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Preliminary communication

S-Sulfinate platinum(II) complexes formed by insertion of SO_2 into Pt—C σ bonds

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Insertion of CO into Pt—C σ bonds is well known[1]. It has been suggested that acyl and sulfonyl derivatives of transition metal compounds show a marked structural similarity[2], and this has prompted us to prepare some new *S*-sulfinate—platinum(II) complexes, namely *trans*-$[PtL_2(SO_2Ph)Cl]$ (L = PEt_3, $AsEt_3$, $SeEt_2$ $TeEt_2$).

When sulfur dioxide is condensed into a Carius tube containing the *trans*-$[PtL_2PhCl]$ complex at —60°, the latter dissolves, giving a yellow or orange solution. No reaction occurs at room temperature, but keeping the mixture at about 45° overnight gives the sulfonyl compounds, which can be isolated after removal of the excess of SO_2 and crystallization of the crude products from acetone—pentane. The elemental analyses of the products were very satisfactory. Table 1 lists IR and NMR data for the prepared complexes.

The stretching frequencies $\nu_{as}(SO_2)$ at about 1190 cm^{-1} and $\nu_{sym}(SO_2)$ at about 1090 cm^{-1} support a structure in which SO_2 has been inserted into the M—C σ bond[2,3]. Furthermore treatment of *trans*-$[Pt(SeEt_2)_2Cl_2]$ with $PhSO_2Na$ in 1/1 ratio in methanol gave a product identical with that isolated from the reaction of SO_2 with *trans*-$[Pt(SeEt_2)_2PhCl]$. In all the compounds described, the value of ν(Pt—Cl) is nearly the same as expected for a *trans* configuration. The value of this stretching frequency at about 300 cm^{-1} indicates a medium *trans* influence for the $PhSO_2$ group bonded to platinum(II). The ^1H NMR spectra (Table 1) are almost identical, and show, in addition to the complex absorption due to phenylic hydrogens at about τ 2.5, a multiplet, arising from coupling between hydrogens of the CH_3 and the ^{195}Pt (33%) of the resonances arising from the CH_2 groups bonded to P, As, Se or Te, and a triplet characteristic of the CH_3 group on the ligand L.

Although we have no kinetic data, we believe, in accord with current opinion[4], that insertions of SO_2 into the Pt—C σ-bonds proceed through an attack of SO_2 on the platinum center followed by the formation of the platinum—sulfinate bond.

Further studies regarding the insertion reactions of SO_2 on Pd—C and Ni—C σ bonds are proceeding.

TABLE 1

IR AND ^{1}H NMR DATA FOR *trans*-[$PtL_2(PhSO_2)Cl$] [a]

Complex	$\nu_{asym}(SO_2)$	$\nu_{sym}(SO_2)$	$\nu(Pt-Cl)$	$\tau(C_6H_5)$	$\tau(CH_2)$	$\tau(CH_3)$
trans-[$Pt(PEt_3)_2(PhSO_2)Cl$]	1187 vs	1093 s	303 s			
trans-[$Pt(AsEt_3)_2(PhSO_2)Cl$]	1185 s br	1090 s	304 s	1.85–2.1 and 2.5–2.73 (5)	8.05m (12)	8.8t (18) J 7.5
trans-[$Pt(SeEt_2)_2(PhSO_2)Cl$]	1200 vs	1098 s	304 s	2.06–2.70 (5)	7.0m (8)	8.62t (12) J 7.5
trans-[$Pt(TeEt_2)_2(PhSO_2)Cl$]	1185 vs	1095 s	301 s	1.9–2.65 (5)	7.08m (8)	8.46t (12) J 7.8

[a] Chemical shifts (τ) are relative to $SiMe_4$ as internal standard, the spectra being measured at 60 Mc/sec 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.

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