Reactions of the Cyclic Platinum(II) Thiolate Complex $[\mathrm{Pt\{SCH_2C(O)CH_2\}(PPh_3)_2}]$ with Electrophiles, and the Single-crystal Structure of $[\{\mathrm{Pt[SCH_2C(O)CH_2](PPh_3)_2{\cdot}HgBr_2}\}_2]$†

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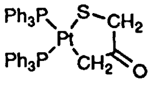
The cyclic thiolato complex $[\mathrm{Pt\{SCH_2C(O)CH_2\}(PPh_3)_2}]$ **1** reacted with alkyl halides RX (MeI, EtBr or $\mathrm{PhCH_2Cl}$) giving the thioether complexes $[\mathrm{Pt\{RSCH_2C(O)CH_2\}X(PPh_3)}]$ with the triphenylphosphine ligand *trans* to the thioether group. ^{31}P-{^{1}H} NMR spectroscopy revealed that the alkylation reactions proceed through a cationic thioether intermediate of the type $[\mathrm{Pt\{RSCH_2C(O)CH_2\}(PPh_3)_2}]^+\mathrm{X}^-$, the rate of formation of which is highly dependent on the reactivity of the alkyl halide. Reaction of **1** with dimethyl sulfate rapidly produced an analogous intermediate which is rather stable in the presence of an excess of dimethyl sulfate as a result of the low nucleophilicity of the methyl sulfate anion. Proton NMR spectroscopy of the complexes $[\mathrm{Pt\{RSCH_2C(O)CH_2\}X(PPh_3)}]$ is consistent with the presence of a rigid metallacycle in solution with the SMe group adopting an axial position. Complex **1** also forms sulfur-donor adducts with 'soft' metal centres such as Hg$^{\mathrm{II}}$ and Ag$^{\mathrm{I}}$. Adduct formation is readily monitored by the influence on the ^{1}H NMR shifts of the metallacyclic $\mathrm{CH_2}$ groups. A single-crystal X-ray diffraction study on the mercury(II) bromide adduct reveals the presence of a 1 : 1 dimeric complex $[\{\mathrm{Pt[SCH_2C(O)CH_2](PPh_3)_2{\cdot}HgBr_2}\}_2]$. The complex contains bridging thiolate ligands with a $\mathrm{BrHg(\mu\text{-}Br)_2HgBr}$ unit and distorted tetrahedrally co-ordinated mercury centres.

Metal thiolate complexes are well known to possess nucleophilic sulfur centres, and alkylation reactions of thiolato complexes have been used previously to synthesise new types of metal–thioether complexes.[1–3] In addition, the powerful ligand properties of metal thiolates have been employed in the synthesis of a range of thiolate-bridged homo- and hetero-bimetallic complexes.[2,4–7] Sulfido-bridged complexes, containing M–S–M groups, have been used in a similar manner.[8–10] In a recent paper[11] we reported the high-yield synthesis of the cyclic platinum(II) thiolate complex $[\mathrm{Pt\{SCH_2C(O)CH_2\}(PPh_3)_2}]$ **1**, together with the related dimeric complex **2**, formed by reaction of **1** with $[\mathrm{Rh_2(\mu\text{-}Cl)_2(CO)_4}]$. The current, continuing interest in the chemistry of metal thiolate complexes[2–5,12] led us to investigate the chemistry of complex **1** in greater detail, and in this paper we describe its reactions with alkyl halides and electrophilic metal complexes.



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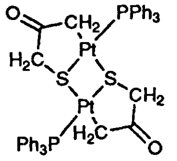

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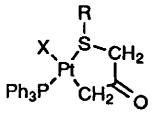
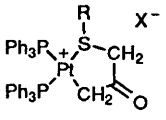


R	X
3a Me	I
3b Et	Br
3c $\mathrm{PhCH_2}$	Cl



R	X
4a Me	I
4b Et	Br
4c $\mathrm{PhCH_2}$	Cl
4d Me	$\mathrm{OSO_3Me}$

Results and Discussion

Treatment of the platinum(II) thiolate complex **1** with an excess of iodomethane in refluxing dichloromethane affords the thioether complex **3a** together with methyltriphenylphosphonium iodide, the cation of which was identified by ^{31}P-{^{1}H} NMR spectroscopy. In a similar fashion to the synthesis of **3a**, reaction of **1** with bromoethane in refluxing chloroform gave the analogous complex **3b**. The platinum complexes can be readily isolated in high yield by extraction with benzene, in which the by-product phosphonium salt is insoluble.

The ^{31}P-{^{1}H} NMR spectra of complexes **3a** and **3b** display a single resonance at *ca.* δ 17, showing coupling to ^{195}Pt of 3972 and 4048 Hz respectively, these values being indicative of a $\mathrm{PPh_3}$ ligand *trans* to the lower *trans*-influence thioether group, as opposed to the alkyl group. Comparison of the values of ^1J(PtP) with the corresponding value for the $\mathrm{PPh_3}$ ligand *trans* to the thiolate moiety in the starting complex **1** confirms the expected lower *trans* influence of the thioether group.[11,13] The ^{13}C-{^{1}H} NMR spectra for **3a** and **3b** showed the expected features, by comparison with **1**.[11] The methyl group was readily distinguished from the metallacyclic $\mathrm{CH_2}$ resonances by means of a distortionless enhancement of polarisation transfer (DEPT) ^{13}C NMR experiment. The $\mathrm{PtCH_2}$ carbon displays the expected large coupling to ^{195}Pt (606.2, **3a**; 628 Hz, **3b**), compared to the

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

thiolate complex **1** (431.0 Hz). These values are consistent with the iodide ligand displaying the expected larger *trans* influence than bromide in platinum(II) complexes.[13] A small coupling to the *cis*-phosphine ligand [$^2J(PC)_{cis}$ 3.0 Hz, **3a**] is also consistent with the *cis* disposition of the PPh_3 and CH_2 moieties. It is well established that *cis* couplings in square-planar d^8 complexes are characteristically much smaller than the corresponding *trans* couplings. The SMe carbon of **3a** shows coupling to ^{31}P of 2.2 Hz, however the corresponding coupling for the $PtSCH_2$ group is significantly smaller, and cannot be resolved, even with the use of a resolution-enhancement technique. A relatively large coupling to ^{195}Pt of 14 Hz is also observed for the SMe group. We tentatively ascribe this to the metallacycle being rigid in solution on the NMR time-scale, with the SMe group in an axial position. Further evidence of this is obtained from the ^1H NMR spectrum, described hereafter. The remaining ^{13}C NMR spectroscopic features were as expected, by comparison with the parent thiolato complex **1**.[11]

The ^1H NMR spectrum of complex **3a** displays the expected multiplet due to the triphenylphosphine ligand, together with a doublet [$^4J(PH)$ 3.92 Hz] due to the methyl group, which also displays the expected ^{195}Pt satellites [$^3J(PtH)$ 33.69 Hz]. By comparison, the corresponding values of $^4J(P_{trans}\text{–Pt–S–C–H})$ and $^3J(\text{Pt–S–C–H})$ for **1** are 1.67 and 30.45 Hz.[11] The increased value of $^4J(PH)$ for **3a** is also consistent with the static structure with the SMe group in an axial environment.

All four methylene protons in the ^1H NMR spectrum of complex **3a** are inequivalent, as a result of the ring geometry. This is illustrated in Fig. 1, which shows the ^1H correlation spectroscopy (COSY) spectrum, together with the methylene and methyl region of the ^1H NMR spectrum, and the static puckered ring structure proposed. One of the methylene protons in **3a** appears at δ 2.84 as a well resolved doublet and clearly displays a large value of $^2J(PtH)$ (121.1 Hz). This proton is assigned to the axial $PtCH_a$ proton, and shows a strong cross-peak to a proton resonance at δ 2.06, thus identifying both inequivalent $PtCH_2$ protons H_a and H_b. It has been observed previously[14–16] that axial substituents on platinacycles show significantly larger ^{195}Pt couplings than do their equatorial counterparts, on account of their proximity to non-bonding electron density, in an axially disposed orbital on platinum, and thus H_b shows a smaller value of $J(PtH)$ than does H_a. The $PtSCH_2$ protons H_c and H_d similarly show cross-peaks to each other. Individual assignment of these protons was initially difficult in $CDCl_3$, due to overlap of one of the resonances with the methyl resonance. However, it is noteworthy that there is a marked chemical shift difference for both the $PtCH_2$ protons and the $PtSCH_2$ protons on moving from $CDCl_3$ to C_6D_6, Table 1, with the $PtCH_2$ protons becoming more deshielded and the $PtSCH_2$ protons more shielded. In C_6D_6 however, the resonance due to H_b is largely obscured by the methyl resonance. Studies of rigid platinacyclic complexes have shown that protons in axial environments characteristically obey a Karplus-type relationship in their coupling to metal-bound phosphine ligands,[14,16] with no coupling of axial protons to *cis*-phosphines being observed. Similar relationships have also been observed for the *anti*-protons of η^3-allyl complexes.[17–19] Inspection of a molecular model of **3a** suggests that the P–Pt–C–H_a torsion angle is around 90°. Thus, it would appear likely that the doublet observed for proton H_a arises due to a geminal coupling of 9.3 Hz to proton H_b. This lies in the range of 6–18 Hz typically observed for geminal couplings in organic molecules.[20] Protons H_c and H_d clearly form a geminal pair, when observed in C_6D_6, with a $^2J(HH)$ coupling of 13.1 Hz, and with H_c showing the larger coupling to ^{195}Pt (43 Hz) due to the axial environment of this proton.

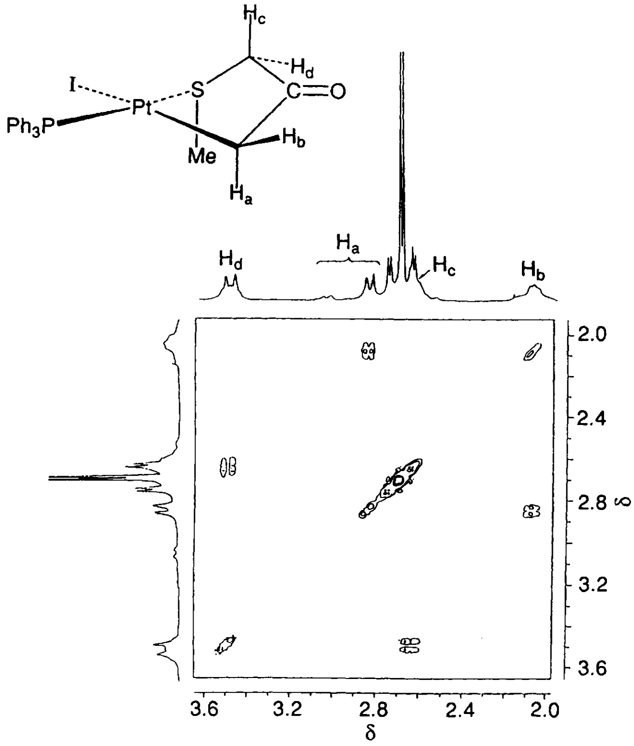


Fig. 1 ^1H COSY NMR spectrum at 300 MHz (excluding PPh_3 resonances) of $[\overline{Pt\{MeSCH_2C(O)}CH_2\}I(PPh_3)]$ **3a** showing the conformation of the metallacycle

Table 1 Comparison of ^1H NMR data for $PtCH_2$ and $PtSCH_2$ protons, in $CDCl_3$ and C_6D_6, for the complex $[\overline{Pt\{MeSCH_2C(O)}CH_2\}I(PPh_3)]$ **3a**

	δ		Coupling constant/Hz[a]	
Proton	$CDCl_3$	C_6D_6	$^2J(HH)$	$J(PtH)$
H_a	2.84	2.92	9.33	121.1
H_b	2.06 (vbr)	*ca.* 2.5 (vbr)[b]	[c]	*ca.* 46
H_c	*ca.* 2.6[b]	2.05	13.1	*ca.* 43
H_d	3.49	2.77	13.3	*ca.* 13
Me[d]	2.70	2.42	—	33.7

[a] Values for SMe, H_a, H_b from $CDCl_3$ solution; H_c, H_d from C_6D_6 solution. [b] Obscured in part by SMe resonance. [c] Not resolved. [d] $J(PH)$ 3.92 Hz; values for other protons not resolved.

The ^1H NMR spectroscopic properties of the thioether metallacycle contrast markedly with the parent thiolato complex **1** in which both $PtCH_2$ protons are equivalent, due to a planar or rapidly inverting metallacycle. Accordingly, we have investigated the variable-temperature NMR behaviour of **3a** in C_6D_6. On warming the solution all four methylene resonances broaden and begin to coalesce at approximately 345 K, but sharpening of the resonances in the rapidly inverting state could not be achieved. The methyl resonance remained sharp between 300 and 345 K. Two inversion processes are possible for the complex: inversion of the thioether and of the metallacycle itself. Inversion of the metallacycle alone maintains the inequivalence of the four methylene protons, and hence thioether inversion, or a combination of this process and metallacycle inversion, has to be invoked to account for the fluxionality of **3a**. Due to coincidental overlapping of broadened resonances at elevated temperatures, the clear identification of a coalescence temperature for the pairs of protons does not appear to be straightforward. The energy barriers to inversion of metal–thioether complexes have been extensively studied, and a number of reviews have appeared.[1,21]

In an attempt to determine the mechanism of formation of complexes **3**, the reaction between **1** and an excess of iodomethane has been monitored by ^{31}P-{^1H} NMR spectroscopy. Immediately after addition of MeI the spectrum revealed quantitative conversion into the cationic alkylated thioether species **4a**. Intermediate **4a** showed an AB doublet of doublets at δ 17.1 and 16.3, with couplings to ^{195}Pt of 2402 and 3777 Hz respectively for PPh_3 ligands *trans* to CH_2 and SMe groups. The larger coupling constant for the PPh_3 ligand *trans* to sulfur is consistent with S-methylation, by comparison with the corresponding values for **1** and **3a**.[11] The coupling constant for the PPh_3 ligand *trans* to CH_2 remains as expected, largely unchanged upon alkylation. Upon standing, the intermediate **4a** slowly transforms over *ca.* 1 h at room temperature into the final thioether product **3a** plus methyltriphenylphosphonium iodide. Complex **4a** has been partly characterised, as described later. As expected due to the lower reactivity of bromoethane towards nucleophiles, the reaction with **1** proceeded much more slowly, generating the intermediate **4b** over *ca.* 24 h at room temperature.

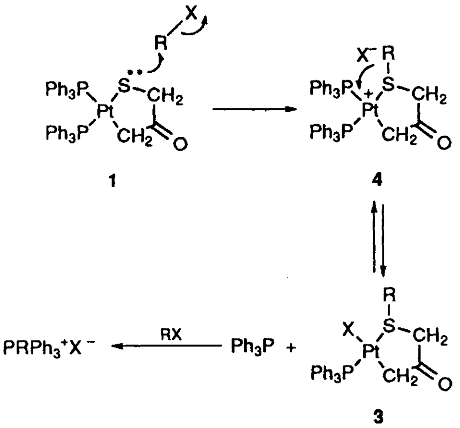
Reactions of complex **1** with alkylating agents which generate poorly nucleophilic anions (compared to iodide), *viz.* benzyl chloride and dimethyl sulfate, were also investigated by ^{31}P-{^{1}H} NMR spectroscopy. With an excess of dimethyl sulfate, complex **1** rapidly and quantitatively generated the cationic thioether complex **4d** the ^{31}P-{^{1}H} NMR spectroscopic properties of which were almost identical to those of the iodide analogue **4a**. Upon standing, **4d** did not rapidly convert into an analogous neutral thioether complex to **3**, but instead decomposed slowly over several days in the NMR tube to a mixture of unidentified products. In a separate experiment, complex **4d** was generated, and isolated from an excess of dimethyl sulfate by trituration with diethyl ether. Subsequent treatment of **4d** with a solution of NBu^n_4I in $CDCl_3$, or separately with iodomethane, did not result in a reaction. Instead, addition of both iodide and iodomethane appears to be necessary for conversion into the observed final product.

In a separate experiment, a mixture of complex **3a** plus $[PMePh_3]I$ was generated from **1** and iodomethane, and separated from the excess of iodomethane by evaporation *in vacuo*. Complex **3a** was then treated with an excess of PPh_3, and ^{31}P-{^{1}H} NMR spectroscopy showed complete conversion into the cationic bis(phosphine) thioether complex **4a** (plus excess of PPh_3 and $PMePh_3^+$) thereby demonstrating the interconvertibility of **3a** and **4a**. The SMe group remains co-ordinated to platinum in the presence of an excess of PPh_3, as evidenced by the presence of the expected doublet, with additional satellites due to ^{195}Pt coupling, observed in the ^{1}H NMR spectrum of the reaction mixture. These results suggest that quaternisation (by MeI) of free PPh_3, generated by nucleophilic attack of I^- at the cationic platinum centre, is an important feature of the proposed mechanism of formation of complexes **3**, depicted in Scheme 1.

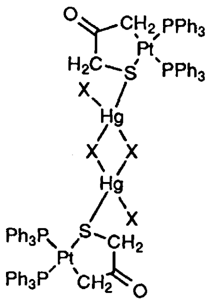
Reaction of complex **1** with benzyl chloride proceeded over the course of *ca.* 24 h at room temperature to generate intermediate **4c**, which showed the characteristic values of ^1J(PtP) for PPh_3 ligands *trans* to SCH_2Ph and CH_2 of 3787 and 2393 Hz respectively. Interestingly, whereas the satellites formed by ^{195}Pt coupling appeared normal, the central resonance for this complex was a single, sharp line. Upon recrystallisation of the complex from dichloromethane–light petroleum, a pale yellow solid was isolated, the ^{31}P-{^{1}H} and ^{13}C-{^{1}H} NMR spectroscopic properties of which were consistent with the benzyl thioether complex **3c**, by comparison with those for **3a** and **3b**. Further characterisation has not been carried out on this complex.

Reactions of complex **1** with various soft, late transition-metal complexes have also been investigated, in order to synthesise thiolate-bridged heterobimetallic complexes. Previously, we reported an initial attempt at the synthesis of such a complex by reaction of **1** with $[Rh_2(\mu-Cl)_2(CO)_4]$ which led to the isolation of the dimeric thiolate-bridged complex **2**.[11] We have subsequently investigated the reactions of **1** with other soft metal centres. Proton NMR spectroscopy of the CH_2 protons provides a convenient method for establishing whether any interaction occurs on addition of solid metal salts to a $CDCl_3$ solution of **1**. The chemical shifts and coupling constants for the $PtSCH_2$ and $PtCH_2$ protons are summarised in Table 2. Complex formation between the thioether group and the halides of mercury(II) is clearly demonstrated by the deshielding of the $PtSCH_2$ protons on co-ordination, with a successive increase being observed on going from HgI_2 to the more electron-withdrawing $HgBr_2$ and $HgCl_2$. The fact that the proton resonances remain little changed, except for these chemical shift changes, indicates that simple co-ordination, as opposed to phosphine-ligand transfer, is occurring. Elemental analysis and energy-dispersive X-ray analysis confirmed the stoichiometry of **5a** as a 1 : 1 adduct between **1** and HgI_2.

In order unambiguously to determine the nature of the mercury adducts, we have carried out a single-crystal X-ray diffraction study on the $HgBr_2$ adduct **5b**, crystals being obtained from a $CDCl_3$ solution on standing. The co-ordination geometry about platinum and sulfur is shown in Fig. 2, together with the atom numbering scheme, whilst Fig. 3 clearly illustrates the dimeric nature of the complex. Selected intramolecular bond lengths and angles and fractional atomic coordinates are given in Tables 3 and 4 respectively. The complex consists of a bromide-bridged $BrHg(\mu-Br)_2HgBr$ unit, with each mercury being complexed by the thiolate sulfur of the platinacycle, the whole molecule being centrosymmetric. Such dimeric, tetrahedral, halide-bridged species are well known in mercury co-ordination chemistry.[1,22] The molecular parameters for the cyclic platinum(II) thiolate moiety are overall very similar to those of the thiolate-bridged dimeric complex **2**, which was structurally characterised previously.[11] Thus, the Pt(1)–S(1) distance in **5b** [2.366(4) Å] is very similar to those in **2** [average 2.374(3) Å]. The co-ordination about the mercury atoms is a distorted tetrahedron, with bond angles about Hg(1) being in the range 91.53(6)–130.6(1) Å, the largest bond angle, as expected, being Br(2)–Hg(1)–S(1), opened out as a result of



Scheme 1



	X
5a	I
5b	Br
5c	Cl

Table 2 Proton NMR spectroscopic data for metallacyclic CH_2 groups of complex **1** on addition of metal salts MX_n

				^3J(PH)/Hz				
Complex	MX_n	δ($PtCH_2$)	^2J(PtH)/Hz	*trans*	*cis*	δ($PtSCH_2$)	^3J(PtH)/Hz	^4J(PH)/Hz
1	—	2.49	62.5	8.36	5.75	3.05	30.5	1.7
5a	HgI_2	2.69	52.3	8.59	4.98	3.44	31.2	*
5b	$HgBr_2$	2.78	50.1	8.58	4.71	3.64	28.1	*
5c	$HgCl_2$	2.85	*ca.* 46	8.55	4.65	3.74	26.5	*
5d	$AgNO_3$	2.60	56.7	8.53	5.07	3.07	28.4	*
	$PbCl_2$	2.49	62.7	8.41	5.72	3.05	31.0	*
	$CdCl_2$	2.50	61.6	*	*	3.05	32.5	*
	$PdCl_2$	2.50	62.7	8.66	5.61	3.06	31.7	2.5

* Not resolved.

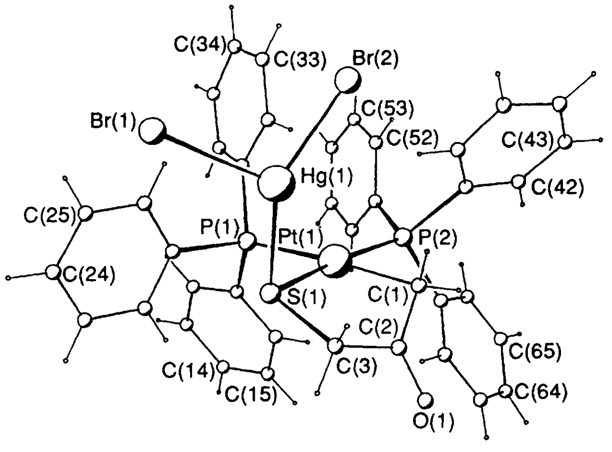


Fig. 2 Molecular structure of the unique half of the dimer $[\{\overline{\mathrm{Pt[SCH_2C(O)C}}\mathrm{H_2](PPh_3)_2 \cdot HgBr_2}\}_2]$ **5b** showing the atom numbering scheme and geometries about S and Pt

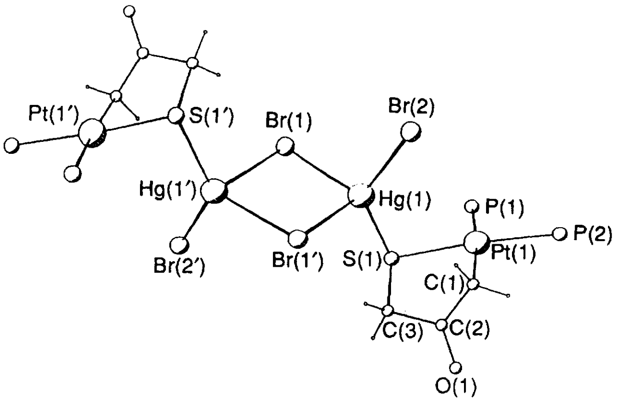


Fig. 3 The centrosymmetric core of the dimer **5b** with phenyl rings omitted for clarity

Table 3 Selected bond lengths (Å) and angles (°) for the dimer $[\{\overline{\mathrm{Pt[SCH_2C(O)C}}\mathrm{H_2](PPh_3)_2 \cdot HgBr_2}\}_2]$ **5b**

Pt(1)–C(1)	2.20(2)	Pt(1)–P(2)	2.276(5)
Pt(1)–P(1)	2.319(4)	Pt(1)–S(1)	2.366(4)
Hg(1)–S(1)	2.463(5)	Hg(1)–Br(2)	2.517(2)
Hg(1)–Br(1)	2.691(2)	Hg(1)–Br(1′)	2.834(2)
S(1)–C(3)	1.85(2)	C(1)–C(2)	1.43(3)
C(2)–O(1)	1.20(2)	C(2)–C(3)	1.52(3)
C(1)–Pt(1)–P(2)	89.4(5)	C(1)–Pt(1)–P(1)	173.7(5)
P(2)–Pt(1)–P(1)	96.9(2)	C(1)–Pt(1)–S(1)	82.2(5)
P(2)–Pt(1)–S(1)	171.5(2)	P(1)–Pt(1)–S(1)	91.5(2)
S(1)–Hg(1)–Br(2)	130.68(12)	S(1)–Hg(1)–Br(1)	117.05(12)
Br(2)–Hg(1)–Br(1)	104.40(7)	C(3)–S(1)–Pt(1)	99.3(6)
C(3)–S(1)–Hg(1)	101.1(7)	Pt(1)–S(1)–Hg(1)	96.9(2)
C(2)–C(1)–Pt(1)	101.9(11)	O(1)–C(2)–C(1)	125(2)
O(1)–C(2)–C(3)	119(2)	C(1)–C(2)–C(3)	115(2)
C(2)–C(3)–S(1)	108.7(12)		

steric interactions between the bulky Br atoms and the platinacycle. The Hg–S bond distance of 2.436(5) Å is comparable to that in the chloride-bridged tetrahydrothiophene complex $[(HgCl_2 \cdot SC_4H_8)_2]$ [2.40(2) Å].[23] The bromide bridges of **5b** are asymmetric [Hg(1)–Br(1) 2.691(2), Hg(1)–Br(1′) 2.834(2) Å], and show the expected lengthening over the terminal Hg(1)–Br(2) bond [2.517(2) Å]. These values are comparable to those of previously structurally characterised Hg–Br compounds (mean 2.762 Å).[24] It is noteworthy that the mercury atoms adopt axial positions on the platinacycle, clearly shown in Fig. 2. This is analogous to the structures elucidated by NMR spectroscopy for the thioether complexes **3**. However, it would seem likely, based on the ^1H NMR spectroscopic properties of complexes **5**, that either the dimeric structure of the solid state does not persist in solution or the complex is fluxional. The presence of a static structure containing an axial S–Hg moiety can be clearly ruled out, since in such a structure all four metallacyclic CH_2 protons would be inequivalent, whereas the spectroscopic features of **5** are overall very similar to those of the starting thiolate complex **1**. The remaining structural features are as expected. The complex crystallises with a molecule of chloroform in the lattice, which has a tendency to be lost upon X-ray irradiation at room temperature.

The amount of deshielding of the $PtCH_2$ protons in the ^1H NMR spectra of complexes **5a**–**5c** when compared to **1** is less marked than for the $PtSCH_2$ protons, as expected. On going along the series **1**, **5a**, **5b**, **5c** there is a regular decrease in the value of ^2J(PtH) for the $PtCH_2$ protons, from 62.5 Hz for **1** to *ca.* 46 Hz for the $HgCl_2$ adduct. A similar regular decrease in the value of ^3J(PtH) is observed for the $PtSCH_2$ protons in the series **5a**–**5c**. There is presumably a lengthening of the Pt–P bond closest to the bulky HgX_2 group (and hence *trans* to the $PtCH_2$ group), with the strongest interaction occurring between **1** and $HgCl_2$. This can be readily observed in the ^{31}P-{^1H} and ^{13}C-{^1H} NMR spectra of complex **5a**, for which the spectroscopic properties are again quite similar to those of **1**, except for changes in chemical shifts and coupling constants. Thus, for the PPh_3 ligand *trans* to CH_2, the value of ^1J(PtP) for **5a** (2358 Hz) is reduced from that in **1** (2434 Hz) due to the *cis* bond-lengthening effect of the Pt–P bond effected by the bulky HgI_2 group. The value of ^1J(PtP) for the PPh_3 ligand *trans* to S is significantly increased, from 3223 for **1** to 3582 Hz for **5a**, as a direct consequence of the lowered *trans* influence of the thiolate ligand on co-ordination to mercury. The ^{13}C-{^1H} NMR spectrum of **5a** shows a $PtCH_2$ resonance having a reduced value of ^1J(PtC) (417.4 Hz), when compared to that of **1** (431.0 Hz). Deshielding of the $PtSCH_2$ carbon from δ 25.9 for **1** to 32.7 for **5a** is also noteworthy. The IR spectrum of **5a** showed a carbonyl stretch at 1678 cm^{-1}, similar to the values of 1650 and

Table 4 Fractional atomic coordinates for $[\{Pt[SCH_2C(O)CH_2](PPh_3)_2\cdot HgBr_2\}_2]$ **5b**

Atom	*x*	*y*	*z*
Pt(1)	0.1848(1)	0.8248(1)	0.0418(1)
Hg(1)	0.4009(1)	0.9231(1)	−0.0022(1)
Br(1)	0.4486(2)	1.0092(1)	−0.1174(1)
Br(2)	0.4902(2)	0.8037(1)	−0.0156(1)
S(1)	0.2384(3)	0.9482(2)	0.0386(3)
P(1)	0.0807(3)	0.8354(3)	−0.0848(3)
P(2)	0.1470(3)	0.7058(3)	0.0637(3)
C(1)	0.2868(11)	0.8278(9)	0.1612(9)
C(2)	0.2595(13)	0.8961(11)	0.1924(11)
C(3)	0.2828(16)	0.9639(10)	0.1475(11)
O(1)	0.2197(10)	0.9029(7)	0.2489(7)
C(11)	−0.0569(12)	0.8314(10)	−0.0876(10)
C(12)	−0.1288(13)	0.8383(9)	−0.1574(11)
C(13)	−0.2339(15)	0.8395(11)	−0.1568(12)
C(14)	−0.2605(16)	0.8351(13)	−0.0836(14)
C(15)	−0.1890(15)	0.8268(13)	−0.0133(13)
C(16)	−0.0849(14)	0.8274(11)	−0.0142(12)
C(21)	0.0878(14)	0.9250(10)	−0.1327(10)
C(22)	0.0230(15)	0.9795(10)	−0.1192(11)
C(23)	0.0269(15)	1.0488(10)	−0.1529(12)
C(24)	0.0988(15)	1.0625(12)	−0.1982(12)
C(25)	0.1664(15)	1.0074(11)	−0.2061(13)
C(26)	0.1610(15)	0.9396(10)	−0.1752(11)
C(31)	0.1166(13)	0.7737(9)	−0.1586(10)
C(32)	0.2214(14)	0.7548(11)	−0.1454(11)
C(33)	0.2561(15)	0.7128(11)	−0.2012(11)
C(34)	0.1891(15)	0.6856(11)	−0.2689(11)
C(35)	0.0850(15)	0.7023(10)	−0.2790(11)
C(36)	0.0535(14)	0.7428(11)	−0.2237(11)
C(41)	0.2627(14)	0.6522(10)	0.1017(10)
C(42)	0.2606(13)	0.5862(10)	0.1414(10)
C(43)	0.3505(16)	0.5475(11)	0.1665(12)
C(44)	0.4378(15)	0.5721(11)	0.1497(12)
C(45)	0.4412(14)	0.6371(10)	0.1071(12)
C(46)	0.3529(14)	0.6769(11)	0.0853(11)
C(51)	0.0792(14)	0.6511(9)	−0.0190(10)
C(52)	0.1352(14)	0.6102(10)	−0.0645(11)
C(53)	0.0838(16)	0.5703(11)	−0.1295(10)
C(54)	−0.0188(17)	0.5694(11)	−0.1550(11)
C(55)	−0.0769(14)	0.6098(11)	−0.1084(11)
C(56)	−0.0257(14)	0.6498(10)	−0.0421(11)
C(61)	0.0723(15)	0.6953(9)	0.1401(10)
C(62)	0.0680(13)	0.7521(10)	0.1938(10)
C(63)	0.0227(14)	0.7413(10)	0.2585(10)
C(64)	−0.0263(14)	0.6767(12)	0.2659(11)
C(65)	−0.0250(14)	0.6189(10)	0.2125(11)
C(66)	0.0208(13)	0.6306(9)	0.1486(10)
Cl(1)	0.8529(6)	0.0170(4)	0.4476(4)
Cl(2)	0.7727(8)	0.1585(7)	0.3881(8)
Cl(3)	0.8390(13)	0.1347(7)	0.5553(7)
C(111)	0.7718(25)	0.1036(25)	0.4618(19)

1684 cm^{-1} observed for complexes **1** and **3a** respectively. These values confirm that there is no interaction between the carbonyl group and the mercury atom.

Negligible or no interaction was observed by ^1H NMR spectroscopy between complex **1** and $PbCl_2$, $CdCl_2$ or $PdCl_2$.

Experimental

General experimental procedures and instrumentation were as described previously.[11] The following reagents were used as supplied from commercial sources: mercury(II) chloride, bromide, red mercury(II) iodide, palladium(II) chloride, cadmium(II) chloride, and dimethyl sulfate (BDH); bromoethane, benzyl chloride (May & Baker Ltd); iodomethane (Merck); lead(II) chloride (Ajax Chemicals, Sydney); silver(I) nitrate (Scientific Supplies Ltd., Auckland). The light petroleum used was in the boiling point range 40–60 °C. The complex $[Pt\{SCH_2C(O)CH_2\}(PPh_3)_2]$ was prepared as described previously.[11] Energy-dispersive X-ray analysis was carried out on a Hitachi S4000 scanning electron microscope. NMR spectra were recorded in $CDCl_3$ unless otherwise specified, using references as described previously.[11]

Synthesis of $[Pt\{MeSCH_2C(O)CH_2\}I(PPh_3)]$ **3a**.—A solution of complex **1**·H_2O (0.300 g, 0.364 mmol) in dichloromethane (20 cm^3) with iodomethane (1 cm^3, large excess) was refluxed for 40 min. The pale yellow solution was evaporated to dryness under reduced pressure to afford a yellow oil which was shown to contain **3a** plus the $PMePh_3{}^+$ ion by ^{31}P-$\{^1H\}$ NMR spectroscopy. The product was extracted with benzene (30 cm^3) and filtered to remove the phosphonium salt. The filtrate was evaporated to dryness under reduced pressure, redissolved in dichloromethane (3 cm^3) and light petroleum (*ca.* 60 cm^3) added to precipitate the product as a pale yellow solid which was filtered off and dried *in vacuo*. Yield 0.219 g (89%) (Found: C, 37.95; H, 3.05. $C_{22}H_{22}IOPPtS$ requires C, 38.45; H, 3.25%), m.p. 195–197 °C; ν(C=O) at 1684 cm^{-1}. NMR: ^{31}P-$\{^1H\}$, δ 17.0 [s, ^1J(PtP) 3972]; ^{13}C-$\{^1H\}$, δ 205.6 [d, C=O, ^3J(PC) 6.5, ^2J(PtC) not resolved], 135.5–127.6 (m, Ph), 37.8 [d, $PtCH_2$, $^2J(PC)_{cis}$ 3.0, ^1J(PtC) 606.2], 36.7 [s, $PtSCH_2$, ^3J(PC) and ^2J(PtC) not resolved], and 23.2 [d, PtSMe, ^3J(PC) 2.2, ^2J(PtC) *ca.* 14 Hz]; for ^1H see Table 1. The ^1H NMR spectrum also showed the expected resonances due to the PPh_3 ligand.

Synthesis of $[Pt\{EtSCH_2C(O)CH_2\}Br(PPh_3)]$ **3b**.—A solution of complex **1**·H_2O (0.060 g, 0.073 mmol) in chloroform (10 cm^3) with bromoethane (1 cm^3, large excess) was refluxed for 24 h. Evaporation to dryness under reduced pressure gave a yellowish oil which was shown to contain product **3b** plus the ethyltriphenylphosphonium ion by ^{31}P-$\{^1H\}$ NMR spectroscopy. The product was extracted with benzene (10 cm^3) and filtered. The filtrate was evaporated to dryness under reduced pressure, redissolved in dichloromethane (2 cm^3) and light petroleum (*ca.* 60 cm^3) added to precipitate the product as pale yellow microcrystals which were filtered off and dried *in vacuo*. Yield 0.038 g (79%), m.p. 152–154 °C (Found: C, 42.65; H, 3.45; Br, 12.15. $C_{23}H_{24}BrOPPtS$ requires C, 42.20; H, 3.70; Br, 12.20%); ν(C=O) at 1684 cm^{-1}. NMR: ^{31}P-$\{^1H\}$, δ 17.2 [s, ^1J(PtP) 4048]; ^{13}C-$\{^1H\}$, δ 207.0 [d, C=O, ^3J(PC) 5.5, ^2J(PtC) not discernible], 134.9–128.2 (m, Ph), 34.3 [d, SCH_2, ^3J(PC) 2.0, ^2J(PtC) not resolved, *ca.* 14], 33.0 [d, SCH_2, ^3J(PC) 2.2, ^2J(PC) not resolved, *ca.* 14], 32.5 [d, $PtCH_2$, ^2J(PC) *cis* 4.2, ^1J(PtC) 628], and 13.8 [d, $PtSCH_3$, ^4J(PC) 3.2, ^3J(PtC) *ca.* 33 Hz].

NMR Study of Alkylation Reactions of Complex **1**.—*General procedure.* Complex **1**·H_2O (*ca.* 40 mg) was dissolved in $CDCl_3$ in a 5 mm NMR tube. An excess of the alkylating agent (about four drops) was added, and the progress of the reaction was followed by ^{31}P-$\{^1H\}$ NMR spectroscopy.

(*a*) *With iodomethane.* Upon addition of iodomethane and acquisition of the spectrum (*ca.* 3 min) there was quantitative conversion of **1** into the thioether complex **4a**. ^{31}P-$\{^1H\}$ NMR: AB spin system, δ 17.1 [^1J(PtP) 2402] and 16.3 [^1J(PtP) 3777, ^2J(PP) 19 Hz]. Over *ca.* 1 h, complex **4a** smoothly transformed into product **3a** plus $PMePh_3{}^+I^-$.

(*b*) *With bromoethane.* Reaction between complex **1** and an excess of EtBr required *ca.* 24 h at room temperature to proceed to completion to the thioether intermediate **4b**, as monitored by ^{31}P-$\{^1H\}$ NMR spectroscopy: **4b**, AB spin system, δ 17.4 [$^1J(PtP)_{trans\ CH_2}$ 2390, ^2J(PP) 17] and 16.2 [$^1J(PtP)_{trans\ S}$ 3757 Hz].

(*c*) *With benzyl chloride*. The ^{31}P-{^{1}H} NMR spectrum showed slow conversion (*ca*. 24 h at room temperature) to intermediate **4c**: AB spin system, δ 16.9 [s, $^1J(\mathrm{PtP})_{trans\ \mathrm{SCH_2Ph}}$ 3787, ^2J(PP) 17 and $^1J(\mathrm{PtP})_{trans\ \mathrm{CH_2}}$ 2393 Hz]. Upon recrystallisation of the product from dichloromethane–light petroleum a pale yellow solid was isolated in high yield, and NMR spectroscopy showed this complex to be the thioether complex **3c**: ^{31}P-{^{1}H}, δ 17.0 [s, ^1J(PtP) 4099]; ^{13}C-{^{1}H}, δ 206.6 [d, C=O, ^3J(PC) 5.7, ^2J(PtC) *ca*. 15.3], 134.9–127.9 (m, Ph), 41.2 (s, br, PtSCH$_2$), 33.1 (s, br, PtSCH$_2$), and 29.8 [d, PtCH$_2$, $^2J(\mathrm{PC})_{cis}$ 3.9, ^1J(PtC) 628.7 Hz].

(*d*) *With dimethyl sulfate*. The ^{31}P-{^{1}H} NMR spectrum showed quantitative and rapid (*ca*. 5 min) conversion into intermediate **4d**. Upon standing overnight the mixture comprised mainly **4d** plus a smaller number of unidentified products presumably formed by decomposition of **4d**. ^{31}P-{^{1}H} NMR of **4d**: AB spin system, δ 17.2 [$^1J(\mathrm{PtP})_{trans\ \mathrm{S}}$ 3691, ^2J(PP) 19.5] and 16.2 [$^1J(\mathrm{PtP})_{trans\ \mathrm{CH_2}}$ 2373 Hz].

Reaction of Complex **3a** *with* PPh$_3$.—Complex **3a** was prepared from **1** and MeI as above, and all volatiles including the excess of MeI were removed *in vacuo*. The residue was dissolved in CDCl$_3$ and an excess of PPh$_3$ added. ^{31}P-{^{1}H} NMR spectroscopy showed complete conversion of **3a** into **4a**, together with excess of PPh$_3$ and PMePh$_3{}^+$ by-product.

Reactions of Complex **1** *with Metal Salts*.—Typically, a 5 mm NMR tube was loaded with complex **1**·H$_2$O (*ca*. 0.025 g) and CDCl$_3$ (1 cm^3), and the ^{1}H NMR spectrum of the pale yellow solution was recorded. Solid metal salt (*ca*. 0.05 g, excess) was added, the tube was shaken vigorously for 5 min and the ^{1}H NMR spectrum was re-recorded. In cases where there was no immediate reaction the NMR tube was allowed to stand overnight and the spectrum re-recorded, whereupon no further change had occurred. Colour changes were observed in the following cases: HgI$_2$ (yellow), HgBr$_2$ (pale yellow), and AgNO$_3$ (pale yellow).

Synthesis of $[\{\overline{\mathrm{Pt[SCH_2C(O)C}}\mathrm{H_2](PPh_3)_2{\cdot}HgI_2\}_2]$ **5a**.—Complex **1**·H$_2$O (0.045 g, 0.055 mmol) was dissolved in chloroform (4 cm^3) and an excess of red mercury(II) iodide added; the mixture was shaken. The solution was allowed to settle, and the clear supernatant decanted from the excess of HgI$_2$. Light petroleum (4 cm^3) was added, and upon standing and slow evaporation yellow microcrystals of complex **5a** formed (0.041 g, 59%), m.p. 168–171 °C (Found: C, 37.05; H, 2.95. C$_{39}$H$_{34}$OP$_2$PtS·HgI$_2$ requires C, 37.10; H, 2.70%); ν(C=O) at 1678 cm^{-1}. Isolated crystals of **5a** had an identical ^{1}H NMR spectrum to that described in the NMR experiment detailed in Table 1. NMR: ^{31}P-{^{1}H}, AB spin system, δ 19.9 [PPh$_3$ *trans* to CH$_2$, ^1J(PtP) 2358, ^2J(PP) 19] and 17.3 [PPh$_3$ *trans* to S, ^1J(PtP) 3582]; ^{13}C-{^{1}H}, δ 203.9 [t, C=O, $^3J(\mathrm{PC})_{trans}$ + $^3J(\mathrm{PC})_{cis}$ 6.3, ^2J(PtC) not resolved], 134.5–127.8 (m, Ph), 47.9 [dd, PtCH$_2$, $^2J(\mathrm{PC})_{trans}$ 63.5, $^2J(\mathrm{PC})_{cis}$ 4.8, ^1J(PtC) 417.4 Hz], and 32.7 (s, br, PtSCH$_2$, coupling constants not resolved). Energy-dispersive X-ray analysis yielded, within experimental error, the expected Pt : Hg : P : I atomic ratio of 1 : 1 : 2 : 2.

Crystal-structure Determination for Complex **5b**.—Yellow crystals of complex **5b** were obtained from a CDCl$_3$ solution, prepared as above for the HgI$_2$ analogue. At room temperature under X-rays the crystals deteriorated (presumably by loss of solvent of crystallisation) but at lower temperatures were completely stable.

Crystal data. (C$_{39}$H$_{34}$Br$_2$HgOP$_2$PtS)$_2$·CDCl$_3$, M = 2336.4, monoclinic, space group $P2_1/n$, a = 13.409(4), b = 18.235(4), c = 17.017(3) Å, β = 102.0(2)°, U = 4070(2) Å^3 (from 25 reflections with $20 < 2\theta < 25°$), λ = 0.710 73 Å, D_c = 2.10 g cm^{-3} for Z = 4, F(000) = 2432, μ(Mo-Kα) = 95 cm^{-1}, T = −143 °C.

Data collection. Nicolet R3 automatic diffractometer, ω scans, on a crystal of dimensions 0.48 × 0.41 × 0.28 mm. A total of 5575 reflections were collected to 2θ$_{\max}$ 45°, of which 5271 were unique (R_{merge} = 0.0576 after absorption correction by the ψ-scan method, $T_{\max,\min}$ 0.399, 0.322), with 3644 observed [$I > 2\sigma(I)$].

Structure analysis and refinement. The structure was solved by automatic interpretation of the Patterson map (SHELXS 86)[25] and developed routinely. A CDCl$_3$ solvation molecule became evident and was included with site occupancy of one, although the tendency for crystals to deteriorate at room temperature suggests that partial loss of lattice solvent occurs readily. Full-matrix least-squares refinement (SHELXL 93)[26] was based on F^2 with all non-hydrogen atoms anisotropic and with hydrogen atoms in calculated positions with a common U_{iso} for each type. The thermal parameters for the CDCl$_3$ of solvation suggested high thermal motion, and non-positive-definite ellipsoids were obtained for some of the carbon atoms, no doubt because of the dominating effect of the heavy atoms in the structure. Refinement converged with R_1 = 0.0551, wR_2 = 0.1107 {$w = [\sigma^2(F_o{}^2) + (0.0593P)^2]^{-1}$ where $P = (F_o{}^2 + 2F_c{}^2)/3$} for $I > 2\sigma(I)$ data and goodness of fit 1.005. The maximum feature in a final difference map was +2.79 e Å^{-3}, adjacent to the solvent molecule, suggesting partial disorder.

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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