# THE CRYSTAL STRUCTURE OF TETRACHLOROBIS(TRIPHENLPHOSPHINE OXIDE)TIN(IV)

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## Abstract

The solid state structure of $[SnCl_4(OPPh_3)_2]$ (1) was determined by the X-ray diffraction method. The results indicate that the complex has a distorted octahedral geometry with the two $OPPh_3$ ligands *cis* to each other: Sn–O = 2.086(2) Å and Sn–Cl = 2.385(1) and 2.395(1) Å. The tin atoms lie on a two-fold axis. The compound crystallizes in the monoclinic space group *C2/c*, with unit cell dimensions $a$ = 13.881(3) Å, $b$ = 12.897(3) Å, $c$ = 19.492(4) Å and $\beta$ = 95.89(3)° for $Z = 4$. The results are discussed in relationship to the IR and NMR data.

## 1. Introduction

In the course of our continuing investigation of the catalytic activity of Group 6 metal carbonyls, we have been particularly intrigued by the role of Lewis acids such as $SnCl_4$ or $GeCl_4$ in the generation of catalytically active species. In a series of papers we have developed synthetic routes to heterobimetallic compounds containing Mo–Sn or W–Sn bonds [1-5]. The latter compounds are the products of the oxidative addition of transition metal and main group metal compounds. However, in the presence of trace amounts of water and oxygen this high-yield synthesis of the heterobimetallic compounds is accompanied by the formation of oxygen-containing products. During the reaction of $[W(CO)_4(NCMe)(PPh_3)]$ with $SnCl_4$ in $CH_2Cl_2$, we generally observed the formation of the oxidative addition product (tungsten(II) compound [6]), but small amounts of $[SnCl_4(OPPh_3)_2]$ (1) and $[HPPh_3]_2[SnCl_6]$ were also formed. Although the structures of numerous tin(IV) complexes containing phosphine oxide as ligands have been determined crystallographically [7-11], $[SnCl_4(OPPh_3)_2]$ (1) has thus far not been studied. Furthermore, we were interested in comparing structural parameters for this compound with those for analogous uranium(IV) [12] and tungsten(IV) [13] compounds.

## 2. Experimental

Reaction of $[W(CO)_4(NCMe)(PPh_3)]$ with $SnCl_4$ in $CH_2Cl_2$ following the experimental details in [6] gave the tungsten(II) compound $[WCl(SnCl_3)(CO)_3((NCMe)(PPh_3)]$ and a small amount of $[SnCl_4(OPPh_3)_2]$ (1). During the slow crystallization from a mixture of $CH_2Cl_2$/heptane, the tungsten(II) compound precipitates as an orange powder and 1 as colourless crystals, which were separated by hand. IR (KBr disc): $\nu$(P=O) 1123 $cm^{-1}$; $^1$H-NMR ($CD_3OD$, 293 K): ($\delta_H$ 7.67 – 7.52 (*Ph*); $^{31}P\{^1H\}$-NMR ($H_3PO_4$ as reference): $\delta_P$ 33.68 in $CD_3OD$ and $\delta_P$ 27.85 in DMSO-$d_6$.

Crystal of chemical formula $C_{36}H_{30}Cl_4O_2P_2Sn$ (1), M.W. = 817.03, monoclinic, space group *C2/c*, $a$ = 13.881(3) Å, $b$ = 12.897(3) Å, $c$ = 19.492(4) Å, $\beta$ = 95.89(3)°, $Z = 4$, $D_{calc}$ = 1.563g $cm^{-3}$. Crystal data for 1 were collected on a Kuma KM4CCD κ-axis diffractometer with graphite-monochromated Mo-$K_\alpha$ radiation, $\mu$(Mo-$K_\alpha$) = 1.168 $mm^{-1}$. The data were corrected for Lorentz and polarisation effects but not for absorption. Data reduction and analysis were carried out using Kuma Diffraction (Wroclaw) programs. The structure was solved by direct methods (SHELXS-97 program) [14] and refined by the full-matrix least-squares method on all $F^2$ data using the SHELXL-97 [15] programs to $R$ values for 1 of $R_1$ = 0.0402 and $wR_2$ = 0.0701. Non-hydrogen atoms were refined with anisotropic thermal parameters; hydrogen atoms were included in the $\Delta\rho$ maps and refined with isotropic displacement parameters.

Crystallographic data have been deposited at the Cambridge Crystallographic Data Centre with deposition no. 171735. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

## 3. Results and Discussion

The molecular structure of $[SnCl_4(OPPh_3)_2]$ (1) is shown in Figure 1. The molecule of 1 is slightly distorted from octahedral geometry, with the oxygen atoms of the triphenylphosphine oxide ligands occupying *cis* positions. The greatest deviation from the ideal octahedral geometry for 1 is manifested in the contraction of the Cl(1)–Sn–Cl(1)' angle to 170.53(4)°. The two *cis* $OPPh_3$ ligands bonded at the same distances from the metal are related by two-fold symmetry. The Sn–Cl bond distances are shorter for the mutually *trans* chlorine, with Sn–Cl(1) of 2.385(1) Å, than for the mutually *cis* chlorine, with Sn–Cl(2) of 2.395(2) Å. The lengthening of the Sn–Cl bond *trans* to the oxygen atom can be accounted for by the *trans* influence of the coordinated phosphine oxide. The Sn–O and Sn–Cl distances in 1 are much shorter than in *trans*-$[SnPh_2Cl_2(OPPh_3)_2]$ (Sn–O = 2.214(4) and Sn–Cl = 2.554(1) Å [9]).

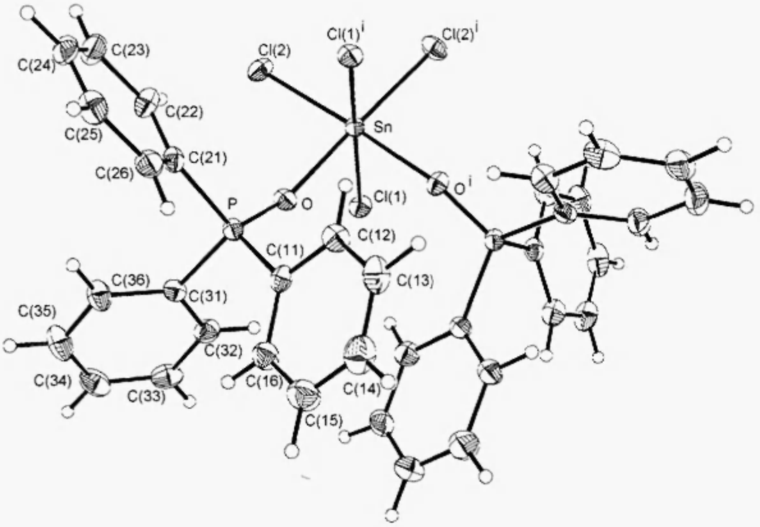

Figure 1. ORTEP drawing of $[SnCl_4(OPPh_3)_2]$ (1) showing the atom numbering scheme. Atoms related by the $C_2$ axis of symmetry are denoted by i. Selected bond lengths (Å) and angles (°): Sn–O 2.086(2), Sn–Cl(1) 2.385(1), Sn-Cl(2) 2.395(1), P–O 1.505(2), O–Sn–O$^i$ 87.02(13), O–Sn–Cl(1)$^i$ 87.43(6), O–Sn–Cl(1) 85.70(7), Cl(1)–Sn–Cl(1) 170.53(4),O–Sn–Cl(2)$^i$ 177.38(7), O$^i$–Sn–Cl(2)$^i$ 90.65(7)Cl(1)$^i$–Sn–Cl(2) 95.40(3), Cl(1)–Sn–Cl(2) 91.20(3), Cl(2)$^i$–Sn–Cl(2) 91.70(5). Symmetry transformations used to generate equivalent atoms: (i) -x, y,-z + 1/2.

The geometry of the $OPPh_3$ shows no unusual features. The phosphorus atoms show tetrahedral coordination. The tetrahedral angles vary from 106.36(16)° to 114.20(14°. The P–O bond, 1.46(1) Å in free $OPPh_3$ [16], is lengthened after coordination to the tin atom to 1.505(2) Å. The Sn–O–P angle of 155.35(14)°, indicating the bent coordination of $OPPh_3$, is much smaller than in the analogous uranium compound (165.1(5)°[12]).

Exactly the same arrangement and symmetry about the metal atom as in **1** has only been observed in the analogous $[UCl_4(OPPh_3)_2]$ [12] and $[WCl_4(OPPh_3)_2]$ [13].

The coordination of the phosphine oxide to Sn is reflected by a shift in the position of the $\nu$(P=O) stretching frequency. Thus the $\nu$(P=O) band in $OPPh_3$ is observed at 1192 $cm^{-1}$, whilst in **1** it is at 1123 $cm^{-1}$. The higher $\Delta\nu$ shift observed for **1** than for $[SnR_2X_2(OPPh_3)_2]$, R = Ph, Me, Bu; X = Cl, Br, NCS [9], suggests greater Lewis acidity for $SnCl_4$ than for the organotin compounds. However, a $\Delta\nu$ shift of 69 $cm^{-1}$ is much smaller than that observed for $[UCl_4(OPPh_3)_2]$ ($\Delta\nu$ = 124 $cm^{-1}$ [12]). The position of the signal in the $^{31}P\{^1H\}$-NMR spectrum of **1** is solvent-dependent ($\delta_P$ = 33.68 in $CH_3OH$-$d_4$ and $\delta_P$ = 27.85 in DMSO-$d_6$).

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