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Isolation and Structure Determination of a Mixed Ligand Platinum Complex containing Trichlorostannane

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Our interest in the isolation and structural characterization of the bimetallic platinum–tin complex containing mixed triethylphosphine and benzamidoxime ligands, PtCl(SnCl$_3$)LL′, (L = PEt$_3$ and L′ = PhC(NH$_2$)=NOH) is manyfold. Metal complexes of low symmetry containing mixed ligands can be useful in studies such as (1) *trans*-effects of ligands having variable electronic and steric parameters [1, 2] (2) asymmetric synthesis catalysed by metal complexes and (3) homogeneous hydrogenation and polymerization catalysis [3]. In particular, platinum-phosphine complexes in conjunction with tin (II) dichloride have been shown in homogeneously catalyse both hydrogenation and hydroformylation reactions [3–6]. Only a small number of mixed ligand complexes of platinum have been reported [7–9]. This is probably due to their tendency to disproportionate into more symmetrical complexes [10]. To the best of our knowledge no single crystal structure of a mixed ligand complex of platinum containing the SnCl$_3^-$ moiety has been determined. Due to our interest in the metal complexes of amidoximes [11], we have used benzamidoxime as one of the ligands in the present studies.

From the reaction of tin(II) dichloride with =PtCl$_2$(PEt$_3$)]$_2$, we have recently isolated a bimetallic dinuclar platinum(II) complex containing the SnCl$_3^-$ ligand, [PtCl(SnCl$_3$)(PEt$_3$)]$_2$ [12] (*1*). This readily undergoes a bridge-splitting reaction with benzamidoxime in CH$_2$Cl$_2$ and from a concentrated solution of this reaction (eqn. 1), crystals of a mixed ligand complex [PtCl(SnCl$_3$)LL′·Et$_2$O], (*2*) (L = PEt$_3$ and L′ = PhC(NH$_2$)=NOH) are isolated in an almost

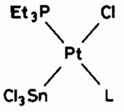
$$[\mathrm{PtCl(SnCl_3)(PEt_3)}]_2 + 2\mathrm{PhC(NH_2)=NOH} \xrightarrow{\mathrm{CH_2Cl_2}}$$

$$2[\mathrm{PtCl(SnCl_3)(PEt_3)(PhC(NH_2)=NOH)}] \qquad (1)$$

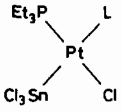
quantitative yield by the addition of diethyl ether. (*Anal.* Found: C, 26.12; H, 4.20; N, 3.67; Cl, 18.35; P, 4.02%. Calcd. for (*2*): C, 36.04; H, 4.21; N, 3.47; Cl, 18.12; P, 3.96%. M.p. = 90–2 °C]. Crystals of *2* hold one mole equivalent of diethylether which could not be removed even when dried under reduced pressure. The presence of diethyl ether is also observed in the ^{1}H NMR spectrum [^{1}H NMR of *2*: δ 0.97 ppm (quintet), J = 7.6 Hz) 9H (methyl protons of PEt$_3$); δ 1.94 ppm (multiplet), 6H (methylene protons of PEt$_3$); δ 1.14 ppm (triplet), J = 6.8 Hz, 6H (methyl protons of Et$_2$O); δ 3.42 ppm (quintet), J = 6.8 Hz, 4H (methylene protons of Et$_2$O); δ 7.49 and 7.27 ppm (multiplets), 5H (phenyl protons of benzamidoxime); δ 5.70 ppm (broad singlet), 2H (–NH$_2$ protons of benzamidoxime); δ 6.91 ppm (broad singlet), 1H (–OH proton of benzmidoxime)].

The ^{31}P NMR spectrum of complex *2* in CH$_2$Cl$_2$/C$_6$D$_6$ shows only one singlet at δ 0.00 ppm (w.r. to. H$_3$PO$_4$) associated with platinum (^{195}Pt) and tin (^{117}Sn and ^{119}Sn) satellite [J^{195}Pt–^{31}P = 3042 Hz and ^{2}J^{117}Sn–^{31}P = 259 Hz, and ^{2}J^{119}Sn–^{31}P = 289 Hz]. The magnitudes of these tin–phosphorus coupling constants are larger than those reported for *trans*-Pt-Cl(SnCl$_3$)(PR$_3$)$_2$ (≅240 Hz) and *trans*-PtH(SnCl$_3$)(PR$_3$)$_2$ (≅200 Hz) [13].

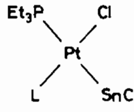
There are several structural configurations possible for a four coordinate platinum (A thru 2C) where benzamidoxime is acting as a monodentate ligand.



2A



2B



2C

The ability of benzamidoxime to coordinate either through the nitrogen of the amino-group or through the nitrogen of the oxime group, makes the assignment even more complicated. Again, the possibility of a structure in which benzamidoxime is acting as a bidentate ligand to give a five coordinate platinum cannot be ruled out on the basis of the above evidence. In order to assign a correct structure of the complex *2*, an X-ray crystal structure determination has been carried out.

The complex crystallizes in the monoclinic system, space group P2$_1$/c with four molecules in the unit cell; the lattice constants are a = 15.945, b = 10.106, c = 18.089, β = 106.67°. Intensity data were collected on a P2$_1$ four-circle automated diffractometer with MoK$_\alpha$-radiation. A total of 4832 independent reflections were measured. Intensities were corrected for Lorentz, polarisation and absorption effects. The structure was determined by heavy-atom techniques and refined by full-matrix least

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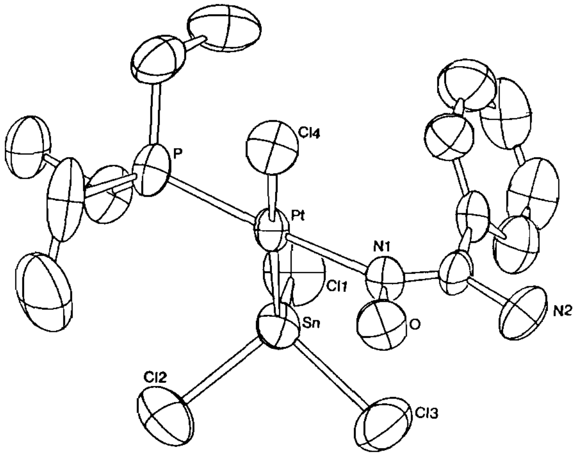

Fig. 1. ORTEP drawing of the complex [PtCl(SnCl$_3$)(PEt$_3$)-(L)] (L = PhC(NH$_2$)=NOH). Phenyl, ethyl, amino- and hydroxyl hydrogen atoms are omitted. Principal bond lengths (A) are: Pt–P = 2.242(3), Sn–Pt = 2.501(1), Cl$_4$Pt = 2.325(3), N$_1$–Pt = 2.097(7), Cl$_1$–Sn = 2.339(3), Cl$_2$Sn = 2.350(3), Cl$_3$–Sn = 2.332(3) and angles (°): Sn–Pt–P = 95.6(1), Cl$_4$–Pt–P = 88.3(1), Cl$_4$Pt–Sn = 175.8(1), N$_1$–Pt–P = 175.4(2), N$_1$–Pt–Sn = 89.1(2) and N$_1$–Pt–Cl$_4$ = 87.0(2).

squares procedures. The final conventional R value is 0.0483 for 3880 observations with $F \geqslant 3\sigma(F)$ and 231 variables.

A perspective view of the molecule *2* is presented in Fig. 1 where the most relevant atoms are labeled. The diethyl ether molecule is not part of the complex *2* and is therefore omitted.

In the compound the Pt atom is four-coordinated and is surrounded in an approximately planar fashion by PEt$_3$ and benzamidoxime, PhC(NH$_2$)=NOH, ligands at mutually *trans* positions, a chlorine and a σ-bonded Sn of the SnCl$_3$ group. The benzamidoxime ligand acts as a monodentate ligand and is coordinated to the platinum through the nitrogen of the oxime group. In the crystal structure of a platinum-tin cluster compound, [(C$_8$H$_{12}$)$_3$Pt$_3$Sn$_2$-Cl$_6$] [14], the average Pt–Sn bond length has been reported to be 2.80 Å. A significantly shorter Pt–Sn (2.50 Å) has been found for complex *2*.

Preliminary results indicate that the above bimetallic complex *2* containing mixed ligands is an active hydrogenation catalyst. A detailed study on the catalytic reactions is currently under investigation.

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