Reaction of Me_2SBr_2 and $Pr^n{}_3PI_2$ with Tin Metal Powder; a Novel Route to Metal Thioether Complexes and the First Tin(IV) Phosphine Complex containing Iodide Ligands

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Tin metal powder reacts readily with both Me_2SBr_2 and $Pr^n{}_3PI_2$ in diethyl ether under ambient conditions, producing the novel $SnBr_4(SMe_2)_2$, which contains both *cis* and *trans* isomers within the unit cell, and the first complex of stoichiometry $SnI_4(PR_3)_2$ to be isolated: both complexes have been crystallographically characterised.

The synthesis of metal complexes by the direct reaction of transition metal powder and dihalotriorganophosphorus compounds, R_3PX_2, is now well established and provides a route to many novel and unexpected products, *e.g.* $[Mn_2I_5(PMe_3)_3]\cdot PMe_3$[1] and $CoI_8(PBu^n{}_3)_3$.[2] More recently we have expanded our studies to investigate the reaction of some heavier group 15 analogues of stoichiometry R_3EX_2 (E = As, Sb) with cobalt metal powder, which has again yielded products that were previously unavailable from conventional synthetic techniques *e.g.* $CoI_3(SbPh_3)_2$[3] and $[Ph_3SbI][CoI_3(SbPh_3)]$.[4]

However, thus far we have concentrated almost exclusively[5] on transition metal powders and compounds of stoichiometry R_3EX_2 (E = P, As, Sb; X = Br, I) *i.e.* those containing a group 15 element. We now report the reaction of unactivated tin metal powder with $Pr^n{}_3PI_2$ to produce the first isolated and structurally authenticated example of a tin complex containing both tertiary phosphine and iodide ligands and, additionally, that Me_2SBr_2 reacts with tin metal powder to produce a tin thioether complex. This proves that the activation of metals by our new synthetic method is not confined to compounds containing a group 15 element, but is also effective for the compound Me_2SBr_2.

$Pr^n{}_3PI_2$ (2 equiv.) reacts with tin metal powder in diethyl ether under anaerobic conditions to produce a red solid in *ca.* 2 d, eqn. (1).

$$2Pr^n{}_3PI_2 + Sn \rightarrow SnI_4(Pr^n{}_3P)_2 \qquad (1)$$

The air sensitive $SnI_4(Pr^n{}_3P)_2$ has been studied using X-ray crystallography† and reveals a *trans* structure, Fig. 1. Although phosphine adducts of tin(IV) halides have received much spectroscopic study,[6] there is only one previously structurally characterised compound of stoichiometry $SnX_4(PR_3)_2$, namely $SnCl_4(PEt_3)_2$ by Pidcock and co-workers.[7] Moreover, information regarding the corresponding iodide complexes is scarce and previous workers[8] have experienced difficulty in their synthesis using conventional techniques, which may have discouraged potential subsequent workers, since there is a paucity of reports regarding the iodo-complexes.[9] Preparation of compounds of stoichiometry $SnI_4(PR_3)_2$ by the method described here is straight forward.

The ability of R_3EX_2 compounds (E = P, As, Sb; X = Br, I) to oxidise crude metal powders must be related to their structure. There is evidence that diorganosulfur dihalides, R_2SX_2,[10] possess solution structures analogous to those of the dihalotriorganophosphorus compounds in diethyl ether,[11] *viz.* the ionic species $[R_2SBr]Br$ compared with $[R_3PX]X$. We were therefore intrigued to know if R_2SX_2 compounds could also oxidise metal powders and, if so, what type of products could be isolated.

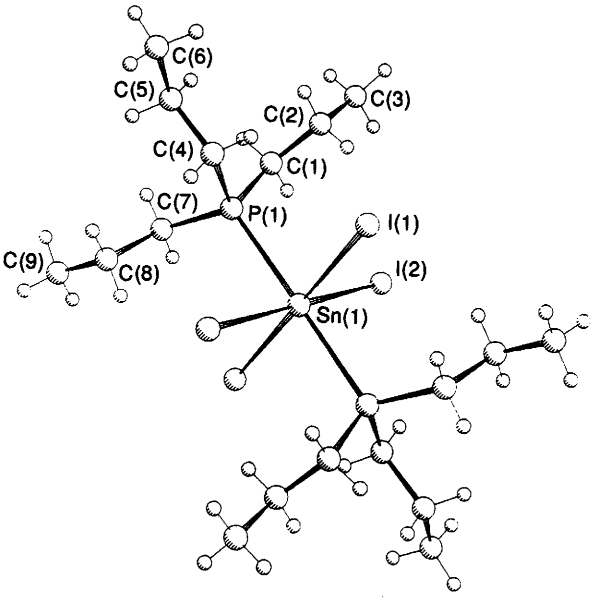

Fig. 1 Selected bond lengths (Å) and angles (°) for $SnI_4(PPr^n{}_3)_2$: Sn(1)–I(1) 2.872(3), Sn(2)–I(2) 2.863(3), Sn(1)–P(1) 2.69(1), P(1)–C(1) 1.86(4), P(1)–C(4) 1.79(4); I(1)–Sn(1)–I(1) 180.00, I(1)–Sn(1)–I(2) 92.2(1), I(1)–Sn(1)–P(1) 88.9(3), I(1)–Sn(1)–P(1) 91.1(3), I(2)–Sn(1)–P(1) 87.8(2), I(2)–Sn(1)–P(1) 92.2(2), P(1)–Sn(1)–P(1) 180.00, Sn(1)–P(1)–C(1) 112(1), Sn(1)–P(1)–C(4) 113(1), Sn(1)–P(1)–C(7) 114(1)

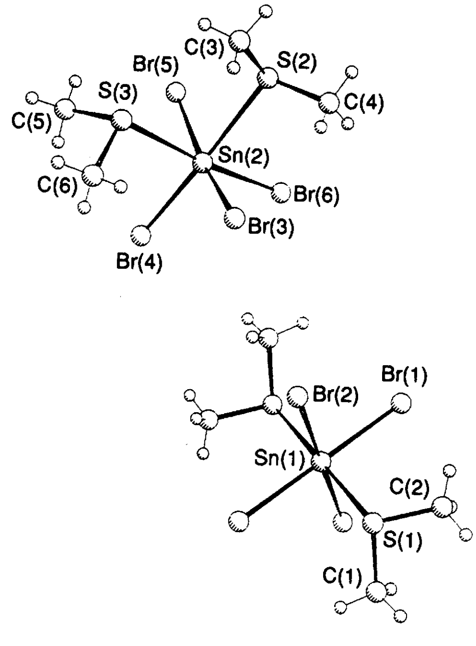

Fig. 2 Selected bond lengths (Å) and angles (°) for $[trans\text{-}(SMe_2)_2SnBr_4]_2[cis\text{-}(SMe_2)_2SnBr_4]$: Sn(1)–Br(1) 2.554(3), Sn(1)–Br(2) 2.554(4), Sn(1)–S(1) 2.65(1), Sn(2)–Br(2) 2.554(4), Sn(2)–Br(4) 2.532(4), Sn(2)–Br(5) 2.557(4), Sn(2)–Br(6) 2.539(4), Sn(2)–S(2) 2.692(9), Sn(2)–S(3) 2.692(8); Br(1)–Sn(1)–Br(2) 89.9(1), Br(1)–Sn(1)–S(1) 95.5(2), S(1)–Sn(1)–S(1) 180.00, Br(3)–Sn(2)–Br(4) 95.9(1), Br(3)–Sn(2)–Br(5) 166.4(1), Br(3)–Sn(2)–Br(6) 93.1(1), Br(3)–Sn(2)–S(2) 88.5 (2), Br(3)–Sn(2)–S(3) 86.8(2), Br(4)–Sn(2)–S(2) 175.5(2), Br(6)–Sn(2)–S(3) 174.0(2)

Unactivated coarse grain tin metal powder reacts with two molar equivalents of Me_2SBr_2 to produce $SnBr_4(SMe_2)_2$ in quantitative yield, eqn. (2).

$$2Me_2SBr_2 + Sn \rightarrow SnBr_4(SMe_2)_2 \qquad (2)$$

Recrystallisation of the pale-yellow powder from diethyl ether produced crystals suitable for single crystal X-ray analysis. The structure[†] of $SnBr_4(SMe_2)_2$ is illustrated in Fig. 2. Surprisingly, the structure analysis reveals that both the *cis* and *trans* isomers are contained within the unit cell in a 2:1 ratio. Several tin(IV) halide complexes containing sulfur donor ligands have been crystallographically characterised;[12–15] generally those with sterically hindered ligands give *trans* adducts *e.g.* $SnBr_4L_2$[11] (L = tetrahydrothiophene), whereas less sterically demanding ligands tend to give *cis* adducts *e.g.* $SnBr_4L_2$[12] (L = 1,3-diethylthiourea). Consequently the isolation of this novel structure, the first of its kind containing both *cis* and *trans* isomers within the unit cell, must arise from this new synthetic route.

In conclusion, the reaction of the compounds R_3PI_2 with tin metal powder provides a simple one-step route to tin(IV) complexes containing iodide ligands, which have proved difficult to synthesise by conventional methods and, more importantly, Me_2SBr_2 is also able to oxidise tin metal powder directly to tin(IV) in a single step under ambient conditions and clearly indicates that this reaction may be used for the facile synthesis of metal thioether complexes. The fact that the complex produced is novel provides further evidence that previously undiscovered materials are available from the reaction of crude metal powders with these powerful oxidising agents.

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Footnote

[†] *Crystal data*: $C_{18}H_{42}SnP_2I_4$, monoclinic, space group $P2_1/c$, a = 8.593(6), b = 11.897(7), c = 15.128(9) Å, β = 93.22(3)°, V = 1544(3) Å^3, Z = 2, D_c = 2.036 g cm^{-3}, T = 296 K, A Rigaku AFC6S diffractometer employing graphite monochromated Mo-Kα radiation (λ = 0.71069 Å) was used for all measurements. A total of 2931 reflections were collected, which yielded 723 observed $[I > 3.60\sigma(I)]$. The structure was solved by direct methods and subject to full-matrix least-squares refinement with all non-hydrogen atoms treated anisotropically and hydrogen atoms fixed in chemically reasonable positions. The final agreement factors were R = 0.063 and R_w = 0.079 for 115 variables.

Cis-trans-$(SC_2H_6)_2SnBr_4$ monoclinic, space group $P2_1/c$, a = 7.617(4), b = 12.382(5), c = 22.744(7) Å, β = 96.07(4)°, V = 2133 Å^3, Z = 6 (2 *trans*-isomers on crystallographic inversion centres and 4 *cis*-isomers in general positions), D_c = 2.627 g cm^{-3}, T = 296 K, a Rigaku A5C6S diffractometer employing graphite monochromated Mo-Kα radiation (λ = 0.71069 Å) was used for all measurements. A total of 3959 reflections were collected, which yielded 1083 observed $[I > 3\sigma(I)]$. The structure was solved by heavy atom techniques and subjected to full-matrix least-squares refinement with all non-hydrogen atoms treated anisotropically and hydrogen atoms fixed in chemically reasonable positions. The final agreement factors were R = 0.055 and R_w = 0.058 for 152 variables.

Atomic coordinates, bond lengths, angles and thermal parameters for both structures have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors Issue No. 1.

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