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COORDINATION CHEMISTRY OF SULPHINES

VI *. COORDINATION OF SULPHINES, XYC=S=O (X, Y = ARYL, S-ARYL, Cl) TO Pd^0 AND Ir^I COMPLEXES. OXIDATIVE ADDITION OF THE C—Cl SIDE BOND OF (*E*)-(RS)ClC=S=O AND (*Z*)-PhClC=S=O TO Pd^0

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Summary

The first Ir^I-sulphine complex has been prepared by treating $[Ir^ICl(cyclo\text{-}C_8H_{14})_2]_2$ with fluorene-9-ylidine-sulphine, $C_{12}H_8C{=}S{=}O$, in the presence of $P(C_6H_{11})_3$ to give *trans*-$[Ir^ICl\{P(C_6H_{11})_3\}_2(C_{12}H_8CSO)]$, in which the sulphine is σ-S coordinated. The complex $[Pd^0(PPh_3)_4]$ reacts with the sulphines, (*p*-Me-$C_6H_4S)_2C{=}S{=}O$, (*E*)-(*p*-$MeC_6H_4S)ClC{=}S{=}O$, and (*Z*)-$PhClC{=}S{=}O$, to form the η^2-CS coordinated sulphine complexes $[Pd^0(PPh_3)_2\{(p\text{-}MeC_6H_4S)_2CSO\}]$, $[Pd^0(PPh_3)_2\{(E)\text{-}(p\text{-}MeC_6H_4S)ClCSO\}]$, and $[Pd^0(PPh_3)_2\{(Z)\text{-}PhClCSO\}]$. In solution $[Pd^0(PPh_3)_2\{(p\text{-}MeC_6H_4S)_2CSO\}]$ does not undergo an oxidative addition reaction of the C—S side bonds, but instead slow dissociation of the sulphine occurs. The complexes $[Pd^0(PPh_3)_2\{(E)\text{-}(p\text{-}MeC_6H_4S)ClCSO\}]$ and $[Pd^0(PPh_3)_2\{(Z)\text{-}PhClCSO\}]$ undergo in solution an oxidative addition of the C—Cl side bonds yielding *trans*-(*E*)- and -(*Z*)-$[Pd^{II}Cl(p\text{-}MeC_6H_4SCSO)(PPh_3)_2]$ and *trans*-(*E*)- and -(*Z*)-$[Pd^{II}Cl(PhCSO)(PPh_3)_2]$, respectively. These reactions proceed at least in part via initially formed *cis* oxidative addition complexes, which subsequently rearrange to the *trans* products.

Introduction

Recently, we reported on the coordination chemistry of sulphines, XYC=S=O, with Pt^0 and Rh^I [1—7]. The sulphines coordinate via η^2-CS to Pt^0 [1,2,5,7] and σ-S or η^3-SCS to Rh^I, depending on the substituents X and Y and the coligands used [1,6,7]. Examples of these sulphine coordination modes are shown in Fig. 1.

* For part V see ref. 1.

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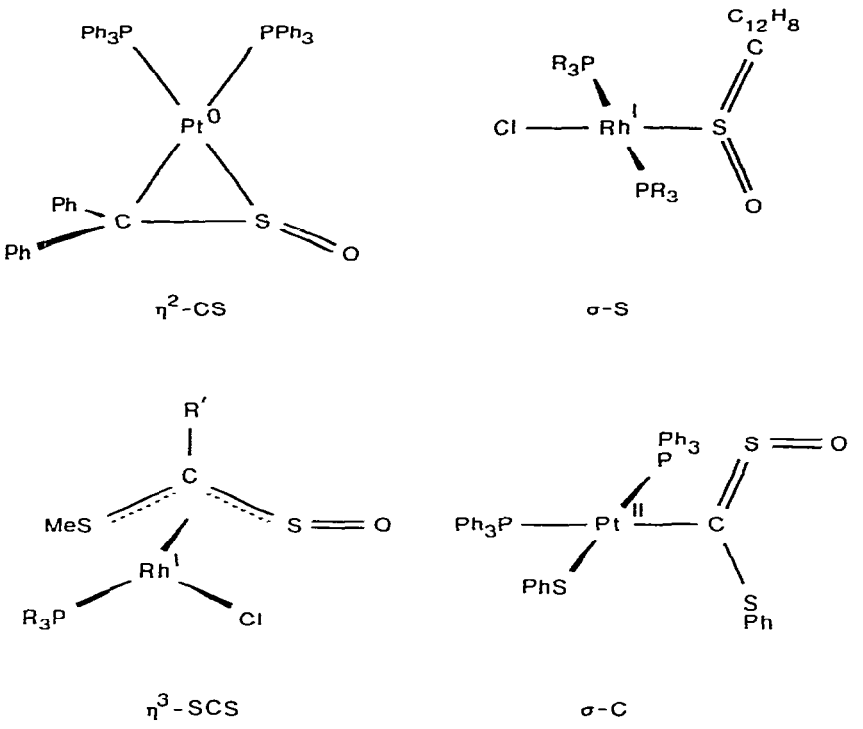

Fig. 1. Examples of η^2-CS, σ-S, η^3-SCS, and σ-C coordination of sulphines.

Sulphines containing C—S side bonds undergo, when coordinated via η^2-CS to $Pt^0(PPh_3)_2$, intramolecular C—S oxidative addition forming σ-C metallo-sulphines. For example the complex $[Pt^0(PPh_3)_2\{(PhS)_2CSO\}]$ is converted into *cis*-(*E*)- and -(*Z*)-$[Pt^{II}(SPh)(PhSCSO)(PPh_3)_2]$ * (see Fig. 1) [3,4,6]. The presence of the more bulky $P(C_6H_{11})_3$ ligand instead of PPh_3 blocks the C—S oxidative addition. This observation enabled the formulation of an overall mechanism for the intramolecular C—S oxidative addition and (*E*)—(*Z*) isomerization processes taking place in η^2-CS coordination compounds as well as for the intramolecular reductive coupling and (*E*)—(*Z*) isomerization processes occurring in the σ-C metallo-sulphines. It was suggested that these processes involve η^3-SCS-coordinated sulphines as key intermediates [5]. The more reactive C—Cl side bond undergoes oxidative addition in $[Pt^0(PR_3)_2\{(E)\text{-}(PhS)ClCSO\}]$ * both for R = Ph and for R = C_6H_{11}, but in the latter case the *cis*-σ-C metallo-sulphines isomerize slowly to the *trans* products, in order to lower the steric interaction between *cis* positioned ligands [5]. Very interesting, but not yet understood, is the observation that C—S oxidative addition does not occur with the σ-S or η^3-SCS coordinated sulphine-Rh^I complexes [1].

* (*E*) and (*Z*) refer to the configuration of the sulphine C=S bond. If they are placed inside the molecular formula, this indicates that the sulphine has the (*E*) or (*Z*) configuration and is coordinated as such (e.g. η^2-CS, σ-S, η^3-SCS). If they 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.

In order to obtain more insight into the role of the metal in rearrangement processes of coordinated sulphines, the reactivity of sulphines towards other low-valent metal centres, such as Pd^0 and Ir^I, has been investigated. This paper deals with the synthesis of the first Ir^I-sulphine complex and oxidative additions of reactive side bonds to "$Pd^0(PPh_3)_2$".

Experimental

Infrared spectra were recorded on Perkin-Elmer 283 or Beckman IR-4250 spectrophotometers. ^1H NMR spectra were recorded on Varian T60A or Bruker WM250 and the $^{31}P\{^1H\}$ NMR spectra on XL100 spectrometers. Elemental analyses were carried out by the Analytical section of the Institute for Organic Chemistry TNO, Utrecht. Molecular weights were determined with a Hewlett-Packard (model 320B) vapour-pressure osmometer.

Preparation of the compounds

The starting complexes $[Pd^0(PPh_3)_4]$ [8] and $[Ir^ICl(C_8H_{14})_2]_2$ [9] (C_8H_{14} = *cyclo*-octene) and the sulphines $C_{12}H_8C{=}S{=}O$ ($C_{12}H_8$ = fluorene-9-ylidene) [10], $(p\text{-}MeC_6H_4S)_2C{=}S{=}O$ [11] and (E)-$(p\text{-}MeC_6H_4S)ClC{=}S{=}O$ [11] were prepared according to literature procedures.

The syntheses of the Pd^0- and Ir^I-sulphine complexes were carried out under N_2 using Schlenk apparatus.

i. trans-$[Ir^ICl\{P(C_6H_{11})_3\}_2(C_{12}H_8CSO)]$. $[Ir^ICl(C_8H_{14})_2]_2$ (0.25 mmol) and $P(C_6H_{11})_3$ (1.0 mmol) were stirred in n-pentane (ca. 25 ml). After 30 min the yellow suspension was cooled to −20°C and a solution of $C_{12}H_8C{=}S{=}O$ (0.5 mmol) in toluene (ca. 15 ml) was slowly added, the temperature being kept below −10°C. The almost clear dark-red solution was allowed to stand at room temperature for at least one hour before filtration followed by solvent evaporation at 25°C. n-Pentane was added to the residue and the mixture was stirred vigorously. The red precipitate was filtered off, and dried in vacuo (Found: C, 59.7; H, 7.5; P, 6.2. Calcd. for $C_{49}H_{74}ClIrOPS$: C, 58.8; H, 7.47; P, 6.19%).

ii. $[Pd^0(PPh_3)_2\{(p\text{-}MeC_6H_4S)_2CSO\}]$. $[Pd^0(PPh_3)_4]$ (0.2 mmol) and $(p\text{-}MeC_6H_4S)_2C{=}S{=}O$ (0.2 mmol) were stirred for 2 h in benzene (ca. 10 ml) at room temperature and the solvent evaporated. n-Pentane was added to the residue and the suspension stirred for ca. 18 h. The light-brown precipitate was filtered off and dried in vacuo. (Found: C, 63.5; H, 4.6; P, 6.6; S, 9.4. *M* 836. Calcd. for $C_{51}H_{44}OP_2PdS_3$: C, 65.3; H, 4.74; P, 6.61; S, 10.3%. *M* 938).

iii. $[Pd^0(PPh_3)_2\{(E)\text{-}(p\text{-}MeC_6H_4S)ClCSO\}]$. $[Pd^0(PPh_3)_4]$ (0.2 mmol) and (E)-$(p\text{-}MeC_6H_4S)ClC{=}S{=}O$ (0.2 mmol) were stirred in a (1 : 1) mixture of benzene and n-pentane (ca. 25 ml) for ca. $1\frac{1}{2}$ h. Further benzene was added until the orange mixture was almost clear. After filtration to remove unreacted $[Pd^0(PPh_3)_4]$ the mixture was concentrated and n-pentane added. The white precipitate was filtered off and dried in vacuo. (Found: C, 62.4; H, 4.4; Cl, 3.8; P, 7.2; S, 6.7. Calcd. for $C_{44}H_{37}ClOP_2PdS_2$: C, 62.2; H, 4.40; Cl, 4.17; P, 7.29; S, 7.55%.).

iv. $[Pd^0(PPh_3)_2\{(Z)\text{-}PhClCSO\}]$. A solution of (Z)-$PhClC{=}S{=}O$ (0.2 mmol) in benzene (ca. 4 cm^3) was added to $[Pd^0(PPh_3)_4]$ (0.2 mmol). The mixture was stirred for 1 h and the white precipitate filtered off, washed with n-pentane,

and dried in vacuo. (Found: C, 63.0; H, 4.3; Cl, 4.1. Calcd. for $C_{43}H_{35}ClOP_2PdS$: C, 64.3; H, 4.40; Cl, 4.41%).

v. trans-(E)-[Pd^{II}Cl(p-MeC$_6$H$_4$SCSO)(PPh$_3$)$_2$]. A concentrated solution of [Pd^0(PPh$_3$)$_2${(*E*)-(*p*-MeC$_6$H$_4$S)ClCSO}] in C_6D_6 was allowed to stand for several days, during which orange crystals of *trans*-(*E*)-[Pd^{II}Cl(*p*-MeC$_6$H$_4$SCSO)-(PPh$_3$)$_2$] slowly separated.

vi. A mixture of trans-(E)- and -(Z)-[Pd^{II}Cl(p-MeC$_6$H$_4$SCSO)(PPh$_3$)$_2$]. A solution of [Pd^0(PPh$_3$)$_2${(*Z*)-PhClCSO}] (70 mg) in $CDCl_3$ (0.4 ml) was allowed to stand for several days. After addition of a layer of n-pentane orange crystalline *trans*-(*E*)- and -(*Z*)-[Pd^{II}Cl(*p*-MeC$_6$H$_4$SCSO)(PPh$_3$)$_2$] formed in the course of several days. (Found: C, 63.7; H, 4.6; Cl, 4.0. *M* 787. Calcd. for $C_{44}H_{37}ClOP_2PdS_2$: C, 62.2; H, 4.40; Cl, 4.17%. *M* 850).

vii. trans-(Z)-[Pd^{II}Cl(p-MeC$_6$H$_4$SCSO)(PPh$_3$)$_2$]. A solution of (*E*)-(*p*-MeC$_6$H$_4$S)ClC=S=O (0.2 mmol) in THF (ca. 3 ml) was added to [Pd^0(PPh$_3$)$_4$] (0.2 mmol). A yellow solid separated from the clear yellow solution and after ca. one hour the mixture was set aside at −20°C for 3 days. The solvent was decanted and the yellow solid washed with n-pentane and dried in vacuo. (Found: C, 62.5; H, 4.38; Cl, 4.31. Calcd. for $C_{44}H_{37}ClOP_2PdS_2$: C, 62.19; H, 4.40; Cl, 4.17%). n-Pentane was added to the mother liquor, more yellow solid separated, and this was filtered off, washed with n-pentane, dried in vacuo, and shown to contain in addition to *trans*-(*Z*)- also some *trans*-(*E*)-[Pd^{II}Cl(*p*-MeC$_6$H$_4$SCSO)(PPh$_3$)$_2$]. (Found: C, 61.4; H, 4.6; Cl, 4.2. Calcd. for $C_{44}H_{37}ClOP_2PdS_2$: C, 62.19; H, 4.40; Cl, 4.17%.)

viii. A mixture of trans-(E)- and -(Z)-[Pd^{II}Cl(PhCSO)(PPh$_3$)$_2$]. Starting from [Pd^0(PPh$_3$)$_2${(*Z*)-PhClCSO}] and following a procedure similar to that in vi, a mixture of *trans*-(*E*)- and -(*Z*)-[Pd^{II}Cl(PhCSO)(PPh$_3$)$_2$] was obtained. This mixture was analyzed spectroscopically.

Results

i. Synthesis and characterization of trans-[Ir^{I}Cl{P(C$_6$H$_{11}$)$_3$}$_2$(C$_{12}$H$_8$CSO)]

The reaction of [Ir^{I}Cl(C$_8$H$_{14}$)$_2$]$_2$ with P(C$_6$H$_{11}$)$_3$ and $C_{12}H_8C{=}S{=}O$, fluorene-9-ylidene-SO, in 1:4:2 molar ratio yielded *trans*-Ir^{I}Cl{P(C$_6$H$_{11}$)$_3$}$_2$(C$_{12}$H$_8$CSO)]. The structure of this Ir-sulphine complex was elucidated by comparison of its IR- and NMR data with those of *trans*-[Rh^{I}Cl{P(C$_6$H$_{11}$)$_3$}$_2$(C$_{12}$H$_8$CSO)] [1] and the free sulphine $C_{12}H_8C{=}S{=}O$.

Analysis established the stoichiometry. The IR spectrum showed three ν(CSO) absorptions, which were very similar to both the free sulphine and the Rh^I sulphine complex. This indicates that the sulphine is not coordinated via its π system, and that the coordination mode is the same as in the Rh^I complex, i.e. σ-S [1]. The presence of a ν(Ir—Cl) absorption at 316 cm^{-1} confirmed the coordination of the Cl atom. The ^{1}H NMR spectra (see Table 1) showed separate resonances for the two *ortho* protons at δ = 10.38 and δ = 8.63 ppm. By analogy to the Rh^I sulphine complex, which has a similar ^{1}H NMR spectrum, the low field resonance is assigned to the *ortho* proton which lies in the deshielding zone of Ir^I, thus implying *syn* orientation with respect to the metal centre and σ-S coordination (see Fig. 2) of the sulphine. Accordingly, the high field resonance is assigned to the *ortho* proton *syn* to the S=O bond, its chemi-

TABLE 1

SPECTROSCOPIC DATA FOR *trans*-[$Ir^{I}Cl\{P(C_6H_{11})_3\}_2(C_{12}H_8CSO)$], [$Pd^{0}(PPh_3)_2(XYCSO)$] (X, Y = aryl, S-aryl, Cl) AND [$Pd^{II}Cl(XCSO)(PPh_3)_2$] (X = aryl, S-aryl)

Compound	IR (KBr mull)		^{31}P NMR in $CDCl_3$			^{1}H NMR ($CDCl_3$, 60 MHz)
	ν(CSO) (cm^{-1})	ν(M—Cl) (cm^{-1})	$\delta(P_a)$ [a] (ppm)	$\delta(P_b)$ [a] (ppm)	$^{2}J(P_a—P_b)$ (Hz)	$\delta(H_{Me})$ [b] (ppm)
trans-[$Ir^{I}Cl\{P(C_6H_{11})_3\}_2(C_{12}H_8CSO)$]	1121, 1090, 1025	319	18.3	—	—	—
[$Pd^{0}(PPh_3)_2\{(p\text{-}MeC_6H_4S)_2CSO\}$]	1022	—	24.0	21.0	19	2.16 2.12
[$Pd^{0}(PPh_3)_2\{(E)\text{-}(p\text{-}MeC_6H_4S)ClCSO\}$]	1035	—	24.9 (24.1) [c]	19.8 (19.1) [c]	19 (15) [c]	2.24
cis-(*E*)-[$Pd^{II}Cl(p\text{-}MeC_6H_4SCSO)(PPh_3)_2$]	*d*	*d*	34.7	18.9	25	*d*
cis-(*Z*)-[$Pd^{II}Cl(p\text{-}MeC_6H_4SCSO)(PPh_3)_2$]	*d*	*d*	32.2	20.8	20	*d*
trans-(*E*)-[$Pd^{II}Cl(p\text{-}MeC_6H_4SCSO)(PPh_3)_2$]	1078, 955	319	23.1 (22.7) [c]	—	—	2.47
trans-(*Z*)-[$Pd^{II}Cl(p\text{-}MeC_6H_4SCSO)(PPh_3)_2$]	987	290	25.9 (25.7) [c]	—	—	2.17
[$Pd^{0}(PPh_3)_2\{(Z)\text{-}PhClCSO\}$]	1015	—	24.2 (23.9) [e]	19.4 (19.4) [e]	14 (13) [e]	—
cis-(*Z*)-[$Pd^{II}Cl(PhCSO)(PPh_3)_2$]	*d*	*d*	34.0 (33.8) [e]	17.9 (17.9) [e]	28 (28) [e]	—
trans-(*E*)-[$Pd^{II}Cl(PhCSO)(PPh_3)_2$]	*f*	*f*	24.5 (24.8) [e]	—	—	—
trans-(*Z*)-[$Pd^{II}Cl(PhCSO)(PPh_3)_2$]	*f*	*f*	25.8 (26.0) [e]	—	—	—

[a] Relative to H_3PO_4 (85%), + = downfield, [b] Relative to Me_4Si. [c] Measured in C_6D_6. [d] Not measured. [e] Measured in CD_2Cl_2. [f] Could not be assigned.

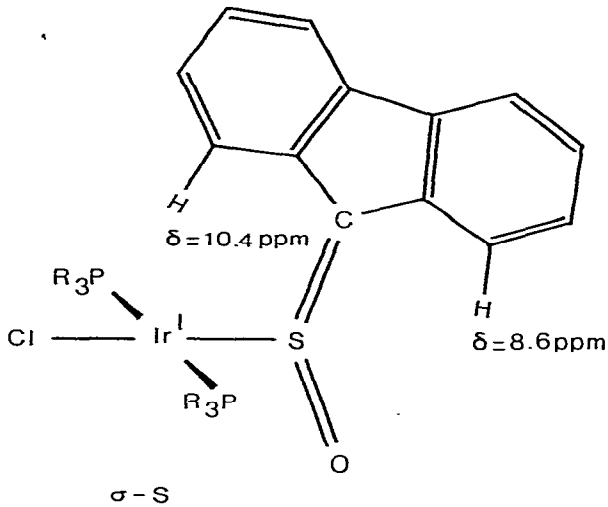

Fig. 2. Structure of *trans*-$[Ir^{I}Cl\{P(C_6H_{11})_3\}_2(C_{12}H_8CSO)]$.

cal shift being almost the same as in the free sulphine [2]. The observation of only one singlet in the ^{31}P NMR spectrum confirmed the *trans* configuration of the phosphine ligands in this complex.

ii. The synthesis and characterization of $[Pd^0(PPh_3)_2\{(p\text{-}MeC_6H_4S)_2CSO\}]$

The Pd-sulphine complex $[Pd^0(PPh_3)_2\{(p\text{-}MeC_6H_4S)_2CSO\}]$ was synthesized from $[Pd^0(PPh_3)_4]$ and $(p\text{-}MeC_6H_4S)_2C{=}S{=}O$. The analytical data were in agreement with a molecule containing two phosphines and one sulphine per Pd atom. The IR spectrum showed only one ν(CSO) absorption at 1022 cm^{-1}, which is indicative of η^2-CS coordination, and the observation of one AB resonance pattern in the ^{31}P NMR spectrum confirmed this [3]. The ^1H NMR spectrum showed two inequivalent Me groups, as observed in the related η^2-CS-Pt complex $[Pt^0(PPh_3)_2\{(p\text{-}MeC_6H_4S)_2CSO\}]$ [2]. One Me group is situated *syn* and the other *anti* with respect to the S=O group (see Fig. 3).

The ^{31}P and ^1H NMR spectra revealed that the complex decomposed very slowly in $CDCl_3$ forming free $(p\text{-}MeC_6H_4S)_2C{=}S{=}O$. After 3 days the ratio of coordinated to free sulphine was ca. 3 : 1. When the solution was kept under N_2 the decomposition rate was considerably lower. The observed molecular weights were significantly less than the calculated value for $[Pt^0(PPh_3)_2\{(p\text{-}MeC_6H_4S)_2CSO\}]$. The results indicate that a dissociation/association equilibrium probably exists between the complex and the free sulphine, and lies predominantly to the side of the complex (see Scheme 1).

SCHEME 1

DISSOCIATION OF THE η^2-CS COMPLEX $[Pd^0(PPh_3)_2\{(p\text{-}MeC_6H_4S)_2CSO\}]$

$$[Pd^0(PPh_3)_2\{(p\text{-}MeC_6H_4S)_2CSO\}] \rightleftharpoons \text{“}Pd^0(PPh_3)_2\text{”} + (p\text{-}MeC_6H_4S)_2C{=}S{=}O$$

When the mixture is treated with O_2, the equilibrium shifts to the right because of irreversible oxidation of the reactive $Pd^0(PPh_3)_2$ fragments. The Pd-sulphine complex did not undergo a C—S oxidative addition reaction, which is in con-

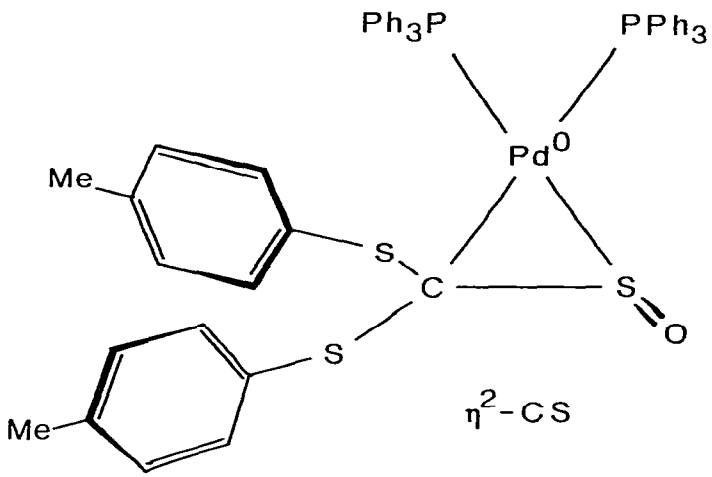

Fig. 3. Structure of $[Pd^0(PPh_3)_2\{(p\text{-}MeC_6H_4S)_2CSO\}]$.

trast with the reaction observed for the corresponding Pt-complex $[Pt^0(PPh_3)_2\{(p\text{-}MeC_6H_4S)_2CSO\}]$.

iii. Syntheses and characterization of the complexes $[Pd^0(PPh_3)_2\{(E)\text{-}(p\text{-}MeC_6H_4S)ClCSO\}]$ and $[Pd^0(PPh_3)_2\{(Z)\text{-}PhClCSO\}]$ and study of the C—Cl oxidative addition

The reaction of $[Pd^0(PPh_3)_4]$ and (E)-$(p\text{-}MeC_6H_4S)ClC{=}S{=}O$ in benzene yielded a yellow solid whose analytical data were consisted with one sulphine and two phosphine ligands per Pd atom. The IR spectrum recorded on this solid showed a strong ν(CSO) absorption at 1035 cm^{-1}, indicative of an η^2-CS complex [3], i.e. $[Pd^0(PPh_3)_2\{(E)\text{-}(p\text{-}MeC_6H_4S)ClCSO\}]$, and weak shoulders at 1078 and 955 cm^{-1}, suggesting [4] the presence of a small amount of the oxidative addition product, (E)-$[Pd^{II}Cl(p\text{-}MeC_6H_4SCSO)(PPh_3)_2]$.

In order to study the C—Cl oxidative addition, we recorded the ^{31}P NMR spectra of solutions of this solid as function of time. The ^{31}P NMR spectra, recorded immediately after dissolution of the solid in $CDCl_3$ and C_6D_6 showed, in addition to a major AB resonance pattern, two AB patterns of minor intensity and two singlets. When the solvent was removed after ca. 15 minutes, the IR spectrum of the resulting yellow solid still showed the absorption of 1035 cm^{-1}, although somewhat lower in intensity compared to the original IR spectrum. The major AB pattern was therefore assigned to the η^2-CS complex $[Pd^0(PPh_3)_2\{(E)\text{-}(p\text{-}MeC_6H_4S)ClCSO\}]$. The assignments of ^{31}P NMR resonance patterns to specific complexes is more difficult than for the corresponding Pt sulphine-phosphine complexes, where useful platinum—phosphorous couplings were present in the spectra. The minor intensity AB pattern with the largest value of $\Delta P = |\delta(P_a) - \delta(P_b)|$ (see Table 1) was assigned to the oxidative addition product, *cis*-(E)-$[Pd^{II}Cl(p\text{-}MeC_6H_4SCSO)(PPh_3)_2]$ and the remaining AB pattern (with the smaller ΔP) to the *cis*-(Z) stereoisomer. Both AB patterns, assigned to the oxidative addition stereoisomers, have somewhat larger $^2J(P_a{-}P_b)$ values than that of the η^2-CS compound. These assignments were

based on the comparison of the Pd compounds with those of the Pt analogs *cis*-(*E*)- and -(*Z*)-[$Pt^{II}Cl(p\text{-}MeC_6H_4SCSO)(PPh_3)_2$], which were very rapidly formed via C—Cl oxidative addition from the η^2-CS complex [$Pt^0(PPh_3)_2$-{(*E*)-(*p*-MeC_6H_4S)ClCSO}] [4]. For the Pt analogs the *cis*-(*E*) isomer had a larger value of ΔP than the *cis*-(*Z*) isomer and the $^2J(P_a—P_b)$ values of both stereoisomers were larger than that of the η^2-CS complex [4].

The ^{31}P NMR spectra of the Pd system showed that the AB patterns slowly disappeared with time, the minor intensity pattern faster than the major one, whereas the intensities of the two singlets increased. When C_6D_6 was used as solvent orange crystals were slowly formed, when only two singlets were present in the ^{31}P NMR spectra. The IR spectrum of this orange solid showed two ν(CSO) absorptions (see Table 1) between 1080 and 950 cm^{-1}, characteristic for (*E*) oxidative addition products [4]. These results indicate that this product is *trans*-(*E*)-[$Pd^{II}Cl(p\text{-}MeC_6H_4SCSO)(PPh_3)_2$]. When n-pentane was added to a similarly aged $CDCl_3$ solution, the IR spectrum of the resulting yellow solid, showed in addition to the two ν(CSO) absorptions of the *trans*-(*E*) isomer an absorption at 987 cm^{-1}, indicative of the (*Z*) oxidative addition product, and using the evidence of a singlet ^{31}P NMR resonance this is assigned to *trans*-(*Z*)-[$Pd^{II}Cl(p\text{-}MeC_6H_4SCSO)(PPh_3)_2$]. In all the IR spectra of the oxidative addition products, absorptions around 300 cm^{-1}, ν(Pd—Cl), were found, indicating, that C—Cl rather than C—S oxidative addition had occurred.

For the final mixture in $CDCl_3$, containing the *trans*-(*E*) and -(*Z*) complexes, comparison of the ^{31}P NMR spectra with the ^1H NMR spectra, in which the lower field Me signal has lower intensity, based on the assumption that the conformations of the *p*-MeC_6H_4SC=S=O groups are the same as in the Pt analogs *, leads to the conclusion that the lower field ^{31}P NMR signal (δ = 25.9 ppm) belongs to the (*Z*) isomer and that at δ = 23.1 ppm to the (*E*) isomer. This conclusion compares well with that for the Pt system, where the ^{31}P NMR resonance of the (*Z*) isomer is also found to low field of the (*E*) isomer.

The reaction of [$Pd^0(PPh_3)_4$] with (*Z*)-PhClC=S=O in benzene yielded a white precipitate, the IR spectrum of which showed one strong ν(CSO) absorption at 1015 cm^{-1}, indicating that the η^2-CS compound [$Pd^0(PPh_3)_2$-{(*Z*)-PhClCSO}] had been formed. The ^{31}P NMR spectrum recorded immediately after dissolution of the white precipitate in $CDCl_3$ or CD_2Cl_2 showed one major and one minor AB resonance pattern, which were assigned to the unchanged complex, and *cis*-(*Z*)-[$Pd^{II}Cl(PhCSO)(PPh_3)_2$], respectively. By analogy to the conversion of [$Pd^0(PPh_3)_2$-{(*E*)-(*p*-MeC_6H_4S)ClCSO}], two singlets at δ = 24.5 and 25.8 ppm (in $CDCl_3$) which increased in intensity upon disappearance of the AB resonance patterns (see Fig. 4), were assigned to *trans*-(*E*)- and -(*Z*)-[$Pd^{II}Cl$-$(PhCSO)(PPh_3)_2$], respectively. After several days, when only singlet resonances were present a white precipitate separated, and its IR spectrum showed weak absorptions at 1070, 990, 980 {ν(CSO)}, and 300 cm^{-1} {ν(Pd—Cl)}. Although these absorptions could not be unambiguously assigned, they suggest that the

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* The Me resonances of *cis*- and *trans*-(*E*)-[$Pt^{II}Cl(p\text{-}MeC_6H_4SCSO)(PPh_3)_2$], in which the *p*-$MeC_6H_4$-S-C=S=O group has an *s-cis* conformation, were shifted downfield with respect to the Me resonances of *cis*- and *trans*-(*Z*)-[$Pt^{II}Cl(p\text{-}MeC_6H_4SCSO)(PPh_3)_2$], which have *gauche* conformations (see ref. 4).

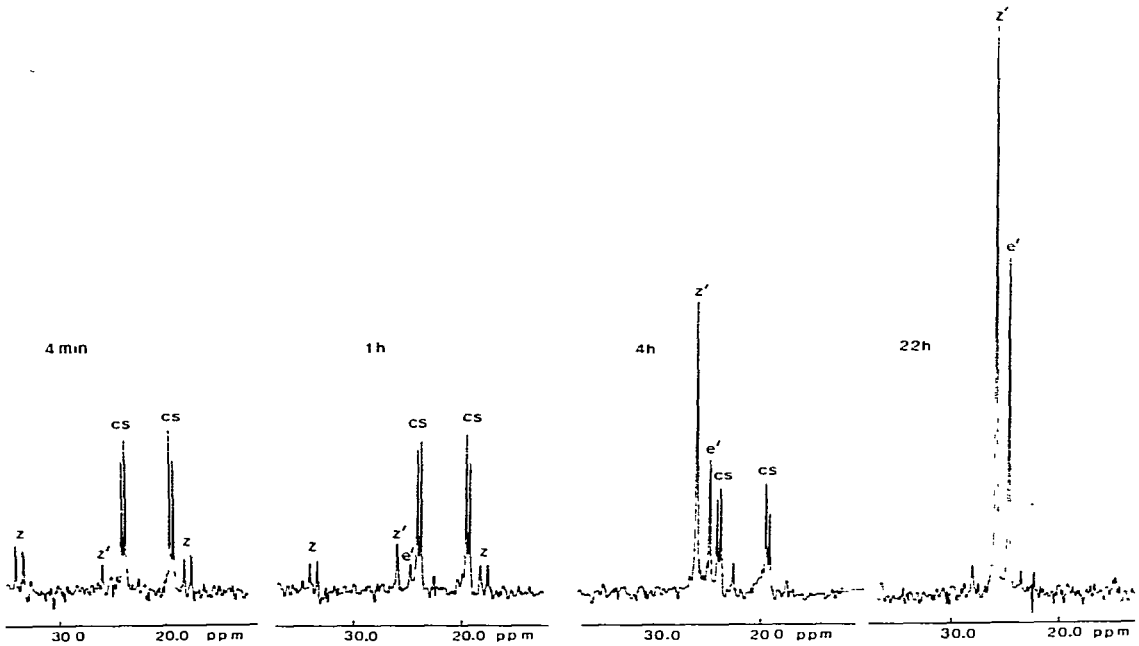

Fig. 4. Conversion of $[Pd^0(PPh_3)_2\{(Z)\text{-PhClCSO}\}]$ (cs) into *cis*-(*Z*)-, *trans*-(*Z*)- and *trans*-(*E*)-$[Pd^{II}Cl(PhCSO)(PPh_3)_2]$, (z), (z') and (e'), respectively, in CD_2Cl_2, followed by ^{31}P NMR.

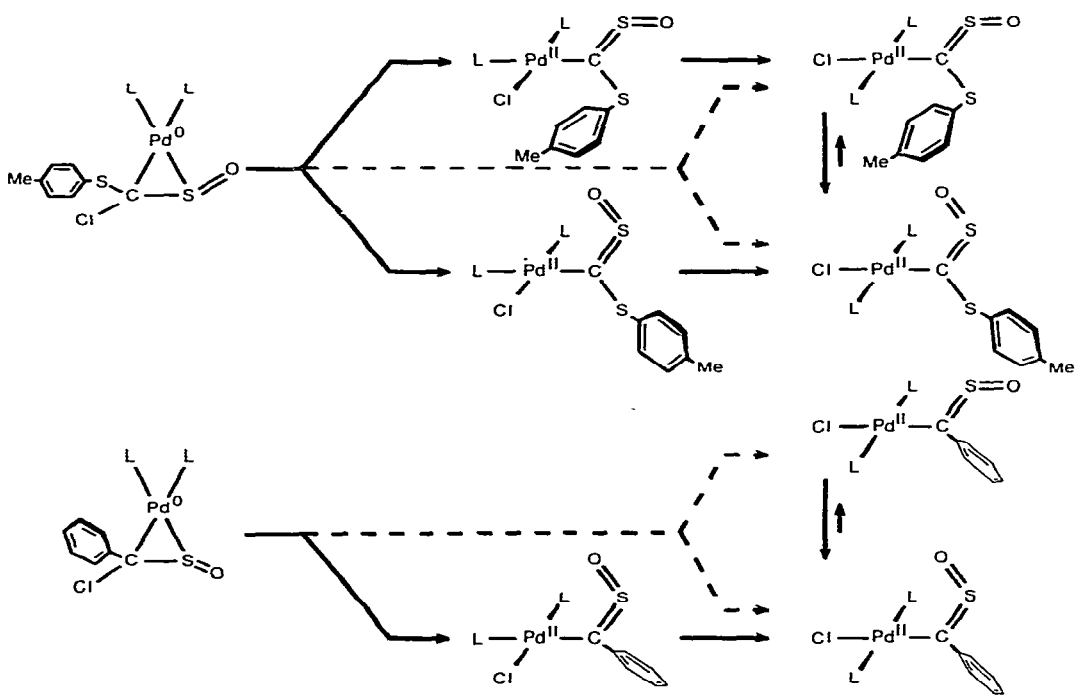

Fig. 5. The C—Cl oxidative addition in $[Pd^0(PPh_3)_2\{(E)\text{-}(p\text{-}MeC_6H_4S)ClCSO\}]$ and $[Pd^0(PPh_3)_2\{(Z)\text{-PhClCSO}\}]$ (L = PPh_3).

white solid contained the oxidative addition complexes *trans*-(*E*)- and -(*Z*)-$[Pd^{II}Cl(PhCSO)(PPh_3)_2]$. This would be in agreement with the assignments of the ^{31}P NMR spectra.

The conversions of $[Pd^0(PPh_3)_2\{(E)\text{-}(p\text{-}MeC_6H_4S)ClCSO\}]$ and $[Pd^0(PPh_3)_2\text{-}\{(Z)\text{-}PhClCSO\}]$ are shown in Fig. 5.

These results clearly illustrate that following η^2-CS coordination, C—Cl oxidative addition occurs, forming *trans* metallo-sulphines. This process proceeds, at least in part, via *cis* products (see Discussion). The ^{31}P NMR spectra showed, that although *trans*-(*E*)-$[Pd^{II}Cl(p\text{-}MeC_6H_4SCSO)(PPh_3)_2]$ was formed faster than the *trans*-(*Z*) stereoisomer, in the final product mixture the *trans*-(*Z*) stereoisomer predominated. This indicates an (*E*)—(*Z*) isomerization equilibrium between the *trans* metallo-sulphines, as found for the Pt analogs [4]. The formation of both *cis*-(*E*)- and -(*Z*)-$[Pd^{II}Cl(p\text{-}MeC_6H_4SCSO)(PPh_3)_2]$ from $[Pd^0(PPh_3)_2\text{-}\{(E)\text{-}(p\text{-}MeC_6H_4S)ClCSO\}]$ is also in agreement with behaviour of the Pt-sulphine complexes [4].

Discussion

The complex *trans*-$[Ir^ICl\{P(C_6H_{11})_3\}_2(C_{12}H_8CSO)]$ is the first example of an Ir-sulphine complex. We have found that reactions of Ir^I complexes with sulphines containing reactive side bonds did not give isolable and defined Ir-sulphine complexes.

Sulphines containing reactive C—S and/or C—Cl side bonds, i.e. (RS)XC=S=O (X = aryl, S-aryl; R = aryl), coordinate to "$Pd^0(PPh_3)_2$" via η^2-CS, the same coordination mode of the C=S=O skeleton being found with "$Pt^0(PPh_3)_2$" [2,3]. No dissociation was observed for the sulphine in the complexes $[Pt^0(PPh_3)_2(XYCSO)]$ (X, Y = aryl, S-aryl, S-alkyl, Cl) in solution, and only intramolecular C—S oxidative addition and (*E*)—(*Z*) isomerization take place [2—7] while slow dissociation of the sulphine was observed in solutions of the complex $[Pd^0(PPh_3)_2\{(p\text{-}MeC_6H_4S)_2CSO\}]$. This indicates that the Pd^0—(η^2-CS) bond is weaker than the Pt^0—(η^2-CS) bond, which may be the result of the lower σ-acceptance and/or poorer π back-donation properties of Pd^0 compared with Pt^0. The fact that the sulphine C=S skeleton in $[Pd^0(PPh_3)_2(C_{12}H_8CSO)]$ rotates around the Pd^0—(η^2-CS) axis, has been ascribed to a difference in π-back-donation properties of Pd^0 and Pt^0 [13], because rotation was not found in $[Pt^0(PR_3)_2(C_{12}H_8CSO)]$ (R = Ph [2,13], C_6H_{11} [5]). This indicates that the properties of the Pd^0—(η^2-CS) bonds are more comparable with those of the Pt^0—(η^2-NS) bonds in $[Pt^0(PPh_3)_2(arylNSO)]$, in which the η^2-NS coordinated sulphinylanilines rotate around the Pt^0—(NS) bond [14].

Although C—S oxidative addition in the complex $[Pd^0(PPh_3)_2\{(p\text{-}MeC_6H_4S)_2\text{-}CSO\}]$ was not found, the η^2-CS complexes $[Pd^0(PPh_3)_2\{(E)\text{-}(p\text{-}MeC_6H_4S)\text{-}ClCSO\}]$ and $[Pd^0(PPh_3)_2\{(Z)\text{-}PhClCSO\}]$ undergo a fast C—Cl oxidative addition. The rate of this oxidative addition is somewhat lower than with the Pt analogs [4,15].

The formation of mainly *trans* oxidative addition products as the ultimate products after η^2-CS coordination of (*E*)-(*p*-MeC_6H_4S)ClC=S=O and (*Z*)-PhCl-C=S=O to $Pd^0(PPh_3)_2$ can be explained in two ways. (i) The C—Cl oxidative addition yields only *cis* products, which subsequently isomerize very rapidly to

trans products. In $CDCl_3$ and CD_2Cl_2 the *cis*-to-*trans* isomerization is considerably faster than the C—Cl oxidative addition because the *cis* products were only detected, in very small amounts, at the beginning of the conversion reaction (see Fig. 5; equations with →). (ii) In addition to a *cis* oxidative addition a *trans* oxidative addition also occurs, with the *cis* products isomerizing to the *trans* products (completing the reaction sequences in Fig. 5 with the reaction arrows ⟶). The preference for formation of mainly *trans* products from C—Cl oxidative additions of organic substrates to $[Pd^0(PPh_3)_4]$ is well documented [16—19]. The η^2-CS complexes $[Pt^0\{P(C_6H_{11})_3\}_2\{(E)\text{-}(RS)ClCSO\}]$ (R = p-MeC_6H_4, Ph) undergo a *cis* C—Cl oxidative addition and slow *cis*-to-*trans* isomerization, finally resulting in only *trans*-(*E*)- and -(*Z*)-$[Pt^{II}Cl(RSCSO)\{P(C_6H_{11})_3\}_2]$ [5,20].

Conclusions

The present results of the coordination chemistry of sulphines lead to three conclusions: (i) $[Ir^ICl\{P(C_6H_{11})_3\}_n(sulphine)]$ complexes are considerably less stable than their Rh analogs $[Rh^ICl\{P(C_6H_{11})_3\}_n(sulphine)]$ when reactive C—S and C—Cl side bonds are present. (ii) The properties of the $[Pd^0(PPh_3)_2(\eta^2\text{-CS-sulphine})]$ complexes are more comparable with those of the $[Pt^0\{P(C_6H_{11})_3\}_2(\eta^2\text{-CS-sulphine})]$ and $[Pt^0(PPh_3)_2(\eta^2\text{-NS-sulphinylaniline})]$ complexes than with those of $[Pt^0(PPh_3)_2(\eta^2\text{-CS-sulphine})]$ complexes. (iii) Because C—S oxidative addition in $[Pd^0(PPh_3)_2\{(p\text{-}MeC_6H_4S)_2CSO\}]$ does not occur and the complexes $[Ir^ICl\{P(C_6H_{11})_3\}_n\{RSC(X)SO\}]$ (X = aryl, S-aryl; R = aryl, alkyl) could not be synthesized, the present results give no further information concerning the role of the metal in the C—S oxidative addition and reductive coupling of sulphine side bonds and the (*E*)—(*Z*) isomerization in coordinated sulphines and metallosulphines.

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