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Note

Tin(IV) to platinum(II) ligand transfer reactions of sulfinyl-containing Lewis bases

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Abstract

The Pt(II) centres in *trans*-[PtCl(μ-Cl)(PEt_3)]$_2$ were shown to be able to abstract sulfinyl-containing Lewis bases from several of their Sn(IV) adducts and form stable Pt(II) complexes. Hexacoordinate Sn(IV) adducts of Ph_2SnCl_2 with disulfoxides of the type $(RSOCH_2)_2$ (R = Pr, Ph), as well as with 1-methyl-2-(methylsulfinyl) imidazole (ImSOMe), had the sulfur-containing ligand abstracted by Pt(II) to form either S-bonded bridging diplatinum complexes (in the case of the disulfoxides) or an N-bonded species (with ImSOMe), as shown by spectroscopic and structural analysis. The ligand abstraction seems to be a general reaction. Only when the Sn(IV) precursor was changed to the particularly stable $MeSnCl_3 \cdot$ ImSOMe complex, in which the tin moiety is strongly acidic, did the reaction not proceed.

Keywords: Crystal structures; Platinum complexes; Sulfoxide complexes; Tin adduct complexes

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1. Introduction

The Sn(IV) metal centre is a 'hard' species and many adducts are known involving Sn(IV)-containing Lewis acids and 'hard' bases, such as oxygen-containing ligands typified by sulfoxides [1,2]. The hard and soft acid–base concept is usually applicable only when comparing competing reactions involving species of similar acidity or basicity [3,4]. Normally the bond strength of a series of adducts is described within the context of 'hard–hard' and 'soft–soft' interactions. The comparative importance of 'hard–hard' versus 'soft–soft' interactions has rarely been addressed.

The reactions described here show how several adducts of Ph_2SnCl_2 with the disulfoxides $RSOCH_2CH_2SOR$ (R = n-Pr and Ph) and with ImSOMe, clearly involving 'hard–hard' interactions, are significantly perturbed in the presence of *trans*-[PtCl(μ-Cl)(PEt_3)]$_2$. Surprisingly the strong Sn(IV)–O and Sn(IV)–N bonds are broken and the ligand is transferred to Pt(II), resulting in the formation of Pt(II)–S and Pt(II)–N bonded complexes. Only the very strongly bonded adduct $MeSnCl_3$ImSOMe did not react in this fashion.

Complexes involving both Sn and Pt, as well as Sn–Pt heterobimetallics, have become increasingly important in recent years, especially in the field of catalysis, and studies of the ligating modes of these metals are needed in order to clarify many points in their chemical behaviour [5].

2. Experimental

The ligands ImSOMe and $(RSOCH_2)_2$ (R = n-Pr, Ph) were prepared as previously reported [2,6]. Four adducts have been prepared and studied, namely $MeSnCl_3$ImSOMe [2], Ph_2SnCl_2ImSOMe [2] and $Ph_2SnCl_2(RSOCH_2)_2$ (R = n-Pr and Ph, respectively). The adducts with the disulfoxides were prepared by refluxing equimolar amounts of acid and base in $CHCl_3$ for 1 h, followed by evaporation and recrystallisation from a 1:1 mixture of n-hexane and MeOH, giving the pure products in 50% yields. *Anal.* of the new adducts: $Ph_2SnCl_2(n\text{-}PrSOCH_2)_2$: Found: C, 43.1; H, 5.1. Calc. for $C_{20}H_{28}O_2S_2Cl_2Sn$: C, 43.3; H, 5.1%. $Ph_2SnCl_2(PhSOCH_2)_2$: Found: C, 49.5; H, 4.1. Calc. for $C_{26}H_{24}O_2S_2Cl_2Sn$: C, 50.2; H, 3.9%.

Trans-[PtCl(μ-Cl)(PEt_3)]$_2$ was prepared according to the literature method [7]. Reactions of the adducts with [PtCl(μ-Cl)(PEt_3)]$_2$ were performed in CH_2Cl_2 in a Schlenk tube using equimolar amounts of the reactants. Stirring the solution for several hours followed by cooling led to the deposition of crystals in yields of pure product varying

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from 55 to 60%. $MeSnCl_3$·ImSOMe did not react with $[PtCl(\mu\text{-}Cl)(PEt_3)]_2$. The other reactions produced the complexes **1–3** listed below.

1: *trans*-$[Pt(Et_3P)Cl_2(ImSOMe)]$: Found: C, 24.9; H, 4.3; N, 5.2. Calc. for $C_{11}H_{23}Cl_2N_2OPSPt$: C, 25.0; H, 4.4; N, 5.3%.

2: *cis*-$[\{Pt(Et_3P)Cl_2\}_2(PrSOCH_2)_2]$: Found: C, 24.7; H, 4.9. Calc. for $C_{20}H_{48}Cl_4O_2P_2S_2Pt_2$: C, 24.5; H, 4.9%.

3: *cis*-$[\{Pt(Et_3P)Cl_2\}_2(PhSOCH_2)_2]$: Found: C, 29.7; H, 4.2. Calc. for $C_{26}H_{44}Cl_4O_2P_2S_2Pt_2$: C, 29.8; H, 4.2%.

Complexes **1–3** were also prepared by direct reaction of the Lewis base with $[PtCl(\mu\text{-}Cl)(PEt_3)]_2$ to give the identical products described above.

IR spectra were obtained in KBr pellets from a 1710 Perkin-Elmer FT spectrometer. ^{31}P, ^{119}Sn and ^{195}Pt NMR spectra were recorded in $CDCl_3$ solution in a 250 MHz Bruker instrument.

The molecular structures of complexes **1** and **2**, obtained from single crystal diffraction studies are shown in Figs. 1 and 2. Data collection in both cases was performed at 293 K.

Crystal data for 1: $C_{11}H_{23}Cl_2N_2OPSPt$, $M=528$, orthorhombic space group *Pbca* (No. 61), $a=17.330(2)$, $b=11.740(4)$, $c=17.502(5)$ Å, $V=3560.9$ Å^3, $Z=4$, $D_{calc}=1.93$ g cm^{-3}. Monochromated Mo Kα radiation $\lambda=.71069$ Å, $\mu=84.6$ cm^{-1}. The structure of the crystal (0.2×0.2×0.2 mm) was solved by routine heavy atom techniques and refined by full-matrix least-squares methods, using an Enraf-Nonius CAD-4 diffractometer, with non-H atoms isotropic. Of 2468 reflections observed, 1493 with $|F^2|>2\sigma(F^2)$ were used in the refinement, which converged at $R=0.034$, $R'=0.043$.

Crystal data for 2: $C_{20}H_{48}Cl_4O_2P_2S_2Pt_2$, $M=978.7$, monoclinic space group *C2/c* (No. 15), $a=11.453(2)$, $b=10.222(3)$, $c=28.242(19)$, $\beta=102.34(4)°$, $V=3229.9$ Å^3, $Z=4$, $D_{calc}=2.01$ g cm^{-3}. Monochromated Mo Kα radiation $\lambda=0.71069$ Å, $\mu=93.2$ cm^{-1}. The structure of the crystal (0.2×0.2×0.1 mm) was solved as in the case in **1**. Of 3145 reflections observed, 2268 with $[F^2]>2\sigma(F^2)$ were used in the refinement, which converged at $R=0.037$, $R'=0.049$. The space group *C2/c* was thus confirmed over *Cc* by the successful structure refinement.

3. Results and discussion

The molecular structure of the adduct $MeSnCl_3$ImSOMe shows that the Sn atom is hexacoordinated and the ligand is attached to the metal by the N and O atoms [2]. The inertness of this adduct towards $[PtCl(\mu\text{-}Cl)(PEt_3)]_2$ is probably due to the strength of the bonds of the chelating base to the very acidic Sn atom [2]. The adduct Ph_2SnCl_2ImSOMe is also likely to be a bidentate species. Table 1 presents IR data for the adducts, their precursors and the resulting Pt(II) complexes. Comparison of the data for free ImSOMe and Ph_2SnCl_2ImSOMe clearly shows a decrease in the SO stretching frequency of the base upon adduct formation, indicative of bonding through the oxygen atom. New SnN bands also appear, and a decrease in the frequency of the SnCl absorptions compared to the free Lewis acid was also noted (see Table 1). A similar decrease in the SO stretching frequency was also observed for the disulfoxides upon complexation, resulting in a sharp band indicating bonding by both oxygen atoms to metal centres.

The decrease in Lewis acidity of Ph_2SnCl_2 compared to $MeSnCl_3$ is apparently sufficient to make Ph_2SnCl_2-ImSOMe more reactive. The structures of the similar Sn(IV)

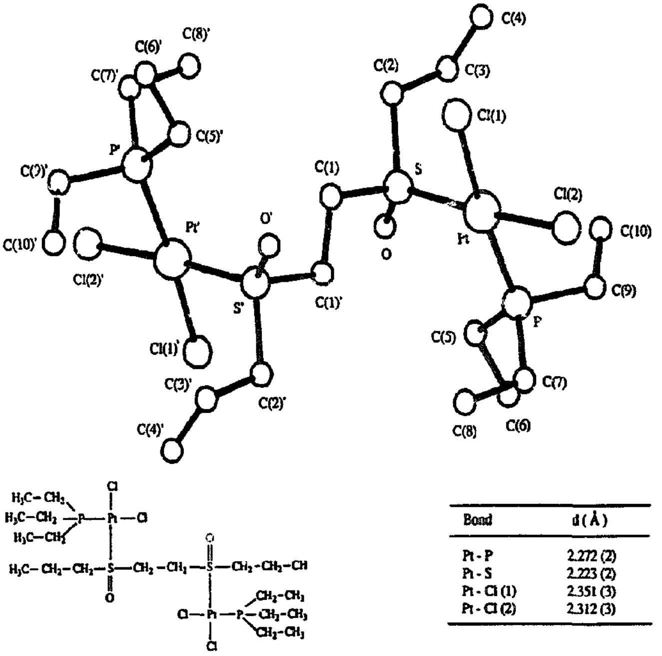
Table 1
Spectroscopic data

Compound	IR absorptions (cm^{-1})				^{119}Sn NMR δ (ppm) relative to Me_4Sn	$^{31}P\{^1H\}$ NMR		^{119}Sn Mössbauer	
	$\bar{\nu}SO$	$\bar{\nu}SnO$	$\bar{\nu}SnN$	$\bar{\nu}SnCl$		δ (ppm) relative to H_3PO_4	$^1J_{PtP}$ (Hz)	δ (mm s^{-1})	Δ (mm s^{-1})
ImSOMe	1020 [a]								
$(PrSOCH_2)_2$	1016								
$(PhSOCH_2)_2$	1037								
$[MeSnCl_3\cdot ImSOMe]$	970 [a]	433 [a]	340 [a]	245 [a]	insoluble			0.91	1.95
$[Ph_2SnCl_2\cdot ImSOMe]$	992 [a]	440 [a]	343 [a]	240 [a]	−105			1.26	3.51
$[Ph_2SnCl_2(PrSOCH_2)_2]$	963	461		240	−168			1.39	3.63
$[Ph_2SnCl_2\cdot (PhSOCH_2)_2]$	998	456		245	−129			1.28	3.73
$[Pt(Et_3P)Cl_2(ImSOMe)]$	1058					1	3467		
$[\{Pt(Et_3P)Cl_2\}_2(PrSOCH_2)_2]$	1142					19	3378		
$[\{Pt(Et_3P)Cl_2\}_2(PhSOCH_2)_2]$	1144					17	3312		
Trans-$[PtCl(\mu\text{-}Cl)(PEt_3)]_2$						12	3836		
$MeSnCl_3$				382 [a]	21			1.20	1.99
Ph_2SnCl_2				364, 356 [a]	−33			1.32	2.85

[a] Ref. [2].

sulfoxide adducts [$Me_2SnCl_2(RSOCH_2)_2$] (R = n-Pr, Ph) have recently been determined [8]. The crystallographic results show that both adducts are polymeric, with the disulfoxide forming a bridge between two organotin(IV) species. It seems likely that the adducts [$Ph_2SnCl_2(RSOCH_2)_2$] (R = n-Pr, Ph) also have a similar structure.

^{119}Sn chemical shift data for the adducts are also presented in Table 1. δ_{Sn} in [$Ph_2SnCl_2ImSOMe$] is − 105 ppm, which lies within the range usually associated with pentacoordination (−90 to −190 ppm [9]). This implies that although in the solid state the tin atom is hexacoordinate, in solution it may become pentacoordinated. Since both [$Ph_2SnCl_2(PrSOCH_2)_2$] and [$Ph_2SnCl_2(PhSOCH_2)_2$] also have similar shifts (−168 and −129 ppm, respectively) which are very different from those assigned to hexacoordinated species (−210 to −400 ppm), we believe that the adducts become



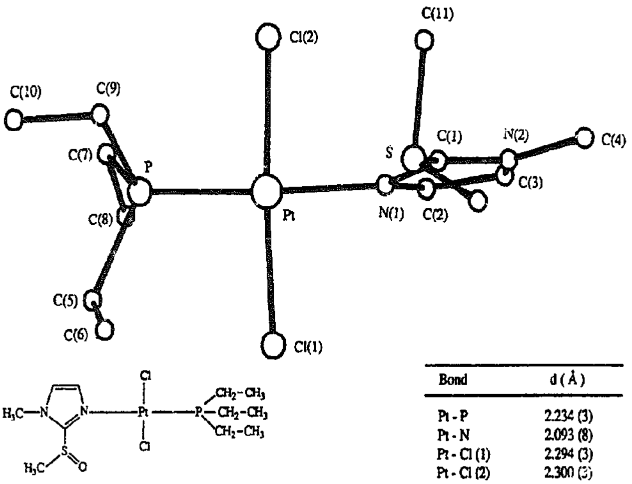
Bond	d(Å)
Pt-P	2.272 (2)
Pt-S	2.223 (2)
Pt-Cl (1)	2.351 (3)
Pt-Cl (2)	2.312 (3)

Fig. 1. The molecular structure of *cis*-[{$Pt(Et_3P)Cl_2$}$_2$($PrSOCH_2$)$_2$].

Table 2
Crystallographic data of the Pt complexes

Parameter	1 [$Pt(Et_3P)Cl_2(ImSOMe)$]	2 [{$Pt(Et_3P)Cl_2$}$_2$($PrSOCH_2$)$_2$]	3 [{$Pt(Et_3P)Cl_2$}$_2$($PhSOCH_2$)$_2$] [a]
Pt–N	2.093(8)		
Pt–S		2.223(2)	2.212(3)
Pt–P	2.234(3)	2.272(2)	2.270(3)
Pt–Cl1	2.294(3)	2.351(3)	2.302(3)
Pt–Cl2	2.300(3)	2.312(3)	2.353(3)
S–O	1.483(10)	1.475(7)	1.475(9)
Cl1–Pt–Cl2	176.1(1)	87.5(1)	86.9(1)
P–Pt–N	174.5(2)		
Cl1–Pt–N	88.4(2)		
Cl2–Pt–N	87.8(2)		
Cl1–Pt–P	94.6(1)	172.68(9)	173.9(1)
Cl2–Pt–P	82.2(1)	85.20(9)	88.6(1)
S–Pt–P		100.06(8)	93.4(1)
S–Pt–Cl1		87.25(8)	91.4(1)
S–Pt–Cl2		174.73(9)	174.3(3)

[a] Data from Ref. [14].



Bond	d (Å)
Pt - P	2.234 (3)
Pt - N	2.093 (8)
Pt - Cl (1)	2.294 (3)
Pt - Cl (2)	2.300 (3)

Fig. 2. The molecular structure of *trans*-[Pt(Et$_3$P)Cl$_2$(ImSOMe)].

pentacoordinated discrete species in solution. These species may be thought of as bridging 2:1 adducts (2 Lewis acids: 1 Lewis base) as is known to occur in [(Ph$_3$SnCl)$_2$-(PrSOCH$_2$)$_2$] [6,10]. Bridging disulfoxide complexes of Pt(II) also occur with Pt(II) as the discussion below will show. In this case, however, the ligand binds the metal through the sulfur atoms.

The ^{119}Sn Mössbauer data for the three Ph$_2$SnCl$_2$ adducts are remarkably close, suggesting they all have similar solid state structures. In the case of MeSnCl$_3$ImSOMe, as the electronegativity of the atoms around Sn(IV) increases the isomer shift is expected to decrease. The data are consistent with the presence of hexacoordinate Sn(IV) in all four cases [11]. Moreover, it has been shown that hexacoordinated monoorganic tin compounds, as well as adducts of monoorganic tin halides, tend to present lower quadrupole splittings than either di- or triorganic species [12,13].

The new complexes obtained from the reactions of the Ph$_2$SnCl$_2$ adducts with [PtCl(μ-Cl)(PEt$_3$)]$_2$ show an increase in the IR absorption frequency of the SO group, as shown in Table 1, indicating that transfer of the Lewis base from the Sn(IV) adducts to Pt(II) results in attachment of the metal via the S atom, unlike the O-bonded precursor adducts.

The structures of all three complexes have been determined. The complex [{Pt(Et$_3$P)Cl$_2$}$_2$(PhSOCH$_2$)$_2$] was shown to have two Cl atoms in a *cis* arrangement around each square planar Pt moiety [14]. The analogous [{Pt(Et$_3$P)Cl$_2$}$_2$(PrSOCH$_2$)$_2$], whose structure is presented here (Fig. 1) is very similar. The pertinent data for both complexes are compared in Table 2. Fig. 2 shows the structure of [Pt(Et$_3$P)Cl$_2$)ImSOMe]. In this monometallic species, in contrast with the preceding cases, the two Cl atoms are *trans* to each other.

Figs. 1 and 2 and data listed in Table 2 show a number of interesting features. **1** is the only monometallic species, and the Pt(II) atom is bonded to the N atom of the Lewis base, which lies *trans* to the phosphine. The two Cl atoms are *trans* to each other (176.1(1)°), in marked contrast with the dimetallic complexes, in which the two Cl atoms are in a *cis* position, with angles of 87.5(1)° (in complex **2**) and 86.9(1)° (in complex **3**), respectively. As expected, this difference in configuration is reflected in the $^1J_{\mathrm{PtP}}$ data (Table 1). Whereas the *cis* complexes exhibit $^1J_{\mathrm{PtP}}$ values of 3378 (**2**) and 3312 (**3**) Hz, the *trans* complex **1** has a $^1J_{\mathrm{PtP}}$ of 3467 Hz.

The SO distances are found to be shorter in complex **2** and complex **3** compared to complex **1**. Even considering that the ligands are different, it is interesting to see that the crystallographic data are in accordance with the IR results shown in Table 1. In **1** there is no bonding to Pt(II) by the SO group, and in **2** and **3** the SO group is S-bonded to the metal.

4. Supplementary material

All other intramolecular distances and angles as well as atomic and thermal parameters are available from the authors on request.

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