

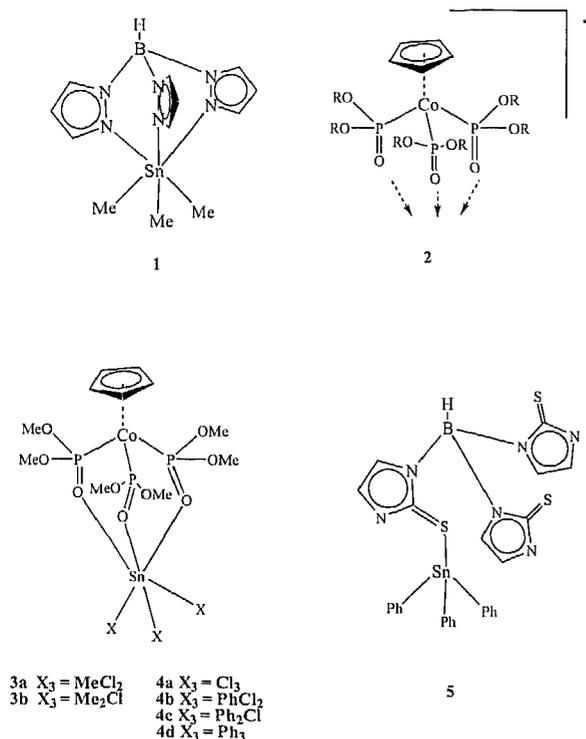
Novel Six-coordinate Aryl- and Alkyltin Complexes

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Introduction

Organo-tin compounds have wide applications as pesticides and as intermediates for organic synthesis.¹ They are invariably Sn(IV) derivatives and are generally four-coordinate.² The mixed organo/chloro compounds of the type R_nSnCl_{4-n} do however have the ability to expand their coordination numbers to five or six. This depends critically on the substituents - with four organic groups, R_4Sn , there is no tendency at all to coordinate extra ligands, while at the other extreme $SnCl_4$ readily forms six-coordinate $[SnCl_4L_2]$ complexes since the electronegative halo groups increase the Lewis acidity of the tin centre.



In a previous study³ it was shown that the complete series of six-coordinate methyl-tin-chloride complexes could be prepared using Trofimenko's tris(pyrazolyl)borate ligand,⁴ including the first example of a six-coordinate trimethyltin centre in $Me_3Sn[(pz)_3BH]$, as in 1.³ The strong tendency of the tris(pyrazolyl)borate ligand to act as a tridentate chelating ligand overcomes the reluctance of the Me_3Sn^+ centre to form three extra bonds.

Recently Klaui⁵ has introduced a new tridentate ligand, $[CpCo\{PO_3R_2\}_3]^-$, 2, (R = Me, Et) which is analogous to the Trofimenko one, but coordinates through three oxygen, rather than nitrogen, atoms. Although this ligand has been quite widely used in transition metal chemistry, there have been no previous reports in organo-tin chemistry, so we are currently investigating this aspect.

Results

The reactions between the Klaui ligand (as the sodium salt) and the organotin chlorides Me_nSnCl_{4-n} or Ph_nSnCl_{4-n} ($n = 0-$

3) generally proceeded smoothly in dichloromethane solution, with elimination of NaCl, to give the corresponding new complexes 3(a-b), 4(a-d). The only example for which no product has yet been isolated is with Me_3SnCl .

To prove that the tin atom was six-coordinate the single-crystal X-ray structures of the Ph_3Sn and the Cl_3Sn derivatives were determined. The structures are illustrated in Figures 1 and 2 and show that the tin is indeed fully complexed - the first example to be established for a Ph_3Sn^+ centre, with a C_3O_3 coordination sphere. As expected the tridentate ligand is more tightly bound for the trichloro example (Sn-O 2.08 Å) than for the triphenyl one (Sn-O 2.21 Å), reflecting the more acidic centre in the former. Other differences are illustrated by the Cl-Sn-Cl and O-Sn-O angles of 87° and 95° respectively for 4a and corresponding C-Sn-C and O-Sn-O angles of 104° and 79° for 4d. While the X-ray structural data is for the solid state only, NMR studies (see below) confirm that the six-coordination is maintained in solution.

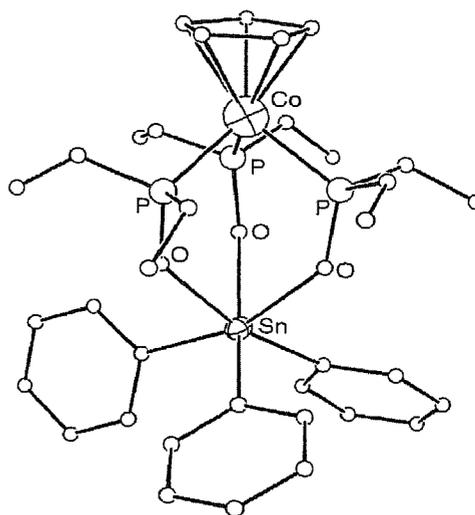


Figure 1. The structure of $[CpCo\{PO_3Me_2\}_3]SnPh_3$

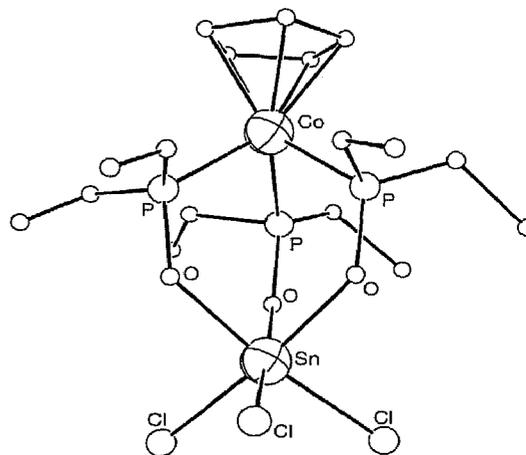


Figure 2. The structure of $[CpCo\{PO_3Me_2\}_3]SnCl_3$

It is interesting that the Ph_3Sn complex of the Klauai ligand formed straightforwardly, while the corresponding Me_3Sn one did not, since for the tris(pyrazolyl)borate system the reverse was found - $\text{Me}_3\text{Sn}\{(\text{pz})_3\text{BH}\}$ was readily isolated⁵ whereas $\text{Ph}_3\text{Sn}\{(\text{pz})_3\text{BH}\}$ has been reported to be unstable.⁶ Reasons for this difference are not yet apparent.

NMR Studies

The new complexes are rich in potential NMR information, with ^1H , ^{13}C , ^{31}P and ^{119}Sn nuclei amenable to study. The ^1H and ^{13}C spectra are complicated by virtual coupling arising from the high symmetry so that, for example, the signals for the Me groups in the $\text{Ph}_3\text{Sn}[\text{CpCo}\{\text{PO}_3\text{Me}_2\}_3]$ example show a complex splitting pattern to the three equivalent P nuclei.

The ^{119}Sn spectra are the most interesting, since the chemical shifts are characteristic of coordination number in solution, and provide information about the structural rigidity of the complexes. For the symmetrical $\text{X}_3\text{Sn}[\text{CpCo}\{\text{PO}_3\text{Me}_2\}_3]$ the ^{119}Sn signal is a quartet, arising from coupling to three equivalent phosphorus atoms, while for the unsymmetrical RCl_2Sn^+ or R_2ClSn^+ complexes the signals are more complicated, indicating some fluxionality. For all of the complexes the ^{119}Sn shifts lie in the -300 to -700 ppm region, where six-coordinate tin is expected, and furthermore they lie on a straight line when plotted against number of Cl groups on the tin (Figure 3). This shows the full series maintains in solution the six-coordination found crystallographically in the solid state.

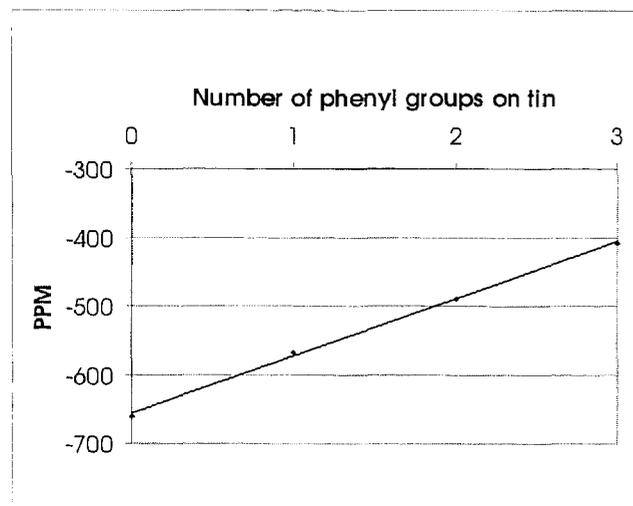


Figure 3. The ^{119}Sn chemical shift versus degree of phenyl substitution for $[\text{CpCo}\{\text{PO}_3\text{Me}_2\}_3]\text{SnX}_3$

Complexes With Tris(methimazolyl)borate Ligand

Another tridentate ligand related to the pyrazolyl-borate and Klauai ligands has been introduced very recently by Reglinski.⁷ This is the tris(methimazolyl)borate anion **5** which coordinates through three sulfur atoms. This is therefore a softer Lewis base than the N- or O-donor analogues, so might be expected to form stable complexes with the relatively soft organotin centres. However our preliminary results show that with Ph_3SnCl , the complex that forms is four-coordinate with only one of the sulfur atoms attached to tin and the other two dangling. This is illustrated in Figure 4. ^{119}Sn NMR for this compound gives a signal at -58 ppm, which shows

that four-coordination is maintained in solution. This is a unique example for this ligand since all other complexes reported so far involve tridentate coordination. Further work is needed to understand the reasons for this behaviour.

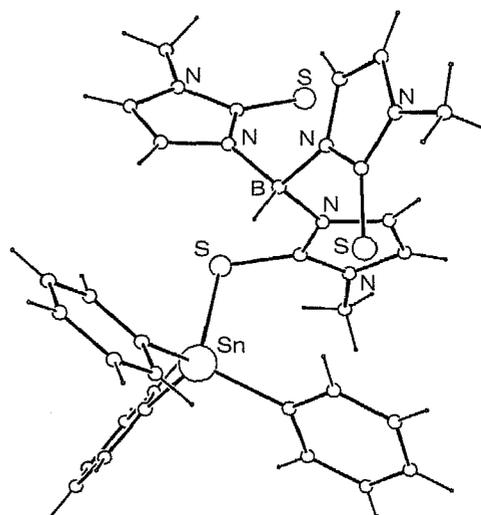


Figure 4. The structure of $[\text{HB}\{\text{C}_3\text{N}_2\text{S}\}_3]\text{SnPh}_3$

Conclusions

The Klauai ligand is clearly useful for enforcing high coordination numbers on alkyl- and aryltin centres. It behaves differently from the pyrazolylborate ligands and so extends the range of compounds known. The related tris(methimazolyl)borate ligands however seem less powerful in encouraging higher coordination in tin chemistry. The three mono-negative tridentate ligands have complementary roles in their coordination chemistry of main group elements.

Acknowledgements

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