ESI

Tin(II) fluoride *vs.* tin(II) chloride – a comparison of their coordination chemistry with neutral ligands

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SUPPLEMENTARY INFORMATION

Table S1 Crystal data and structure refinement details

Compound	$[CH_2(PMe_3)_2][SnCl_3]_2$	$[(o\text{-}C_6H_4(PMe_2)_2CH_2]I_2.dmso$	$[Ph_2P(H)(CH_2)_2P(H)Ph_2][SnCl_3]_2$
Formula	$C_7H_{20}Cl_6P_2Sn_2$	$C_{11}H_{18}I_2P_2.Me_2SO$	$C_{26}H_{26}Cl_6P_2Sn_2$
M/g mol^{-1}	616.25	544.12	850.49
Crystal system	monoclinic	monoclinic	monoclinic
Space group (No.)	$P2_1/c$ (14)	$P2_1/c$ (14)	$P2_1/c$ (14)
a/Å	8.793(3)	9.035(2)	11.407(5)
b/Å	20.570(6)	20.046(5)	16.501(6)
c/Å	10.823(4)	11.377(3)	9.233(4)
α/°	90	90	90
β/°	104.374(4)	95.021(4)	113.011(6)
γ/°	90	90	90
U/Å^3	1896.4(11)	2052.6(9)	1599.6(11)

Z	4	4	2
μ(Mo-Kα) /mm^{-1}	3.628	3.315	2.178
F(000)	1176	1048	828
Total reflections	11751	9685	9358
Unique reflections	4304	4638	3635
R_{int}	0.062	0.027	0.046
Goodness-of-fit on F^2	0.991	0.954	1.137
R_1[b] [$I_o > 2\sigma(I_o)$]	0.046	0.020	0.056
R_1 (all data)	0.064	0.023	0.066
wR_2[b] [$I_o > 2\sigma(I_o)$]	0.079	0.043	0.082
wR_2 (all data)	0.087	0.043	0.086

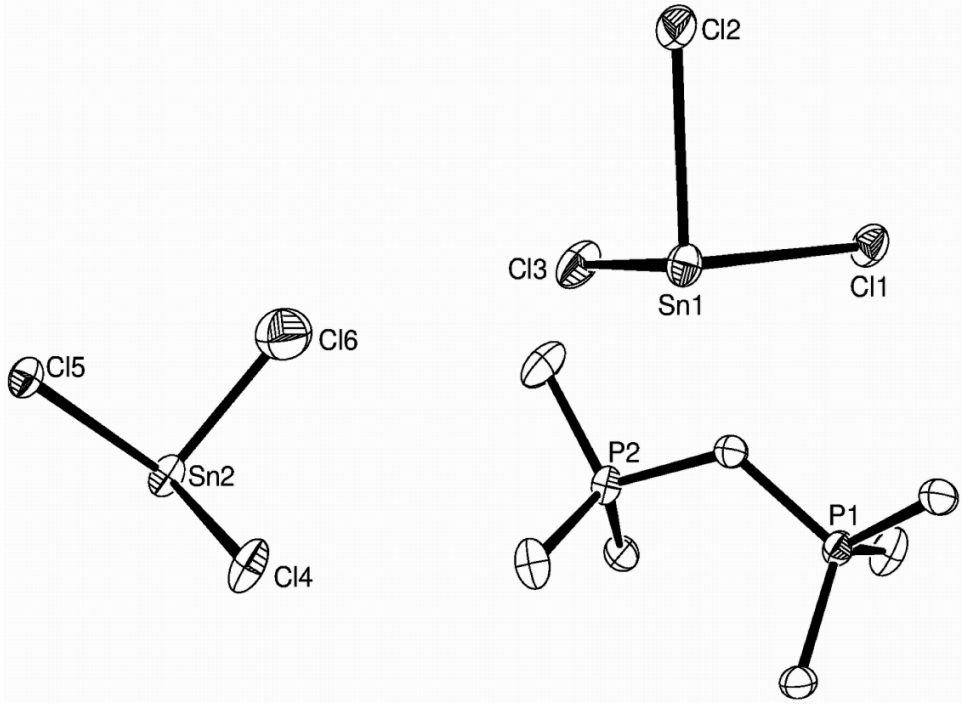

Fig S1. Structure of $[CH_2(PMe_3)_2][SnCl_3]_2$ with atom numbering scheme Thermal ellipsoids are drawn at 50% probability. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Sn1–Cl1 = 2.5507(16), Sn1–Cl2 = 2.5482(17), Sn1–Cl3 = 2.5299(16), Sn2–Cl4 = 2.5455(16), Sn2–Cl5 = 2.5445(17), Sn2–Cl6 = 2.337(2), P1–C4 = 1.814(6), P2–C4 = 1.803(5); P1–C4–P2 = 122.2(3).

Positional disorder was observed for the phosphonium cations based around P1 and P4; the use of DFIX was necessary to restrain the P–C bonds to a sensible length. A second dataset of the same compound was obtained with the *c* axis of the unit cell ~1/3rd of the length (hence the cell volume was also ~1/3rd of the size and Z = 8). However, there were clear (albeit weak) reflections which corresponded to the longer axis hence the larger cell was determined as correct.

1,1,3,3-tetramethylbenzodiphospho-1,3-diium diiodide

Diiodomethane (0.268 g, 1.0 mmol) was added to a solution of diphos (0.198 g, 1.0 mmol) in PhMe (20 mL) and refluxed for 16 h. A white precipitate formed which, upon cooling, was allowed to settle. The solid was isolated by decanting away the supernatant and drying *in vacuo*. Yield 0.440 g, 95%. Required for for $C_{11}H_{18}I_2P_2$ (465.9): C, 28.3; H, 3.9. Found: C, 28.8; H, 4.0%. ^{1}H NMR(d^6-dmso, 295 K): 2.56 (d, J_{HP} = 16.1 Hz, [12H]), 3.93 (t, J_{HP} = 13.7 Hz, [2H]), 8.17–8.25 (m, [2H]), 8.51–8.60 (m, [2H]). ^{13}C{^{1}H} NMR (d^6-dmso 295 K): 11.42 (d, J_{CP} = 50.8 Hz), 100.40 (s), 129.63 (s), 131.90 (t, J_{CP} = 10.7 Hz), 135.81 (d, J_{CP} = 6.8 Hz). ^{31}P{^{1}H} NMR (d^6-dmso, 295 K): 50.4.

The structure is shown in Fig S2.

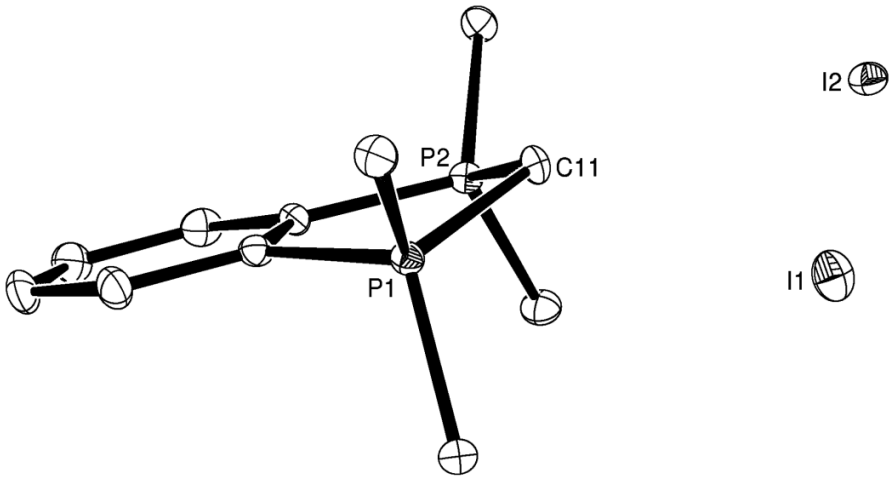

Figure S2. Crystal structure of [*o*-$C_6H_4(PMe_2)_2(CH_2)$]$I_2 \cdot Me_2SO$ showing the atom numbering scheme. Ellipsoids are drawn at the 50% probability level and H atoms and the dmso solvent molecule are omitted for clarity. Selected bond lengths (Å) and angles (°): P1–C11 = 1.8073(19), P2–C11 = 1.8130(19); P1–C11–P2 = 107.62(11).

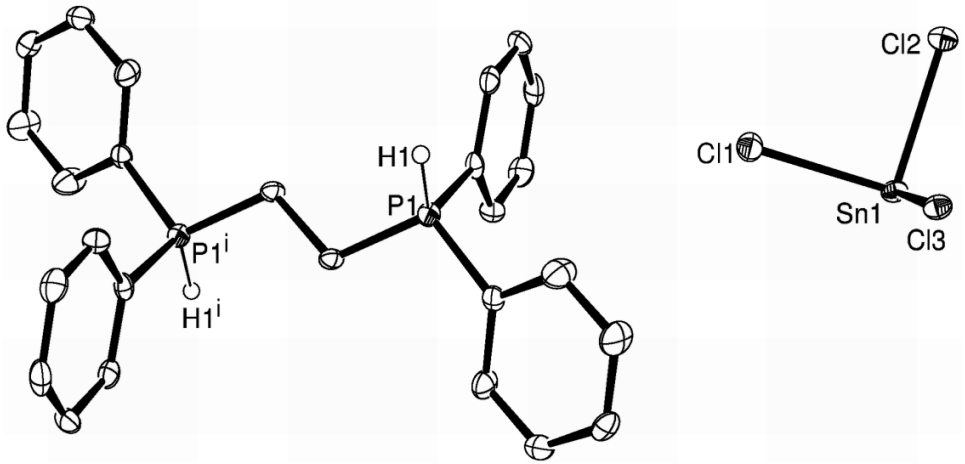

Figure S3 The structure of $[Ph_2P(H)(CH_2)_2P(H)Ph_2][SnCl_3]_2$ showing the cation and one anion. Ellipsoids are drawn at the 50% probability level and H atoms (bar PH) are omitted for clarity. Symmetry code 2–x, 1–y, 2–z Selected bond lengths (Å) and angles (°): P1–H1 = 1.37(5), Cl1–Sn1 = 2.5061(15) Cl2–Sn1 = 2.5064(16), Cl3–Sn1 = 2.5457(15), Cl1–Sn1–Cl2 = 91.28(5), Cl1–Sn1–Cl3 = 90.27(5), Cl2–Sn1–Cl3 = 90.68(4).