectrum reveals the presence of the PPh_3 ligand at δ 25.9 showing couplet to ^{195}Pt (2275.4 Hz) characteristic of PPh_3 *trans* to CH_2. The $P(OMe)_3$ ligand appears at δ 111.8 showing the characteristically large value of $^1J(PtP)$ of 5175.8 Hz. For the minor isomer **7b**, the PPh_3 ligand appears at δ 22.7, the value of $^1J(PtP)$ of *ca.* 3153 Hz being indicative of PPh_3 *trans* to thiolate. The ^1H and $^{13}C-\{^1H\}$ NMR spectral features of **7** are as expected for a mixed phosphine–phosphite complex. Reaction of **2** with an excess of tri-*n*-butylphosphine in dichloromethane yields an analogous mixed-ligand complex **8**, again with the major isomer **8a** having PPh_3 *trans* to CH_2. The attempted reaction of **2** with triphenyl phosphite was unsuccessful. However, reaction of **2** with an excess of trimethyl phosphite in refluxing dichloromethane leads to displacement of both triphenylphosphine ligands, giving the bis(phosphite) complex **9**, which has been characterised by $^{31}P-\{^1H\}$, ^1H and $^{13}C-\{^1H\}$ NMR spectroscopy. Thus, the $^{31}P-\{^1H\}$ NMR spectrum of complex **9** shows two inequivalent $P(OMe)_3$ resonances showing couplings to ^{195}Pt of 3735.4 and 5000.0 Hz, for phosphites *trans* to CH_2 and S respectively. The $^{13}C-\{^1H\}$ and ^1H NMR spectra also show two sets of resonances for the two inequivalent phosphites. Complex **9** was found to decompose on standing in air, and consequently satisfactory microanalytical data have not been obtained for this complex.

All of the monosubstituted complexes show the expected carbonyl stretching band in the range 1649–1683 cm^{-1}, while complexes **4**–**6** containing isocyanide ligands show the strong CN stretch for this group in the range 2147–2183 cm^{-1}. It is worth noting that for the 2,6-xylyl isocyanide complex **6**, two carbonyl and two isocyanide stretches can be observed, presumably attributable to the major and minor isomers of this complex.

It is worth noting that a number of μ-sulfido complexes of platinum(II) have been prepared previously using the nucleophilic displacement of platinum-bound chloride by sulfide.[18,19] These complexes were found to show pronounced nucleophilic behaviour at the sulfur centre. In addition, other non-bridged thiolato complexes of the platinum metals have found use in the construction of homo- and hetero-bimetallic complexes.[1,2,20] Accordingly, we have investigated the reaction of complex **2** with the labile metal complex $[Rh_2(\mu-Cl)_2(CO)_4]$, which led to a mixture of products, as shown by $^{31}P-\{^1H\}$ NMR spectroscopy. By means of column chromatography on Al_2O_3, the thiolate-bridged dimeric complex $[\{\overline{Pt[SCH_2C(O)C}H_2](PPh_3)\}_2]$ **10** was isolated in moderate yield and characterised by means of a single-crystal X-ray diffraction study. Selected intramolecular bond distances and angles are given in Table 1, and the molecular structure, together with the atom numbering scheme are shown in Fig. 2. The structure confirms the five-membered metallacyclic nature of the thiolate complexes described in this paper. The complex has a *trans* disposition of

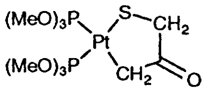

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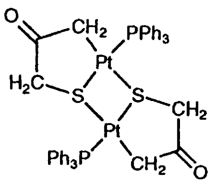
Table 1 Selected intramolecular bond lengths (Å) and angles (°) for $[\{\overline{Pt[SCH_2C(O)C}H_2](PPh_3)\}_2]$ **10** with estimated standard deviations in parentheses

P(1)–Pt(1)	2.232(3)	S(2)–Pt(2)	2.371(3)
P(2)–Pt(2)	2.234(3)	Pt(1)–C(3)	2.097(11)
S(1)–Pt(1)	2.381(2)	Pt(2)–C(6)	2.072(9)
S(2)–Pt(1)	2.373(3)	Pt(1) ··· Pt(2)	3.088(1)
S(1)–Pt(2)	2.371(3)		
P(1)–Pt(1)–S(2)	105.3(1)	P(2)–Pt(2)–C(6)	92.7(3)
P(1)–Pt(1)–C(3)	88.4(3)	S(1)–Pt(2)–S(2)	79.9(1)
S(1)–Pt(1)–S(2)	79.6(1)	S(2)–Pt(2)–C(6)	84.7(3)
S(1)–Pt(1)–C(3)	86.9(3)	Pt(1)–S(1)–Pt(2)	81.1(1)
P(2)–Pt(2)–S(1)	102.6(1)	Pt(1)–S(2)–Pt(2)	81.2(1)
$SCH_2C(O)CH_2$ ligands			
S(1)–C(1)	1.832(12)	S(2)–C(4)	1.831(10)
C(1)–C(2)	1.508(15)	C(4)–C(5)	1.513(16)
C(2)–C(3)	1.460(14)	C(5)–C(6)	1.447(14)
C(2)–O(2)	1.207(12)	C(5)–O(1)	1.227(14)
S(1)–C(1)–C(2)	102.1(7)	S(2)–C(4)–C(5)	108.1(7)
C(1)–C(2)–C(3)	114.6(9)	C(4)–C(5)–C(6)	113.8(11)
Pt(1)–C(3)–C(2)	104.5(8)	Pt(2)–C(6)–C(5)	103.2(7)
C(1)–C(2)–O(2)	120.4(11)	C(4)–C(5)–O(1)	119.7(11)
Triphenylphosphine ligands			
P(1)–C(11)	1.824(6)	P(2)–C(41)	1.826(6)
P(1)–C(21)	1.823(6)	P(2)–C(51)	1.826(5)
P(1)–C(31)	1.810(8)	P(2)–C(61)	1.839(7)
C(11)–P(1)–C(21)	100.3(4)	C(41)–P(2)–C(51)	100.2(3)
C(11)–P(1)–C(31)	106.3(4)	C(41)–P(2)–C(61)	106.3(4)
C(21)–P(1)–C(31)	107.5(4)	C(51)–P(2)–C(61)	104.0(4)



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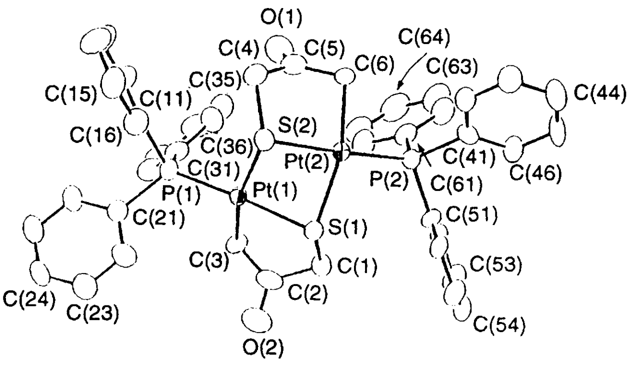

Fig. 2 Molecular structure of $[\{\overline{Pt[SCH_2C(O)C}H_2](PPh_3)\}_2]$ **10** (non-hydrogen atoms only) showing the atom numbering scheme

PPh_3 ligands about the Pt_2S_2 core, with the carbonyl groups of the two thiolate metallacycles also adopting a *trans* arrangement. The structure shows no unexceptional features; thus the platinum–sulfur and platinum–phosphorus distances are highly comparable to those in the related thiolate-bridged complex $[\{Pt(SCH_2Ph)(\mu\text{-}SCH_2Ph)(PMePh_2)\}_2]$.[3] It would seem likely that the rhodium complex employed in the synthesis of **10** has acted as a triphenylphosphine abstraction reagent, however, no attempt was made to identify rhodium-triphenylphosphine complexes in the reaction mixture. Investigations into the reactivity of complex **2** with other labile metal complexes are in progress.

Experimental

Reactions were carried out under a nitrogen atmosphere using solvents which were purified prior to use by distillation under nitrogen from the following drying agents: dichloromethane (P_4O_{10}), diethyl ether (sodium benzophenone ketyl), light petroleum (b.p. range 40–60 °C) (calcium hydride), methanol (magnesium methoxide) and acetone (calcium sulfate). The new platinum complexes were recrystallised using non-deoxygenated solvents. The $^{31}P\text{-}\{^1H\}$ NMR spectra were recorded in CH_2Cl_2 solution on a JEOL FX90Q spectrometer at 36.23 MHz, using an external D_2O lock and 85% H_3PO_4 (δ 0.0) as external reference (by the tube replacement method). Positive values are to high frequency (low field). The ^1H and $^{13}C\text{-}\{^1H\}$ NMR spectra were recorded on a Bruker AC300P spectrometer (^1H, 300.13 MHz; ^{13}C, 74.47 MHz) in $CDCl_3$, and were referenced relative to residual solvent peaks. Infrared spectra were recorded as KBr discs either on a Perkin-Elmer 580, or on a Bio-Rad FTS-40 spectrophotometer. Far-IR spectra were recorded on the powdered sample in diffuse reflectance mode, against a powdered polyethylene background. Raman spectra were recorded on powdered material contained in a glass capillary using a SPEX Ramalog spectrometer. Melting points were recorded on a Reichert hot-stage apparatus and are uncorrected.

The following reagents were used as supplied from commercial sources: 1,3-dichloroacetone (Aldrich), sodium sulfide nonahydrate (BDH), trimethyl phosphite (BDH), triphenyl phosphite (Aldrich) and tri-*n*-butyl phosphine (Koch-Light). The following compounds were prepared by literature procedures, or minor modifications thereof: $[Pt(\eta^2\text{-}C_2H_4)(PPh_3)_2]$,[21] $[Pt(\eta^2\text{-}trans\text{-}PhCH{=}CHPh)(PPh_3)_2]$,[22] *tert*-butyl isocyanide,[23] *n*-butyl isocyanide,[23] 2,6-xylyl isocyanide[24] and $[Rh_2(\mu\text{-}Cl)_2(CO)_4]$.[25]

Synthesis of *cis*-$[PtCl\{CH_2C(O)CH_2Cl\}(PPh_3)_2]$ **1**.—A mixture of $[Pt(\eta^2\text{-}C_2H_4)(PPh_3)_2]$ (0.40 g, 0.53 mmol) and 1,3-dichloroacetone (0.10 g, 0.79 mmol) in diethyl ether (20 cm^3) was stirred for 2 h. The white microcrystalline solid was filtered off, washed with diethyl ether, and dried *in vacuo* at 40 °C to yield complex **1** (0.44 g, 96%) (Found: C, 55.5; H, 4.1; Cl, 8.2. $C_{39}H_{34}Cl_2OP_2Pt$ requires C, 55.5; H, 4.1; Cl, 8.4%), m.p. > 210 °C (decomp.), melting at 258–260 °C; ν(C=O) at 1678s cm^{-1}. NMR: $^{31}P\text{-}\{^1H\}$ AB spin system, δ 20.6 [d, ^1J(PtP) 2075.2, ^2J(PP) 17.1] and 18.1 [d, ^1J(PtP) 4257.8]; ^1H, δ 7.60–7.11 (m, 30 H, Ph), 4.49 (s, 2 H, CH_2Cl) and 2.63 [dd, 2 H, $PtCH_2$, $^3J(PH)_{trans}$ 10.5, $^3J(PH)_{cis}$ 5.3, ^2J(PtH) 73.8]; $^{13}C\text{-}\{^1H\}$, δ 204.7 [d, C=O, ^3J(PC) 5.4, ^2J(PtC) 42.2], 135.3–126.8 (m, Ph), 50.7 (s, CH_2Cl) and 36.9 [dd, $PtCH_2$, $^2J(PC)_{trans}$ 78.6, $^2J(PC)_{cis}$ 3.8, ^1J(PtC) 444.3 Hz].

Compound **1** can be prepared in an identical manner, in comparable yield, starting with $[Pt(\eta^2\text{-}trans\text{-}PhCH{=}CHPh)(PPh_3)_2]$.

Synthesis of $[Pt\{SCH_2C(O)CH_2\}(PPh_3)_2]{\cdot}H_2O$ **2**.—To a suspension of *cis*-$[PtCl\{CH_2C(O)CH_2Cl\}(PPh_3)_2]$ **1** 0.360 g, 0.426 mmol) in methanol–acetone (1 : 1, 30 cm^3) was added sodium sulfide nonahydrate (0.160 g, 0.666 mmol). The mixture was brought to reflux for 1 min, cooled to room temperature and evaporated to dryness under reduced pressure to afford a grey solid. The product was extracted with dichloromethane (30 cm^3), and after filtration to remove sodium salts, the clear pale yellow solution was reduced in volume to *ca.* 5 cm^3 and light petroleum (*ca.* 60 cm^3) was added. The pale yellow precipitate was filtered off, washed with light petroleum and dried *in vacuo* to give 0.303 g (86%) of **2**. Recrystallisation from dichloromethane–light petroleum gave pale yellow platy crystals (Found: C, 56.7; H, 4.4. $C_{39}H_{34}OP_2PtS{\cdot}H_2O$ requires C, 56.7; H, 4.4%), m.p. > 210 °C (decomp.); ν(C=O) at 1650s cm^{-1}. Fast atom bombardment (FAB) mass spectrum (positive ion mode, *m*-nitrobenzyl alcohol matrix); $[M + H]^+$ at *m*/*z* 808. NMR: $^{31}P\text{-}\{^1H\}$, AB spin system, δ 25.8 [d, ^1J(PtP) 2434.1, ^2J(PP) 19.5] and 21.7 [d, ^1J(PtP) 3222.7]; ^1H, δ 7.49–7.19 (m, 30 H, Ph), 3.05 [d, 2 H, $PtSCH_2$, ^4J(PH) 1.67, ^3J(PtH) 30.45], 2.49 [dd, 2 H, $PtCH_2$, $^3J(PH)_{trans}$ 8.36, $^3J(PH)_{cis}$ 5.75, ^2J(PtH) 62.54] and 2.04 (s, br, 2 H, H_2O); $^{13}C\text{-}\{^1H\}$, δ 207.3 [dd, C=O, $^3J(PC)_{trans}$ 9.6, $^3J(PC)_{cis}$ 5.9, ^2J(PtC) not discernible due to broadness of satellites and overlap with central resonance], 134.9–127.6 (m, Ph), 46.0 [dd, $PtCH_2$, $^2J(PC)_{trans}$ 65.0, $^2J(PC)_{cis}$ 5.1, ^1J(PtC) 431.0 Hz] and 25.9 (s, br, $PtSCH_2$, coupling constants not determinable).

Synthesis of $[Pt\{SCH_2C(O)CH_2\}(CNBu^t)(PPh_3)]$ **4**.—A solution of **2** (0.150 g, 0.182 mmol) in dichloromethane with *tert*-butyl isocyanide (0.1 cm^3, excess) was refluxed for 30 min. Evaporation to dryness under reduced pressure yielded a pale yellow oil. $^{31}P\text{-}\{^1H\}$ NMR spectroscopy showed resonances due to the product (two isomers **4a** and **4b** in a 72 : 28 ratio) plus liberated triphenylphosphine (δ −5.3). Two recrystallisations from dichloromethane–light petroleum gave a pale yellow microcrystalline solid which was filtered off, washed with light petroleum, and dried *in vacuo* to afford 0.103 g (90%) of product (Found: C, 49.3; H, 4.5; N, 2.2. $C_{26}H_{28}NOPPtS$ requires C, 49.7; H, 4.5; N, 2.2%), m.p. 186–187 °C; ν(CN) at 2183vs, ν(C=O) at 1677m (sh) and 1652vs cm^{-1}. NMR for major isomer **4a**: $^{31}P\text{-}\{^1H\}$, δ 17.7 [s, ^1J(PtP) 2153.3]; ^1H, δ 7.57–7.36 (m, 15 H, Ph), 3.03 [s, 2 H, $PtSCH_2$, ^3J(PtH) 33.37, ^4J(PH) not discernible], 3.01 [d, 2 H, $PtCH_2$, $^3J(PH)_{trans}$ 9.54, ^2J(PtH) 64.59] and 1.11 (s, 9 H, Bu^t); $^{13}C\text{-}\{^1H\}$, δ 211.0 [d, C=O, ^3J(PC) 6.0, ^2J(PtC) not resolved], 134.5–128.3 (m, Ph), 57.7 [s, br, $C(CH_3)_3$, ^3J(PtC) *ca.* 17], 37.3 [d, $PtCH_2$, $^2J(PC)_{trans}$ 66.0, ^1J(PtC) 419.4], 29.7 [s, $C(CCH_3)_3$] and 28.7 [d, $PtSCH_2$, ^3J(PC) 4.4, ^2J(PtC) *ca.* 12 Hz]. NMR for minor isomer **4b**: $^{31}P\text{-}\{^1H\}$, δ 19.3 [s, ^1J(PtP) 3137.2]; ^1H, δ 2.32 [d, $PtCH_2$, $^3J(PH)_{cis}$ 5.27, ^2J(PtH) 64.42] and 1.12 (s, Bu^t) ($PtSCH_2$ resonance not observed due to overlap); $^{13}C\text{-}\{^1H\}$, δ 212.3 [d, C=O, ^3J(PC) *ca.* 9.6], 39.0 [d, $PtCH_2$, $^2J(PC)_{cis}$ 4.6, ^1J(PtC) not discernible] and 27.4 [d, br, $PtSCH_2$, ^3J(PC) *ca.* 2 Hz, ^2J(PtC) not discernible].

Synthesis of $[Pt\{SCH_2C(O)CH_2\}(CNBu^n)(PPh_3)]$ **5**.—This complex was prepared in comparable percentage yield as for **4**, using *n*-butyl isocyanide (Found: C, 49.2; H, 4.6; N, 2.1. $C_{26}H_{28}NOPPtS$ requires C, 49.7; H, 4.5; N, 2.2%), m.p. 126–130 °C. NMR: $^{31}P\text{-}\{^1H\}$, δ 17.6 [s, ^1J(PtP) 2155.7 Hz].

Synthesis of $[Pt\{SCH_2C(O)CH_2\}(CNC_6H_3Me_2\text{-}2,6)(PPh_3)]$ **6**.—2,6-Xylyl isocyanide (0.018 g, 0.137 mmol) was added to a stirred solution of **2** (0.100 g, 0.121 mmol) in dichloromethane (10 cm^3), and the mixture stirred at 30 °C for 20 min. The solvent was removed under reduced pressure and the residue triturated with diethyl ether (10 cm^3) to remove triphenylphosphine and excess isocyanide. Crystallisation from dichloromethane–diethyl ether afforded pale yellow crystals of **6** (0.063 g, 77%) (Found: C, 53.0; H, 4.2; N, 2.1. $C_{30}H_{28}NOPPtS$ requires C, 53.3; H, 4.2; N, 2.1%), m.p. partial melting 172–176 °C, then decomposition with liberation of $CNC_6H_3Me_2$-2,6 at 180–210 °C, further partial melting 211–215 °C; ν(CN) at 2147vs and 2160m (sh) cm^{-1}; ν(C=O) at 1654m (sh) and 1683s cm^{-1}. NMR spectroscopy reveals the presence of a major isomer

Table 2 Fractional atomic coordinates for $[\mathrm{Pt}\{\mathrm{SCH_2C(O)CH_2}\}(\mathrm{PPh_3})]_2$ **10**

Atom	*x*	*y*	*z*
Pt(1)	−0.234 41(4)	−0.101 56(3)	0.250 04(3)
Pt(2)	0.063 37(4)	0.004 02(3)	0.104 73(3)
S(1)	−0.134 72(26)	0.083 73(19)	0.179 91(21)
S(2)	−0.100 00(26)	−0.151 61(20)	0.090 96(20)
P(1)	−0.341 57(28)	−0.268 00(20)	0.326 81(22)
P(2)	0.223 25(27)	0.144 99(20)	0.116 74(21)
O(1)	0.116 3(8)	−0.261 9(7)	0.155 1(7)
O(2)	−0.401 7(9)	0.139 9(7)	0.387 4(6)
C(1)	−0.162 5(11)	0.162 7(8)	0.289 1(8)
C(2)	−0.302 5(12)	0.098 5(10)	0.358 7(9)
C(3)	−0.306 7(11)	−0.017 2(8)	0.380 3(8)
C(4)	−0.007 7(11)	−0.264 6(8)	0.072 9(9)
C(5)	0.108 4(12)	−0.215 4(9)	0.095 7(10)
C(6)	0.194 6(10)	−0.108 8(8)	0.047 7(8)
C(11)	−0.327 7(8)	−0.397 6(5)	0.254 9(6)
C(12)	−0.293 6(8)	−0.491 9(5)	0.273 4(6)
C(13)	−0.285 2(8)	−0.589 1(5)	0.216 2(6)
C(14)	−0.310 7(8)	−0.592 0(5)	0.140 5(6)
C(15)	−0.344 8(8)	−0.497 7(5)	0.122 0(6)
C(16)	−0.353 3(8)	−0.400 5(5)	0.179 2(6)
C(21)	−0.527 7(5)	−0.288 5(6)	0.395 7(5)
C(22)	−0.593 5(5)	−0.204 4(6)	0.397 0(5)
C(23)	−0.736 0(5)	−0.221 0(6)	0.449 8(5)
C(24)	−0.812 7(5)	−0.321 7(6)	0.501 2(5)
C(25)	−0.746 9(5)	−0.405 8(6)	0.499 9(5)
C(26)	−0.604 4(5)	−0.389 2(6)	0.447 2(5)
C(31)	−0.277 2(8)	−0.282 7(6)	0.405 8(7)
C(32)	−0.358 9(8)	−0.297 2(6)	0.502 8(7)
C(33)	−0.298 6(8)	−0.299 2(6)	0.559 0(7)
C(34)	−0.156 5(8)	−0.286 6(6)	0.518 2(7)
C(35)	−0.075 0(8)	−0.272 1(6)	0.421 4(7)
C(36)	−0.135 3(8)	−0.270 2(6)	0.365 1(7)
C(41)	0.378 1(6)	0.197 9(5)	0.008 1(4)
C(42)	0.411 0(6)	0.131 8(5)	−0.073 6(4)
C(43)	0.527 9(6)	0.172 5(5)	−0.157 2(4)
C(44)	0.612 0(6)	0.279 3(5)	−0.159 2(4)
C(45)	0.579 2(6)	0.345 4(5)	−0.077 5(4)
C(46)	0.462 3(6)	0.304 7(5)	0.006 1(4)
C(51)	0.170 0(7)	0.279 5(4)	0.166 9(5)
C(52)	0.178 4(7)	0.331 6(4)	0.245 7(5)
C(53)	0.136 9(7)	0.435 0(4)	0.279 3(5)
C(54)	0.086 9(7)	0.486 4(4)	0.234 2(5)
C(55)	0.078 4(7)	0.434 3(4)	0.155 4(5)
C(56)	0.120 0(7)	0.330 8(4)	0.121 7(5)
C(61)	0.281 5(8)	0.104 5(6)	0.193 7(5)
C(62)	0.417 1(8)	0.136 8(6)	0.177 4(5)
C(63)	0.450 7(8)	0.111 8(6)	0.243 7(5)
C(64)	0.348 8(8)	0.054 3(6)	0.326 3(5)
C(65)	0.213 3(8)	0.021 9(6)	0.342 6(5)
C(66)	0.179 6(8)	0.046 9(6)	0.276 4(5)

6a (71%) having the PPh_3 ligand *trans* to the CH_2 group, and a minor isomer **6b** (29%) with PPh_3 *trans* to S. NMR for major isomer **6a**: ^{31}P-{^{1}H}, δ 18.8 [s, ^1J(PtP) 2143.6]; ^{1}H, δ 7.63–6.94 (m, 18 H, aromatic), 3.22 [d, 2 H, $PtCH_2$, $^3J(\mathrm{PH})_{trans}$ 9.35, ^2J(PtH) 63.93], 3.08 [s, 2 H, $PtSCH_3$, ^3J(PtH) 33.43] and 1.92 (s, 6 H, Me); ^{13}C-{^{1}H}, δ 210.9 [d, C=O, ^3J(PC) 5.7, ^2J(PtC) not resolved], 141.2–127.8 (m, aromatic), 37.6 [d, $PtCH_2$, $^2J(\mathrm{PC})_{trans}$ 65.5, ^1J(PtC) 423.8], 29.1 [d, br, $PtSCH_2$, $^3J(\mathrm{PC})_{cis}$ 4.6 Hz, ^2J(PtC) not resolved] and 18.4 (s, Me). NMR for minor isomer **6b**: ^{31}P-{^{1}H}, δ 19.6 [s, ^1J(PtP) 3222.5]; ^{1}H, distinct observed resonances at δ 3.17 [d, $PtSCH_2$, $^4J(\mathrm{PH})_{trans}$ 2.42, *J*(PtH) not discernible due to overlap], 2.44 [d, $PtCH_2$, $^3J(\mathrm{PH})_{cis}$ 5.23, ^2J(PtH) 62.96] and 1.97 (s, Me); ^{13}C-{^{1}H} resonances observed at δ 212.1 [d, C=O, ^3J(PC) 9.6, ^2J(PtC) not discernible], 40.3 [d, $PtCH_2$, $^2J(\mathrm{PC})_{cis}$ 4.9, ^1J(PtC) not discernible], 27.6 [d, br, $PtSCH_2$, $^3J(\mathrm{PC})_{trans}$ *ca.* 2.3, ^2J(PtC) *ca.* 16.2 Hz] and 15.3 (s, Me).

Synthesis of $[\mathrm{Pt}\{\mathrm{SCH_2C(O)CH_2}\}\{\mathrm{P(OMe)_3}\}(\mathrm{PPh_3})]$ **7**.—To a solution of **2** (0.150 g, 0.182 mmol) in dichloromethane (10 cm^3) was added dropwise with stirring, 1 equivalent of trimethyl phosphite as a solution in dichloromethane (0.17 mol dm^{-3}, 1.09 cm^3). After 10 min the solvent was removed under reduced pressure, and ^{31}P-{^{1}H} NMR spectroscopy indicated a mixture of product **7** and triphenylphosphine. The product was triturated with diethyl ether and then recrystallised from dichloromethane–light petroleum to yield white microcrystals of **7** as a mixture of major (94%) and minor (6%) isomers (0.098 g, 80%) (Found: C, 43.1; H, 4.3. $C_{24}H_{28}O_4P_2PtS$ requires C, 43.0; H, 4.2%), m.p. 155–162 °C, with liberation of $P(OCH_3)_3$; ν(C=O) at 1649s cm^{-1}. NMR for major isomer **7a**: ^{31}P-{^{1}H}, δ 111.8 [d, $P(OMe)_3$, ^1J(PtP) 5175.8, ^2J(PP) 31.7] and 25.9 [d, PPh_3, ^1J(PtP) 2275.4, ^2J(PP) 31.7]; ^{1}H, δ 7.56–7.10 (m, 15 H, Ph), 3.38 [d, 9 H, $P(OMe)_3$, ^3J(PH) 12.59, ^2J(PtH) not resolved], 3.08 [d, 2 H, $PtSCH_2$, $^4J(\mathrm{PH})_{trans}$ 4.19, ^3J(PtH) 27.49] and 2.90 [dd, 2 H, $PtCH_2$, $^3J(\mathrm{PH})_{trans}$ 8.57, $^3J(\mathrm{PH})_{cis}$ 4.71, ^2J(PtH) 60.52]; ^{13}C-{^{1}H}, δ 208.5 [dd, C=O, $^3J(\mathrm{PC})_{trans}$ 10.0, $^3J(\mathrm{PC})_{cis}$ 6.2, ^2J(PtC) not resolved], 134.8–127.6 (m, Ph), 52.1 [d, $P(OMe)_3$, ^2J(PC) 1.8, ^3J(PtC) *ca.* 13], 38.0 [dd, $PtCH_2$, $^2J(\mathrm{PC})_{trans}$ 63.1, $^2J(\mathrm{PC})_{cis}$ 7.8, ^1J(PtC) 416.7 Hz] and 29.1 [s, br, $PtSCH_2$, ^3J(PC) and ^2J(PtC) not resolved]. NMR for minor isomer **7b**: ^{31}P-{^{1}H}, δ 115.5 [d, $P(OMe)_3$, ^1J(PtP) *ca.* 4034, ^2J(PP) 31.7] and 22.7 [d, PPh_3, ^1J(PtP) *ca.* 3153 Hz].

Synthesis of $[\mathrm{Pt}\{\mathrm{SCH_2C(O)CH_2}\}(\mathrm{PBu^n_3})(\mathrm{PPh_3})]$ **8**.—To a solution of **2** (0.100 g, 0.121 mmol) in dichloromethane (10 cm^3) was added tributylphosphine (0.1 cm^3, excess), and the mixture was stirred at 30 °C for 40 min. Evaporation to dryness under reduced pressure yielded a white solid which was triturated with light petroleum (10 cm^3). The residue was recrystallised from dichloromethane–light petroleum to afford **8** as a white powder (0.079 g, 87%) (Found: C, 52.7; H, 6.2. $C_{33}H_{46}OP_2PtS$ requires C, 53.0; H, 6.2%), m.p. partial melting > 125 °C, melting at 182–185 °C; ν(C=O) at 1683m (sh) and 1653vs cm^{-1}. NMR for major isomer **8a**: ^{31}P-{^{1}H}, δ 22.7 [d, PPh_3, ^1J(PtP) 2404.8, ^2J(PP) 17.1] and −0.71 [d, PBu^n_3, ^1J(PtP) 3022.5, ^2J(PP) 17.1]; ^{1}H, δ 7.68–7.34 (m, 15 H, Ph), 3.02 [d, 2 H, $PtSCH_2$, $^4J(\mathrm{PH})_{trans}$ 2.50, ^3J(PtH) 29.10], 2.82 [dd, 2 H, $PtCH_2$, $^3J(\mathrm{PH})_{trans}$ 8.66, $^3J(\mathrm{PH})_{cis}$ 5.31, ^2J(PtH) 63.66], 1.50–1.13 (m, 27 H, CH_2, PBu^n_3) and 0.79 [t, 9 H, CH_3, PBu^n_3, ^3J(HH) 6.88]; ^{13}C-{^{1}H}, δ 209.2 [dd, C=O, $^3J(\mathrm{PC})_{trans}$ 9.0, $^3J(\mathrm{PC})_{cis}$ 5.8, *J*(PtC) not resolved], 134.9–127.9 (m, Ph), 41.7 [dd, $PtCH_2$, $^2J(\mathrm{PC})_{trans}$ 67.6, $^2J(\mathrm{PC})_{cis}$ 6.3, ^1J(PtC) 444.5], 29.3 (s, br, PBu^n_3), 26.4 [s, PBu^n_3, *J*(PtC) 21.3 Hz], 24.4–23.6 (m, $PtSCH_2$ and PBu^n_3) and 13.6 (s, CH_3). A resonance due to the $PtCH_2$ protons of the minor isomer **8b** (< 1%) was observed in the ^{1}H NMR spectrum at δ 2.21 [dd, $^3J(\mathrm{PH})_{trans}$ 8.8, $^3J(\mathrm{PH})_{cis}$ 5.5, ^2J(PtH) 58.28 Hz].

Synthesis of $[\mathrm{Pt}\{\mathrm{SCH_2C(O)CH_2}\}\{\mathrm{P(OMe)_3}\}_2]$ **9**.—To a solution of **2** (0.150 g, 0.182 mmol) in dichloromethane (20 cm^3) was added trimethyl phosphite (0.1 cm^3, excess) and the mixture was refluxed for 15 min. Evaporation to dryness under reduced pressure afforded a very pale yellow oil which was triturated with light petroleum and then recrystallised from dichloromethane–light petroleum to give the product **9** as a white microcrystalline solid (0.081 g, 84%), m.p. 68–71 °C. NMR: ^{31}P-{^{1}H}, δ 119.7 [d, $P(OMe)_3$, ^1J(PtP) 3735.4, ^2J(PP) 46.4] and 114.2 [d, $P(OMe)_3$, ^1J(PtP) 5000.0]; ^{1}H, δ 3.68 [d, 9 H, $P(OMe)_3$, ^3J(PH) 5.78], 3.64 [d, 9 H, $P(OMe)_3$, ^3J(PH) 6.27], 3.10 [d, 2 H, $PtSCH_2$, $^4J(\mathrm{PH})_{trans}$ 4.48, ^3J(PtH) 28.83] and 2.72 [dd, 2 H, $PtCH_2$, $^3J(\mathrm{PH})_{trans}$ 12.86, $^3J(\mathrm{PH})_{cis}$ 4.68, ^2J(PtH), 58.14]; ^{13}C-{^{1}H}; δ 211.2 [t, $^3J(PC)_{trans}$ + $^3J(PC)_{cis}$ 9.1, ^2J(PtC) not discernible], 52.6 [d, P(OMe)$_3$, ^2J(PC) 1.5, ^3J(PtC) *ca.* 11.5], 52.4 [d, P(OMe)$_3$, ^2J(PC) 1.4, ^3J(PtC) 14.8], 39.2 [dd, PtCH$_2$, $^2J(PC)_{trans}$ 96.5, $^2J(PC)_{cis}$ 7.5, ^1J(PtC) 396.3] and 27.4 [t, PtSCH$_2$, $|^3J(PC)_{trans}$ + $^3J(PC)_{cis}|$ 4.0 Hz]. The product decomposes on standing in air, and satisfactory microanalytical data were not obtained.

Attempted Reaction of **2** *with Triphenyl Phosphite*.—A solution of **2** (0.12 g, mmol) in dichloromethane (20 cm^3) was refluxed with triphenyl phosphite (0.1 cm^3, 0.382 mmol) for 20 min. Evaporation to dryness under reduced pressure gave a pale yellow oil that was shown to contain unreacted **2** by ^{31}P-{^{1}H} NMR spectroscopy.

Reaction of **2** *with* [Rh$_2$(μ-Cl)$_2$(CO)$_4$].—To a solution of **2** (0.190 g, 0.230 mmol) in dichloromethane (25 cm^3) was added [Rh$_2$(μ-Cl)$_2$(CO)$_4$] (0.046 g, 0.118 mmol) in dichloromethane (10 cm^3) to give an orange solution which was refluxed for 1 h. The deep orange solution was evaporated to dryness under reduced pressure to afford a deep orange oil which was shown to contain a number of products by ^{31}P-{^{1}H} NMR spectroscopy. Column chromatography on Al$_2$O$_3$, eluting first with CH$_2$Cl$_2$ gave a uncharacterised non-phosphorus containing yellow band, and then with CH$_2$Cl$_2$–MeOH (2:1 v/v) gave an orange band, which was collected and evaporated under reduced pressure. Crystallisation from dichloromethane–light petroleum gave the product as a pale yellow-brown powder which was filtered off and dried *in vacuo* to give 0.085 g of crude [{Pt[SCH$_2$C(O)CH$_2$](PPh$_3$)}$_2$] **10**, m.p. 180 °C (decomp.), ν(C=O) at 1672s cm^{-1}. Slow recrystallisation from dichloromethane–light petroleum gave a small number of deep orange-red crystals which were characterised by a single-crystal X-ray diffraction study.

Crystal Structure Determination of Complex **10**.—An orange-red crystal of approximate dimensions 0.09 × 0.24 × 0.22 mm was glued to the end of a thin glass fibre using epoxy resin. The unit-cell parameters were determined by least-squares refinement of ω measurements for different layers.[26] Intensities of 5628 reflections in the range $7 \leqslant 2\theta \leqslant 50°$ and [±*h*, ±*k*, *l*(0–17)] were measured on a Stoe Stadi-2 Weissenberg diffractometer, with an ω-scan technique. The data were corrected for Lorentz and polarisation effects to give 3683 reflections with $I \geqslant 3\sigma(I)$.

Crystal data. [{Pt[SCH$_2$C(O)CH$_2$](PPh$_3$)}$_2$], M = 1091.01, triclinic, space group $P\bar{1}$, a = 11.427(7), b = 12.030(7), c = 16.299(4) Å, α = 97.03(6), β = 60.79(4), γ = 104.30(3)°, U = 1895.06 Å^3, Z = 2, D_c = 1.912 g cm^{-3}, $F(000)$ = 1048, Mo-Kα radiation, λ = 0.710 69 Å, μ(Mo-Kα) = 72.92 cm^{-1}

The position of the two platinum atoms were located and the structure solved by conventional Patterson techniques using SHELX 76.[27] Scattering factors were taken from ref. 28. All subsequent calculations were carried out using SHELX 76. Phenyl rings were included as rigid groups with D_{6h} symmetry and C–C distances of 1.395 Å. The hydrogen atoms of the phenyl and methyl groups were included in calculated positions (C–H 1.08 Å) and had fixed isotropic thermal parameters. All non-hydrogen atoms were refined with anisotropic thermal parameters during the final cycles of refinement. An analytical absorption correction was applied to the data using the Gaussian integration method employed by SHELX 76, the maximum and minimum transmission factors being 0.5581 and 0.2537 respectively. Final cycles of least-squares refinement used a weighting parameter $w = 1.388/(\sigma^2F + gF^2)$ (g = 0.000 24) and gave final residual indices of R = 0.0341 and R' = 0.0313. The average shift/e.s.d. = 0.006 (max. = ±0.149). The final Fourier difference map had maximum and minimum values of +1.51 and −1.14 e Å^{-3} respectively. 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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