Characterization and X-Ray Structure of the Adduct Formed Between Triphenyltin Chloride and Dicyclohexylphosphinyl-N-methyl(thioformamide): Ph₃Sn[Cy₂P(O)C(S)N(H)Me]Cl

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Abstract

The reaction of Ph₃SnCl and Cy₂P(O)C(S)N(H)Me yields the air-stable adduct Ph₃Sn[Cy₂P(O)-C(S)N(H)Me]Cl which features a trigonal bipyramidal tin atom geometry with a chlorine atom [Sn-Cl 2.4236(9) Å] and an oxygen atom [Sn-O 2.523(2) Å], derived from a monodentate phosphinyl(thioformamide) ligand, occupying the axial positions. The pale-yellow crystals are monoclinic, space group $P2_1/c$ with unit cell dimensions a 10.050(1), b 16.501(1), c 19.273(1) Å, β $102.12(1)^\circ$, Z 4; the structure was refined to final R 0.031 by using 5384 reflections.

Introduction

There are a number of coordination possibilities associated with the phosphorus(V) ligands of the general formula $R_2P(O)C(S)N(H)R'$ (R, R' = alkyl or aryl) (1). Crystallographic evidence shows that monodentate coordination, through the sulfur atom exclusively, is found in the recently characterized Au[Cy₂P(O)C(S)N(H)Me]Cl adduct.¹ When the related [Ph₂P(O)C(S)N(H)Ph] ligand is deprotonated, bidentate coordination, through the oxygen and sulfur atoms, is found in the [Mo(CO)₂(PPh₃)(Ph₂P(O)C(S)NPh)₂] complex.² The interaction of such ligands towards tin and indeed other main group elements has not been reported. However, there are reports of the interaction between the phosphorus(III) precursors of (1), i.e. $R_2PC(S)N(H)R'$ (2), and tin.^{3,4} The crystal structures of Ph₃Sn[R₂PC(S)NPh], R = Ph³ and R = Cy,⁴ show that coordination occurs through the sulfur atom leading to a tetrahedral tin centre in both cases;



¹Siasios, G., and.Tiekink, E. R. T., Aust. J. Chem., 1995, 48, 757.

- ² Ambrosius, H. P. M. M., Bosman, W. P., and Cras, J. A., J. Organomet. Chem., 1981, 215, 201.
- ³ Dakternieks, D., Hoskins, B. F., and Rolls, C. L., Aust. J. Chem., 1988, 41, 195.
- ⁴ Dakternieks, D., Hoskins, B. F., and Rolls, C. L., Aust. J. Chem., 1986, 39, 1221.

Manuscript received 7 April 1995

0004-9425/95/091659\$05.00

 $Sn \cdots N$ separations of $2 \cdot 728(3)$ and $2 \cdot 788(3)$ Å, respectively, were not regarded as significant interactions. Interestingly, the behaviour of these compounds in solution was different in that for $Ph_3Sn[Cy_2PC(S)NPh]$ two isomers were detected in solution whereas only one isomer was found for the other derivative.⁴ As a continuation of an investigation of the structural characteristics of ligands (1) and (2) and their complexes, the interaction of (1) with Ph_3SnCl has been studied.

Experimental

I.r. spectra were measured in KBr disks on a Perkin Elmer 1720X Fourier-transform spectrometer. ¹H and ¹³C n.m.r. spectra were recorded in CDCl₃ solutions on an ACP300 n.m.r. spectrometer, and ³¹P n.m.r. spectra were measured on a Bruker CXP300 n.m.r. spectrometer at 121.5 MHz with internal 85% H₃PO₄ in D₂O as the reference. F.a.b. mass spectra were obtained on a VG ZAB 2HF instrument equipped with an f.a.b. source. Argon was used as the exciting gas with the source pressure typically 10^{-6} mbar; the f.a.b. voltage was 7 kV and the current 1 mA. The ion accelerating potential was 8 kV and the matrix employed was 3-nitrobenzyl alcohol. The complex was made up as a c. 0.5 mol dm⁻³ solution in dichloromethane; a drop was added to a drop of the matrix and the mixture was applied to the f.a.b. probe tip.

Synthesis

T le R₂P(O)C(S)N(H)R', R = Cy or Ph and R' = Me or Ph, ligands were prepared by the literature method.⁵ The only new compound isolated was one that contained the R = Cy and R' = Me ligand. A benzene solution (20 cm^3) of Cy₂P(O)C(S)N(H)Me (200 mg, 0.696 mmol) was added to a benzene solution (20 cm^3) of a 1.08 mol. equiv. of Ph₃SnCl (253 mg) with stirring for 3.5 h. The solvent was allowed to evaporate, the residue taken up in dichloromethane, the solution centrifuged and the supernatant solution allowed to evaporate. Recrystallization from hot ethanol solution yielded pale-yellow crystals suitable for the X-ray study; yield 30%, m.p. 131–132°C (dec.). ¹H n.m.r. (300.13 MHz, SiMe₄ internal reference): δ 9.33, br, NH; 7.65–7.59, ortho Ph; 7.51–7.45, meta, para Ph; 3.23, dd, ⁴J(P,H) 1.47, ³J(H,H) 5.05 Hz, Me; 2.17–2.29, br, CH; 1.21–1.99, m, CH₂. ¹³C n.m.r. (75.47 MHz, SiMe₄): δ 198.5, d, Cq, ¹J(P,C) 74.5 Hz; 137.5, C1 Ph; 136.1, d, C3 Ph, ³J(Sn,C) 49.1 Hz; 130.4, d, C4 Ph, ⁴J(Sn,C) 13.8 Hz; 129.1, d, C2 Ph, ²J(Sn,H) 63.6 Hz; 34.9, d, CH, ¹J(P,C) 64.3 Hz; 34.8, s, Me; 26.3–24.8, m, CH₂.

X-Ray Crystallography

Intensity data for a crystal 0.32 by 0.40 by 0.48 mm were measured on a Rigaku AFC6R diffractometer fitted with graphite-monochromatized Mo K α radiation, $\lambda 0.71073$ Å; the $\omega : 2\theta$ scan technique was employed to measure data up to a maximum Bragg angle of $27 \cdot 5^{\circ}$. The data set was corrected for Lorentz and polarization effects⁶ and an empirical absorption correction was applied so that the range of transmission factors was 0.901-1.045.⁷ Of the 8126 reflections measured, 7706 were unique and of these 5384 satisfied the $I \geq 3.0\sigma(I)$ criterion of observability and were used in the subsequent analysis.

Crystal data.—C₃₂H₄₁ClNOPSSn, M 672·9, monoclinic, space group $P_{2_1/c}$, a 10·050(1), b 16·501(1), c 19·273(1) Å, β 102·12(1)°, V 3125·0(4) Å³, Z 4, D_c 1·430 g cm⁻³, F(000) 1384, μ 10·66 cm⁻¹.

The structure was solved by direct methods,⁸ and refined by a full-matrix least-squares procedure based on F.⁶ Non-hydrogen atoms were refined with anisotropic thermal parameters

⁵ Ojima, I., Akiba, K., and Inamoto, N., Bull. Chem. Soc. Jpn, 1969, 42, 2975.

⁶ teXsan, Structure Analysis Package, Molecular Structure Corporation, Texas, U.S.A., 1992.
⁷ Walker, N., and Stuart, D., Acta Crystallogr., Sect. A, 1983, 39, 158.

⁸ Sheldrick, G. M., shelx76, Program for the Automatic Solution of Crystal Structure, Göttingen, Germany, 1986.

Atom	x	y	z	Atom	x	у	z	
Sn	0.04442(2)	0.24620(1)	0.27298(1)	C(36)	0.5311(3)	0.2027(2)	0.4612(2)	
Cl	-0.1866(8)	0.2841(6)	0.2180(5)	C(41)	0.0895(3)	0.3450(2)	0.3441(1)	
S(1)	0.5290(8)	-0.0119(5)	0.3945(6)	C(42)	0.2125(3)	0.3520(2)	0.3896(2)	
P(1)	0.4061(7)	0.1434(4)	0.3314(4)	C(43)	0.2406(4)	0.4155(2)	0.4365(2)	
O(2)	0.2759(2)	0.1885(1)	0.3261(1)	C(44)	0.1447(4)	0.4725(2)	0.4381(2)	
N(1)	0.2759(2)	0.0299(2)	0.3860(1)	C(45)	0.0217(4)	0.4672(2)	0.3932(2)	
C(1)	0·3959(3)	0.0465(2)	0.3746(1)	C(46)	-0.0060(3)	0.4041(2)	0.3463(2)	
C(2)	0·2436(3)	-0.0449(2)	0.4175(2)	C(51)	-0.0155(3)	0.1399(2)	0.3173(2)	
C(21)	0.4394(3)	0.1223(2)	0.2458(1)	C(52)	-0.0298(3)	0.1409(2)	0.3862(2)	
C(22)	0·3358(3)	0.0632(2)	0.2053(2)	C(53)	-0.0762(4)	0.0737(3)	0.4164(2)	
C(23)	0.3510(4)	0.0546(2)	0.1297(2)	C(54)	-0.1085(3)	0.0061(2)	0.3783(3)	
C(24)	0.4931(4)	0.0298(2)	0.1253(2)	C(55)	-0.0933(4)	0.0033(2)	0.3105(3)	
C(25)	0·5955(4)	0.0879(2)	0.1656(2)	C(56)	-0.0480(3)	0.0697(2)	0.2802(2)	
C(26)	0 · 5833(3)	0.0957(2)	0.2421(2)	C(61)	0.1165(3)	0.2515(2)	0.1782(2)	
C(31)	0·5486(3)	0.1933(2)	0.3850(2)	C(62)	0.0427(4)	0.2182(2)	0.1165(2)	
C(32)	0·5745(3)	0.2747(2)	0.3542(2)	C(63)	0.0870(4)	0.2242(3)	0.0541(2)	
C(33)	0.6936(3)	0.3167(2)	0.4007(3)	C(64)	0.2020(5)	0.2648(3)	0.0526(2)	
C(34)	0.6774(4)	0.3248(2)	0.4754(3)	C(65)	0.2771(4)	0.2986(2)	0.1117(2)	
C(35)	0.6536(4)	0.2441(2)	0.5059(2)	C(66)	0.2344(3)	0.2915(2)	0.1753(2)	

Table 1. Fractional atomic coordinates for $Ph_3Sn[Cy_2P(O)C(S)N(H)Me]Cl$



Fig. 1. Molecular structure of $Ph_3Sn[Cy_2P(O)C(S)N(H)Me]Cl$ showing the crystallographic numbering scheme.

and the hydrogen atoms were included in the model in their calculated positions (C–H, N–H 0.97 Å). The refinement was continued until convergence employing σ weights; the analysis of variance showed no special features indicating that an appropriate weighting scheme had been applied. Final values for R and R_w were 0.031 and 0.034, respectively; the fractional atomic coordinates are listed in Table 1 and the numbering scheme employed is shown in Fig. 1 (drawn with ORTEP⁹ at 15% probability ellipsoids). The teXsan package,⁶ installed on an Iris Indigo workstation, was employed for all calculations. Complete lists of bond distances and angles, thermal parameters, hydrogen atom parameters and structure factor tables have been deposited with the Australian Journal of Chemistry, P.O. Box 89, East Melbourne, Vic. 3002.

Results and Discussion

The mixing of Ph_3SnCl with an equimolar amount of $Cy_2P(O)C(S)N(H)Me$ in benzene solution yields the adduct $Ph_3Sn[Cv_2P(O)C(S)N(H)Me]Cl$; the same product was isolated when the reaction was attempted in the presence of Et_3N . When analogous reactions were attempted for the R = Cy, R' = Ph and R = Ph, R' = Meor Ph ligands, in both the absence and presence of Et_3N , the starting materials were recovered. A spectroscopic analysis of Ph₃Sn[Cy₂P(O)C(S)N(H)Me]Cl confirmed the stoichiometry of the compound. In the i.r. spectrum, recorded as a KBr disk, absorptions due to ν (N–H) were found at 3056 and 3018 cm⁻¹, those due to μ (NCS) at 1520 and 1362 cm⁻¹, and $\nu(P=O)$ at 1180 cm⁻¹. Except for the second $\nu(NCS)$ absorption, which had shifted to higher frequency (by 24 cm^{-1}), all the other absorptions were in positions similar to those observed for the uncoordinated ligand. In the f.a.b. mass spectrum the molecular ion was not observed; however, the most abundant ion corresponded to $[M-Cl]^+$ (m/z 638). Other tin-containing peaks in the low molecular weight region were assigned to $[M-Ph]^+$ (m/z)595, relative abundance 13%) and $[M - Cl, Ph]^+$ (560, 22%). Peaks due to $[(Cy_2P(O)C(S)N(H)Me)_2]^+ (576, 38), [(Cy_2P(O)C(S)N(H)Me)_2 - C(S)N(H)Me]^+ (576, 38), [(Cy_2P(O)C(S)N(H)Me)_2 - C(S)N(H)Me)_2 - C(S)N(H)Me]^+ (576, 38), [(Cy_2P(O)C(S)N(H)Me)_2 - C(S)N(H)Me)_2 - C(S)N(H)Me]^+ (576, 38), [(Cy_2P(O)C(S)N(H)Me)_2 - C(S)N(H)Me)_2 - C(S)N(H)M$ (501, 38) and $[{(Cy_2P(O)C(S)N(H)Me)_2 - 2C(S)N(H)Me}] = [{Cy_2P(O)}_2H]^+$ (429, 63) were also detected. The only peak in the high molecular weight region was assigned tentatively as $[Ph_7Sn_3O_2H]$ (929, 28). In CDCl₃ solution, the integration of the 1 H n.m.r. spectrum (see Experimental) was consistent with the formulation of the compound, and the resonances due to the ligand were observed in positions similar to those of the uncoordinated ligand. Similarly, the ${}^{13}C$ n.m.r. data resembled closely those observed for the free ligand. Notable was the observation that the quaternary carbon atom appeared as a doublet centred about 198.5 ppm with ${}^{1}J(P,C)$ 74.5 Hz compared with 197.9 ppm and 70.0 Hz in the free ligand. The $^{31}\mathrm{P}$ n.m.r. data, measured on the dissolved crystals, were also similar to those of the parent ligand, i.e. $48 \cdot 4$ ppm in the adduct, cf. $47 \cdot 9$ ppm; at reduced temperatures (i.e. down to 215 K) there was a small downfield shift to 49.5 ppm. In summary, the spectroscopic evidence confirmed the presence of both the Ph_3SnCl and $Cy_2P(O)C(S)N(H)Me$ entities consistent with the formation of an adduct. A crystallographic investigation substantiates this.

The molecular structure of $Ph_3Sn[Cy_2P(O)C(S)N(H)Me]Cl$ is shown in Fig. 1 and selected interatomic parameters are listed in Table 2. The structure is molecular, there being no significant intermolecular interactions <3.6 Å involving the non-hydrogen atoms in the lattice. The tin atom is five-coordinate and exists

⁹ Johnson, C. K., ORTEP-II, Report ORNL-5138, Oak Ridge National Laboratory, Tennessee, U.S.A., 1976.

in a distorted trigonal bipyramidal geometry. The trigonal plane is defined by the carbon atoms of three phenyl substituents (the sum of the C–Sn–C angles is $357 \cdot 3^{\circ}$), and the axial positions are occupied by the chlorine atom and an oxygen atom derived from the phosphinyl(thioformamide) ligand; the Cl–Sn–O(2) angle is $172 \cdot 73(5)^{\circ}$. In this description, the tin atom lies 0.1981(4) Å out of the trigonal plane in the direction of the chlorine atom. The dihedral angles between each pair of the three phenyl groups containing the C(41), C(51) and C(61) atoms are as follows: C(41-46)/C(51-56), $85 \cdot 5^{\circ}$; C(41-46)/C(61-66), $110 \cdot 4^{\circ}$; C(51-56)/C(61-66), $39 \cdot 7^{\circ}$.

Atoms	Parameter	Atoms	Parameter
Sn-Cl	$2 \cdot 4236(9)$	Sn-O(2)	$2 \cdot 523(2)$
Sn-C(41)	$2 \cdot 117(3)$	Sn-C(51)	2.094(3)
Sn-C(61)	$2 \cdot 103(3)$	S(1) - C(1)	$1 \cdot 628(3)$
P(1) - O(2)	$1 \cdot 490(2)$	P(1) - C(1)	$1 \cdot 816(3)$
P(1) - C(21)	1.785(3)	P(1) - C(31)	1.783(3)
N(1) - C(1)	$1 \cdot 299(3)$	N(1)-C(2)	$1 \cdot 443(4)$
Cl-Sn-O(2)	$172 \cdot 73(5)$	Cl-Sn-C(41)	96 .06(8)
Cl-Sn-C(51)	$93 \cdot 63(7)$	Cl-Sn-C(61)	94.72(8)
O(2)-Sn-C(41)	$88 \cdot 49(9)$	O(2) - Sn - C(51)	80.69(8)
O(2) - Sn - C(61)	$84 \cdot 94(9)$	C(41) - Sn - C(51)	$114 \cdot 9(1)$
C(41)-Sn-C(61)	$117 \cdot 7(1)$	C(51) - Sn - C(61)	$124 \cdot 7(1)$
O(2) - P(1) - C(1)	$109 \cdot 8(1)$	O(2) - P(1) - C(21)	$111 \cdot 5(1)$
O(2)-P(1)-C(31)	$113 \cdot 3(1)$	C(1) - P(1) - C(21)	$106 \cdot 9(1)$
C(1)-P(1)-C(31)	$104 \cdot 9(1)$	C(21)-P(1)-C(31)	110.0(1)
Sn-O(2)-P(1)	159.7(1)	C(1) - N(1) - C(2)	$123 \cdot 4(3)$
S(1) - C(1) - P(1)	$120 \cdot 4(2)$	S(1) - C(1) - N(1)	$125 \cdot 6(2)$
P(1)-C(1)-N(1)	$114 \cdot 0(2)$		

Table 2. Selected bond distances (Å) and angles (degrees) for $Ph_{3}Sn[Cy_{2}P(O)C(S)N(H)Me]Cl$

The phosphinyl(thioformamide) ligand, which adopts a Z conformation about the C(1)-N(1) bond, coordinates exclusively in the monodentate mode as there is no evidence of other interactions, either intra- or inter-molecular, involving the sulfur atom. The C(1)=S(1) separation of 1.628(3) Å substantiates this observation as the equivalent separation in the crystal structure of Cy₂P(O)C(S)N(H)Me is 1.630(3) Å.¹⁰ Of interest are the parameters associated with the Sn–O and P=O bonds. The P=O separations are equal within experimental error in the present structure [1.490(2) Å] and in the structure of Cy₂P(O)C(S)N(H)Me, i.e. 1.480(2) Å, and are indicative of P=O double bonds. It has been noted previously in the literature that the P=O separations in triorganophosphine oxide adducts of tin-containing compounds do not vary significantly and are independent of the magnitude of the Sn–O separation.¹¹ However, despite this conclusion, it is noteworthy that all of the comparable bond distances and angles describing both the coordinated and uncoordinated Cy₂P(O)C(S)N(H)Me ligands are equal within experimental error. This observation, coupled with the minimal changes in the

¹⁰ Siasios, G., and Tiekink, E. R. T., Z. Kristallogr., in press.

¹¹ Gielen, M., Pan, H., and Tiekink, E. R. T., Bull. Soc. Chim. Belg., 1993, 102, 447.

spectroscopic characteristics of the free and coordinated $Cy_2P(O)C(S)N(H)Me$ ligands, points to the formation of a weak adduct only between Ph_3SnCl and the $Cy_2P(O)C(S)N(H)Me$ ligand.

Acknowledgments

The grant from a Commonwealth Postgraduate Award to V.J.H., and the support of the crystallographic facility by the Australian Research Council are gratefully acknowledged.