Journal of Organometallic Chemistry, 179 (1979) 411—419

COORDINATION CHEMISTRY OF SULFINES

I. SYNTHESIS AND CHARACTERIZATION OF THE COMPLEXES $Pt(PPh_3)_2(XYCSO)$ (X, Y = ARYL, S-ARYL, S-ALKYL, Cl). COORDINATION VIA THE C=S-π-BOND

JOHAN W. GOSSELINK, GERARD VAN KOTEN *, KEES VRIEZE

Anorganisch Chemisch Laboratorium, J.H. van 't Hoff Instituut, University of Amsterdam, Nieuwe Achtergracht 166, 1018 WV Amsterdam (The Netherlands)

BINNE ZWANENBURG and BEN H.M. LAMMERINK

Department of Organic Chemistry, University of Nijmegen, Toernooiveld, 6525 ED Nijmegen (The Netherlands)

(Received April 30th, 1979)

Summary

Reactions of $Pt(PPh_3)_4$ with the sulfines, XYC=S=O, (X, Y = aryl, S-aryl, S-alkyl, Cl) yield coordination compounds of the type $Pt(PPh_3)_2(XYCSO)$. Infrared, ^{31}P and ^1H NMR spectra reveal that in all cases the sulfine ligand is coordinated side-on via the C=S π-bond (Pt—η^2-CS). Reactions of $Pt(PPh_3)_4$ with either the *E*- or *Z*-isomer of $(p\text{-}CH_3C_6H_4)(CH_3S)CSO$ yields the corresponding *E*- or *Z*-coordination compound, $Pt(PPh_3)_2[E\text{-}(p\text{-}CH_3C_6H_4)(CH_3S)CSO]$ or $Pt(PPh_3)_2[Z\text{-}(p\text{-}CH_3C_6H_4)(CH_3S)CSO]$, indicating that the configuration of the sulfine ligand is retained upon coordination to the $Pt(PPh_3)_2$ unit. The compounds $Pt(PPh_3)_2(XYCSO)$, containing reactive C—X and/or C—Y bonds (X, Y = S-aryl, S-alkyl, Cl), undergo a rearrangement in solution to give complexes of the type $PtX(PPh_3)_2(YCSO)$.

Introduction

Sulfines (XYC=S=O), are heterocumulenic systems, related to sulfinylanilines (Ar—N=S=O) and diarysulfurdiimines (Ar—N=S=N—Ar) which are being studied in our laboratory [1,2]. Their synthesis, chemical reactivity and structure have been extensively investigated by Zwanenburg et al. [3—11]. Sulfines show synthetically useful reactions such as cyclo-addition with dienes and 1,3-

---

* To whom correspondence should be addressed.

dipoles, and nucleophilic additions. Recently, we found that heterocumulenes can be activated and transformed in a specific way by complex formation to low valent metals [1]. In this paper we describe the first results of a study of the coordination properties of sulfines towards low valent metal centres, it being argued that such complex formation might well influence the reactivity of the sulfines.

Sulfines (XYCSO) have a bent planar structure [16,17]. In the case of two non-equivalent substituents at carbon ($X \neq Y$) the molecule exists in two isomeric forms, which are not interconverted at room temperature [12—17]. Hitherto only a few metal complexes of sulfines have been reported in the literature. Dittmer et al. [18] oxidized $Fe(CO)_3(H_2C{=}CHCH{=}S)$ to yield two isomers of the sulfine complex $Fe(CO)_3(H_2C{=}CHCH{=}S{=}O)$, in which the sulfine ligand is suggested to coordinate via C=C and C=S. Carlsen [19] reported the sulfine complex $TiCl_4 \cdot Ph_2CSO$, in which the sulfine molecule is assumed to be bound to $TiCl_4$ by weak electrostatic forces. In an attempt to prepare a sulfine complex, Alper [20] found that $Fe_2(CO)_9$ deoxygenated $(p\text{-}CH_3OC_6H_4)_2CSO$ to give the *ortho*-metallated diarylthioketon—iron complex $Fe(CO)_3[(p\text{-}CH_3OC_6H_4)(p\text{-}CH_3O\overline{C_6H_3C(S)H]Fe}(CO)_3$.

Recently, the coordination behaviour of Ar—N=S=O to platinum(0), rhodium(I) and iridium(I) was reported by Meij et al. [2]. $Pt(PPh_3)_2(Ar{-}NSO)$ contains η^2-NS bonded ArNSO, while in the case of $RhCl[P(\text{isopropyl})_3]_2$-(Ar—NSO) the ligand is coordinated either via η^2-NS or via η^1-S. It is noteworthy, that *N*-sulfinylanilines can be isolated in only one isomeric form (i.e. the *cis*). Sulfines (XYCSO) are expected to be more versatile in their coordination behaviour, as in the case $X \neq Y$ the ligand exists in two stable isomeric forms, so that the coordination behaviour of each isomer can be studied independently. In the case, where the sulfine molecule contains reactive C—X and/or C—Y bonds (e.g., X, Y = S-aryl, S-alkyl, Cl) in addition to coordination via the cumulene fragment, insertion of the metal centre into these bonds can be expected. Such insertions by platinum(0) and rhodium(I) have been observed, for example, with $(CH_3)_2NC(S)X$ (X = S-aryl, S-alkyl, Cl) [21] and $\overline{SCH_2CH_2SC}{=}S$ [22].

In this paper the reactions of $Pt(PPh_3)_4$ with the sulfines: thiofluorenone-S-oxide (X, Y = fluorene); diphenylsulfine (X = Y = Ph); *E*-*p*-tolyl(phenylthio)-sulfine ($X = p\text{-}CH_3C_6H_4$; Y = PhS); *E*- and *Z*-*p*-totyl-(methylthio)sulfine ($X = p\text{-}CH_3C_6H_4$; $Y = CH_3S$); bis(phenylthio)sulfine (X = Y = PhS); and its *p*-tolyl analog ($X = Y = p\text{-}CH_3C_6H_4S$); *p*-methoxyphenylthio(*p*-tolylthio)sulfine ($X = p\text{-}CH_3C_6H_4S$, $Y = p\text{-}CH_3OC_6H_4S$, a mixture of two isomers); chloro(phenylthio)sulfine (X = Cl, Y = SPh, one isomer only) and *Z*-chloro(phenyl)sulfine (X = Cl, Y = Ph) are described.

Experimental

Reactions were carried out under N_2 in a Schlenk apparatus. The infrared spectra were recorded on a Perkin—Elmer 283 or a Beckman IR-4250 spectrophotometer. The ^1H NMR spectra were recorded on a Varian T60 A and the $^{31}P\{^1H\}$ NMR spectra on a Varian XL 100 spectrometer. Elemental analysis were carried out by the Analytical Section of the Institute for Organic Chemistry TNO, Utrecht (The Netherlands).

TABLE 1

ANALYTICAL DATA AND MOLECULAR WEIGHTS

Compound	Analysis (Found (calcd.) (%))						Mol. wt. [a] (Found (calcd))
	C	H	P	S	Cl	O	
$Pt(PPh_3)_2(Ph_2CSO)$	63.4 (63.01)	4.7 (4.33)	6.5 (6.63)	3.1 (3.43)	0.00 (0.00)		897 (934)
$Pt(PPh_3)_2$(fluoreneSO)	63.1 (63.15)	4.1 (4.12)	6.3 (6.65)	3.3 (3.44)			
$Pt(PPh_3)_2[E\text{-}(p\text{-}CH_3C_6H_4)(PhS)CSO]$	61.8 (61.27)	4.6 (4.33)	6.0 (6.32)	6.9 (6.54)		1.7 (1.63)	931 (980)
$Pt(PPh_3)_2[E\text{-}(p\text{-}CH_3C_6H_4)(CH_3S)CSO]$	57.5 (58.87)	4.4 (4.40)	6.3 (6.75)	6.4 (6.98)		1.5 (1.69)	
$Pt(PPh_3)_2[Z\text{-}(p\text{-}CH_3C_6H_4)(CH_3S)CSO]$	57.0 (58.87)	4.5 (4.40)					
$Pt(PPh_3)_2[(PhS)_2CSO]$	60.2 (58.96	4.4 (4.05)	5.8 (6.21)	9.3 (9.64)		1.7 (1.62)	1036 (998)
$Pt(PPh_3)_2[(p\text{-}CH_3C_6H_4S)_2CSO]$	59.7 (59.69)	4.6 (4.33)	5.6 (6.04)	8.2 (9.37)			
$Pt(PPh_3)_2[(p\text{-}CH_3C_6H_4S)(p\text{-}CH_3OC_6H_4S)CSO] \cdot C_7H_8$	60.6 (61.41)	4.8 (4.63)				2.8 (2.82)	
$Pt(PPh_3)_2(Z\text{-}PhClCSO)$	57.9 (57.88)	4.1 (3.96)				1.7 (1.79)	

[a] By osmometry in $CHCl_3$.

Starting materials

$Pt(PPh_3)_4$ [23] and the sulfines [3] were prepared by literature procedures.

Syntheses of the platinum—sulfine complexes

A general procedure for the synthesis of the platinum—sulfine complexes $Pt(PPh_3)_2(XYCSO)$ is as follows: $Pt(PPh_3)_4$ (0.2 mmol) and XYCSO (0.2 mmol) were stirred in benzene or toluene (about 2 cm^3). $Pt(PPh_3)_2(XYCSO)$, precipitated as a white solid, was filtered off, washed with benzene or toluene (about 2 cm^3) and n-hexane, and dried in vacuo. The yield (40 to 90%) depends on the solubility of $Pt(PPh_3)_2(XYCSO)$ in the solvents used. The analytical data are listed in Table 1.

In the case of $Pt(PPh_3)_2[E$- or Z-$(p\text{-}CH_3C_6H_4)(CH_3S)CSO]$, an excess of free ligand was needed during the synthesis in order to obtain pure products. Pure $Pt(PPh_3)_2[(PhS)ClCSO]$ could not be isolated because the insertion product $PtCl(PPh_3)_2[(PhS)CSO]$ also precipitated from the reaction mixture.

Testing of the stability of $Pt(PPh_3)_2(XYCSO)$

After recording the ^{31}P NMR spectra, n-hexane was added to the $CDCl_3$ solutions. In each case a white precipitate was formed, which was filtered off, washed with n-hexane, and dried in vacuo. The infrared spectra of these precipitates were almost identical to those of the pure compounds. This result indicates that the complexes are stable in solution and towards air during the period necessary for recording the ^{31}P NMR spectra.

Results and discussion

$Pt(PPh_3)_4$ reacts with sulfines, XYCSO, to give complexes of the stoichiometry $Pt(PPh_3)_2(XYCSO)$, which are monomeric in chloroform (see Table 1).

$$Pt(PPh_3)_4 + XYCSO \rightarrow Pt(PPh_3)_2(XYCSO) + 2PPh_3$$

The structure of the platinum—sulfine complexes has been studied by ^1H and ^{31}P NMR and infrared spectroscopy. The close resemblance of the spectroscopic data for these complexes (see Table 2, 3 and 4) indicate that all the sulfine ligands are coordinated to the Pt atom in the same way, via the C=S=O fragment and not via one or both S atoms of the substituents X and Y. In principle the C=S=O moiety has various possibilities for coordination to platinum(0) viz., coordination via η^2-CS, η^1-S, η^2-SO and η^1-O). In the light of the electronic structure of the C=S=O function [11] the η^2-CS or η^1-S coordination modes are likely to be much more favourable than the latter two possibilities for coordination. As will be shown below the spectroscopic data indicate η^2-CS coordination [24].

The ^1H NMR spectra of the free sulfines show a downfield shift for the *ortho* protons *syn* to the SO group (see Fig. 1, *ortho* protons with asterisks) in the case of fluoreneSO, Ph_2CSO, E-$(p\text{-}CH_3C_6H_4)(PhS)CSO$ and E-$(p\text{-}CH_3C_6H_4)(CH_3S)CSO$ as compared with the other aromatic protons. This is due to the deshielding effect of the SO group [10]. Upon coordination these protons are shifted upfield by approximately 0.7 ppm (see Table 2), resulting in a masking by the PPh_3 protons except for $Pt(PPh_3)_2$(fluoreneSO). A similar

TABLE 2

^{1}H NMR DATA FOR $Pt(PPh_3)_2(XYCSO)$ AND XYCSO

Compound	δ(ortho proton(s)) [a,b]		δ(CH_3) [a]	
	Pt complex	Free ligand	Pt complex	Free ligand
$Pt(PPh_3)_2$(fluorene-SO)	7.85	8.55	—	—
$Pt(PPh_3)_2(Ph_2CSO)$	*c*	7.80	—	—
$Pt(PPh_3)_2[E\text{-}(p\text{-}CH_3C_6H_4)(PhS)CSO]$	*c*	8.10	2.15	2.30
$Pt(PPh_3)_2[E\text{-}(p\text{-}CH_3C_6H_4)(CH_3S)CSO]$	*c*	8.02	2.25 [d]	2.40; 2.30
$Pt(PPh_3)_2[Z\text{-}(p\text{-}CH_3C_6H_4)(CH_3S)CSO]$	—	—	2.25; 2.10	2.48; 2.40
$Pt(PPh_3)_2[(p\text{-}CH_3C_6H_4S)_2CSO]$	—	—	2.04; 2.00 [e]	2.35; 2.30
$Pt(PPh_3)_2[(p\text{-}CH_3C_6H_4S)(p\text{-}CH_3OC_6H_4S)CSO]$ [f]	—	—	2.13; 2.16 [e,g] 3.63; 3.66 [e,h]	2.34; 2.38 [g] 3.78; 3.80 [h]
$Pt(PPh_3)_2(p\text{-}CH_3C_6H_4NSO)$ [2]	6.78	7.58	2.05	2.32

[a] δ(ppm) relative to TMS, internal reference. [b] Only *ortho*-protons syn to the SO group (see Fig. 1). [c] *Ortho*-protons are obscured by other aromatic protons of the complex. [d] CH_3S and $p\text{-}CH_3C_6H_4$ accidently have the same chemical shift. [e] Measured on a Varian HA 100 spectrometer. [f] A mixture of two isomers. [g] δ(CH_3). [h] δ(OCH_3).

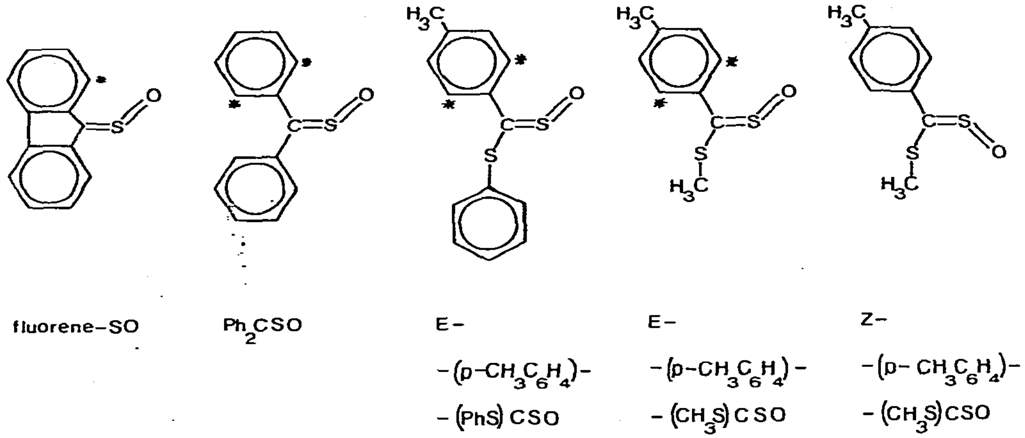

Fig. 1. Structures of some sulfines.

shift (0.9 ppm) is found in the case of $Pt(PPh_3)_2(Ar—NSO)$, where the aryl and SO groups are situated *syn* in both the complex and the free ligand [2]. This indicates that coordination in $Pt(PPh_3)_2(XYCSO)$ and $Pt(PPh_3)_2(Ar—NSO)$ is similar i.e. η^2-CS bonded sulfine (see Fig. 1).

The infrared data (see Table 3) support this view. In previous studies of the free ligand, strong absorptions in the region 1150—900 cm^{-1} have been assigned to vibrations of the CSO moiety [3—12]. In the sulfine complex $Fe(CO)_3(H_2C{=}CHCH{=}S{=}O)$ the absorption at 1030 cm^{-1} is assigned to $\nu(SO)$ [18], whereas in the complexes $Pt(PPh_3)_2(Ar—NSO)$ it has been established that the absorption between 1056 and 1040 cm^{-1} arises from the $\nu(SO)$ vibration [2]. Therefore it is plausible to assign the strong absorption at 1025—1005 cm^{-1} in the present complexes to $\nu(SO)$. Unfortunately the $\nu(C{=}S)$ of the coordinated sulfine molecule could not be assigned.

^{31}P NMR spectra (see Table 4) revealed that the PPh_3 ligands are in *cis* positions and are inequivalent at room temperature. Moreover the spectra of $Pt(PPh_3)_2[E\text{-}(p\text{-}CH_3C_6H_4)(CH_3S)CSO]$ did not change on lowering the temperature to —40° C. This shows that no rotation about the Pt—(CS) bond occurs on NMR time scale. In contrast to the rigid structure of the platinum—sulfine complexes, rotation around the Pt—(NS) bond in $Pt(PPh_3)_2(Ar—NSO)$ is observed at room temperature [2], which points to a stronger π-backbonding in the Pt—(CS) bond compared with the Pt—(NS) bond.

Most interesting is the fact that starting from the two sulfine isomers $E\text{-}(p\text{-}CH_3C_6H_4)(CH_3S)CSO$ or $Z\text{-}(p\text{-}CH_3C_6H_4)(CH_3S)CSO$ two different platinum—sulfine complexes can be isolated and that these are distinguishable by ^{31}P and ^{1}H NMR. This indicates that the configuration of the sulfine is retained upon coordination to the $Pt(PPh_3)_2$ unit via η^2-C=S. The structures and ^{31}P NMR spectra of both coordination compounds are shown in Fig. 2. This result accounts for the observation, that starting from $E\text{-}(p\text{-}CH_3C_6H_4)(PhS)CSO$, Z-PhClCSO and (PhS)ClCSO (one isomer) in all cases only one coordination compound, $Pt(PPh_3)_2[E\text{-}(p\text{-}CH_3C_6H_4)(PhS)CSO]$, $Pt(PPh_3)_2(Z\text{-}PhClCSO)$ and $Pt(PPh_3)_2[(PhS)ClCSO]$, respectively, was isolated. Accordingly, starting from a mixture of the two isomers of the sulfine $(p\text{-}CH_3C_6H_4S)(p\text{-}CH_3OC_6H_4S)CSO$ a

TABLE 3

INFRARED ABSORPTIONS (cm^{-1}) AND ASSIGNMENTS FOR Pt(PPh$_3$)$_2$(XYCSO) AND XYCSO (KBr-mulls) [a]

Compound	Pt complex		Free ligand CSO vibrations
	ν(SO)	other ligand vibrations	
Pt(PPh$_3$)$_2$(fluorene-SO)	1006	1220, 953, 617, 387, 329	1116, 1085, 1016
Pt(PPh$_3$)$_2$(Ph$_2$CSO)	1011 (998 [b]; 998 [c])	600, 331	1109, 1005
Pt(PPh$_3$)$_2$[*E*-(p-CH$_3$C$_6$H$_4$)(PhS)CSO]	1020	1502, 809, 322	1112, 1010, 1000
Pt(PPh$_3$)$_2$[*E*-(p-CH$_3$C$_6$H$_4$)(CH$_3$S)CSO]	1006	1503, 810, 324	1110, 1006
Pt(PPh$_3$)$_2$[*Z*-(p-CH$_3$C$_6$H$_4$)(CH$_3$S)CSO]	1010	1501, 810, 335	1121, 1014
Pt(PPh$_3$)$_2$[(PhS)$_2$CSO]	1016 (998 [b]; 1011 [c])	344	1110, 993, 945
Pt(PPh$_3$)$_2$[(p-CH$_3$C$_6$H$_4$S)$_2$CSO]	1012	802, 338	1109, 995, 947
Pt(PPh$_3$)$_2$[(p-CH$_3$C$_6$H$_4$S)(p-CH$_3$OC$_6$H$_4$S)CSO] [d]	1022	820, 800, 340	1115, 1002, 946
Pt(PPh$_3$)$_2$(*Z*-PhClCSO)	1008	592, 337, 317	1135, 1019, 914
Pt(PPh$_3$)$_2$[(PhS)ClCSO]	1017	338	1150, 1020, 925

[a] Absorptions from the Pt(PPh$_3$)$_2$-unit are not tabulated. [b] Measured in CHCl$_3$. [c] Measured in CH$_2$Cl$_2$. [d] A mixture of two isomers, indistinguishable by infrared spectroscopy.

TABLE 4

^{31}P{^{1}H}NMR DATA FOR Pt(PPh$_3$)$_2$(XYCSO) [a]

Compound	^1J(Pt—P$_a$) (Hz)	^1J(Pt—P$_b$) (Hz)	^2J(P$_a$—P$_b$) (Hz)	δ(P$_a$) (ppm)	δ(P$_b$) (ppm)
Pt(PPh$_3$)$_2$(fluoreneSO)	3561	3491	11	23.4	20.6
Pt(PPh$_3$)$_2$(Ph$_2$CSO)	3718	3256	17	21.5	19.6
Pt(PPh$_3$)$_2$[*E*-(p-CH$_3$C$_6$H$_4$)(PhS)CSO]	3622	3490	12	21.1	19.3
Pt(PPh$_3$)$_2$[*E*-(p-CH$_3$C$_6$H$_4$)(CH$_3$S)CSO]	3675	3419	13	21.6	19.9
Pt(PPh$_3$)$_2$[*Z*-(p-CH$_3$C$_6$H$_4$)(CH$_3$S)CSO]	3603	3345	11	20.5	19.6
Pt(PPh$_3$)$_2$[(PhS)$_2$CSO]	3596	3531	8	20.0	19.1
Pt(PPh$_3$)$_2$[(p-CH$_3$C$_6$H$_4$S)$_2$CSO]	3602	3523	8	20.5	19.5
Pt(PPh$_3$)$_2$[(p-CH$_3$C$_6$H$_4$S)(p-CH$_3$OC$_6$H$_4$S)CSO] [b]	3604	3525	7	20.6	19.6
Pt(PPh$_3$)$_2$[(PhS)ClCSO]	3539	3343	7	20.6	18.1
Pt(PPh$_3$)$_2$(*Z*-PhClCSO)	3581	3156	11	21.8	18.8
Pt(PPh$_3$)$_2$(p-CH$_3$C$_6$H$_4$NSO) [2]	3483	4580	11	20.0	16.6

[a] δ(ppm) relative to H$_3$PO$_4$ (85%); upfield = —; in CDCl$_3$. [b] A mixture of the two possible isomers, which have the same ^{31}P NMR spectrum.

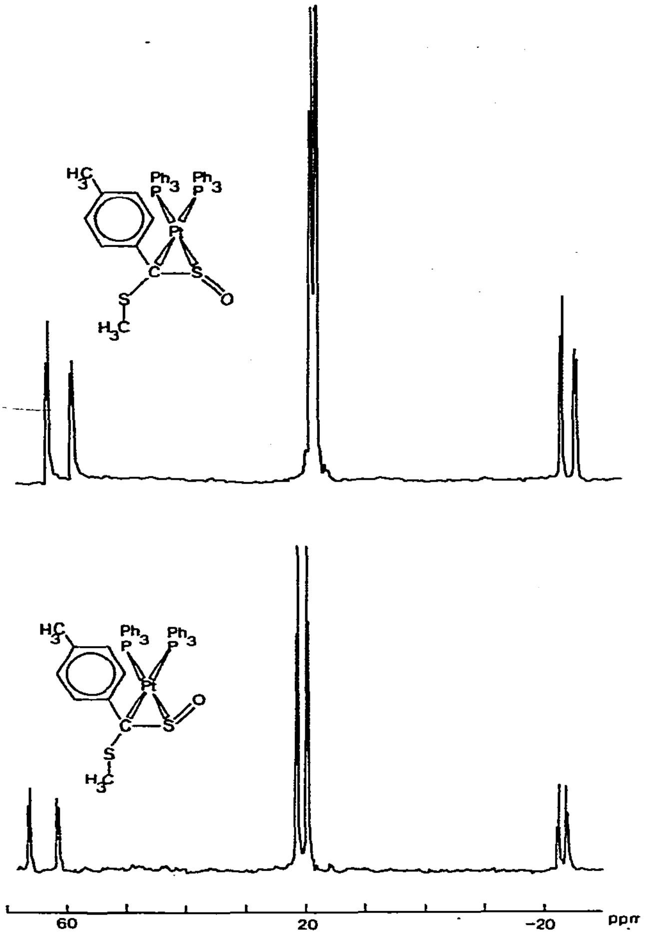

Fig. 2. Structures and ^{31}P NMR spectra of $Pt(PPh_3)_2[Z\text{-}(p\text{-}CH_3C_6H_4)(CH_3S)CSO]$ and $Pt(PPh_3)_2[E\text{-}(p\text{-}CH_3C_6H_4)(CH_3S)CSO]$.

mixture of two isomeric coordination compounds, $Pt(PPh_3)_2[(p\text{-}CH_3C_6H_4S)(p\text{-}CH_3OC_6H_4S)CSO]$, was isolated, as was shown by ^1H NMR spectroscopy (see Table 2, two OCH_3 singlets and two CH_3 singlets).

The complexes $Pt(PPh_3)_2$(fluorene-SO) and $Pt(PPh_3)_2(Ph_2CSO)$ are indefinitely stable in solution. In contrast the complexes $Pt(PPh_3)_2(XYCSO)$ containing a reactive C—X and/or C—Y (X, Y = S-aryl, S-alkyl, Cl) bonds undergo rearrangement in solution according to the equation:

$Pt(PPh_3)_2(XYCSO) \rightarrow PtX(PPh_3)_2(YCSO)$

(X = Cl, S-aryl, S-alkyl; Y = aryl, S-aryl)

A detailed report concerning these rearrangements as well as the molecular structure of a representative of this novel type of heterocumulene metal-complexes will be subject of a forthcoming paper.

Acknowledgements

We wish to thank Dr. R. Meij and Miss A.M.F. Brouwers for their continuous interest, and Mr. J.M. Ernsting for recording the ^{31}P NMR spectra and measuring the molecular weights.

References

1 R. Meij, D.J. Stufkens and K. Vrieze, J. Organometal. Chem., 144 (1978) 239.
2 R. Meij, D.J. Stufkens and K. Vrieze, J. Organometal. Chem., 155 (1978) 323; 164 (1979) 353.
3 G.E. Veenstra and B. Zwanenburg, Recl Trav. Chim. Pays-Bas, 95 (1976) 28, 37, 195, 202. Tetrahedron, 34 (1978) 1585.
4 B.F. Bonini, G. Maccagnani, G. Mazzanti and B. Zwanenburg, Gazz. Chim. Ital., 107 (1977) 283, 289.
5 B.F. Bonini, G. Maccagnani, L. Thijs and B. Zwanenburg, Tetrahedron Lett., (1973) 3569.
6 B.F. Bonini, G. Maccagnani, G. Mazzanti, L. Thijs, H.P.M.M. Ambrosius and B. Zwanenburg, J. Chem. Soc. Perkin I, (1977) 1468.
7 B. Zwanenburg, L. Thijs, J.B. Broens and J. Strating, Recl Trav. Chim. Pays-Bas, 91 (1972) 443.
8 L. Thijs, J. Strating and B. Zwanenburg, Recl Trav. Chim. Pays-Bas, 91 (1972) 1345.
9 A. Tangerman, B. Zwanenburg, Recl Trav. Chim. Pays-Bas, 96 (1977) 196.
10 A. Tangerman, B. Zwanenburg, J. Chem. Soc. Perkin II, (1974) 1141, 1143; (1975) 352, 916; Tetrahedron Lett., (1972) 5329; (1973) 79, 5195.
11 J. van Lierop, A. van der Avoird and B. Zwanenburg, Tetrahedron, 33 (1977) 539.
12 J.P. Snijder and D.N. Harpp, J. Chem. Soc. Chem. Commun., (1972) 1305.
13 B.F. Bonini, L. Lunazzi, G. Maccagnani and G. Mazzanti, J. Chem. Soc. Perkin I, (1973) 2314.
14 J.F. King and T. Durst, J. Amer. Chem. Soc., 85 (1963) 2676.
15 A. Tangerman, PhD Thesis, Nijmegen, 1974.
16 Th.W. Hummelink, Cryst. Struct. Commun., 4 (1975) 441.
17 R.B. Bates and G.A. Wolfe, J. Amer. Chem. Soc., 90 (1968) 6854.
18 D.C. Dittmer, K. Takahashi, M. Iwanami, A.I. Tsai, P.L. Chang, B.B. Bildner and I.K. Stamos, J. Amer. Chem. Soc., 95 (1973) 6113; 98 (1976) 2795.
19 L. Carlsen, Chem. Ind., 16 (1978) 733.
20 H. Alper, J. Organometal. Chem., 84 (1975) 347.
21 A.W. Gal, PhD Thesis, Nijmegen, 1977.
22 E.D. Dobrzynski and R.J. Angelici, J. Organometal. Chem., 76 (1974) C53.
23 F.R. Hartley, Organomet. Chem. Rev. Sect. A, 6 (1970) 119.
24 *Note added in proof*
The preliminary results of an X-ray structure determination by Dr. A.L. Spek (University of Utrecht) of $Pt(PPh_3)_2$(fluoreneSO) · $\frac{1}{2}C_6H_6$ established the presence of a fluoreneSO ligand which is η^2-CS bonded to platinum(0). The Pt and P atoms as well as the C=S bond are situated in the same plane (C—S 1.76, Pt—C 2.12 and Pt—S 2.32 Å; present R 0.05).