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Displacement Reactions of *cis*-$[Pt^{II}Cl(R'SCSO)(PR_3)_2]$ (R = Ph, C_6H_{11}; R' = aryl) with Nucleophiles.

Formation with $R'S^-$ of an η^2-CS Coordinated Sulphine $(R'S)_2C{=}S{=}O$ by Reductive Coupling [1]

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A cyclic process to synthesize sulphines in the coordination sphere of platinum has been tested by stepwise reactions. Step i: *The Cl atoms in the metallo–sulphines* cis-*$[Pt^{II}Cl(R'SCSO)(PR_3)_2]$ (R = Ph, C_6H_{11}; R' =* p-*MeC_6H_4) were displaced by $R''S^-$ (R'' =* p-*MeC_6H_4,* p-*$MeOC_6H_4$) leading to the metallo–sulphines* cis-*$[Pt^{II}(SR'')(R'SCSO)(PR_3)_2]$, with only (*E*)-(*Z*) isomerization being found and no scrambling between R'S and R''S groups.* Step ii: *These metallo–sulphines in the case of R = C_6H_{11} were not detected, they are unstable because of the steric interaction between the bulky co-ligands and undergo immediate C–S reductive coupling forming the η^2-CS coordinated sulphine compounds $[Pt^0\{P(C_6H_{11})_3\}_2\{(R''S)(R'S)CSO\}]$.* Step iii: *These latter η^2-CS coordinated sulphines could be displaced by (*E*)-$(R'S)ClC{=}S{=}O$ forming the highly unstable η^2-CS compound $[Pt^0\{P(C_6H_{11})_3\}_2\{(E)\text{-}(R'S)ClCSO\}]$ which undergoes an immediate C–Cl oxidative addition and reforms the starting metallo–sulphine* cis-*$[Pt^{II}Cl(R'SCSO)\{P(C_6H_{11})_3\}_2]$ (*Step iv*). Two complications prevent this cyclic process becoming a catalytic cycle: (*i*) slow* cis-*to*-trans *isomerization of the metallo–sulphines* cis-*$[Pt^{II}Cl(R'SCSO)\{P(C_6H_{11})_3\}_2]$ and (*ii*) decomposition during the sulphine displacement (*Step iii*). Test reactions showed that the sulphine $(R'S)_2C{=}S{=}O$ is formed faster* via *direct displacement in (*E*)-$(R'S)ClC{=}S{=}O$ by $R''S^-$ than by the cyclic process. When the bidentate ligand $Et_2NCS_2^-$ is used as displacing ligand dissociation of one PR_3 group is initiated instead of C–S reductive coupling, forming the metallo–sulphines $[Pt^{II}(S_2CNEt_2)(R'SCSO)(PR_3)]$.*

Introduction

The coordination chemistry of sulphines, XYC=S=O (X, Y = aryl, S-aryl, S-alkyl, Cl) is currently being studied in our laboratory. Several coordination modes of these heterocumulenic systems have been established, *i.e.* η^2-CS to $M^0(PR_3)_2$ (M = Pt, Pd; R = C_6H_{11}, Ph), [1–3, 5–7] σ-S to *trans*-$M^ICl(PR_3)_2$ (M = Rh, Ir; R = C_6H_{11}, i-C_3H_7) [1, 8] and for the sulphines containing one or two C–S side bonds coordination *via* η^3-SCS to $Rh^ICl(PR_3)$ (R = C_6H_{11}, i-C_3H_7) [8]. Furthermore, sulphines containing C–S and/or C–Cl side bonds undergo, when coordinated to $M^0(PR_3)_2$ (M = Pt, Pd; R = Ph, C_6H_{11}) C–S and C–Cl, oxidative addition resulting in formation of metallo–sulphines *cis*- and *trans*-$[M^{II}X(YCSO)(PR_3)_2]$ (X = S-aryl, S-alkyl, Cl; Y = aryl, S-aryl) [2, 3, 6, 7], as well as C–S reductive coupling (the reverse process). No evidence has been found for the C–Cl reductive coupling process.

In the literature two examples of the synthesis of sulphines in a metal coordination sphere have been reported. Dittmer *et al.* synthesized $[Fe^0(CO)_3\{H_2CC(H)C(H){=}S{=}O\}]$ by oxidizing the complex $[Fe^0(CO)_3\{H_2CC(H)C(H){=}S\}]$ [9], whereas Götzfried and Beck synthesized $[Pt^0(PPh_3)_2(C_{12}H_8CSO)]$ ($C_{12}H_8$ = fluorene) by reaction of $[Pt^0(PPh_3)_2(SO_2)]$ with $(Me_3Si)(C_{12}H_8)C^-Li^+$ [10].

In view of the considerable insight gained into the factors determining the coordination mode of the sulphine as well as the cleavage and formation of reactive side bonds [1–8], we directed our research to the synthesis of novel, unstable sulphines in the coordination sphere of a metal.

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[†] (*E*) and (*Z*) refer to the configuration around 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 coordinated as such (η^2-CS, σ-S, η^3-SCS). 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 coordination.

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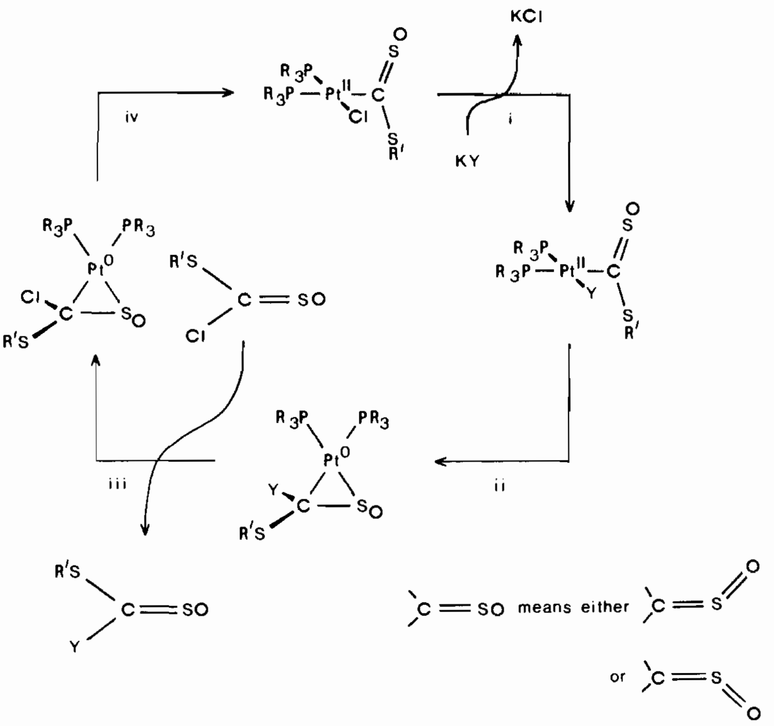

Fig. 1. A possible route for the synthesis of sulphine (R'S)YC=S=O in the coordination sphere of Pt.

Displacement of the Cl atom in *cis*-[$Pt^{II}Cl(R'SCSO)(PR_3)_2$] (R = Ph, C_6H_{11}; R' = aryl) by a nucleophile Y^- should give the substituted metallo–sulphine *cis*-[$Pt^{II}Y(R'SCSO)(PR_3)_2$] (reaction *i* in Fig. 1). Initiation of a subsequent reductive coupling would then result in formation of a C–Y bond forming a new sulphine η^2-CS coordinated to $Pt^0(PR_3)_2$ (reaction *ii* in Fig. 1). When a displacement of this sulphine (R'S)YC=S=O by (R'S)ClC=S=O (reaction *iii* in Fig. 1) could be accomplished, both the unstable η^2-CS complex [$Pt^0(PR_3)_2\{(R'S)ClSO\}$], reforming *via* C–Cl oxidative addition *cis*[$Pt^{II}Cl(R'SCSO)(PR_3)_2$], and the new sulphine (R'S)YC=S=O, could be synthesized.

In this paper we present the results of a first exploration of this synthetic route, involving attempts to test it for the syntheses of already known sulphines. Each of the steps shown in Fig. 1 could be demonstrated in separate reactions. It was hoped that, based on these results, the synthesis of otherwise unstable sulphines *e.g.* (R"O)(R'S)(RC=S=O could also be achieved in the coordination sphere of a metal.

Experimental

Infrared spectra were recorded on a Perkin-Elmer 283 spectrophotometer. ^1H NMR spectra were recorded on a Varian T-60A and a Bruker WM 250, ^{31}P NMR spectra on a Varian XL 100 spectrometer. Elemental analyses were carried out by the Analytical Section of the Institute for Organic Chemistry TNO, Utrecht (The Netherlands).

The sulphines $(p\text{-}MeC_6H_4S)_2C=S=O$ [11] and the metallo–sulphines *cis*-(*E*)- and -(*Z*)-[$Pt^{II}Cl(R'SCSO)(PPh_3)_2$] (R' = Ph, $p\text{-}MeC_6H_4$) [4] and *cis*-(*E*)-*trans*-(*E*)- and *trans*-(*Z*)-[$Pt^{II}Cl(p\text{-}MeC_6H_4SCSO)\{P(C_6H_{11})_3\}_2$] [5] were prepared according to literature procedures. The reactants $KSC_6H_4Me\text{-}p$ and $KSC_6H_4OMe\text{-}p$ were prepared by the reaction of $p\text{-}MeC_6H_4SH$ and $p\text{-}MeOC_6H_4SH$ with KOH. All further reagents are commercially available.

(i) General procedure for reactions between [$Pt^{II}Cl(p\text{-}MeC_6H_4SCSO)(PR_3)_2$] (R = Ph, C_6H_{11}) and KSR' (R' = $p\text{-}MeC_6H_4$, $p\text{-}MeOC_6H_4$)

To a solution of [$Pt^{II}Cl(p\text{-}MeC_6H_4SCSO)(PR_3)_2$] (R = Ph, C_6H_{11}; 0.1 mmol) in $CDCl_3$ (*ca.* 2 ml) or a mixture of $CDCl_3$ (*ca.* 1 ml) and CD_3OD (*ca.* 1 ml) was added an excess of KSR' (R' = $p\text{-}MeC_6H_4$ or $p\text{-}MeOC_6H_4$; *ca.* 0.5 mmol). The reaction mixture was stirred for several days. Unreacted KSR' was then removed by filtration. ^{31}P and ^1H NMR spectra were recorded to identify the products by comparison with the data of the pure compounds. In the case of R= Ph addition of a layer of n-pentane resulted over a period of several days in the precipitation of the substituted metallo–sulphines. Elemental analyses were in accord with a formulation of $[Pt^{II}(SR')(p\text{-}MeC_6H_4SCSO)(PPh_3)_2]$.

(ii) Displacement of (p-$MeC_6H_4S)_2C{=}S{=}O$ in $[Pt^0\{P(C_6H_{11})_3\}_2\{(p\text{-}MeC_6H_4S)_2CSO\}]$ by (E)-(p-$MeC_6H_4S)ClC{=}S{=}O$

A mixture of $[Pt^0\{P(C_6H_{11})_3\}_2\{(p\text{-}MeC_6H_4S)_2CSO\}]$ (0.1 mmol) and (*E*)-(*p*-$MeC_6H_4S)ClC{=}S{=}O$ (0.1 mmol) was stirred in $CDCl_3$ (0.5 ml). Displacement of the η^2-CS coordinated sulphine (*p*-$MeC_6H_4S)_2C{=}S{=}O$ by the sulphine (*E*)-(*p*-$MeC_6H_4S)ClC{=}S{=}O$ was followed by ^{31}P NMR for 7 days. The reaction products were identified by comparison of the ^{31}P NMR spectra of the reaction mixture with those of the pure complexes $[Pt^0\{P(C_6H_{11})_3\}_2\{(p\text{-}MeC_6H_4S)_2CSO\}]$, *cis*-(*E*)-, *trans*-(*E*)- and *trans*-(*Z*)-$[Pt^{II}Cl(p\text{-}MeC_6H_4SCSO)\{P(C_6H_{11})_3\}_2]$.

(iii) Displacement of Cl in (E)-(p-$MeC_6H_4S)ClC{=}S{=}O$ by p-$MeOC_6H_4S$ in $CDCl_3$ with or without cis-(E)-$[Pt^{II}Cl(p\text{-}MeC_6H_4SCSO)\{P(C_6H_{11})_3\}_2]$

Two mixtures of (*E*)-(*p*-$MeC_6H_4S)ClC{=}S{=}O$ (0.75 mmol) and KSC_6H_4OMe-*p* (0.75 mmol) in $CDCl_3$ (1 ml), one of which contained *cis*-(*E*)-$[Pt^{II}Cl(p\text{-}MeC_6H_4SCSO)\{P(C_6H_{11})_3\}_2]$ (0.18 mmol) were stirred for 16 hours. Undissolved KSC_6H_4OMe-*p* and KCl were filtered off and the reaction mixtures, which contained mainly (*E*)- and (*Z*)-(*p*-$MeOC_6H_4S$)(*p*-$MeC_6H_4S)C{=}S{=}O$, were investigated by ^1H NMR spectroscopy.

(iv) Synthesis of (E)-$[Pt^{II}(S_2CNEt_2)(R'SCSO)(PR_3)]$ ($R = R' = Ph$; $R = C_6H_{11}$, $R' =$ p-MeC_6H_4)

A mixture of *cis*-(*E*)-$[Pt^{II}Cl(R'SCSO)(PR_3)_2]$ (*ca.* 0.2 mmol; R = R' = Ph; R = C_6H_{11}, R' = *p*-MeC_6H_4) and $NaS_2CNEt_2{\cdot}3H_2O$ (*ca.* 0.6 mmol) were stirred in a mixture of CH_2Cl_2 (*ca.* 15 ml) and CH_3OH (*ca.* 15 ml) for 4 days. After the solvents had been removed *in vacuo* benzene was added (*ca.* 15 ml). The mixture was stirred for ½ h and then filtered to remove NaCl and unreacted NaS_2CNEt_2. The filtrate was concentrated and stirred for one night. In the case of R = R' = Ph impure white (*E*)-$[Pt^{II}(S_2CNEt_2)(PhSCSO)(PPh_3)]$ precipitated, which could be crystallized from $CDCl_3$/n-pentane as orange crystals. *Anal.* Calc. for (*E*)-$[Pt^{II}(S_2CNEt_2)(PhSCSO)(PPh_3)]{\cdot}0.1CDCl_3$: C, 45.93; H and D, 3.88. Cl, 1.35; N, 1.78%; M, 788. Found: C, 46.2; H and D, 3.97; Cl, 1.48; N, 1.65%; M($CHCl_3$), 750. In the case of R = C_6H_{11} and R' = *p*-MeC_6H_4 addition of n-pentane to the C_6H_6 solution resulted in precipitation of impure, white (*E*)-$[Pt^{II}(S_2CNEt_2)(p\text{-}MeC_6H_4SCSO)\{P(C_6H_{11})_3\}]$ which could be recrystallized from $CDCl_3$/n-pentane as orange crystals. The white compound was analyzed by spectroscopic methods, which also showed the presence of some (*Z*) isomer.

(v) Synthesis of cis-(Z)-$[Pt^{II}I(p\text{-}MeC_6H_4SCSO)(PPh_3)_2]$

A suspension of *cis*-$[Pt^{II}Cl(p\text{-}MeC_6H_4SCSO)(PPh_3)_2]$ (0.2 mmol; mixture of (*E*) and (*Z*) stereoisomers) and KI (100 fold excess) in $CHCl_3$ (2 ml) was stirred for 3 days. The mixture was filtered to remove KCl and unreacted KI, the solvent was removed *in vacuo* and the residue washed with n-pentane. Spectroscopic methods showed that the residue also contained, in addition to the major product *cis*-(*Z*)-$[Pt^{II}I(p\text{-}MeC_6H_4SCSO)(PPh_3)_2]$, a minor amount of the *cis*-(*E*) stereoisomer. The product could be purified by recrystallization from $CDCl_3$/n-pentane yielding orange crystalline *cis*-$[Pt^{II}I(p\text{-}MeC_6H_4SCSO)(PPh_3)_2]$, as the (*Z*) with a small amount of the (*E*) stereoisomer.

Results

(i) The formation of cis-$[Pt^{II}(SC_6H_4X\text{-}p)(p\text{-}MeC_6H_4SCSO)(PPh_3)_2]$ via displacement of Cl in cis-$[Pt^{II}Cl(p\text{-}MeC_6H_4SCSO)(PPh_3)_2]$ by SC_6H_4X-p (X = Me, MeO)

The reaction of *cis*-(*Z*)-$[Pt^{II}Cl(p\text{-}MeC_6H_4SCSO)(PPh_3)_2]$ containing a minor amount of the *cis*-(*E*) isomer with excess of KSC_6H_4X-*p* (X = Me, OMe) in $CDCl_3$ resulted in the displacement of Cl and formation of the metallo–sulphines *cis*-(*E*)- and -(*Z*)-$[Pt^{II}(SC_6H_4X\text{-}p)(p\text{-}MeC_6H_4SCSO)(PPh_3)_2]$ (*ca.* 1:4 molar ratio for X = Me; *ca.* 1:1 molar ratio for X = MeO; see Fig. 2a).

The products present in the reaction mixtures were identified by comparison of the ^{31}P and ^1H NMR spectra with those of equimolar mixtures of *cis*-(*E*)- and -(*Z*)-$[Pt^{II}(SC_6H_4Me\text{-}p)(p\text{-}MeC_6H_4SCSO)(PPh_3)_2]$ in $CDCl_3$ and an equimolar mixture of *cis*-(*E*)- and -(*Z*)-$[Pt^{II}(SC_6H_4OMe\text{-}p)(p\text{-}MeC_6H_4SCSO)(PPh_3)_2]$ and *cis*-(*E*)- and -(*Z*)-$[Pt^{II}(SC_6H_4Me\text{-}p)(p\text{-}MeOC_6H_4SCSO)(PPh_3)_2]$ in $CDCl_3$ [4]. ^{31}P NMR spectra showed that even after *ca.* ½ h. 50% of the Cl atoms in the starting metallo–sulphines had already been displaced, but nevertheless the reaction mixtures were stirred for 3 days. The absence of ν(Pt–Cl) absorption in the IR spectra of the isolated products confirmed that they contained no Cl. The ^1H NMR spectra recorded on the final reaction mixtures showed the presence of unracted KSC_6H_4X-*p*, as well as unidentifiable materials which are probably products of the reaction of KSC_6H_4X-*p* with the solvent.

Product identification in the case of X = MeO needs some explanation. The ^{31}P NMR spectra recorded on the final reaction mixtures showed two AB resonance patterns (complete with Pt satellites) consistent with the presence of one (*E*) and of one (*Z*) metallo–sulphine [4]. The ^1H NMR spectra contained no MeO resonances lower than $\delta = 3.9$ ppm,

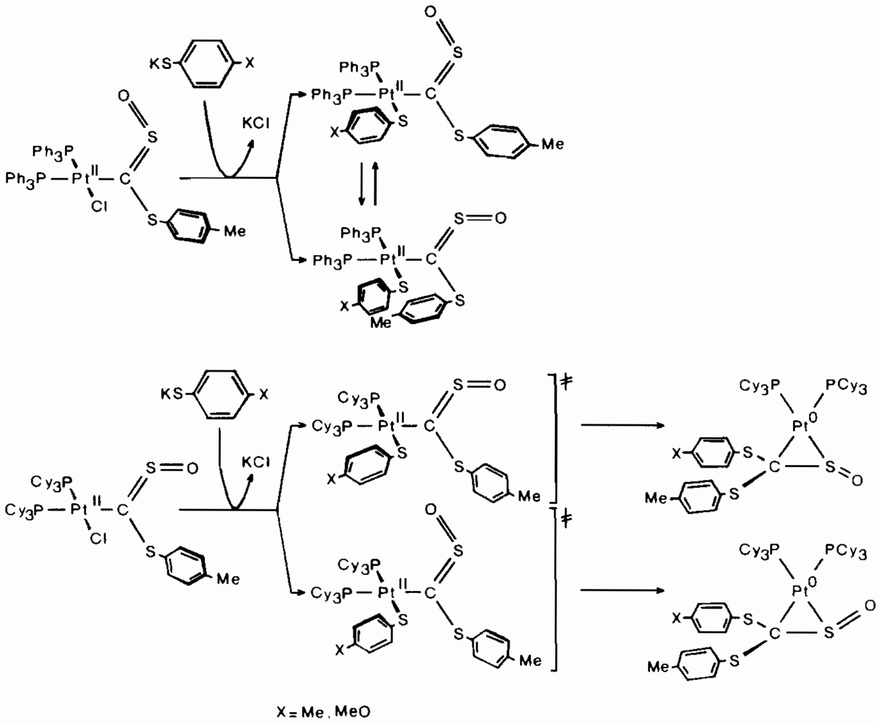

Fig. 2. The substitution of Cl in *cis*-[$Pt^{II}Cl$(*p*-MeC_6H_4SCSO)($(PR_3)_2$)] (R = Ph, C_6H_{11}) by *p*-XC_6H_4SK (X = Me, MeO) in $CDCl_3$.

pointing to the absence of products containing an (*E*)-$PtC(SC_6H_4OMe$-*p*)=S=O fragment. (These fragments were found to have *s-cis* conformations [4] bringing the MeO groups into the deshielding cone of Pt^{II} which resulted in a downfield shift of the MeO protons to 3.9 ppm)*. Because ^{31}P NMR spectra, recorded on the final reaction mixture, were not in accord with the metallo-sulphines *cis*-(*E*)- and (*Z*)-[$Pt^{II}(SC_6H_4$-*Me-p*)(*p-Me*$C_6H_4SCSO)(PPh_3)_2$], possible products from intermolecular scrambling, the product must be *cis*-(*E*)-[$Pt^{II}(SC_6H_4$*OMe-p*)(*p-Me*$C_6H_4SCSO)$-$(PPh_3)_2$], resulting from the direct displacement with KSC_6H_4OMe-*p*. Because scrambling of the *p*-XC_6H_4S groups did not occur for the (*E*) stereoisomers, even after prolonged reaction time (several weeks), this reaction is also not to be expected for the (*Z*)-stereoisomers. Consequently, the other ^{31}P NMR AB resonance pattern is now assigned to *cis*-(*Z*)-[$Pt^{II}(SC_6H_4$-*OMe-p*)(*p-Me*$C_6H_4SCSO)(PPh_3)_2$].

The difference in the (*E*)-(*Z*) ratio between starting complexes (*ca.* 1:9) and products (3:1) in the case of a 1:1 mixture of $CDCl_3$ and CD_3OD used as a solvent, showed that the displacement involved (*E*)-(*Z*) isomerization.

These displacement reactions established the first step in the syntheses of sulphines in the coordination sphere of Pt (see Fig. 1, reaction *i*).

(ii) The formation of the η^2*-CS compound* [$Pt^0\{P(C_6H_{11})_3\}_2\{$(p-$XC_6H_4S$)(p-$MeC_6H_4S)CSO\}$] *via displacement of Cl in* cis-(E)-[$Pt^{II}Cl$(p-$MeC_6H_4SCSO)\{P(C_6H_{11})_3\}_2$] *by* SC_6H_4X-p *(X = Me, MeO)*

A mixture containing mainly the η^2-CS compound [$Pt^0\{P(C_6H_{11})_3\}_2\{$(*E*)-(*p*-$MeC_6H_4S)ClCSO\}$] and a minor amount of the metallo–sulphine *cis*-(*E*)-[$Pt^{II}Cl$(*p*-$MeC_6H_4SCSO)\{P(C_6H_{11})_3\}$], was allowed to react with a suspension of KSC_6H_4X-*p* (X = Me, MeO) in $CDCl_3$. Because the η^2-CS compound undergoes a very fast C–Cl oxidative addition in $CDCl_3$, the metallo–sulphine *cis*-(*E*)-[$Pt^{II}Cl$(*p*-MeC_6H_4-$SCSO)\{P(C_6H_{11})_3\}_2$] was the actual starting complex. In the case of X = Me the reaction resulted in formation of the η^2-CS complex [$Pt^0\{P(C_6H_{11})_3\}_2$ $\{$(*p*-$MeC_6H_4S)_2CSO\}$] while in the case of X = MeO a mixture of [$Pt^0\{P(C_6H_{11})_3\}_2\{$(*E*)-(*p*-$MeOC_6H_4S$)-(*p*-$MeC_6H_4S)CSO)\}$] and [$Pt^0\{P(C_6H_{11})_3\}_2\{$(*Z*)-(*p*-$MeOC_6H_4S$)(*p*-$MeC_6H_4S)CSO\}$] was obtained (see Fig. 2b). Furthermore, the same impurities, arising from reaction of KSC_6H_4X-*p* with the solvent, were present as in the case of the reaction with the PPh_3 complexes (see Section i). The η^2-CS compounds were identified by comparison of the ^{31}P and ^1H

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*In reference 4 values of the MeO resonances for *cis*-(*E*)- and -(*Z*)-[$Pt^{II}(SC_6H_4Me$-*p*)(*p*-$MeOC_6H_4SCSO)(PPh_3)_2$] and *cis*-(*E*)- and -(*Z*)-[$Pt^{II}(SC_6H_4OMe$-*p*)(*p*-$MeC_6H_4SCSO)$-$(PPh_3)_2$] were incorrectly tabulated. The correct values are 3.90, 3.68, 3.77 and 3.70 ppm (relative to Me_4Si).

TABLE I. Spectroscopic Data.

Compound	Isomer	IR (KBr mull)		^{31}P-NMR (in CDCl$_3$)					^{1}H-NMR (in CDCl$_3$)				
		ν(CSO) (cm^{-1})	ν(Pt–Cl) {ν(C=N)} (cm^{-1})	^{1}J(Pt–P$_a$) (Hz)	^{1}J(Pt–P$_b$) (Hz)	^{2}J(P$_a$–P$_b$) (Hz)	δ(P$_a$)^{a} (ppm)	δ(P$_b$)^{a} (ppm)	δ(Me)^{b} (ppm)	δ(MeO)^{b} (ppm)	δ(H$_o$)^{b,c} (ppm)	δ(H$_m$)^{b,d} (ppm)	^{2}J(H$_o$–H$_m$) (Hz)
[$Pt^{II}Cl(RSCSO)(PPh_3)_2$]^{e}	*cis-(E)*	1075 947	295	3892^{g}	2285^{h}	17	12.2^{g}	17.1^{h}	2.63	–			
	cis-(Z)	978	298	4003^{g}	2202^{h}	18	14.4^{g}	15.7^{h}	2.34	–			
	trans-(E)			2738^{i}	–	–	19.9^{i}	–	2.50	–			
	trans-(Z)			2805^{i}	–	–	22.8^{i}	–	2.22	–			
[$Pt^{0}\{P(C_6H_{11})_3\}_2\{(RS)ClCSO\}$]^{e}	*(E)*	1002	–										
[$Pt^{II}Cl(RSCSO)\{P(C_6H_{11})_3\}_2$]^{e}	*cis-(E)*	1070 945		3730^{g}	2251^{h}	15	15.8^{g}	12.2^{h}	2.32	–	8.01	7.08	7.5
	trans-(E)	1060 950	279	2416^{i}	–	–	14.7^{i}	–	2.31	–	8.47		7.5
	trans-(Z)			2490^{i}	–	–	17.7^{i}	–		–			
[$Pt^{II}(SR)(RSCSO)(PPh_3)_2$]^{e}	*cis-(E)*	1073 946	–	2965^{j}	2448^{h}	20	15.9^{j}	18.8^{h}	2.66 2.17	–			
	cis-(Z)			3052^{j}	2301^{h}	21	18.9^{j}	17.2^{h}	2.29 2.19	–			
[$Pt^{II}(SR')(RSCSO)(PPh_3)_2$]^{e,f} #	*cis-(E)*	1075 948	–	2940^{j}	2457^{h}	20	15.8^{j}	18.9^{h}	2.60	3.77			
	cis-(Z)			3035^{j}	2311^{h}	22	18.7^{j}	17.2^{h}	2.20	3.70			
[$Pt^{0}\{P(C_6H_{11})_3\}_2\{(RS)_2CSO\}$]^{e}		1016	–	3475^{k}	3470^{k}	12	26.8^{k}	27.8^{k}	2.15 2.12	–			7.5
[$Pt^{0}\{P(C_6H_{11})_3\}_2\{(R'S)(RS)CSO\}$]^{e,f}	*(E)*	1020	–	3473^{k}	3469^{k}	12	26.8^{k}	27.8^{k}	2.25	3.69			
	(Z)	1020	–	3503^{k}	3438^{k}	11	27.0^{k}	27.3^{k}	2.20	3.70			
[$Pt^{II}I(RSCSO)(PPh_3)_2$]^{e}	*cis-(E)*	1070 945	–	–					2.61	–			
	cis-(Z)	978	–	3801^{l}	2232^{h}	17	13.5^{l}	10.5^{h}	2.27	–			
[$Pt^{II}(S_2CNEt_2)(PhSCSO)(PPh_3)_2$]	*(E)*	1072 947	1525	3621^{j}	–	–	11.5^{j}	–	–	–			
	(Z)	970	1530	3680^{j}	–	–	14.5^{j}	–	–	–			
[$Pt^{II}(S_2CNEt_2)(RSCSO)\{P(C_6H_{11})_3\}$]^{e}	*(E)*	1063 933	1521	3436^{j}	–	–	17.2^{j}	–		–			
	(Z)			3500^{j}	–	–	19.9^{j}	–		–			

^{a}Relative to H_3PO_4 (85%), + = downfield. ^{b}Relative to Me_4Si. ^{c}H$_o$: *ortho* protons. ^{d}H$_m$: *meta* protons. ^{e}R = *p*-MeC$_6$H$_4$. ^{f}R' = *p*-MeOC$_6$H$_4$. ^{g}P$_a$: *trans* to Cl. ^{h}P$_b$: *trans* to C. ^{i}P$_a$: *trans to P.* ^{j}P$_a$: *trans* to S. ^{k}P$_a$, P$_b$: *trans* to C=S. ^{l}P$_a$: *trans to I.*

NMR spectra recorded on the final mixtures, with those of the pure compounds synthesized *via* the reaction of $[Pt^0\{P(C_6H_{11})_3\}_2]$ and the corresponding free sulphines [5].

The formation of both stereoisomers of $[Pt^0\{P(C_6H_{11})_3\}_2\{(p\text{-}MeOC_6H_4S)(p\text{-}MeC_6H_4S)CSO\}]$ starting from pure *cis*-(*E*)-$[Pt^{II}Cl(p\text{-}MeC_6H_4SCSO)\{P(C_6H_{11})_3\}_2]$ is thought to proceed *via* a displacement of Cl by $p\text{-}MeOC_6H_4S$ in combination with an (*E*)-(*Z*) isomerization, as also found for the PPh_3 complexes, followed by C–S reductive coupling. However, the immediately formed substituted metallo–sulphines *cis*-(*E*)- and -(*Z*)-$[Pt^{II}(SC_6H_4OMe\text{-}p)(p\text{-}MeC_6H_4SCSO)\{P(C_6H_{11})_3\}_2]$ could not be detected in the reaction mixtures with ^{31}P NMR spectroscopy, even after a short reaction time (½ h), probably because of high lability of these metallo–sulphines towards C–S reductive coupling (see Fig. 2b).

Besides the displacement reaction a slight amount of the metallo–sulphine, *cis*-(*E*)-$[Pt^{II}Cl(p\text{-}MeC_6H_4SCSO)\{P(C_6H_{11})_3\}_2]$ underwent a *cis*-to-*trans* isomerization followed by an (*E*)-(*Z*) isomerization, forming the metallo–sulphines *trans*-(*E*) and -(*Z*)-$[Pt^{II}Cl(p\text{-}MeC_6H_4SCSO)\{P(C_6H_{11})_3\}_2]$ which were identified with ^{31}P NMR spectroscopy. This isomerization reaction was already investigated for *cis*-(*E*)-$[Pt^{II}Cl(PhSCSO)\{P(C_6H_{11})_3\}_2]$ [5]. The *trans*-metallo–sulphines are unreactive towards displacement of Cl by $SC_6H_4X\text{-}p$ anion, as established by a separate reaction from which the *trans*-(*E*) isomer could be isolated (see Table I). Earlier attempts to isolate *trans*-metallo–sulphines failed [5].

The displacement reactions discussed in this section, in which bulky phosphines were used as co-ligands, resulted in the syntheses of sulphines in the coordination sphere of platinum (see Fig. 1, reaction *ii*).

*(iii) Attempts to synthesize (*E*)- and (*Z*)-(*p*-$MeOC_6H_4S$)(*p*-MeC_6H_4S)C=S=O from (*E*)-(*p*-MeC_6H_4S)ClC=S=O and KSC_6H_4OMe-*p* in $CDCl_3$, via a cyclic process involving Pt complexes.*

To complete the process shown in Fig. 1, the reaction between the η^2-CS complex $[Pt^0\{P(C_6H_{11})_3\}_2\{(p\text{-}MeC_6H_4S)_2CSO\}]$ and the free sulphine (*E*)-$(p\text{-}MeC_6H_4S)ClC{=}S{=}O$ (1:1 molar ratio) in $CDCl_3$ has been followed by ^{31}P NMR spectroscopy. After 1½ days the resonance patterns of $[Pt^0\{P(C_6H_{11})_3\}_2\{(p\text{-}MeC_6H_4S)_2CSO\}]$, *cis*- and *trans*-(*E*)-$[Pt^{II}Cl(p\text{-}MeC_6H_4SCSO)\{P(C_6H_{11})_3\}_2]$ (*ca.* 1:1:0.3 molar ratio) could be identified. Some minor signals obviously belonging to decomposition products were also detected. After 4 days the starting complex and the *cis*-(*E*)-metallo–sulphine disappeared and in addition to the *trans*-(*E*) the *trans*-(*Z*)metallo–sulphine was also present, as well as an increased amount of decomposition products.

^{31}P NMR spectroscopy showed that the metallo–sulphine *cis*-(*E*)-$[Pt^{II}Cl(p\text{-}MeC_6H_4SCSO)\{P(C_6H_{11})_3\}_2]$ did not react with the free sulphine $(p\text{-}MeC_6H_4S)_2C{=}S{=}O$, but instead underwent a slow *cis*-to-*trans* and (*E*)-(*Z*) isomerization, as expected [5]. Because of the great lability of C–Cl sulphine side bonds towards oxidative addition at Pt^0 centres [4, 5], there will never be an equilibrium situation between the η^2-CS compounds $[Pt^0\{P(C_6H_{11})_3\}_2\{(p\text{-}MeC_6H_4S)_2CSO\}]$ and $[Pt^0\{P(C_6H_{11})_3\}_2\{(E)\text{-}(p\text{-}MeC_6H_4S)ClCSO\}]$ and the corresponding free sulphines.

These observations reveal that the metallo–sulphine *cis*-(*E*)-$[Pt^{II}Cl(p\text{-}MeC_6H_4SCSO)\{P(C_6H_{11})_3\}_2]$ can be resynthesized by displacement of the formed η^2-CS coordinated sulphine $(p\text{-}MeC_6H_4S)_2C{=}S{=}O$ in the final Pt-product by the original sulphine (*E*)-$(p\text{-}MeC_6H_4S)ClC{=}S{=}O$. The cyclic process, shown in Fig. 1, is completed for Y = $SC_6H_4Me\text{-}p$, although the formation of $(p\text{-}MeC_6H_4S)_2C{=}S{=}O$ could not be followed because of the complexity of the ^1H NMR spectra of the reaction mixture. No isolation attempts were made. The reformed starting complex *cis*-(*E*)-$[Pt^{II}Cl(p\text{-}MeC_6H_4SCSO)\{P(C_6H_{11})_3\}_2]$ in principle can undergo a displacement reaction with $KSC_6H_4OMe\text{-}p$ in a second cycle (see Fig. 1).

In order to study whether the cyclic process of Fig. 1 could be converted into a useful route for the synthesis of (*E*)- and (*Z*)-$(p\text{-}MeOC_6H_4S)(p\text{-}MeC_6H_4S)C{=}S{=}O$, the reaction between (*E*)-$(p\text{-}MeC_6H_4S)ClC{=}S{=}O$ and $KSC_6H_4OMe\text{-}p$ (1:1 molar ratio) in the presence of a small amount of *cis*-(*E*)-$[Pt^{II}Cl(p\text{-}MeC_6H_4SCSO)\{P(C_6H_{11})_3\}_2]$ was followed by ^1H NMR. In a control experiment the same reaction was studied but in this case no Pt complexes were present. The ^1H NMR spectra showed in both reactions the slow formation of (*E*)- and (*Z*)-$(p\text{-}MeOC_6H_4S)(p\text{-}MeC_6H_4S)C{=}S{=}O$ and no indication was obtained for any influence of the metallo–sulphine on the product formation.

The study of separate reactions of Fig. 1 for Y = $SC_6H_4X\text{-}p$ (X = Me, MeO) showed that the sulphine displacement (see Fig. 1, reaction *iii*) is most likely the rate determinant in the product formation *via* the cyclic process. Furthermore, the sulphine displacement proceeded considerably slower than the displacement of Cl in the free sulphine (*E*)-$(p\text{-}MeC_6H_4S)ClC{=}S{=}O$ of the control experiment (see above). From this it can be concluded that the formation of (*E*)- and (*Z*)-$(p\text{-}MeOC_6H_4S)(p\text{-}MeC_6H_4S)C{=}S{=}O$ in the reaction mixture containing (*E*)-$(p\text{-}MeC_6H_4S)ClC{=}S{=}O$, $KSC_6H_4OMe\text{-}p$, and *cis*-(*E*)-$[Pt^{II}Cl(p\text{-}MeC_6H_4SCSO)\{P(C_6H_{11})_3\}_2]$ (a small amount) proceeded almost completely *via* the direct displacement of Cl by $SC_6H_4OMe\text{-}p$ in the free sulphine.

*(iv) The synthesis of (*E*)- and (*Z*)-$[Pt^{II}(S_2CNEt_2)(R'SCSO)(PR_3)]$ (R = R′ = Ph; R = C_6H_{11}, R′ = *p*-MeC_6H_4)*

The reaction of *cis*-(*E*)-$[Pt^{II}Cl(PhSCSO)(PPh_3)_2]$ with $NaS_2CNEt_2{\cdot}H_2O$ in a mixture of CH_2Cl_2 and

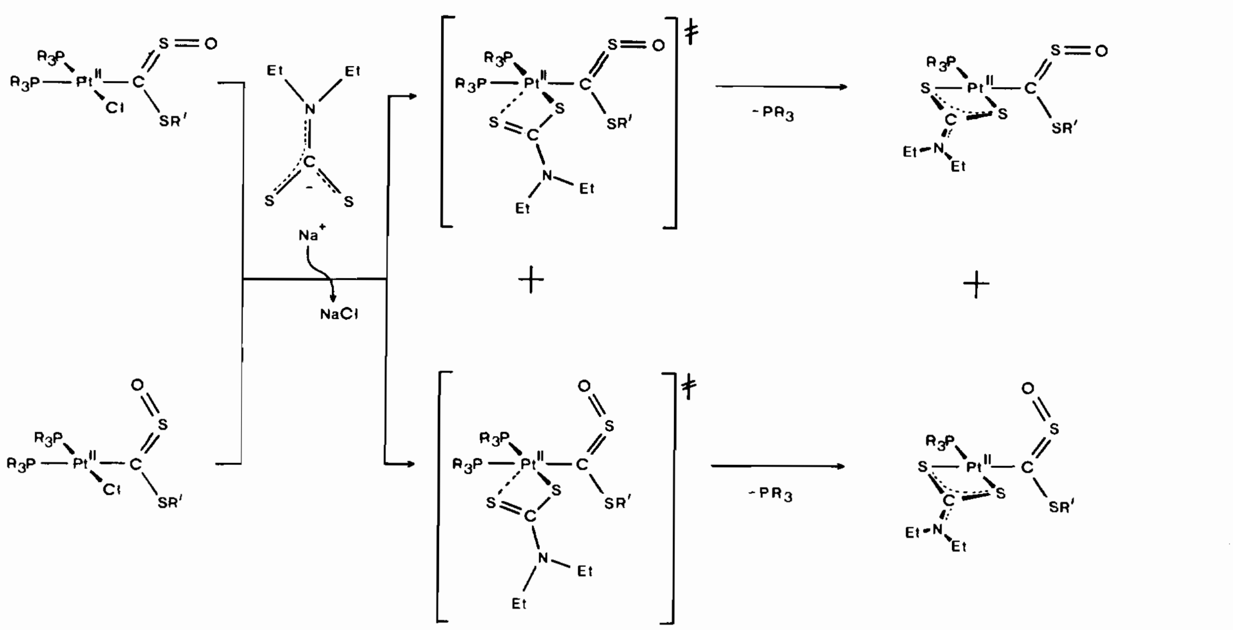

Fig. 3. The syntheses and structures of (*E*)- and (*Z*)-[Pt^{II}(S$_2$CNEt$_2$)(R'SCSO)(PR$_3$)] (R = R' = Ph; R = C$_6$H$_{11}$, R' = *p*-MeC$_6$H$_4$).

MeOH yielded the metallo–sulphine (*E*)-[Pt^{II}(S$_2$CNEt$_2$)(PhSCSO)(PPh$_3$)] with small amounts of its (*Z*) stereoisomer (*Z*)-[Pt^{II}(S$_2$CNEt$_2$)(PhSCSO)(PPh$_3$)] and an unknown impurity. When the product was recrystallized from CDCl$_3$/n-pentane the (*E*) stereoisomer could be collected as orange crystals, of which elemental analyses and molecular weight determinations established the stoichiometry and monomeric nature respectively (see Experimental). The IR spectra of both the impure and recrystallized product showed two ν(CSO) absorptions (see Table I) at 1072 and 943 cm^{-1} and no ν(Pt–Cl) absorption, pointing to an (*E*)-Pt^{II}(PhSCSO) metallo–sulphine fragment, in which the Cl atom is displaced by the Et$_2$NCS$_2$ ligand. This ligand is chelate bonded and its IR ν(C=N) absorption is fully comparable with this absorption in [Rh^{III}Cl(η^2-CSMe$_2$NCS)(Me$_2$NCS$_2$)(PPh$_3$)$_2$], which contained a chelate bonded dithiocarbamato ligand [12], [Rh^{I}(S$_2$CNMe$_2$)(PPh$_3$)$_2$] [13], [Pt^{II}(S$_2$CNMe$_2$)(PPh$_3$)$_2$]$^+$Br$^-$ [13], and [Pt^{II}(S$_2$CNMe$_2$)(σ-C-Me$_2$NCS)(PPh$_3$)] [14], in which the bidentate character was established by spectroscopic methods. The ^{1}H NMR data showed two unequivalent Et groups, consistent with an asymmetric arrangement around Pt, having one S atom of the dithiocarbamato ligand coordinated *trans* to a PPh$_3$ and the other *trans* to the PhS–C=S=O group. The fact that the two Et resonances are anisochronous points to a hindered rotation around the C$\cdots$N bond, as also found for [Pt^{II}(S$_2$CNEt$_2$)(η^2-CS–SCNMe$_2$)(PPh$_3$)] [14]. The ^{1}J(Pt–P) value of 3621 Hz found in the ^{31}P NMR spectrum of (*E*)-[Pt^{II}(S$_2$CNEt$_2$)(PhSCSO)(PPh$_3$)] was comparable with those of 3700–3100 Hz, reported for P atoms coordinated to Pt^{II} in [Pt^{II}H{Me$_2$NC(S)NC(S)NMe$_2$}(PPh$_3$)], [Pt^{II}Cl{Me$_2$NC(S)NC(S)NMe$_2$}(PPh$_3$)], and [Pt^{II}{Me$_2$NC(S)NC(S)NMe$_2$}(PPh$_3$)$_2$]$^+$Cl$^-$, in which the dithiobiuret ligands are bonded *via* both S atoms in a chelate fashion [13]. The ^{31}P NMR spectrum of the reaction mixture also showed two minor resonances of which one could be assigned to (*Z*)-[Pt^{II}(S$_2$CNEt$_2$)(PhSCSO)(PPh$_3$)] because of its ^{1}J(Pt–P) value of 3680 Hz comparable with that of the (*E*) stereoisomer but the nature of the other product is still unknown. When a mixture of *cis*-(*Z*)- and -(*E*)-[Pt^{II}Cl(PhSCSO)(PPh$_3$)$_2$] was used in the displacement reaction, the resonance patterns of (*E*)- and (*Z*)-[Pt^{II}(S$_2$CNEt$_2$)(PhSCSO)(PPh$_3$)] and the unknown product had almost equal intensity.

Starting from the P(C$_6$H$_{11}$)$_3$ complex [Pt^0{P(C$_6$H$_{11}$)$_3$}$_2${(*E*)-(*p*-MeC$_6$H$_4$S)ClCSO}] the ^{31}P NMR spectrum recorded on a CDCl$_3$ solution of the reaction products (see Experimental) showed a major signal, each with Pt satellites with ^{1}J(Pt–P) values of 3436 and 3500 Hz, respectively. Addition of a layer of n-pentane to the solution resulted in formation of orange crystals of which the IR spectrum showed two ν(CSO) absorptions at 1063 and 933 cm^{-1} and no ν(Pt–Cl) absorption. Therefore the major ^{31}P NMR resonance pattern was assigned to (*E*)-[Pt^{II}(S$_2$CNEt$_2$)(*p*-MeC$_6$H$_4$SCSO){P(C$_6$H$_{11}$)$_3$}] and the minor pattern to the corresponding (*Z*) stereoisomer.

The difference in chemical shift of the P atom between (*E*)- and (*Z*)-[Pt^{II}(S$_2$CNEt$_2$)(R'SCSO)-

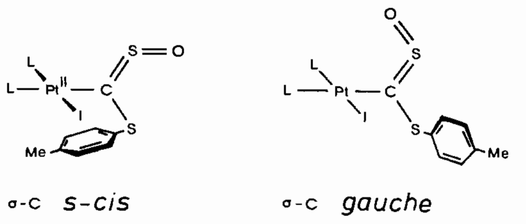

Fig. 4. Structures of *cis*-(*E*)- and -(*Z*)-[Pt^{II}I(*p*-MeC$_6$H$_4$-SCSO)L$_2$] (L = PPh$_3$).

(PR$_3$)] defined as $\Delta(P) = \delta(P_E) - \delta(P_Z)$ (where P_E stands for the P atom in the (*E*) stereoisomer, and P_Z for that in the (*Z*) stereoisomer) is found to be –2.9 ppm for R = Ph and –2.7 ppm for R = C$_6$H$_{11}$, which is in good agreement with the value of –2.9 ppm found for P atoms *cis* coordinated to a R′SC=S=O fragement in several metallo–sulphines [4, 5].

The differences in $^1J(Pt–P)$ values between (*E*)- and (*Z*)-[Pt^{II}(S$_2$CNEt$_2$)(R′SCSO)(PR$_3$)], defined as $\Delta(^1J) = {}^1J(Pt–P_E) - {}^1J(Pt–P_Z)$, were found to be –59 Hz for R = Ph and –64 Hz for R = C$_6$H$_{11}$, values falling to the low end of the range of –118 to –67 Hz found for $\Delta(^1J)$ for P atoms coordinated *cis* to a R′S–C=S=O fragment in several metallo–sulphines [4, 5].

(v) Halogen exchange in cis-*[Pt^{II}Cl(*p*-MeC$_6$H$_4$SCSO)(PPh$_3$)$_2$]*

The reaction mixture of *cis*-(*E*)- and -(*Z*)-[Pt^{II}Cl-(*p*-MeC$_6$H$_4$SCSO)(PPh$_3$)$_2$] with a suspension of KI in CDCl$_3$ resulted in the slow formation of *cis*-(*Z*)-[Pt^{II}I(*p*-MeC$_6$H$_4$SCSO)(PPh$_3$)$_2$] together with a small amount of the *cis*-(*E*) stereoisomer.

The IR spectrum recorded on the reaction products showed the absence of a ν(Pt–Cl) in agreement with the displacement of Cl. Furthermore, they showed one ν(CSO) absorption at 978 cm^{-1}, characteristic of (*Z*) metallo–sulphines and weak absorptions at *ca.* 1070 and 945 cm^{-1}, indicative of the presence of an (*E*) stereoisomer. The ^{1}H NMR spectra recorded on a CDCl$_3$ solution of the reaction products showed a major singlet at 2.27 and a minor singlet at 2.61 ppm, assigned to (*Z*)- and (*E*)-[Pt^{II}-I(*p*-MeC$_6$H$_4$SCSO)(PPh$_3$)$_2$] respectively. The lower field shift of the resonance belonging to the (*E*) stereoisomer compared to that of the (*Z*) stereoisomer is caused by a *s-cis* conformation of the *p*-MeC$_6$H$_4$S–C=S=O fragment in the (*E*) stereoisomer and a *gauche* conformation in the (*Z*) stereoisomer, which was found for the Cl analogues (see Fig. 4) [4]. Because the (*E*) stereoisomer is present in a very low concentration, the ^{31}P NMR spectrum recorded on a CDCl$_3$ solution of the final reaction product showed one AB resonance pattern (complete with Pt satellites). This pattern established the (*Z*) stereoisomer as being *cis*-(*Z*)-[Pt^{II}I(*p*–MeC$_6$H$_4$SCSO)-(PPh$_3$)$_2$]. Because the *trans*-(*Z*) isomer is absent, the (*E*) isomer is also thought to have the PPh$_3$ groups in *cis* positions. The smaller $^1J(Pt–P)$ value of 2232 Hz was assigned to the P atom *trans* to the C atom, and the other {$^1J(Pt–P)$ = 3801 Hz} to the P atom *trans* to the I atom. This assignment was based on the assumption that the C atom has a greater *trans* influence than does the I atom. Comparison of the ^{31}P NMR data of the *cis*(*Z*) isomer with those of its analogue (see Table I) confirmed this assignment: On going from X = Cl to X = I in the complexes *cis*-(*Z*)-[Pt^{II}X(*p*-MeC$_6$H$_4$SCSO)(PPh$_3$)$_2$] the $^1J(Pt–P_X)$ (P atom *trans* to X atom) changed more than the $^1J(Pt–P_C)$ value, *i.e.* 202 Hz decrease *versus* 30 Hz increase. By contrast the $\delta(P_X)$ value changed less than the $\delta(P_C)$ value, *i.e.* 0.9 ppm *versus* 5.2 ppm upfield. This is in agreement with the different bulkiness of the halogen atoms which has more influence on the chemical shift of the *cis* ligands than that of the *trans* ligand.

Discussion

In previous reports we showed that η^3-SCS coordinated sulphines are the most likely key intermediates or transition states in the intramolecular C–S oxidative addition and (*E*)-(*Z*) isomerization of the η^2-CS compounds [Pt^0(PR$_3$)$_2${(*E*)- or (*Z*)-(R′S)XCSO}], as well as the intramolecular C–S reductive coupling and (*E*)-(*Z*) isomerization reactions of the corresponding metallo–sulphines (σ-C) *cis*-(*E*)- and -(*Z*)-[Pt^{II}(SR′)(XCSO)(PPh$_3$)$_2$] (X = aryl, S-aryl; R′ = aryl, alkyl; R = Ph, C$_6$H$_{11}$) [5]. Upon formation of *cis*-[Pt^{II}(SR″)(R′SCSO)(PPh$_3$)$_2$] by a displacement reaction (see Results section *i*) only (*E*)–(*Z*) isomerization and no scrambling of *p*-XC$_6$H$_4$S (X = Me, MeO) was found. This result is additional support for the overall mechanism. It excludes occurrence of (*E*)–(*Z*) isomerization in *cis*-[Pt^{II}(SR″)(R′SCSO)-(PPh$_3$)$_2$] *via* η^2-CS compounds [Pt^0(PPh$_3$)$_2${(R″S)-(R′S)CSO}] as intermediates because scrambling of R″S and R′S groups would then be expected. This latter possibility was proposed as an alternative route for the (*E*)–(*Z*) isomerization in metallo–sulphines [4].

The metallo–sulphines *cis*-(*E*)- and -(*Z*)-[Pt^{II}-(SR″)(R′SCSO){P(C$_6$H$_{11}$)$_3$}$_2$], which were expected to be initially formed *via* displacement of Cl in *cis*-(*E*)-[Pt^{II}Cl(R′SCSO){P(C$_6$H$_{11}$)$_3$}$_2$] by R″S, could not be detected. They contain two bulky phosphines in *cis* position leading to a less favourable steric interaction than in the *trans* metallo–sulphines and the η^2-CS complexes. In principle two pathways are available for these unstable metallo–sulphines to release the steric interaction; (*i*) *cis*-to-*trans* isomerization as was found for the metallo–sulphine *cis*-(*E*)-

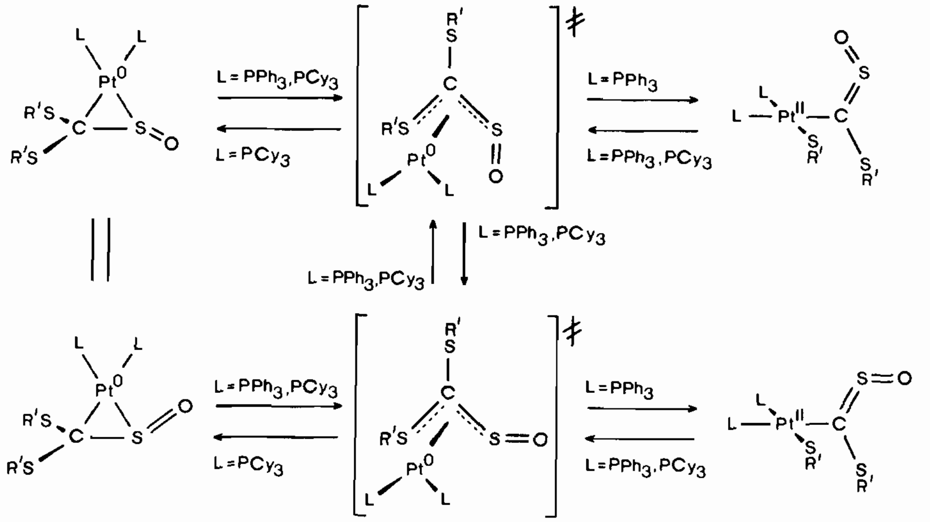

Fig. 5. The influence of the phosphines on the intramolecular rearrangements of sulphines on Pt^0(PR$_3$)$_2$ centres.

$[\mathrm{Pt^{II}Cl(R'SCSO)\{P(C_6H_{11})_3\}_2}]$ [5]. (*ii*) C–S reductive coupling resulting in formation of three-coordinate Pt^0 complexes, the process actually observed. Reduction of steric interaction in the metallo–sulphine *cis*-(*E*)-$[\mathrm{Pt^{II}Cl(R'SCSO)\{P(C_6H_{11})_3\}_2}]$ by C–Cl reductive coupling is an unlikely process, because of the greater reactivity of C–Cl compared with C–S side bonds towards oxidative addition to Pt^0 [4, 5].

The immediate formation of the η^2-CS compounds $[\mathrm{Pt^0\{P(C_6H_{11})_3\}_2\{(R''S)(R'S)CSO\}}]$ from the metallo–sulphines *cis*-$[\mathrm{Pt^{II}(SR'')(R'SCSO)\{PC_6H_{11})_3\}_2}]$ is the first example of irreversible C–S sulphine side bond reductive coupling. It is thought to proceed *via* the same mechanism as was deduced for the C–S reductive coupling in *cis*-$[\mathrm{Pt^{II}(SMe)(R'CSO)(PPh_3)_2}]$ (R' = aryl) [5], *i.e.* C–S reductive coupling followed by gliding of the Pt^0(PR$_3$)$_2$ unit from the C–S side bond along the S–C=S frame to the C=S bond with η^3-SCS coordinated sulphines as intermediates or transition states. The reverse occurs when PPh$_3$ is the co-ligand: The η^2-CS compounds $[\mathrm{Pt^0(PPh_3)_2\{(R''S)(R'S)CSO\}}]$ undergo irreversible C–S oxidative addition, *via* η^3-SCS coordinated intermediates. The intramolecular rearrangements of sulphines on Pt^0(PR$_3$)$_2$ centres can therefore be steered to either C–S bond cleavage or C–S bond formation by using the correct co-ligands. This interesting effect of the phosphine co-ligand is summarized in Fig. 5, taking into account the general mechanism for C–S oxidative addition, reductive coupling and (*E*)–(*Z*) isomerization.

The absence of scrambling of R'S and R''S groups also indicated, that the displacement reaction proceeds *via* attack of R''S on the Pt atom. The alternative process, *i.e.* attack of R''S on the C atom of the (R'S)C=S=O fragment would lead to formation of (R''S)(R'S)C=S=O and thus would result in effective scrambling. However, determination of the precise mechanism requires kinetic measurements [15]. In the absence of such information a mechanism for the *cis*-to-*trans* isomerization could not be deduced. This isomerization reaction proceeds fortunately at a considerably lower rate than the displacement reactions.

The formation of the metallo–sulphines (*E*)- and (*Z*)-$[\mathrm{Pt^{II}(S_2CNEt_2)(R'SCSO)(PR_3)}]$ from the displacement reactions with NaS$_2$CNEt$_2$ possibly proceeds *via* intermediates in which two phosphines are coordinated to Pt and the dithiocarbamato coordinated in a monodentate or a bidentate fashion with one S atom on a fifth coordination place (see Fig. 3). In a second step one PR$_3$ group dissociates, thus demonstrating another possibility for diminishing steric interaction between two *cis* positioned bulky P(C$_6$H$_{11}$)$_3$ groups.

When R''S is the nucleophile the C–S sulphine side bond reductive coupling is the essential step in the synthesis of sulphines in the coordination sphere of Pt according to the cyclic process, shown in Fig. 1. Three side reactions so far prevent this cyclic process becoming catalytic: (*i*) Isomerization of *cis*-$[\mathrm{Pt^{II}Cl(R'SCSO)\{P(C_6H_{11})_3\}_2}]$ into *trans* isomers, the latter being unreactive towards Cl displacement, (*ii*) decomposition during the displacement of the η^2-CS coordinated sulphine in $[\mathrm{Pt^0\{P(C_6H_{11})_3\}_2\{(\textit{p}\text{-}MeC_6H_4S)_2CSO\}}]$ by the original sulphine (*E*)-(*p*-MeC$_6$H$_4$S)ClC=S=O, which is a very slow reaction compared with the displacement, C–S reductive coupling, and C–Cl oxidative addition reaction, and (*iii*) *cis*-to-*trans* isomerization in the formed metallo–sulphines *cis*-$[\mathrm{Pt^{II}Y(R'SCSO)(PR_3)_2}]$, which does not occur in case of Y = SC$_6$H$_4$X-*p*, but in principle like side reaction (*i*) be competitive to the C–Y reductive coupling process*.

Finally, it must be noted that the synthesis of sulphines of the type (R″S)(R′S)C=S=O according to the cyclic process shown in Fig. 1 cannot compete with the direct synthesis of sulphines by known organic routes. This process may prove useful for the syntheses of other sulphines, which either cannot be synthesized by organic routes or which are unstable as free molecules, but are expected to stabilized by coordination to a metal core.

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*Preliminary results for Y = MeO showed that in case of $P(C_6H_{11})_3$ as co-ligands instead of C–O reductive coupling *cis*-to-*trans* isomerization occurred. Therefore it is impossible to synthesize the unknown sulphine (R′S)(MeO)C=S=O *via* the cyclic process.

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