Co-ordination Chemistry of Sulphines. Part 3.[1] Oxidative Addition of the Carbon–Chlorine Bond of (*E*)-Chloro(arylthio)-sulphine, (*E*)-(RS)ClCSO, to Tetrakis(triphenylphosphine)platinum(0) and of a Carbon–Sulphur Bond in $[Pt^0(PPh_3)_2\{(RS)_2CSO\}]$ by an Intramolecular Process. *X*-Ray Crystal and Molecular Structure of *cis*-(*E*)-$[Pt^{II}(PhS)(PhSCSO)(PPh_3)_2]\cdot C_6H_6$ [†]

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The platinum–sulphine complexes $[Pt^0(PPh_3)_2\{(RS)_2CSO\}]$ (R = Ph or C_6H_4Me-*p*), in which the sulphines are η^2-CS co-ordinated, undergo in solution ($CDCl_3$) complete and intramolecular oxidative addition of a C–S bond to Pt^0 yielding an equilibrium mixture of the stereoisomers *cis*-(*E*)- and *cis*-(*Z*)-$[Pt^{II}(RS)(RSCSO)(PPh_3)_2]$. An *X*-ray crystal and molecular structure analysis of *cis*-(*E*)-$[Pt^{II}(PhS)(PhSCSO)(PPh_3)_2]\cdot C_6H_6$ revealed that in this stereoisomer the Pt and O atoms are situated *anti*, the (PPt)(S)C=S=O fragment is coplanar and perpendicular to the P_2Pt plane, and that the phenyl ring of the PhS–C=S=O fragment is folded under the Pt atom resulting in an *s-cis* conformation. Hydrogen-1 n.m.r. studies revealed that the *p*-MeC_6H_4S–C=S=O fragment has the same *s-cis* conformation in *cis*-(*E*)-$[Pt^{II}(p\text{-}MeC_6H_4S)(p\text{-}MeC_6H_4SCSO)(PPh_3)_2]$ in $CDCl_3$ as in *cis*-(*E*)-$[Pt^{II}(PhS)(PhSCSO)(PPh_3)_2].C_6H_6$ in the solid state and (*Z*)-(2,4,6-$Me_3C_6H_2$)(PhS)CSO in $CDCl_3$, while in *cis*-(*Z*)-$[Pt^{II}(p\text{-}MeC_6H_4S)(p\text{-}MeC_6H_4SCSO)(PPh_3)_2]$ it has a *gauche* conformation, the same as in (*E*)-(2,4,6-$Me_3C_6H_2$)-(PhS)CSO. An equimolar mixture of the two stereoisomers of $[Pt^0(PPh_3)_2\{(RS)(R'S)CSO\}]$ (R' = C_6H_4OMe-*p*; R = C_6H_4Me-*p*) in $CDCl_3$ is completely converted into an equimolar mixture of *cis*-(*E*)- and *cis*-(*Z*)-$[Pt^{II}(RS)(R'SCSO)(PPh_3)_2]$ and *cis*-(*E*)- and *cis*-(*Z*)-$[Pt^{II}(R'S)(RSCSO)(PPh_3)_2]$. These complexes have the same conformations as *cis*-(*E*)- and *cis*-(*Z*)-$[Pt^{II}(RS)(RSCSO)(PPh_3)_2]$. The mechanism of the intramolecular oxidative addition taking as example $[Pt^0(PPh_3)_2\{(RS)_2CSO\}]$ could be gliding movements of the $Pt^0(PPh_3)_2$ unit along two different S–C=S frames *via* two stereoisomeric intermediates $[Pt^0(PPh_3)_2\{(E)\text{-}RSC(SR)SO\}]$ and $[Pt^0(PPh_3)_2\{(Z)\text{-}RSC(SR)SO\}]$, in which the sulphines are η^3-SCS co-ordinated in a pseudo-allylic fashion. Sulphines containing a C–Cl and a C–S side bond, *e.g.* (*E*)-(RS)ClCSO (R = Ph, C_6H_4Me-*p*) gave a fast oxidative addition of the C–Cl bond to Pt^0 yielding the stereoisomers, *cis*-(*E*)-, *cis*-(*Z*)-, *trans*-(*E*)-, and *trans*-(*Z*)-$[Pt^{II}Cl(RSCSO)(PPh_3)_2]$. In the case where R = C_6H_4Me-*p*, ^1H n.m.r. evidence has revealed that the RS–C=S=O fragments in the *cis*-(*E*) and *trans*-(*E*) stereoisomers have a *s-cis* conformation, while in *cis*-(*Z*) and *trans*-(*Z*) a *gauche* conformation exists.

SULPHINES, XYC=S=O, have a bent planar structure [2-7] and are heterocumulenic systems,[2-7] related to sulphinylanilines (aryl–N=S=O) and diarylsulphurdi-imines (aryl–N=S=N–aryl), the chemistry of which is being studied in our laboratory.[8]

Recently, we reported the first metal–sulphine complexes, $[Pt^0(PPh_3)_2(XYCSO)]$ (X,Y = aryl, *S*-aryl, *S*-alkyl, or Cl), which were synthesized by reaction of stable sulphines with $[Pt^0(PPh_3)_4]$.[9] The sulphines in these compounds are η^2-CS co-ordinated, as established by an *X*-ray crystal-structure determination for one representative, *i.e.* $[Pt^0(PPh_3)_2$(fluorene-9-ylidenesulphine)].[1]

Furthermore, we reported the intramolecular rearrangements of the co-ordination stereoisomers $[Pt^0(PPh_3)_2\{(E)\text{-}(MeS)RCSO\}]$ [‡] and $[Pt^0(PPh_3)_2\{(Z)\text{-}(MeS)RCSO\}]$ (R = Ph or C_6H_4Me-*p*) [1,10] independently synthesized with retention of configuration from the respective (*E*) and (*Z*) sulphine stereoisomers of (MeS)RCSO.[9] When either $[Pt^0(PPh_3)_2\{(E)\text{-}(MeS)RCSO\}]$ or $[Pt^0(PPh_3)_2\{(Z)\text{-}(MeS)RCSO\}]$ was brought into solution an equilibrium mixture was obtained containing the oxidative-addition stereoisomers *cis*-(*E*)- and *cis*-(*Z*)-$[Pt^{II}(MeS)(RCSO)(PPh_3)_2]$, the co-ordination stereoisomer $[Pt^0(PPh_3)_2\{(E)\text{-}(MeS)RCSO\}]$, and only traces of the co-ordination stereoisomer $[Pt^0(PPh_3)_2\{(Z)\text{-}(MeS)RCSO\}]$. From this observation it was concluded that besides the oxidative addition of the C–S side bond in the co-ordination stereoisomers, a reductive coupling reaction had also occurred in the oxidative-addition stereoisomers. Moreover, the presence of the co-ordination stereoisomer $[Pt^0(PPh_3)_2\{(Z)\text{-}(MeS)RCSO\}]$ in only trace amounts indicates that the (*Z*) co-ordination stereoisomer is thermodynamically less stable than the (*E*) form and both of the oxidative-addition stereoisomers.

We describe herein the intramolecular oxidative addition of co-ordinated sulphines containing two C–S side bonds, (RS)(R'S)CSO (R, R' = Ph, C_6H_4Me-*p*, or C_6H_4OMe-*p*) to the $Pt^0(PPh_3)_2$ fragment and the oxidative addition of sulphines containing one C–S and one C–Cl side bond (*E*)-(RS)ClCSO (R = Ph or C_6H_4Me-*p*) to $[Pt^0(PPh_3)_4]$. Furthermore, an analysis is given of the configuration of the oxidative-addition products, *i.e.*

[†] *cis*-(*E*)-Phenylthio(phenylthiosulphinylmethyl)bis(triphenylphosphine)platinum(II)-benzene (1/1).

[‡] (*E*) and (*Z*) refer to the configuration of the sulphine C=S bond. If these are placed inside the molecular formula, this indicates that the sulphine has the (*E*) or (*Z*) configuration and is co-ordinated as such (*e.g.* η^2-CS). If these are placed before the molecular formula, this indicates that the PtXC=S=O entity as a whole has the (*E*) or (*Z*) configuration, with σ-C co-ordination.

cis-(*E*)- and *cis*-(*Z*)-$[Pt^{II}(RS)(RSCSO)(PPh_3)_2]$ (R,R′ = Ph, C_6H_4Me-*p*, or C_6H_4OMe-*p*) and *cis*-(*E*)-, *cis*-(*Z*)-, *trans*-(*E*)-, and *trans*-(*Z*)-$[Pt^{II}Cl(RSCSO)(PPh_3)_2]$ (R = Ph or C_6H_4Me-*p*) in both the solid state and solution ($CDCl_3$). As part of this study, the solid-state molecular structure of a representative oxidative-addition product, *cis*-(*E*)-$[Pt^{II}(PhS)(PhSCSO)(PPh_3)_2]\cdot C_6H_6$, was determined by single-crystal *X*-ray structure analysis.

EXPERIMENTAL

Infrared spectra were recorded on a Perkin-Elmer 283 spectrophotometer. Hydrogen-1 and ^{31}P-$\{^1H\}$ n.m.r. spectra were recorded on Varian-T60A, -HA100, or -XL100 spectrometers. Elemental analyses were carried out by the Analytical Section of the Institute for Organic Chemistry TNO, Utrecht. Molecular weights were determined with a Hewlett–Packard (model 320 B) vapour-pressure osmometer.

Preparation of the Compounds.—In most cases reactions were followed by ^{31}P-$\{^1H\}$ n.m.r. and the spectral parameters used for compound identification. The co-ordination compounds, $[Pt^0(PPh_3)_2\{(RS)(R'S)CSO\}]$ [9] (R = R′ = Ph or C_6H_4Me-*p*; R = C_6H_4Me-*p*, R′ = C_6H_4OMe-*p*, mixture of two stereoisomers in a *ca.* 1 : 1 mol ratio), and the sulphines $(RS)_2CSO$ [11] and (*E*)-(RS)ClCSO [11] (R = Ph or C_6H_4Me-*p*) were prepared according to literature procedures. All reactions except (*i*) were carried out under a N_2 atmosphere using Schlenk apparatus.

(*i*) *Conversion of* $[Pt^0(PPh_3)_2\{(RS)(R'S)CSO\}]$ (R = R′ = Ph or C_6H_4Me-*p*; R = C_6H_4Me-*p*, R′ = C_6H_4OMe-*p*, *mixture of the two stereoisomers in a* ca. 1 : 1 *mol ratio*). (*a*) On standing at room temperature for 36 h a solution of $[Pt^0(PPh_3)_2\{(RS)_2CSO\}]$ (50 or 100 mg) in $CDCl_3$ (*ca.* 0.4 cm³) yielded a *ca.* 1 : 1 mixture of *cis*-(*E*)- and *cis*-(*Z*)-$[Pt^{II}(RS)(RSCSO)(PPh_3)_2]$. Addition of a layer of n-hexane to such a mixture ($CHCl_3$ solution; R = Ph) yielded over a period of days yellow *cis*-(*E*)-$[Pt^{II}(PhS)(PhSCSO)(PPh_3)_2]\cdot 0.7\ CHCl_3$. Yield 70% (Found: C, 57.4; H, 4.1; Cl, 2.5; P, 5.9; S, 9.1. Calc. for $C_{49.7}H_{40.7}Cl_{2.1}OP_2PtS_3$: C, 57.75; H, 3.95; Cl, 2.40; P, 6.00; S, 9.30%).

(*b*) Under conditions identical to those described in (*i*) (*a*) $[Pt^0(PPh_3)_2\{(RS)(R'S)CSO\}]$ yielded after 36 h an approximately equimolar mixture of the four stereoisomers *cis*-(*E*)- and *cis*-(*Z*)-$[Pt^{II}(p\text{-}MeC_6H_4S)(p\text{-}MeOC_6H_4SCSO)(PPh_3)_2]$ and *cis*-(*E*)- and *cis*-(*Z*)-$[Pt^{II}(p\text{-}MeOC_6H_4S)(p\text{-}MeC_6H_4SCSO)(PPh_3)_2]$.

(*ii*) *Preparation of* cis-(E)-$[Pt^{II}(PhS)(PhSCSO)(PPh_3)_2]\cdot C_6H_6$. $[Pt^0(PPh_3)_4]$ (0.2 mmol) and $(PhS)_2CSO$ (0.2 mmol) were stirred together in benzene (*ca.* 4 cm³) for a few minutes. Upon standing at room temperature yellow *cis*-(*E*)-$[Pt^{II}(PhS)(PhSCSO)(PPh_3)_2]\cdot C_6H_6$ slowly crystallized out. The solution was decanted off and the crystals dried *in vacuo* (Found: C, 60.2; H, 4.4; O, 1.7; P, 5.7; S, 8.7%. *M* 980. Calc. for $C_{55}H_{46}OP_2PtS_3$: C, 61.4; H, 4.30; O, 1.50; P, 5.75; S, 8.95%. *M* 1 076).

(*iii*) *Preparation of a mixture of* $[Pt^0(PPh_3)_2\{(p\text{-}MeC_6H_4S)_2CSO\}]$, cis-(E)- *and* cis-(Z)-$[Pt^{II}(p\text{-}MeC_6H_4S)(p\text{-}MeC_6H_4SCSO)(PPh_3)_2]$. $[Pt^0(PPh_3)_4]$ (0.2 mmol) and $(p\text{-}MeC_6H_4S)_2CSO$ (0.2 mmol) were stirred in benzene (2 cm³) for 2 min and set aside for a few days at 4 °C. n-Hexane (0.5 cm³) was added, after which a yellow-white powder precipitated within a few days. This precipitate was filtered off, washed with n-hexane, and dried *in vacuo*.

(*iv*) *Preparation of a mixture of* $[Pt^0(PPh_3)_2\{(p\text{-}MeC_6H_4S)_2CSO\}]$ *and* cis-(E)-$[Pt^{II}(p\text{-}MeC_6H_4S)(p\text{-}MeC_6H_4SCSO)(PPh_3)_2]$. $[Pt^0(PPh_3)_4]$ (0.2 mmol) and $(p\text{-}MeC_6H_4S)_2CSO$ (0.2 mmol) were stirred in toluene (2 cm³) for 2 min. After standing at −20 °C for 24 h n-hexane was added resulting in slow precipitation of a white solid, which was filtered off, washed with n-hexane, and dried *in vacuo*.

(*v*) *Preparation of* cis-(E)-$[Pt^{II}Cl(p\text{-}MeC_6H_4SCSO)(PPh_3)_2]$. $[Pt^0(PPh_3)_4]$ (0.2 mmol) and (*E*)-$(p\text{-}MeC_6H_4S)ClCSO$ (0.2 mmol) were stirred overnight in benzene, toluene, or dichloromethane (*ca.* 3 cm³). A white precipitate was formed which was filtered off, washed with n-hexane, and dried *in vacuo* (Found: C, 51.2; H, 3.8; Cl, 10.3; P, 5.8; S, 5.7. Calc. for *cis*-(*E*)-$[Pt^{II}Cl(p\text{-}MeC_6H_4SCSO)(PPh_3)_2]\cdot 1.2\ CH_2Cl_2$, $C_{45.2}H_{39.4}Cl_{3.4}OP_2PtS_2$: C, 52.2; H, 3.80; Cl, 11.6; P, 5.95; S, 6.15%). In some reactions using toluene as solvent the precipitate appeared to consist of a mixture of the stereoisomers *cis*-(*E*)-, *cis*-(*Z*)-, and *trans*-(*Z*)-$[Pt^{II}Cl(p\text{-}MeC_6H_4SCSO)(PPh_3)_2]$ (Found: C, 56.6; H, 4.1; P, 6.4. Calc. for $C_{44}H_{37}ClOP_2PtS_2$: C, 56.3; H, 4.00; P, 6.60%).

(*vi*) *Preparation of* cis-(E)-$[Pt^{II}Cl(PhSCSO)(PPh_3)_2]$. $[Pt^0(PPh_3)_4]$ (0.2 mmol) and (*E*)-(PhS)ClCSO (0.2 mmol) were stirred in benzene (*ca.* 3 cm³) for one night. The white precipitate formed was filtered off, washed with n-hexane, and dried *in vacuo*. Mostly, the precipitate was pure *cis*-(*E*)-$[Pt^{II}Cl(PhSCSO)(PPh_3)_2]$ (Found: C, 56.3; H, 4.1; Cl, 3.7; O, 1.7; P, 6.2; S, 6.8. Calc. for $C_{43}H_{35}ClOP_2PtS_2$: C, 55.8; H, 3.85; Cl, 3.85; O, 1.75; P, 6.70; S, 6.95%). In a few cases the precipitate also contained, in addition to *cis*-(*E*)-$[Pt^{II}Cl(PhSCSO)(PPh_3)_2]$, stereoisomeric *cis*-(*Z*)-$[Pt^{II}Cl(PhSCSO)(PPh_3)_2]$.

(*vii*) *Preparation of a mixture of* $[Pt^0(PPh_3)_2\{(E)\text{-}(PhS)ClSCO\}]$ *and* cis-(E)-$[Pt^{II}Cl(PhSCSO)(PPh_3)_2]$. $[Pt^0(PPh_3)_4]$ (0.2 mmol) and (*E*)-(PhS)ClCSO (0.2 mmol) were stirred in toluene (*ca.* 3 cm³) for one night. The white precipitate, which was filtered off, washed with n-hexane, and dried *in vacuo*, consisted of a mixture of $[Pt^0(PPh_3)_2\{(E)\text{-}(PhS)ClCSO\}]$ and *cis*-(*E*)-$[Pt^{II}Cl(PhSCSO)(PPh_3)_2]$.

Crystal-structure Determination of cis-(E)-$[Pt^{II}(PhS)(PhSCSO)(PPh_3)_2]\cdot C_6H_6$.—*Crystal data.* Orthorhombic, space group $P2_12_12_1$, $a = 10.28(1)$, $b = 21.45(2)$, $c = 21.65(2)$ Å, $U = 4\,774$ Å³, $D_m = 1.48 \pm 0.02$ g cm^{-3} (by flotation in H_2O–$ZnCl_2$), $Z = 4$, $D_c = 1.497$ g cm^{-3}, $F(000) = 2\,160$, $\mu(\text{Cu-}K_\alpha) = 76.23$ cm^{-1}.

The quality of a transparent yellow crystal, of dimensions 0.025 × 0.025 × 0.018 cm, was examined by preliminary Weissenberg photographs. The crystal was transferred to a Nonius CAD4 computer-controlled diffractometer for data collection. Accurate values of the unit-cell parameters and the crystal orientation matrix were determined at ambient temperature from a least-squares treatment of the angular settings of 18 carefully centred reflections (Cu-K_α radiation, $\lambda = 1.541\,8$ Å). The intensities (4 527) were measured by using a θ—2θ scan of which 4 349 were significantly above the background intensity $[I > 2.5\sigma(I)]$. The crystal was oriented along the [011] axis. No correction was made for absorption. The structure was solved by use of a Patterson function to find the platinum atom and a difference-Fourier map to locate the other, non-hydrogen, atoms. The refinement was carried out by means of a block-diagonal least-squares procedure, using a Cruickshank weighting scheme $[W = (A + F_{obs.} + B \times F_{obs.}{}^2)^{-1}$ with $A = 2.140\,0$ and $B = 0.013\,5]$, resulting in a final R value of 0.061%. The Pt, S, and P atoms were refined anisotropically, the C and O atoms of the C=S=O fragment isotropically, and all phenyl rings as rigid groups. From a final difference synthesis less than half the number of hydrogen atoms were found and therefore their positions were not refined.

The molecular structure (with the numbering of the atoms) is shown in Figure 1. Table 1 contains the atomic parameters and Table 2 relevant bond lengths and bond angles.

TABLE 1

Positional parameters of non-hydrogen atoms of *cis*-(*E*)-$[Pt^{II}(PhS)(PhSCSO)(PPh_3)_2]\cdot C_6H_6$

Atom	*X*	*Y*	*Z*
Pt	0.021 88(5)	0.415 21(2)	0.192 70(2)
P(1)	0.099 9(3)	0.502 9(1)	0.140 5(2)
P(2)	0.056 6(3)	0.345 1(1)	0.114 8(1)
S(3)	0.000 5(4)	0.487 5(2)	0.275 4(2)
S(4)	−0.018 4(4)	0.291 8(2)	0.293 1(2)
S	−0.228 6(4)	0.347 8(2)	0.231 4(2)
C	−0.069(1)	0.348 2(6)	0.241 2(6)
O	−0.301(2)	0.296 5(8)	0.264 0(8)
C(101)	0.214 1(8)	0.544 8(3)	0.188 8(3)
C(102)	0.310 4(8)	0.509 7(3)	0.218 3(3)
C(103)	0.406 7(8)	0.539 7(3)	0.252 8(3)
C(104)	0.406 7(8)	0.604 8(3)	0.257 9(3)
C(105)	0.310 5(8)	0.639 9(3)	0.228 4(3)
C(106)	0.214 1(8)	0.609 9(3)	0.193 8(3)
C(107)	0.187 5(8)	0.497 3(3)	0.066 0(3)
C(108)	0.115 7(8)	0.492 7(3)	0.011 3(3)
C(109)	0.180 1(8)	0.488 4(3)	−0.045 4(3)
C(110)	0.316 2(8)	0.488 6(3)	−0.047 5(3)
C(111)	0.387 9(8)	0.493 3(3)	0.007 2(3)
C(112)	0.323 6(8)	0.497 6(3)	0.063 9(3)
C(113)	−0.035 5(8)	0.556 0(3)	0.121 0(3)
C(114)	−0.161 4(8)	0.543 3(3)	0.141 9(3)
C(115)	−0.263 9(8)	0.582 8(3)	0.125 5(3)
C(116)	−0.240 5(8)	0.635 0(3)	0.088 2(3)
C(117)	−0.114 5(8)	0.647 6(3)	0.067 3(3)
C(118)	−0.012 0(8)	0.608 1(3)	0.083 7(3)
C(201)	0.230 3(8)	0.341 8(3)	0.098 2(3)
C(202)	0.281 1(8)	0.341 6(3)	0.038 3(3)
C(203)	0.415 7(8)	0.339 3(3)	0.029 4(3)
C(204)	0.499 4(8)	0.337 2(3)	0.080 3(3)
C(205)	0.448 7(8)	0.337 3(3)	0.140 2(3)
C(206)	0.314 1(8)	0.339 6(3)	0.149 1(3)
C(207)	−0.039 0(9)	0.359 4(4)	0.047 0(4)
C(208)	−0.137 2(9)	0.404 4(4)	0.050 2(4)
C(209)	−0.217 4(9)	0.415 0(4)	−0.000 8(4)
C(210)	−0.199 5(9)	0.380 7(4)	−0.055 1(4)
C(211)	−0.101 4(9)	0.335 6(4)	−0.058 4(4)
C(212)	−0.021 2(9)	0.325 0(4)	−0.007 3(4)
C(213)	0.009 6(8)	0.263 1(3)	0.128 5(3)
C(214)	0.098 0(8)	0.218 8(3)	0.150 6(3)
C(215)	0.054 9(8)	0.159 0(3)	0.165 8(3)
C(216)	−0.076 6(8)	0.143 4(3)	0.158 9(3)
C(217)	−0.164 9(8)	0.187 6(3)	0.136 9(3)
C(218)	−0.121 8(8)	0.247 5(3)	0.121 7(3)
C(31)	−0.126 0(9)	0.464 2(3)	0.327 4(3)
C(32)	−0.096 0(9)	0.428 7(3)	0.379 6(3)
C(33)	−0.192 9(9)	0.415 2(3)	0.423 0(3)
C(34)	−0.319 7(9)	0.437 2(3)	0.414 0(3)
C(35)	−0.349 7(9)	0.472 7(3)	0.361 7(3)
C(36)	−0.252 8(9)	0.486 1(3)	0.318 4(3)
C(41)	0.151(1)	0.299 3(4)	0.300 2(3)
C(42)	0.227(1)	0.245 5(4)	0.296 1(3)
C(43)	0.362(1)	0.249 5(4)	0.302 5(3)
C(44)	0.421(1)	0.307 4(4)	0.313 0(3)
C(45)	0.345(1)	0.361 3(4)	0.317 0(3)
C(46)	0.210(1)	0.357 2(4)	0.310 6(3)
C(01)	−0.271(1)	0.242 9(5)	0.416 6(5)
C(02)	−0.173(1)	0.248 2(5)	0.460 9(5)
C(03)	−0.174(1)	0.209 8(5)	0.513 0(5)
C(04)	−0.274(1)	0.166 0(5)	0.520 8(5)
C(05)	−0.372(1)	0.160 7(5)	0.476 5(5)
C(06)	−0.371(1)	0.199 2(5)	0.424 4(5)

RESULTS

(*i*) *Description of the Structure of* cis-(E)-$[Pt^{II}(PhS)(PhSCSO)(PPh_3)_2]\cdot C_6H_6$.—The crystal structure of *cis*-(*E*)-$[Pt^{II}(PhS)(PhSCSO)(PPh_3)_2]\cdot C_6H_6$ consists of four discrete complex molecules per unit cell. The molecules of benzene occupy interstitial sites in the crystal lattice.

The Pt atom is square planar co-ordinated by two P atoms in *cis* positions, the C atom of the C=S=O functionality, and the S atom of the independent PhS group. The interatomic distances between these atoms clearly show that the PtP_2 group has inserted into one of the C–S side bonds of $(PhS)_2CSO$. The atoms S(4), Pt, C(41), C, and O are coplanar and this plane is almost perpendicular to the plane through Pt, P(1), and P(2). The PtSC=S=O unit is planar similar to the planarity of the XYC=S=O skeleton in the free sulphines.[2-7] The O atom is *anti* with respect to the Pt atom, while the phenyl ring of the PhS–C=S=O group is folded under the Pt atom leading to an *s-cis* conformation of this fragment. These structural features bear analogy to the conformation of the free sulphines (*Z*)-$(2,4,6\text{-}Me_3C_6H_2)(PhS)CSO$.[12]

TABLE 2

Relevant bond distances and angles for *cis*-(*E*)-$[Pt^{II}(PhS)(PhSCSO)(PPh_3)_2]\cdot C_6H_6$

(*a*) Bond distances (Å)

Pt–P(1)	2.337(3)	P(2)–C(207)	1.794(3)
Pt–P(2)	2.287(3)	P(2)–C(213)	1.847(3)
Pt–S(3)	2.379(4)	S(3)–C(31)	1.791(4)
Pt–C	2.01(1)	C–S(4)	1.73(1)
P(1)–C(101)	1.810(8)	C–S	1.65(1)
P(1)–C(107)	1.852(8)	S(4)–C(41)	1.752(5)
P(1)–C(113)	1.846(8)	S–O	1.51(2)
P(2)–C(201)	1.824(4)		

(*b*) Bond angles (°)

P(1)–Pt–P(2)	96.9(1)	Pt–P(2)–C(207)	114.0(2)
P(1)–Pt–S(3)	82.6(1)	Pt–P(2)–C(213)	117.8(2)
P(2)–Pt–C	89.3(4)	Pt–S(3)–C(31)	111.0(2)
S(3)–Pt–C	91.7(4)	C–S(4)–C(41)	107.0(5)
Pt–P(1)–C(101)	110.0(3)	Pt–C–S(4)	134.1(8)
Pt–P(1)–C(107)	122.4(3)	Pt–C–S	113.5(7)
Pt–P(1)–C(113)	110.4(3)	S(4)–C–S	112.4(8)
Pt–P(2)–C(201)	108.9(1)	C–S–O	115.7(9)

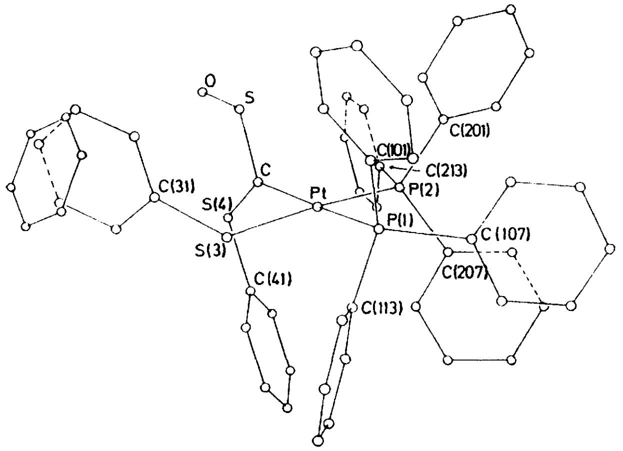


FIGURE 1 ORTEP drawing of *cis*-(*E*)-$[Pt^{II}(PhS)(PhSCSO)(PPh_3)_2]\cdot C_6H_6$

The C=S=O skeleton of the sulphine molecule after oxidative addition has a close resemblance to the C=S=O fragment of free sulphines as illustrated by comparison of the crystallographic data of the complex *cis*-(*E*)-$[Pt^{II}(PhS)(PhSCSO)(PPh_3)_2]\cdot C_6H_6$ and the free sulphines (*Z*)-$(2,4,6\text{-}Me_3C_6H_2)\{PhS(O)_2\}CSO$,[13] (*E*)-$(2,4,6\text{-}Me_3C_6H_2)\{PhS(O)_2\}CSO$,[13] (*Z*)-$(2,4,6\text{-}Me_3C_6H_2)\{PhS(O)\}CSO$,[13] (*E*)-$(2,4,6\text{-}Me_3C_6H_2)$-

$\{PhS(O)\}CSO$,[13] and $\overline{SCH_2CH_2SCSO}$,[3] *i.e.* C–S distance: 1.65(1) *vs.* 1.622(2), 1.640(7), 1.614(6), 1.628(5), and 1.64(1) Å; S–O distance: 1.51(2) *vs.* 1.466(3), 1.432(7), 1.464(5), 1.470(5), and 1.50(1) Å; and C–S–O angle: 115.7(9) *vs.* 115.2(2), 113.3(4), 113.3(3), 112.4(3), and 109.4(7)°.

Because of the close resemblance between free sulphines and *cis*-(*E*)-$[Pt^{II}(PhS)(PhSCSO)(PPh_3)_2]$, the latter compound may also be called a metal-substituted sulphine. This complex and the *cis*-(*Z*) stereoisomer retain comparability to free sulphines even in solution, as discussed below.

(*ii*) *Structure of* cis-(E)- *and* cis-(Z)-$[Pt^{II}(RS)(RSCSO)(PPh_3)_2]$ (R = Ph *or* C_6H_4Me-*p*).—Based on the structure of *cis*-(*E*)-$[Pt^{II}(PhS)(PhSCSO)(PPh_3)_2]\cdot C_6H_6$ the two strong cumulene vibrations [ν(CSO) = 1 079 and 950 cm⁻¹] in the i.r. spectrum (KBr mull) of this compound can be taken as characteristic of this specific stereoisomer.

Infrared spectra (KBr mulls) recorded on mixtures of *cis*-(*E*)- and *cis*-(*Z*)-$[Pt^{II}(RS)(RSCSO)(PPh_3)_2]$ in various mol ratios showed that only one cumulene absorption [ν(CSO)] can be assigned to the *cis*-(*Z*) stereoisomer. Despite the absence of an unambiguous explanation for the presence of a single ν(CSO) absorption, this phenomenon may be used as a criterion for identification of (*Z*) oxidative-addition stereoisomers. Phosphorus-31 n.m.r. spectra recorded directly after dissolving *cis*-(*E*)-$[Pt^{II}(PhS)(PhSCSO)(PPh_3)_2]\cdot C_6H_6$ in $CDCl_3$ show two AB resonance patterns (complete with ^{195}Pt satellites) in a *ca.* 4 : 1 mol ratio. The magnitude and similarity of the ^{31}P chemical-shift and coupling data strongly suggest that the solution contains the two oxidative products *cis*-(*E*)-$[Pt^{II}(PhS)(PhSCSO)(PPh_3)_2]$ [$^1J(Pt–P_C)$, 2 446; $^1J(Pt–P_S)$, 2 985 Hz] and in smaller amounts the *cis*-(*Z*) stereoisomer [$^1J(Pt–P_C)$, 2 300; $^1J(Pt–P_S)$, 3 060 Hz]. On the basis of *trans* influence the smaller coupling [$^1J(Pt–P_C)$] in each case may be attributed to the P atom *trans* to the C atom of the PhS-C=S=O group and the larger [$^1J(Pt–P_S)$] to P *trans* to S of the PhS group.[14–16] We have seen, that in the *cis*-(*E*) stereoisomers the O and Pt atoms are situated *anti*. By analogy to free sulphines with the non-equivalent substituents at C, which exist in two isomeric forms, we assume that in the *cis*-(*Z*) stereoisomers both the atoms are situated *syn*.

More detailed information concerning the structures of both stereoisomers can be derived from the ¹H n.m.r. spectra. We have seen that in the solid state *cis*-(*E*)-$[Pt^{II}(PhS)(PhSCSO)(PPh_3)_2]$ exists in a conformation (*s-cis*) where the phenyl ring of the PhS–C=S=O group is positioned ***anti*** to the C=S bond and thereby lies in proximity to the metal centre (see Figures 1 and 2). It is not unreasonable therefore to expect that in *cis*-(*E*)-$[Pt^{II}(p\text{-}MeC_6H_4S)(p\text{-}MeC_6H_4SCSO)(PPh_3)_2]$ the *p*-MeC_6H_4S group of the sulphine fragment should be similarly aligned. This would bring the Me group into the deshielding zone of the platinum atom and accordingly produce a downfield shift[17–20] (compared to the other Me groups), which is indeed observed (see Table 3). This geometry is, as mentioned above, the same as that deduced for (*Z*)-(2,4,6-$Me_3C_6H_2$)(PhS)CSO in solution[12] [see Figures 2(*a*) and 3(*a*)]. The Me group of the *p*-MeC_6H_4S-C=S=O fragment in the *cis*-(*Z*) stereoisomer does not show a downfield shift pointing to the conformation of the sulphine ligand in this stereoisomer being similar to that of (*E*)-(2,4,6-$Me_3C_6H_2$)(PhS)CSO, which is *gauche* in solution[12] [see Figures 2(*b*) and 3(*b*)].

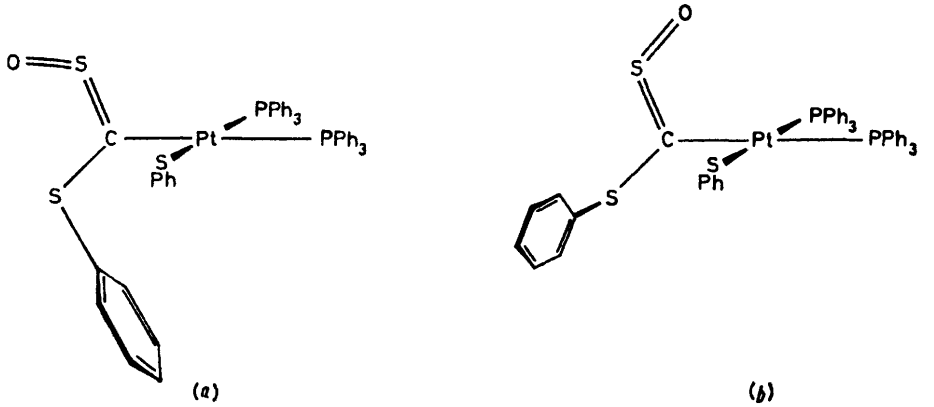


FIGURE 2 The oxidative-addition stereoisomers *cis*-(*E*)- (*a*) and *cis*-(*Z*)-$[Pt^{II}(PhS)(PhSCSO)(PPh_3)_2]$ (*b*)

(*iii*) *Conversion of* $[Pt^0(PPh_3)_2\{(RS)_2CSO\}]$ *into* cis-(E)- *and* cis-(Z)-$[Pt^{II}(RS)(RSCSO)(PPh_3)_2]$ (R = Ph *or* C_6H_4Me-*p*).—Upon standing in $CDCl_3$, the co-ordination compound $[Pt^0(PPh_3)_2\{(RS)_2CSO\}]$ changed completely within 36 h into the stereoisomeric oxidative-addition products, *cis*-(*E*)- and *cis*-(*Z*)-$[Pt^{II}(RS)(RSCSO)(PPh_3)_2]$. This could be readily followed by ^{31}P n.m.r. spectroscopy. No concentration dependency of this reaction was found, which shows that oxidative addition occurs intramolecularly; fully analogous to the conversions of the co-ordination products $[Pt^0(PPh_3)_2\{(E)\text{-}(MeS)RCSO\}]$ and $[Pt^0(PPh_3)_2\{(Z)\text{-}(MeS)RCSO\}]$ described previously.[1,9]

In the first hours of the reaction the concentration of *cis*-(*Z*)-$[Pt^{II}(RS)(RSCSO)(PPh_3)_2]$ is considerably higher than that of the corresponding *cis*-(*E*) stereoisomer, but invariably the final mixture contained the two products in a *ca.* 1 : 1 mol ratio. This suggests, that the thermodynamic stability of the two complexes is similar, but that the *cis*-(*Z*) stereoisomer is kinetically preferred. This result also indicates the existence of an equilibrium between these two stereoisomers. The results are summarized in the Scheme.

Diffusion of n-hexane into the final reaction mixture (see Experimental section) gave rise to the precipitation of only *cis*-(*E*)-$[Pt^{II}(RS)(RSCSO)(PPh_3)_2]\cdot xCDCl_3$ (x = 0.7 for R = Ph), which was identified by its two cumulene i.r. absorptions. When this precipitate was redissolved in $CDCl_3$ a mixture of both *cis* oxidative-addition stereoisomers in a *ca.* 1 : 1 mol ratio was immediately formed. Dissolution of *cis*-(*E*)-$[Pt^{II}(PhS)(PhSCSO)(PPh_3)_2]\cdot C_6H_6$ in $CDCl_3$ produced immediately a mixture of *cis*-(*E*)- and *cis*-(*Z*)-$[Pt^{II}(PhS)(PhSCSO)(PPh_3)_2]$ in a mol ratio of *ca.* 4 : 1. These results, which are based on ^{31}P n.m.r. data, are further proof for the existence of an equilibrium between the *cis*-(*E*) and *cis*-(*Z*) stereoisomers, although the differences in the rate of isomerization in the different experiments cannot as yet be explained (see Discussion).

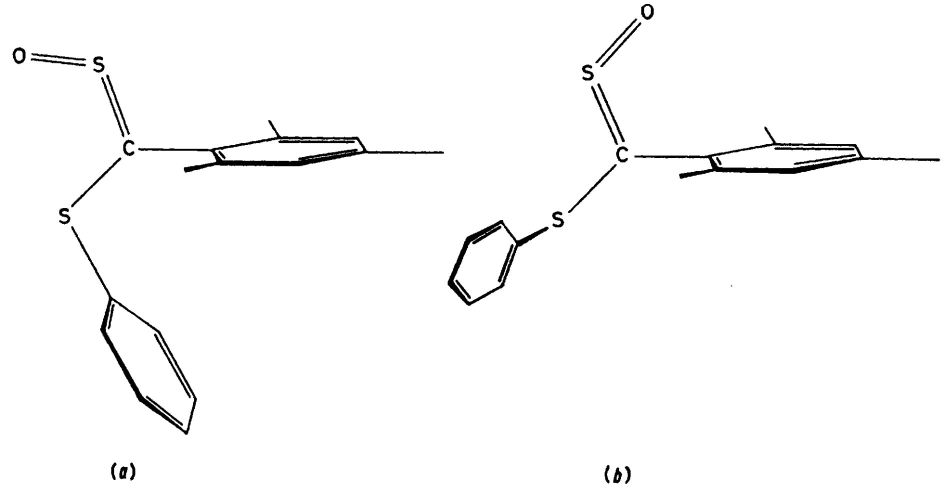
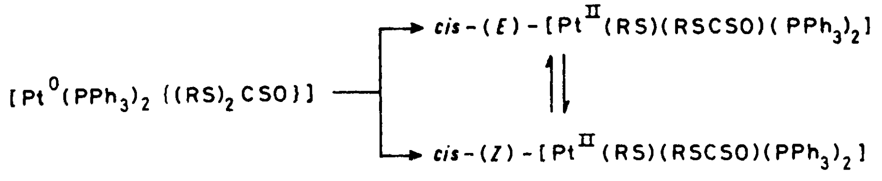


FIGURE 3 The free sulphines (*Z*)- (*a*) and (*E*)-$(2,4,6\text{-}Me_3C_6H_2)(PhS)CSO$ (*b*)

Precise adjustment of the procedure for the synthesis of $[Pt^0(PPh_3)_2\{(RS)_2CSO\}]$ enabled us to isolate from benzene solution *cis*-(*E*)-$[Pt^{II}(PhS)(PhSCSO)(PPh_3)_2]\cdot C_6H_6$ in crystalline form. Addition of n-hexane to reaction mixtures of $[Pt^0(PPh_3)_4]$ and $(p\text{-}MeC_6H_4S)_2CSO$ in toluene resulted in the isolation of not only $[Pt^0(PPh_3)_2\{(p\text{-}MeC_6H_4S)_2CSO\}]$ but also *cis*-(*E*)-$[Pt^{II}(p\text{-}MeC_6H_4S)(p\text{-}MeC_6H_4SCSO)(PPh_3)_2]$. When benzene was used as a solvent *cis*-(*Z*)-$[Pt^{II}(p\text{-}MeC_6H_4S)(p\text{-}MeC_6H_4SCSO)(PPh_3)_2]$ was also precipitated. These results show that in benzene and toluene oxidative addition also takes place and by application of very subtle changes in the procedures the reaction of $[Pt^0(PPh_3)_4]$ and $(RS)_2CSO$ can be steered towards the formation of specific complexes. With respect to the elucidation of the origin of the solvent dependency of the oxidative-addition reaction it was regrettable that owing to low solubility the behaviour of $[Pt^0(PPh_3)_2\{(RS)_2CSO\}]$ in toluene and benzene could not be followed by ^{31}P n.m.r.



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(*iv*) *Conversion of the Mixture of the Two Stereoisomers of* $[Pt^0(PPh_3)_2\{(p\text{-}MeC_6H_4S)(p\text{-}MeOC_6H_4S)CSO\}]$, *in a* ca. 1 : 1 *Mol Ratio.*—In view of the different nature of the substituents on the C=S=O fragment in $(p\text{-}MeOC_6H_4S)(p\text{-}MeC_6H_4S)CSO$ and the intramolecular reaction process of the oxidative addition [see section (*iii*)] it would be expected that a mixture of the two co-ordination stereoisomers of $[Pt^0(PPh_3)_2\{(p\text{-}MeOC_6H_4S)(p\text{-}MeC_6H_4S)CSO\}]$ should give rise to the formation of four *cis* oxidative-addition stereoisomers. Indeed *cis*-(*E*)- and *cis*-(*Z*)-$[Pt^{II}(p\text{-}MeC_6H_4S)(p\text{-}MeOC_6H_4SCSO)(PPh_3)_2]$ and *cis*-(*E*)- and *cis*-(*Z*)-$[Pt^{II}(p\text{-}MeOC_6H_4S)(p\text{-}MeC_6H_4SCSO)(PPh_3)_2]$ are formed (24 h, $CDCl_3$) in a *ca.* 1 : 1 : 1 : 1 mol ratio.

By comparison of the ^{31}P n.m.r. spectra recorded on the final reaction mixture with those of *cis*-(*E*)- and *cis*-(*Z*)-$[Pt^{II}(RS)(RSCSO)(PPh_3)_2]$ the individual ^{31}P n.m.r. spectral data of the four products could be elucidated (see Table 3 and Figure 4). The chemical-shift and ^1J(Pt–P) data confirm that these compounds are oxidative-addition stereoisomers. Hydrogen-1 n.m.r. spectra of the final product mixture show one Me resonance and one MeO resonance shifted downfield with respect to the other Me and MeO resonances. These signals have been assigned to the $p\text{-}MeOC_6H_4S\text{–}C\text{=}S\text{=}O$ fragment in *cis*-(*E*)-$[Pt^{II}(p\text{-}MeC_6H_4S)(p\text{-}MeOC_6H_4SCSO)(PPh_3)_2]$ and the $p\text{-}MeC_6H_4S\text{–}C\text{=}S\text{=}O$ fragment in *cis*-(*E*)-$[Pt^{II}(p\text{-}MeOC_6H_4S)(p\text{-}MeC_6H_4SCSO)(PPh_3)_2]$ by analogy to the *s-cis* conformation of *cis*-(*E*)-$[Pt^{II}(p\text{-}MeC_6H_4S)(p\text{-}MeC_6H_4SCSO)(PPh_3)_2]$ [see section (*i*)].

(*v*) *Reaction of* $[Pt^0(PPh_3)_4]$ *with* (E)-(RS)ClCSO * (R =

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* Carbon-13 and ^1H n.m.r. measurements of (RS)ClCSO show that it is only composed of one stereoisomer but do not indicate with certainty which isomer [(*E*) or (*Z*)] is present. The fact that the reaction with $[Pt^0(PPh_3)_4]$ yields mostly *cis*-(*E*)-$[Pt^{II}Cl(RSCSO)(PPh_3)_2]$ suggests that the ligand exists as the (*E*) isomer.

TABLE 3

Spectroscopic data

Compound	Stereoisomer	I.r. data [a]		^{31}P n.m.r. data [b]									^{1}H n.m.r. data [c]	
		ν(CSO)	ν(Pt–Cl)	^1J(Pt–P$_C$)	^1J(Pt–P$_S$)	^1J(Pt–P$_{Cl}$)	^1J(Pt–P$_P$)	^2J(P–P)	δ(P$_C$)	δ(P$_S$)	δ(P$_{Cl}$)	δ(P$_P$)	δ(Me)	δ(MeO)
		m^{-1}		Hz					p.p.m.				p.p.m.	
$[Pt^{II}(PhS)(PhSCSO)(PPh_3)_2]$	*cis*-(*E*) [d]	1 079, 950		2 446	2 985			20	18.8	16.2				
	cis-(*Z*)	980		2 298	3 073			21	17.2	19.1				
$[Pt^{II}(p\text{-}MeC_6H_4S)(p\text{-}MeC_6H_4SCSO)(PPh_3)_2]$	*cis*-(*E*)	1 073, 946		2 448	2 965			20	19.0	16.2			2.57; 2.21	
	cis-(*Z*)	979		2 301	3 052			22	17.5	19.2			2.18; 2.16	
$[Pt^{II}(p\text{-}MeOC_6H_4S)(p\text{-}MeC_6H_4SCSO)(PPh_3)_2]$	*cis*-(*E*)	[e]		2 458	2 944			20	19.1	16.0			2.50	3.09
	cis-(*Z*)	[e]		2 306	3 038			22	17.4	18.9			2.12	3.07
$[Pt^{II}(p\text{-}MeC_6H_4S)(p\text{-}MeOC_6H_4SCSO)(PPh_3)_2]$	*cis*-(*E*)	[e]		2 443	2 969			20	18.9	16.3			2.14	3.40
	cis-(*Z*)	[e]		2 314	3 054			22	17.5	19.1			2.09	3.09
$[Pt^{II}Cl(PhSCSO)(PPh_3)_2]$	*cis*-(*E*)	1 080, 949	295	2 294		3 886		18	17.4		12.5			
	cis-(*Z*)	978	298	2 205		4 004		18	16.0		14.7			
	trans-(*E*)	[f]	[f]				2 729					20.0		
$[Pt^{II}Cl(p\text{-}MeC_6H_4SCSO)(PPh_3)_2]$	*cis*-(*E*)	1 075, 947	302	2 285		3 892		18	17.4		12.4		2.63	
	cis-(*Z*)	979	303	2 201		4 003		17	16.0		14.7		2.34	
	trans-(*E*)	[f]	[f]				2 738					19.9	2.50	
	trans-(*Z*)	979 [g]	303 [g]				2 805					22.8	2.22	

[a] KBr mulls. [b] In CDCl$_3$, δ (p.p.m.) relative to to H$_3$PO$_4$ (85%), low field positive. [c] In CDCl$_3$, δ (p.p.m.) relative to SiMe$_4$, internal reference. [d] C$_6$H$_6$ adduct. [e] Complexes were not isolated. [f] Absorptions are not assigned. [g] Absorptions are tentatively assigned.

Ph *or* C_6H_4Me-*p*).—This reaction can be summarised in an equation (see below). The reactions in benzene, toluene,

$$[\mathrm{Pt^0(PPh_3)_4}] + (E)\text{-}(\mathrm{RS})\mathrm{ClCSO} \longrightarrow [\mathrm{Pt^0(PPh_3)_2}\{(E)\text{-}(\mathrm{RS})\text{-}\mathrm{ClCSO}\}] + cis\text{-}(E)\text{-}, cis\text{-}(Z)\text{-, and } trans\text{-}(Z)\text{-}[\mathrm{Pt^{II}Cl(RSCSO)(PPh_3)_2}]$$

and dichloromethane resulted in each case in white precipitates (see Experimental section) which, however, had different compositions.

When toluene was used as solvent for R = Ph a mixture of $[Pt^0(PPh_3)_2\{(E)$-$(PhS)ClCSO\}]$ and *cis*-(*E*)-$[Pt^{II}Cl(PhSCSO)(PPh_3)_2]$ was isolated. Dissolving this mixture in $CDCl_3$ resulted in rapid conversion of $[Pt^0(PPh_3)_2\{(E)$-$(PhS)ClCSO\}]$ into *cis*-(*E*)-$[Pt^{II}Cl(PhSCSO)(PPh_3)_2]$; a minor amount of *trans*-(*E*)-$[Pt^{II}Cl(PhSCSO)(PPh_3)_2]$ was also present. Sometimes *cis*-(*Z*)-$[Pt^{II}Cl(PhSCSO)(PPh_3)_2]$ also precipitated with *cis*-(*E*)-$[Pt^{II}Cl(PhSCSO)(PPh_3)_2]$ when benzene was used as a solvent. No explanation has yet been found for this lack of reproducibility. From the reaction of (*E*)-(*p*-$MeC_6H_4S)ClCSO$ using benzene or dichloromethane as solvent only *cis*-(*E*)-$[Pt^{II}Cl(p$-$MeC_6H_4SCSO)(PPh_3)_2]$ was isolated. This was the main product when toluene was used as solvent, but sometimes a mixture of *cis*-(*E*)-, *cis*-(*Z*)-, and *trans*-(*Z*)-$[Pt^{II}Cl(p$-$MeC_6H_4SCSO)(PPh_3)_2]$ was precipitated. After dissolving the latter mixture in $CDCl_3$ *trans*-(*E*)-$[Pt^{II}Cl(p$-$MeC_6H_4SCSO)(PPh_3)_2]$ was also slowly formed.

The stereoisomer *cis*-(*E*)-$[Pt^{II}Cl(RSCSO)(PPh_3)_2]$ was characterized by i.r., ^1H and ^{31}P n.m.r. spectroscopy. The i.r. spectrum showed two strong cumulene vibrations [ν(CSO), see Table 3] both in the solid state (KBr mull) and in $CHCl_3$ solution. As pointed out above, this characterizes a conformation for the oxidative-addition product in which the Pt atom is *anti* to the O atom [(*E*)-stereoisomer]. The medium absorption at *ca.* 300 cm^{-1}, absent in the i.r. spectra of *cis*-(*E*)-$[Pt^{II}(PhS)(PhSCSO)(PPh_3)_2]\cdot C_6H_6$, has been assigned to ν(Pt–Cl), confirming that oxidative addition of the C–Cl bond has taken place. Phosphorus-31 n.m.r. data fully support this view, ^1J(Pt–P) values of *ca.* 2 300 and 3 900 Hz are found and are consistent with P atoms *trans* to C and Cl atoms respectively.[14-16,21] Hydrogen-1 n.m.r. spectra of *cis*-(*E*)-$[Pt^{II}Cl(p$-$MeC_6H_4SCSO)(PPh_3)_2]$ show a Me resonance at low field, comparable to the situation found for *cis*-(*E*)-$[Pt^{II}(p$-$MeC_6H_4S)(p$-$MeC_6H_4SCSO)(PPh_3)_2]$ (see above), indicating an *s-cis* conformation for the *p*-MeC_6H_4S–C=S=O fragment (see Figure 5 and Table 3).

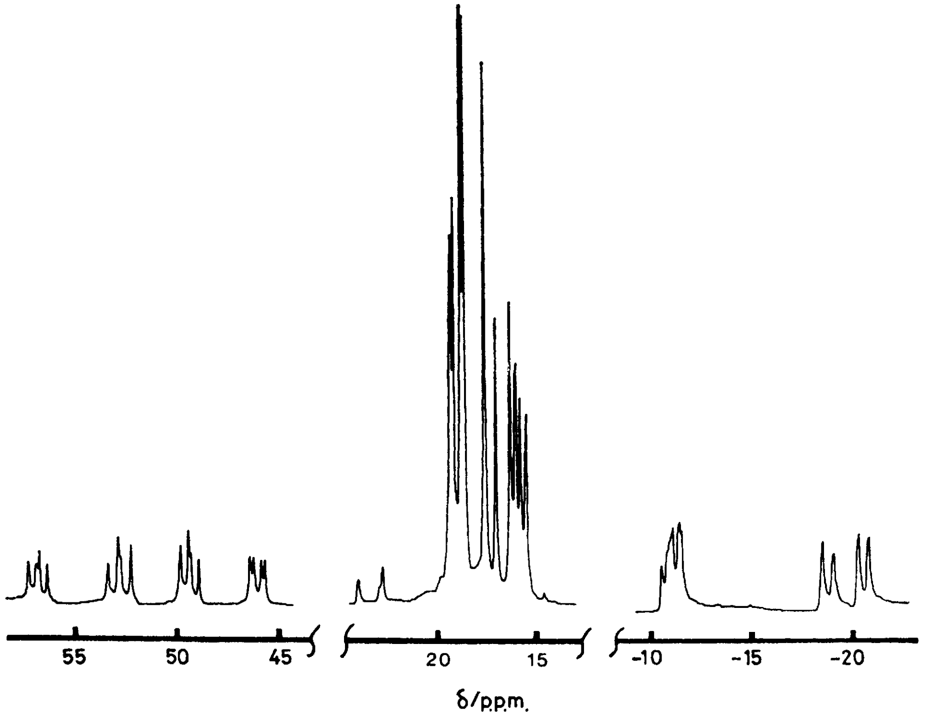


FIGURE 4 ^{31}P n.m.r. spectrum recorded on a mixture of *cis*-(*E*)- and *cis*-(*Z*)-$[Pt^{II}(p$-$MeOC_6H_4S)(p$-$MeC_6H_4SCSO)(PPh_3)_2]$ and *cis*-(*E*)- and *cis*-(*Z*)-$[Pt^{II}(p$-$MeC_6H_4S)(p$-$MeOC_6H_4SCSO)(PPh_3)_2]$ in $CDCl_3$ in an equimolar ratio

Although the other three stereoisomers [*cis*-(*Z*), *trans*-(*E*), and *trans*-(*Z*)] could not be isolated separately, they could be identified by ^1H and ^{31}P n.m.r. in solution and by i.r. spectroscopy (KBr mulls). Phosphorus-31 n.m.r. spectra of several mixtures of these stereoisomers showed one isomer with $^1J(Pt$–$P_C)$ *ca.* 2 200 (P *trans* to C [14-16,21]) and $^1J(Pt$–$P_{Cl})$ *ca.* 4 000 Hz (P *trans* to Cl [14-16,21]) consistent with *cis*-(*Z*)-$[Pt^{II}Cl(RSCSO)(PPh_3)_2]$. The i.r. spectra again showed a medium absorption at *ca.* 300 cm^{-1} [ν(Pt–Cl)] as a consequence of the oxidative addition of the C–Cl bond to Pt^0. Only one cumulene absorption [ν(CSO)] was found in the i.r. spectrum, which could be assigned to *cis*-(*Z*)- and/or *trans*-(*Z*)-$[Pt^{II}Cl(RSCSO)(PPh_3)_2]$. By analogy to the features of *cis*-(*Z*)-$[Pt^{II}(RS)(RSCSO)(PPh_3)_2]$ the chloro-derivative will have the Pt and O atoms situated *syn*. In the ^1H n.m.r. spectra recorded on a mixture of the four stereoisomers the Me resonance assigned to *cis*-(*Z*)-[Pt^{II}Cl(p-MeC$_6$H$_4$SCSO)(PPh$_3$)$_2$], by comparison of signal intensities in the ^{1}H and the corresponding ^{31}P n.m.r. spectra, lies *ca.* 0.3 p.p.m. upfield with respect to that of *cis*-(*E*)-[Pt^{II}Cl(p-MeC$_6$H$_4$SCSO)(PPh$_3$)$_2$]. Since the same behaviour is found for *cis*-(*E*)- and *cis*-(*Z*)-[Pt^{II}(p-MeC$_6$H$_4$S)(p-MeC$_6$H$_4$SCSO)(PPh$_3$)$_2$] the p-MeC$_6$H$_4$S–C=S=O fragment in *cis*-(*Z*)-[Pt^{II}Cl(p-MeC$_6$H$_4$SCSO)(PPh$_3$)$_2$] must have a ***gauche*** conformation. Likewise *s-cis* and ***gauche*** conformations are assigned to *cis*-(*E*)- and *cis*-(*Z*)-[Pt^{II}Cl(PhSCSO)(PPh$_3$)$_2$] respectively (see Figure 5).

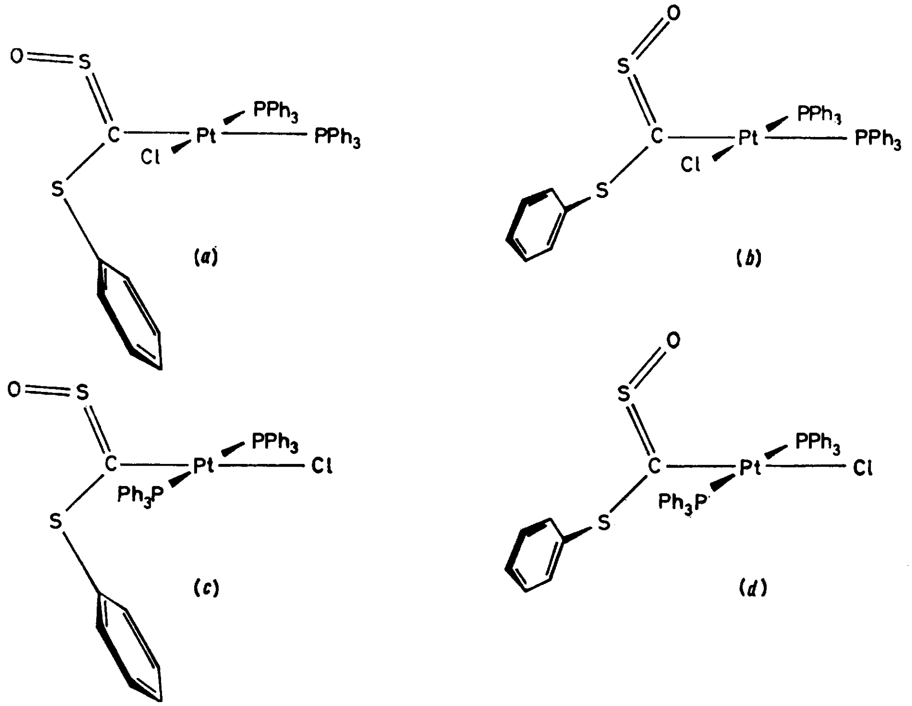


FIGURE 5 The oxidative-addition stereoisomers *cis*-(*E*)- (*a*), *cis*-(*Z*)- (*b*), *trans*-(*E*)- (*c*), and *trans*-(*Z*)-[Pt^{II}Cl(PhSCSO)(PPh$_3$)$_2$] (*d*)

Finally, ^{31}P n.m.r. spectra show that the stereoisomers *trans*-(*E*)- and *trans*-(*Z*)-[Pt^{II}Cl(p-MeC$_6$H$_4$SCSO)(PPh$_3$)$_2$] are also present in the reaction mixture; the ^1J(Pt–P$_P$) values of 2 738 and 2 805 Hz respectively are consistent with P atoms *trans* to P atoms.[14,15,22,23] The possibility that these resonances in the ^{31}P n.m.r. spectra arise from decomposition products can be ruled out, because elemental analysis of mixtures of at least three stereoisomers (two *cis* and one *trans* stereoisomer) were satisfactory (see Experimental section). Hydrogen-1 n.m.r. spectra show that the Me resonances assigned to the two *trans* stereoisomers are separated by *ca.* 0.3 p.p.m., indicating that the p-MeC$_6$H$_4$-S–C=S=O fragments in *trans*-(*E*)- and *trans*-(*Z*)-[Pt^{II}Cl(p-MeC$_6$H$_4$SCSO)(PPh$_3$)$_2$] have *s-cis* and *gauche* conformations, respectively, similar to the *cis* analogues. *trans*-(*E*)-[Pt^{II}Cl(PhSCSO)(PPh$_3$)$_2$] was recognized as the (*E*) isomer by comparison of its ^{31}P n.m.r. data with those of *trans*-(*E*)- and *trans*-(*Z*)-[Pt^{II}Cl(p-MeC$_6$H$_4$SCSO)(PPh$_3$)$_2$].

TABLE 4

Influence of the sulphine geometry on the ^{31}P n.m.r. data of [Pt^{II}X(RSCSO)(PPh$_3$)$_2$] (X = R′S or Cl)

Compounds	^1J(Pt–P$_C$)$_E$ – ^1J(Pt–P$_C$)$_Z$ /Hz	^1J(Pt–P$_S$)$_E$ – ^1J(Pt–P$_S$)$_Z$ /Hz	^1J(Pt–P$_{Cl}$)$_E$ – ^1J(Pt–P$_{Cl}$)$_Z$ /Hz	^1J(Pt–P$_P$)$_E$ – ^1J(Pt–P$_P$)$_Z$ /Hz	δ(P$_C$)$_E$ – δ(P$_C$)$_Z$ /p.p.m.	δ(P$_S$)$_E$ – δ(P$_S$)$_Z$ /p.p.m.	δ(P$_{Cl}$)$_E$ – δ(P$_{Cl}$)$_Z$ /p.p.m.	δ(P$_P$)$_E$ – δ(P$_P$)$_Z$ /p.p.m.
cis-[Pt^{II}(PhS)(PhSCSO)(PPh$_3$)$_2$]	148	−88			1.6	−2.9		
cis-[Pt^{II}(p-MeC$_6$H$_4$S)(p-MeC$_6$H$_4$SCSO)(PPh$_3$)$_2$]	147	−87			1.5	−3.0		
cis-[Pt^{II}(p-MeOC$_6$H$_4$S)(p-MeC$_6$H$_4$SCSO)(PPh$_3$)$_2$]	152	−94			1.7	−2.9		
cis-[Pt^{II}(p-MeC$_6$H$_4$S)(p-MeOC$_6$H$_4$SCSO)(PPh$_3$)$_2$]	129	−85			1.4	−2.8		
cis-[Pt^{II}Cl(PhSCSO)(PPh$_3$)$_2$]	89		−118		1.4		−2.2	
cis-[Pt^{II}Cl(p-MeC$_6$H$_4$SCSO)(PPh$_3$)$_2$]	84		−111		1.4		−2.3	
trans-[Pt^{II}Cl(p-MeC$_6$H$_4$SCSO)(PPh$_3$)$_2$]				−67				−2.9

(*vi*) ***Influence of the Sulphine Geometry in*** [Pt^{II}X(RSCSO)(PPh$_3$)$_2$] (X = Cl, SR′; R,R′ = Ph, C$_6$H$_4$Me-p, *or* C$_6$H$_4$OMe-p) *on* ^{31}P *N.M.R. Parameters*.—On changing the sulphine geometry in [Pt^{II}X(RSCSO)(PPh$_3$)$_2$] (X = Cl, SR′; R,R′ = Ph, C$_6$H$_4$Me-p, or C$_6$H$_4$OMe-p) from the Pt *anti* with respect to the O atom to the Pt *syn* with respect to the O atom [the respective (*E*) and (*Z*) stereoisomers of the oxidative-addition products] the following observations may be made (see Table 4).

There is an opposite effect on the chemical-shift and Pt–P coupling data for the P atoms lying in the PtCSO plane and for those *trans* to the X group. For the former the shifts are to high field with decreasing ^1J(Pt–P) whilst the latter are characterized by low-field shifts and increasing ^1J(Pt–P) values. For example, for the P atoms *trans* to the C atoms an upfield shift of *ca.* 1.5 p.p.m. has been found for all *cis* oxidative-addition products, while ^1J(Pt–P$_C$) decreases by *ca.* 144 Hz for *cis*-$[Pt^{II}(R'S)(RSCSO)(PPh_3)_2]$ and by *ca.* 86 Hz for *cis*-$[Pt^{II}Cl(RSCSO)(PPh_3)_2]$. For the P atoms *cis* to the C atoms in all the oxidative-addition products a downfield shift of *ca.* 2.7 p.p.m. has been observed, while the ^1J(Pt–P) values increase, *i.e. ca.* 89 Hz for ^1J(Pt–P$_S$) in *cis*-$[Pt^{II}(R'S)(RSCSO)(PPh_3)_2]$; *ca.* 115 Hz for ^1J(Pt–P$_{Cl}$) in *cis*-$[Pt^{II}Cl(RSCSO)(PPh_3)_2]$; and 67 Hz for ^1J(Pt–P$_P$) in *trans*-$[Pt^{II}Cl(RSCSO)(PPh_3)_2]$.

The oxidative-addition products *cis*-$[Pt^{II}(MeS)(RCSO)(PPh_3)_2]$ show similar trends, although they are numerically different. This indicates that the direction of these changes is not caused by the conformation of the RS group of the RS–C=S=O fragment (*s-cis* or *gauche*) but merely by the geometry of the C=S=O system itself (*syn* or *anti*).

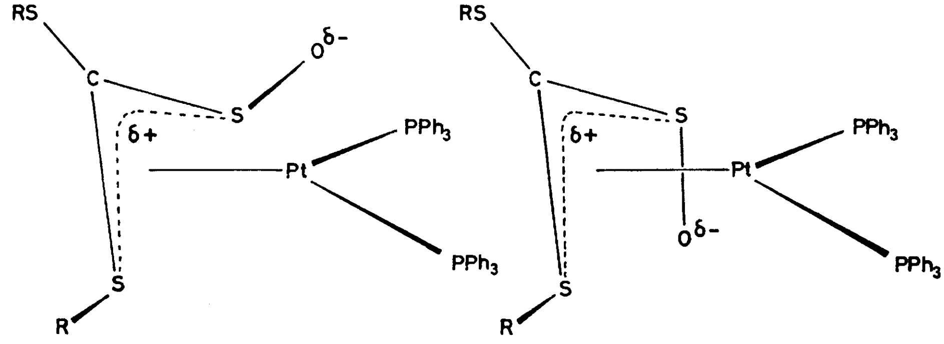
Perhaps a weak interaction between the platinum *d* and the SO π orbitals in the (*Z*) stereoisomers is responsible for the changes in the ^1J(Pt–P) values on going from (*E*)- to (*Z*)-$[Pt^{II}X(RSCSO)(PPh_3)_2]$.

DISCUSSION

(*i*) *Oxidative Addition of* $(RS)_2CSO$ *to* $[Pt^0(PPh_3)_4]$.—The results show that co-ordination of the sulphine $(RS)_2CSO$ to the $Pt^0(PPh_3)_2$ fragment is followed by an intramolecular oxidative addition of one of the C–S side bonds yielding the two stereoisomers *cis*-(*E*)- and *cis*-(*Z*)-$[Pt^{II}(RS)(RSCSO)(PPh_3)_2]$ which are closely related to the oxidative-addition stereoisomers *cis*-(*E*)- and *cis*-(*Z*)-$[Pt^{II}(MeS)(RCSO)(PPh_3)_2]$ already reported by us.[1,10] Based on their close resemblance to the free sulphines (*Z*)- and (*E*)-$(2,4,6\text{-}Me_3C_6H_2)(PhS)CSO$ [12] such organometallic complexes may be called metal-substituted sulphines.

In our previous paper a mechanism was proposed for the intramolecular oxidative addition of the sulphines in $[Pt^0(PPh_3)_2\{(E)\text{-}(MeS)RCSO\}]$ and $[Pt^0(PPh_3)_2\{(Z)\text{-}(MeS)RCSO\}]$.[1] This mechanism can be extended to the solution behaviour of $[Pt^0(PPh_3)_2\{(RS)_2CSO\}]$; with η^2-CS co-ordination of the sulphines, the $Pt^0(PPh_3)_2$ unit may glide along either of the two S–C=S frames to one C–S side bond. Depending on which side is chosen the intermediates in this motion are $[Pt^0(PPh_3)_2\{(E)\text{-}RSC(SR)SO\}]$ or $[Pt^0(PPh_3)_2\{(Z)\text{-}RSC(SR)SO\}]$ in which the sulphines are η^3-SCS co-ordinated (see Figure 6).

From the first isomer, insertion of the $Pt^0(PPh_3)_2$ unit into the C–S side bond *anti* with respect to the O atom yields *cis*-(*E*)-$[Pt^{II}(RS)(RSCSO)(PPh_3)_2]$, whereas oxidative addition of the other C–S side bond in the second isomer results in formation of *cis*-(*Z*)-$[Pt^{II}(RS)(RSCSO)(PPh_3)_2]$.



(*a*) (*b*)

FIGURE 6 The pseudo-allylic intermediates $[Pt^0(PPh_3)_2\{(E)\text{-}RSC(SR)SO\}]$ (*a*) and $[Pt^0(PPh_3)_2\{(Z)\text{-}RSC(SR)SO\}]$ (*b*)

It is interesting to note that the complete conversion of $[Pt^0(PPh_3)_2\{(RS)_2CSO\}]$ in $CDCl_3$ is comparable with the almost quantitative conversion of $[Pt^0(PPh_3)_2\{(Z)\text{-}(MeS)RCSO\}]$, whereas $[Pt^0(PPh_3)_2\{(E)\text{-}(MeS)RCSO\}]$ remains in equilibrium with the oxidative-addition stereoisomers.[1,10] This phenomenon suggests that co-ordination compounds of the type $[Pt^0(PPh_3)_2\{(RS)XCSO\}]$ ($X = SR$ or R) in which the sulphines are η^2-CS co-ordinated are thermodynamically unstable in $CDCl_3$ with respect to the corresponding oxidative-addition products, if they contain a C–S side bond *syn* to the S=O bond. That insertion into this C–S side bond is also kinetically more favourable can also be deduced from the fact that in the first few hours of the solution reaction of $[Pt^0(PPh_3)_2\{(p\text{-}MeC_6H_4S)_2CSO\}]$ more *cis*-(*Z*)- than *cis*-(*E*)-$[Pt^{II}(p\text{-}MeC_6H_4S)(p\text{-}MeC_6H_4SCSO)(PPh_3)_2]$ is present. Since the final reaction mixtures contained these two products in an almost 1 : 1 mol ratio, these oxidative-addition stereoisomers must isomerize.

Three routes for this isomerization are considered. First a direct isomerization, which may be catalyzed by impurities. Isomerization of free sulphines resulting from attack of base on the S atom of the C=S=O moiety is known.[24] A second route could be an isomerization *via* a η^3-SCS *pseudo*-allylic structure, with an equilibrium between the two *pseudo*-allylic intermediates $[Pt^0(PPh_3)_2\{(E)\text{-}RSC(SR)SO\}]$ and $[Pt^0(PPh_3)_2\{(Z)\text{-}RSC(SR)SO\}]$. Recent results in rhodium–sulphine chemistry indicate, that the complexes $[Rh^ICl\{P(C_6H_{11})_3\}\{(E)\text{-}MeSC(R)SO\}]$ and $[Rh^ICl\{P(C_6H_{11})_3\}\{(Z)\text{-}MeSC(R)SO\}]$, in which the sulphines are thought to be η^3-SCS co-ordinated, mutually isomerize.[25] The third possibility involves an intramolecular reductive coupling of RS and RSCSO, analogous to the reductive coupling of MeS and RCSO in *cis*-(*E*)-[Pt^{II}(MeS)(RCSO)(PPh$_3$)$_2$],[1,10] followed by the oxidative addition of the other C–S side bond. This implies equilibria between the co-ordination compound and the much more favoured oxidative-addition stereoisomers.

It is clear from the present results, that further work is needed to distinguish between these three possibilities. Accordingly, at this moment it is not possible to indicate which factors are responsible for the rate of isomerization and the relative thermodynamic stability of the oxidative-addition stereoisomers.

(*ii*) *Oxidative Addition of* (E)-(RS)ClCSO *to* [Pt^0(PPh$_3$)$_4$].—The co-ordination compounds [Pt^0(PPh$_3$)$_2${(*E*)-(RS)ClCSO}] are markedly less stable than the co-ordination compounds which possess only C–S side bonds (see above). A rapid oxidative addition of the C–Cl bond to Pt^0(PPh$_3$)$_2$ takes place, yielding a variety of stereoisomers of general molecular formula [Pt^{II}Cl(RSCSO)(PPh$_3$)$_2$].

This greater reactivity of the C–Cl bond compared to the C–S bond as regards oxidative addition to Pt^0 is well documented, *e.g.* [Pt^0(PPh$_3$)$_4$] reacts with Me$_2$NC(S)Cl[26] to give *cis*-[Pt^{II}Cl{C(S)NMe$_2$}(PPh$_3$)$_2$] but not with Me$_2$NC(S)SMe[27] and (EtS)$_2$CS.[28]

The instability of the co-ordination compounds, [Pt^0(PPh$_3$)$_2${(*E*)-(RS)ClCSO}] hampered the study of their conversion by ^{31}P n.m.r., which makes a mechanistic discussion inadvisable. It has not yet been possible for the reaction of [Pt^0(PPh$_3$)$_4$] with (*E*)-(RS)ClCSO to be steered to specific complex formation by changing the reaction conditions. In general *cis*-(*E*)-[Pt^{II}Cl(RSCSO)(PPh$_3$)$_2$] was formed, but sometimes also the other stereoisomers *cis*-(*Z*) and *trans*-(*Z*) precipitated from the reaction mixture.

By studying the oxidative addition of (*E*)-(RS)ClCSO to [Pt^0(PPh$_3$)$_4$] we hoped to gain more insight into the mechanism of the isomerization of the RSCSO moiety in the complexes [Pt^{II}X(RSCSO)(PPh$_3$)$_2$] (X = Cl or SR). In view of the high reactivity of the C–Cl bond towards low-valent metal centres, *pseudo*-allylic intermediates become less likely, while a reductive coupling of Cl and RSCSO in the oxidative-addition products is also not to be expected. The only process therefore which seems likely in these oxidative-addition compounds would be a direct isomerization, perhaps catalysed by impurities. It was observed that *cis*-(*E*)-[Pt^{II}Cl(*p*-MeC$_6$H$_4$SCSO)(PPh$_3$)$_2$] did not isomerize in solution (CDCl$_3$) during 3 h. [Pt^0(PPh$_3$)$_2${(*E*)-(PhS)ClCSO}] produced only *cis*-(*E*)-[Pt^{II}Cl(PhSCSO)(PPh$_3$)$_2$] even after 24 h, indicating that this *cis*-(*E*) complex does not isomerize to *cis*-(*Z*)-[Pt^{II}Cl(PhSCSO)(PPh$_3$)$_2$]. In a mixture of *trans*-(*Z*)-, *cis*-(*E*)-, and *cis*-(*Z*)-[Pt^{II}Cl(*p*-MeC$_6$H$_4$SCSO)(PPh$_3$)$_2$] in CDCl$_3$ during a few days the *trans*-(*E*) stereoisomer is also formed. This stereoisomer must originate from the *trans*-(*Z*) stereoisomer since the amounts of both the *cis* stereoisomers remained constant (based on ^{31}P n.m.r. measurements). Therefore it can be concluded that both stereoisomers of *cis*-[Pt^{II}Cl(RSCSO)(PPh$_3$)$_2$] do not mutually isomerize, and the stereoisomers of *trans*-[Pt^{II}Cl(RSCSO)(PPh$_3$)$_2$] give rise to an isomerization during the time necessary for a complete isomerization of the stereoisomers of *cis*-[Pt^{II}(RS)(RSCSO)(PPh$_3$)$_2$]. We are now able to extrapolate these results to the stereoisomers of *cis*-[Pt^{II}(RS)(RSCSO)(PPh$_3$)$_2$] and conclude that direct isomerization between *cis*-(*E*) and *cis*-(*Z*) oxidative-addition stereoisomers is unlikely.

Preliminary results show that the Cl atom in *cis*-(*E*)-[Pt^{II}Cl(*p*-MeC$_6$H$_4$SCSO)(PPh$_3$)$_2$] can be substituted by PhS yielding a mixture of the four possible stereoisomers of *cis*-[Pt^{II}(R'S)(RSCSO)(PPh$_3$)$_2$] (R,R' = Ph, C$_6$H$_4$Me-*p*; R $\neq$ R') in mol ratios which depend on the reaction conditions. This substitution reaction, which will be the subject of a following paper, may have great synthetic importance if reductive coupling can be initiated. This would then constitute an attractive method for the synthesis of otherwise unstable sulphines in the co-ordination sphere of platinum.

(*iii*) *Concluding Remarks*.—Sulphines, XYC=S=O, can be divided into four groups, according to their reactivity to [Pt^0(PPh$_3$)$_4$].

1. *Sulphines lacking reactive side bonds* (X=Y=aryl). Reaction of these sulphines with [Pt^0(PPh$_3$)$_4$] gives stable co-ordination complexes, *i.e.* [Pt^0(PPh$_3$)$_2$(XYCSO)] in which the sulphines are η^2-CS co-ordinated.

2. *Sulphines with one* C–S *side bond*. These sulphines give rise to stereoisomeric co-ordination complexes [Pt^0(PPh$_3$)$_2${(*E*)-(RS)R'CSO}] and [Pt^0(PPh$_3$)$_2${(*Z*)-(RS)R'CSO}]. In this case co-ordination of the sulphine has been found to give η^2-CS co-ordination and retention of configuration. These co-ordination stereoisomers are in equilibrium with the oxidative-addition stereoisomers *cis*-(*E*)- and *cis*-(*Z*)-[Pt^{II}(RS)(R'CSO)(PPh$_3$)$_2$]. The relative thermodynamic stability of the co-ordination stereoisomers depends on the configuration of the co-ordinated sulphine.

3. *Sulphines with two* C–S *side bonds*. After formation of an η^2-CS co-ordination compound [Pt^0(PPh$_3$)$_2${(RS)$_2$CSO}], a complete intramolecular oxidative-addition reaction of one of the C–S side bonds occurs yielding the stereoisomers *cis*-(*E*)- and *cis*-(*Z*)-[Pt^{II}(RS)(RSCSO)(PPh$_3$)$_2$]. Co-ordination compounds [Pt^0(PPh$_3$)$_2$(XYCSO)] containing a C–S side bond *syn* to the S=O unit (groups 2 and 3) are unstable in CDCl$_3$ with respect to their corresponding oxidative-addition products, while co-ordination compounds with no C–S side bond *syn* to the S=O group (group 2) have almost the same thermodynamic stability as their corresponding oxidative-addition products.

4. *Sulphines containing a* C–Cl *side bond*. The co-ordination compounds [Pt^0(PPh$_3$)$_2${(*E*)-(RS)ClCSO}] are very unstable in CDCl$_3$ and undergo fast oxidative addition of the C–Cl bond yielding the stereoisomers, *cis*-(*E*)-, *cis*-(*Z*)-, *trans*-(*E*)-, and *trans*-(*Z*)-[Pt^{II}Cl(RSCSO)(PPh$_3$)$_2$].

Thermal parameters for the non-hydrogen atoms of *cis*-(*E*)-[Pt^{II}(PhS)(PhSCSO)(PPh$_3$)$_2$]·C$_6$H$_6$ and observed and calculated structure factors are available as Supplementary Publication No. SUP 22895 (33 pp.).*

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1979, Index issue.

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