Correspondence to: Professor B K Nicholson

Chemistry Department

University of Waikato

Private Bag 3105

Hamilton

New Zealand

Email: b.nicholson@waikato.ac.nz

Fax: 64 7 838 4219

Six-coordinate organotin(IV) complexes formed using the Kläui ligands; $[CpCo\{P(OR')_2O\}_3]SnR_{3-n}Cl_n$.

Nicholas C. Lloyd, Brian K Nicholson* and Alistair L. Wilkins.

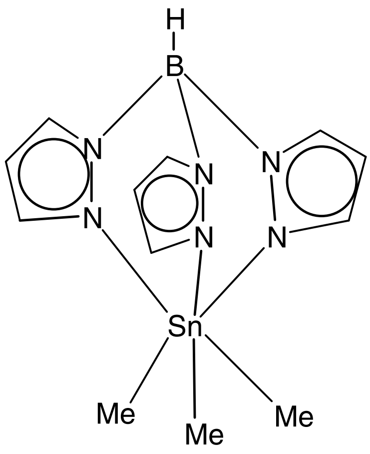
Department of Chemistry, University of Waikato, Private Bag 3105, Hamilton, New Zealand.

Abstract.

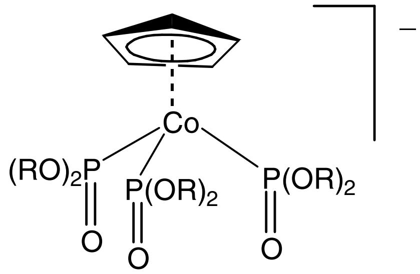
The complexes $[CpCo\{P(OR')_2O\}_3]SnR_{3-n}Cl_n$ [R' = Me, Et; R = Ph, Me] are readily prepared from the corresponding organotin chloride and the sodium salt of the Kläui ligands. The X-ray crystal structures of the full series are reported for R = Ph, n = 0-3, and these show that they are all six-coordinate, including the Ph_3Sn derivative which is the first example of a SnC_3O_3 coordination sphere. ^{1}H, ^{13}C, ^{31}P and ^{119}Sn NMR spectra are reported, and interpreted in terms of significant second-order effects and fluxional processes.

1. Introduction.

The coordination chemistry of organo-tin(IV) is well developed.[1] As is entirely predictable, for R_nSnX_{4-n} (R = alkyl, aryl; X = Cl, Br, etc) the tendency towards increased coordination number decreases as the number of R groups increases. Hence, while $RSnX_3$ readily forms six-coordinate complexes with a wide range of Lewis bases, corresponding R_3SnX rarely forms analogous hexa-coordinate species.[2] There appear to be only five structurally-characterised six-coordinate tin complexes which incorporate a R_3Sn^+ group, all involving strongly chelating or pincer-type ligands.[3] The first of these to be reported was the reasonably-stable $Me_3Sn[pz_3BH]$ (**1**),[4] and several subsequent studies described related pyrazolyl-borate complexes.[5] These included $Ph_3Sn[pz_3BH]$ which was however found to be too unstable for structural characterisation.[6,7] The higher coordination numbers found for these compounds are a consequence of the strong tendency for the tripodal Trofimenko-type pyrazolyl-borate ligands to be tridentate.[8]



(1)



(**2**) L^{Me} R = Me
L^{Et} R = Et

An analogous type of mono-negative tridentate ligand which encourages strong coordination are the Kläui ligands **2**.[9] These have been found to give many novel complexes of the d- and f-block elements. In contrast, there have been few studies in which **2** has been used to form derivatives of the p-block elements. For Group 14 these have been restricted to $L^R{}_2M$ (M = Si, Sn, Pb)[10] and to recently described inorganic four-coordinate Ge(II) and six-coordinate Ge(IV) derivatives of the type $L^{Et}GeCl$ and $L^{Et}Ge(N_3)_3$ respectively.[11] The only organometallic p-block example of which we are aware is Me_2ClSnL^{Me}.[12]

We now report the preparation of the series $Me_nCl_{3-n}SnL^R$ (R = Me) and $Ph_nCl_{3-n}SnL^R$ (R = Me, Et) together with selected structures and spectroscopic properties. This includes the structure of Ph_3SnL^{Me}, which is the first example for a Sn(IV) compound with a SnC_3O_3 coordination sphere. Some aspects of this work have been briefly communicated elsewhere.[13]

2. Experimental

2.1 General Methods.

The new compounds were generally stable in air, but reactions involving organotin chlorides were carried out under dry nitrogen conditions, using purified solvents. ^{1}H, $^{13}C\{^{1}H\}$, $^{31}P\{^{1}H\}$ and $^{119}Sn\{^{1}H\}$ NMR spectroscopy was performed on a Bruker Avance series DRX 300 or 400 MHz machine at 303 K in $CDCl_3$ unless otherwise noted. ^{31}P spectra were referenced to orthophosphoric acid and ^{119}Sn spectra were referenced to $SnMe_4$. For variable temperature ^{119}Sn NMR corrections were applied for shifts in the signal, arising from variations in temperature. Resolution of spectra was, on average, ^{1}H 0.09 Hz, ^{13}C 0.55 Hz, ^{31}P 1.2 Hz, ^{119}Sn 1.2 Hz. Data processing and collection used the XWIN NMR V3.1 software suite. Where necessary, resolution enhancement was used, to allow confused and overlapping patterns to be seen. This was done by either altering the line-broadening factor (LB) or by setting a negative LB value (dependent on the nucleus in question: -1 Hz for ^{1}H and ^{13}C, ranging to –20 Hz for ^{31}P and ^{119}Sn due to the natural line width) and a GB value of 0.3 Hz. Scalar coupling constants were measured directly by observation from the spectra without simulation of second-order effects.

The organo-tin compounds were purchased from Aldrich, while the Kläui ligands NaL^{Me} and NaL^{Et} were from Strem.

2.2 Preparation of $PhMeSnCl_2$. (c.f. ref 14)

$PhSnCl_3$ (3.02 g, 10 mmol) in a Schlenk flask under nitrogen was cooled to $0^{o}C$ in an ice bath. $SnMe_4$ (1.79 g, 10 mmol) was added dropwise, with stirring. After addition was complete, stirring was continued for half an hour. The mixture was pumped under vacuum at room temperature for several hours to remove the Me_3SnCl by-product. The residue (2.74 g, 97 %) was checked by GC-MS to establish purity, giving >95 % $MePhSnCl_2$. ^{1}H NMR: δ 1.35 (CH_3, s), 7.68 – 7.52 (C_6H_5, m); ^{13}C NMR: δ 4.80 (CH_3, s), 129.6 (*m*-Ph, s), 131.7 (*p*-Ph, s), 134.6 (*o*-Ph, s), 138.8 (*i*-Ph, s); ^{119}Sn: δ 55.1.

*2.3. Preparation of Ph_3SnL^{Me} (**3**).*

A solution of NaL^{Me} (0.500 g, 1.05 mmol) was dissolved in the minimum amount of CH_2Cl_2 (*ca* 5 mL) in a round-bottomed flask. A solution of Ph_3SnCl (0.405 g, 1.05 mmol) in CH_2Cl_2 (*ca* 5 mL) was added in one portion with stirring, and the mixture was stirred for 30 min. The cloudy mixture was filtered through a small column of Florisil and the solvent removed from the yellow solution by rotary evaporation. The residue was recrystallised from CH_2Cl_2 / petroleum spirits at -20°C giving yellow crystals of Ph_3SnL^{Me} (0.64 g, 76 %). Anal. Calcd for $C_{29}H_{38}CoO_9P_3Sn$: C, 43.48; H, 4.78. Found: C, 43.54, 4.53. ^{1}H NMR: δ 3.51 (CH_3, vq), 5.10 (Cp, s), 7.24 (*m*, *p*-Ph, m), 7.83 (*o*-Ph, d, J = 7.4 Hz, tin satellites $^3J_{^{119}Sn-^1H}$ = 69 Hz, $^3J_{^{117}Sn-^1H}$ = 57 Hz); ^{13}C NMR: δ 52.4 (CH_3, vq, $^2J_{^{31}P-^{13}C}$ = 3 Hz), 89.1 (Cp, s), 126.5 (*p*-Ph, s, tin satellites $^4J_{^{119}Sn-^{13}C;\ ^{117}Sn-^{13}C\ (av)}$ = 15.6 Hz), 126.8 (*m*-Ph, s, tin satellite $^3J_{^{119}Sn-^{13}C;\ ^{117}Sn-^{13}C\ (av)}$ = 64.8 Hz), 136.9 (*o*-Ph, s, tin satellite $^2J_{^{119}Sn-^{13}C;\ ^{117}Sn-^{13}C\ (av)}$ = 49.5 Hz), 154.9 (*i*-Ph, q, $^3J_{^{31}P-^{13}C}$ = 3.5 Hz, tin satellites $^1J_{^{119}Sn-^{13}C;}$ = 746 Hz, $^1J_{^{117}Sn-^{13}C}$ = 720 Hz); ^{31}P NMR: δ 117 (s); ^{119}Sn NMR: δ -408 (q, $^2J_{^{31}P-^{119}Sn}$ = 82 Hz).

*2.4. Preparation of Ph_2ClSnL^{Me} (**4**).*

Using the same method, Ph_2SnCl_2 (0.361 g, 1.05 mmol) was reacted with NaL^{Me} (0.500 g, 1.05 mmol) in CH_2Cl_2 (5 mL) to give yellow crystals of Ph_2ClSnL^{Me} after purification and recrystallisation from CH_2Cl_2 and petroleum spirits (0.49 g, 62 %). Calcd for $C_{23}H_{33}ClCoO_9P_3Sn$: C, 36.37; H 4.38. Found C, 36.92, H, 4.46. ^{1}H NMR: δ 3.44 (CH_3, t, $^3J_{^{31}P-^1H}$ = 5.3 Hz), 3.52 (CH_3, d, $^3J_{^{31}P-^1H}$ = 10.6 Hz), 3.85 (CH_3, t, $^3J_{^{31}P-^1H}$ = 5.4 Hz), 5.12 (Cp, s), 7.21 (*m, p*-Ph, m), 7.82 (*o*-Ph, d, J = 6.6 Hz, tin satellites $^2J_{^{119}Sn-^1H}$ = 94.2 Hz, $^2J_{^{117}Sn-^1H}$ = 79.4 Hz); ^{13}C NMR: δ 52.6 (CH_3, br m), 53.7 (CH_3, br t, J = 4.3 Hz), 89.4 (Cp, s), 127.2 (*m*-Ph, s, tin satellite $^3J_{^{119}Sn-^{13}C;\ ^{117}Sn-^{13}C\ (av)}$ = 90 Hz), 127.2 (*p*-Ph, s, tin satellite $^4J_{^{119}Sn-^{13}C;\ ^{117}Sn-^{13}C\ (av)}$ = 18 Hz), 135.3 (*o*-Ph, s, tin satellite $^2J_{^{119}Sn-^{13}C;\ ^{117}Sn-^{13}C\ (av)}$ = 62 Hz), 154.3 (*i*-Ph, q, $^3J_{^{31}P-^{13}C}$

= 3.5 Hz, tin satellites $^1J_{^{119}Sn - ^{13}C}$ = 1047 Hz, $^1J_{^{117}Sn - ^{13}C}$ = 997 Hz); ^{31}P NMR δ 119 (m). ^{119}Sn NMR: δ -491 (d of t, $^2J_{^{31}P - ^{119}Sn}$ = 94, 62 Hz)

*2.5. Preparation of $PhCl_2SnL^{Me}$ (**5**).*

Using the same method, $PhSnCl_3$ (0.307 g, 1.05 mmol) was reacted with NaL^{Me} (0.500 g, 1.05 mmol) in CH_2Cl_2 (5 ml) to give yellow crystals of $PhCl_2SnL^{Me}$ (0.44 g, 58 %). Calcd for $C_{17}H_{28}Cl_2CoO_9P_3Sn$: C, 28.44, H, 3.93. Found C, 28.16 H, 3.97. ^{1}H NMR: δ 3.47 (CH_3, m), 3.75 (CH_3, m), 3.82 (CH_3, m), 5.12 (Cp, s), 7.25 (*m, p*-Ph, m), 7.83 (*o*-Ph, d, *J* = 6.6 Hz, tin satellites $^3J_{^{119}Sn - ^1H}$ = 138.6 Hz, $^3J_{^{117}Sn - ^1H}$ = 130.4 Hz); ^{13}C NMR: δ 52.8 (CH_3, m), 53.7 (CH_3, m), 54.0 (CH_3, m), 89.7 (Cp, s,), 127.6 (*m*-Ph, s, $^3J_{^{119}Sn - ^{13}C;\ ^{117}Sn - ^{13}C\ (av)}$ = 146 Hz), 128.2 (*p*-Ph, s, tin satellite $^4J_{^{119}Sn - ^{13}C;\ ^{117}Sn - ^{13}C\ (av)}$ = 28 Hz), 133.8 (*o*-Ph, s, tin satellite $^2J_{^{119}Sn - ^{13}C;\ ^{117}Sn - ^{13}C\ (av)}$ = 78 Hz), 153.5 (*i*-Ph, m, tin satellite $^1J_{^{119}Sn - ^{13}C;\ ^{117}Sn - ^{13}C\ (av)}$ = 1720 Hz); ^{31}P NMR: δ 117 (br, s); ^{119}Sn NMR: δ -569 (m).

*2.6. Preparation of Cl_3SnL^{Me} (**6**).*

Similarly, $SnCl_4$ (0.1642 g, 0.63 mmol) was reacted with NaL^{Me} (0.300 g, 0.63 mmol) in CH_2Cl_2 (5 ml) to give yellow crystals of Cl_3SnL^{Me} (0.16 g, 38 %). Calcd for $C_{11}H_{23}Cl_3CoO_9P_3Sn$: C, 19.54, H, 3.43. Found C, 19.68, H, 3.34. ^{1}H NMR: δ 3.80 (CH_3, vq, $^3J_{^{31}P - ^1H}$ = 3.8 Hz), 5.22 (Cp, s). ^{13}C NMR: δ 54.0 (CH_3, vq, $^2J_{^{31}P - ^{13}C}$ = 3.3 Hz), 89.9 (Cp, s). ^{31}P NMR: δ 121 (s). ^{119}Sn NMR: δ -661 (br,s).

*2.7. Attempted Preparation of Me_3SnL^{Me} (**7**).*

Using the same method, Me_3SnCl (0.209 g, 1.05 mmol) with NaL^{Me} (0.500 g, 1.05 mmol) in CH_2Cl_2 (5 ml) gave yellow crystals of a complex mixture of products, apparently Me_2ClSnL^{Me}, $MeCl_2SnL^{Me}$ and NaL^{Me} (see discussion).

*2.8. Preparation of Me_2ClSnL^{Me} (**8**).*

Similarly, Me_2SnCl_2 (0.2307 g, 1.05 mmol) was reacted with NaL^{Me} (0.500 g, 1.05 mmol) in CH_2Cl_2 (5 ml) to give yellow crystals of Me_2ClSnL^{Me} (0.40 g, 60 %). Calcd for $C_{13}H_{29}ClCoO_9P_3Sn$: C, 24.59, H, 3.66. Found C, 24.95; H, 4.50. ^{1}H NMR: δ 0.43 (CH_3-Sn), s, $^2J_{^{119}Sn-^1H}$ = 76 Hz), 3.62 (CH_3-O, pseudo q, $^3J_{^{31}P-^1H}$ = 3.4 Hz), 5.03 (Cp, s). ^{13}C NMR: δ 14.0 (CH_3-Sn, q, $^3J_{^{31}P-^{13}C}$ = 3.3 Hz, tin satellites $^1J_{^{119}Sn-^{13}C}$ = 713 Hz, $^1J_{^{117}Sn-^{13}C}$ = 682 Hz), 52.5 (CH_3-O, br s), 89.3 (Cp, s); ^{31}P NMR: δ 117 (br s). ^{119}Sn NMR: δ -340 (q, $^2J_{^{31}P-^{119}Sn}$ = 88 Hz).

*2.9. Preparation of $MeCl_2SnL^{Me}$ (**9**).*

Similarly, $MeSnCl_3$ (0.252 g, 1.05 mmol) and NaL^{Me} (0.500 g, 1.05 mmol) in CH_2Cl_2 (5 ml) gave yellow crystals of $MeCl_2SnL^{Me}$ (0.55 g, 80 %). Calcd for $C_{12}H_{26}Cl_2CoO_9P_3Sn$: C, 21.98, H, 3.97. Found C, 22.04, H, 3.97. ^{1}H NMR: δ 0.98 (Me-Sn, s, tin satellites $^2J_{^{119}Sn-^{13}C}$ = 135 Hz, $^2J_{^{117}Sn-^{13}C}$ = 131 Hz), 3.63 (CH_3-O, m), 3.75 (CH_3-O, m), 5.13 (Cp, s). ^{13}C NMR: δ 19.2 (CH_3-Sn, pseudo q, $^3J_{^{31}P-^{13}C}$ = 3.5 Hz, tin satellites $^1J_{^{119}Sn-^{13}C}$ = 1274 Hz, $^1J_{^{117}Sn-^{13}C}$ = 1218 Hz), 52.6 (CH_3-O, m), 53.5 (CH_3-O, m), 54.0 (CH_3-O, m), 89.7 (Cp, s); ^{31}P NMR: δ 119 (br, s); ^{119}Sn NMR: δ -509 (m).

*2.10. Preparation of $PhMeClSnL^{Me}$ (**10**).*

As above, $PhMeSnCl_2$ (0.237 g, 0.84 mmol) with NaL^{Me} (0.400 g, 0.84 mmol) in CH_2Cl_2 (5 ml) gave a yellow solid. Several recrystallizations were attempted, but were not successful because of rearrangement reactions. This compound was only characterised by its ^{119}Sn NMR shift (see discussion).

*2.11. Preparation of Ph_3SnL^{Et} (**11**).*

Using the same method, Ph_3SnCl (0.345 g, 0.896 mmol) was reacted with NaL^{Et} (0.500 g, 0.896 mmol) in CH_2Cl_2 (5 mL) to give yellow crystals of Ph_3SnL^{Et} (0.53 g, 67 %). Calcd for $C_{35}H_{50}CoO_9P_3Sn$: C, 47.48; H, 5.69. Found C, 47.48, H, 5.59. ^{1}H NMR: δ 1.17 (CH_3, t, J =

7.1 Hz), 3.92 (CH_2, m), 5.07 (Cp, s), 7.25 (*m*, *p*-Ph, m), 7.80 (*o*-Ph, d, *J* = 6.6 Hz, tin satellites $^3J_{^{119}Sn-^1H}$ = 68 Hz, $^3J_{^{117}Sn-^1H}$ = 54 Hz); ^{13}C NMR: δ 16.5 (CH_3, vq, $^3J_{^{31}P-^{13}C}$ = 1.9 Hz), 60.9 (CH_2, vq, $^2J_{^{31}P-^{13}C}$ = 3.1 Hz), 89.5 (Cp, s), 126.3 (*p*-Ph, s, tin satellite $^4J_{^{119}Sn-^{13}C;\,^{117}Sn-^{13}C\,(av)}$ = 13 Hz), 126.6 (*m*-Ph, s, tin satellite $^3J_{^{119}Sn-^{13}C}$ = 66 Hz, $^3J_{^{117}Sn-^{13}C}$ *J* = 64 Hz), 136.9 (*o*-Ph, s, tin satellite $^2J_{^{119}Sn-^{13}C;\,^{117}Sn-^{13}C\,(av)}$ $^2J_{av}$ = 49 Hz), 155.4 (*i*-Ph, q, $^3J_{^{31}P-^{13}C}$ = 3.6 Hz, tin satellite $^1J_{^{119}Sn-^{13}C}$ = 750 Hz, $J_{^{117}Sn-^{13}C}$ = 717 Hz); ^{31}P NMR: δ 114 (s); ^{119}Sn NMR: δ -413 (q, $^2J_{^{119}Sn-^{31}P}$ = 82 Hz).

*2.12. Preparation of Ph_2ClSnL^{Et} (**12**).*

Similarly, Ph_2SnCl_2 (0.308 g, 0.896 mmol) was reacted with NaL^{Et} (0.500 g, 0.896 mmol) in CH_2Cl_2 (5 mL) to give yellow crystals (from $CDCl_3$) of Ph_2ClSnL^{Et} (0.18 g, 24 %). Calcd for $C_{29}H_{45}ClCoO_9P_3Sn.2CHCl_3$: C, 34.33; H, 4.55. Found C, 34.92; 5.03. ^{1}H NMR: δ 1.08 (CH_3, t, *J* = 7.1 Hz), 1.14 (CH_3, t, *J* = 7.1 Hz), 1.31 (CH_3, t, *J* = 7.1 Hz), 3.85 (CH_2, m), 4.27 (CH_2, m), 5.07 (Cp, s), 7.20 (*m*, *p*-Ph, m), 7.81 (*o*-Ph, d, *J* = 7.0 Hz, $^3J_{^{119}Sn-^1H}$ = 92 Hz, $^3J_{^{117}Sn-^1H}$ = 80 Hz). ^{13}C NMR: δ 16.3 (CH_3, m), 16.6 (CH_3, t, *J* = 2.9 Hz), 61.3 (CH_2, m), 62.2 (CH_2, t, *J* = 4.5 Hz), 89.6 (Cp, s), 127.0 (*p*-Ph, s, tin satellite $^4J_{^{119}Sn-^{13}C;\,^{117}Sn-^{13}C\,(av)}$ = 18 Hz), 126.9 (*m*-Ph, s, tin satellite $^3J_{^{119}Sn-^{13}C}$ = 91 Hz, $^3J_{^{117}Sn-^{13}C\,(av)}$ = 88 Hz), 135.3 (*o*-Ph, s, tin satellite $^2J_{^{119}Sn-^{13}C;\,^{117}Sn-^{13}C\,(av)}$ = 61 Hz), 154.8 (*i*-Ph, q, $^3J_{^{31}P-^{13}C}$ = 3.5 Hz, tin satellites $^1J_{^{119}Sn-^{13}C}$ = 1044 Hz, $^1J_{^{117}Sn-^{13}C}$ = 1004 Hz). ^{31}P NMR: δ 116 (m). ^{119}Sn NMR: δ -495 (d of t, $^2J_{^{119}Sn-^{31}P}$ = 92, 62 Hz)

*2.13. Preparation of $PhCl_2SnL^{Et}$ (**13**).*

Similarly, $PhSnCl_3$ (0.345 g, 0.896 mmol) was reacted with NaL^{Et} (0.500 g, 0.896 mmol) in CH_2Cl_2 (5 mL) to give yellow crystals of $PhCl_2SnL^{Et}$ (0.57 g, 79 %). Calcd for $C_{24}H_{40}Cl_2CoO_9P_3Sn.CHCl_3$: C, 32.13, H, 4.53. Found C, 32.71, H, 4.80. ^{1}H NMR: δ 1.08 (CH_3, t, *J* = 7.1 Hz), 1.27 (CH_3, t, *J* = 7.0 Hz), 1.29 (CH_3, t, *J* = 7.0 Hz), 3.85 (CH_2, m), 4.25

(CH_2, m), 5.09 (Cp, s), 7.24 (*m*, *p*-Ph, m), 7.81 (*o*-Ph, d, *J* = 7.1 Hz, tin satellites $^{3}J_{^{119}Sn-^{1}H}$ = 142 Hz, $^{3}J_{^{117}Sn-^{1}H}$ = 133 Hz); ^{13}C NMR: δ 16.3 (CH_3, m), 16.5 (CH_3, m), 61.8 (CH_2, m), 62.5 (CH_2, m), 62.9 (CH_2, m), 89.9 (Cp, s), 128.0 (*p*-Ph, s, tin satellite $^{4}J_{^{119}Sn-^{13}C;\,^{117}Sn-^{13}C\,(av)}$ = 28 Hz), 127.3 (*m*-Ph, s, tin satellite $^{3}J_{^{119}Sn-^{13}C;}$ = 146 Hz, $^{3}J_{^{117}Sn-^{13}C\,(av)}$ = 139 Hz), 133.7 (*o*-Ph, s, tin satellite $^{2}J_{^{119}Sn-^{13}C;\,^{117}Sn-^{13}C\,(av)}$ = 77 Hz), 153.8 (*i*-Ph, m, tin satellites $^{1}J_{^{119}Sn-^{13}C;\,^{117}Sn-^{13}C\,(av)}$ = 1729 Hz); ^{31}P NMR: δ 116 (s); ^{119}Sn NMR: δ -570 (m)

2.14. Xray Crystallography

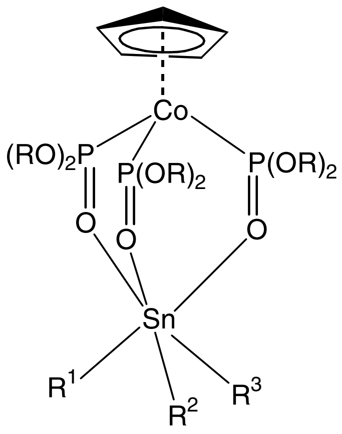
Data were collected on a Bruker SMART CCD diffractometer using standard procedures. They were solved by direct methods and refined (on F_o^2) using the SHELX programs [15] running under WinGx.[16] Crystal data and refinement details are in Table 1. Special details for each: Ph_3SnL^{Me} (**3**) crystallized with two independent molecules in the asymmetric unit; Cl_3SnL^{Me} (**6**) was located on a mirror plane which led to disorder involving the Cp ring and the Me groups so hydrogen atoms were not included in the refinement and the precision of the determination was reduced; $PhCl_2SnL^{Me}$ (**5**) crystallized with a molecule of CH_2Cl_2 in the lattice but was otherwise straightforward; Ph_2ClSnL^{Et} (**12**) also had disorder, involving the CH_2 portion of the the Et groups but this was readily modelled. The structures are illustrated in Figs 1-4 with selected bond parameters included in the captions.

3. Results and discussion

3.1 Preparation of the complexes.

Synthesis of the new complexes **3-13** was generally straightforward, by combining equal amounts of the appropriate organotin chloride with NaL^R in CH_2Cl_2 (Eqn 1).

$$R_{3-n}SnCl_n + NaL^R \rightarrow R_{3-n}SnCl_{n-1}L^R + NaCl \qquad \text{(eqn 1)}$$



3 R = Me $R^1 = R^2 = R^3$ = Ph
4 R = Me $R^1 = R^2$ = Ph R^3 = Cl
5 R = Me R^1 = Ph $R^2 = R^3$ = Cl
6 R = Me $R^1 = R^2 = R^3$ = Cl
7 R = Me $R^1 = R^2 = R^3$ = Me
8 R = Me $R^1 = R^2$ = Me R^3 = Cl
9 R = Me R^1 = Me $R^2 = R^3$ = Cl
10 R = Me R^1 = Me R^2 = Ph R^3 = Cl
11 R = Et $R^1 = R^2 = R^3$ = Ph
12 R = Et $R^1 = R^2$ = Ph R^3 = Cl
13 R = Et R^1 = Ph $R^2 = R^3$ = Cl

Recrystallisation generally yielded pure, air-stable compounds in good yields and these were characterized by elemental analysis and NMR spectroscopy. The structures of **3**, **5**, **6** and **12** were also determined. No indication of ligand rearrangements equivalent to that observed for reactions of NaL^{Et} with $ZrCl_4$ was seen with the tin halides.[17]

Attempts to form Me_3SnL^{Me} by reaction of Me_3SnCl with NaL^{Me} unexpectedly gave only Me_2ClSnL^{Me}. This has clearly arisen via a redistribution reaction:

$2Me_3SnCl$ • $Me_4Sn + Me_2SnCl_2$ (eqn 2)

followed by reaction of the Me_2SnCl_2 with the Kläui ligand. Although redistribution reactions like that of eqn 2 are well known, they are not usually significant under such mild conditions (25°C, CH_2Cl_2) so in this case must be promoted by $[L^R]^-$. Because of the higher Lewis acidity of Me_2SnCl_2, preferential reaction to give Me_2ClSnL^{Me} would shift the equilibrium of eqn 2 to the right. There was ^{119}Sn NMR evidence of corresponding redistribution processes in the other syntheses, especially for Ph_3SnL^R, but these were slower and did not affect the yields.

Similarly, a pure sample of $MePhClSnL^{Me}$ could not be isolated because scrambling led to other combinations. However the ^{119}Sn NMR (see below) could be deduced from the mixture since the impurity peaks were well-separated from the main component.

3.2. X-ray crystal structures.

The structures of a full series of compounds, $Ph_{3-n}Cl_nSnL^R$ were determined, to confirm the six-coordination in each case and to monitor the changes in bond parameters across the series.

The crystal structure of Ph_3SnL^{Me} (**3**) revealed two structurally-equivalent independent molecules in the asymmetric unit. The geometry of one is illustrated in Fig 1 and averaged bond parameters are given in the caption. The tin atom is clearly six-coordinate, a very rare example for a tri-organotin centre and the first with a SnC_3O_3 coordination sphere. The geometry about the tin atom is distorted octahedral, with average O-Sn-O angles of 79.4° and C-Sn-C of 103.3°. This will be a consequence of the small bite of the L^{Me} ligand and the steric interactions between the three *fac* Ph groups. The Sn-C bonds are 2.174(3)Å, compared with 2.122Å in Ph_3SnCl, [18] and the Sn-O bonds average 2.239(2)Å which indicates reasonably strong bonding – for comparison Sn-O distances around 2.40Å and 2.30Å are found respectively for five-coordinate $R_3SnCl(O{=}PPh_3)$ and $R_2SnCl_2(O{=}PPh_3)$ complexes (R = Me, Ph).[19]

The structures of the remaining members of the series are illustrated in Figs 2-4, and bond parameters are included in the captions. Table 2 compares selected parameters amongst the different compounds. These show the following trends from the Ph_3SnL^{Me} example **3** to the Cl_3SnL^{Me} complex **6**:

(i) Both the Sn-C and Sn-Cl bond lengths decrease as the Ph groups are replaced by Cl, with the Sn-Cl bond length in Cl_3SnL^{Me} at 2.368 Å being slightly shorter than the corresponding distance in a number of $Cl_3Sn[(pz)_3BH]$ examples (typically 2.37-2.38Å), [5-7] suggesting similar bonding;

(ii) The Sn-O bonds also decrease across the series, with those *trans* to C being consistently shorter than those *trans* to Cl in the two examples where both are present, which is the opposite of what would be expected given the relative *trans* influences of C and Cl;

(iii) The P=O bonds also decrease slightly as the L^R ligand becomes more tightly bonded to Sn;

(iv) The complexes tend more towards octahedral across the series, from C-Sn-C and O-Sn-O angles of 103.3° and 79.4° respectively for Ph_3SnL^{Me} to Cl-Sn-Cl and O-Sn-O angles of 95.0° and 86.6° for Cl_3SnL^{Me}.

These trends can all be explained by the increasing Lewis acidity of the tin atom as less-bulky but more-electronegative Cl atoms replace Ph groups.

3.3. NMR Spectra.

The complexes prepared in this study are particularly interesting for NMR study. They have several active nuclei (^{1}H, ^{13}C, ^{31}P and ^{119}Sn), have symmetry that leads to virtual coupling effects, and show temperature-affected fluxional behaviour. Full data for each compound are listed in the experimental section.

3.3.1. ^{1}H and ^{13}C Spectra

For all of the compounds, the cyclopentadienyl rings give single ^{1}H and ^{13}C resonances at *ca* δ 5.1 and 89 ppm respectively, only marginally shifted from those of the free ligand with no discernible coupling to the other nuclei present.

For the OMe groups on the L^{Me} compounds (and the OEt groups on L^{Et}) the spectra gave ^{1}H and ^{13}C patterns complicated by virtual coupling effects, as has been analysed for other complexes with the Kläui ligands.[20] Ph_3SnL^{Me} (**3**) is an example with C_{3V} symmetry. In the ^1H spectrum the methyl protons gave a multiplet at 3.51 ppm, with virtual coupling to the phosphorus nuclei which can be analyzed as an $A_{18}X_3$ spin system. This "virtual quartet" is symmetrical, with $^3J_{P-H}$ = 3.6 Hz, 2.9 Hz, and 3.6 Hz. The effect is more noticeable in the coordinated species than in the free ligand where the couplings are unsymmetrical $^3J_{P-H}$ = 3.5 Hz, 3.1 Hz and 3.6 Hz. Similarly in the ^{13}C spectrum the methyl carbons gave a virtual quartet at 52.4 ppm, of four lines of equal intensity, $^2J_{P-C}$ = 3.1 Hz. This was from the six equivalent carbons, coupling to the three equivalent phosphorus, in an A_6X_3 [CpCo{**P**(O**C**H_3)$_2$O}$_3$SnPh$_3$] spin system. As in the proton spectra, this is slightly shifted from 50.7 ppm in the free ligand, the coupling constant is also slightly increased from $^2J_{P\text{-}C}$ = 2.6 Hz.

Cl_3SnL^{Me} (**6**) also has C_{3V} symmetry, so the ^1H and ^{13}C methyl signals appeared as the expected virtual quartet. Analysis was the same as for Ph_3SnL^{Me} and details are given in the experimental section.

In Ph_2ClSnL^{Me} (**4**) the idealized symmetry is lowered from C_{3V} to C_S. The spectra are mainly first order so analysis is reasonably straightforward. The ^1H NMR signals of the methyl groups now show three distinct peaks – a triplet at 3.44 ppm with $^3J_{P\text{-}H}$ = 5.3 Hz, a doublet at 3.52 ppm with $^3J_{P\text{-}H}$ = 10.6 Hz, and a triplet at 3.85 ppm with $^3J_{P\text{-}H}$ = 5.4 Hz. (Fig 5).

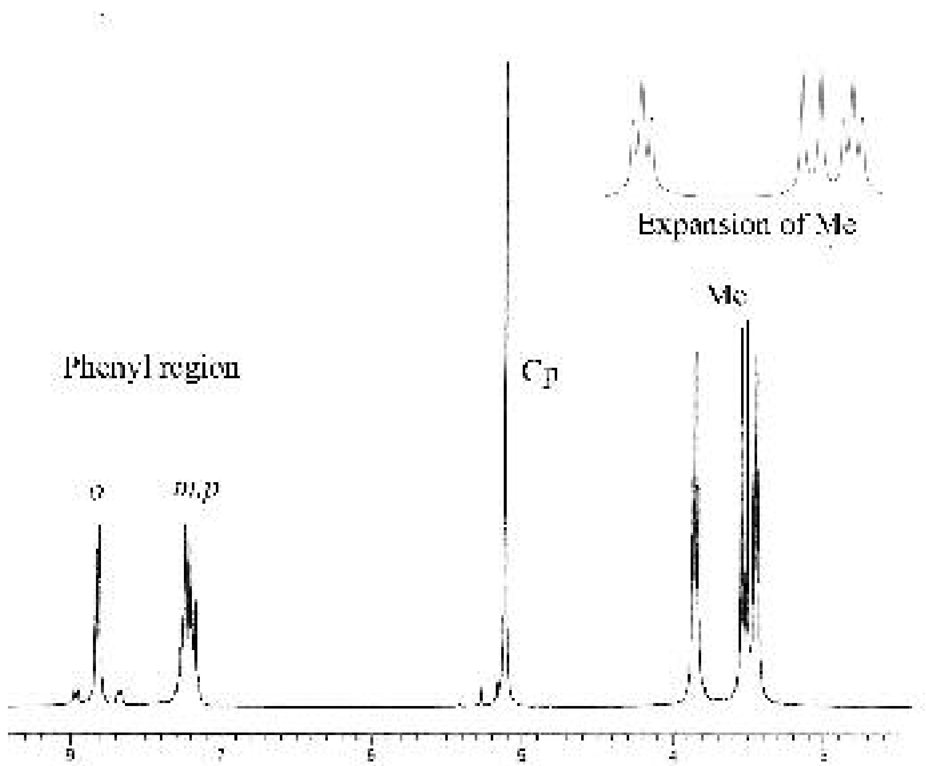
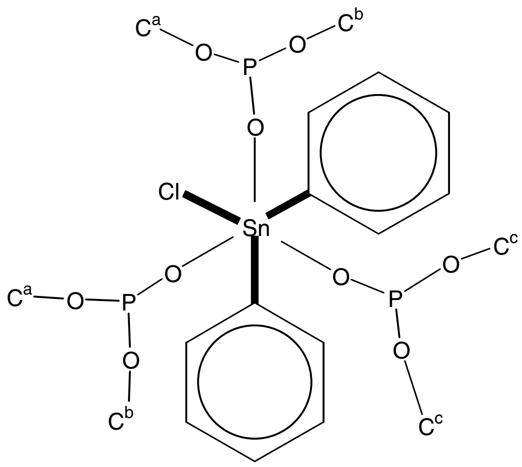


Figure 5. [1]H NMR spectrum of Ph_2ClSnL^{Me}.



(14)

The three methyl signals can be explained with the help of **14**. This shows a projection of the molecule, indicating the three distinct methyl groups, marked as C_a, C_b, and C_c. C_a and C_b, are on phosphorus *trans* to phenyl groups, and these show two similar triplets, with virtual coupling to two equivalent P nuclei in an $A_{12}X_2$ spin system. The remaining, C_c, only shows a doublet, coupling to one P nucleus, in an A_6X spin system

Similarly the methyl signals in the ^{13}C NMR spectrum of Ph_2ClSnL^{Me} (**4**) show two multiplets, the one at 52.6 ppm ($^2J_{P\text{-}C}$ = 4.6 and 4.4 Hz), twice the intensity of the other at 53.7 ppm ($^2J_{P\text{-}C}$ = 4.5 and 4.2 Hz). The coupling is caused by two equivalent and one unique phosphorus atoms, but the pattern has second order characteristics as the intensities of the lines are not as predicted in simple terms.

The same pattern essentially repeats for the other Ph compound with C_s symmetry, $PhCl_2SnL^{Me}$ (**5**) where the ^1H and ^{13}C spectra again gave three multiplets for the OMe groups, but with more pronounced second-order affects which led to distorted shapes.

The phenyl-tin analogues formed with the L^{Et} ligand showed essentially the same type of behaviour for the OR groups on the ligand, other than the obvious extra complexity arising the Et *vs* the Me group.

For the methyl-tin compounds the ligand signals are moderated by more rapid fluxionality. Thus for Me_2ClSnL^{Me} (**8**) the OCH_3 signals appear as a quartet from three pseudo-equivalent phosphorus atoms, while the ^{13}C shows a broad unresolved single peak for the OCH_3 groups. The methyl groups on the tin atom show a resolved quartet in the ^{13}C but no phosphorus coupling could be resolved for the ^1H signal at 0.43 ppm, which is shifted considerably upfield from that in Me_2SnCl_2 at 1.21 ppm.

For $MeCl_2SnL^{Me}$ (**9**) the lower symmetry is more apparent, with two distorted multiplets (2:1 intensity ratio) for the ^1H and three separate complex multiplets for the ^{13}C for the ligand OCH_3 groups, as seen for the Ph_2ClSnL^{Me} compound. The ^{13}C of the tin-methyl is still a second-order quartet.

For the ^{1}H and ^{13}C spectra of all of the compounds, varying the temperature between 300 K and 220 K had little affect on the patterns observed, despite the evidence from the ^{119}Sn spectra (discussed below) that the molecules are fluxional at ambient temperature.

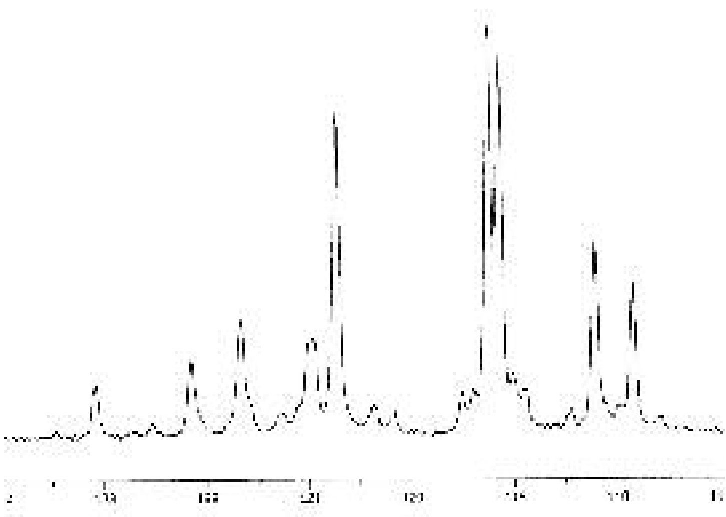
3.3.2. ^{31}P NMR Spectra

The ^{31}P NMR signal for Ph_3SnL^{Me} was a single broad peak at 117 ppm.

This is only slightly shifted from the free ligand at 112 ppm. On cooling to 220 K, coupling could be resolved from tin satellites, $^{2}J_{Sn\text{-}P}$= 77 Hz. Similarly for Cl_3SnL^{Me} there was a single broad peak at room temperature, but cooling to resolve any coupling was precluded by poor solubility.

For Ph_2ClSnL^{Me} (**4**) at 300 K the ^{31}P NMR spectrum is difficult to interpret, because of the broad line-width of the pattern. At 220 K, the line-width is reduced, allowing the signal to be resolved (Fig 6). Processing with resolution enhancement (LB = -5 Hz, and GB = 0.3 Hz) facilitated the interpretation of the observed multiplicity. It was assessed as a heavily distorted second order system, which can be described as an ABC pattern, where B and C are only slightly different in chemical environment.

Figure 6. ^{31}P spectrum at 220 K of Ph_2ClSnL^{Me}.

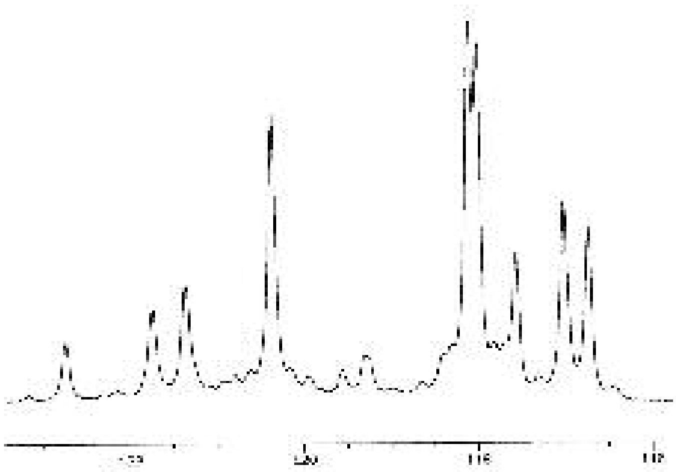


The A part of the signal at 122 ppm shows coupling with B, J_{AB} = 172 Hz, which then shows coupling to C, J_{AC} = 113 Hz to give a heavily distorted doublet of doublets.

The part of the signal which is closer to the B and C parts of the signal was increased in intensity as would be expected in a second order system. This hinders immediate recognition of the multiplicity. The B part of the signal, at 119 ppm, shows coupling to A as a doublet J_{AB} = 172 Hz, and the C part of the signal, also at 119 ppm, also shows coupling to A as a doublet J_{AC} = 113 Hz, both of which are distorted and close to overlapping. J_{BC} coupling is too small to show any resolvable features.

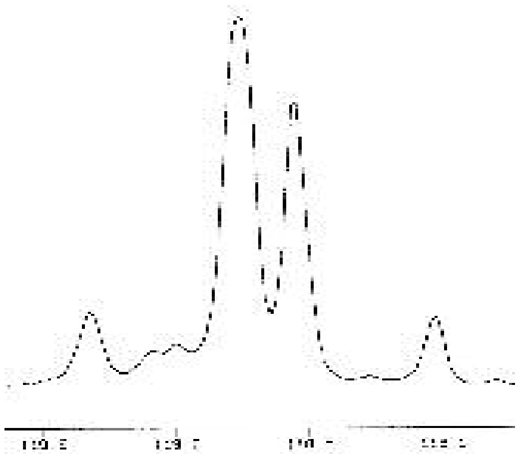
The ^{31}P NMR spectrum for Me_2ClSnL^{Me} was a broad multiplet at 300 K, but on cooling to 220 K a similar complex pattern as was seen for Ph_2ClSnL^{Me} could be distinguished and interpreted the same way. The spectrum recorded here (Fig 7) is more complex than that reported previously for the same compound, where it was recorded in CD_2Cl_2 at 202 K and was analysed as an AB_2 spin system with δ_A = 119, δ_B = 117, J_{AB} = 146 Hz.[12]

Figure 7. ^{31}P NMR spectrum of Me_2ClSnL^{Me} at 220 K.



The ^{31}P spectrum for $PhSnCl_2L^{Me}$ was a very broad single peak at 300 K. On cooling to 220 K, the signal resolved into a complicated multiplet (Fig 8) which could not be fully analysed.

Figure 8. ^{31}P NMR spectrum of $PhCl_2SnL^{Me}$ at 220 K



Similarly for $MeCl_2SnL^{Me}$ the ^{31}P spectrum at 300 K was a single broad peak, which at 220 K gave a similar pattern to that of the $PhCl_2SnL^{Me}$ analogue.

3.3.3. ^{119}Sn NMR Spectra.

The ^{119}Sn NMR shifts gave a perfectly linear relationship to the number of Ph groups for both of the $Ph_{3-n}Cl_nSnL^R$ series (R = Me, Et). This linear relationship is unusual, as the four-coordinate $Ph_{4-n}SnCl_n$ series does not give a simple correlation.[21] However the six-coordinate tin pyrazolyl-borate series, $R_{3-n}Cl_nSn[(pz)_3BH]$ also showed linear plots.[7]

Although the chemical shifts were straightforward, the actual patterns were complex.

The ^{119}Sn spectrum for Ph_3SnL^{Me} at 300 K showed the expected quartet at -408 ppm, with AX_3 coupling to three equivalent phosphorus nuclei. The coupling observed was $^2J_{Sn-P}$= 82 Hz. At 220 K the quartet was more clearly resolved, and the coupling was $^2J_{Sn-P}$= 79 Hz which matches the coupling for the tin satellites in the ^{31}P spectrum. Ph_3SnL^{Et} also gave the predicted quartet, at -413 ppm, slightly shifted from that of Ph_3SnL^{Me} at -408 ppm but with the same coupling constant $^2J_{Sn-P}$ = 82 Hz.

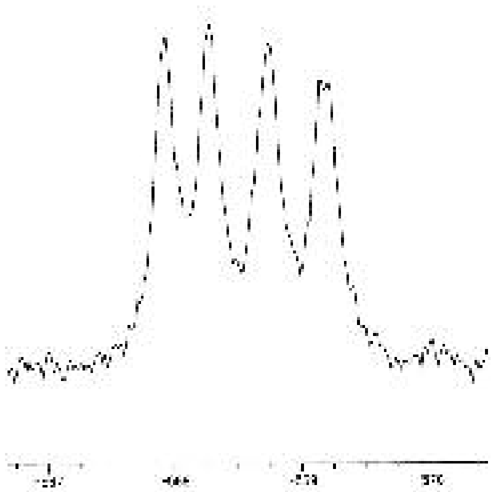
For Cl_3SnL^{Me} where the same pattern was expected there was only a single broad peak at 300 K. However at 220 K the signal appeared as a poorly resolved quartet, δ -661 ppm, $^2J_{Sn\text{-}P}$ = 16 Hz. Further analysis was hampered by low solubility.

For Ph_2ClSnL^{Me} the ^{119}Sn NMR spectrum at 300 K is a first order doublet ($J_{Sn\text{-}P}$= 94 Hz) of triplets ($J_{Sn\text{-}P}$ = 62 Hz). This can be described as an AX_2Y system where A is tin and X and Y are phosphorus. There was little change between this and the spectrum run at 220 K.

For Me_2ClSnL^{Me} the ^{119}Sn spectra at 300 K showed an apparent quartet which was resolved as the temperature was lowered into a doublet of triplets as seen for Ph_2ClSnL^{Me}. The temperature at which the pattern could be first resolved was 260 K. Clearly the methyl example is more fluxional than the Ph analogue, but otherwise analysis is straightforward. The Sn-P coupling constants differ between the Ph and Me examples, with Me_2ClSnL^{Me} having 105 Hz and 75 Hz and Ph_2ClSnL^{Me} having 94 Hz, and 62 Hz respectively.

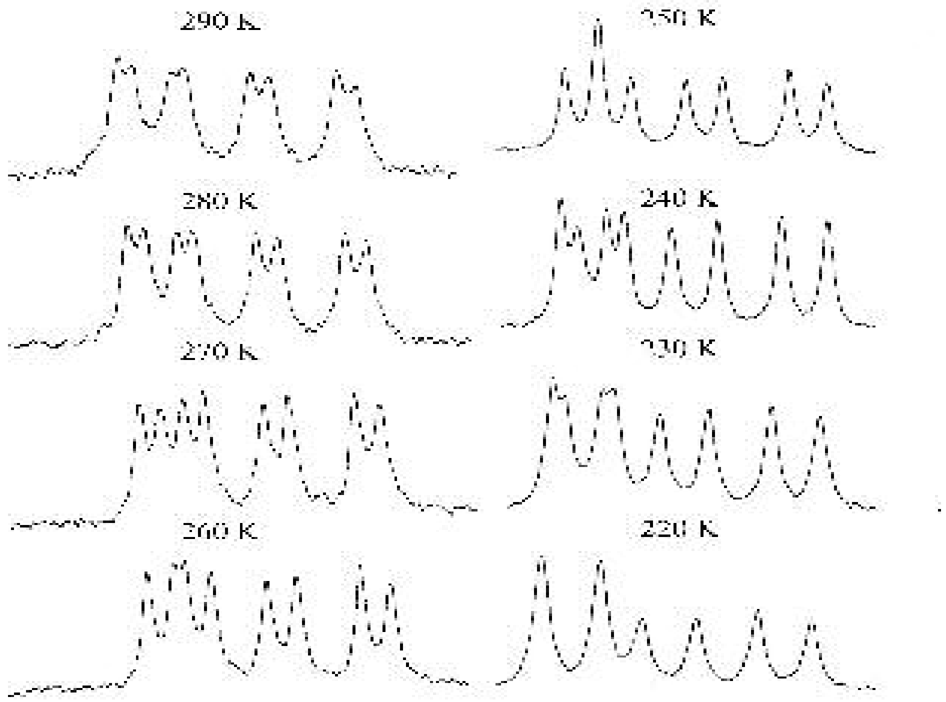
In contrast, the ^{119}Sn spectra for $PhCl_2SnL^{Me}$ were much more complex. At 300 K four equally sized peaks were found (Fig 9), centred at -568.5 ppm.

Figure 9. ^{119}Sn NMR spectrum of $PhSnCl_2L^{Me}$ at 300 K



As the temperature was lowered, to 220 K, the spectra varied before reaching what appeared to be three doublets, with the intensities in the ratio 2:1:1 (Fig 10).

Figure 10. ^{119}Sn NMR spectra of $PhSnCl_2L^{Me}$, from 290 K to 220 K

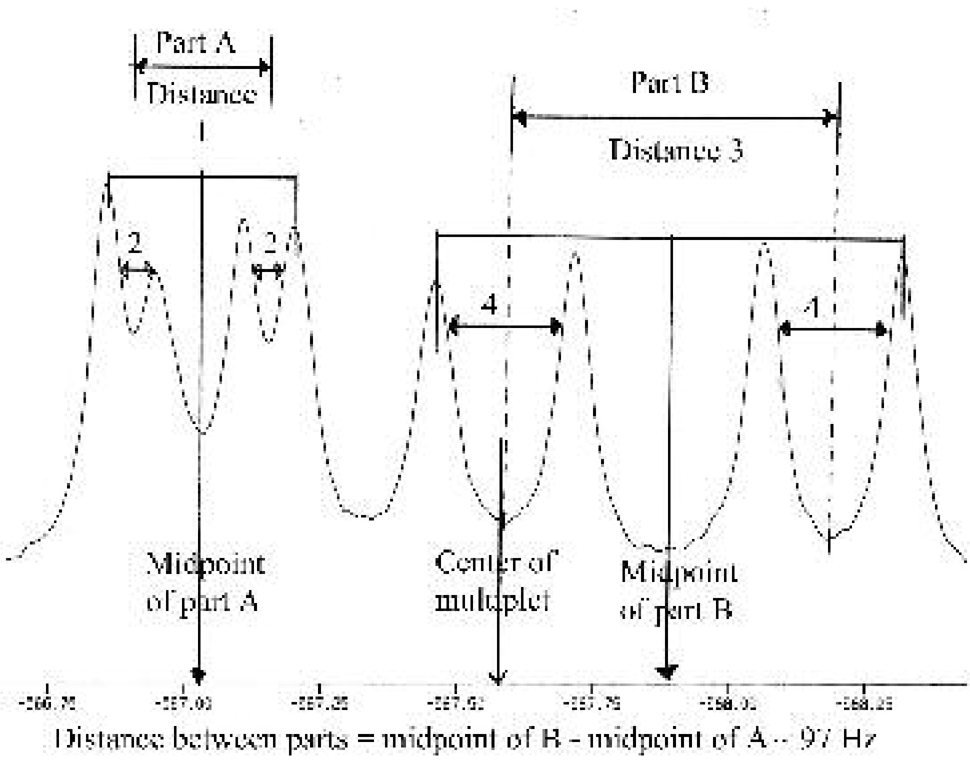


The apparent splitting parameters are listed in Table 3, as defined in Figure 11.

Table 3. Variation in parameters from the ^{119}Sn NMR variable temperature spectra of $PhCl_2SnL^{Me}$

Temp. (K)	Distance 1 (Hz)	Distance 2 (Hz)	Distance 3 (Hz)	Distance 4 (Hz)
300	39.0	(nil)	52.4	(nil)
290	33.8	8.2	56.1	12.0
280	31.8	10.2	58.2	13.7
270	28.8	13.5	59.9	15.9
260	24.1	17.4	61.5	19.7
250	20.3	20.3	63.4	22.9
240	28.3	10.2	67.6	28.4
230	30.4	6.7	68.3	29.8
220	36.0	nil	70.8	33.1

Figure 11. Interpretation of the ^{119}Sn NMR spectrum of $PhCl_2SnL^{Me}$



A full explanation of the spectral behavior was not found. Very similar patterns were repeated for $PhCl_2SnL^{Et}$ and $MeCl_2SnL^{Me}$, which shows the variations are reproducible for all of the $R'Cl_2SnL^R$ compounds.

The complex $PhMeClSnL^{Me}$ (**10**) was prepared to perhaps aid the understanding of the $PhSnCl_2L^{Me}$ and $MeSnCl_2L^{Me}$ spectra. It should be a chiral compound, with three distinct phosphorus environments leading to a ^{119}Sn NMR spectrum which should be a doublet of doublets of doublets, in an AXYZ spin system.

At 300 K, the ^{119}Sn spectra of this compound showed a complex multiplet, centered at -417.2 ppm. However, on cooling to 220 K the expected doublet of doublets of doublets was resolved, as eight lines of equal intensity. $^2J_{Sn\text{-}P\,(A)}$, $^2J_{Sn\text{-}P\,(B)}$ and $^2J_{Sn\text{-}P\,(C)}$ were 81.2 Hz, 57.6 Hz and 100.0 Hz respectively.

4. Conclusion

The Klaui ligands are excellent for tri-coordination to organotin(IV) centres, conferring six-coordination with even the least Lewis-acidic tin atoms. Resulting compounds are stable, crystalline substances that are essentially air-stable – certainly more so than the corresponding complexes with the pyrazolylborate ligands. The symmetry of the resulting complexes leads to complex NMR, further affected by room temperature fluxionality.

5. Supplementary material.

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos 292221-292224. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Rd., Cambridge CB2 1EZ, UK (e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

Full Supplementary Tables of NMR data and copies of variable temperature NMR spectra can be obtained from the authors (b.nicholson@waikato.ac.nz).

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Table 1

Crystal data and refinement details.

	$Cl_3SnL^{Me}.CH_2Cl_2$ (6).CH_2Cl_2	**$PhCl_2SnL^{Me}.CH_2Cl_2$ (5).CH_2Cl_2**	**Ph_2ClSnL^{Et} (12)**	**Ph_3SnL^{Me} (3)**
Formula	$C_{12}H_{25}Cl_5CoO_9P_3Sn$.	$C_{18}H_{30}Cl_4CoO_9P_3Sn$	$C_{29}H_{45}ClCoO_9P_3Sn$	$C_{29}H_{38}CoO_9P_3Sn$
M_r	761.10	802.75	843.63	801.12
T(K)	203	168	168	200
crystal system	orthorhombic	triclinic	triclinic	monoclinic
space group	Pnma	P-1	P-1	$P2_1/c$
a (Å)	17.6545(2)	8.677(4)	10.046(2)	19.301(1)
b(Å)	12.2563(2)	9.786(5)	11.615(3)	20.636(1)
c(Å)	12.1295(2)	18.524(9)	17.083(4)	18.565(1)
α(deg)	90	75.037(6)	94.972(3)	90
β(deg)	90	87.385(6)	90.299(3)	117.954(1)
γ(deg)	90	67.783(6)	114.862(3)	90
V($Å^3$)	2624.57(7)	1404.3(11)	1799.9(7)	6531.6(1)
Z	4	2	2	8
ρ(g cm^{-3})	1.926	1.898	1.557	1.629
μ(mm^{-1})	2.31	2.08	1.41	1.47
Size (mm^3)	0.55x0.50x0.38	0.65x0.50x0.22	0.42x0.25x0.15	0.40x0.17x0.10
F(000)	1504	800	860	3248
$θ_{max}$(deg)	27.6	26.5	26.5	27.5
Reflns collected	26033	17794	23586	39294
Unique reflns	3131	5502	7302	14254
Parameters	178	331	403	803
R_1 [I > 2σ(I)]	0.0952	0.0484	0.0216	0.0322
wR_2 (all data)	0.2388	0.1073	0.0556	0.0773
GOF on F^2	1.309	1.171	1.033	1.071

Table 2
Selected bond parameters for complexes

	Ph_3SnL^{Me}(**3**)	Ph_2ClSnL^{Et}(**12**)	$PhCl_2SnL^{Me}$(**5**)	Cl_3SnL^{Me}(**6**)
Bond lengths (Å)				
Sn-C	2.174(3)	2.170(2)	2.111(5)	
Sn-Cl		2.452(1)	2.385(1)	2.368(5)
Sn-O(*trans* to C)	2.239(2)	2.157(2)	2.044(4)	
Sn-O(*trans* to Cl)		2.181(1)	2.099(3)	2.074(12)
P=O	1.512(2)	1.517(1)	1.498(4)	1.490(13)
Bond angles (degrees)				
O-Sn-O	79.4(1)	82.30(5)	84.9(1)	86.6(1)
C-Sn-C	103.3(1)	104.3(1)		
C-Sn-Cl		98.07(5)	97.4(1)	
Cl-Sn-Cl			97.4(1)	95.0(2)

Captions to Figures

Figure 1. The structure of Ph_3SnL^{Me} (**3**). Bond parameters include: Sn(1)-O(11) 2.213(2), Sn(1)-O(21) 2.248(2), Sn(1)-O(31) 2.229(2) Sn(1)-C(41) 2.172(3), Sn(1)-C(51) 2.177(3) Sn(1)-C(61) 2.174(3) Å, O-Sn-O (av.) 79.4(1)°, C-Sn-C (av.) 103.3(1)°.

Figure 2. The structure of Ph_2ClSnL^{Et} (**12**). Bond parameters include: Sn(1)-O(11) 2.156(1), Sn(1)-O(21) 2.182(2), Sn(1)-O(31) 2.159(1), Sn(1)-C(41) 2.170(2),Sn(1)-C(51) 2.170(2), Sn(1)-Cl(1) 2.4523(7) Å, O-Sn-O (av.) 82.3(1)°, C(41)-Sn-C(51) 104.3(1)°, C(41)-Sn-Cl(1) 98.14(5)°, C(51)-Sn-Cl(1) 98.01(5)°.

Figure 3. The structure of $PhCl_2SnL^{Me}$ (**5**). Bond parameters include: Sn(1)-O(11) 2.044(4), Sn(1)-O(21) 2.111(3), Sn(1)-O(31) 2.071(3), Sn(1)-C(41) 2.111(5), Sn(1)-Cl(1) 2.385(2 0, Sn(1)-Cl(2) 2.385(2) Å, O-Sn-O (av.) 84.9(1)°, Cl(1)-Sn-C(41) 99.3(1)°, Cl(2)-Sn-C(41) 95.5(1)°, Cl(1)-Sn-Cl(2) 97.40(5)°.

Figure 4. The structure of Cl_3SnL^{Me} (**6**). Bond parameters include: Sn(1)-O(1) 2.084(9), Sn(1)-O(2) 2.064(12), Sn(1)-Cl(1) 2.367(5), Sn(1)-Cl(2) 2.369(4) Å, O-Sn-O (av.) 86.6(2)°, Cl-Sn-Cl (av.) 95.0(2)°.

Figure 5. ^{1}H NMR spectrum of Ph_2ClSnL^{Me}.

Figure 6. ^{31}P spectrum of Ph_2ClSnL^{Me} at 220 K.

Figure 7. ^{31}P NMR spectrum of Me_2ClSnL^{Me} at 220 K.

Figure 8. ^{31}P NMR spectrum of $PhCl_2SnL^{Me}$ at 220 K

Figure 9. ^{119}Sn NMR spectrum of $PhCl_2SnL^{Me}$ at 300 K.

Figure 10. ^{119}Sn NMR spectra of $PhCl_2SnL^{Me}$, from 290 K to 220 K.

Figure 11. Interpretation of the ^{119}Sn NMR spectrum of $PhCl_2SnL^{Me}$

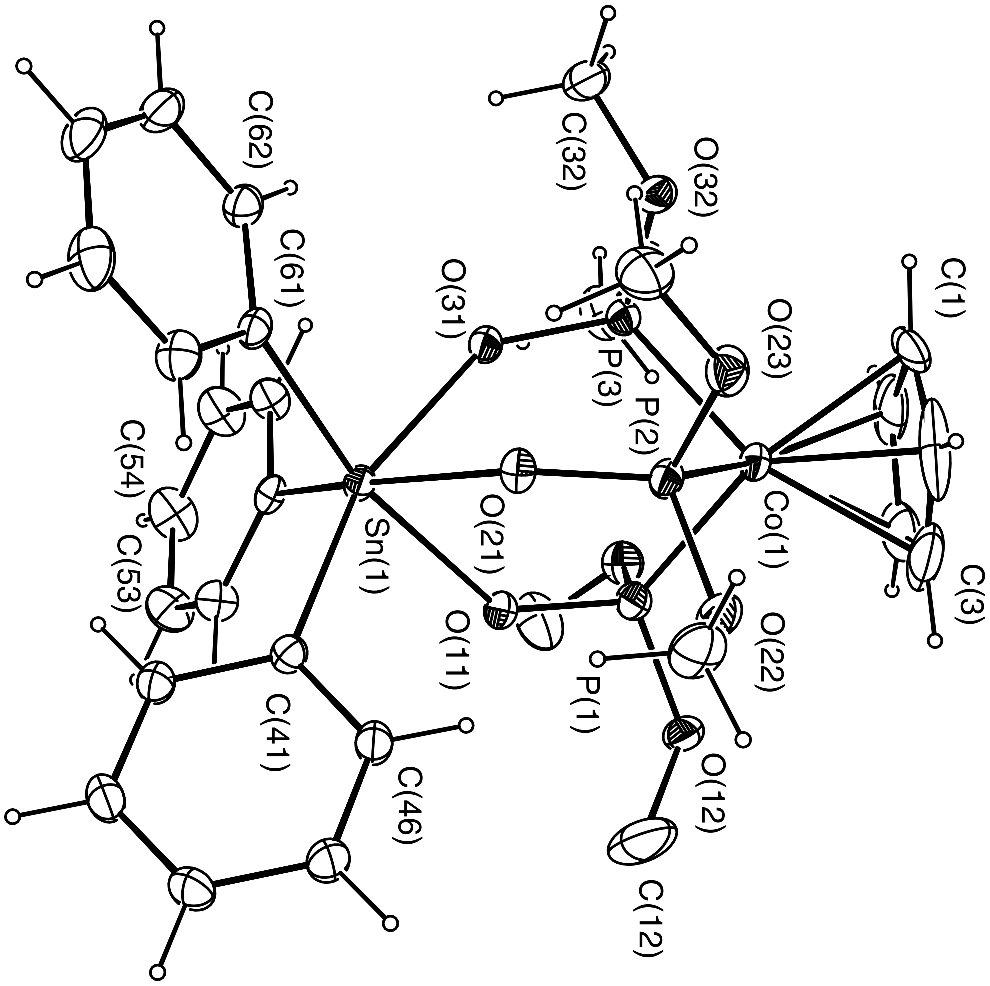

C(62)
C(32)
O(32)
C(61)
O(31)
O(23)
C(1)
P(3)
P(2)
C(54)
Sn(1)
O(21)
Co(1)
C(53)
C(3)
O(11)
O(22)
P(1)
C(41)
O(12)
C(46)
C(12)

Figure 1

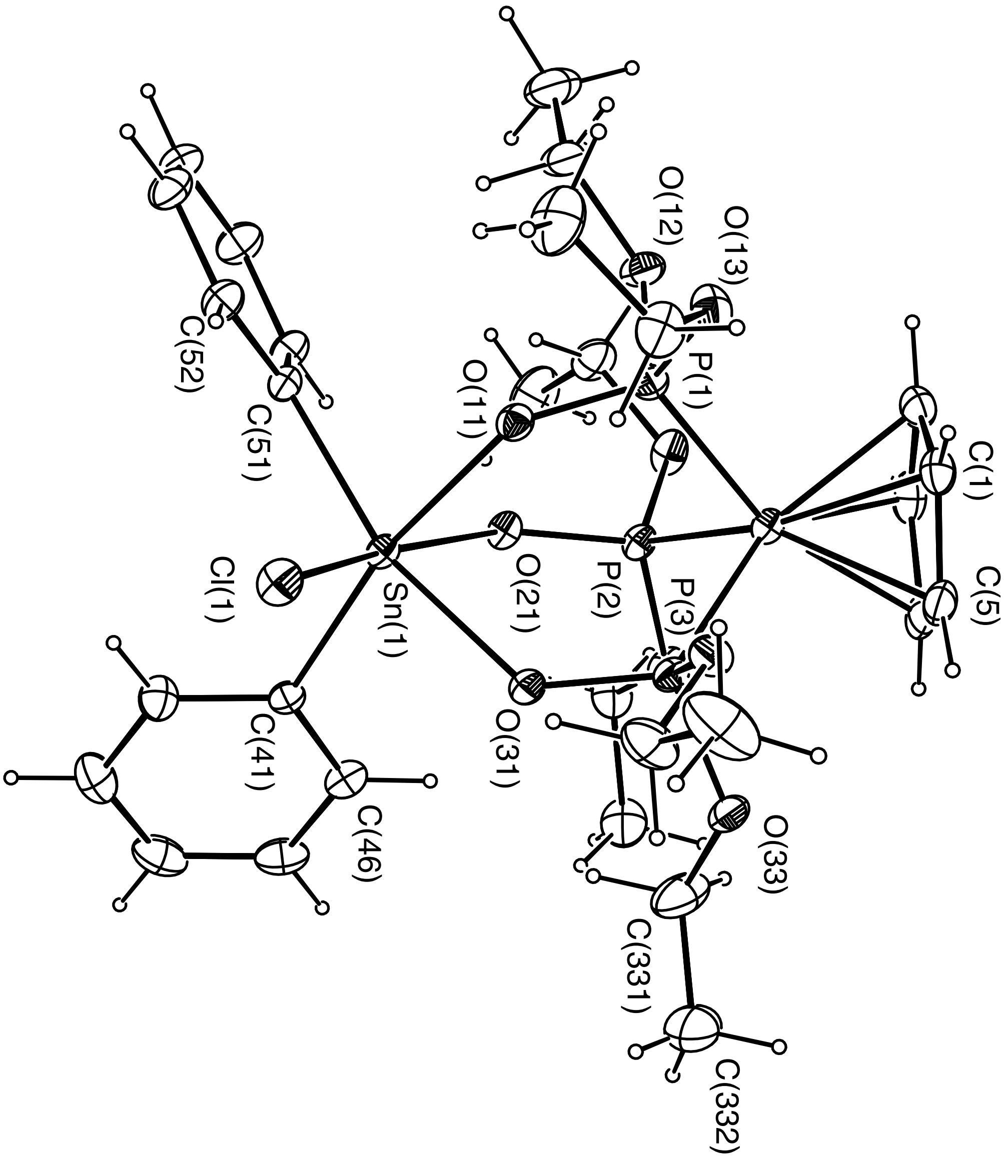

O(12)
O(13)
P(1)
C(1)
C(5)
C(52)
C(51)
O(11)
Cl(1)
Sn(1)
O(21)
P(2)
P(3)
C(41)
C(46)
O(31)
O(33)
C(331)
C(332)

Figure 2

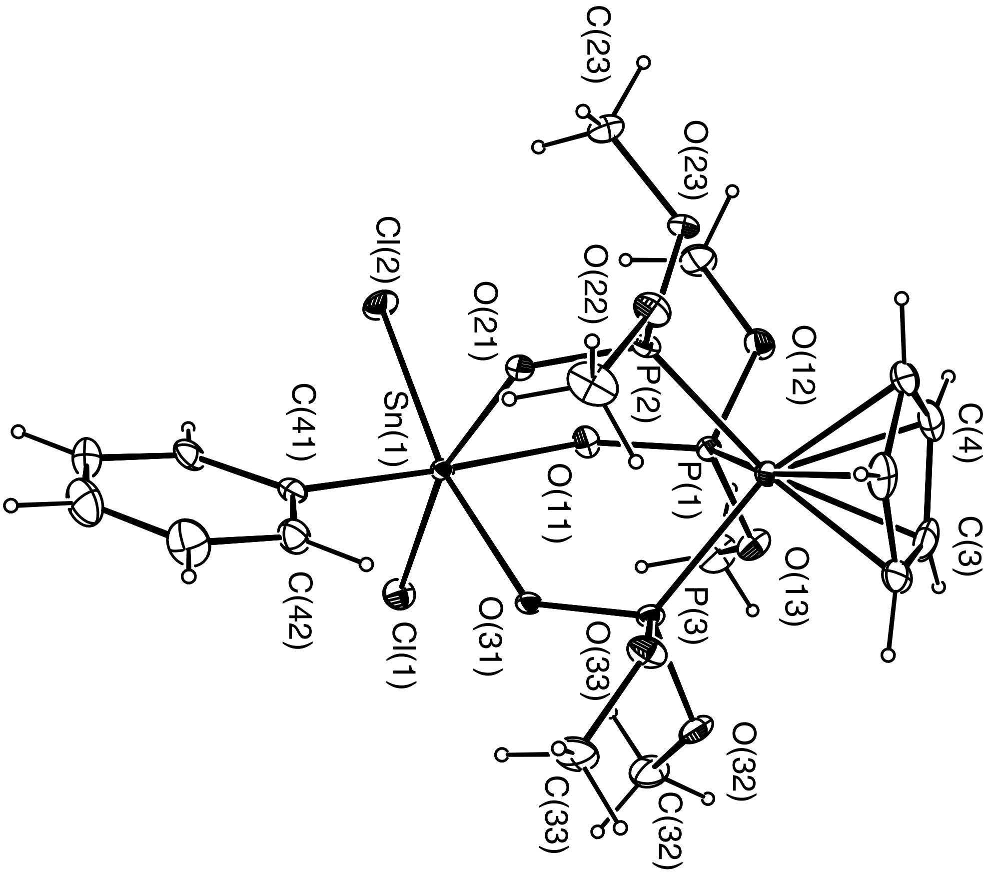
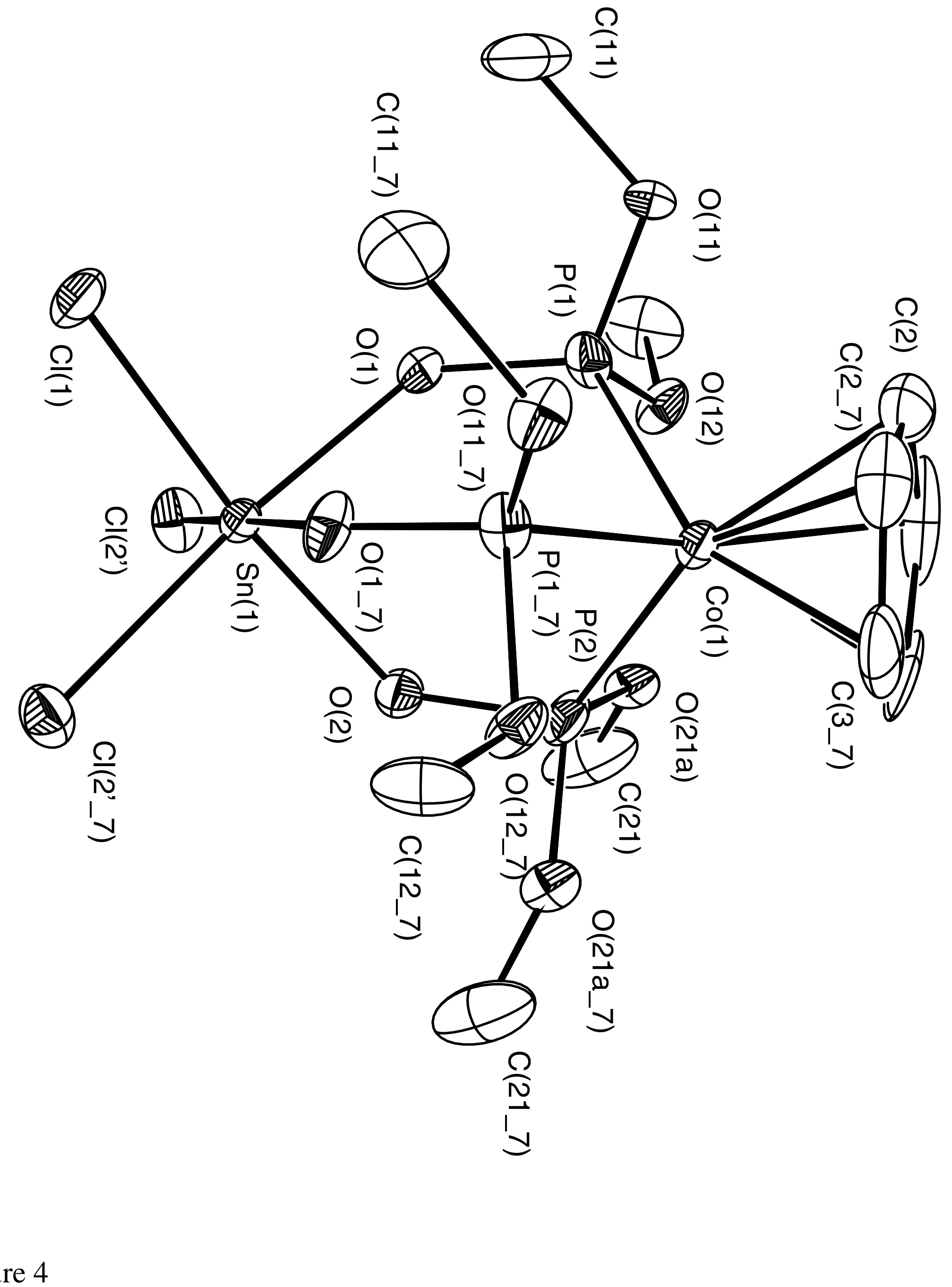

C(23)
O(23)
Cl(2)
O(22)
O(21)
P(2)
O(12)
Sn(1)
C(41)
C(4)
P(1)
O(11)
C(3)
O(13)
P(3)
C(42)
Cl(1)
O(31)
O(33)
O(32)
C(33)
C(32)

Figure 3



C(11)
C(11_7)
O(11)
P(1)
C(2)
C(2_7)
O(1)
O(12)
Cl(1)
O(11_7)
Cl(2')
Sn(1)
O(1_7)
P(1_7)
P(2)
Co(1)
O(2)
O(21a)
C(3_7)
Cl(2'_7)
O(12_7)
C(21)
C(12_7)
O(21a_7)
C(21_7)

Figure 4