Co-ordination Chemistry of Electron-rich Poly(organosulphur) Compounds. Part 2.[1] Comparative Data on Reactions of Di-μ-chloro-bis[chloro(triethylphosphine)platinum(II)], and the Crystal and Molecular Structure of *cis*-μ-2,2-Bis(methylthio)ethene-1,1-dithiolato-*SS''* : *S'S'''*-bis[chloro(triethylphosphine)platinum(II)] †

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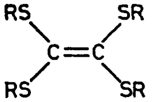
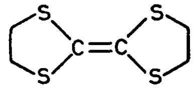
The tetrakis(alkylthio)-olefins $C_2(SR)_4$ (R = Me or Et) react with $[\{PtCl_2(PEt_3)\}_2]$ in hot xylene to yield *cis*- and *trans*-$[(Et_3P)ClPt\{S(RS)C{=}C(SR)S\}PtCl(PEt_3)]$; with $C_2(SEt)_4$ there is spectroscopic evidence for intermediates, *cis*- and *trans*-$[(Et_3P)Cl_2Pt\{RS(RS)C{=}C(SR)(SR)\}PtCl_2(PEt_3)]$ (R = Et). In contrast, the cyclic olefin $[\dot{:}CSCH_2CH_2S]_2$ forms the *SS''*-bonded *cis*-$[PtCl(PEt_3)(olefin)][PtCl_3(PEt_3)]$; similar behaviour is found with $C_2(NMe_2)_4$ and *o*-$C_6H_4(NMe_2)_2$, the corresponding cations being $[PtCl\{C_2(NMe_2)_4\text{-}NN''\}(PEt_3)]^+$ (6) and $[PtCl\{o\text{-}C_6H_4(NMe_2)_2\text{-}NN'\}(PEt_3)]^+$, respectively. The salt $[PtCl\{C_2(NMe_2)_4\text{-}NN''\}(PEt_3)][PtCl_3(PEt_3)]$ readily transforms into $[C_2(NMe_2)_4][Pt^{II}Cl_3(PEt_3)]_2$ on dissolution in dimethylformamide. A single-crystal *X*-ray analysis of the title complex shows that it has approximate C_2 symmetry with each platinum atom bound to a chelating ligand attached at one end by a thiolate sulphur atom and at the other by a thioether S atom; the average bond lengths are 2.25(1) and 2.33(1) Å, respectively. Interaction of Pt with the C=C π orbitals is unlikely because the distance of closest approach is *ca.* 3.1 Å. The average Pt–P and Pt–Cl distances are 2.26(1) and 2.34(1) Å, respectively. Bond lengths [1.34(4) (C=C) and 1.75(3) (C=S) Å] in the 2,1,1-dithiolate ligand indicate essentially localised double and single bonds.

In Part 1 we described reactions between a tetrakis(alkylthio)-olefin, (1)—(3), and a Group 6 metal(0) carbonyl, $[M(CO)_6]$ or $[M(CO)_3(NCMe)_3]$.[1] The products were mononuclear co-ordination compounds, in which the olefin behaved either as a two- or four-electron donor, by virtue of *S*- or *SS''*-ligation. We now report on the reactions of the same olefins with di-μ-chloro-bis[chloro(triethylphosphine)platinum(II)], (4) (see Scheme).

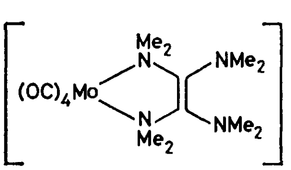


(1) R = Me, (2) R = Et



(3)

Complex (4) is a reagent known to be susceptible to bridge cleavage by a nucleophile. For example, with nitrogen analogues of (3), $[\dot{:}CN(R)CH_2CH_2NR]_2$ [abbreviated as $L^R{}_2$] the complexes *cis*- and *trans*-$[PtCl_2L^R(PEt_3)]$ (R = Me or Et) were obtained.[2] The open-chain electron-rich olefin $C_2(NMe_2)_4$ has not previously been examined in this context, but by contrast did not offer a route to Group 6 metal-carbene complexes [although $M\{C(NMe_2)_2\}$ derivatives are known [3]], and instead gave *NN''* complexes, as in (A).[4] Accordingly, we have extended the present study to include $C_2(NMe_2)_4$ and *o*-$C_6H_4(NMe_2)_2$; the latter was taken as a model source of *NN'*-chelate complexes. The results are summarised in the Scheme and in Tables 1 and 2. A communication described preliminary data on complex (5).[5]



(A)

RESULTS AND DISCUSSION

The olefin $C_2(NMe_2)_4$ readily reacted with the complex $[\{PtCl_2(PEt_3)\}_2]$ (4) to form the pale yellow 1 : 1 adduct (6). In order to assist in its structural elucidation by ^1H n.m.r. and i.r. spectroscopy, the reaction of complex (4) with *o*-$C_6H_4(NMe_2)_2$ to form adduct (7) was carried out. The essential similarity in the spectroscopic properties of adducts (6) and (7), especially their ^1H n.m.r. spectra [chemical shifts, $^4J(^{31}P{-}^1H)$, and $^3J(^{195}Pt{-}^1H)$ of the various $N{-}CH_3$ protons (Table 2)], provides the basis for the *NN''*-bonding assignment of $C_2(NMe_2)_4$ to Pt^{II} in the former. This evidence was taken to establish the cation $[PtCl\{C_2(NMe_2)_4\text{-}NN''\}(PEt_3)]^+$ for salt (6), and the anion $[PtCl_3(PEt_3)]^-$ is already known.[6]

Salt (6) was unstable in solution: attempted recrystallisation from dimethylformamide (dmf), CH_2Cl_2, or Me_2CO gave $[C_2(NMe_2)_4][Pt^{II}Cl_3(PEt_3)]_2$ (8). However, it was possible to record the ^1H n.m.r. spectrum of (6) in $(CD_3)_2CO$, although decomposition at *ca.* 20 °C was complete within *ca.* 30 min. The dication [4] and anion [6] of salt (8) are well known, and its structure was therefore deduced by i.r. and ^1H n.m.r. spectroscopy. The decomposition path (6) $\longrightarrow$ (8) was not further investigated. However, $[\{PtCl(H)(PEt_3)\}_2]$ is a possible co-product of (8).[7]

The reaction of (1) or (2) with (4) followed an unexpected course, the final products being the binuclear complexes $[(Et_3P)ClPt\{S(RS)C{=}C(SR)S\}PtCl(PEt_3)]$, (5) or (9). It is thus seen that S–R cleavage has accompanied sulphur co-ordination; S→M co-ordination evidently weakens the adjacent S–Et bond. The bridg-

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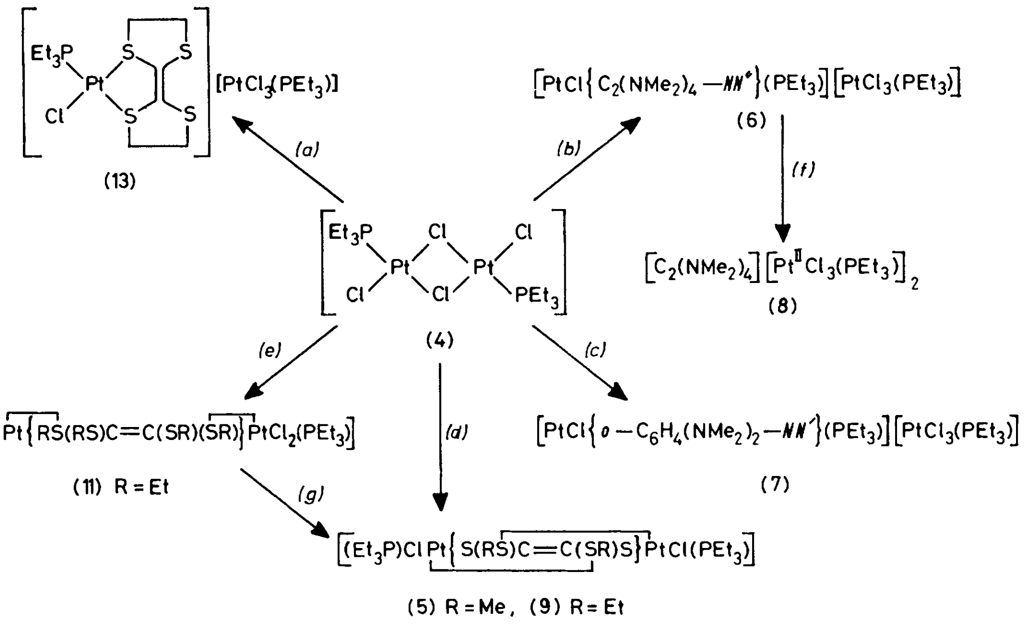
† No reprints available.



SCHEME Reactions of (*i*) $C_2(SR)_4$ (R = Me or Et), (*ii*) $[\dot{:}CSCH_2CH_2S]_2$, (*iii*) $C_2(NMe_2)_4$, or (*iv*) o-$C_6H_4(NMe_2)_2$ with $[\{PtCl_2(PEt_3)\}_2]$.

(*a*) $[\dot{:}CSCH_2CH_2S]_2$, PhMe, 100 °C, 30 min; (*b*) $C_2(NMe_2)_4$, C_6H_6, 25 °C, 12 h; (*c*) o-$C_6H_4(NMe_2)_2$, C_6H_6, 25° C, 3 h; (*d*) $C_2(SR)_4$ (R = Me or Et),xylene, 120 °C, 2 h; (*e*) $C_2(SEt)_4$, PhMe, −40 to 0 °C; (*f*) dmf–OEt_2, −30 °C, 12 h [*via* recrystallisation of (6)]; (*g*) xylene, 120 °C 2 h

ing ligand in complexes (5) and (9) is the quadridentate dianion (10), which may be regarded as intermediate between the potentially quadri-*S*-dentate olefin (1) or (2) and the as yet unknown bridging tetrathiolate $[C_2S_4]^{4-}$. It will be noted that complexes (5) and (9) arise from loss of 2RCl (R = Me or Et) from a possible 2 : 1 adduct be-

TABLE 1

Platinum(II) complexes derived from $C_2(NMe_2)_4$, $C_2(SR_4$ (R = Me or Et), or related donors, and their characterisation

	Complex	Yield (%)	M.p. (θ_c/°C)	Colour	Analysis (%) [a] C	H	N
(6)	$[PtCl\{C_2(NMe_2)_4\text{-}NN''\}(PEt_3)][PtCl_3(PEt_3)]$ [b]	90	91—150 (slow decomp.)	Pale yellow	27.4 (27.3)	5.7 (5.6)	5.7 (5.8)
(7)	$[PtCl\{o\text{-}C_6H_4(NMe_2)_2\text{-}NN'\}(PEt_3)][PtCl_3(PEt_3)]$	95	126—127	Pale yellow	28.6 (28.3)	5.1 (5.0)	3.2 (3.0)
(8)	$[C_2(NMe_2)_4][Pt^{II}Cl_3(PEt_3)]_2$	35	220 (decomp.)	Pale yellow	25.6 (25.4)	5.2 (5.2)	5.3 (5.4)
(5)	$[(Et_3P)ClPt\{S(MeS)C{=}C(SMe)S\}PtCl(PEt_3)]$ [c]	75	230—232 (decomp.)	Yellow	22.6 (22.1)	4.2 (4.3)	
(9)	$[(Et_3P)ClPt\{S(EtS)C{=}C(SEt)S\}PtCl(PEt_3)]$	75	240	Yellow	23.9 (23.8)	4.4 (4.4)	
(13)	$[PtCl\{[\dot{:}C(S)CH_2CH_2S]_2\text{-}SS''\}(PEt_3)][PtCl_3(PEt_3)]$	70		Yellow	22.3 (22.1)	4.1 (3.9)	

[a] Calculated values are given in parentheses. [b] Cl, 15.1 (14.7%). [c] Cl, 8.3 (8.2); P, 7.5 (7.1%).

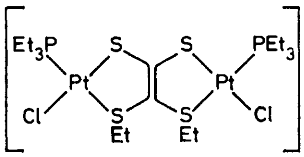
TABLE 2

Selected ^{1}H n.m.r. [a] and i.r. spectroscopic [b] data for some platinum(II) complexes (see Table 1)

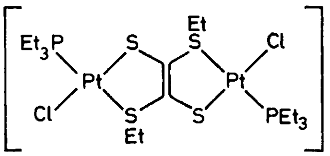
Complex	Solvent	N.m.r. N–CH_3	N.m.r. S–CH_3 (S–CH_2–)	I.r. ν(Pt–Cl)	I.r. Others
(6)	$(CD_3)_2CO$	6.86 (t of d),[c] 6.56 (t of d) [d] 6.99,[e] 7.02 [e]		338 (sh), 335s, 277s	540w,[f] 445w
(7)	$CDCl_3$	6.70 (t of d),[h] 6.20 (t of d)		336s, 276s	540w,[f] 440w [g]
(8)	$S(CD_3)_2O$	6.50, 6.80		335s, 277s	445w,[g] 1 665s
(5)	$CDCl_3$		7.30 (t of d) [k]	326s, 292m	
(9)	$CDCl_3$		6.5—7.2 (m)	325s, 290s	440w[j]
(13)	$CDCl_3$		6.6 (m)	348s, 346 (sh); 338m, 335 (sh)	445w [g]

[a] Values quoted in τ relative to $SiMe_4$ (τ 10): all the peaks are singlets unless otherwise stated (d = doublet, t = triplet, and m = multiplet). [b] Values quoted for $\nu_{max.}$ in cm^{-1}; (s = strong, m = medium, w = weak, and sh = shoulder). [c] N–CH_3 *trans* to PEt_3, ^4J[P–( )–H] 3.0 ,^3J[Pt–( )–H] 20 Hz. [d] N–CH_3 *cis* to PEt_3, ^4J[P–( )–H] <1.5, ^3J[Pt–( )–H] 46 Hz. [e] Non-co-ordinated N–CH_3 groups. [f] ν(Pt–N). [g] ν(Pt–P). [h] N–CH_3 *trans* to PEt_3, ^4J[P–( )–H] *ca.* 4, ^3J[Pt–( )–H] 22 Hz. [i] N–CH_3 *cis* to PEt_3, ^4J[P–( )–H] <1, ^3J[Pt–( )–H] 46 Hz. [j] $\nu(CN_2)_{asym}$. [k] ^4J[P–( )–H] 4, ^3J[Pt–( )–H] 24 Hz.

tween the olefin (1) or (2) and the platinum substrate (4). Unsuccessful attempts were made to prepare $[(Et_3P)_2Pt\{S(S)C{=}C(S)S\}Pt(PEt_3)_2]$ by further thermal elimination of 2RCl from (5) or (9) by reaction with $2PEt_3$.

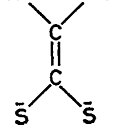


(9a)



(9b)

The assignment of stereochemistry to the binuclear complexes (5) and (9) is, in the final analysis, dependent on the *X*-ray data for (5a). However, the n.m.r. and i.r. results are consistent with the proposal (see Scheme), although ^{31}P n.m.r. spectra of the ethyl complex show the presence of *cis* (9a) and *trans* (9b) isomers.



(10)

The reaction between $C_2(SEt)_4$ (2) and complex (4) was followed by ^{31}P n.m.r. spectroscopy in order to find evidence for a possible intermediate to formation of (9). It was expected that S$\rightarrow$Pt co-ordination may precede S–Et cleavage. The olefin $C_2(SEt)_4$ was chosen in preference to the lower homologue $C_2(SMe)_4$ (1) for reasons of solubility. The spectra were recorded immediately on mixing the reactants in xylene [Figure 1(*a*)] and after heating to 100 °C for 2 h [Figure 1(*b*)]. There is no obvious reason why only one isomer of complexes (5) or (9) should be formed and indeed the final ^{31}P spectrum (*b*) shows two sets of triplets, centred on 127.2 [$^1J(^{195}Pt-^{31}P)$ 3 354.5] and 128.0 p.p.m. [$^1J(^{195}Pt-^{31}P)$ 3 281.2 Hz], the former assignable to the *cis* isomer (9a) and the latter, because of the similarity of chemical shift and coupling constant, to the *trans*-complex (9b).

The initial spectrum (*a*) shows four sets of triplets: two of these are due to the final products (9a) and (9b) (at 127.1 and 127.9 p.p.m. respectively), and the other two to their respective intermediates (11a) and (11b). These signals are centred at 126.7 [$^1J(^{195}Pt-^{31}P)$ 3 354.3] and 127.6 p.p.m. [$^1J(^{195}Pt-^{31}P)$ 3 281 Hz]; because of the almost identical ^1J values to those for (9a) and (9b), the former is taken as characteristic of a *cis* isomer (11a), and the latter of the *trans* complex (11b). Moreover, the close correspondence not only in ^1J values but also in chemical shifts between the final, (9), and intermediate, (11), products, suggests that the latter are also binuclear and have similar Pt–P environments. Initially, we considered that a monomeric species (12) might be implicated; this, however, should be an intermediate to both final products (9a) and (9b), and is therefore ruled out.

Hydrogen-1 n.m.r. spectra were also examined in a similar way: namely, by comparing the spectrum obtained (*i*) immediately after mixing the binuclear platinum sub-

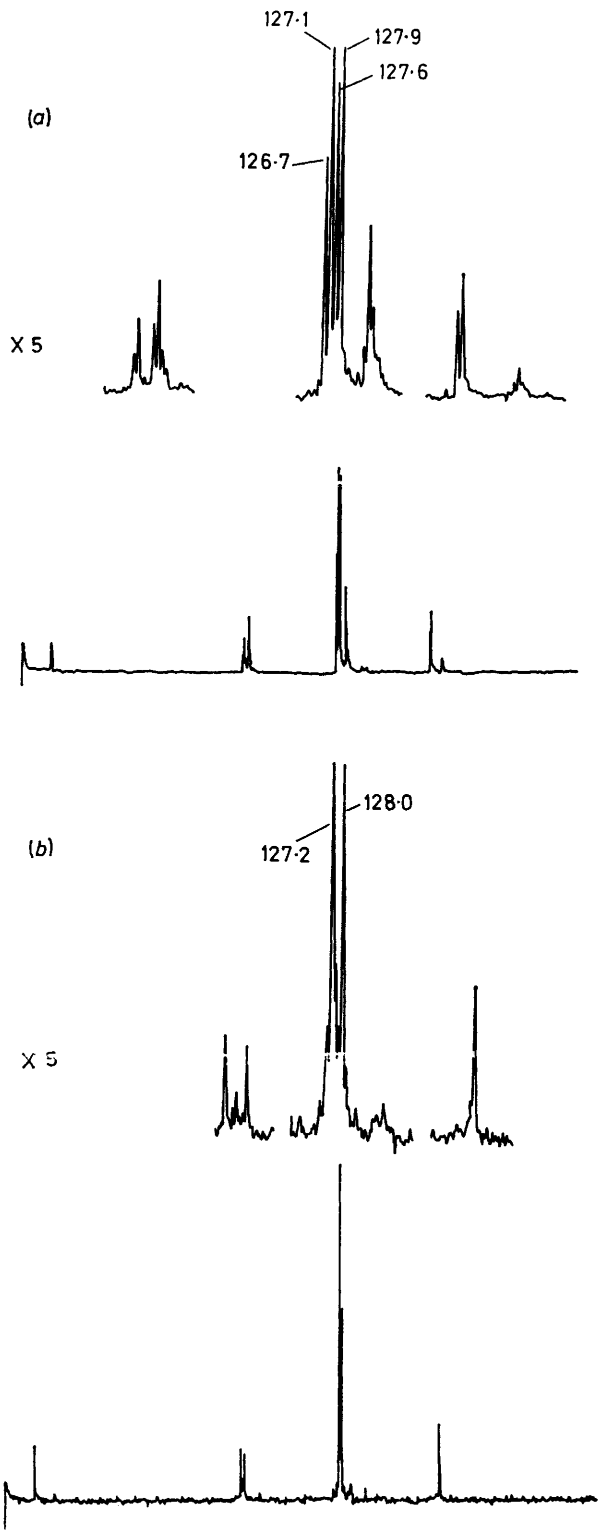
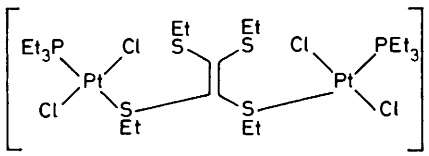
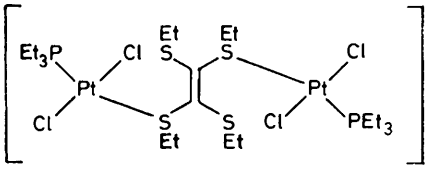


FIGURE 1 The ^{31}P n.m.r. spectra of an equimolar mixture of $C_2(SEt)_4$ and $[\{PtCl_2(PEt_3)\}_2]$ in xylene at 20 °C: (*a*) immediately after mixing, and (*b*) after heating at 100 °C for 2 h

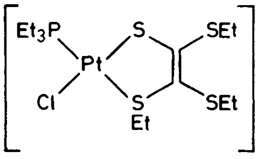
strate (4) and $C_2(SEt)_4$ (2) in xylene and (*ii*) after heating the mixture for 2 h at 100 °C; although there were some differences, the spectra were too complicated for useful assignments.



(11a)

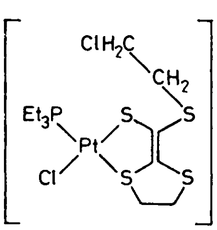


(11b)



(12)

As mentioned previously, there is a clear distinction between cyclic and acyclic tetra-aminoethylenes; only the former afford carbenemetal complexes, although both may form *NN''*-metal adducts. For the sulphur analogues such as $C_2(SR)_4$ and [:$\dot{C}SCH_2CH_2\dot{S}$]$_2$ (3) there is a difference in behaviour, but it is concerned with C–S rather than C=C fission. Thus olefin (3) leads only to an *S,S''*-Pt^{II} complex (13), and C–S cleavage to products such as (14)—(16) is presumably energetically unfavourable.



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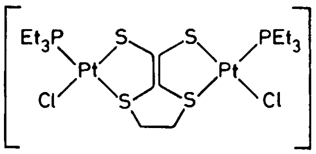

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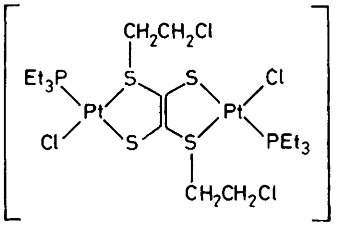

(16)

Spectroscopic Properties.—Hydrogen-1 n.m.r. and i.r. spectroscopic data are given in Table 2. Although rapid decomposition of the salt (6) occurs in solution, the ^{1}H n.m.r. spectrum was obtained in $(CD_3)_2CO$. Four signals are attributed to the olefin fragment: two of these showed ^4J[^{31}P–( )–^{1}H] and ^3J[^{195}Pt–( )–H] couplings and are assigned to the heteroatom donor substituents. The other two signals were singlets, separated by only τ 0.03 and are the CH_3 protons of the different non-co-ordinating N atoms. A similar spectrum was obtained from (7), the ^3J and ^4J values and chemical shifts of the CH_3 substituents of the co-ordinating N atoms being very similar to those for salt (6).

The values of the coupling constants ^3J and ^4J for the heteroatom donor CH_3 substituents in (5)—(7) are remarkably consistent, those *trans* to PEt_3 being in the range 20—24 (^3J) and 3—4 Hz (^4J), and those *trans* to Cl$^-$ being 46 (^3J) and <1—1.5 Hz (^4J). These distinctions are a clear reflection of the differing *trans* influence of the P and Cl atoms;[8] the precise nature of the heteroatom donor (N or S) seems to have little effect on the values of ^3J or ^4J.[9] The similarity of ^3J constants indicates a similar dihedral angle between the planes (*i*) Pt–N–C and N–C–H and (*ii*) Pt–S–C and S–C–H, and likewise the ^4J values are also considered to show this angular dependence.[10]

For complexes (9) and (11) the values of ^{31}P n.m.r. chemical shifts (*ca.* 127—128 p.p.m.) and coupling constants [^1J(^{195}Pt–^{31}P) *ca.* 3 320 Hz] are fairly typical of *trans*-Et_3P–Pt–X:[10,11] *e.g.* in the carbene complex *cis*-[Pt{$\dot{C}N(Me)CH_2CH_2\dot{N}Me$}$Cl_2(PEt_3)$], ^1J(^{195}Pt–^{31}P) 3 720 Hz and δ(PEt_3) 136.2 p.p.m.;[12] the value of ^1J(^{195}Pt–^{31}P) is strongly dependent on the *trans* influence of the group X,[11,13] the greater its magnitude the smaller is the *trans* influence. For example, in Et_3P–Pt^{II}–Cl (*trans*) ^1J(^{195}Pt–^{31}P) is 3 454 Hz, but in Et_3P–Pt^{II}–PBu^n_3 (*trans*) ^1J(^{195}Pt–^{31}P) is 2 270 Hz.[11] The coupling constant of 3 320 Hz in [$(Et_3P)ClPt${S(RS)C=C(SR)S}$PtCl(PEt_3)$] suggests that S$^-$ in (9) has a slightly greater *trans* influence than Cl$^-$, in the region expected for an anionic ligand.[8,11]

The complexes containing the [$PtCl_3(PEt_3)$]$^-$ anion, (6)—(8) and (13), had ν(Pt–Cl) (Table 2) in good agreement with the previously reported bands at 330 and 271 cm^{-1} in [NPr^n_4][$PtCl_3(PEt_3)$].[6] The ν(Pt–Cl) values for the cationic fragments of complexes (6), (7), and (13) are not easily distinguished from ν_{asym}[$PtCl_2$(*trans*)], but for the first two salts are believed to be at *ca.* 338 and 336 cm^{-1} respectively; complex (13) exhibits several bands in the 330—350 cm^{-1} region, which is expected to include ν(Pt–S). Thus, *cis*-[$PtCl_2(SEt_2)_2$] exhibits[14] ν($PtCl_2$) at 330 and 318 cm^{-1} and *cis*-[$PtCl_2${S(Ph)CH_2CH_2SPh-*SS''*}] has ν(PtS_2) at 350 and 329 cm^{-1}.[15] We suggest, therefore, that the band at 348 cm^{-1} of (13) arises from the Pt–S (*trans* to Cl) vibration, whereas ν(PtCl) is at 338 cm^{-1}.

Crystal Structure of cis-[(Et_3P)Cl-Pt{S(MeS)C=C(SMe)S}$PtCl(PEt_3)$] (5a).— The final molecular configuration of complex (5a) is illustrated as an ORTEP drawing in Figure 2,[16] which also shows some relevant bond lengths; further details are in Table 3. It can be seen that two geminal SMe groups of the

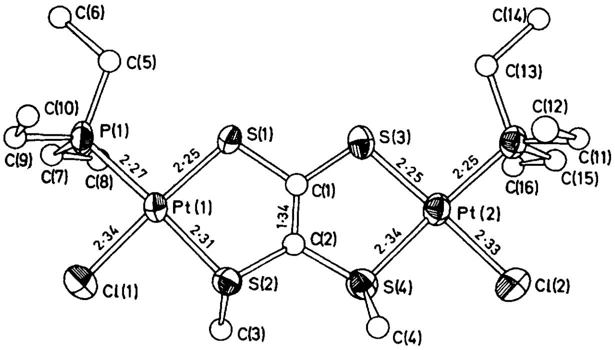

FIGURE 2 An ORTEP drawing of *cis*-[(Et$_3$P)ClPt{S(MeS)C=C(SMe)S}PtCl(PEt$_3$)] showing 50% thermal vibration ellipsoids for the anisotropic atoms and some pertinent bond lengths (Å)

tetrasubstituted ethene (1) have been demethylated to form a new ligand, 2,2-bis(methylthio)ethene-1,1-dithiolate, which bridges two platinum atoms. Thus each platinum atom is complexed by a chelating ligand attached at one end by a thiolate sulphur atom and at the other by a thioether sulphur atom. The averages of the two types of platinum–sulphur bond distances are 2.253 and 2.325 Å respectively.

TABLE 3

Bond lengths and angles for complex (5a). Estimated standard deviations are given in parentheses in units of the last significant digit

(*a*) Bonds (Å)

Pt(1)–S(1)	2.253(10)	S(4)–C(4)	1.85(5)
Pt(1)–S(2)	2.311(9)	P(1)–C(5)	1.84(4)
Pt(1)–P(1)	2.267(10)	P(1)–C(7)	1.86(4)
Pt(1)–Cl(1)	2.340(11)	P(1)–C(9)	1.80(4)
Pt(2)–S(3)	2.253(10)	P(2)–C(11)	1.89(5)
Pt(2)–S(4)	2.335(10)	P(2)–C(13)	1.83(3)
Pt(2)–P(2)	2.249(10)	P(2)–C(15)	1.81(4)
Pt(2)–Cl(2)	2.334(11)	C(5)–C(6)	1.57(5)
C(1)–C(2)	1.34(4)	C(7)–C(8)	1.51(7)
C(1)–S(1)	1.79(4)	C(9)–C(10)	1.54(6)
C(1)–S(3)	1.74(4)	C(11)–C(12)	1.53(6)
C(2)–S(2)	1.73(3)	C(13)–C(14)	1.57(5)
C(2)–S(4)	1.75(3)	C(15)–C(16)	1.52(7)
S(2)–C(3)	1.82(4)		

(*b*) Angles (°)

S(1)–Pt(1)–S(2)	89.6(3)	C(2)–S(2)–C(3)	102(2)
S(1)–Pt(1)–P(1)	93.1(4)	Pt(2)–S(3)–C(1)	103(1)
S(2)–Pt(1)–Cl(1)	87.5(4)	Pt(2)–S(4)–C(2)	104(1)
P(1)–Pt(1)–Cl(1)	89.9(4)	Pt(2)–S(4)–C(4)	106(2)
S(3)–Pt(2)–S(4)	88.0(4)	C(2)–S(4)–C(4)	104(2)
S(3)–Pt(2)–P(2)	94.9(4)	Pt(1)–P(1)–C(5)	114(1)
S(4)–Pt(2)–Cl(2)	88.8(4)	Pt(1)–P(1)–C(7)	108(1)
P(2)–Pt(2)–Cl(2)	88.4(4)	Pt(1)–P(1)–C(9)	115(1)
S(1)–C(1)–S(3)	112(2)	Pt(2)–P(2)–C(11)	112(1)
S(1)–C(1)–C(2)	122(3)	Pt(2)–P(2)–C(13)	116(1)
S(3)–C(1)–C(2)	126(3)	Pt(2)–P(2)–C(15)	113(1)
S(2)–C(2)–S(4)	120(2)	P(1)–C(5)–C(6)	112(3)
S(2)–C(2)–C(1)	122(2)	P(1)–C(7)–C(8)	111(3)
S(4)–C(2)–C(1)	118(2)	P(1)–C(9)–C(10)	115(3)
Pt(1)–S(1)–C(1)	103(1)	P(2)–C(11)–C(12)	109(3)
Pt(1)–S(2)–C(2)	103(1)	P(2)–C(12)–C(14)	116(2)
Pt(1)–S(2)–C(3)	108(1)	P(2)–C(15)–C(16)	111(3)

(*c*) Torsion angles (°)

Pt(1)–P(1)–C(5)–C(6)	176	Pt(2)–P(2)–C(11)–C(12)	−51
C(7)–P(1)–C(5)–C(6)	56	C(13)–P(2)–C(11)–C(12)	76
C(9)–P(1)–C(5)–C(6)	−56	C(15)–P(2)–C(11)–C(12)	−173
Pt(1)–P(1)–C(7)–C(8)	−54	Pt(2)–P(2)–C(13)–C(14)	−179
C(5)–P(1)–C(7)–C(8)	69	C(11)–P(2)–C(13)–C(14)	56
C(9)–P(1)–C(7)–C(8)	−177	C(15)–P(2)–C(13)–C(14)	−53
Pt(1)–P(1)–C(9)–C(10)	66	Pt(2)–P(2)–C(15)–C(16)	58
C(5)–P(1)–C(9)–C(10)	−62	C(11)–P(2)–C(15)–C(16)	179
C(7)–P(1)–C(9)–C(10)	−175	C(13)–P(2)–C(15)–C(16)	−70

The Pt–S (thioether) distance (2.325 Å) compares well with the value of 2.30 Å for the Pd–S distance in di-μ-bromo-bis[bromo(dimethyl sulphide)palladium(II)],[17] although a slightly larger ***trans*** influence of the phosphine might have been expected. The Pt–S(thiolate) bond distance (2.25 Å) is rather shorter than other comparable bonds. The Pt–S distance in bis(dimethyl-*o*-thiophenylarsine)platinum(II) is 2.308 Å,[18] and in bis(pentafluorophenylthiolato)bis(tri-n-butylphosphine)platinum(II) the Pt–S distance is 2.36 Å.[19] In the bis[*cis*-1,2-bis(trifluoromethyl)ethene-1,2-dithiolato]gold(III) anion the Au–S distances average 2.291 Å,[20] and in a dithioaromatic acid complex of Pt^{II} the Pt–S distance is 2.31 Å.[21]

Another molecule which contains a 2-thioalkylethene-1-thiolate chelating ligand is the adduct formed by addition of cyclohexadiene across two *cis*-sulphur atoms of the complex bis(*cis*-1,2-diphenylethene-1,2-dithiolato)-palladium,[22] where the Pd–S (thiolate) distance averages 2.28 Å and the Pd–S (thioether) distance averages 2.30 Å.

In complex (5a) there is the possibility of each platinum atom interacting ***via*** the sulphur atoms, both with the ethylene π bond and possibly with each other. A certain amount of π-bonding character in the Pt–S(thiolate) bonds would be consistent with the relatively short bond lengths. However, in the 1,1-dithiolate ligand the bond lengths of 1.34 Å for the C=C bond and 1.74 Å for the C–S bonds indicate essentially localised double and single bonds, respectively. Any direct interaction of the platinum atom with the ethylene π orbitals seems unlikely in view of the distance involved (3.1 Å).

The average Pt–P and Pt–Cl distances (2.26 and 2.335 Å) are within the ranges observed in other complexes,[23] and are consistent with the ***trans*** influence of sulphur ligands in square-planar Pt^{II} lengthening the bond ***trans*** to it by ***ca.*** 0.02 Å, as has been observed in the two isomers of dichlorodi-μ-thiocyanato-bis[(tri-n-propylphosphine)platinum(II)].[24]

Complex (5a) as a whole has approximate C_2 symmetry. The deviations of the atoms from the mean plane through the heavy atoms is given in Table 4. It can be seen that the two tetrahedral sulphur atoms S(2) and S(4) are twisted very slightly out of the plane of the molecule on the opposite side to the methyl group attached to

TABLE 4

Distances (Å) of atoms from the mean plane through the heavy atoms; the equation of the mean plane is defined as

$$0.5030X - 0.7010Y - 0.5056Z = -2.9543$$

where X, Y, and Z are the co-ordinates (Å) with respect to the Cartesian axis system ***a,b,c*** *

(*a*) Atoms defining the plane

Pt(1) 0.07, Pt(2) −0.05, S(1) −0.02, S(2) 0.17, S(3) −0.08, S(4) −0.26, P(1) −0.03, P(2) 0.11, Cl(1) −0.01, Cl(2) 0.09

(*b*) Other atoms

C(1) −0.07, C(2) −0.07, C(3) −1.37, C(4) 1.25, C(5) 0.15, C(6) −0.03, C(7) −1.69, C(8) −2.81, C(9) 1.16, C(10) 2.63, C(11) 1.71, C(12) 2.89, C(13) 0.06, C(14) 0.16, C(15) −1.18, C(16) −2.56

them. The triethylphosphine ligands are orientated so as to have one ethyl group lying in the plane of the molecule on the opposite side to the chlorine atom, with the angles P(1)–Pt(1)–S(1) and P(2)–Pt(2)–S(3) both *ca.* 5° greater than the other angles subtended at the platinum atoms. This conformation has been seen in the corresponding thiocyanate-bridged platinum(II) complex [24] and may be a consequence of steric interactions with the non-bonded lone pairs on the chlorine atom. The remaining ethyl groups are bent back above and below the phosphorus atom, possibly to minimise intermolecular contacts.

There are no intermolecular contacts significantly shorter than the sum of the relevant van der Waals radii.

EXPERIMENTAL

General Procedures.—All the reactions were performed under an atmosphere of dinitrogen using conventional Schlenk-tube techniques. Halogenated solvents were dried over P_4O_{10}, hydrocarbon solvents from sodium, and then distilled under nitrogen. Infrared spectra were recorded on a Perkin-Elmer 457 grating spectrophotometer using CsI plates, ^1H n.m.r. spectra using a Varian T60 spectrometer, and ^{31}P n.m.r. spectra on a JEOL FT100 spectrometer. The starting materials $[\{PtCl_2(PEt_3)\}_2]$ (4),[7] $[{:}C(SR)_2]_2$, (1) and (2), and $[{:}\overline{C(S)CH_2CH_2S}]_2$ (3) were obtained according to published methods.[1]

Reactions of Di-μ-chloro-bis[chloro(triethylphosphine)platinum(II)], $[\{PtCl_2(PEt_3)\}_2]$.—(*a*) *With tetrakis(dimethylamino)ethene.* To complex (4) (0.69 g, 0.90 mmol) dissolved in benzene (50 cm^3) was added freshly distilled tetrakis(dimethylamino)ethene (0.25 g, 1.28 mmol) and the mixture stirred (25 °C, 12 h). The pale yellow precipitate was removed by filtration, washed with OEt_2 (5 × 10 cm^3) and dried *in vacuo* to give *chloro[tetrakis(dimethylamino)ethene-NN″](triethylphosphine)platinum*(II) *trichloro(triethylphosphine)platinate*(II) (6) (0.69 g, 80%). Attempts to recrystallise complex (6) from dmf–acetone–OEt_2 afforded pale yellow crystals of *tetrakis(dimethylamino)ethane-*1,2*-diylium bis[trichloro(triethylphosphine)platinate*(II)] (8) (0.35 g, 35%).

(*b*) *With tetrakis(methylthio)ethene.* Complex (4) (0.38 g, 0.50 mmol) and tetrakis(methylthio)ethene (0.11 g, 0.5 mmol) were heated (120 °C, 20 min) in xylene (15 cm^3). The solution was allowed to cool (20 °C) and addition of C_6H_{14} and cooling (−25 °C, 24 h) afforded yellow crystals of μ-2,2-*bis(methylthio)ethene*-1,1-*dithiolato*-SS″:S′S‴-*bis*-[*chloro(triethylphosphine)platinum*(II)] (5) (0.24 g, 75%).

(*c*) *With tetrakis(ethylthio)ethene.* Using the procedure of (*b*), the bis(ethylthio)ethene analogue was similarly prepared from tetrakis(ethylthio)ethene and complex (4). Cooling (−25 °C) the xylene filtrate after addition of C_6H_{14} afforded yellow crystals of μ-2,2-*bis(ethylthio)ethene*-1,1-*dithiolato*-SS″:S′S‴-*bis[chloro(triethylphosphine)platinum*(II)].

(*d*) *With* o-*phenylenebis(dimethylamine).* To complex (4) (0.25 g, 0.32 mmol) in benzene (30 cm^3) was added *o*-phenylenebis(dimethylamine) (0.16 g, 1.0 mmol) and the mixture was stirred (25 °C, 3 h). The solution became pale yellow and eventually a pale yellow precipitate formed which was removed by filtration and washed with C_6H_{14} to give *chloro[*o*-phenylenebis(dimethylamine)*-NN′]*(triethylphosphine)platinum*(II) *trichloro(triethylphosphine)platinate*(II) (7) (0.29 g, 95%).

(*e*) *With bi*(1,3-*dithiacyclopent*-2-*ylidene*). Complex (4) (0.38 g, 0.50 mmol) and bi(1,3-dithiacyclopent-2-ylidene) (0.10 g, 0.50 mmol) were stirred together in toluene (10 cm^3, 100 °C, 30 min) to deposit a pale yelow solid. This was filtered off, washed with OEt_2 (2 × 10 cm^3), and recrystallised from CH_2Cl_2–OEt_2 (10 cm^3, 1 : 1) by flotation, affording pale yellow crystals of [*bi*(1,3-*dithiacyclopent*-2-*ylidene*)-SS″]*chloro(triethylphosphine)platinum*(II) *trichloro(triethylphosphine)platinate*(II) (13).

Phosphorus-31 *N.M.R. Experiments to follow the Reaction between Complex* (4) *and Tetrakis(ethylthio)ethene.*—Complex (4) (0.19 g, 0.25 mmol) and $C_2(SEt)_4$ (0.56 g, 0.25 mmol) were mixed in toluene (1 cm^3, previously cooled to −78 °C). The mixture was warmed (0 °C) and transferred to an 8-mm ^{31}P n.m.r. tube and the spectrum recorded (25 °C) [Figure 1(*a*)]. The mixture was then heated (100 °C, 2 h) and the spectrum re-recorded [Figure 1(*b*)].

Attempted Isolation of the Intermediate (11a).—Complex (4) (0.19 g, 0.25 mmol) was suspended in toluene (5 cm^3) and on addition of $C_2(SEt)_4$ (0.056 g, 0.25 mmol) the initially insoluble dimer quickly went into solution. The solvent was removed *in vacuo*, the residue stirred in OEt_2 (5 cm^3, 2 h), filtered, and dried *in vacuo*. The resulting yellow solid could not be isolated in a crystalline form, and it was not possible to obtain consistent analytical data for this solid.

Crystal Data for Complex (5a)—$C_{14}H_{36}Cl_2P_2Pt_2S_4$, $M = 879.8$, Monoclinic, $a = 7.552(2)$, $b = 30.193(6)$, $c = 12.018(2)$ Å, $\beta = 96.70(1)°$, $U = 2\ 721.6$ Å^3, $Z = 4$, $D_c = 2.15$ g cm^{-3}, Mo-K_α radiation, $\lambda = 0.709\ 26$ Å, μ(Mo-K_α) = 114.0 cm^{-1}, $F(000) = 1\ 664$. Systematic absences: *hkl* for $(h + k)$ odd and *h0l* for *l* odd, space group *Cc* (no. 9).

Complex (5a) crystallised from xylene–hexane solution as clusters of long, very thin, golden needles elongated along the *a* axis. A section of dimensions *ca.* 0.5 × 0.05 × 0.03 mm, cut from one of these, was used for the structure analysis. Preliminary cell dimensions were derived from precession and Weissenberg films and the systematic absences indicated the space group to be either *Cc* or *C*2/*c*, the former being later confirmed by a successful structure analysis. The crystal was then transferred to a Hilger and Watts Y290 four-circle diffractometer and accurate cell dimensions were derived by least-squares treatment of accurate 2θ values for 12 reflections. Intensity data for reflections with $\theta < 15°$ were collected using the ω—2θ step-scan technique with Mo-K_α radiation (graphite-crystal monochromator). Each reflection was measured in 72 half-second steps and background counts of 18 s each were measured at each end of the scan. Three standard reflections were remeasured after every 100 reflections and showed no significant variation. The data were corrected for Lorentz and polarisation effects, but not for absorption. Data were classified as significant if $I > 3\sigma(I)$ based on counting statistics. After averaging of equivalent reflections there were 1 061 significant reflections out of a total of 1 275, and only these reflections were used in the structure solution and refinement.

The Patterson map was interpreted as showing two platinum atoms in the asymmetric unit of space group *Cc*. The remaining non-hydrogen atoms were located by successive difference-Fourier maps. Full-matrix least-squares refinement of atom parameters with temperature factors anisotropic for platinum and isotropic for the remaining atoms converged at *R* 0.038. The real and imaginary components of anomalous dispersion were included for the Pt, Cl, P, and S atoms. The scattering factors and dispersion corrections were taken from ref. 25. A refinement of the equivalent enantiomeric structure converged at R 0.042, indicating that the correct enantiomer was that originally chosen. Reverting to the correct enantiomer, refinement was continued with anisotropic temperature factors for all the non-carbon atoms and with reflection data given empirical weightings defined as $w = 1/\{1 + [(F_o - 150)/186]^2\}$ derived from an analysis of $\langle w\Delta^2\rangle$ and $|F|$. In addition, the 041 reflection was given a weighting of zero since it may be affected by extinction. Convergence was reached at R 0.032 when the maximum shift of a parameter was less than 0.02 of the corresponding estimated standard deviation (e.s.d.) and the e.s.d. of an observation of unit weighting was 1.01. A final difference-Fourier synthesis was everywhere less than ± 0.6 e Å^{-3}. No attempt was made to locate the hydrogen atoms. Final atom parameters are shown in Table 5, and a list of final observed and calculated structure factors and thermal parameters has been deposited as Supplementary Publication No. SUP 22285 (7 pp.).*

TABLE 5

Final atomic co-ordinates ($\times 10^4$) with estimated standard deviations in parentheses

Atom	x	y	z
Pt(1)	0 000	0 566.0(4)	2 500
Pt(2)	0 591.8(2.2)	1 938.9(4)	−1 297.1(1.3)
S(1)	1 958(12)	1 088(3)	2 097(8)
S(2)	−1 765(12)	0 731(4)	0 850(7)
S(3)	2 212(13)	1 731(4)	0 311(9)
S(4)	−1 682(12)	1 477(3)	−0 819(9)
P(1)	1 629(15)	0 383(4)	4 140(9)
P(2)	2 674(13)	2 402(3)	−1 822(8)
Cl(1)	−2 234(14)	0 074(4)	2 902(11)
Cl(2)	−1 152(15)	2 097(4)	−2 983(9)
C(1)	0 896(48)	1 326(12)	0 831(31)
C(2)	−0 698(36)	1 187(9)	0 359(23)
C(3)	−0 383(44)	0 970(11)	1 212(28)
C(4)	−2 033(59)	1 053(14)	−1 930(38)
C(5)	3 852(45)	0 636(11)	4 339(28)
C(6)	4 874(57)	0 530(15)	5 522(36)
C(7)	0 427(53)	0 583(14)	5 308(33)
C(8)	−0 000(71)	1 069(18)	5 193(45)
C(9)	1 912(50)	−0 201(12)	4 379(32)
C(10)	3 023(53)	−0 438(14)	3 562(32)
C(11)	3 461(58)	2 226(15)	−3 193(37)
C(12)	3 998(60)	1 737(15)	−3 112(37)
C(13)	4 673(44)	2 467(11)	−0 821(27)
C(14)	6 114(49)	2 795(12)	−1 179(32)
C(15)	1 840(56)	2 957(13)	−2 115(35)
C(16)	1 092(61)	3 154(15)	−1 101(39)

Initial data reduction was carried out with local programs, and the solution and refinement of the structure was carried out with the '*X*-RAY '70' system.[26]

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1978, Index issue.