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Intramolecular Rearrangements of Sulfines Coordinated to Platinum. A Unique Equilibrium between Oxidative-Addition Stereoisomers *cis*-(*E*)- and *cis*-(*Z*)-Bis(triphenylphosphine)(methylthio)(arylsulfine)platinum(II) and the Two Stereoisomers of the Reductive Coupling Product Bis(triphenylphosphine)[aryl(methylthio)sulfine]platinum(0). Crystal and Molecular Structure of Bis(triphenylphosphine)(9-sulfinylfluorene)platinum(0)-0.5-Benzene^{1,2}

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An X-ray single-crystal study has revealed the molecular structure of bis(triphenylphosphine)(9-sulfinylfluorene)platinum(0)-0.5-benzene, $[\text{Pt}^0(\text{PPh}_3)_2(\text{C}_{12}\text{H}_8\text{CSO})] \cdot 0.5\text{C}_6\text{H}_6$: monoclinic space group $C2/c$ with unit cell dimensions $a = 12.951$ (4) Å, $b = 17.958$ (5) Å, $c = 37.088$ (8) Å, $\beta = 98.48$ (2)°, $V = 8531.8$ Å³, and $Z = 8$. The crystal structure was solved by standard Patterson and Fourier techniques. Anisotropic blocked full-matrix least-squares refinement with 5884 observed diffractometer data converged to $R_F = 0.038$ ($R_{wF} = 0.041$). The sulfine, $\text{C}_{12}\text{H}_8\text{CSO}$, is coordinated via η^2 -CS to the $\text{Pt}(\text{PPh}_3)_2$ unit. By comparison with the planar free sulfines, the C=S bond is lengthened and the C_{12}H_8 and SO groups bend out of plane. In CDCl_3 the coordination compounds $[\text{Pt}^0(\text{PPh}_3)_2(\text{E})-(\text{MeS})\text{RCSO}]$ and $[\text{Pt}^0(\text{PPh}_3)_2(\text{Z})-(\text{MeS})\text{RCSO}]$ ($\text{R} = \text{Ph}$, $p\text{-MeC}_6\text{H}_4$; η^2 -CS coordinated sulfine stereoisomers) were both converted into an equilibrium mixture of the oxidative-addition stereoisomers *cis*-(*E*)- and *cis*-(*Z*)- $[\text{Pt}^{\text{II}}(\text{MeS})(\text{PPh}_3)_2(\text{RCSO})]$ (in which the $\text{Pt}^0(\text{PPh}_3)_2$ unit is inserted into the C-S side bond) and one coordination stereoisomer, $[\text{Pt}^0(\text{PPh}_3)_2(\text{E})-(\text{MeS})\text{RCSO}]$. Individually, the *cis*-*E* and *cis*-*Z* stereoisomers were likewise converted into the same equilibrium mixture upon dissolution in CDCl_3 , which further illustrates the existence of a unique equilibrium between oxidative addition and reductive coupling products. Only traces of the specific stereoisomer $[\text{Pt}^0(\text{PPh}_3)_2(\text{Z})-(\text{MeS})\text{RCSO}]$ were found in the equilibrium mixture, indicating that η^2 -CS coordinated sulfines which contain a C-S side bond *syn*, as opposed to *anti* (with respect to the SO group), are more reactive toward oxidative addition to Pt^0 . A mechanism is proposed for the intramolecular oxidative-addition process, i.e., gliding movements along S-C=S frames via stereoisomeric intermediates $[\text{Pt}^0(\text{PPh}_3)_2(\text{E})-\text{MeSC}(\text{R})\text{SO}]$ and $[\text{Pt}^0(\text{PPh}_3)_2(\text{Z})-\text{MeSC}(\text{R})\text{SO}]$, in which the sulfines are η^3 -SCS coordinated.

Introduction

Sulfines (thioetone S-oxides, $\text{XYC}=\text{S}=\text{O}$) have a bent planar structure and exist in two stereoisomeric forms if $X \neq Y$. They are heterocumulenic systems,³⁻⁸ related to the sulfinylanilines ($\text{ArN}=\text{S}=\text{O}$) and arylsulfur diimides ($\text{ArN}=\text{S}=\text{NAr}$), whose chemistry is being studied in our laboratory.⁹ The synthesis, chemical reactivity, and structure of sulfines

have been extensively investigated by Zwanenburg et al.¹⁰⁻¹⁷

Dittmer et al.¹⁸ synthesized the first metal-sulfine complexes, i.e., two stereoisomers of $[\text{Fe}(\text{CO})_3(\text{H}_2\text{C}=\text{CHCH}=\text{S}=\text{O})]$, containing an η^2 -CS coordinated sulfine moiety, by oxidation of $[\text{Fe}(\text{CO})_3(\text{H}_2\text{C}=\text{CHCH}=\text{S})]$ with hydrogen peroxide.

A proper choice of the nature of the metal center for sulfine coordination is important; Alper¹⁹ found that ($p\text{-MeOC}_6\text{H}_4$)₂C=S=O was deoxygenated by $[\text{Fe}_2(\text{CO})_9]$, rather than forming an iron-sulfine complex. Götzfried and Beck²⁰ found that the reaction of $[\text{W}(\text{CO})_5(\text{THF})]$ with 9-sulfinylfluorene ($\text{C}_{12}\text{H}_8\text{C}=\text{S}=\text{O}$) yielded unstable $[\text{W}(\text{CO})_5(\text{C}_{12}\text{H}_8\text{CSO})]$, which decomposed forming thiofluorenone. Recently, we reported²¹ the first series of metal-sulfine complexes, i.e., $[\text{Pt}^0(\text{PPh}_3)_2(\text{XYCSO})]$ ($X, Y = \text{aryl}, S\text{-aryl}, S\text{-alkyl}, \text{Cl}$), which were synthesized from stable sulfines. Spectroscopic data suggest that the sulfine ligands in these complexes are η^2 -CS coordinated. Furthermore, since we found that (*E*)- $(\text{MeS})\text{RC}=\text{S}=\text{O}$ ($\text{R} = \text{Ph}, p\text{-MeC}_6\text{H}_4$) reacted with $[\text{Pt}^0(\text{PPh}_3)_4]$, resulting in the formation of $[\text{Pt}^0(\text{PPh}_3)_2(\text{E})-(\text{MeS})\text{RCSO}]$, while from the *Z* stereoisomer $[\text{Pt}^0(\text{PPh}_3)_2(\text{Z})-(\text{MeS})\text{RCSO}]$ was obtained, stereospecific coordination is indicated. Independently, Götzfried and Beck²⁰ have synthesized the metal-sulfine complexes $[\text{M}^0(\text{PPh}_3)_2(\text{R}_1\text{R}_2\text{CSO})]$ ($\text{M} = \text{Pt}, \text{Pd}; \text{R}_1\text{R}_2 = \text{C}_{12}\text{H}_8$ and $\text{R}_1 = 2\text{-methoxy-1-naphthyl}, \text{R}_2 = \text{H}$).

It is of interest that sulfines that have RS substituents on carbon may after η^2 -CS coordination undergo an oxidative-addition reaction of the C-S single bond; such reactions have

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- (1) Coordination Chemistry of Sulfines. 2. See ref 21 for part 1.
- (2) *E* and *Z* refer to the configuration of the sulfine C=S bond. If these are placed inside the molecular formula, this indicates that the sulfine has the *E* or *Z* configuration and is coordinated as such (η^2 -CS or η^3 -SCS). If these are placed before the molecular formula, this indicates that the $\text{PtXC}=\text{S}=\text{O}$ entity as a whole has the *E* or *Z* configuration, with η^1 -C coordination.
- (3) Hummelink, Th. W. *Cryst. Struct. Commun.* **1975**, *4*, 441-444; Ph.D. Thesis, University of Nijmegen, 1974.
- (4) Bates, R. B.; Wolfe, G. A. *J. Am. Chem. Soc.* **1968**, *90*, 6854-6855.
- (5) Snijder, J. P.; Harpp, D. N. *J. Chem. Soc., Chem. Commun.* **1972**, 1305-1306.
- (6) Bonini, B. F.; Lunazzi, L.; Maccagnani, G.; Mazzanti, G. *J. Chem. Soc., Perkin Trans. 1* **1973**, 2314-2319.
- (7) King, J. F.; Durst, T. *J. Am. Chem. Soc.* **1963**, *85*, 2676-2677.
- (8) Tangerman, A. Ph.D. Thesis, University of Nijmegen, 1974.
- (9) Meij, R.; Stufkens, D. J.; Vrieze, K. *J. Organomet. Chem.* **1978**, *144*, 239-253; **1978**, *155*, 323-336; **1979**, *164*, 353-370. Vrieze, K.; van Koten, G. *Recl. Trav. Chim. Pays-Bas* **1980**, *99*, 145-153.
- (10) Veenstra, G. E.; Zwanenburg, B. *Recl. Trav. Chim. Pays-Bas* **1976**, *95*, 28-30, 37-39, 195-201, 202-205; *Tetrahedron* **1978**, *34*, 1585-1592.
- (11) Bonini, B. F.; Maccagnani, G.; Mazzanti, G.; Zwanenburg, B. *Gazz. Chim. Ital.* **1977**, *107*, 283-287, 289-292.
- (12) Bonini, B. F.; Maccagnani, G.; Thijs, L.; Zwanenburg, B. *Tetrahedron Lett.* **1973**, 3569-3572.
- (13) Bonini, B. F.; Maccagnani, G.; Mazzanti, G.; Thijs, L.; Ambrosius, H. P. M. M.; Zwanenburg, B. *J. Chem. Soc., Perkin Trans. 1* **1977**, 1468-1471.
- (14) Zwanenburg, B.; Thijs, L.; Broens, J. B.; Strating, J. *Recl. Trav. Chim. Pays-Bas* **1972**, *91*, 443-451.
- (15) Thijs, L.; Strating, J.; Zwanenburg, B. *Recl. Trav. Chim. Pays-Bas* **1972**, *91*, 1345-1351.
- (16) Tangerman, A.; Zwanenburg, B. *Recl. Trav. Chim. Pays-Bas* **1977**, *96*, 196-199; *J. Chem. Soc., Perkin Trans. 2* **1974**, 1141-1145; **1975**, 916-924; *Tetrahedron Lett.* **1972**, 5329-5332.

- (17) van Lierop, J.; van der Avoird, A.; Zwanenburg, B. *Tetrahedron* **1977**, *33*, 539-545.
- (18) Dittmer, D. C.; Takahashi, K.; Iwanami, M.; Tsai, A. I.; Chang, P. L.; Bildner, B. B.; Stamos, I. K. *J. Am. Chem. Soc.* **1973**, *95*, 6113-6114; **1976**, *98*, 2795-2803.
- (19) Alper, H. *J. Organomet. Chem.* **1975**, *34*, 347-350.
- (20) Götzfried, F.; Beck, W. *J. Organomet. Chem.* **1980**, *191*, 329-338.
- (21) Gosselink, J. W.; van Koten, G.; Vrieze, K.; Zwanenburg, B.; Lammerink, B. H. M. *J. Organomet. Chem.* **1979**, *179*, 411-419.

been previously reported, e.g., for $\overline{\text{SCH}_2\text{CH}_2\text{SC}=\text{S}}$.²² In this paper we report the oxidative addition of the η^2 -CS coordinated sulfines in $[\text{Pt}^0(\text{PPh}_3)_2](E)\text{-}(\text{MeS})\text{RC}(\text{SO})]$ and $[\text{Pt}^0(\text{PPh}_3)_2](Z)\text{-}(\text{MeS})\text{RC}(\text{SO})]$ ($R = \text{Ph}, p\text{-MeC}_6\text{H}_4$). This leads to the formation of the stereoisomers *cis*-(*E*)- and *cis*-(*Z*)- $[\text{Pt}^{\text{II}}(\text{MeS})(\text{PPh}_3)_2(\text{RC}(\text{SO}))]$, which are representatives of a novel type of metal-sulfine complex.²³ In solution the oxidative addition and the coordination (reductive coupling) stereoisomers from these complexes are in equilibrium.

The X-ray structure determination of $[\text{Pt}^0(\text{PPh}_3)_2(\text{C}_{12}\text{H}_8\text{CSO})]\cdot 0.5\text{C}_6\text{H}_6$ has been carried out and is, to our knowledge, the first reported structure analysis of an η^2 -CS bonded sulfine-metal complex.

Experimental Section

IR spectra were recorded on a Perkin-Elmer 283 spectrophotometer. ¹H and ³¹P NMR spectra were recorded on a Varian T60A, HA 100, or XL 100 spectrometer. Molecular weights were determined with a Hewlett-Packard vapor-pressure osmometer, Model 320 B. Elemental analyses were carried out by the Analytical Section of the Institute for Organic Chemistry TNO, Utrecht, The Netherlands.

Preparation of the Compounds. The sulfines, $\text{C}_{12}\text{H}_8\text{CSO}$,²⁴ (*E*)- and (*Z*)-(R'S)RC(SO) ($R = \text{Ph}, p\text{-MeC}_6\text{H}_4$; $R' = \text{Me}, ^{13}\text{CH}_3$),¹⁰ and the coordination compounds $[\text{Pt}^0(\text{PPh}_3)_2](E)\text{-}(\text{R}'\text{S})\text{RC}(\text{SO})]$ and $[\text{Pt}^0(\text{PPh}_3)_2](Z)\text{-}(\text{R}'\text{S})\text{RC}(\text{SO})]$ ($R = p\text{-MeC}_6\text{H}_4, \text{Ph}$ and $R' = \text{Me}$; $R = \text{Ph}$ and $R' = ^{13}\text{CH}_3$)²¹ were prepared according to literature procedures.

$[\text{Pt}^0(\text{PPh}_3)_2(\text{C}_{12}\text{H}_8\text{CSO})]\cdot 0.5\text{C}_6\text{H}_6$. Under a nitrogen atmosphere with the use of Schlenk apparatus, $[\text{Pt}^0(\text{PPh}_3)_4]$ (0.2 mmol) and $\text{C}_{12}\text{H}_8\text{CSO}$ (0.2 mmol) were stirred in benzene (ca. 2 cm³) for ca. 2 min. After the mixture was allowed to stand at room temperature, yellow crystals of $[\text{Pt}^0(\text{PPh}_3)_2(\text{C}_{12}\text{H}_8\text{CSO})]\cdot 0.5\text{C}_6\text{H}_6$ formed, which were isolated by decantation. Anal. Calcd for $\text{C}_{52}\text{H}_{41}\text{OP}_2\text{PtS}$: C, 64.32; H, 4.26; P, 6.38; S, 3.30. Found: C, 64.4; H, 4.4; P, 6.7; S, 3.2.

cis-(*E*)- $[\text{Pt}^{\text{II}}(\text{MeS})(\text{PPh}_3)_2(p\text{-MeC}_6\text{H}_4\text{CSO})]\cdot 0.8\text{CDCl}_3$. A layer of hexane was placed on a CDCl_3 solution of $[\text{Pt}^0(\text{PPh}_3)_2](E)\text{-}(\text{MeS})(p\text{-MeC}_6\text{H}_4\text{CSO})]$ and *cis*-(*E*)- and *cis*-(*Z*)- $[\text{Pt}^{\text{II}}(\text{MeS})(\text{PPh}_3)_2(p\text{-MeC}_6\text{H}_4\text{CSO})]$ in ca. 1:1:1 molar ratio (the latter mixture was obtained from $[\text{Pt}^0(\text{PPh}_3)_2](E)\text{-}(\text{MeS})(p\text{-MeC}_6\text{H}_4\text{CSO})]$ or $[\text{Pt}^0(\text{PPh}_3)_2](Z)\text{-}(\text{MeS})(p\text{-MeC}_6\text{H}_4\text{CSO})]$). During 2 days slow precipitation of yellow crystalline *cis*-(*E*)- $[\text{Pt}^{\text{II}}(\text{MeS})(\text{PPh}_3)_2(p\text{-MeC}_6\text{H}_4\text{CSO})]\cdot 0.8\text{CDCl}_3$ occurred; yield ca. 60%. Anal. Calcd for $\text{C}_{45.8}\text{H}_{40}\text{Cl}_{2.4}\text{OD}_{0.8}\text{P}_2\text{PtS}_2$: C, 54.23; H, 4.14; Cl, 8.39; O, 1.58. Found: C, 54.1; H, 4.1; Cl, 8.3; O, 1.4. Molecular weight (CHCl_3): calcd, 1014; found, 957.

A 4:1 Molar Mixture of *cis*-(*Z*)- and *cis*-(*E*)- $[\text{Pt}^{\text{II}}(\text{MeS})(\text{PPh}_3)_2(p\text{-MeC}_6\text{H}_4\text{CSO})]$. Under nitrogen atmosphere with the use of Schlenk apparatus, $[\text{Pt}^0(\text{PPh}_3)_4]$ (0.2 mmol) and a mixture of (*E*)- and (*Z*)- $(\text{MeS})(p\text{-MeC}_6\text{H}_4\text{CSO})]$ (0.2 mmol) were stirred in benzene (2–3 cm³) for about 2 min. After a few days yellow crystalline *cis*-(*Z*)- and *cis*-(*E*)- $[\text{Pt}^{\text{II}}(\text{MeS})(\text{PPh}_3)_2(p\text{-MeC}_6\text{H}_4\text{CSO})]$ (molar ratio 4:1) were formed; total yield 45%. Anal. Calcd for $\text{C}_{45}\text{H}_{40}\text{OP}_2\text{PtS}_2$: C, 58.87; H, 4.40; O, 1.74. Found: C, 59.0; H, 4.5; O, 1.8. When the same procedure was followed with (*E*)- $(\text{MeS})\text{PhCSO}$, $[\text{Pt}^0(\text{PPh}_3)_2][(E)\text{-}(\text{MeS})\text{PhCSO}]$ was isolated exclusively, instead of the expected *cis*-(*Z*)- $[\text{Pt}^{\text{II}}(\text{MeS})(\text{PPh}_3)_2(\text{PhCSO})]$.

Crystallographic Data. Crystal data for $[\text{Pt}^0(\text{PPh}_3)_2(\text{C}_{12}\text{H}_8\text{CSO})]\cdot 0.5\text{C}_6\text{H}_6$: yellow, monoclinic, space group $C2/c$, $Z = 8$, unit cell parameters $a = 12.951$ (4) Å, $b = 17.958$ (5) Å, $c = 37.088$ (8) Å, $\beta = 98.48$ (2)°, $V = 8531.8$ Å³, $d(\text{obsd}) = 1.49$ (1) g/cm³, $d(\text{calcd}) = 1.512$ g/cm³, mol wt 971.0, $F(000) = 3880$, $\mu(\text{Mo K}\alpha) = 32.9$ cm⁻¹.

The quality of a crystal was examined by preliminary Weissenberg photographs; it was then transferred to an Enraf-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

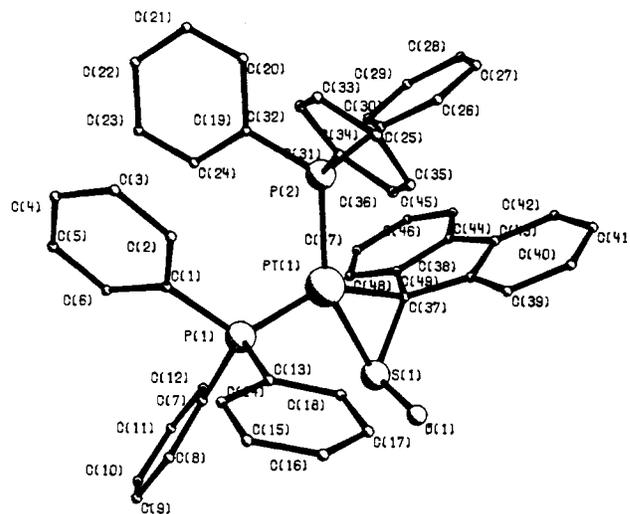


Figure 1. PLUTO drawing³¹ of $[\text{Pt}^0(\text{PPh}_3)_2(\text{C}_{12}\text{H}_8\text{CSO})]$.

of the angular settings of 24 carefully centered reflections (Mo $K\alpha$ radiation; $\lambda = 0.71069$ Å).²⁵ The standard deviations in the lattice parameters were obtained from the comparison of the deviations from integer values of the indexes, calculated with the orientational matrix, for the angular settings of the orientation reflections as described by Duisenberg.²⁶

Data Collection and Reduction. Intensity data up to $\theta = 25^\circ$ were collected in the $\omega/2\theta$ scan mode with the CAD4 diffractometer using zirconium-filtered Mo $K\alpha$ radiation. The applied scan angle was $\Delta\omega = (0.45 + 0.35 \tan \theta)^\circ$. Two standard reflections (114 and 135) were used, and their intensities were monitored after every 0.5 h of X-ray exposure time. There was no indication of decay during data collection. A total of 6591 unique reflections were collected of which 5884 with $I > 2.5\sigma(I)$ were used in subsequent structure analysis. Correction for absorption: crystal dimensions (110 → 110) 0.26 mm, (001 → 001) 0.25 mm, (110 → 110) 0.45 mm; minimum/maximum correction 1.43/1.56. Corrections for Lorentz and polarization effects, fluctuations in the reference reflections (3%), and data averaging were carried out in the usual way.

Structure Determination. The structure was solved with the application of standard Patterson and Fourier techniques refined by anisotropic blocked full-matrix least-squares techniques. Hydrogen atoms were included at calculated positions and refined in the riding mode on the parameters of the atom to which they were attached. Refinement converged to a final $R_F = 0.038$ ($R_{wF} = 0.041$) with $w^{-1} = [\sigma^2(F) + 0.001F^2]/0.1175$ for 5884 observed reflections.²⁷ A final difference Fourier synthesis showed no significant features. Calculations were carried out either with the ILIAS system,²⁸ on an in-house Data General Eclipse/S230 minicomputer, or on the Cyber 175 of the university computer center (XRAY76²⁹ (ABSORB), ORTEP,³⁰ PLUTO³¹). The atomic coordinates and the thermal parameters are tabulated in Table I.

Results

i. Description of the Structure of $[\text{Pt}^0(\text{PPh}_3)_2(\text{C}_{12}\text{H}_8\text{CSO})]\cdot 0.5\text{C}_6\text{H}_6$. The crystal structure of $[\text{Pt}^0(\text{PPh}_3)_2(\text{C}_{12}\text{H}_8\text{CSO})]\cdot 0.5\text{C}_6\text{H}_6$ consists of eight discrete sulfine complexes per unit cell and four molecules of benzene, which

- (22) Dobrzynski, E. D.; Angelici, R. J. *J. Organomet. Chem.* **1974**, *76*, C53–C55.
 (23) Gosselink, J. W.; Brouwers, A. M. F.; van Koten, G.; Vrieze, K. *J. Chem. Soc., Chem. Commun.* **1979**, 1045–1047.
 (24) van der Leij, M.; Porskamp, P. A. T. W.; Lammerink, B. H. M.; Zwanenburg, B. *Tetrahedron Lett.* **1978**, 811–814.

- (25) "CAD-4 Users Manual"; Enraf-Nonius: Delft, The Netherlands, 1972.
 (26) Duisenberg, A. J. M. "Collected Abstracts of the First European Enraf-Nonius CAD-4 Users Meeting, Paris, June 1974"; Enraf-Nonius: Delft, 1974.
 (27) The function minimized was $\sum(w(|F_o| - |F_c|))^2$. The refinement was on F . The unweighted and weighted residuals are defined as follows: $R_F = (\sum|F_o| - |F_c|)/\sum|F_o|$ and $R_{wF} = [(\sum w(|F_o| - |F_c|))^2 / (\sum w|F_o|^2)]^{1/2}$.
 (28) ILIAS system: a locally modified and extended minicomputer implementation of the SHELX-76 system of G. Sheldrick.
 (29) Stewart, J. M., Ed. Technical Report TR-446 of the Computer Science Center; University of Maryland Press: College Park, Md., 1976.
 (30) Johnson, C. K. "ORTEP", Report ORNL-3794; Oak Ridge National Laboratory: Oak Ridge, Tenn., 1965.
 (31) PLUTO: program for the preparation of crystal structure drawings by S. Motherwell and modified by B. Clegg.

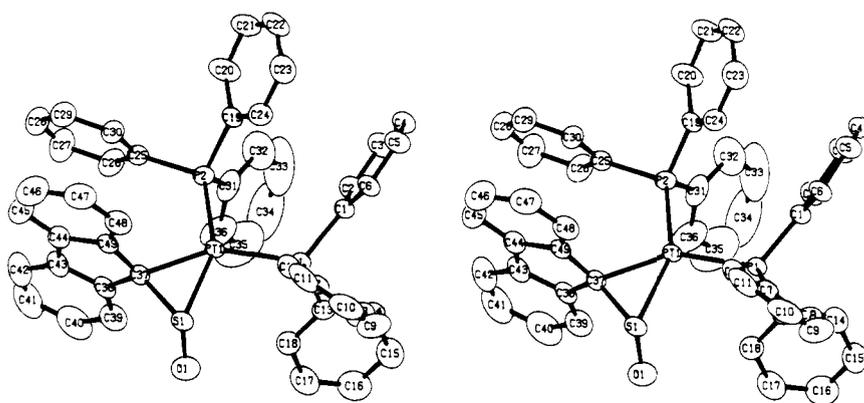


Figure 2. ORTEP³⁰ stereoview of [Pt⁰(PPh₃)₂(C₁₂H₈CSO)].

occupy interstitial sites. The molecular geometry and the adopted numbering scheme is shown in a PLUTO³¹ drawing (Figure 1). Thermal vibrational ellipsoids are shown in an ORTEP³⁰ stereoview (Figure 2). Relevant interatomic distances and bond angles are listed in Tables II and III, respectively. All bond distances and angles are within the expected range. Least-squares planes are given in Table IV.

The coordination around platinum is approximately planar, comprising the two mutually *cis* P atoms and the C=S bond. P(1) and P(2) are only 0.03 and 0.17 Å, respectively, out of the plane determined by Pt(1), S(1), and C(37) on the side of O(1). The dihedral angle between the least-squares plane through the C₁₂H₈C fragment and the plane through Pt(1), S(1), C(37) is 90°. The angle between the line through C(37) and S(1) and the least-squares plane through the C₁₂H₈C fragment is 32° (cf. K⁺[Pt^{II}Cl₃(C₂H₄)];³² the angle between the C=C vector and the planes through the CH₂ fragments is 16°). This points to a change of the hybridization at the C atom of the C=S=O moiety from sp² to sp³ as a result of the η²-CS coordination. A similar change is found for the N atom of the sulfinylaniline 2,4,6-Me₃C₆H₂N=S=O upon η²-NS coordination to the Pt⁰(PPh₃)₂ unit, as has been established by comparison of the electron diffraction data of (*Z*)-MeN=S=O^{3,33} and the crystal structure data of [Pt⁰(PPh₃)₂(2,4,6-Me₃C₆H₂NSO)].⁹ The latter compound is isoelectronic and isostructural with the present Pt-sulfine complex. The S=O group in the present complex is also bent out of the original free sulfine plane upon η²-CS coordination as evidenced by the dihedral angle between the planes through Pt(1), C(37), S(1) and C(37), S(1), O(1) which differs markedly from 90° (75°). The S=O bond length (1.471 (6) Å) and the C=S=O bond angle (113.9 (3)°) hardly differ from those in free sulfines (varying from 1.432 (7) to 1.50 (1) Å and from 109.4 (7) to 115.2 (2)°, respectively)^{3,4} and in *cis*-(*E*)-[Pt^{II}(PhS)(PPh₃)₂(PhSCSO)]·C₆H₆ (1.51 (2) Å and 115.7 (9)°, respectively).^{23,24} The π coordination causes a lengthening of the C=S bond. This bond distance in the present complex is 1.762 (5) Å, while in the free sulfines it varies from 1.50 (1) to 1.640 (7) Å^{3,4} and in the metal-substituted sulfine *cis*-(*E*)-[Pt^{II}(PhS)(PPh₃)₂(PhSCSO)]·C₆H₆ it is 1.65 (1) Å.^{23,34}

ii. Structures of [Pt⁰(PPh₃)₂[(*E*)-(MeS)RCSO]] and [Pt⁰(PPh₃)₂[(*Z*)-(MeS)RCSO]] (R = Ph, *p*-MeC₆H₄). As a result of the known molecular structure of [Pt⁰(PPh₃)₂(C₁₂H₈CSO)]·0.5C₆H₆, valuable spectroscopic assignment

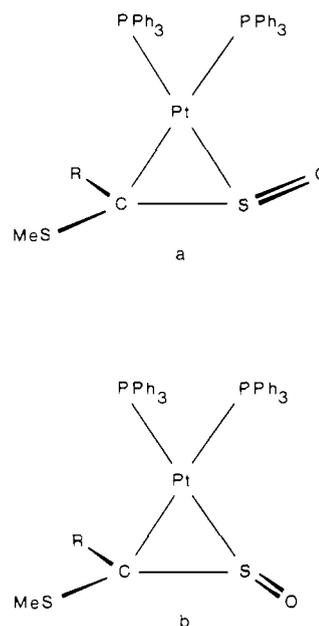


Figure 3. Structures of [Pt⁰(PPh₃)₂[(*E*)-(MeS)RCSO]] (a) and [Pt⁰(PPh₃)₂[(*Z*)-(MeS)RCSO]] (b) (R = *p*-MeC₆H₄, Ph).

criteria for η²-CS bonded sulfines are now available. For example, in the IR spectra the observation of one strong cumulene absorption (ν(CSO), probably mainly ν(SO)) at ca. 1010 cm⁻¹ (KBr mull) is indicative of this type of coordination. Furthermore, the ³¹P NMR spectra, recorded directly after dissolution of the compounds in CDCl₃, are characteristic, showing two nonequivalent ¹J(Pt-P) values between 3700 and 3200 Hz.²¹ On this basis the stereoisomers [Pt⁰(PPh₃)₂[(*E*)-(MeS)RCSO]] and [Pt⁰(PPh₃)₂[(*Z*)-(MeS)RCSO]] contain η²-CS bonded (MeS)RCSO (see Figure 3 and Table V).

By synthesizing the ¹³C-enriched coordination stereoisomers [Pt⁰(PPh₃)₂[(*E*)-(¹³CH₃S)PhCSO]] and [Pt⁰(PPh₃)₂[(*Z*)-(¹³CH₃S)PhCSO]], we are able to assign the ¹J(Pt-P) values to the specific P atoms. The ³¹P NMR spectra recorded on CDCl₃ solutions of these complexes showed a ⁴J(¹³C-P) coupling of 10 Hz as well as a coupling on the P atom of the *E* isomer with ¹J(Pt-P) = 3428 Hz and a coupling in the *Z* isomer with ¹J(Pt-P) = 3360 Hz. These ¹J(Pt-P) values now can be assigned to P atoms *trans* to C atoms of the C=S=O moieties. On the other P atoms, coordinated *trans* to the S atoms of the C=S=O moieties, no ⁴J(¹³C-P) coupling is found.

iii. Structures and Assignment of the Spectroscopic Data of *cis*-(*E*)- and *cis*-(*Z*)-[Pt^{II}(MeS)(PPh₃)₂(RCSO)] (R = Ph, *p*-MeC₆H₄). Under particular conditions the reaction of

(32) Love, R. A.; Koetzle, T. F.; Williams, G. J. B.; Andrews, L. C.; Bau, R. *Inorg. Chem.* **1975**, *14*, 2653-2657.

(33) Beagly, B.; Chantrelle, S. J.; Kirby, R. G.; Schmidling, D. G. *J. Mol. Struct.* **1975**, *25*, 319-327.

(34) Gosselink, J. W.; van Koten, G.; Brouwers, A. M. F.; Overbeek, O. J. *Chem. Soc., Dalton Trans.* **1981**, 342-352.

Table I. Positional and Thermal Parameters^a and Their Esd's^b for [Pt⁰(PPh₃)₂(C₁₂H₈CSO)]·0.5C₆H₆

atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U</i> (1,1)	<i>U</i> (2,2)	<i>U</i> (3,3)	<i>U</i> (2,3)	<i>U</i> (1,3)	<i>U</i> (1,2)
Pt(1)	0.13050 (1)	-0.06602 (1)	0.39076 (1)	0.0331 (1)	0.0238 (1)	0.0497 (2)	0.00066 (9)	0.00101 (9)	-0.00258 (8)
S(1)	0.0657 (1)	-0.18396 (7)	0.39871 (5)	0.0451 (8)	0.0249 (7)	0.085 (1)	0.0037 (7)	0.0040 (7)	-0.0041 (6)
P(1)	0.3063 (1)	-0.08842 (8)	0.39457 (4)	0.0333 (7)	0.0277 (6)	0.0555 (9)	-0.0009 (6)	0.0018 (6)	-0.0022 (5)
P(2)	0.1065 (1)	0.05811 (7)	0.37643 (4)	0.0421 (7)	0.0272 (7)	0.0458 (8)	0.0043 (6)	0.0068 (6)	0.0002 (6)
O(1)	0.0638 (4)	-0.2329 (3)	0.3668 (2)	0.080 (3)	0.052 (3)	0.113 (4)	-0.015 (3)	0.020 (3)	-0.003 (3)
C(1)	0.3987 (4)	-0.0121 (3)	0.4036 (2)	0.037 (3)	0.033 (3)	0.055 (3)	-0.005 (2)	0.003 (2)	-0.004 (2)
C(2)	0.4058 (5)	0.0405 (3)	0.3765 (2)	0.053 (4)	0.042 (3)	0.067 (4)	0.008 (3)	0.009 (3)	-0.007 (3)
C(3)	0.4682 (5)	0.1030 (4)	0.3837 (2)	0.060 (4)	0.044 (4)	0.084 (5)	0.010 (3)	0.008 (4)	-0.012 (3)
C(4)	0.5241 (5)	0.1134 (3)	0.4181 (2)	0.049 (4)	0.037 (3)	0.095 (5)	-0.003 (3)	0.010 (4)	-0.010 (3)
C(5)	0.5180 (5)	0.0621 (3)	0.4454 (2)	0.058 (4)	0.048 (4)	0.071 (4)	-0.008 (3)	-0.001 (3)	-0.008 (3)
C(6)	0.4576 (4)	-0.0008 (3)	0.4376 (2)	0.043 (3)	0.033 (3)	0.077 (4)	0.001 (3)	-0.004 (3)	-0.008 (2)
C(7)	0.3507 (4)	-0.1511 (3)	0.4325 (2)	0.041 (3)	0.028 (3)	0.068 (4)	-0.003 (2)	-0.001 (3)	-0.009 (2)
C(8)	0.4361 (5)	-0.1972 (4)	0.4331 (2)	0.071 (4)	0.051 (4)	0.074 (5)	-0.002 (3)	-0.002 (4)	0.014 (3)
C(9)	0.4716 (7)	-0.2379 (4)	0.4652 (3)	0.097 (6)	0.046 (4)	0.099 (6)	0.003 (4)	-0.022 (5)	0.026 (4)
C(10)	0.4240 (7)	-0.2316 (4)	0.4949 (2)	0.103 (6)	0.046 (4)	0.072 (5)	0.013 (4)	-0.022 (5)	-0.022 (4)
C(11)	0.3374 (6)	-0.1873 (4)	0.4941 (2)	0.074 (5)	0.068 (5)	0.061 (4)	0.008 (4)	-0.011 (4)	-0.038 (4)
C(12)	0.2997 (5)	-0.1468 (3)	0.4629 (2)	0.047 (3)	0.048 (3)	0.072 (4)	0.000 (3)	0.002 (3)	-0.010 (3)
C(13)	0.3406 (4)	-0.1312 (3)	0.3536 (2)	0.051 (3)	0.031 (3)	0.058 (4)	0.002 (2)	0.011 (3)	0.001 (2)
C(14)	0.4422 (5)	-0.1328 (4)	0.3456 (2)	0.060 (4)	0.072 (4)	0.087 (5)	-0.024 (4)	0.024 (4)	-0.019 (3)
C(15)	0.4644 (6)	-0.1671 (5)	0.3140 (2)	0.073 (5)	0.097 (6)	0.105 (7)	-0.029 (5)	0.046 (5)	-0.023 (4)
C(16)	0.3853 (7)	-0.1998 (5)	0.2902 (2)	0.110 (7)	0.094 (6)	0.072 (5)	-0.024 (5)	0.031 (5)	-0.016 (5)
C(17)	0.2867 (6)	-0.1988 (5)	0.2981 (2)	0.077 (5)	0.088 (6)	0.071 (5)	-0.022 (4)	0.011 (4)	-0.023 (4)
C(18)	0.2624 (5)	-0.1653 (3)	0.3295 (2)	0.053 (4)	0.053 (3)	0.063 (4)	-0.011 (3)	0.006 (3)	-0.001 (3)
C(19)	0.1736 (4)	0.1275 (3)	0.4066 (2)	0.039 (3)	0.036 (3)	0.070 (4)	-0.007 (3)	0.012 (3)	-0.010 (2)
C(20)	0.1567 (6)	0.2059 (4)	0.3983 (2)	0.093 (6)	0.047 (4)	0.107 (6)	-0.012 (4)	0.010 (5)	-0.019 (4)
C(21)	0.2082 (7)	0.2568 (4)	0.4215 (3)	0.078 (6)	0.033 (4)	0.20 (1)	-0.018 (5)	0.007 (7)	-0.012 (4)
C(22)	0.2764 (7)	0.2363 (5)	0.4507 (3)	0.072 (5)	0.078 (6)	0.17 (1)	-0.064 (6)	0.041 (6)	-0.041 (5)
C(23)	0.2909 (6)	0.1609 (5)	0.4602 (2)	0.062 (5)	0.096 (6)	0.091 (6)	-0.037 (5)	0.007 (4)	-0.010 (4)
C(24)	0.2384 (5)	0.1081 (3)	0.4377 (2)	0.056 (4)	0.048 (3)	0.058 (4)	-0.010 (3)	0.020 (3)	-0.006 (3)
C(25)	-0.0280 (4)	0.0914 (3)	0.3726 (2)	0.041 (3)	0.026 (2)	0.063 (4)	0.008 (2)	0.007 (3)	-0.000 (2)
C(26)	-0.0900 (5)	0.1040 (4)	0.3395 (2)	0.060 (4)	0.067 (4)	0.067 (5)	0.006 (3)	0.002 (3)	0.021 (3)
C(27)	-0.1903 (6)	0.1300 (5)	0.3396 (3)	0.056 (4)	0.101 (6)	0.104 (7)	0.008 (5)	-0.008 (4)	0.024 (4)
C(28)	-0.2314 (6)	0.1452 (4)	0.3704 (3)	0.053 (4)	0.062 (4)	0.114 (7)	0.007 (4)	0.013 (4)	0.011 (3)
C(29)	-0.1701 (5)	0.1310 (4)	0.4033 (2)	0.066 (4)	0.059 (4)	0.101 (6)	-0.013 (4)	0.037 (4)	-0.005 (3)
C(30)	-0.0699 (5)	0.1041 (3)	0.4043 (2)	0.048 (3)	0.045 (3)	0.071 (4)	0.002 (3)	0.018 (3)	0.002 (3)
C(31)	0.1451 (5)	0.0760 (4)	0.3319 (2)	0.052 (4)	0.079 (5)	0.051 (4)	0.026 (3)	0.019 (3)	0.022 (3)
C(32)	0.2050 (7)	0.1357 (5)	0.3244 (3)	0.099 (7)	0.106 (7)	0.101 (8)	0.049 (6)	0.024 (6)	-0.013 (5)
C(33)	0.2359 (9)	0.1380 (8)	0.2890 (4)	0.091 (7)	0.24 (2)	0.14 (1)	0.14 (1)	0.041 (7)	0.011 (8)
C(34)	0.201 (1)	0.087 (1)	0.2628 (3)	0.13 (1)	0.35 (2)	0.067 (7)	0.05 (1)	0.042 (7)	0.07 (1)
C(35)	0.148 (1)	0.0297 (9)	0.2721 (3)	0.24 (2)	0.22 (1)	0.069 (7)	-0.015 (8)	0.061 (9)	0.05 (1)
C(36)	0.1164 (7)	0.0241 (5)	0.3049 (2)	0.124 (8)	0.100 (7)	0.069 (5)	-0.004 (4)	0.034 (5)	0.031 (6)
C(37)	-0.0219 (4)	-0.1085 (3)	0.3916 (2)	0.033 (3)	0.030 (3)	0.061 (4)	0.003 (2)	0.002 (2)	-0.003 (2)
C(38)	-0.1018 (4)	-0.1037 (3)	0.3581 (2)	0.039 (3)	0.036 (3)	0.075 (4)	0.002 (3)	-0.003 (3)	-0.011 (2)
C(39)	-0.0941 (6)	-0.1236 (4)	0.3228 (2)	0.064 (5)	0.065 (4)	0.086 (5)	-0.007 (4)	-0.005 (4)	-0.008 (3)
C(40)	-0.1797 (8)	-0.1126 (5)	0.2962 (3)	0.106 (7)	0.105 (7)	0.069 (6)	-0.000 (5)	-0.020 (5)	-0.031 (6)
C(41)	-0.2708 (7)	-0.0838 (6)	0.3055 (3)	0.069 (6)	0.107 (7)	0.118 (8)	0.029 (6)	-0.043 (6)	-0.019 (5)
C(42)	-0.2783 (6)	-0.0638 (4)	0.3405 (3)	0.046 (4)	0.083 (6)	0.140 (9)	0.030 (6)	-0.009 (5)	-0.007 (4)
C(43)	-0.1940 (5)	-0.0753 (3)	0.3671 (2)	0.041 (3)	0.044 (4)	0.094 (5)	0.013 (3)	-0.003 (3)	-0.010 (3)
C(44)	-0.1801 (5)	-0.0630 (3)	0.4068 (2)	0.047 (3)	0.032 (3)	0.099 (5)	0.009 (3)	0.020 (3)	-0.006 (2)
C(45)	-0.2504 (6)	-0.0378 (4)	0.4291 (3)	0.063 (4)	0.054 (4)	0.122 (7)	0.006 (5)	0.040 (5)	0.003 (4)
C(46)	-0.2178 (8)	-0.0345 (5)	0.4652 (3)	0.107 (7)	0.079 (6)	0.113 (8)	-0.004 (5)	0.065 (6)	-0.000 (5)
C(47)	-0.1167 (8)	-0.0541 (4)	0.4807 (3)	0.105 (7)	0.062 (5)	0.108 (7)	-0.012 (4)	0.043 (6)	-0.017 (5)
C(48)	-0.0459 (6)	-0.0782 (4)	0.4590 (2)	0.067 (4)	0.052 (4)	0.065 (4)	-0.001 (3)	0.017 (4)	-0.014 (3)
C(49)	-0.0781 (4)	-0.0835 (3)	0.4219 (2)	0.040 (3)	0.025 (2)	0.084 (4)	-0.001 (3)	0.013 (3)	-0.009 (2)
C(50)	0.5	0.2157 (9)	0.25	0.090 (9)	0.11 (1)	0.09 (1)	0.0	-0.005 (8)	0.0
C(51)	0.4749 (6)	0.1762 (6)	0.2180 (3)	0.070 (5)	0.152 (9)	0.090 (7)	0.034 (7)	0.006 (5)	0.016 (6)
C(52)	0.4748 (7)	0.1026 (6)	0.2173 (3)	0.092 (7)	0.106 (7)	0.100 (7)	-0.019 (6)	-0.002 (5)	-0.004 (6)
C(53)	0.5	0.0642 (8)	0.25	0.11 (1)	0.08 (1)	0.15 (2)	0.0	0.00 (1)	0.0

atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U</i> , Å ²	atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U</i> , Å ²
H(2)	0.3626 (5)	0.0321 (3)	0.3496 (2)	0.08	H(27)	-0.2386 (6)	0.1387 (5)	0.3136 (3)	0.08
H(3)	0.4725 (5)	0.1437 (4)	0.3625 (2)	0.08	H(28)	-0.3094 (6)	0.1672 (4)	0.3692 (3)	0.08
H(4)	0.5730 (5)	0.1620 (3)	0.4236 (2)	0.08	H(29)	-0.2004 (5)	0.1412 (4)	0.4285 (2)	0.08
H(5)	0.5598 (5)	0.0710 (3)	0.4724 (2)	0.08	H(30)	-0.0234 (5)	0.0924 (3)	0.4303 (2)	0.08
H(6)	0.4563 (4)	-0.0425 (3)	0.4585 (2)	0.08	H(32)	0.2262 (7)	0.1794 (5)	0.3441 (3)	0.08
H(8)	0.4755 (5)	-0.2017 (4)	0.4094 (2)	0.08	H(33)	0.2889 (9)	0.1810 (8)	0.2829 (4)	0.08
H(9)	0.5379 (7)	-0.2746 (4)	0.4658 (3)	0.08	H(34)	0.218 (1)	0.093 (1)	0.2353 (3)	0.08
H(10)	0.4541 (7)	-0.2617 (4)	0.5194 (2)	0.08	H(35)	0.128 (1)	-0.0137 (9)	0.2522 (3)	0.08
H(11)	0.2985 (6)	-0.1838 (4)	0.5179 (2)	0.08	H(36)	0.0674 (7)	-0.0221 (5)	0.3103 (2)	0.08
H(12)	0.2311 (5)	-0.1123 (3)	0.4623 (2)	0.08	H(39)	-0.0227 (6)	-0.1470 (4)	0.3159 (2)	0.08
H(14)	0.5041 (5)	-0.1070 (4)	0.3642 (2)	0.08	H(40)	-0.1750 (8)	-0.1272 (5)	0.2683 (3)	0.08
H(15)	0.5438 (6)	-0.1685 (5)	0.3083 (2)	0.08	H(41)	-0.3371 (7)	-0.0766 (6)	0.2844 (3)	0.08
H(16)	0.4021 (7)	-0.2257 (5)	0.2655 (2)	0.08	H(42)	-0.3496 (6)	-0.0398 (4)	0.3471 (3)	0.08
H(17)	0.2253 (6)	-0.2246 (5)	0.2794 (2)	0.08	H(45)	-0.3285 (6)	-0.0211 (4)	0.4176 (3)	0.08
H(18)	0.1831 (5)	-0.1657 (3)	0.3353 (2)	0.08	H(46)	-0.2724 (8)	-0.0164 (5)	0.4828 (3)	0.08
H(20)	0.1055 (6)	0.2235 (4)	0.3742 (2)	0.08	H(47)	-0.0933 (8)	-0.0497 (4)	0.5098 (3)	0.08

Table I (Continued)

atom	x/a	y/b	z/c	U, Å ²	atom	x/a	y/b	z/c	U, Å ²
H(21)	0.1937 (7)	0.3154 (4)	0.4166 (3)	0.08	H(48)	0.0328 (6)	-0.0932 (4)	0.4706 (2)	0.08
H(22)	0.3201 (7)	0.2780 (5)	0.4675 (3)	0.08	H(50)	0.5	0.2755 (9)	0.25	0.12
H(23)	0.3439 (6)	0.1442 (5)	0.4840 (2)	0.08	H(51)	0.4545 (6)	0.2065 (6)	0.1927 (3)	0.12
H(24)	0.2475 (5)	0.0501 (3)	0.4451 (2)	0.08	H(52)	0.4562 (7)	0.0729 (6)	0.1919 (3)	0.12
H(26)	-0.0604 (5)	0.0940 (4)	0.3142 (2)	0.08	H(53)	0.5	0.0039 (8)	0.25	0.12

^a The temperature factor has the form of $\exp(-T)$, where $T = 8\pi^2 U(\sin \theta/\lambda)^2$ for isotropic atoms and $T = 2\pi^2 \sum_i h(i)h(j)U(i,j)i^*j^*$ for anisotropic atoms. i^* and j^* are reciprocal axial lengths and $h(i)$'s are Miller indices. ^b Esd's in parentheses.

Table II. Bond Distances (Å) for [Pt⁰(PPh₃)₂(C₁₂H₃CSO)]·0.5C₆H₆

Pt(1)-S(1)	2.313 (1)	C(10)-C(11)	1.37 (1)	C(32)-C(33)	1.43 (2)
Pt(1)-P(1)	2.295 (1)	C(11)-C(12)	1.39 (1)	C(33)-C(34)	1.36 (2)
Pt(1)-P(2)	2.302 (1)	C(13)-C(14)	1.389 (9)	C(34)-C(35)	1.32 (2)
Pt(1)-C(37)	2.122 (5)	C(13)-C(18)	1.389 (8)	C(35)-C(36)	1.34 (1)
S(1)-O(1)	1.471 (6)	C(14)-C(15)	1.39 (1)	C(37)-C(38)	1.499 (8)
S(1)-C(37)	1.762 (5)	C(15)-C(16)	1.38 (1)	C(37)-C(49)	1.495 (9)
P(1)-C(1)	1.818 (5)	C(16)-C(17)	1.35 (1)	C(38)-C(39)	1.37 (1)
P(1)-C(7)	1.828 (6)	C(17)-C(18)	1.39 (1)	C(38)-C(43)	1.384 (9)
P(1)-C(13)	1.817 (6)	C(19)-C(20)	1.451 (9)	C(39)-C(40)	1.38 (1)
P(2)-C(19)	1.809 (6)	C(19)-C(24)	1.367 (8)	C(40)-C(41)	1.38 (1)
P(2)-C(25)	1.827 (5)	C(20)-C(21)	1.36 (1)	C(41)-C(42)	1.37 (2)
P(2)-C(31)	1.824 (7)	C(21)-C(22)	1.34 (1)	C(42)-C(43)	1.38 (1)
C(1)-C(2)	1.392 (9)	C(22)-C(23)	1.40 (1)	C(43)-C(44)	1.47 (1)
C(1)-C(6)	1.389 (8)	C(23)-C(24)	1.37 (1)	C(44)-C(45)	1.39 (1)
C(2)-C(3)	1.387 (9)	C(25)-C(26)	1.384 (9)	C(44)-C(49)	1.406 (8)
C(3)-C(4)	1.38 (1)	C(25)-C(30)	1.383 (9)	C(45)-C(46)	1.34 (1)
C(4)-C(5)	1.38 (1)	C(26)-C(27)	1.38 (1)	C(46)-C(47)	1.40 (1)
C(5)-C(6)	1.379 (8)	C(27)-C(28)	1.36 (1)	C(47)-C(48)	1.38 (1)
C(7)-C(8)	1.379 (9)	C(28)-C(29)	1.38 (1)	C(48)-C(49)	1.38 (1)
C(7)-C(12)	1.39 (1)	C(29)-C(30)	1.380 (9)	C(50)-C(51)	1.38 (1)
C(8)-C(9)	1.41 (1)	C(31)-C(32)	1.38 (1)	C(51)-C(52)	1.32 (2)
C(9)-C(10)	1.34 (1)	C(31)-C(36)	1.38 (1)	C(52)-C(53)	1.39 (1)

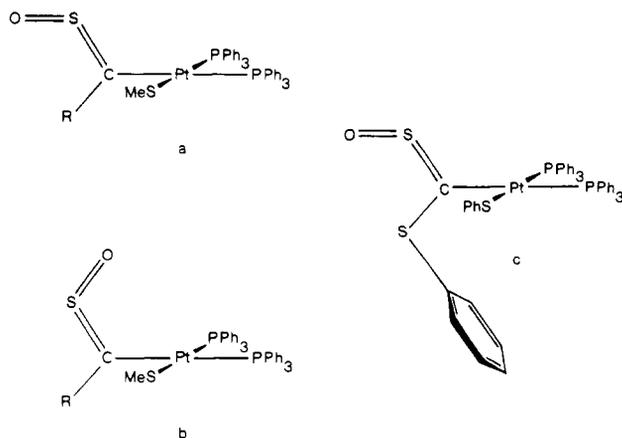


Figure 4. Structures of *cis*-(*E*)- and *cis*-(*Z*)-[Pt^{II}(MeS)(PPh₃)₂(RCSO)] (a and b, respectively; R = *p*-MeC₆H₄, Ph) and *cis*-(*E*)-[Pt^{II}(PhS)(PPh₃)₂(PhSCSO)]³⁴ (c).

[Pt⁰(PPh₃)₄] with (PhS)₂CSO afforded directly *cis*-(*E*)-[Pt^{II}(PhS)(PPh₃)₂(PhSCSO)]·C₆H₆, and the molecular structure and stereochemistry of this product were unambiguously established by an X-ray crystal structure determination.^{23,34} This confirmed the oxidative addition of one C-S side bond to Pt⁰ as well as the anti position of the Pt and O atoms (*E* stereoisomer see Figure 4c). The two strong cumulene absorptions (ν (CSO)) in the IR spectra, 1079 and 950 cm⁻¹ (see Table V),^{23,34} may be taken as a criterion for this specific *E* stereoisomer. IR spectra recorded on *cis*-(*E*)-[Pt^{II}(MeS)(PPh₃)₂(*p*-MeC₆H₄CSO)]·0.8CDCl₃ (KBr mull) also show two cumulene (ν (CSO)) vibrations (see Table V), and this complex is therefore characterized as the *E* stereoisomer. IR spectra recorded on a 4:1 molar mixture of *cis*-(*Z*)- and *cis*-(*E*)-[Pt^{II}(MeS)(PPh₃)₂(*p*-MeC₆H₄CSO)] show only one cumulene absorption assignable to the *Z* stereoisomer (see Table V). Despite the absence of an un-

ambiguous explanation for a single cumulene absorption, this phenomenon may be used for identification of *Z* oxidative-addition stereoisomers.³⁴

³¹P NMR spectra recorded on CDCl₃ solutions of mixtures of *cis*-(*E*)- and *cis*-(*Z*)-[Pt^{II}(MeS)(PPh₃)₂(RCSO)] (R = Ph, *p*-MeC₆H₄) with different molar ratios (see section iv) show two AB resonance patterns (together with ¹⁹⁵Pt satellites). The similarity and magnitude of the ³¹P chemical shifts and coupling data strongly indicate that both compounds are oxidative-addition stereoisomers (see Table V and Figure 4). The assignment of a particular AB resonance pattern to a specific stereoisomer (*cis*-*E* or *cis*-*Z*) is based on comparison both with the ³¹P NMR data of *cis*-(*E*)- and *cis*-(*Z*)-[Pt^{II}(PhS)(PPh₃)₂(PhSCSO)]^{23,34} and with the relative intensities of the cumulene absorptions in the IR spectra, taking into account a possible isomerization in solution (see Discussion). On the basis of trans influence, the smaller coupling in each AB resonance pattern may be attributed to the P atom trans to the C atom of the RC=S=O group (¹J(Pt-P_c)) and the larger to the P trans to S of the MeS group (¹J(Pt-P_s)).³⁵⁻³⁷

¹H NMR (60 and 100 MHz) spectra recorded on the final equilibrium mixture in CDCl₃ show ³J(Pt-H) = 52 Hz on the MeS signals of *cis*-(*E*)- and *cis*-(*Z*)-[Pt^{II}(MeS)(PPh₃)₂(*p*-MeC₆H₄CSO)]. Further splitting of the MeS signals of these compounds by the P nuclei was also detected, giving rise to a complex multiplet structure which was not further analyzed. Two resonances around δ 8.2 (relative to Me₄Si) in the ¹H NMR spectra recorded on the final equilibrium mixture are assigned to the ortho aryl protons of the *p*-MeC₆H₄C=S=O group of *cis*-(*E*)-[Pt^{II}(MeS)(PPh₃)₂(*p*-MeC₆H₄CSO)] by analogy to the downfield shift of the ortho aryl protons of free sulfoxes, which lie in the deshielding zone of the S=O groups.⁸

(35) Allen, F. H.; Pidcock, A. *J. Chem. Soc. A* **1968**, 2700-2704.

(36) Anderson, S. J.; Goggin, P. L.; Goodfellow, R. J. *J. Chem. Soc., Dalton Trans.* **1976**, 1959-1964.

(37) Carty, A. J. *Inorg. Chem.* **1976**, *15*, 1956-1959.

Table III. Bond Angles (Deg) for $[\text{Pt}^0(\text{PPh}_3)_2(\text{C}_{12}\text{H}_8\text{CSO})] \cdot 0.5\text{C}_6\text{H}_6$

S(1)-Pt(1)-P(1)	101.94 (5)	C(21)-C(22)-C(23)	120.9 (8)
S(1)-Pt(1)-P(2)	151.28 (5)	C(22)-C(23)-C(24)	118.5 (7)
S(1)-Pt(1)-C(37)	46.6 (1)	C(19)-C(24)-C(23)	121.6 (6)
P(1)-Pt(1)-P(2)	106.42 (5)	P(2)-C(25)-C(26)	122.9 (5)
P(1)-Pt(1)-C(37)	148.5 (1)	P(2)-C(25)-C(30)	118.5 (4)
P(2)-Pt(1)-C(37)	104.9 (1)	C(26)-C(25)-C(30)	118.6 (6)
Pt(1)-S(1)-O(1)	114.1 (2)	C(25)-C(26)-C(27)	118.4 (7)
Pt(1)-S(1)-C(37)	61.0 (2)	C(26)-C(27)-C(28)	123.7 (8)
O(1)-S(1)-C(37)	113.9 (3)	C(27)-C(28)-C(29)	117.6 (7)
Pt(1)-P(1)-C(1)	120.0 (2)	C(28)-C(29)-C(30)	120.3 (8)
Pt(1)-P(1)-C(7)	110.6 (2)	C(25)-C(30)-C(29)	121.4 (6)
Pt(1)-P(1)-C(13)	112.7 (2)	P(2)-C(31)-C(32)	123.9 (6)
C(1)-P(1)-C(7)	101.4 (2)	P(2)-C(31)-C(36)	117.2 (6)
C(1)-P(1)-C(13)	103.8 (3)	C(32)-C(31)-C(36)	118.8 (8)
C(7)-P(1)-C(13)	107.2 (3)	C(31)-C(32)-C(33)	116.7 (9)
Pt(1)-P(2)-C(19)	119.2 (2)	C(32)-C(33)-C(34)	122 (1)
Pt(1)-P(2)-C(25)	115.4 (2)	C(33)-C(34)-C(35)	118 (1)
Pt(1)-P(2)-C(31)	109.5 (2)	C(34)-C(35)-C(36)	123 (1)
C(19)-P(2)-C(25)	100.9 (3)	C(31)-C(36)-C(35)	121 (1)
C(19)-P(2)-C(31)	105.5 (3)	Pt(1)-C(37)-S(1)	72.4 (2)
C(25)-P(2)-C(31)	104.9 (3)	Pt(1)-C(37)-C(38)	119.7 (4)
P(1)-C(1)-C(2)	119.3 (4)	Pt(1)-C(37)-C(49)	117.4 (4)
P(1)-C(1)-C(6)	122.5 (4)	S(1)-C(37)-C(38)	121.2 (4)
C(2)-C(1)-C(6)	118.0 (5)	S(1)-C(37)-C(49)	119.6 (4)
C(1)-C(2)-C(3)	120.7 (6)	C(38)-C(37)-C(49)	104.7 (4)
C(2)-C(3)-C(4)	119.8 (6)	C(37)-C(38)-C(39)	129.6 (6)
C(3)-C(4)-C(5)	120.4 (6)	C(37)-C(38)-C(43)	109.5 (6)
C(4)-C(5)-C(6)	119.1 (6)	C(39)-C(38)-C(43)	120.8 (6)
C(1)-C(6)-C(5)	121.9 (6)	C(38)-C(39)-C(40)	118.6 (7)
P(1)-C(7)-C(8)	122.7 (5)	C(39)-C(40)-C(41)	120.2 (9)
P(1)-C(7)-C(12)	117.2 (4)	C(40)-C(41)-C(42)	121.2 (9)
C(8)-C(7)-C(12)	119.9 (6)	C(41)-C(42)-C(43)	118.9 (8)
C(7)-C(8)-C(9)	118.8 (7)	C(38)-C(43)-C(42)	120.2 (8)
C(8)-C(9)-C(10)	121.0 (7)	C(38)-C(43)-C(44)	108.4 (6)
C(9)-C(10)-C(11)	120.3 (7)	C(42)-C(43)-C(44)	131.4 (7)
C(10)-C(11)-C(12)	120.4 (7)	C(43)-C(44)-C(45)	130.5 (6)
C(7)-C(12)-C(11)	119.6 (6)	C(43)-C(44)-C(49)	109.2 (6)
P(1)-C(13)-C(14)	122.8 (5)	C(45)-C(44)-C(49)	120.3 (7)
P(1)-C(13)-C(18)	118.6 (5)	C(44)-C(45)-C(46)	118.0 (8)
C(14)-C(13)-C(18)	118.6 (6)	C(45)-C(46)-C(47)	123 (1)
C(13)-C(14)-C(15)	120.5 (6)	C(46)-C(47)-C(48)	120.2 (9)
C(14)-C(15)-C(16)	120.0 (8)	C(47)-C(48)-C(49)	118.4 (7)
C(15)-C(16)-C(17)	119.5 (8)	C(37)-C(49)-C(44)	108.1 (6)
C(16)-C(17)-C(18)	121.6 (7)	C(37)-C(49)-C(48)	131.3 (5)
C(13)-C(18)-C(17)	119.7 (6)	C(44)-C(49)-C(48)	120.6 (6)
P(2)-C(19)-C(20)	119.7 (5)	C(51)-C(50)-C(51) ^a	118 (1)
P(2)-C(19)-C(24)	121.7 (4)	C(50)-C(51)-C(52)	122 (1)
C(20)-C(19)-C(24)	118.6 (6)	C(51)-C(52)-C(53)	119 (1)
C(19)-C(20)-C(21)	118.4 (7)	C(52)-C(53)-C(52) ^a	120 (1)
C(20)-C(21)-C(22)	121.8 (7)		

^a 1 - x, y, 1/2 - z.

Surprisingly, ³¹P NMR spectra recorded on the ¹³C-enriched compounds *cis*-(*E*)- and *cis*-(*Z*)-[Pt^{II}(¹³CH₃S)(PPh₃)₂-(PhCSO)] show a ³J(¹³C-P) coupling of 9 Hz on the P atoms trans to the C=S=O groups, whereas on the P atoms trans to the ¹³CH₃S groups no ³J(¹³C-P) coupling was found. Although there is no certain explanation for this phenomenon, it may be a consequence of the conformation of the ¹³CH₃S-Pt fragment.

iv. Conversion of [Pt⁰(PPh₃)₂[(*E*)-(MeS)RCSO]] and [Pt⁰(PPh₃)₂[(*Z*)-(MeS)RCSO]] into *cis*-(*E*)- and *cis*-(*Z*)-[Pt^{II}(MeS)(PPh₃)₂(RCSO)] (R = Ph, *p*-MeC₆H₄). Although the coordination stereoisomers [Pt⁰(PPh₃)₂[(*E*)-(MeS)RCSO]] and [Pt⁰(PPh₃)₂[(*Z*)-(MeS)RCSO]] are stable in the solid state, in solution (CDCl₃ or C₆H₆) an intramolecular oxidative addition of the C-S side bond to the Pt⁰(PPh₃)₂ unit occurs. As an illustration, the conversion of [Pt⁰(PPh₃)₂[(*Z*)-(MeS)RCSO]] followed by ³¹P NMR is shown in Figure 5.

Irrespective of the starting material, either [Pt⁰(PPh₃)₂[(*E*)-(MeS)RCSO]] or [Pt⁰(PPh₃)₂[(*Z*)-(MeS)RCSO]], after 2 days in CDCl₃ an equilibrium mixture is formed, consisting of [Pt⁰(PPh₃)₂[(*E*)-(MeS)RCSO]] and *cis*-(*E*)- and *cis*-(*Z*)-[Pt^{II}(MeS)(PPh₃)₂(RCSO)] (R = *p*-MeC₆H₄, Ph).^{23,34} In

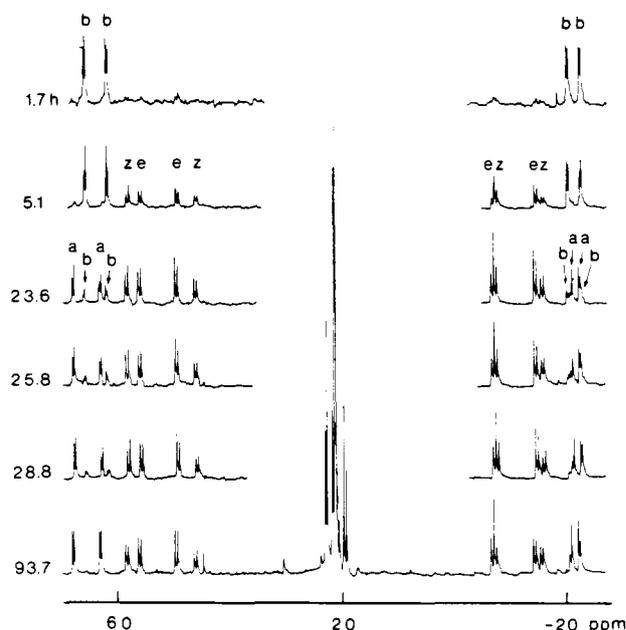
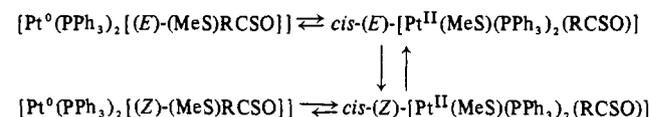


Figure 5. Conversion of [Pt⁰(PPh₃)₂[(*Z*)-(MeS)(*p*-MeC₆H₄)CSO]] (b) into *cis*-(*E*)- and *cis*-(*Z*)-[Pt^{II}(MeS)(PPh₃)₂(*p*-MeC₆H₄)CSO]] (e and z, respectively) and [Pt⁰(PPh₃)₂[(*E*)-(MeS)(*p*-MeC₆H₄)CSO]] (a), followed by ³¹P NMR in CDCl₃.

Scheme I. Equilibrium of Oxidative-Addition and Coordination Stereoisomers in CDCl₃ (R = *p*-MeC₆H₄, Ph)



(*Z*)-[Pt^{II}(MeS)(PPh₃)₂(RCSO)] in a molar ratio of ca. 1:1:1 for R = *p*-MeC₆H₄ and ca. 2:1:1 for R = Ph. Only traces of [Pt⁰(PPh₃)₂[(*E*)-(MeS)RCSO]] have been found. After *cis*-(*E*)-[Pt^{II}(MeS)(PPh₃)₂(*p*-MeC₆H₄)CSO]]·0.8CDCl₃ is dissolved in CDCl₃, ³¹P NMR spectra show the initial presence of a mixture of both oxidative-addition stereoisomers *cis*-(*E*)- and *cis*-(*Z*)-[Pt^{II}(MeS)(PPh₃)₂(*p*-MeC₆H₄)CSO]] in a ca. 1:1 molar ratio. In ca. 1 day the coordination stereoisomer [Pt⁰(PPh₃)₂[(*E*)-(MeS)(*p*-MeC₆H₄)CSO]] is gradually formed until again the same equilibrium mixture (vide supra) is obtained. It is important to note that a mixture of *cis*-(*Z*)- and *cis*-(*E*)-[Pt^{II}(MeS)(PPh₃)₂(*p*-MeC₆H₄)CSO]] in CDCl₃ with a molar ratio of ca. 4:1 (on the basis of the initial ³¹P NMR spectra) results likewise in the formation of the same equilibrium mixture (vide supra) on standing for 1 day.

Discussion

The results presented above indicate the existence of an equilibrium between the coordination stereoisomers [Pt⁰(PPh₃)₂[(*E*)-(MeS)RCSO]] and [Pt⁰(PPh₃)₂[(*Z*)-(MeS)RCSO]] and the oxidative-addition stereoisomers *cis*-(*E*)- and *cis*-(*Z*)-[Pt^{II}(MeS)(PPh₃)₂(RCSO)] (R = *p*-MeC₆H₄, Ph). Accordingly, in addition to the oxidative-addition reaction, the backward reaction, i.e., the reductive coupling of MeS and R-C=S=O groups, must occur. Hence, we are dealing with a unique equilibrium, which is summarized in Scheme I.

The nature of the geometry of the sulfine determines the relative thermodynamic stability of the coordination and oxidative-addition stereoisomers. This is clearly illustrated by the observation of only traces of the specific coordination stereoisomer [Pt⁰(PPh₃)₂[(*Z*)-(MeS)RCSO]] and, furthermore, by the complete conversion of [Pt⁰(PPh₃)₂[(*RS*)₂CSO]] to the oxidative-addition stereoisomers, *cis*-(*E*)- and *cis*-(*Z*)-[Pt^{II}(RS)(PPh₃)₂(RCSO)] (R = *p*-MeC₆H₄, Ph).^{23,34} In

Table IV

Least-Squares Plane Analysis for $[\text{Pt}^0(\text{PPh}_3)_2(\text{C}_{12}\text{H}_8\text{CSO})] \cdot 0.5\text{C}_6\text{H}_6$

plane	atoms	max dev, ^a Å	eq of the least-squares plane ^b			
			P	Q	R	S
1	C(1)–C(6)	0.02 (1)	-10.666	8.863	14.756	1.586
2	C(7)–C(12)	0.01 (1)	7.139	13.713	9.318	4.449
3	C(13)–C(18)	0.005 (4)	1.209	-15.519	17.628	8.686
4	C(19)–C(24)	0.03 (2)	-10.949	0.464	24.194	8.015
5	C(25)–C(30)	0.01 (1)	4.468	16.855	-1.543	0.828
6	C(31)–C(36)	0.04 (2)	10.235	-9.430	7.262	3.183
7	C(37)–C(49)	0.05 (4)	4.258	16.785	-6.752	-4.605
8	C(38)–C(43)	0.01 (1)	4.528	16.558	-8.004	-5.052
9	C(44)–C(49)	0.01 (1)	4.169	16.896	-5.635	-4.107
10	C(37), C(38), C(43), C(44), C(49)	0.02 (1)	4.252	16.782	-6.834	-4.606
11	Pt(1), S(1), C(37)		-0.578	2.758	36.454	13.989
12	Pt(1), S(1), P(1), P(2), C(37)	0.05 (3)	-0.606	3.475	36.204	13.793
13	O(1), S(1), C(37)		-9.920	-10.011	15.938	7.545

Relevant Interplanar Angles (Deg)									
1,2	89	5,6	77	8,10	2	7,13	35	3,12	72
1,3	69	7,8	2	9,10	2	10,11	90	4,12	55
2,3	64	7,9	2	7,11	90	10,13	35	5,12	80
4,5	75	7,10	0	7,12	88	1,12	66	6,12	80
4,6	59	8,9	4	11,13	75	2,12	63		

^a Standard deviations of atoms defining the plane are in parentheses. ^b Equation in direct space fractional coordinates: $Px + Qy + Rz = S$.

Table V. Spectroscopic Data

compd	IR, ^a $\nu(\text{CSO})$	³¹ P NMR ^b				¹ H NMR ^b				ref
		¹ J(Pt–P _a)	¹ J(Pt–P _b)	² J(P _a –P _b)	$\delta(\text{P}_a)$	$\delta(\text{P}_b)$	$\delta(\text{MeS})$	$\delta(p\text{-MeC}_6\text{H}_4)$	³ J(Pt–SMe)	
$[\text{Pt}^0(\text{PPh}_3)_2(\text{C}_{12}\text{H}_8\text{CSO})] \cdot 0.5\text{C}_6\text{H}_6$	1006	3561	3491	11	23.4	20.6				
$[\text{Pt}^0(\text{PPh}_3)_2[(E)\text{-}(\text{MeS})(p\text{-MeC}_6\text{H}_4)\text{CSO}]]$	1006	3675	3419	13	21.6	19.9	2.25	2.25		21
$[\text{Pt}^0(\text{PPh}_3)_2[(Z)\text{-}(\text{MeS})(p\text{-MeC}_6\text{H}_4)\text{CSO}]]$	1010	3603	3345	11	20.5	19.6	2.10	2.25		21
$[\text{Pt}^0(\text{PPh}_3)_2[(E)\text{-}(\text{MeS})\text{PhCSO}]]$	1015	3668	3428	12	21.6	19.7	2.25			
$[\text{Pt}^0(\text{PPh}_3)_2[(Z)\text{-}(\text{MeS})\text{PhCSO}]]$	1009	3592	3360	10	20.6	19.6	2.10			
<i>cis</i> -(<i>E</i>)- $[\text{Pt}^{\text{II}}(\text{MeS})(\text{PPh}_3)_2(p\text{-MeC}_6\text{H}_4\text{CSO})]$	1065, 962	2297 ^d	2872 ^e	20	20.2 ^d	19.7 ^e	2.04	2.22	52	
<i>cis</i> -(<i>Z</i>)- $[\text{Pt}^{\text{II}}(\text{MeS})(\text{PPh}_3)_2(p\text{-MeC}_6\text{H}_4\text{CSO})]$	975	2179 ^d	3013 ^e	21	18.2 ^d	20.2 ^e	2.04	2.22	52	
<i>cis</i> -(<i>E</i>)- $[\text{Pt}^{\text{II}}(\text{MeS})(\text{PPh}_3)_2(\text{PhCSO})]$	<i>c</i>	2308 ^d	2867 ^e	21	20.1 ^d	19.5 ^e	2.05		52	
<i>cis</i> -(<i>Z</i>)- $[\text{Pt}^{\text{II}}(\text{MeS})(\text{PPh}_3)_2(\text{PhCSO})]$	<i>c</i>	2190 ^d	3008 ^e	20	18.2 ^d	20.0 ^e	2.05		52	
<i>cis</i> -(<i>E</i>)- $[\text{Pt}^{\text{II}}(\text{PhS})(\text{PPh}_3)_2(\text{PhSCSO})] \cdot \text{C}_6\text{H}_6$	1079, 950	2446 ^d	2985 ^e	20	18.8	16.2				23, 34

^a KBr mull; ν values given in cm^{-1} . ^b In CDCl_3 ; J values in Hz. ^c Compound could not be isolated (see Experimental Section). ^d P_a: trans to C atom. ^e P_b: trans to S atom.

both the coordination compounds $[\text{Pt}^0(\text{PPh}_3)_2[(Z)\text{-}(\text{MeS})\text{RCSO}]]$ and $[\text{Pt}^0(\text{PPh}_3)_2[(E)\text{-}(\text{MeS})\text{RCSO}]]$, the SO group is situated syn with respect to a C–S bond. That the nature of the substituent R also has some influence on the thermodynamic stability of the coordination products is apparent from the amount of $[\text{Pt}^0(\text{PPh}_3)_2[(E)\text{-}(\text{MeS})\text{RCSO}]]$ present in the final equilibrium mixture, i.e., ca. 30% for R = *p*-MeC₆H₄ and ca. 50% for R = Ph.

From the ³¹P NMR data it was concluded that the rates of the oxidative-addition processes were unchanged upon altering the concentration of the starting complexes $[\text{Pt}^0(\text{PPh}_3)_2[(E)\text{-}(\text{MeS})(p\text{-MeC}_6\text{H}_4)\text{CSO}]]$ and $[\text{Pt}^0(\text{PPh}_3)_2[(Z)\text{-}(\text{MeS})(p\text{-MeC}_6\text{H}_4)\text{CSO}]]$. Therefore, the oxidative-addition and reductive coupling reactions are thought to occur intramolecularly.

A possible mechanism for the oxidative-addition reaction could comprise the following sequence. After η^2 -CS coordination of the sulfine, the $\text{Pt}^0(\text{PPh}_3)_2$ unit glides along the S=C=S fragment to the C–S side bond. This is followed by an oxidative addition of this bond to Pt^0 . Accordingly, the reductive coupling process is thought to be the reverse of this process.

An obvious intermediate or transition state in the gliding movement could be an η^3 -SCS, pseudoallylic coordinated sulfine (see Figure 6). In this intermediate the Pt atom is four-coordinated by the bidentate pseudoallylic sulfine and the two phosphine ligands, between which the P–Pt–P angle has

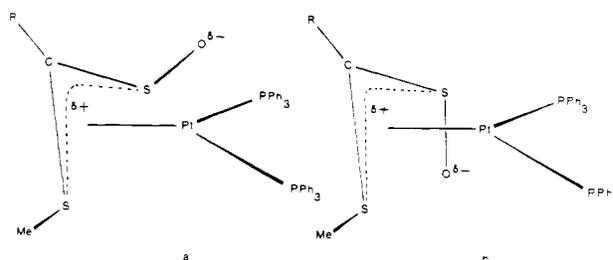


Figure 6. Structures of $[\text{Pt}^0(\text{PPh}_3)_2[(E)\text{-}(\text{MeS})(p\text{-MeC}_6\text{H}_4)\text{SO}]]$ (a) and $[\text{Pt}^0(\text{PPh}_3)_2[(Z)\text{-}(\text{MeS})(p\text{-MeC}_6\text{H}_4)\text{SO}]]$ (b), pseudoallylic intermediates.

decreased as compared to the η^2 -CS coordinated complexes. The pseudoallylic stereoisomer $[\text{Pt}^0(\text{PPh}_3)_2[(E)\text{-}(\text{MeS})(p\text{-MeC}_6\text{H}_4)\text{SO}]]$ would then be the corresponding intermediate in the conversion of $[\text{Pt}^0(\text{PPh}_3)_2[(E)\text{-}(\text{MeS})\text{RCSO}]]$ into *cis*-(*E*)- $[\text{Pt}^{\text{II}}(\text{MeS})(\text{PPh}_3)_2(\text{RCSO})]$.

Preliminary results indicate that the sulfines in the complexes $[\text{Rh}^{\text{I}}\text{Cl}(\text{PR}'_3)[(E)\text{-}(\text{MeS})(\text{R})\text{SO}]]$ and $[\text{Rh}^{\text{I}}\text{Cl}(\text{PR}'_3)[(Z)\text{-}(\text{MeS})(\text{R})\text{SO}]]$ (R = Ph, *p*-MeC₆H₄; R' = *c*-Hx, *i*-C₃H₇) are η^3 -SCS coordinated.³⁸

The observations that the conversion of $[\text{Pt}^0(\text{PPh}_3)_2[(E)\text{-}(\text{MeS})\text{RCSO}]]$ yielded some *cis*-(*Z*)- $[\text{Pt}^{\text{II}}(\text{MeS})(\text{PPh}_3)_2$

(38) Gosselink, J. W.; Brouwers, A. M. F.; van Koten, G.; Vrieze, K., to be submitted for publication.

(RCSO)] and that $[\text{Pt}^0(\text{PPh}_3)_2[(Z)\text{-(MeS)RCSO}]]$ likewise gave rise to *cis*-(*E*)- $[\text{Pt}^{\text{II}}(\text{MeS})(\text{PPh}_3)_2(\text{RCSO})]$ illustrate that during the oxidative-addition reaction isomerization of the sulfine skeleton occurs. Three types of isomerization pathway are possible:

First, there could be an equilibrium between the pseudoallylic intermediates, analogous to the *syn*-*anti* interchange found in the complexes $[\text{PdCl}(\text{PR}_3)(\eta^3\text{-H}_2\text{CC}(\text{H})\text{CH}_2)]$.³⁹

Second, a direct equilibrium between the two oxidative-addition stereoisomers *cis*-(*E*)- and *cis*-(*Z*)- $[\text{Pt}^{\text{II}}(\text{MeS})(\text{PPh}_3)_2(\text{RCSO})]$ can be envisaged, perhaps catalyzed by trace impurities. Isomerization under influence of base has been observed for free sulfines.⁴⁰

A third possibility could be a process involving an impurity-catalyzed isomerization of free sulfine (generated by a dissociative process of the coordination compounds) followed by recoordination of the sulfine.

In order to gain more insight into the isomerization of oxidative-addition stereoisomers, we have studied the isomerization of *cis*-(*E*)- and *cis*-(*Z*)- $[\text{Pt}^{\text{II}}\text{Cl}(\text{PPh}_3)_2(\text{RCSO})]$ ($\text{R} = p\text{-MeC}_6\text{H}_4, \text{Ph}$), oxidative-addition products of the sulfine (*E*)-(RS)ClCSO. The lability of the C-Cl bond with respect toward oxidative addition to Pt^0 should prohibit both a reductive coupling reaction of Cl and $\text{RSC}=\text{S}=\text{O}$ and the existence of pseudoallylic intermediates. The results will be described in a forthcoming paper.³⁴ In order to investigate

the isomerization of coordination stereoisomers in absence of an oxidative-addition process, we are now studying the complexes $[\text{Pt}^0(\text{P}(\text{c-Hx})_3)_2[(E)\text{-(MeS)PhCSO}]]$ and $[\text{Pt}^0(\text{P}(\text{c-Hx})_3)_2[(Z)\text{-(MeS)PhCSO}]]$. The bulkiness of the $\text{P}(\text{c-Hx})_3$ groups should make oxidative addition less attractive because *cis*-positioned $\text{P}(\text{c-Hx})_3$ ligands in a square-planar Pt^{II} complex would be unfavorable. In contrast we might anticipate that pseudoallylic intermediates can still be formed.

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Registry No. $[\text{Pt}^0(\text{PPh}_3)_2(\text{C}_{12}\text{H}_8\text{CSO})]\cdot 0.5\text{C}_6\text{H}_6$, 75701-23-4; *cis*-(*E*)- $[\text{Pt}^{\text{II}}(\text{MeS})(\text{PPh}_3)_2(p\text{-MeC}_6\text{H}_4\text{CSO})]$, 73358-19-7; *cis*-(*Z*)- $[\text{Pt}^{\text{II}}(\text{MeS})(\text{PPh}_3)_2(p\text{-MeC}_6\text{H}_4\text{CSO})]$, 73367-11-0; $\text{Pt}^0(\text{PPh}_3)_2[(E)\text{-(MeS)}(p\text{-MeC}_6\text{H}_4)\text{CSO}]$, 72539-18-5; $\text{Pt}^0(\text{PPh}_3)_2[(Z)\text{-(MeS)}(p\text{-MeC}_6\text{H}_4)\text{CSO}]$, 72581-76-1; $\text{Pt}^0(\text{PPh}_3)_4$, 14221-02-4; $\text{Pt}^0(\text{PPh}_3)_2[(E)\text{-(MeS)PhCSO}]$, 75701-24-5; $\text{Pt}^0(\text{PPh}_3)_2[(Z)\text{-(MeS)PhCSO}]$, 75764-72-6; *cis*-(*E*)- $[\text{Pt}^{\text{II}}(\text{MeS})(\text{PPh}_3)_2(\text{PhCSO})]$, 75701-09-6; *cis*-(*Z*)- $[\text{Pt}^{\text{II}}(\text{MeS})(\text{PPh}_3)_2(\text{PhCSO})]$, 75764-66-8.

Supplementary Material Available: A table of observed and calculated structure factors for $[\text{Pt}^0(\text{PPh}_3)_2(\text{C}_{12}\text{H}_8\text{CSO})]\cdot 0.5\text{C}_6\text{H}_6$ (41 pages). Ordering information is given on any current masthead page.

(39) Vrieze, K. "Dynamic Nuclear Magnetic Resonance Spectroscopy"; Jackman, L. M., Cotton, F. A., Eds.; Academic Press: New York, 1975; pp 441-487.

(40) Bonini, B. F.; Maccagnani, G. *J. Chem. Soc., Perkin Trans. 2* 1978, 1218-1224.

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Isomers of Cobalt(III) Complexes Containing Quadridentate Ligands with a Six-Membered Chelate Ring. Optically Active 2,3,2-tet Derivatives

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The preparation and characterization are described for the isomers for the (4*R*,6*R*)-4,6-dimethyl-3,7-diaza-1,9-nonanediamine (5*R*,7*R*-Me₂-2,3,2-tet) and for the (6*R*,8*R*)-6,8-dimethyl-2,5,9,12-tetraazatridecane (1,5*R*,7*R*,11-Me₄-2,3,2-tet) complexes of the type *trans*- $[\text{CoCl}_2(\text{tetraamine})]^+$. The isomers are designated by the different configurations of asymmetric nitrogens. The following isomers were isolated: *S,S* and *R,S* for the former and *R,S,S,R*, *S,R,S,S*, and *R,S,S,S* for the latter ligand. The six-membered ring in the *R,S* and *S,R,S,S* isomers has the chair conformation with an axial and an equatorial C-methyl group. The six-membered part for the *S,S*, *R,S,S,R*, and *R,S,S,S* isomers adopts a λ skew-boat conformation with two equatorial C-methyl groups. The ratio of the *S,S* and *R,S* isomers for the *trans*- $[\text{CoCl}_2(5*R*,7*R*\text{-Me}_2\text{-2,3,2-tet})]^+$ at equilibrium was evaluated to be 2:1 ($\Delta G = 1.92 \text{ kJ mol}^{-1}$). All the isomers of the *trans*- $[\text{CoCl}_2(5*R*,7*R*\text{-Me}_2\text{-2,3,2-tet})]^+$ and *trans*- $[\text{CoCl}_2(1,5*R*,7*R*,11\text{-Me}_4\text{-2,3,2-tet})]^+$ produce $\Delta\text{-}\beta\text{-(S,S)-}[\text{CoCO}_3(5*R*,7*R*\text{-Me}_2\text{-2,3,2-tet})]^+$ and $\Delta\text{-}\beta\text{-(R,S,S,S)-}[\text{CoCO}_3(1,5*R*,7*R*,11\text{-Me}_4\text{-2,3,2-tet})]^+$, respectively, by the reaction with carbonate ion in an aqueous solution. The (*R,R*)-2,4-pentanediamine parts in these carbonato complexes were considered to adopt chair conformations with one methyl group axial and the other equatorial. These carbonato complexes were converted to the *trans*-dichloro complexes with the same configurations about the nitrogen centers.

Introduction

The stereochemistry of cobalt(III) complexes of tetraamine ligands with a six-membered chelate ring has been of recent interest.¹⁻³ The methyl groups substituted in diamines or

tetraamines affect significantly the configurations of metal complexes. Two conformations are possible for the (*R,R*)-2,4-pentanediamine (*R,R*-ptn) coordinated to a metal ion as a bidentate ligand. The chair conformation has one axial methyl group, the other being equatorial. In the λ skew-boat conformation, however, both methyl groups are disposed equatorially. Both conformations were actually observed in

(1) Hamilton, H. G., Jr.; Alexander, M. D. *Inorg. Chem.* 1966, 5, 2060-2061.

(2) Bosnich, B.; Gillard, R. D.; McKenzie, E. D.; Webb, G. A. *J. Chem. Soc. A* 1966, 1331-1339.

(3) Hamilton, H. G.; Alexander, M. D. *J. Am. Chem. Soc.* 1967, 89, 5065-5067.

(4) Brubaker, G. R.; Schaefer, D. P. *Inorg. Chem.* 1970, 9, 2373-2374.

(5) Brubaker, G. R.; Schaefer, D. P. *Inorg. Chem.* 1971, 10, 811-814.

(6) Brubaker, G. R.; Schaefer, D. P. *Inorg. Chem.* 1971, 10, 968-975.

(7) Alexander, M. D.; Hamilton, H. G., Jr. *Inorg. Chem.* 1969, 8, 2131-2134.

(8) Payne, N. C. *Inorg. Chem.* 1972, 11, 1376-1381.