Intramolecular Rearrangements of Sulphines Co-ordinated to Pt Involving Insertion and Reductive Coupling Reactions. *X*-Ray Crystal and Molecular Structure of (*E*)-[$\mathrm{Pt^{II}(PhS)(PPh_3)_2(PhSCSO)]\cdot C_6H_6}$, a New Type of Heterocumulene–Metal Complex†

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Summary The $\mathrm{Pt^0(PPh_3)_2}$-unit in $[\mathrm{Pt^0(PPh_3)_2(XYCSO)}]$ (X = Y = *S*-aryl or X = *S*-alkyl, Y = aryl, both stereoisomers), in which the sulphine XYCSO is η^2-CS co-ordinated, inserts into a C–S bond yielding an equilibrium mixture consisting of two stereoisomers (*E*)- and (*Z*)-$[\mathrm{Pt^{II}X(PPh_3)_2(YCSO)}]$ and varying amounts of $[\mathrm{Pt^0(PPh_3)_2(XYCSO)}]$, depending on the geometry of the co-ordinated sulphine.

Sulphines (XYCSO) are heterocumulenic systems, which, in principle, can co-ordinate to metal centres *via* the CSO-unit in a variety of ways, *i.e.*, *via* η^1-S, η^1-O, η^2-CS, or η^2-SO. Moreover, when X and Y are non-equivalent the planar bent sulphine molecule[1,2] exists as two stereoisomers, thus resulting in two metal–sulphine stereoisomers on complexation {*cf.*, $[\mathrm{Pt(PPh_3)_2\{(p\text{-}MeC_6H_4)(MeS)CSO\}}]$,[3] and $[\mathrm{Fe(CO)_3(H_2C{=}CHCH{=}S{=}O)}]$,[4] which contain η^2-CS co-ordinated XYCSO}. When X,Y=*S*-aryl, *S*-alkyl, or Cl, in addition to co-ordination, insertion of the metal centre into the C–X or C–Y bond might also take place.

We now report the co-ordination behaviour of XYCSO to $\mathrm{Pt^0}$. We shall concentrate on intramolecular rearrangement processes of co-ordinated sulphine involving C–S bond breaking and bond formation.

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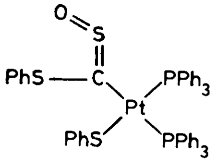
† Throughout this article, (*E*) and (*Z*) refer to the configuration of the sulphine C=S bond. If these are placed inside the molecular formula, this indicates that the sulphine has the (*E*) or (*Z*) configuration, and is co-ordinated as such (η^2) through the C=S bond. If these are placed outside the molecular formula, this indicates that the Pt(PhS)C=S=O co-ordinated entity as a whole has the (*E*) or (*Z*) configuration, co-ordination being through a Pt–C σ-bond.



(*E*) - (3b)

The sulphines (**1a**—**e**) react with [Pt^0(PPh$_3$)$_4$] to form (**2a**—**e**) (see Scheme), containing η^2-CS co-ordinated XYCSO. Separate reactions with the stereoisomers (**1d**) or (**1e**) yield the corresponding isomeric complexes (**2d**) or (**2e**), indicating that the configuration of the sulphine is retained upon co-ordination to Pt^0.[3] In the absence of reactive side-bonds, *cf.* (**1a**), the corresponding co-ordination compound (**2a**) remains stable in solution at room temperature. In contrast the Pt^0(PPh$_3$)$_2$-unit in (**2b,c**) (X = Y = *S*-aryl) inserts intramolecularly and irreversibly in solution (25 °C, in *ca.* 24 h) into one of the C–S bonds, yielding two isomeric insertion products (*E*)- and (*Z*)-(**3b,c**) (see Scheme).

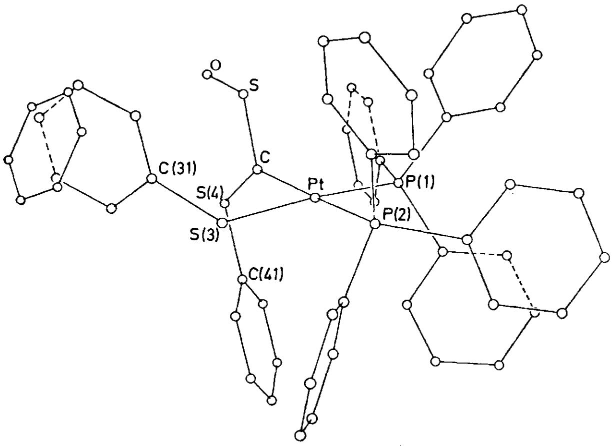


FIGURE. ORTEP drawing of the molecular structure of (*E*)-(**3b**) Important bond angles and distances are: Pt–C, 2·01(1); Pt–P(1), 2·336(4); Pt–P(2), 2·287(3); Pt–S(3), 2·379(4); C–S, 1·65(1); S–O, 1·50(2); C–S(4), 1·73(1) Å; <P(1)–Pt–S(3), 82·6(1); P(1)–Pt–P(2), 96·8(1); P(2)–Pt–C, 89·3(4); C–Pt–S(3), 91·7(4); Pt–C–S, 113·5(7); Pt–C–S(4), 134·1(8); S(4)–C–S, 112·4(8); C–S–O, 115·7(9); C–S(4)–C(41), 107·0(5); Pt–S(3)–C(31), 111·0(2)°.

Compound (*E*)-(**3b**) crystallizes preferentially from benzene. A single-crystal *X*-ray structure determination shows that this isomer has the structural formula (*E*)-[Pt$^{\text{II}}$(PhS)(PPh$_3$)$_2$(PhSCSO)]·C$_6$H$_6$ (see Figure). *Crystal data*: orthorhombic, with cell dimensions $a = 10{\cdot}28$, $b = 21{\cdot}44$, $c = 21{\cdot}65$ Å, $U = 4774$ Å^3, $Z = 4$, space group $P2_12_12_1$. 4349 independent reflections from a total of 4527, which were measured on a Nonius CAD-4 diffractometer using Cu-K_α radiation, have been considered as observed [$I > 2{\cdot}5\sigma(I)$]. The final *R*-factor is 0·06.‡

The Pt-atom lies in the sulphine plane, which is perpendicular to the plane through P(1)PtP(2) and is situated *anti* with respect to the O-atom. The PhSCSO-fragment has the same *s-cis* configuration in both (*E*)-(**3b**) and the free sulphine (*Z*)-(2,4,6-Me$_3$C$_6$H$_2$)(PhS)CSO.[5] On the basis of this observation and by analogy with the stereoisomerism found in the free sulphines (where X ≠ Y), the O and Pt atoms in (*Z*)-(**3b**)§ are thought to be situated *syn*.

Interestingly, in (**2b**) and (**2e**) the Pt^0(PPh$_3$)$_2$ unit also inserts in the C–S bond, yielding, irrespective of whether (**2d**) or (**2e**) is used as starting material, a *ca.* 1 : 1 : 1 mixture of (**2d**), (*E*)-(**3d**), and (*Z*)-(**3d**)¶ (see Scheme). Surprisingly, only traces of (**2e**) are present in the final reaction mixture. ^{31}P-N.m.r. spectra recorded on a solution of (*E*)-(**3d**) in CDCl$_3$ showed the initial presence of (*E*)- and (*Z*)-(**3d**) in a 1 : 1 molar ratio, whilst, over a period of *ca.* 24 h, (**2d**) was formed until a 1 : 1 : 1 equilibrium was reached. These observations show that the insertion and co-ordination products [(*E*)- and (*Z*)-(**3d**), and (**2d**) and (**2e**), respectively] are in equilibrium. Reformation of (**2d**) implies that a reductive coupling of MeS and *p*-MeC$_6$H$_4$CSO takes place in the insertion products.

The present results indicate the influence of the geometry of the sulphine ligand and Pt–CSO fragment on the thermodynamic stability of the complexes. This is clearly illustrated by the absence of the specific co-ordination product, [Pt^0(PPh$_3$)$_2${(*Z*)-(*p*-MeC$_6$H$_4$)(MeS)CSO}] (**2e**) in the equilibrium mixture, which contains [Pt^0(PPh$_3$)$_2${(*E*)-(*p*-MeC$_6$H$_4$)(MeS)CSO}] (**2d**), and (*E*)- and (*Z*)-[Pt$^{\text{II}}$(MeS)(PPh$_3$)$_2$(*p*-MeC$_6$H$_4$CSO)] (*E*)- and (*Z*)-(**3d**), and by the quantitative formation of the insertion products (*E*)- and (*Z*)-[Pt$^{\text{II}}$(RS)(PPh$_3$)$_2$(RSCSO)] (*E*)- and (*Z*)-(**3b,c**) from [Pt^0(PPh$_3$)$_2${(RS)$_2$CSO}] (**2b,c**). In these co-ordination products (**2b,c,e**) the O-atom is situated *syn* to an S-atom.

A detailed study of these systems, which are unique, because both insertion and co-ordination products are present in equilibrium, might provide better insight into

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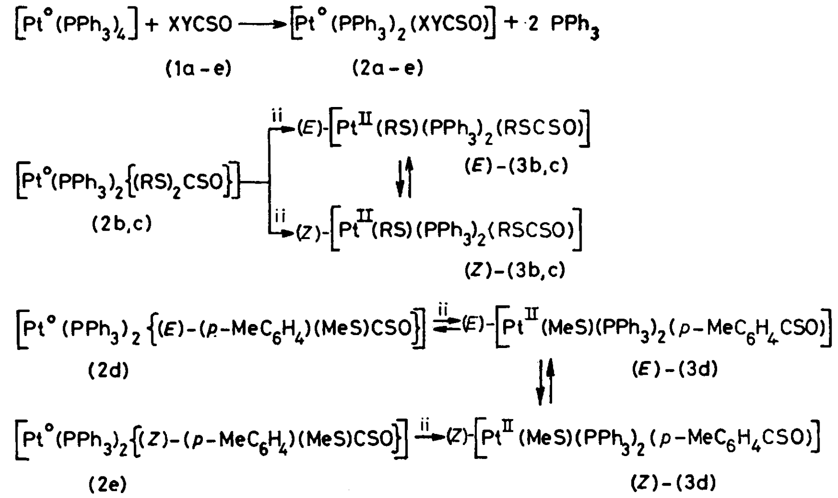
‡ All Pt, P, and S atoms have been refined anisotropically; the carbon atoms belonging to phenyl rings have been refined as ideal groups and the C and O atoms of the CSO-fragment have been refined isotropically. The refinement has been carried out by means of a block diagonal least-square programme, using a Cruickshank weighting scheme. No attempt has been made to localize the H-atoms. The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

§ ^{31}P-N.m.r. data of the insertion products are (*E*)-(**3b**): ^1J(Pt–P$_C$) 2448 Hz, ^1J(Pt–P$_S$) 2985 Hz, and (*Z*)-(**3b**): ^1J(Pt–P$_C$) 2296 Hz and ^1J(Pt–P$_S$) 3073 Hz (P$_C$ and P$_S$, respectively P *trans* to C and P *trans* to S). The i.r. spectra (KBr-mulls) of (*E*)- and (*Z*)-(**3b**) show different CSO-vibrations: (*E*)-(**3b**) 1079(s) and 950(s) cm^{-1} and (*Z*)-(**3b**) 980(s) cm^{-1}. The ^{1}H-n.m.r. spectra of (*E*)- and (*Z*)-(**3c**) show that the Me-group of the *p*-MeC$_6$H$_4$SCSO fragment in (*E*)-(**3c**) is shifted 0·1 p.p.m. downfield compared to the free ligand. This is due to the fact that this group lies in the deshielding zone of Pt$^{\text{II}}$ [*cf. s-cis* conformation of (*E*)-(**3b,c**)]. The Me-group of the *p*-MeC$_6$H$_4$S–Pt-fragment in both *E*- and *Z*-(**3c**) and of the *p*-MeC$_6$H$_4$SCSO-fragment in *Z*-(**3c**) is shifted 0·3 p.p.m. upfield compared to the free ligand, indicating a *gauche* conformation for the *p*-MeC$_6$H$_4$SCSO–Pt-fragment in (*Z*)-(**3c**), as was found for (*E*)-(2,4,6-Me$_3$C$_6$H$_2$)(PhS)CSO (ref.5).

¶ ^{31}P-N.m.r. data, for (*E*)-(**3d**) [^1J(Pt–P$_C$) 2317 Hz and ^1J(Pt–P$_S$) 2873 Hz] and *Z*-(**3d**) [^1J(Pt–P$_C$) 2159 Hz and ^1J(Pt–P) 3016 Hz], when compared with those of (*E*)- and (*Z*)-(**3b**), indicate that these compounds are also insertion products.



a; X, Y = fluoren-9-ylidene
b; X = Y = PhS
c; X = Y = *p*-MeC$_6$H$_4$S
d; X = MeS, Y = *p*-MeC$_6$H$_4$ (*E*-isomer)
e; X = MeS, Y = *p*-MeC$_6$H$_4$ (*Z*-isomer)
i, in benzene or toluene; ii, in CDCl$_3$
R = Ph or *p*-MeC$_6$H$_4$

SCHEME

the intimate mechanisms involved in oxidative insertion and reductive coupling reactions of heterocumulenes on transition metal centres.**

We thank Prof. B. Zwanenburg and Mr. B. H. M. Lammerink of the Department of Organic Chemistry, University of Nijmegen (The Netherlands), for their assistance and useful comments during the syntheses of the sulphines.

(*Received*, 15*th June* 1979; *Com.* 631.)

** Preliminary experiments revealed that in *trans*-[Rh^{I}Cl(PCy$_3$)$_2$(fluorene-9-ylidene–SO)] (Cy = cyclohexyl) [^1J(Rh–P) 113 Hz, δ(P) 28·8 p.p.m. (relative to 80% H$_3$PO$_4$), ν(CSO) 1118, 1090, and 1022 cm^{-1} (KBr-mulls)] the sulphine ligand is η^1-S bonded. The reaction of [(PCy$_3$)$_2$Rh^{I}Cl(C$_8$H$_{14}$)] with *Z*-(*p*-MeC$_6$H$_4$)(MeS)CSO afforded [Rh^{I}Cl(PCy$_3$){(*Z*)-(*p*-MeC$_6$H$_4$)(MeS)CSO}] [^1J(Rh–P) 185 Hz, δ(P) 51·0 p.p.m. (relative to 80% H$_3$PO$_4$), ν(SO) 1046 cm^{-1} (KBr-mulls), ^3J(Rh–SCH$_3$) 3 Hz] instead of insertion products. In this compound the sulphine is probably co-ordinated *via* the S-atom and the C=S-fragment.

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