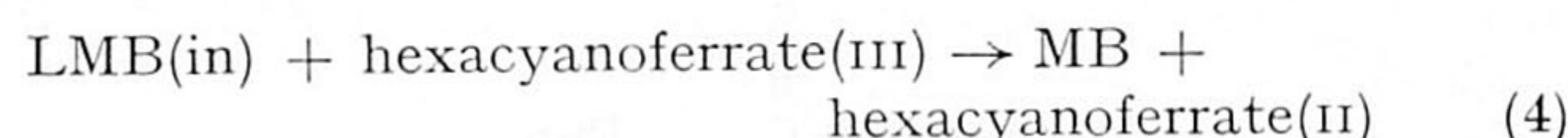
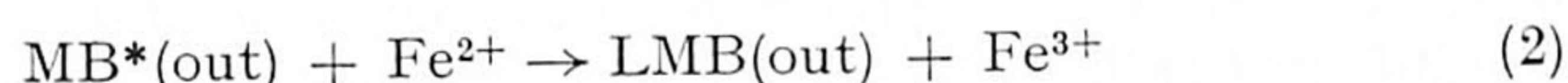
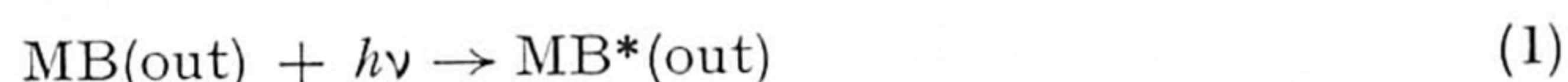


TABLE. Relative reduction rates of hexacyanoferrate(III) under different conditions

Methylene Blue/ 10 ⁻⁵ M	FeCl ₂ /M	Light ^a	Relative rates
4.0	0.01	+	4.0
2.4	0.01	+	2.5
1.2	0.01	+	1.0
0	0.01	+	0
1.2	0	+	0
1.2	0.01	-	0

^a + Irradiated, - non-irradiated.

either hexacyanoferrate(III), iron(II) chloride or light no reduction was observed. The reduction rate was found to increase linearly with Methylene Blue concentration. Neither hexacyanoferrate(III) nor iron(II) chloride penetrated the phospholipid wall. Self reduction of Methylene Blue and hexacyanoferrate(III) does not occur, as described previously. From these results, it is clear that hexacyanoferrate(III) is an electron acceptor and iron(II) chloride is an electron donor. The reaction is thought to proceed via steps (1)–(4).



where MB = Methylene Blue, LMB = leuco Methylene Blue, out = outside, in = inside.

This electron transfer does not occur under ordinary conditions for the following reasons. First, the redox potential of iron(II) chloride (E_0' 0.77 V) is higher than that of hexacyanoferrate(III) (E_0' 0.33 V). Secondly, iron(II) chloride reacts rapidly with potassium hexacyanoferrate(III) to form a deep blue precipitate of iron(II) hexacyanoferrate(III) (Turnbull's Blue). When the vesicle containing potassium hexacyanoferrate(III) inside and iron(II) chloride outside was destroyed by the addition of detergent, the dispersion soon turned deep blue and Turnbull's Blue was precipitated.

Thus we have carried out a photosensitized reduction of hexacyanoferrate(III) by iron(II) chloride in the liposome system. This reaction is noteworthy because it cannot be observed in the ordinary system.

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¹ M. Mangel, *Biochim. Biophys. Acta*, 1976, **430**, 459.

² Y. Toyoshima, M. Morino, H. Motoki, and M. Sukigara, *Nature*, 1977, **265**, 187.

³ J. W. Otvos and M. Calvin, *Nature*, 1978, **274**, 507; *Internat. J. Energy Res.*, 1979, **3**, 80.

⁴ M. Mangel, D. Bevns, and A. Ilani, *J. Membrane Biol.*, 1975, **20**, 171.

⁵ H. Ti. Tien and S. P. Verna, *Nature*, 1969, **227**, 1232.

⁶ Y. Sudo and F. Toda, *Nature*, 1979, **279**, 807.

⁷ C. H. Lea, D. H. Rhodes, and R. D. Stoll, *Biochemistry*, 1975, **60**, 353.

Intramolecular Rearrangements of Sulphines Co-ordinated to Pt Involving Insertion and Reductive Coupling Reactions. X-Ray Crystal and Molecular Structure of (*E*)-[Pt^{II}(PhS)(PPh₃)₂(PhSCSO)]·C₆H₆, a New Type of Heterocumulene–Metal Complex†

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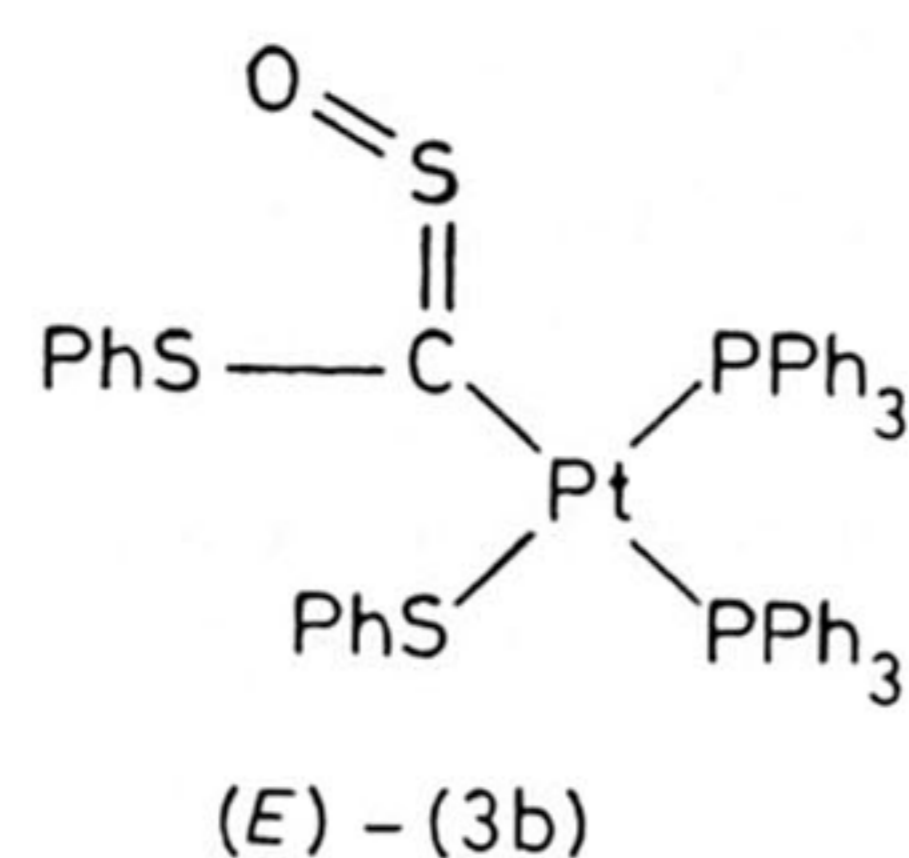
Summary The Pt⁰(PPh₃)₂-unit in [Pt⁰(PPh₃)₂(XYCSO)] (X = Y = S-aryl or X = S-alkyl, Y = aryl, both stereoisomers), in which the sulphine XYCSO is η²-CS co-ordinated, inserts into a C–S bond yielding an equilibrium mixture consisting of two stereoisomers (*E*)- and (*Z*)-[Pt^{II}X(PPh₃)₂(YCSO)] and varying amounts of [Pt⁰(PPh₃)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* η¹-S, η¹-O, η²-CS, or

η²-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.*, [Pt(PPh₃)₂{(p-MeC₆H₄)(MeS)CSO}],³ and [Fe(CO)₃(H₂C=CHCH=S=O)],⁴ which contain η²-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 Pt⁰. We shall concentrate on intramolecular rearrangement processes of co-ordinated sulphine involving C–S bond breaking and bond formation.

† 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 (η²) 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.



The sulphines (**1a—e**) react with $[\text{Pt}^0(\text{PPh}_3)_4]$ 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 $\text{Pt}^0(\text{PPh}_3)_2$ -unit in (**2b,c**) ($\text{X} = \text{Y} = \text{S-aryl}$) 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).

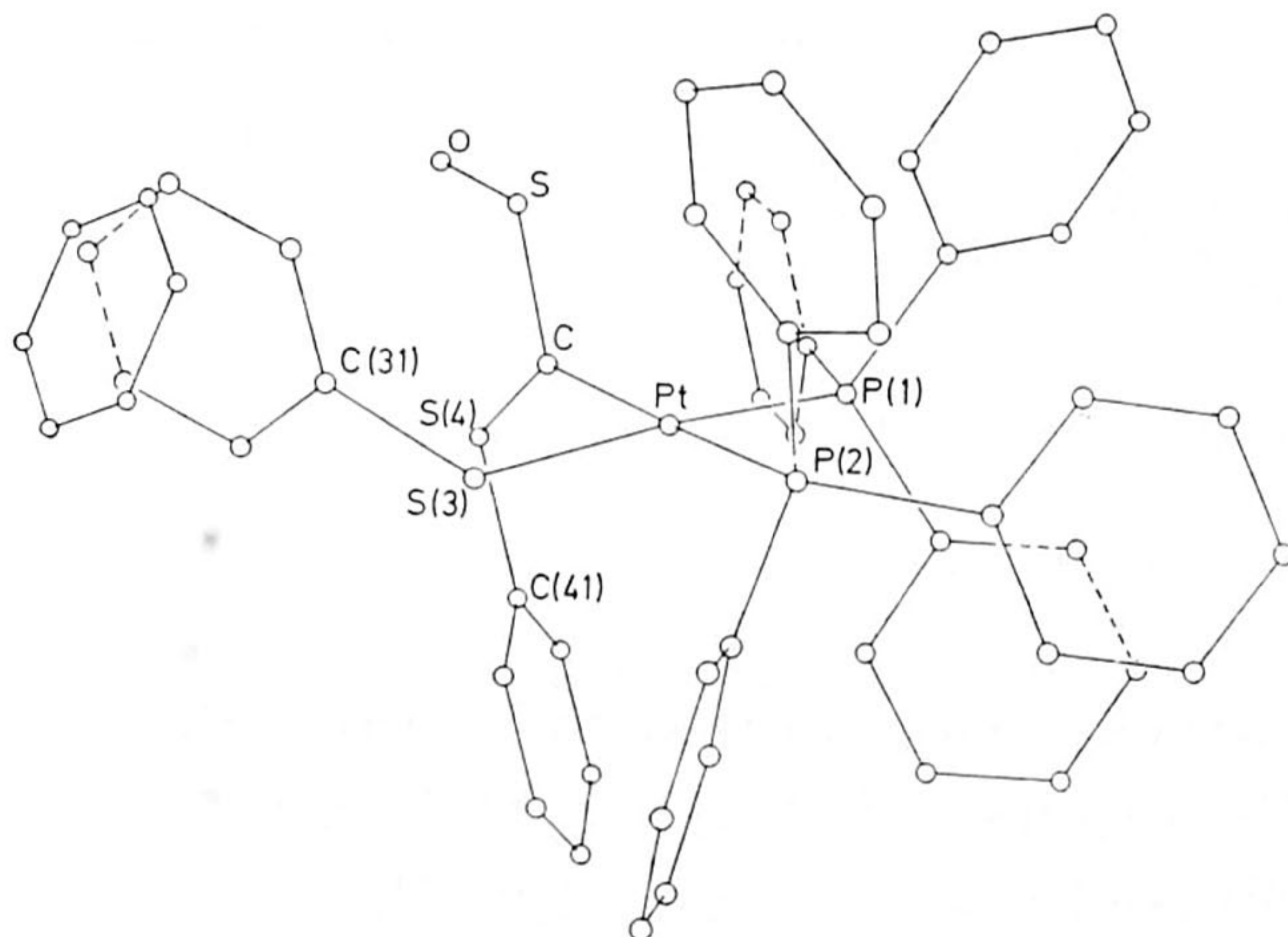


FIGURE. ORTEP drawing of the molecular structure of (*E*)-(**3b**). Important bond angles and distances are: Pt–C, 2.01(1); Pt–P(1), 2.336(4); Pt–P(2), 2.287(3); Pt–S(3), 2.379(4); C–S, 1.65(1); S–O, 1.50(2); C–S(4), 1.73(1) Å; \angle P(1)–Pt–S(3), 82.6(1); P(1)–Pt–P(2), 96.8(1); P(2)–Pt–C, 89.3(4); 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)°.

‡ 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.

§ ³¹P-N.m.r. data of the insertion products are (*E*)-(**3b**): $^1J(\text{Pt}-\text{P}_c)$ 2448 Hz, $^1J(\text{Pt}-\text{P}_s)$ 2985 Hz, and (*Z*)-(**3b**): $^1J(\text{Pt}-\text{P}_c)$ 2296 Hz and $^1J(\text{Pt}-\text{P}_s)$ 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 ¹H-n.m.r. spectra of (*E*)- and (*Z*)-(**3c**) show that the Me-group of the *p*-MeC₆H₄SCSO 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^{II} [*cf.* *s-cis* conformation of (*E*)-(**3b,c**)]. The Me-group of the *p*-MeC₆H₄S–Pt-fragment in both *E*- and *Z*-(**3c**) and of the *p*-MeC₆H₄SCSO-fragment in *Z*-(**3c**) is shifted 0.3 p.p.m. upfield compared to the free ligand, indicating a *gauche* conformation for the *p*-MeC₆H₄SCSO–Pt-fragment in (*Z*)-(**3c**), as was found for (*E*)-(2,4,6-Me₃C₆H₂)(PhS)CSO (ref.5).

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

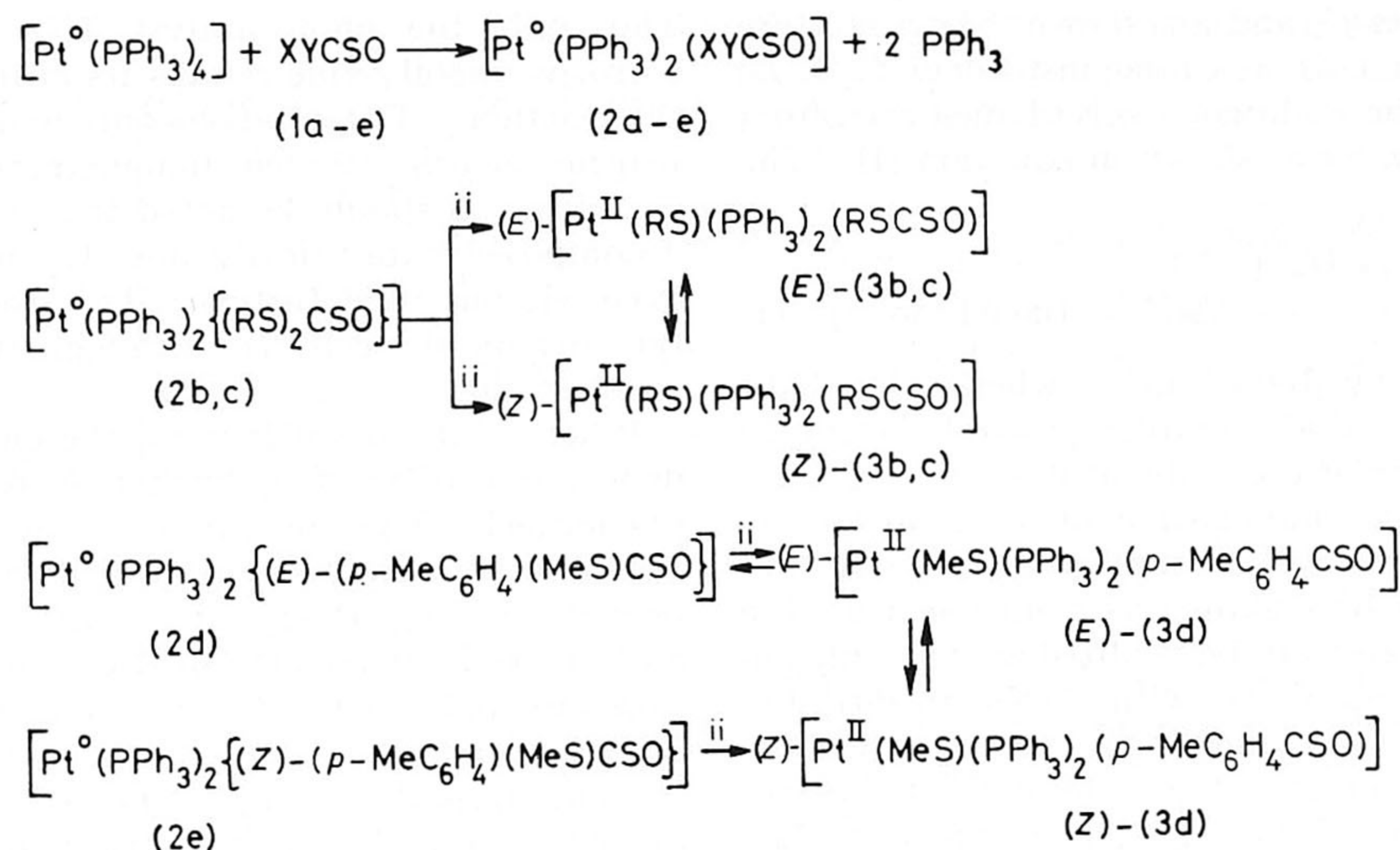
Compound (*E*)-(**3b**) crystallizes preferentially from benzene. A single-crystal X-ray structure determination shows that this isomer has the structural formula (*E*)- $[\text{Pt}^{\text{II}}(\text{PhS})(\text{PPh}_3)_2(\text{PhSCSO})] \cdot \text{C}_6\text{H}_6$ (see Figure). *Crystal data*: orthorhombic, with cell dimensions $a = 10.28$, $b = 21.44$, $c = 21.65$ Å, $U = 4774$ Å³, $Z = 4$, 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 [$I > 2.5\sigma(I)$]. 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-Me₃C₆H₂)(PhS)CSO.⁵ On the basis of this observation and by analogy with the stereoisomerism found in the free sulphines (where $\text{X} \neq \text{Y}$), the O and Pt atoms in (*Z*)-(**3b**)§ are thought to be situated *syn*.

Interestingly, in (**2b**) and (**2e**) the $\text{Pt}^0(\text{PPh}_3)_2$ 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. ³¹P-N.m.r. spectra recorded on a solution of (*E*)-(**3d**) in CDCl₃ 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*-MeC₆H₄CSO 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, $[\text{Pt}^0(\text{PPh}_3)_2\{(Z)-(p\text{-MeC}_6\text{H}_4)(\text{MeS})\text{CSO}\}]$ (**2e**) in the equilibrium mixture, which contains $[\text{Pt}^0(\text{PPh}_3)_2\{(E)-(p\text{-MeC}_6\text{H}_4)(\text{MeS})\text{CSO}\}]$ (**2d**), and (*E*)- and (*Z*)- $[\text{Pt}^{\text{II}}(\text{MeS})(\text{PPh}_3)_2-(p\text{-MeC}_6\text{H}_4\text{CSO})]$ (*E*)- and (*Z*)-(**3d**), and by the quantitative formation of the insertion products (*E*)- and (*Z*)- $[\text{Pt}^{\text{II}}(\text{RS})(\text{PPh}_3)_2(\text{RSCSO})]$ (*E*)- and (*Z*)-(**3b,c**) from $[\text{Pt}^0(\text{PPh}_3)_2\{(\text{RS})_2\text{CSO}\}]$ (**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



- a; X, Y = fluorene-9-ylidene
 b; X = Y = PhS
 c; X = Y = *p*-MeC₆H₄S
 d; X = MeS, Y = *p*-MeC₆H₄ (*E*-isomer)
 e; X = MeS, Y = *p*-MeC₆H₄ (*Z*-isomer)
 i, in benzene or toluene; ii, in CDCl₃
 R = Ph or *p*-MeC₆H₄

SCHEME

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

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of Nijmegen (The Netherlands), for their assistance and useful comments during the syntheses of the sulphines.

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** Preliminary experiments revealed that in *trans*-[Rh^ICl(PCy₃)₂(fluorene-9-ylidene-SO)] (Cy = cyclohexyl) [¹J(Rh-P) 113 Hz, δ(P) 28.8 p.p.m. (relative to 80% H₃PO₄), ν(CSO) 1118, 1090, and 1022 cm⁻¹ (KBr-mulls)] the sulphine ligand is η¹-S bonded. The reaction of [(PCy₃)₂Rh^ICl(C₈H₁₄)] with *Z*-(*p*-MeC₆H₄)(MeS)CSO afforded [Rh^ICl(PCy₃)₂{*Z*-(*p*-MeC₆H₄)(MeS)CSO}] [¹J(Rh-P) 185 Hz, δ(P) 51.0 p.p.m. (relative to 80% H₃PO₄), ν(SO) 1046 cm⁻¹ (KBr-mulls), ³J(Rh-SCH₃) 3 Hz] instead of insertion products. In this compound the sulphine is probably co-ordinated *via* the S-atom and the C=S-fragment.

¹ Th. W. Hummelink, *Cryst. Struct. Comm.*, 1975, **4**, 441.

² R. B. Bates and G. A. Wolfe, *J. Amer. Chem. Soc.*, 1968, **90**, 6854.

³ J. W. Gosselink, G. van Koten, K. Vrieze, B. Zwanenburg, and B. H. M. Lammerink, *J. Organometallic Chem.*, 1979, 179, in the press.

⁴ D. C. Dittmer, K. Takahashi, M. Iwanami, A. I. Tsai, P. L. Chang, B. B. Bildner, and I. K. Stamos, *J. Amer. Chem. Soc.*, 1973, **95**, 6113; *ibid.*, 1976, **98**, 2795.

⁵ A. Tangerman and B. Zwanenburg, *J.C.S. Perkin II*, 1975, 352.

Production of H₂ and CO from Liquid Water and Carbon using Solar Energy

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Summary Gaseous H₂, CO, and CO₂ were produced from water and carbon by photocatalytic processes using TiO₂-RuO₂ as a catalyst.

THE utilization of solar energy is of importance in view of the energy and raw material crises, and several photocatalytic reactions have been reported.¹ Coal gasification or liquefaction is also a topic of current interest. We have therefore studied the use of solid carbon (in place of coal or coke) and liquid water as raw materials for the production of gaseous products by a photocatalytic process.

We report here that gaseous H₂ and CO were produced at around room temperature when an aqueous suspension of carbon with TiO₂-RuO₂ as catalyst was illuminated.

Typically, TiO₂ (30 mg) (Katayama Co.), RuO₂ catalyst (10 mg) (Rare Metallic Co.), and active carbon (0.5 mg) (Katayama Co.) were mixed and rubbed in an agate mortar, and suspended in neutral water (10 ml) in a Pyrex cell which was then evacuated. The mixture was illuminated with a 500 W Xe lamp for 12 h and the gas evolved was trapped at -197 and -78 °C, and analysed by mass spectrometry. The gas was not condensed at -197 °C,