Synthesis, Characterization, Crystal Structures, and Reactions of Trigonal Bipyramidal Tin(IV) Complexes Containing a Tetradentate Tripodal Tristhiolatophosphine Ligand. Use in the One-Step Synthesis of an Iron(IV) Complex

Kerry A. (Fusie) Clark,† T. Adrian George,*,† Tom J. Brett,† Charles R. Ross, II,‡ and Richard K. Shoemaker†

Department of Chemistry, University of Nebraska−Lincoln, Lincoln, Nebraska 68588-0304, and Department of Structural Biology, St. Jude Children's Research Hospital, Memphis, Tennessee 38105-2794

Received November 29, 1999

Trigonal bipyradimal complexes of tin(IV) such as BuSn-[$P(C_6H_4$-2-$O)_3$] and ZSn[$N(CH_2CH_2X)_3$] (Chart 1)[1,2] are well-known where four of the five coordination sites are occupied by the four donor atoms of a tetradentate tripodal ligand. Most of the ligands in this category are trianions produced by the deprotonation of proligands such as alcohols, thiols, or amines. Although tin(IV) complexes are known with ligands containing a combination of three sulfurs and one nitrogen atom,[2,3] and three oxygens and one phosphorus atom,[2] no examples have been reported with the soft-base combination of three sulfurs and one phosphorus atom. Trigonal bipyramidal complexes containing the ligand $[P(C_6H_3\text{-3-R}-S)_3]^{3-}$ (R = H or Ph) have been reported for Tc,[4] Fe,[5,6] Ni,[7] and Re.[8] Here, we report the synthesis and crystal structure of three trigonal bipyramidal complexes of tin-(IV): PhSn(PS_3) (**1**), PhSn($P'S_3$) (**2**), and PhSn($P''S_3$) (**3**), where $(PS_3)^{3-} = [P(C_6H_4\text{-2-S})_3]^{3-}$, $(P'S_3)^{3-} = [P(C_6H_3\text{-5-Me-2-S})_3]^{3-}$, and $(P''S_3)^{3-} = [P(C_6H_3\text{-3-Me}_3\text{Si-2-S})_3]^{3-}$. Complex **3** undergoes a metathesis reaction with $FeCl_3$ to form the purple iron(IV) complex [FeCl($P''S_3$)][9] in one step.

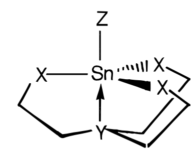
The reaction of $PhSnCl_3$ in tetrahydrofuran (thf) at 0 °C with the trilithium salt of the ligand, generated in situ from the thiol and *n*-BuLi (3 equiv), produced the corresponding PhSn(IV) complex:[10−12]

$$PhSnCl_3 + PS_3Li_3 \rightarrow PhSn(PS_3) + 3LiCl \qquad (1)$$

The ligands PS_3H_3 and $P''S_3H_3$ were prepared by the method of Block et al.,[13] and $P'S_3H_3$ was prepared by an adaption of this method starting with *p*-MeC_6H_4SH. The three complexes showed very different solubility properties. The trimethylsilyl-substituted product was soluble in almost all common organic solvents, whereas the unsubstituted product showed limited solubility except in thf.

Each complex displays a singlet in the ^{31}P NMR spectrum. The resonance occurs at ca. −63 ppm, with tin satellites ($J_{P-Sn} \approx 1100$ Hz) and carbon satellites ($J_{P-C} \approx 73$ Hz) for PhSn(PS_3) and PhSn($P''S_3$). The resonance for PhSn($P'S_3$) occurs at −58 ppm. The resonances in the room temperature ^{1}H and ^{13}C NMR spectra of PhSn(PS_3) and PhSn($P''S_3$) are unambiguously assigned using heteronuclear multiple-quantum coherence and heteronuclear multiple-bond correlation. Low-temperature (178 K) ^{1}H NMR spectra show no broadening of any signals.

Chart 1



X = O; Y = N; Z = Alkyl, Aryl

X = S, Y = N; Z = Me or *t*-Bu

Crystals of PhSn(PS_3),[14] PhSn($P'S_3$),[15] and PhSn($P''S_3$)[16] were obtained from cooled (0 °C) thf/hexane solutions and structures

* To whom correspondence should be addressed. E-mail: tageorge@unlserve.unl.edu.

† University of Nebraska−Lincoln.

‡ St. Jude Children's Research Hospital.

(1) Verkade, J. G. *Coord. Chem. Rev.* **1994**, *137*, 233.

(2) Tzschach, A.; Jurkschat, K. *Comments Inorg. Chem.* **1983**, *3*, 35.

(3) Jurkschat, K.; Mügge, C.; Tzschach, A.; Zschunke, A.; Fischer, G. W. *Z. Anorg. Allg. Chem.* **1980**, *463*, 123.

(4) (a) de Vries, N.; Davison, A.; Jones, A. G. *Inorg. Chim. Acta* **1989**, *165*, 9. (b) de Vries, N.; Cook, J.; Jones, A. G.; Davison, A. *Inorg. Chem.* **1991**, *30*, 2662.

(5) Franolic, J. D.; Millar, M.; Koch, S. A. *Inorg. Chem.* **1995**, *34*, 1981.

(6) Hsu, H.-F.; Koch, S. A.; Popescu, C. V.; Münck, E. *J. Am. Chem. Soc.* **1997**, *119*, 8371.

(7) Nguyen, D. H.; Hsu, H.-F.; Millar, M.; Koch, S. A.; Achim, C.; Bominaar, E. L.; Münck, E. *J. Am. Chem. Soc.* **1996**, *118*, 8963.

(8) For [Re(PS_3)(PPh_3)], see ref 8 in the following. Dilworth, J. R.; Hutson, A. J.; Lewis, J. S.; Miller, J. R.; Zheng, Y.; Chen, Q.; Zubieta, J. *J. Chem. Soc., Dalton Trans.* **1996**, 1093.

(9) Niemoth-Anderson, J. D.; Clark, K. A. (Fusie); George, T. A.; Ross, C. R., II. *J. Am. Chem. Soc.*, in press.

(10) PhSn(PS_3) (**1**): *n*-BuLi (0.48 mL, 1.2 mmol) was added to a solution containing PS_3H_3 (0.16 g, 0.46 mmol) in thf (40 mL) at 0 °C. After the solution was stirred for 35 min, a solution of $PhSnCl_3$ (0.14 g, 0.45 mmol) in thf (10 mL) was added. The solution was stirred for 1 h at 0 °C before solvent was removed in vacuo. CH_2Cl_2 (40 mL) was added, and the resulting suspension was extracted with water (3 × 40 mL). The yellow CH_2Cl_2 layer was separated and dried over $MgSO_4$. The solution was removed from $MgSO_4$ via syringe, and then CH_2Cl_2 was removed in vacuo. Pentane (15 mL) was added and the mixture placed in the freezer (−18 °C, 5.5 h). The cream-colored solid was collected by filtration, washed with chilled benzene, and dried in vacuo to yield 0.15 g (60%) of product. Crystals suitable for X-ray diffraction studies were grown from a cooled (12 °C) thf/hexane solution (3:1 by volume) over 2 days. ^{1}H NMR (δ, thf/DMSO-d_6): 8.11 (t, 3H, J = 7.75 Hz, 6-*H*, C_6H_4), 7.66 (app d, 2H, J = 7.15 Hz, *2*, *6*-H, C_6H_5), 7.53 (t, 3H, J = 7.75 Hz, 4-*H*, C_6H_4), 7.46−7.39 (m, 3H, 3, 4, 5-*H*, C_6H_5), 7.32 (app t, 3H, J = 7.87 Hz, 3-*H*, C_6H_4), 7.13 (t, 3H, J = 7.51 Hz, 5-*H*, C_6H_4). ^{31}P{^{1}H} NMR (δ, thf-d_8): −63.30 (s, J(P−^{119}Sn) = 1105 Hz, J(P−^{117}Sn) = 1056 Hz, J(PC) = 75.80 Hz). High-resolution EIMS (*m/z*): found 551.9 (M^+). From calcd MS: $C_{24}H_{17}PS_3{}^{120}Sn$, 551.9247.

(11) PhSn($P''S_3$) (**3**): Anal. Calcd for $C_{33}H_{41}PS_3Si_3Sn\cdot 2H_2O\cdot 0.33CH_2Cl_2$: C, 48.10; H, 5.53. Found: C, 48.07; H, 5.51. ^{1}H NMR (δ, CD_2Cl_2): 7.78 (td, 3H, J = 7.75 Hz, J = 1.51 Hz, 6-*H*, C_6H_3), 7.71 (dt, 2H, J = 7.39 Hz, J = 1.25 Hz, 2, 6-*H*, C_6H_5), 7.60 (dt, 3H, J = 7.16 Hz, J = 1.25 Hz, 4-*H*, C_6H_3), 7.53−7.47 (m, 3H, 3,4,5-*H*, C_6H_5), 7.19 (td, 3H, J = 7.39 Hz, J = 1.35 Hz, 5-*H*, C_6H_3), 1.55 (br, H_2O), 0.423 (s, 27H, Me$_3$-Si). ^{1}H NMR (δ, thf-d_8): 8.02 (t, 3H, J = 7.37 Hz, 6-*H*, C_6H_3), 7.70 (d, 2H, J = 6.94 Hz, 2, 6-*H*, C_6H_5), 7.56 (d, 3H, J = 7.01 Hz, 4-*H*, C_6H_3), 7.50 (t, 2H, J = 7.08 Hz, 3, 5-*H*, C_6H_5), 7.45 (d, 1H, J = 7.29 Hz, 4-*H*, C_6H_5), 7.18 (t, 3H, J = 7.17 Hz, 5-*H*, C_6H_3), 5.03 (s, CH_2Cl_2), 2.92 (br, H_2O), 0.399 (s, 27H, Me_3Si). ^{31}P{^{1}H} NMR (δ, CD_2Cl_2): −63.85 (s, J(P−^{119}Sn) = 1161 Hz, J(P−^{117}Sn) = 1109 Hz, J(PC) = 69.46 Hz). Low-resolution FABMS (*m/z*): found 769.4 (M + H)$^+$. From calcd MS: $C_{33}H_{41}PS_3{}^{120}Sn$, 768.044.

(12) PhSn($P'S_3$) (**2**): ^{31}P{^{1}H} NMR (δ, CD_2Cl_2): −57.99 (s, J(P−^{119}Sn) = 1127 Hz, J(P−^{117}Sn) = 1080 Hz).

(13) Block, E.; Ofori-Okai, G.; Zubieta, J. *J. Am. Chem. Soc.* **1989**, *111*, 2327.

(14) Crystal data for PhSn(PS_3) (**1**) ($C_{24}H_{17}PS_3Sn$) (293 K): monoclinic, *P*2-(1)/*c*, a = 10.041(2) Å, b = 12.990(3) Å, c = 17.548(4) Å, $\alpha = \gamma$ = 90°, β = 96.94(3)°, V = 2272.1(8) Å^3, z = 4. Final least-squares refinement on F^2 using 4296 unique reflections and 262 parameters yielded R_1 = 0.0386 (wR2 = 0.0949) and GOF = 1.016.

(15) Crystal data for PhSn($P'S_3$) (**2**) ($C_{27}H_{23}PS_3Sn$) (293 K): monoclinic, *P*2-(1)/*c*, a = 10.641(2) Å, b = 15.354(3) Å, c = 15.384(3) Å, $\alpha = \gamma$ = 90°, β = 91.85(3)°, V = 2512.2(9) Å^3, z = 4. Final least-squares refinement on F^2 using 4757 unique reflections and 290 parameters yielded R_1 = 0.0410 (wR2 = 0.1114) and GOF = 1.071.

10.1021/ic991371n CCC: $19.00
Published on Web 05/11/2000

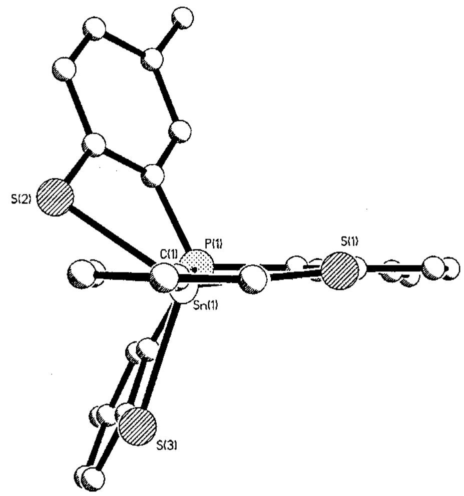


Figure 1. Structure of PhSn(P′S$_3$) (**2**) with hydrogen atoms omitted and the following selected bond distances (Å) and angles (deg): Sn−C(1) = 2.1412(38); Sn−P = 2.5125(9); Sn−S(1) = 2.5120(12); Sn−S(2) = 2.5723(12); Sn−S(3) = 2.4448(12); C(1)−Sn−P = 169.32(10); C(1)−Sn−S(1) = 94.70(11); C(1)−Sn−S(2) = 98.27(11); C(1)−Sn−S(3) = 105.61(11); S(1)−Sn−S(2) = 137.96(4); S(1)−Sn−S(3) = 111.85(4); S(2)−Sn−S(3) = 102.80(4).

determined by X-ray diffraction. In all three complexes, tin is above the S$_3$ plane. Whereas [FeCl(P″S$_3$)] displays C_{3v} symmetry, in both **1** and **3** the plane of the three sulfur atoms has been rotated by more than 13° about the pseudo-3-fold axis of Sn(PS$_3$), possibly to avoid a close *o*-phenyl(Sn)−hydrogen to sulfur interaction. This form of distortion contrasts with those reported in the anions [Ni(P(C$_6$H$_3$-3-Ph-2-S)$_3$)(CO)]$^{-}$ [7] and [Fe$_2$(μ-S$_2$)-(P(C$_6$H$_4$-2-S)$_3$)$_2$]$^{2-}$,[5] where two of the S−M−S angles are significantly greater than 120° and the third angle is significantly less than 120°.

The structure of PhSn(P′S$_3$) (Figure 1) shows the plane of the phenyl(Sn) group to be almost coplanar with the plane containing SnPS(1) and the corresponding *m*-tolyl group. This orientation may be the result of hydrogen-bonding between S(1) and the hydrogen atom on C(2) of the phenyl group: S(1)−H(2) = 2.6792(11) Å. Perhaps as a result of this orientation, the P−Sn−C(1) vector is not linear (169°).

Both methyl[17] and *n*-butyl[18] derivatives were prepared by the reactions of PS$_3$Li$_3$ with MeSnCl$_3$ and *n*-BuSnCl$_3$, respectively, as described above. Although both complexes were isolated and characterized, crystals suitable for X-ray diffraction studies have not been obtained. Pale-yellow crystals were obtained during attempts to crystallize *n*-BuSn(PS$_3$) from a pyridine/acetone solution. The crystal structure showed the compound to be oxidized, dimerized ligand (OPS$_3$)$_2$ (**4**).[19] The (OPS$_3$)$_2$ molecule contains two ligands that are coupled through a S−S bond. Within each original ligand the remaining two sulfurs form a S−S bond and each phosphorus has been oxidized to a phosphine oxide.

The stability of the crystallographically characterized iron(IV) complexes [FeX(P″S$_3$)] where X = Cl, Br, or I[9] in nonpolar solvents prompted us to attempt the preparation of these complexes by transmetalation[20] using PhSn(P″S$_3$). Thus, solid FeCl$_3$ (2 equiv) was added slowly to a yellow solution of PhSn(P″S$_3$) in CH$_2$Cl$_2$. The solution turned purple as soon as solid FeCl$_3$ encountered the stirred solution of PhSn(P″S$_3$). After the addition was complete, water was added to remove salts. After the water layer was removed, the CH$_2$Cl$_2$ layer was dried over MgSO$_4$, and then solvent was removed in vacuo. The purple solid was purified by crystallization from a benzene/pentane solution (1:3, v:v) at −18 °C. The yield was 46%. The ^{1}H and ^{31}P spectra of the purple product were identical to those of an authentic sample of [FeCl(P″S$_3$)]. In this reaction FeCl$_3$ is the source of {FeCl} and the oxidizing agent that converts putative [Fe(P″S$_3$)] to [FeCl-(P″S$_3$)]:

$$\mathrm{PhSn(P''S_3) + FeCl_3 \rightarrow [Fe(P''S_3)] + PhSnCl_3} \qquad (2)$$

$$\mathrm{[Fe(P''S_3)] + FeCl_3 \rightarrow [FeCl(P''S_3)] + FeCl_2} \qquad (3)$$

The yield of [FeCl(P″S$_3$)] is a function of the ratio of reactants and the reaction time. Thus, the reaction of FeCl$_3$ (1.6 equiv) and PhSn(P″S$_3$) (1 equiv) for 1.5 h in CH$_2$Cl$_2$ resulted in equal amounts of [FeCl(P″S$_3$)] and unreacted PhSn(P″S$_3$) being detected. With 3 equiv of FeCl$_3$ for 1.5 h, the yield of [FeCl(P″S$_3$)] was about the same but there was no unreacted PhSn(P″S$_3$). Instead, a number of non-tin-containing phosphine compounds were formed including the oxidized, dimerized ligand (OP″S$_3$)$_2$. When this latter reaction was stirred for 3 h, the yield of [FeCl-(P″S$_3$)] was reduced considerably. With 5.8 equiv of FeCl$_3$ for 1.5 h, the yield of [FeCl(P″S$_3$)] was zero. These results are not surprising because FeCl$_3$ was shown to slowly decompose [FeCl-(P″S$_3$)] in CH$_2$Cl$_2$. For example, when FeCl$_3$ (0.8 equiv) was stirred with [FeCl(P″S$_3$)] (1 equiv) in CH$_2$Cl$_2$, a small amount of unreacted FeCl(P″S$_3$)] together with (OP″S$_3$)$_2$ was observed in the ^{31}P NMR spectrum. However, when this reaction was repeated with more than 1 equiv of FeCl$_3$, the purple color due to [FeCl-(P″S$_3$)] disappeared almost immediately and only (OP″S$_3$)$_2$ was observed in the ^{31}P NMR spectrum.

Further work is in progress (i) to explore the chemistry of PhSn-(PS$_3$) and (ii) to compare the crystal structures of RSn(PS$_3$)-type complexes with those determined by calculation.

Acknowledgment. We thank the National Science Foundation EPSCoR Grant, the Research Corporation, the University of Nebraska, Center for Materials Research and Analysis for support of this work and Stephanie Cornet for experimental assistance.

Supporting Information Available: Fully labeled figures for compounds **1**−**4**, selected bond distances and bond angles for **1** and **3**, ^{13}C NMR data for **1** and **3**, and four X-ray crystallographic files that are in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

IC991371N

(16) Crystal data for PhSn(P″S$_3$) (**3**) (C$_{33}$H$_{41}$PS$_3$Si$_3$Sn) (293 K): triclinic, $P\bar{1}$, a = 10.111(2) Å, b = 14.737(3) Å, c = 15.342(3) Å, α = 112.86(3)°, β = 107.21(3)°, γ = 90.75(3)°, V = 1990.8(7) Å^3, z = 2. Final least-squares refinement on F^2 using 6552 unique reflections and 371 parameters yielded R_1 = 0.0556 (wR2 = 0.1418) and GOF = 1.127.

(17) For MeSn(PS$_3$). ^{31}P{^{1}H} NMR (δ, pyridine/CD$_2$Cl$_2$): −44.11 (s, J(P−^{119}Sn) = 1837 Hz, J(P−^{117}Sn) = 1756 Hz, J(PC) = 77.31 Hz). Low-resolution FABMS (m/z): 490.9 (M + H)$^+$. From calcd MS: C$_{19}$H$_{15}$-PS$_3$^{120}Sn, 489.910.

(18) For n-BuSn(PS$_3$). ^{31}P{^{1}H} NMR (δ, CD$_2$Cl$_2$): −57.96 (s, J(P−^{119}Sn) = 1302 Hz, J(P−^{117}Sn) = 1245 Hz, J(PC) = 75.29 Hz). Low-resolution FABMS (m/z): 533.1 (M + H)$^+$. From calcd MS: C$_{19}$H$_{15}$PS$_3$^{120}Sn, 532.964.

(19) Crystal data for (OPS$_3$)$_2$·py (**4**·py) (C$_{36}$H$_{24}$O$_2$P$_2$S$_6$·C$_5$H$_5$N) (293 K): monoclinic, $P2(1)/n$, a = 9.943(2) Å, b = 13.408(3) Å, c = 28.629(6) Å, α = γ = 90°, β = 96.30(3)°, V = 3793.6(13) Å^3, z = 4. Final least-squares refinement on F^2 using 4418 unique reflections and 471 parameters yielded R_1 = 0.0637 (wR2 = 0.1562) and GOF = 1.045. ^{31}P{^{1}H} NMR (δ, CD$_2$Cl$_2$): 44.47 (s).

(20) Transmetalation reactions involving transfer of tetradentate tripodal ligands from tin to transition metals have been reported. Plass, W.; Verkade, J. G. *J. Am. Chem. Soc.* **1992**, *114*, 2275.