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INSERTION OF SULPHUR DIOXIDE INTO PLATINUM–CARBON σ-BONDS

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SUMMARY

Insertion reactions of sulphur dioxide with Pt–C σ-bonded complexes are described. These occur at about 50° in a Carius tube. The complexes obtained are of the *S*-sulphinate type, as indicated by their IR spectra. The *S*-sulphinate group shows a medium *trans*-effect. A comparison between carbon monoxide and sulphur dioxide insertions shows that the sulphur dioxide reactions are faster, probably because of the greater electrophilicity of sulphur dioxide.

INTRODUCTION

In recent years a considerable amount of information on sulphur dioxide insertion reactions with transition metal alkyl, aryl, alkenyl and alkinyl compounds has accumulated, and two reviews have recently appeared on the subject[1,2]. Although a comparison between the insertion behaviour of carbon monoxide and sulphur dioxide has been attempted, there are differences between the mechanisms of these insertions. Reactions of CO with Pt–C and Pd–C σ-bonded complexes have been studied in many cases[3], but no study has been carried out on the analogous Ni–C σ-bonded compounds. However reactions of SO_2 with such compounds have been reported[4]. Furthermore the insertion reaction of SO_2 with the bis(triethylphosphine)-π-allylplatinum chloride has been studied[5]; and Chatt and Mingos[6] succeeded in preparing *p*-toluenesulphinatoplatinum(II) complexes containing Pt–S bonds by bringing sodium *p*-toluenesulphinate into reaction with complexes of the type PtL_2Cl_2. In order to compare CO and SO_2 insertion reactions, we prepared some new *S*-sulphinate-platinum(II) complexes by inserting SO_2 into a Pt–C σ-bond. A preliminary communication on this subject has already appeared[7].

EXPERIMENTAL

Starting materials as *trans*-PtL_2RCl (L = PEt_3, $AsEt_3$, $SeEt_2$, $TeEt_2$) and *cis*-$Pt(PPh_3)_2Ph_2$ were prepared as previously described[8,9]. The *trans*-$Pt(SeEt_2)_2Ph_2$ complex was obtained by treating *trans*-$Pt(SeEt_2)_2Cl_2$ with PhMgCl (molar ratio 1/4) in ether, at room temperature, and was identified by elemental analysis and IR spectroscopy (m.p. 79–82°). The *trans*-$Pt(PPh_3)_2(CH_2CN)Cl$ was obtained by oxidative addition of $ClCH_2CN$ to $Pt(PPh_3)_4$. The sulphur dioxide was supplied by Matheson, and passed through concentrated H_2SO_4 and a P_4O_{10}–$CaCl_2$ column before condensation at −75°. IR spectra were recorded with a Perkin–Elmer model 457 spectrometer. ^1H NMR spectra were recorded with a Jeol 60 MHz spectrometer. Melting points were determined on a Fisher–Jones hot stage apparatus. Elemental analyses were by Alfred Bernhardt, Microanalytisches laboratorium, Mülheim, Germany. Physical properties and analytical data are listed in Table 1.

TABLE 1

PHYSICAL PROPERTIES AND ANALYTICAL DATA

Compound	*Colour*	*M.p. (°C)*	*Analysis found (calcd.) (%)*			
			C	*H*	*Cl*	*S*
trans-$Pt(PEt_3)_2(PhSO_2)Cl$	White	132–135	35.31 (35.62)	5.46 (5.64)	5.66 (5.84)	4.96 (5.28)
trans-$Pt(PEt_3)_2(CH_3SO_2)Cl$	White	64–67	28.76 (28.59)	5.77 (6.09)	6.35 (6.49)	5.56 (5.87)
trans-$Pt(AsEt_3)_2(PhSO_2)Cl$	White	79–83	30.79 (31.06)	5.09 (5.06)	5.25 (5.10)	4.32 (4.61)
trans-$Pt(SeEt_2)_2(PhSO_2)Cl$	Pale-yellow	90–93	25.91 (26.07)	3.82 (3.75)	5.24 (5.49)	4.53 (4.97)
trans-$Pt(SeEt_2)_2(p\text{-}ClC_6H_4SO_2)Cl$	White	117–120	25.04 (24.71)	3.59 (3.55)	10.39 (10.42)	4.55 (4.71)
trans-$Pt(SeEt_2)_2(PhSO_2)_2$	White	139–142	31.60 (31.96)	4.16 (4.02)		8.36 (8.53)
trans-$Pt(TeEt_2)_2(PhSO_2)Cl$	Ivory	73–75	22.45 (22.62)	3.56 (3.39)	4.61 (4.77)	4.09 (4.32)

Preparation of trans-$Pt(PEt_3)_2(PhSO_2)Cl$

trans-Chlorophenylbis(triethylphosphine)platinum(II) (120 mg, 0.22 mmoles) was placed in a Carius tube (height 250 mm, diameter 20 mm). Sulphur dioxide was flushed through the tube which was cooled at −78°. Condensation of SO_2 was continued until all the starting material had dissolved to form a red solution (ca. 2.5 ml required). The tube was sealed, and the mixture maintained at 50° for about 6 h; during this time the solution became pale yellow. After evaporation of the excess of SO_2, the oily residue was extracted with $CHCl_3$, and the extract was filtered and treated with pentane to precipitate a white solid. Crystallization from dichloromethane/pentane gave white crystals.

Preparation of trans-$Pt(PEt_3)_2(CH_3SO_2)Cl$

By a procedure similar to that described above, 115 mg (0.24 mmoles) of *trans*-$Pt(PEt_3)_2(CH_3)Cl$ and ca. 2 ml of liquid sulphur dioxide gave 95 mg of *trans*-chloro-*S*-methylsulphinatobis(triethylphosphine)platinum(II) as a white powder. The product was crystallized several times from chloroform/ether.

Preparation of trans-$Pt(AsEt_3)_2(PhSO_2)Cl$

Sulphur dioxide was condensed into a Carius tube containing *trans*-Pt-

$(AsEt_3)_2PhCl$ (100 mg, 0.16 mmoles) at −78° until the solid had completely dissolved (ca. 2 ml required). The red solution was kept at 50° for 8 h, during which it became pale yellow. After evaporation of the excess of SO_2, the residue was extracted with acetone, and petroleum ether (b.p. 40–70°) was added. Crystallization from chloroform/ether gave the product as a white powder.

Preparation of trans-Pt(SeEt$_2$)$_2$(PhSO$_2$)Cl

Sulphur dioxide was condensed into a Carius tube containing *trans*-chlorophenylbis(diethylselenide)platinum(II) (160 mg, 0.23 mmoles). By a procedure similar to that described above, the product was obtained after several crystallizations from acetone/pentane. The same product was obtained by adding a solution of 92 mg of $PhSO_2Na$ in methanol to a suspension of 300 mg of *trans*-dichlorobis(diethylselenide)platinum(II) stirred in the same solvent. After 6 h the solvent was evaporated, and the residue washed with water and dried. The product was crystallized from acetone/pentane.

Preparation of trans-Pt(SeEt$_2$)$_2$(p-ClC$_6$H$_4$SO$_2$)Cl

Sulphur dioxide was condensed into a Carius tube containing *trans*-$Pt(SeEt_2)_2$-$(p\text{-}ClC_6H_4)Cl$ (110 mg, 0.18 mmoles) at −78°. The mixture was kept at 50° for about 8 h. By a procedure similar to that described above a white product was obtained from acetone/pentane.

Preparation of trans-Pt(SeEt$_2$)$_2$(PhSO$_2$)$_2$

By condensing sulphur dioxide into a Carius tube containing *trans*-$Pt(SeEt_2)_2$-Ph_2 (150 mg, 0.24 mmoles) a red solution was obtained. The sealed tube was kept at 50° overnight, during which the colour turned to pale yellow and a white precipitate was formed. The excess of SO_2 was evaporated, and the solid residue dissolved in chloroform and filtered. Addition of pentane to the concentrated solution gave a white solid.

Preparation of trans-Pt(TeEt$_2$)$_2$(PhSO$_2$)Cl

By a procedure similar to that described above, 130 mg (0.19 mmoles) of *trans*-$Pt(TeEt_2)_2PhCl$ and ca. 1.5 ml of liquid sulphur dioxide gave 98 mg of *trans*-chloro-*S*-phenylsulphinatobis(diethyltelluride)platinum(II) as a white powder. The product was crystallized from acetone/pentane.

RESULTS AND DISCUSSION

When sulphur dioxide is condensed in a Carius tube containing the *trans*-PtL_2RCl ($L = PEt_3$, $AsEt_3$, $SeEt_2$, $TeEt_2$; R = organic group) complexes at −60° the latter dissolve to give yellow or orange solutions. When the mixture is left for about 8 h at room temperature, there is no reaction, but if it is kept at 50° in a sealed tube for about 6 h, *trans*-$PtL_2(RSO_2)Cl$ complexes are formed. The products are white or pale yellow, are air stable and are not electrolytes. *trans*-$Pt(TeEt_2)_2(SO_2Ph)$-Cl differs from the other complexes in that it slowly decomposes.

Table 2 lists IR and ^1H NMR data for the prepared complexes. The IR spectra in the 800–1250 cm^{-1} region are consistent with the presence of *S*-bonded sulphinate

TABLE 2

IR AND ^{1}H NMR DATA[a]

Complex	$\nu_{asym}(SO_2)$	$\nu_{sym}(SO_2)$	$\nu(Pt\text{–}Cl)$	$\tau(C_6H_5)$	$\tau(CH_2)$	$\tau(CH_3)$
trans-$Pt(PEt_3)_2(PhSO_2)Cl$	1187 vs	1093 s	303 s			
trans-$Pt(PEt_3)_2(CH_3SO_2)Cl$	1192 vs	1095 s	302 s			
trans-$Pt(AsEt_3)_2(PhSO_2)Cl$	1185 s(br)	1090 s	304 s	1.85–2.1 2.50–2.73(5)	8.05 m(12)	8.8 t(18) *J* 7.5
trans-$Pt(SeEt_2)_2(PhSO_2)Cl$	1200 vs	1098 s	304 s	2.06–2.70(5)	7.0 m(8)	8.62 t(12) *J* 7.5
trans-$Pt(SeEt_2)_2(p\text{-}ClC_6H_4SO_2)Cl$	1204 vs		296 s	2.15–2.64(4)	6.92 m(8)	8.57 t(12) *J* 7.5
trans-$Pt(SeEt_2)_2(PhSO_2)_2$	1196 vs	1089 vs		2.10–2.62(10)	6.85 m(8)	8.75 t(12) *J* 7.5
trans-$Pt(TeEt_2)_2(PhSO_2)Cl$	1185 vs	1095 s	301 s	1.90–2.65(5)	7.08 m(8)	8.46 t(12) *J* 7.8

[a] Chemical shifts (τ) are relative to $SiMe_4$ as internal standard, the spectra being measured at 60 MHz and integrated. Abbreviation: m = multiplet, t = 1/2/1 triplet, *J* = coupling constant with the proton of the CH_2 group, vs = very strong, s = strong, br = broad. Values in parentheses are the relative intensities of the protons.

groups coordinated with platinum(II). The stretching frequencies $\nu_{as}(SO_2)$ at about 1190 cm^{-1} and $\nu_{sym}(SO_2)$ at about 1090 cm^{-1} in fact support a structure in which SO_2 has been inserted into the Pt–C σ-bond to give an *S*-sulphinate compound[10,11]. On the other hand, by treating *trans*-$Pt(SeEt_2)_2Cl_2$ with $PhSO_2Na$ in methanol, at a 1/1 ratio, we were able to obtain a compound identical with that produced by the insertion reaction between SO_2 and *trans*-$Pt(SeEt_2)_2PhCl$. The behaviour of Pt^{II} in giving *S*-sulphinate complexes is in accord with its soft character[12].

The ^{1}H NMR spectra (Table 2) are almost identical for the complexes $PtL_2(PhSO_2)Cl$ ($L = SeEt_2$, $TeEt_2$, PEt_3, $AsEt_3$) and $Pt(SeEt_2)_2(PhSO_2)_2$, and show, in addition to the complex absorption due to the phenylic hydrogens centered at about τ 2.5, first a multiplet, arising from the coupling between hydrogens of CH_3, ^{195}Pt (33%) and ^{31}P (when P is present), of the resonances arising from the CH_2 groups bonded to P, As, Se or Te, and, second, a triplet characteristic of the CH_3 group on the ligand L.

As expected for a *trans* configuration of the complexes, the stretching frequency $\nu(Pt\text{–}Cl)$ (Table 2) is insensitive to variation of the neutral coordinated ligands; the value of about 302 cm^{-1} is found also in other *S*-sulphinate platinum(II) complexes[6], and indicates a medium *trans* influence for the $PhSO_2$ group bonded to platinum(II). We cannot say whether this *trans*-effect is inductive or mesomeric. It is possible that the *S*-sulphinate is a good σ-donor group[13], but the question must remain open.

It is important to note that the insertion of SO_2 into the platinum(II) complexes, does not occur at room temperature. This must be due to kinetic factors. The alkyl and aryl platinum(II) complexes must be considered the most inert of the compounds so far studied in reactions with SO_2. Insertions of CO show a similar behaviour, although in this case more drastic conditions are required. In contrast, insertion of SO_2 into a Ni–C σ-bond in a complex such as $(\pi\text{-}C_5H_5)Ni(PR_3)CH_3$ to give $(\pi\text{-}C_5H_5)Ni(PR_3)(SO_2CH_3)$ occurs quite rapidly at room temperature[4]. Furthermore the reaction conditions and the values $\nu_{as}(SO_2)$ and $\nu_{sym}(SO_2)$ are not sensitive to the electron withdrawing properties of the Cl atom in the *p*-chlorophenyl derivative.

No detectable reaction was observed when the *trans*-$Pt(PPh_3)_2(CH_2CN)Cl$ was kept overnight at 60° in the presence of SO_2. Clearly the strength of the platinum–carbon bond has an important influence on these reactions. The complexes $(\pi\text{-}C_5H_5)Fe(CO)_2CH_2CN$ and $(\pi\text{-}C_5H_5)Mo(CO)_3CH_2CN$ similarly fail to react with SO_2[1,14]. *trans*-$Pt(SeEt_2)_2(SO_2Ph)_2$ obtained by inserting SO_2 into *trans*-$Pt(SeEt_2)_2Ph_2$ is the first example of a mononuclear complex containing more than one sulphinate group bonded to a d^8 metal. *cis*-$Pt(PPh_3)_2Ph_2$ also reacted with SO_2 to give a white product containing the coordinated *S*-sulphinate group, but the elemental analysis was not satisfactory.

In conclusion, although SO_2 and CO both insert into platinum–carbon σ-bonds, the reactions with SO_2 are faster than those with CO. Probably the greater electrophilicity of SO_2 plays an important role in determining this behaviour.

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