Journal of Organometallic Chemistry, 87 (1975) 67–82

THERMODYNAMICS OF METAL–LIGAND BOND FORMATION

XVI*. BASE ADDUCTS OF SOME ORGANOTIN COMPOUNDS

Y. FARHANGI** and D.P. GRADDON***

School of Chemistry, University of New South Wales, Kensington, N.S.W. 2033 (Australia)

(Received September 20th, 1974)

Summary

Thermodynamic data have been obtained by calorimetric titration in benzene solution at 30° for reaction of organotin compounds with Lewis bases; data are reported for forty acid/base systems.

Ph_3SnCl forms 1/1 adducts of low stability with pyridine (py) or 4-methylpyridine (4-mepy). Ph_2SnCl_2, Me_2SnCl_2, Bu_2SnCl_2 and $Bu_2Sn(NCS)_2$ form simultaneously 1/1 and 1/2 adducts with py or 4-mepy and 1/1 adducts with 2,2′-bipyridine or 1,10-phenanthroline (phen); the enthalpies of formation of the phen adducts are similar to those of 1/2 adducts with 4-mepy. With $BuSnCl_3$ and $PhSnCl_3$ it was not possible to obtain data for each step in addition of pyridine or 4-mepy. Adduct stabilities increase with increasing chloride substitution and in the order Bu < Me < Ph; adducts of $Bu_2Sn(NCS)_2$ are more stable than those of Bu_2SnCl_2.

Tributylphosphine does not react with Ph_3SnCl but gives 1/1 adducts with the other tin compounds; only $PhSnCl_3$ adds a second molecule of this base. The 1/1 adducts are more stable than those with heterocyclic bases. Tributylamine brings about disproportionation of the compounds R_2SnX_2 to R_4Sn and SnX_4NBu_3.

Introduction

During the last ten years there has been considerable interest in the behav-

---

[*] For part XV see ref. 1.

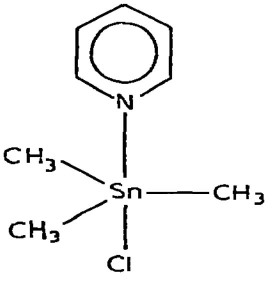
[**] Department of Chemistry, Faculty of Science, University of Tabriz, Tabriz, Iran.

[***] For correspondence.

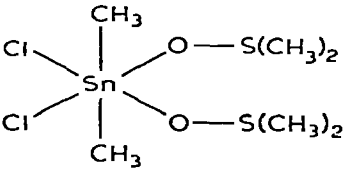
iour of tin(IV) halides and organotin halides as Lewis acids. While the tin tetraalkyls and tetraaryls show no evidence of Lewis acidity the tin(IV) halides are strong Lewis acids, forming 1/1 and 1/2 adducts with a wide variety of bases. In solution in non-donor solvents tin(IV) chloride forms very stable 1/2 adducts with cyclic ethers such as tetrahydrofuran [2]: in benzene solution at 25° the enthalpies of adduct formation ($-\Delta H$) are about 100-120 kJ mol^{-1} with adduct formation constants of 10^4-10^8 l^2 mol^{-2}. Esters and ketones form less stable adducts and two steps can be distinguished, corresponding to successive formation of 1/1 and 1/2 adducts [3]; the enthalpies of adduct formation are about 45 kJ mol^{-1} for the addition of each molecule of base, but the first formation constant is rather larger than the second: K_1 about 20-80, K_2 about 5-25 l mol^{-1}. Nitriles and some other ketones and esters form only 1/1 adducts [4] with enthalpies of formation of 30-60 kJ mol^{-1} and K between 3-16 l mol^{-1} in benzene solution at 25°. Solid 1/2 adducts have been isolated with unidentate heterocyclic bases and 1/1 adducts with bidentate bases [5, 6].

The organotin halides, R_nSnX_{4-n}, are intermediate in Lewis acidity between R_4Sn and SnX_4, the acidity generally increasing as the proportion of halide increases. Me_3SnCl forms a 1/1 adduct with pyridine which has been shown by X-ray analysis [7] to have trigonal-bipyramidal stereochemistry with *trans*, apical N and Cl atoms, the tin atom being 5-coordinate (Structure I). Equilibrium studies in carbon tetrachloride solution at 26° show that Me_3SnCl is only a weak Lewis acid [8, 9]: the formation constants for 1/1 adducts with a variety of bases lie between 0.4 and 10 l mol^{-1} with enthalpies of formation from 25-40 kJ mol^{-1}.

Solid 1/2 adducts have been isolated of the halides R_2SnCl_2 with unidentate heterocyclic bases and dimethyl sulphoxide, as have 1/1 adducts with 2,2'-bipyridine and 1,10-phenanthroline. Mössbauer, dipole moment and nuclear quadrupole studies of the adducts $R_2SnCl_2B_2$ (B = base) show that the R groups are *trans* and the Cl atoms *cis* in octahedral complexes [10-12] and the two *cis* base molecules may be replaced by one molecule of a bidentate base. Similar results are found [13, 14] for the thiocyanate complexes $R_2Sn(NCS)_2$(bidentate base). These results are supported by the crystal structure determination [15] of the adduct with dimethyl sulphoxide $Me_2SnCl_2(dmso)_2$ (Structure II). In the 1/1 adduct of $Me_2Sn(NCS)_2$ with 2,6,2',2''-terpyridine the molecule has pentagonal-bipyramidal stereochemistry, the tin atom being surrounded by five coplanar nitrogen atoms and two *trans*, apical methyl groups [16].



(I)



(II)

Few equilibrium studies have been made on these systems. The formation of 1/1 adducts of organotin chlorides with 2,2'-bipyridine in acetonitrile solution at 25° occurs with enthalpies of adduct formation of about 50 kJ mol^{-1} and formation constants between 10^3 and 10^4 l mol^{-1}, but there is some uncertainty of the extent to which the solvent may be coordinated, as it certainly is in acetonitrile solutions of $SnCl_4$ [17]. In benzene solution data have been obtained [18] for the addition of 2,2'-bipyridine to Oct_2SnCl_2, $Oct_2Sn(NCS)_2$ and $Bu_2Sn(NCS)_2$ at 30° and these results are discussed in detail below. It has also been shown [19] that various organotin halides form adducts of low stability with aromatic amines in ether solution.

This paper reports thermodynamic data, obtained by calorimetric titration in benzene solution at 30°, for the reaction of the tin compounds Ph_3SnCl, Ph_2SnCl_2, Me_2SnCl_2, Bu_2SnCl_2, $Bu_2Sn(NCS)_2$, $BuSnCl_3$ and $PhSnCl_3$ with unidentate and bidentate heterocyclic bases; also with tributylphosphine, comparison of which with the nitrogen donors allows some assessment of the hard/soft character of the tin compounds as Lewis acids; also with tributylamine, which is shown to induce disproportionation in the tin compounds.

Experimental

Materials

Organotin chlorides were obtained from Research Organic/Inorganic Chemical Corp., Sun Valley, California and purified by crystallisation from ethanol or distillation under reduced pressure; purity was checked by elemental analysis for carbon and hydrogen. $Bu_2Sn(NCS)_2$ was prepared from Bu_2SnCl_2 and potassium thiocyanate by a standard method [20], crystallised from ethanol and the purity checked by analysis for carbon, hydrogen and nitrogen.

Pyridine was purified by heating under reflux with potassium permanganate before distillation. 4-Methylpyridine, tributylphosphine and tributylamine were purified by distillation. 2,2'-Bipyridine and 1,10-phenanthroline hydrate were crystallised from ethanol. Merck chromatographic grade 2-methylpyridine was used without further purification, apart from drying. All liquid nitrogeneous bases were dried over solid anhydrous potassium carbonate.

Benzene for use as solvent was purified by freezing, distilling and dried over calcium hydride.

Calorimetry

Calorimetric titrations in benzene solution were carried out in an LKB 8700-2 titration calorimeter. Details of the technique used have been described previously [21]. Briefly, successive additions of liquid base or benzene solution of base were made to 100 ml of a benzene solution of the tin compound and the heat change measured after each addition of base. The enthalpy of reaction was calculated from the extrapolated, integrated heat of reaction after correcting for dilution effects (Q_∞). The adduct formation constant (K) was then calculated at each point in the titration and the value of Q_∞ refined to give the most consistent values of K. In reactions of stoichiometry 1/1 the optimum range of formation constant is $10 < K < 1000$ within which the standard deviation of K in a single titration is about ± 5%, rising when $K > 1000$ until the limit of measurement of about 10^5. Within the optimum range of K the enthalpy is reproducible within about ± 2%, but the accuracy of ΔH becomes less as K becomes smaller and measurement of ΔH becomes unreliable when $K < 1$.

In the tables of results all data are the average of at least three titrations. Uncertainties given for K are the sum of the mean deviation from different titrations and the average standard deviation in each titration; uncertainties given for ΔH are mean deviations; uncertainties in ΔG and ΔS are derived.

In many of these systems the calorimetric data could not be fitted assuming simple 1/1 or 1/2 equilibria. In these cases, where it is known from other evidence that both 1/1 and 1/2 adducts are likely to be formed, the titration data were fitted by assuming both adducts were formed simultaneously and that the equilibrium system could be described by the four parameters K_1, K_2, ΔH_1 and ΔH_2. The values of these parameters were obtained by trial and error and refined by variation of individual values of K by ± 10%. In all these systems the values of K_1 and K_2 were of the same order of magnitude (except for some thiocyanates) and the fitting of computed curves to experimental data was sufficiently sensitive to allow assessment of uncertainties in each formation constant of about ± 20% and about ± 20% in individual values of the two enthalpies; uncertainties in the overall enthalpy, ΔH_{1+2}, were smaller, typically less than ± 10%. In one case where the individual values of K_1 and K_2 were both < 10 the uncertainties are larger and even the overall enthalpy of reaction is imprecise because the reaction only proceeds about two-thirds to completion under the experimental conditions. With the strongest Lewis acids, $BuSnCl_3$ and $PhSnCl_3$ individual values of K_1 and K_2 were too large to be determined and only the overall enthalpy could be obtained.

Results and discussion

Tin compounds R_3SnCl

Attempts to carry out calorimetric titrations of tributyltin chloride with a wide range of bases with N, P or O donors were unsuccessful; unless the enthalpies of formation of adducts of these bases are quite unusually small (less than 5 kJ mol^{-1}), this shows that these adducts are of low stability, $K < 1$. A value of $K = 1.9$ l mol^{-1} has previously been obtained spectrophotometrically [9] for the formation of the adduct of pyridine with Me_3SnCl in carbon tetrachloride solution; formation constants of Lewis acid/base compounds are usually fairly similar in benzene and carbon tetrachloride and adducts of Bu_2SnCl_2 are less stable than those of Me_2SnCl_2 (below), so that a value of $K < 1$ for adducts of Bu_3SnCl is likely and this falls below the limits of our measurement technique.

Triphenyltin chloride formed 1/1 adducts of low stability with pyridine and 4-methylpyridine; details and thermodynamic data are given in Table 1. No evidence was found for the formation of adducts in benzene solution by Ph_3SnCl with 2-methylpyridine, 2,2'-bipyridine, 1,10-phenanthroline, tributylphosphine or tributylamine.

The enthalpies of formation of the adducts of Ph_3SnCl with pyridine and 4-methylpyridine, about 40 kJ mol^{-1}, are comparable to those of many other adducts of heterolytic bases with neutral compounds of metals and, as in many

TABLE 1

THERMODYNAMIC DATA FOR FORMATION OF 1/1 ADDUCTS OF Ph_3SnCl WITH PYRIDINE AND 4-METHYLPYRIDINE IN BENZENE SOLUTION AT 30°

Base	$[Ph_3SnCl]$ (mmol l^{-1})	K (l mol^{-1})	$-\Delta H^0$ (kJ mol^{-1})	$-\Delta G^0$ (kJ mol^{-1})	$-\Delta S^0$ (J K^{-1} mol^{-1})
py	14.8	1.24 ± 0.05	41.0	0.55 ± 0.10	133 ± 1
	25.7	1.09 ± 0.02	41.0	0.22 ± 0.05	135 ± 1
	71.0	1.06 ± 0.04	41.0	0.15 ± 0.08	135 ± 1
	Mean	1.13 ± 0.11	41.0 ± 0.0	0.31 ± 0.24	134 ± 2
4-mepy	7.0	2.27 ± 0.02	45.5	2.07 ± 0.02	143 ± 1
	27.1	2.28 ± 0.03	45.2	2.08 ± 0.03	142 ± 1
	71.7	2.41 ± 0.02	43.8	2.22 ± 0.02	137 ± 1
	Mean	2.32 ± 0.08	44.8 ± 0.7	2.12 ± 0.13	141 ± 3

of the other systems, the 4-methylpyridine adduct is a little more stable and has a slightly more negative enthalpy of formation, reflecting the greater base strength of this base. There is no evidence for addition of a second molecule of base to Ph_3SnCl and the tin atom may be regarded as having a coordination number of five which cannot be easily increased; a trigonal-bipyramidal structure may be proposed for the adducts, with *trans*, apical N and Cl atoms, analogous to that found in $Me_3SnCl \cdot py$ [7].

The failure of Ph_3SnCl to form adducts with 2,2′-bipyridine or 1,10-phenanthroline is most interesting and suggests that the coordination number of the tin atom cannot be raised above five. The failure of tributylphosphine to react is also interesting, since this base forms more stable 1/1 adducts with tin compounds of the types R_2SnCl_2 and $RSnCl_3$ (below) than do heterocyclic bases. It seems possible that the 5-coordinate adducts such as $Ph_3SnCl \cdot py$ may have a special stability associated with the coplanarity of the three phenyl groups and that this may not be compatible with possible demands of a coordinated phosphorus atom in an apical site for some degree of double bonding.

Tin compounds R_2SnCl_2

The compounds Ph_2SnCl_2, Me_2SnCl_2 and Bu_2SnCl_2 all reacted in a similar manner with pyridine or 4-methylpyridine: the titration curves obtained could not be fitted for formation of 1/1 or 1/2 adducts but fitted well for simultaneous formation of both adducts (eqns. 1 and 2). The fit of experimental points to

$$R_2SnCl_2 + B \rightleftharpoons R_2SnCl_2B \tag{1}$$

$$R_2SnCl_2B + B \rightleftharpoons R_2SnCl_2B_2 \tag{2}$$

computed titration curves using four parameters, K_1, K_2, ΔH_1, and ΔH_2 is shown in Figs. 1-4 and the best-fit results for all systems are summarised in Table 2, which also includes data for $Bu_2Sn(NCS)_2$. When $Bu_2Sn(NCS)_2$ was titrated two distinct steps could be observed with $K_1 \gg K_2$, but in the other cases although $K_1 > K_2$ the difference was only small and the enthalpies of addition of the two base molecules were not significantly different.

TABLE 2

THERMODYNAMIC DATA FOR ADDITION OF PYRIDINE AND 4-METHYLPYRIDINE TO ORGANOTIN COMPOUNDS R_2SnX_2 IN BENZENE SOLUTION AT 30°

R	X	Base	$[R_2SnX_2]$ (mmol l^{-1})	K_1 (l mol^{-1})	$-\Delta H_1^0$ (kJ mol^{-1})	$-\Delta G_1^0$ (kJ mol^{-1})	$-\Delta S_1^0$ (J K^{-1} mol^{-1})	K_2 (l mol^{-1})	$-\Delta H_2^0$ (kJ mol^{-1})	$-\Delta G_2^0$ (kJ mol^{-1})	$-\Delta S_2^0$ (J K^{-1} mol^{-1})	$-\Delta H_{1+2}^0$ (kJ mol^{-1})
Ph	Cl	py	1.39-6.85	80 ± 20	48 ± 10	11 ± 1	122 ± 30	60 ± 20	57 ± 10	10 ± 1	155 ± 30	105 ± 5
Ph	Cl	4-mepy	0.95-6.21	200 ± 50	50 ± 10	13 ± 1	121 ± 30	150 ± 50	56 ± 10	13 ± 1	143 ± 30	106 ± 5
Me	Cl	py	3.11-10.90	17 ± 5	45 ± 10	7 ± 1	125 ± 30	13 ± 5	28 ± 10	6 ± 1	71 ± 30	73 ± 5
Me	Cl	4-mepy	0.95-10.62	40 ± 10	60 ± 10	9 ± 1	167 ± 30	30 ± 10	18 ± 10	9 ± 1	34 ± 30	78 ± 5
Bu	Cl	py	2.14-7.06	5 ± 2	40 ± 10	4 ± 1	117 ± 30	5 ± 2	22 ± 10	4 ± 1	53 ± 30	62 ± 10
Bu	Cl	4-mepy	1.61-8.50	12 ± 3	62 ± 10	6 ± 1	184 ± 30	10 ± 3	18 ± 10	6 ± 1	40 ± 30	78 ± 10
Bu	NCS	py	1.10-4.83	$\approx 10^4$	45 ± 5	≈23	73 ± 20	100 ± 15	35 ± 5	12 ± 1	77 ± 20	80 ± 5
Bu	NCS	4-mepy	0.59-4.23	$\approx 10^4$	52 ± 5	≈23	96 ± 20	130 ± 15	46 ± 5	12 ± 1	111 ± 20	98 ± 5

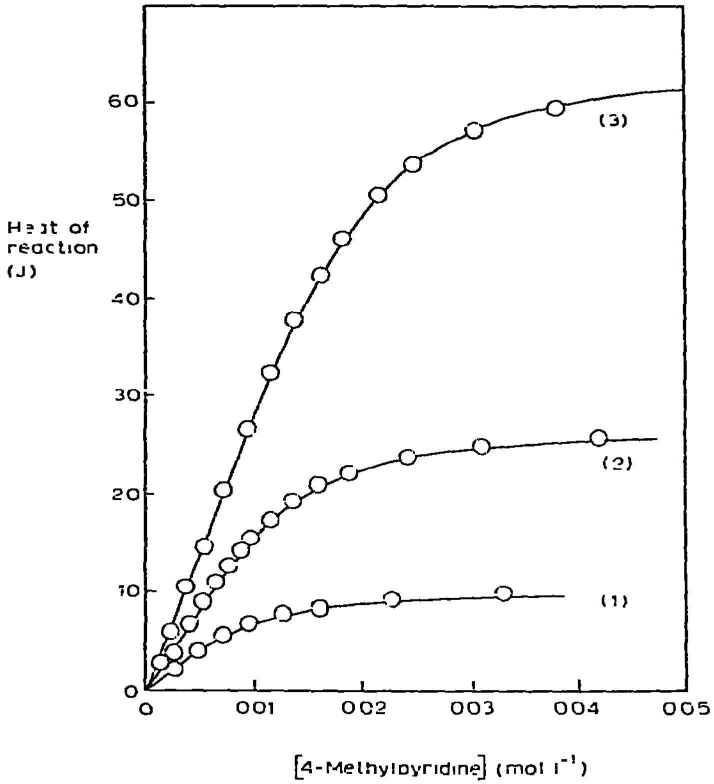


Fig. 1. Calorimetric titration of Ph_2SnCl_2 with 4-methylpyridine. Curves computed using K_1 = 200, K_2 = 150, ΔH_1 = -50, ΔH_2 = -56 kJ mol^{-1}. Experimental points for [Ph_2SnCl_2] = 0.00095 (1), 0.00260 (2) and 0.00621 (3) mol l^{-1}.

There is a quite distinct difference in the stabilities of the adducts of the three tin compounds; these decrease in the order: $Ph_2SnCl_2 > Me_2SnCl_2 > Bu_2SnCl_2$. The greater stability of the adducts of Ph_2SnCl_2 arises from the more negative enthalpies of formation and may be attributed to the inductive effect of the phenyl groups. The small difference between the stabilities of the adducts of Me_2SnCl_2 and Bu_2SnCl_2, however, is not accompanied by any significant differences in enthalpy of formation and is more probably due to the steric effect of the larger butyl group.

The very high stabilities of the 1/1 adducts with $Bu_2Sn(NCS)_2$ arise partly from an inductive effect, shown by the more negative enthalpy of adduct formation compared with adducts of Bu_2SnCl_2. A major factor, however, is the lower entropy resistance to adduct formation, shown by comparison of the data for Ph_2SnCl_2 and $Bu_2Sn(NCS)_2$: despite nearly equal enthalpies of formation, the adducts of $Bu_2Sn(NCS)_2$ are a hundred times more stable than those of Ph_2SnCl_2. This entropy stabilisation of the 1/1 adducts of $Bu_2Sn(NCS)_2$ may be attributed to the much reduced steric effect of the narrow rod-like NCS groups; this effect is, however, restricted to formation of the 1/1 adduct and the presence of NCS groups apparently does little to facilitate the addition of the second molecule of base.

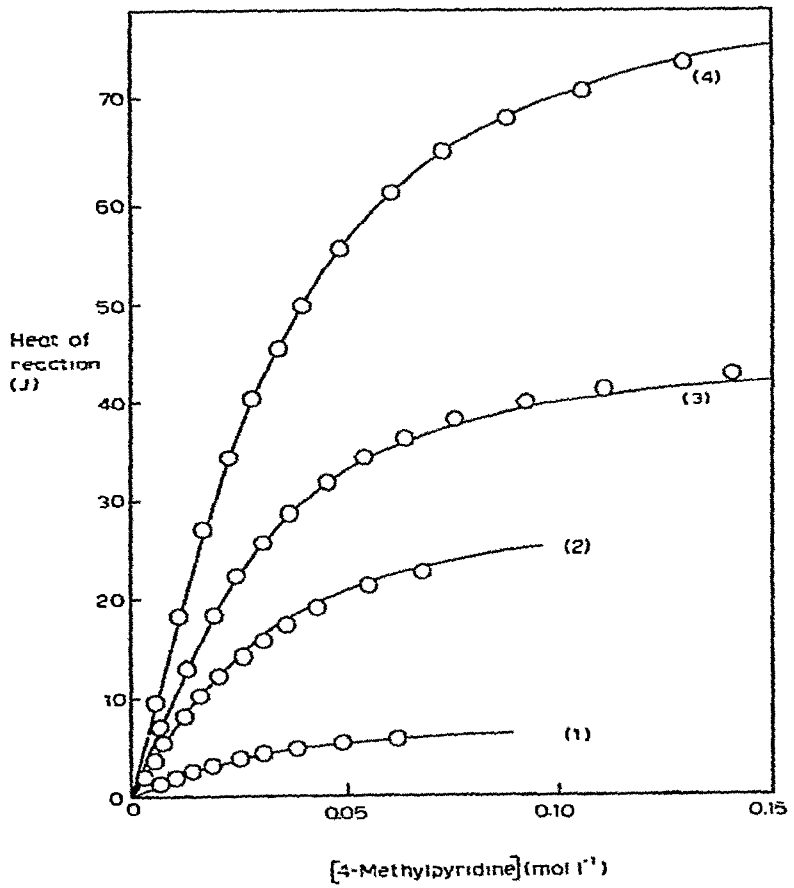


Fig. 2. Calorimetric titration of Me_2SnCl_2 with 4-methylpyridine. Curves computed for $K_1 = 40$, $K_2 = 30$, $\Delta H_1 = -60$, $\Delta H_2 = -18$ kJ mol^{-1}. Experimental points for $[Me_2SnCl_2] = 0.00095$ (1), 0.00363 (2), 0.00589 (3) and 0.0106 (4) mol l^{-1}.

TABLE 3

THERMODYNAMIC DATA FOR FORMATION OF 1/1 ADDUCTS OF ORGANOTIN COMPOUNDS R_2SnX_2 WITH 2,2'-BIPYRIDINE AND 1,10-PHENANTHROLINE IN BENZENE SOLUTION AT 30°

R	X	Base	$[R_2SnX_2]$ (mol l^{-1})	K (l mol^{-1})	$-\Delta H^0$ (kJ mol^{-1})	$-\Delta G^0$ (kJ mol^{-1})	$-\Delta S^0$ (J K^{-1} mol^{-1})
Ph	Cl	bipy	0.61-1.58	6.4×10^3	81.8 ± 1.5	22 ± 2	198 ± 12
Ph	Cl	phen	0.47-1.67	2×10^5	107.0 ± 3.0	31 ± 3	250 ± 20
Me	Cl	bipy	0.59-2.17	123 ± 4	64.8 ± 0.6	12.1 ± 0.2	174 ± 3
Me	Cl	phen	0.53-2.05	5×10^4	86.0 ± 1.0	27 ± 3	195 ± 13
Bu	Cl	bipy	0.97-7.60	40.3 ± 1.3	62.1 ± 0.0	9.3 ± 0.1	174 ± 1
Bu	Cl	phen	0.66-3.18	5×10^4	84.3 ± 1.3	27 ± 3	189 ± 14
Bu	NCS	bipy	0.61-2.45	$>10^4$	70.7 ± 1.9	>23	<158
Bu	NCS	phen	0.57-2.11	$>10^5$	84.7 ± 2.2	>29	<184

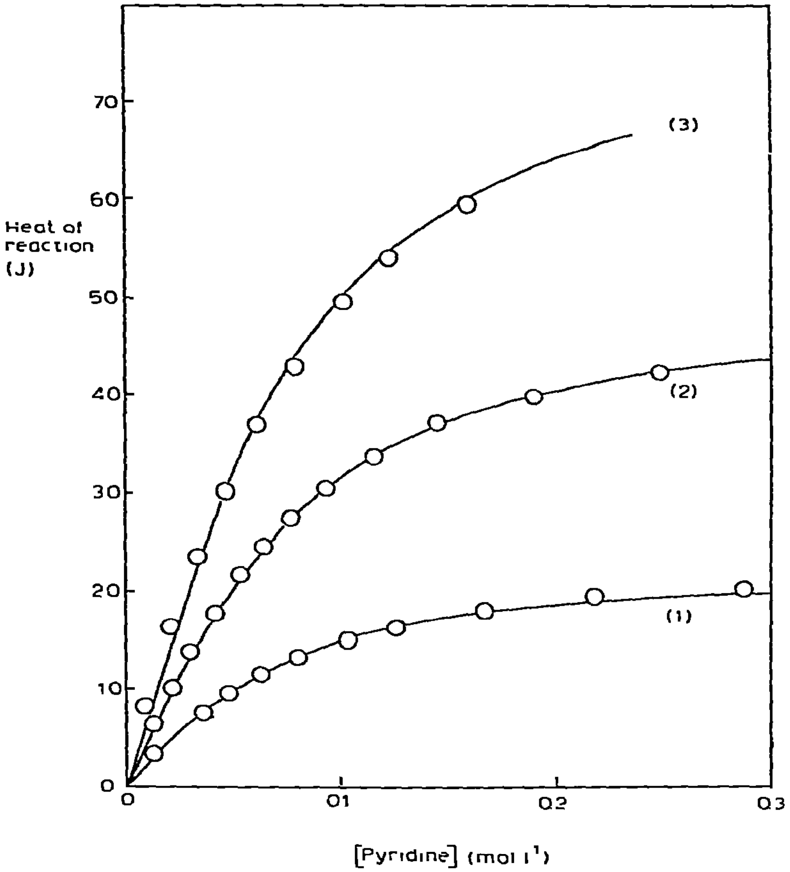


Fig. 3. Calorimetric titration of Me_2SnCl_2 with pyridine. Curves computed for $K_1 = 17$, $K_2 = 13$, $\Delta H_1 = -45$, $\Delta H_2 = -28$ kJ mol^{-1}. Experimental points for $[Me_2SnCl_2] = 0.00311$ (1), 0.00681 (2), 0.0109 (3) mol l^{-1}.

Thermodynamic data were also obtained for the formation of 1/1 adducts of the compounds R_2SnX_2 with 2,2′-bipyridine and 1,10-phenanthroline. Results are summarised in Table 3. The enthalpies of formation of the 1,10-phenanthroline adducts are close to those for addition of two molecules of 4-methylpyridine, showing that both nitrogen atoms are coordinated; this is supported by the very high stabilities of these adducts, which reflect a chelate effect.

The 2,2′-bipyridine adducts are of lower stability than those of 1,10-phenanthroline and have less negative enthalpies of formation. The present data for the formation of $Bu_2Sn(NCS)_2$bipy are in exact agreement with those previously reported [18] by Wardell ($K = 1.5 \times 10^4$, $-\Delta H = 70.4 \pm 1.2$ kJ mol^{-1}). The present results for the formation of the adduct $Bu_2SnCl_2 \cdot$ bipy also compare well with those reported by Wardell for addition of 2,2′-bipyridine to Oct_2SnCl_2 ($K = 27$, $-\Delta H = 53.2$ kJ mol^{-1}). The slightly lower stability and less negative enthalpy of formation of the adduct of the octyl compound may be correlated with small changes in inductive and steric effects and continue the trend already apparent in Table 3 on changing from methyl to butyl. The much lower stabilities of the bipyridine adducts of Me_2SnCl_2 and Bu_2SnCl_2 than the corresponding

TABLE 4

THERMODYNAMIC DATA FOR REACTION OF 2-METHYLPYRIDINE WITH Ph_2SnCl_2, Me_2SnCl_2 AND $Bu_2Sn(NCS)_2$ IN BENZENE SOLUTION AT 30°

Reaction	[Sn] (mmol l^{-1})	K	$-\Delta H^0$ (kJ mol^{-1})	$-\Delta G^0$ (kJ mol^{-1})	$-\Delta S^0$ (J K^{-1} mol^{-1})
Ph_2SnCl_2 + 2-mepy $\rightleftharpoons$ $Ph_2SnCl_2$2-mepy	3.00-10.60	4.5 ± 0.4	70 ± 0	3.8 ± 0.3	248 ± 1
2 Me_2SnCl_2 + 2-mepy $\rightleftharpoons$ $(Me_2SnCl_2)_2$2-mepy	4.58-19.30	334 ± 17	90 ± 1	14.6 ± 0.3	248 ± 3
$Bu_2Sn(NCS)_2$ + 2-mepy $\rightleftharpoons$ $Bu_2Sn(NCS)_2$2-mepy	0.61-3.07	$\approx 10^4$	56 ± 1	≈23	≈109
$Bu_2Sn(NCS)_2$2-mepy + 2-mepy $\rightleftharpoons$ $Bu_2Sn(NCS)_2(2\text{-mepy})_2$	0.61-3.07	10.2 ± 0.7	45 ± 1	5.8 ± 0.2	130 ± 4

TABLE 5

THERMODYNAMIC DATA FOR REACTION OF $BuSnCl_3$ AND $PhSnCl_3$ WITH HETEROCYCLIC BASES IN BENZENE SOLUTION AT 30°

Reaction	[Sn] (mmol l^{-1})	K	$-\Delta H^0$ (kJ mol^{-1})	$-\Delta G^0$ (kJ mol^{-1})	$-\Delta S^0$ (J K^{-1} mol^{-1})
$BuSnCl_3$ + 2-mepy $\rightleftharpoons$ $BuSnCl_3$ · 2-mepy	2.94-11.12	1×10^4	80 ± 5	≈23	≈188
$BuSnCl_3$ · 2-mepy + 2-mepy $\rightleftharpoons$ $BuSnCl_3(2\text{-mepy})_2$	2.94-11.12	30 ± 5	34 ± 5	8.6 ± 0.4	84 ± 18
$BuSnCl_3$ + 2 py $\rightleftharpoons$ $BuSnCl_3(py)_2$	2.29-9.44	4×10^5	116 ± 5	≈32	≈280
$BuSnCl_3$ + 2(4-mepy) $\rightleftharpoons$ $BuSnCl_3(4\text{-mepy})_2$	3.32-11.26	1×10^6	125 ± 5	≈35	≈300
$BuSnCl_3$ + bipy $\rightleftharpoons$ $BuSnCl_3$ · bipy	0.52-4.42	1×10^5	104 ± 1	≈20	<250
$BuSnCl_3$ + phen $\rightleftharpoons$ $BuSnCl_3$ · phen	0.49-0.83	$>10^5$	128 ± 1	>20	<330
$PhSnCl_3$ + 2 py $\rightleftharpoons$ $PhSnCl_3(py)_2$	0.44-3.59	$>10^6$	139 ± 7	>35	<340
$PhSnCl_3$ + 2(4-mepy) $\rightleftharpoons$ $PhSnCl_3(4\text{-mepy})_2$	0.58-2.47	$>10^6$	140 ± 0	>35	<350
$PhSnCl_3$ + bipy $\rightleftharpoons$ $PhSnCl_3$ · bipy	1.08-4.80	$>10^5$	130 ± 4	>20	<340
$PhSnCl_3$ + phen $\rightleftharpoons$ $PhSnCl_3$ · phen	0.41-1.61	$>10^6$	144 ± 2	>35	<360

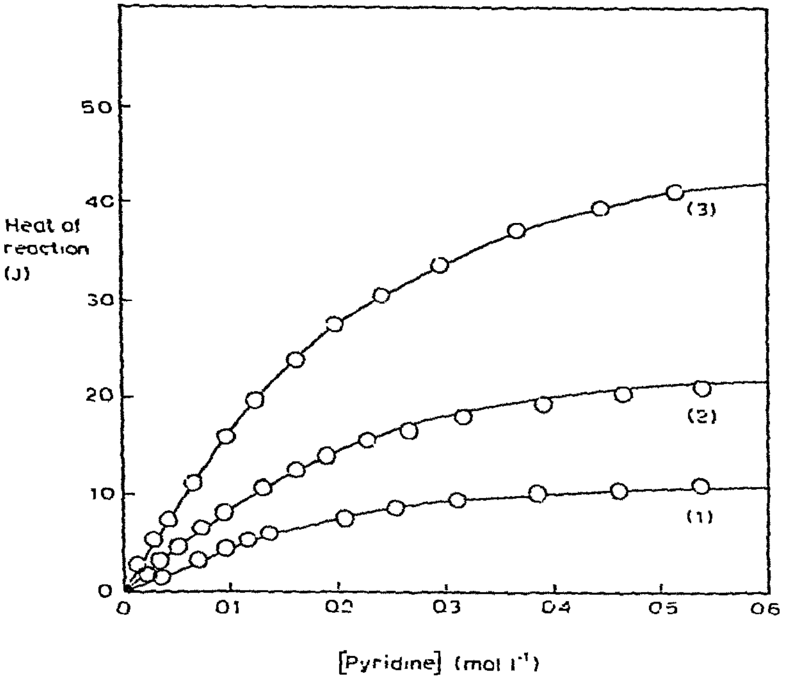


Fig. 4. Calorimetric titration of Bu_2SnCl_2 with pyridine. Curves computed for $K_1 = 6$, $K_2 = 5$, $\Delta H_1 = -40$, $\Delta H_2 = -22$ kJ mol^{-1}. Experimental points for $[Bu_2SnCl_2] = 0.00244$ (1), 0.00413 (2) and 0.00796 (3) mol l^{-1}.

phenanthroline adducts arise from less negative enthalpies of formation and probably reflect less satisfactory N—Sn orbital overlap, due to strain or twisting in the bipyridine molecule.

The reaction of 2-methylpyridine with the compounds R_2SnX_2 vary from one compound to another. With $Bu_2Sn(NCS)_2$ two molecules of base are added successively with $-\Delta H_1 > -\Delta H_2$ and $K_1 \gg K_2$. The enthalpies of reaction are similar to those with 4-methylpyridine and there is little difference between the values of K_1 with the two bases, but K_2 is much smaller with 2-methylpyridine. Apparently the narrow, rod-like NCS groups raise no steric barrier to entry of the first molecule of 2-methylpyridine, but the effect of the *ortho* methyl group becomes important when the second molecule is added. Data are given in Table 4.

Under the experimental conditions only one molecule of 2-methylpyridine adds to Ph_2SnCl_2; the 1/1 adduct is of low stability (Table 4) but the enthalpy of adduct formation is more negative than for the 1/1 adducts with pyridine or 4-methylpyridine (Table 2). Comparison with Ph_3SnCl (Table 1) shows that the higher enthalpy of reaction can be attributed to the inductive effect of the second chlorine atom, while there is little change in adduct stabilities because of the closeness of the experimental temperature to the isoequilibrium temperatures.

The similarity of isoequilibrium temperatures for the formation of $Ph_2SnCl_2 \cdot$ 2-mepy (318 K), $Ph_3SnCl \cdot$ py (306 K) and $Ph_3SnCl \cdot$ 4-mepy (317 K) argues for structural similarity of the adducts. By comparison the isoequilibrium temperatures for the formation of $Ph_2SnCl_2 \cdot$ py and $Ph_2SnCl_2 \cdot$ 4-mepy are much higher (about 400 K) and these adducts probably have different structures with smaller enthalpies of formation but stabilised by entropy factors. All these requirements can be met by the following possible structures: for $Ph_3SnCl \cdot B$ and $Ph_2SnCl_2 \cdot$ 2-mepy trigonal-bipyramidal molecules with *trans*, apical N and Cl atoms, as observed [7] in $Me_3SnCl \cdot py$; for the other $R_2SnX_2 \cdot B$ molecules fluxional 5-coordinate structures. Fluxional structures are common in 5-coordinate compounds and their importance in tin(IV) compounds has been recently discussed [22]; such structures could be expected to react readily with further base molecules and to be stabilised by entropy factors, they could also be rendered unstable by the steric interference of the *ortho* methyl group in coordinated 2-methylpyridine adducts.

Data could not be obtained for addition of 2-methylpyridine to Bu_2SnCl_2 because of adduct precipitation. With Me_2SnCl_2 titration curves were obtained which could only be fitted by assuming formation of a 2/1 adduct according to eqn. 3; the structure of the adduct formed is not known. Dissociation by a

$$2\,Me_2SnCl_2 + \text{2-mepy} \rightleftharpoons (Me_2SnCl_2)_2\text{2-mepy} \quad (3)$$

reaction such as eqn. 4 is not consistent with the thermometric titration data,

$$(Me_2SnCl_2)_2\text{2-mepy} \rightleftharpoons Me_3SnCl + MeSnCl_3\text{2-mepy} \quad (4)$$

but there are special features of this system which lower the accuracy of the experimental results and make interpretation very uncertain: the adduct formation constant is small and the reaction proceeds little more than half way to completion with the highest base concentration which can be achieved, furthermore 2-methylpyridine has a large heat of dilution in benzene and this inevitably lowers the accuracy of measured heat changes.

Tin compounds $RSnCl_3$

Replacement of a third alkyl or aryl group by chlorine leads to a further increase in Lewis acidity, as shown by the data for reactions of $BuSnCl_3$ and $PhSnCl_3$ in Table 5.

Titration of $BuSnCl_3$ with 2-methylpyridine revealed two distinct steps, corresponding to formation of 1/1 and 1/2 adducts; titration of $PhSnCl_3$ with 2-methylpyridine was frustrated by adduct precipitation. With pyridine or 4-methylpyridine both tin compounds gave 1/2 adducts, the stabilities of which were too high to allow determination of data for successive base additions; titrations with 2,2′-bipyridine or 1,10-phenanthroline showed formation of 1/1 adducts of high stability. The enthalpy data for these reactions show the similarity of enthalpies of formation of adducts with one molecule of phenanthroline or two molecules of unidentate base, the enthalpies of formation of adducts with bipyridine are slightly smaller as in many other systems.

The enthalpies of adduct formation by the compounds $RSnCl_3$ are consistently more negative than with R_2SnCl_2 showing the effect of continuing replacement of R by Cl in increasing the Lewis acidity of the tin compounds. Precipitation of adducts from solution prevented the extension of these observations to corresponding adducts of the tin(IV) halides.

Adducts of organotin compounds with tributylphosphine

Thermodynamic data are shown in Table 6 for the reaction of the various

TABLE 6

THERMODYNAMIC DATA FOR FORMATION OF 1/1 ADDUCTS OF ORGANOTIN COMPOUNDS WITH TRIBUTYLPHOSPHINE IN BENZENE SOLUTION AT 30°

Compound	Concn. (mmol l^{-1})	K ($l\ mol^{-1}$)	$-\Delta H^0$ (kJ mol^{-1})	$-\Delta G^0$ (kJ mol^{-1})	$-\Delta S^0$ (J $K^{-1} mol^{-1}$)
Ph_2SnCl_2	2.23-11.00	1.9×10^4	73.7 ± 1.2	25 ± 2	161 ± 10
Me_2SnCl_2	2.44-6.93	1002 ± 60	54.0 ± 1.6	17.4 ± 0.3	121 ± 7
Bu_2SnCl_2	1.73-10.33	322 ± 17	54.8 ± 0.8	14.5 ± 0.2	133 ± 4
$Bu_2Sn(NCS)_2$	0.69-2.56	$>10^4$	78.0 ± 1.7	>23.2	<182
$BuSnCl_3$	0.47-1.73	2×10^4	92.6 ± 0.2	25 ± 2	222 ± 7
$PhSnCl_3$	0.54-2.42	$>10^5$	94.3 ± 0.5	>29	<215
$PhSnCl_3PBu_3$	0.54-2.42	2420 ± 100	75.1 ± 1.8	19.6 ± 0.2	181 ± 7

tin compounds with tributylphosphine. This base did not react with R_3SnCl; with $PhSnCl_3$ two molecules of base were added in distinct steps with $-\Delta H_1 > -\Delta H_2$ and $K_1 \gg K_2$; in all other cases only one molecule of base added in solution, the tin atom becoming 5-coordinate.

The failure to add a second molecule of base (except for $PhSnCl_3$) suggests some steric interference and this is supported by comparison with the data for addition of the first molecule of pyridine (Table 2): the isoequilibrium temperature for the formation of 1/1 adducts with pyridine (400-450 K) is 50-100 K higher than for tributylphosphine adducts and these latter are less stable than would be expected from their more negative enthalpies of formation; nevertheless these more negative enthalpies are responsible for the tributylphosphine adducts being much more stable than corresponding adducts with unidentate nitrogeneous bases.

It would be expected that tin(IV) compounds, in which the metal atom has achieved the electronic structure of xenon and also carries a large formal charge, would behave as a Lewis acid of "hard" or "A" character. It is thus surprising to find 1/1 adducts with a phosphine which are more stable than adducts with nitrogenous bases and also have more negative enthalpies of formation; it seems likely that some degree of double-bonding occurs in the Sn—P bonds in these adducts.

Reactions with tertiary aliphatic amines

To assess the posibility that double-bonding might also be occurring in the Sn—N bonds in adducts with heterocyclic bases, calorimetric titrations were attempted with a variety of unidentate and bidentate tertiary amines. With bidentate amines, such as *N,N,N',N'*-tetramethyl-1,2-diaminoethane, these attempts were frustrated by the precipitation of adducts, but satisfactory titrations were achieved with tributylamine and tin compounds of the types R_2SnX_2 and $RSnX_3$; R_3SnX did not react.

With all the compounds of the type R_2SnX_2 the titration results showed near-quantitative addition of half a mole of base to each mole of tin compound, followed by incomplete addition of a further half mole of base; the titration curves for this second step in the reaction fitted well the equations for a 1/1 equilibrium. (Fig. 5). These results are consistent with an initial step involving

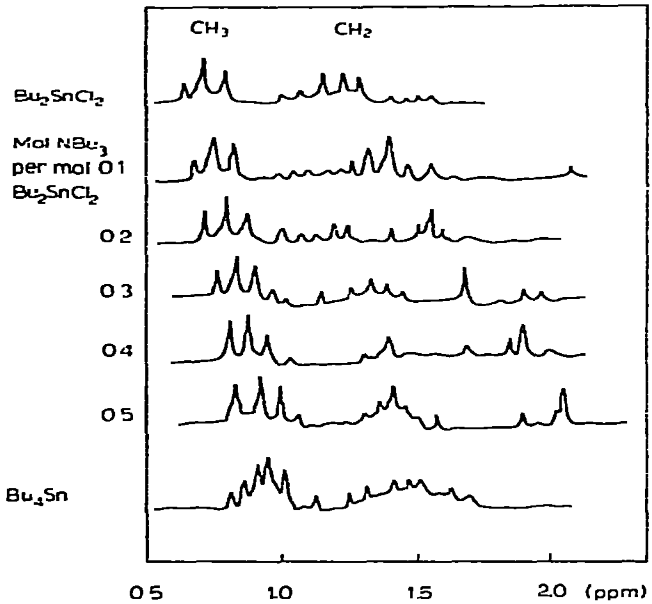


Fig. 6. Proton NMR spectra of benzene solutions of $SnBu_4$ and Bu_2SnCl_2, both 3×10^{-3} mol l^{-1}, and Bu_2SnCl_2 containing various proportions of NBu_3.

disproportionation of the tin compound, according to either eqn. 5 or 6. Compounds of the types R_4Sn and R_3SnX have both been found not to react with NBu_3 and would take no further part in the reaction. The next step would then be addition of a second molecule of base to the half of the original tin which is now more highly chlorinated (eqn. 7 or 8).

$$2\,R_2SnX_2 + B = R_4Sn + SnX_4B \tag{5}$$

$$2\,R_2SnX_2 + B = R_3SnX + RSnX_3B \tag{6}$$

$$SnX_4B + B \rightleftharpoons SnX_4B_2 \tag{7}$$

$$RSnX_3B + B \rightleftharpoons RSnX_3B_2 \tag{8}$$

To distinguish between these two possibilities solutions of Bu_2SnCl_2 (3.00×10^{-3} *M*) in benzene were prepared, containing various proportions of tributylamine up to half the concentration of the tin compound. Proton NMR spectra of these solutions showed clearly the shift of the $SnBu\text{-}CH_3$ and CH_2 proton resonances towards those of $SnBu_4$ as the tributylamine concentration approaches half that of the tin compound (Fig. 6), showing that the initial disproportionation is the reaction shown in eqn. 9. If this reaction is truly quantitative, the following step involves only the addition of base to $SnCl_4NBu_3$ and should give the same thermodynamic parameters for each compound of the type R_2SnCl_2, but quite different parameters for $Bu_2Sn(NCS)_2$. The data obtained are summarised in Table 7.

$$2\,Bu_2SnCl_2 + NBu_3 = Bu_4Sn + SnCl_4NBu_3 \tag{9}$$

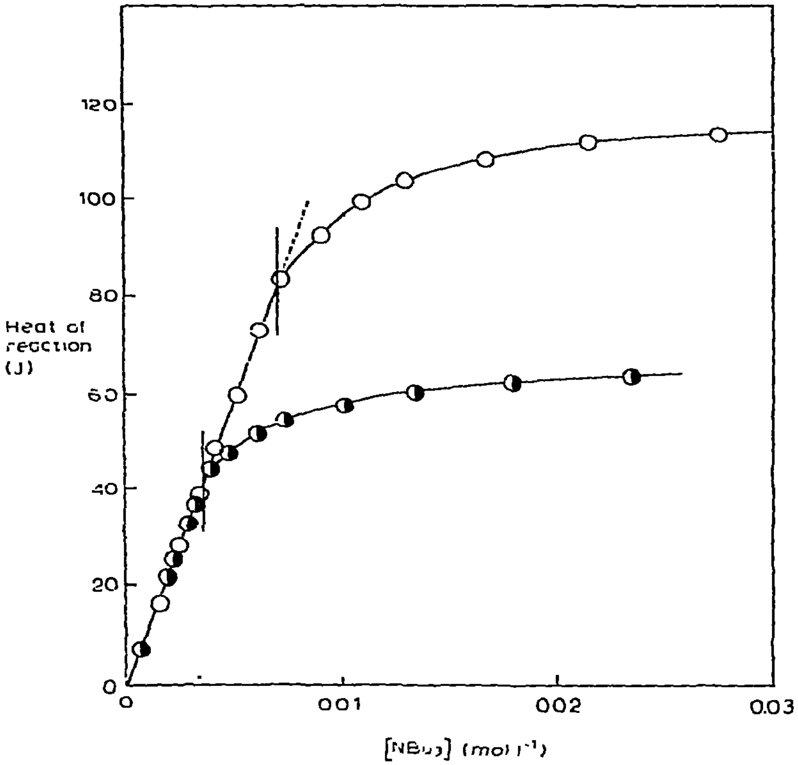


Fig. 5. Calorimetric titration of Bu_2SnCl_2 with NBu_3. Experimental points for $[Bu_2SnCl_2] = 0.00727$ (◑) and 0.0142 (○) mol l^{-1}; vertical lines show where $[NBu_3] = ½[Bu_2SnCl_2]$.

The values of K_2 and ΔH_2 observed for Ph_2SnCl_2, Me_2SnCl_2 and Bu_2SnCl_2 are not the same, but the differences are no larger than could be expected if the disproportionation step is not quite quantitative, so that some of the enthalpy change for this step "spills over" into the next. As expected the data obtained for $Bu_2Sn(NCS)_2$ are very different from those for the chloro compounds and K_2 and ΔH_2 for this system may be attributed to reaction 10.

$$Sn(NCS)_4NBu_3 + NBu_3 \rightleftharpoons Sn(NCS)_4(NBu_3)_2 \qquad (10)$$

TABLE 7

APPARENT THERMODYNAMIC DATA IN BENZENE SOLUTION AT 30° FOR THE REACTIONS:

$$2\,R_2SnX_2 + NBu_3 \rightleftharpoons R_4Sn + SnX_4NBu_3 \qquad (1)$$

$$SnX_4NBu_3 + NBu_3 \rightleftharpoons SnX_4(NBu_3)_2 \qquad (2)$$

R	X	[Sn] (mmol l^{-1})	$-\Delta H_1^0$ (kJ mol^{-1})	K_2 (l mol^{-1})	$-\Delta H_2^0$ (kJ mol^{-1})
Ph	Cl	1.15-6.31	133 ± 2	347 ± 27	85 ± 3
Me	Cl	3.78-10.90	115 ± 1	127 ± 6	62 ± 1
Bu	Cl	3.92-14.21	116 ± 5	219 ± 9	64 ± 2
Bu	NCS	0.61-3.07	142 ± 4	3430 ± 340	147 ± 10

Calorimetric titrations were also carried out with tributylamine and the tin compounds $BuSnCl_3$ and $PhSnCl_3$, but it was not found possible to fit the titration curves by assuming any simple combination of likely disproportiona and addition reactions and it seems probable that these compounds react accc ing to some more complex scheme of equilibria; the overall heats of reaction observed were very large: -231 ± 4 and -259 ± 6 kJ mol^{-1} respectively.

Acknowledgement

We are grateful to the Australian Research Grants Committee for suppor this work; to Mr. V. Pickles of the University of New South Wales for NMR spectra; to the University of Tabriz for a fellowship to one of us (Y.F.).

References

1 Y. Farhang and D.P. Graddon, Aust. J. Chem., 27 (1974) 2103.
2 F.J. Cioffi and S.T. Zenchelsky, J. Phys. Chem., 67 (1963) 357.
3 J.J. Myher and K.E. Russell, Can. J. Chem., 42 (1964) 1555.
4 J. Laane and T.L. Brown, Inorg. Chem., 3 (1964) 148.
5 G. Vandrish and M. Onyszchuk, J. Chem. Soc. A, (1970) 3327.
6 R.C. Paul, S.C. Ahluwalia and R. Parakash, Indian J. Chem., 6 (1968) 464.
7 R. Hulme, J. Chem. Soc., (1963) 1524.
8 N.A. Matwiyoff and R.S. Drago, Inorg. Chem., 3 (1964) 337.
9 T.F. Bolles and R.S. Drago, J. Amer. Chem. Soc., 87 (1965) 5015; 88 (1966) 3921, 5730.
10 M.A. Mullins and C. Curran, Inorg. Chem., 6 (1967) 2017.
11 K.L. Jaura and V.K. Verma, J. Inorg. Nucl. Chem., 35 (1973) 2361.
12 V.S. Petrosayan, N.S. Yashina, O.A. Reutov et al., J. Organometal. Chem., 52 (1973) 315, 321, 333.
13 M.A. Mullins and C. Curran, Inorg. Chem., 7 (1968) 2584.
14 J.C. May and C. Curran, J. Organometal. Chem., 39 (1972) 289.
15 N.W. Isaacs and C.H.L. Kennard, J. Chem. Soc. A, (1970) 1257.
16 D.V. Naik and W.R. Scheidt, Inorg. Chem., 12 (1973) 272.
17 G. Matsubayashi, Y. Kawasaki, T. Tanaka and R. Okawara, J. Inorg. Nucl. Chem., 28 (1966) 2937.
18 J.L. Wardell, J. Chem. Soc. A, (1971) 2628.
19 J.L. Wardell, J. Organometal. Chem., 9 (1967) 89; 10 (1967) 53.
20 J.H. Holloway, G.P. McQuillan and D.S. Ross, J. Chem. Soc. A, (1969) 2505.
21 D.P. Graddon and K.B. Heng, Aust. J. Chem., 24 (1971) 1781.
22 J. Nasielski, Pure Appl. Chem., 30 (1972) 449.