Reactions of some Tin(II) and Tin(IV) Compounds with the Dodecahydro-*nido*-decaborate(2−) Ion, $[B_{10}H_{12}]^{2-}$ †

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The new ionic compounds $[Ph_4As]_2[B_{10}H_{12}]$ and $[Ph_3MeP]_2[B_{10}H_{12}]$ react with anhydrous $SnCl_2$ to give metallic tin, HCl, salts of *closo*-$[B_{10}H_{10}]^{2-}$, and salts of the *nido*-stannadecaborate ion $[B_{10}H_{12}SnCl_2]^{2-}$ which has been shown by ^{119}Sn Mössbauer spectroscopy to be a tin(II) complex. The corresponding reactions with Me_2SnCl_2 yield $[B_{10}H_{10}]^{2-}$ salts and also the novel tin(II) ion $[Me_2SnCl_2]^{2-}$ as well as the chelated ion $[B_{10}H_{12}Me_2SnCl_2]^{2-}$ which has been shown by Mössbauer spectroscopy to be a tin(IV) derivative. I.r. and ^{11}B n.m.r. data are discussed and structures proposed. The compound Et_2SnCl_2 reacted to give $[Ph_4As]_2[B_{10}H_{12}Et_2SnCl_2]$ but Ph_2SnCl_2 did not lead to isolable stannaborate species.

THE incorporation of Group 4 elements other than carbon into polyhedral borane species has proved unusually elusive although a few carbaborane derivatives of silicon, germanium, and tin are known.[1] Silicon and its heavier congeners (including lead) also bond directly to some of the smaller boranes though the attachment is exopolyhedral.[2] Only one report has previously appeared on polyhedral metallo-derivatives of decaborane and Group 4 elements, namely the preparation of $Me_2GeB_{10}H_{12}$ and $Me_2SnB_{10}H_{12}$.[3] This is perhaps surprising in view of the numerous *closo*- and *nido*-carbadecaborane species which are now known and the ready propensity of the dianion $[B_{10}H_{12}]^{2-}$ to act as a tetra*hapto*, bidentate, four-electron donor to both transition and main-group metals.[4] Some years ago we prepared and characterized several tin(II) and tin(IV) derivatives of the dodecahydrodecaborate(2−) ion [5] and the growing interest in such compounds prompts us now to publish the results. The corresponding derivatives of lead are very much less stable and reduction to metallic lead is difficult to avoid.[6]

RESULTS AND DISCUSSION

The direct reaction of metal alkyls with decaborane frequently yields metallaboranes [4] but this route proved unsuccessful with tin possibly because of the polymeric nature of its dialkyls. Reaction of sodium dodecahydrodecaborate(2−) with tin halides and organotin halides was also ineffective, but use of the methyltriphenylphosphonium and tetraphenylarsonium salts of $[B_{10}H_{12}]^{2-}$ led to several stannadecaborane complexes. The new compounds $[Ph_3MeP]_2[B_{10}H_{12}]$ and $[Ph_4As]_2[B_{10}H_{12}]$ were prepared by addition of a methylene chloride solution of the corresponding bromides to a solution of $Na_2[B_{10}H_{12}]$ in tetrahydrofuran (thf). After removal of the sodium bromide the required salts were precipitated by further addition of thf. The salts were recrystallized from methylene chloride–thf to yield small orange-yellow crystals, soluble without decomposition in methylene chloride and dimethyl sulphoxide but insoluble in thf, diethyl ether, and water. The electrical conductivity of a 10^{-3}M solution of $[Ph_4As]_2[B_{10}H_{12}]$ was almost identical with that of the known 2 : 1 electrolyte $[Ph_4As]_2[B_{10}H_{10}]$.

The reaction of $[Ph_4As]_2[B_{10}H_{12}]$ in methylene chloride with a solution of anhydrous $SnCl_2$ in thf gave rise to a number of products and at least two modes of reaction could be discerned [equations (1) and (2)]. Metallic

$$[Ph_4As]_2[B_{10}H_{12}] + SnCl_2 \longrightarrow Sn + 2HCl + [Ph_4As]_2[B_{10}H_{10}] \quad (1)$$

$$[Ph_4As]_2[B_{10}H_{12}] + SnCl_2 \longrightarrow [Ph_4As]_2[B_{10}H_{12}SnCl_2] \quad (2)$$

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† This work was carried out in the Department of Chemistry, The University of Newcastle upon Tyne during the period 1967—1970.

[1] R. W. Rudolph, R. L. Voorhees, and R. E. Cochoy, *J. Amer. Chem. Soc.*, 1970, **92**, 3351; V. Chowdhry, W. R. Pretzer, D. N. Rai, and R. W. Rudolph, *ibid.*, 1973, **95**, 4560; A. Tabereaux and R. N. Grimes, *Inorg. Chem.*, 1973, **12**, 792; C. G. Savory and M. G. H. Wallbridge, *J.C.S. Dalton*, 1972, 918.

[2] D. F. Gaines and T. V. Iorns, *J. Amer. Chem. Soc.*, 1967, **89**, 4249; 1968, **90**, 6617; J. C. Calabrese and L. F. Dahl, *ibid.*, 1971, **93**, 6042.

[3] R. E. Loffredo and A. D. Norman, *J. Amer. Chem. Soc.*, 1971, **93**, 5587.

[4] N. N. Greenwood and I. Ward, *Chem. Soc. Rev.*, 1974, **3**, 231.

[5] B. Youll, Ph.D. Thesis, University of Newcastle upon Tyne, 1970.

[6] N. N. Greenwood and E. Kunze, unpublished work, 1972.

tin and the tetraphenylarsonium salt of *closo*-decahydrodecaborate(2−) were precipitated from solution immediately following the appearance of a transient red colouration. It is notable in this reaction that rearrangement of *nido*-$[B_{10}H_{12}]^{2-}$ to *closo*-$[B_{10}H_{10}]^{2-}$ occurs by abstraction of hydrogen atoms to form HCl, the implied oxidation of the borate anion being compensated for by reduction of $SnCl_2$ to metallic tin. The metallaborane complex $[Ph_4As]_2[B_{10}H_{12}SnCl_2]$ was isolated as a pale yellow crystalline solid on addition of diethyl ether to the filtered reaction mixture. The equivalent reaction using $[Ph_3MeP]_2[B_{10}H_{12}]$ was entirely analogous and led to the corresponding products. $[Ph_3MeP]_2[B_{10}H_{12}SnCl_2]$ was found to be much more soluble than the corresponding tetraphenylarsonium salt and was isolated by addition of benzene to the mixture after removal of a red oil produced on addition of diethyl ether. Detailed analytical and physical data on these compounds are in the Experimental section. The $[B_{10}H_{10}]^{2-}$ salts were identified by boron analysis and their characteristic ^{11}B n.m.r. spectrum of two doublets of relative areas 1 : 4.

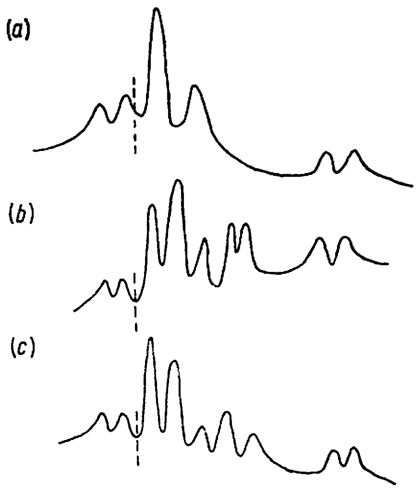

FIGURE 1 28·8 MHz ^{11}B N.m.r. spectra of stannadecaborate ions in thf solution relative to Et_2O,BF_3 as external standard (broken line): (*a*) $[Ph_4As]_2[B_{10}H_{12}SnCl_2]$; (*b*) $[Ph_4As]_2[B_{10}H_{12}Me_2SnCl_2]$; (*c*) $[Ph_4As]_2[B_{10}H_{12}Et_2SnCl_2]$. Numerical values of chemical shifts and *J*(B–H) coupling constants are in the text

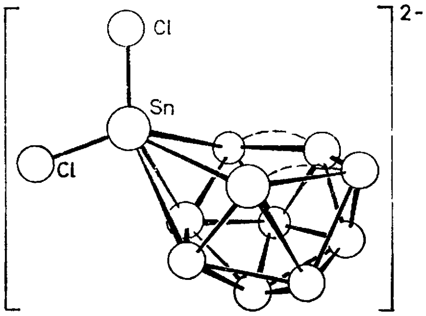

FIGURE 2 Proposed structure of the $[B_{10}H_{12}SnCl_2]^{2-}$ ion; each boron is bonded to a terminal H atom and the positions of the two bridging H atoms are shown by broken lines

The i.r. spectra of the salts of $[B_{10}H_{12}SnCl_2]^{2-}$ were complex because of the nature of the cations, but absorptions in the B–H and Sn–Cl regions were clearly visible at 2 490 (shoulder at 2 350 cm^{-1}) and at 292 and 257 cm^{-1} respectively. The ^{11}B n.m.r. spectrum of $[B_{10}H_{12}SnCl_2]^{2-}$ at 28·87 MHz comprised a succession of poorly resolved doublets (Figure 1). Detailed structural assignment is not possible, but it is clear that the electronic distribution within the $B_{10}H_{12}$ moiety has been considerably modified by co-ordination. Coupling constants are in the range expected for B–H terminal (see Experimental section).

On the basis of the foregoing chemical and physical evidence, and by analogy with numerous other metallaboranes,[4] it is possible to formulate the $[B_{10}H_{12}SnCl_2]^{2-}$ ion as a *nido*-stannadecaborate (Figure 2). A similar structure was recently proposed for the neutral species $Me_2GeB_{10}H_{12}$ and $Me_2SnB_{10}H_{12}$.[3] However, a subtle bonding problem arises because it is not clear whether the ion is a tin(II) compound formed by chelation of $SnCl_2$ by the ligand $[B_{10}H_{12}]^{2-}$ or a tin(IV) compound in which two hydrogen atoms of $[B_{10}H_{14}]^{2-}$ have been substituted by a bridging tin atom. To resolve this uncertainty the ^{119}Sn Mössbauer spectrum of $[Ph_4As]_2[B_{10}H_{12}SnCl_2]$ was obtained at liquid-nitrogen temperature. The spectrum consisted of a doublet with a chemical isomer shift relative to $BaSnO_3$ of δ 3·17 ± 0·03 mm s^{-1} and a quadrupole splitting of Δ 1·26 ± 0·03 mm s^{-1}. This is well within the expected range for Sn^{II} complexes (δ 2·3—4·2 mm s^{-1}) [7] and excludes the possibility of Sn^{IV} for which δ is always $<2{\cdot}0$ mm s^{-1}. The observed values for δ and Δ are both close to those for known complexes of $SnCl_2$.[7] The values can also be compared with those recently published [8] for the *closo*-carbaborane derivatives of tin(II), 3-Sn-1,2-$C_2B_9H_{11}$, namely δ 4·67 ± 0·04 mm s^{-1} relative to $^{119}SnO_2$ and Δ 3·83 ± 0·4 mm s^{-1}.

In an attempt to prepare metallaborane complexes of Sn^{IV}, a solution of $[Ph_4As]_2[B_{10}H_{12}]$ in methylene chloride was treated with dimethyltin dichloride dissolved in thf. The reaction was even more complex than that with anhydrous $SnCl_2$ and products isolated included $[Ph_4As]_2[B_{10}H_{10}]$, $[Ph_4As]_2[Me_2SnCl_2]$, $[Ph_4As]_2[B_{10}H_{12}Me_2SnCl_2]$, and HCl. The *closo*-$[B_{10}H_{10}]^{2-}$ salt precipitated when the reacting solutions were mixed and the tetraphenylarsonium salts of $[Me_2SnCl_2]^{2-}$ and $[B_{10}H_{12}Me_2SnCl_2]^{2-}$ were precipitated on addition of diethyl ether to the filtrate; subsequent separation was effected by a series of fractional crystallizations using mixtures of thf and diethyl ether. The corresponding series of reactions starting with $[Ph_3MeP]_2[B_{10}H_{12}]$ were analogous, but the products proved to be less easily separable and the reaction was consequently less satisfactory as a preparative route. Reactions of Et_2SnCl_2 with $[Ph_4As]_2[B_{10}H_{12}]$ and $[Ph_3MeP]_2[B_{10}H_{12}]$ gave the quaternary arsonium and phosphonium salts of $[B_{10}H_{10}]^{2-}$ and $[B_{10}H_{12}Et_2SnCl_2]^{2-}$, the latter being soluble in thf and insoluble in diethyl ether, thus

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[7] N. N. Greenwood and T. C. Gibb, 'Mössbauer Spectroscopy,' Chapman and Hall, London, 1971.

[8] R. W. Rudolph and V. Chowdhry, *Inorg. Chem.*, 1974, **13**, 248.

enabling them to be purified by recrystallization from a mixture of the two solvents. Similar reactions with Ph_2SnCl_2 gave only small yields of $[Ph_4As]_2[B_{10}H_{10}]$ and $[Ph_3MeP]_2[B_{10}H_{10}]$ and no stannadecaborate complexes were isolated.

The i.r. spectrum of $[Ph_4As]_2[B_{10}H_{12}Me_2SnCl_2]$ was too complex to permit a detailed structural assignment of the co-ordination about the tin atom but the results are consistent with (though they do not rigorously establish) *trans*-$SnMe_2$, *cis*-$SnCl_2$, and chelation of Me_2SnCl_2 by $[B_{10}H_{12}]^{2-}$ (Figure 3). B–H Absorptions occurred at 2 500 cm^{-1} with a shoulder at 2 350 cm^{-1}; an absorption assignable to Sn–Me occurred at 565 cm^{-1} and Sn–Cl absorptions at 330 cm^{-1} (and possibly at 280 cm^{-1}) respectively. The ^{11}B n.m.r. spectra of the tetraphenylarsonium salts of $[B_{10}H_{12}Me_2SnCl_2]^{2-}$ and $[B_{10}H_{12}Et_2SnCl_2]^{2-}$ are in Figure 1. The baselines slope badly because of the high-gain settings required by the low concentration of boron in solution and this militates against precise determination of relative peak areas. However the broad features of the spectra are evident and lead to the numerical data cited in the Experimental section.

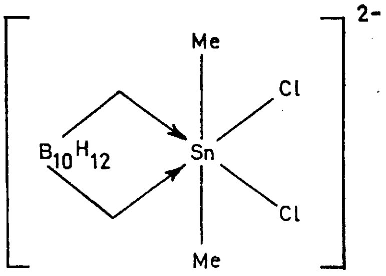

FIGURE 3 Proposed structure of the $[B_{10}H_{12}Me_2SnCl_2]^{2-}$ ion

The ^{119}Sn Mössbauer spectrum of $[Ph_4As]_2$-$[B_{10}H_{12}Me_2SnCl_2]$ at 77 K confirmed the presence of Sn^{IV}:[7] chemical isomer shift δ 1·75 ± 0·01 mm ms^{-1} relative to $BaSnO_3$, quadrupole splitting Δ 3·13 mm s^{-1}. The large value of the quadrupole splitting is again consistent with a *trans*-disposition of the two methyl groups,[7] though compounds which are closely related structurally are not available to strengthen this diagnosis.[9,10]

Although peripheral to the main theme of this work, attention should also be drawn to the isolation of the unusual ion $[Me_2SnCl_2]^{2-}$, isoelectronic with Me_2TeCl_2. A structure analogous to that of TeF_4 and based on a trigonal bipyramid with an equatorial non-bonding pair of electrons might therefore be envisaged. The i.r. spectrum of $[Ph_4As]_2[Me_2SnCl_2]$ showed two strong bands in the Sn–Me stretching region at 540 and 510 cm^{-1} and two bands in the Sn–Cl stretching region, a narrow band of 370 cm^{-1} and a broad one centred at 270 cm^{-1}. The ion $[Me_2SnCl_2]^{2-}$ is formally a tin(II) compound and its formation from the tin(IV) compound Me_2SnCl_2 during ' oxidation ' of $[B_{10}H_{12}]^{2-}$ to $[B_{10}H_{10}]^{2-}$ parallels the formation of tin metal from tin(II) chloride in the first sequence of reactions.

EXPERIMENTAL

Reactions were carried out in an atmosphere of dry oxygen-free nitrogen in a glove-box. Solvents were distilled from lithium aluminium tetrahydride or calcium hydride under an atmosphere of nitrogen.

The i.r. spectra of most of the compounds were examined as Nujol mulls between plates of KBr or CsI. High-resolution spectra in the range 4 000—400 cm^{-1} were recorded on a Perkin-Elmer 125 grating spectrophotometer and medium-resolution spectra down to 250 cm^{-1} were obtained on a Perkin-Elmer 457 grating spectrophotometer. Far-i.r. spectra in the range 400—20 cm^{-1} were obtained on an R.I.I.C. Fourier-transform FS520 spectrometer using a Melinex beam divider and Polythene windows. Proton n.m.r. spectra were obtained at 90 MHz and ^{11}B spectra at 28·87 MHz on a Bruker Spectrospin spectrometer; Et_2O,BF_3 was used as external standard. Mössbauer spectra were obtained at 77 K on an N.S.E.C. model AM-1 spectrometer using a source of $Ba^{119}SnO_3$ and computed by means of programs written by Dr. T. C. Gibb. Electrical conductivity was measured at 25 °C by means of a cell with platinum-black electrodes and a Wayne–Kerr Universal Bridge model B221 which allowed both resistance and capacitance balancing.

Analysis was by Parr-bomb degradation. Boron was determined on the filtrate after acidification with hydrochloric acid and boiling to remove dissolved carbon dioxide. The solution was adjusted to pH 6·3 using dilute sodium hydroxide and then after adding a large excess of mannitol was titrated to pH 8·0 with 0·1M-sodium hydroxide. Chlorine was determined by Volhard's method. Tin was usually precipitated as sulphide from acidified aliquot portions of the Parr filtrate and then ignited to the oxide to constant weight. However, in the presence of arsenic the tin determinations tended to be high due to precipitation of arsenic sulphide prior to ignition. This problem was solved by reducing the arsenic to As^{III} with phosphorous acid and precipitating the sulphide in the presence of a high concentration of fluoride ions. The tin was not precipitated under these conditions, but could be precipitated by Cupferron after removal of arsenic sulphide; the precipitate was then ignited and weighed as SnO_2. Arsenic was determined as the sulphide after reduction of aliquot portions of the Parr filtrate by phosphorous acid; the precipitate was washed on the sinter successively with 8M-hydrochloric acid saturated with hydrogen sulphide, carbon disulphide, and ethanol, before drying at 105 °C. Phosphorus was determined as phosphate by precipitation of ammonium magnesium phosphate hexahydrate and ignition to magnesium pyrophosphate. Where phosphorus occurred in the presence of tin, it was first precipitated as triammonium dodecamolybdophosphate(3–). Carbon and hydrogen analyses were by Beller Mikroanalytische Laboratorium, Gottingen, and Alfred Bernhardt Mikroanalytische Laboratorium, Engelskirchen, Germany. Analytical data on the stannadecaborane complexes are in the Table.

Preparations.—*Bis(tetraphenylarsonium) dodecahydro*-nido-*decaborate*(2–). A solution of $[Ph_4As]Br$ (1·41 g, 2·86 mmol) in CH_2Cl_2 (15 cm^3) was added to a solution of $Na_2[B_{10}H_{12}]$,2thf (0·47 g, 1·43 mmol) in thf (35 cm^3). A transient red colouration was rapidly followed by the simultaneous precipitation of a white solid (NaBr) and an

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[9] N. W. G. Debye, E. Rosenberg, and J. J. Zuckerman, *J. Amer. Chem. Soc.*, 1968, **90**, 3234.

[10] P. G. Hendricker, *Inorg. Chem.*, 1968, **8**, 2328.

orange-yellow solid (A). The solids were filtered and weighed (0·93 g). Further addition of thf to the filtrate yielded more orange-yellow solid (0·21 g) which was in turn collected by filtration and added to the initial mixture. The resulting pale yellow solution was evaporated to *ca.* 15 cm^3 and diethyl ether was added slowly. A pale yellow crystalline solid (B) (0·32 g) was precipitated. The mixture of NaBr and (A) was extracted with methylene chloride and gradual addition of thf to the extract yielded small, bright yellow, *needles* of $[Ph_4As]_2[B_{10}H_{12}]$ (55% yield) (Found: C, 55·1; H, 5·3; As, 17·2; B, 12·5. $[Ph_4As]_2[B_{10}H_{12}]$ requires C, 65·0; H, 5·9; As, 16·9; B, 12·2%). The pale yellow crystalline solid was recrystallized similarly by the gradual addition of diethyl ether to a solution in thf. The product (yield 13%) was probably the mixed derivative $[Ph_4As]Na[B_{10}H_{12}]$ (Found: C, 42·7; H, 4·7; As, 19·5; B, 16·15; Na, 1·0. $[Ph_4As]Na[B_{10}H_{12}]$ requires C, 54·8; H, 6·1; As, 14·2; B, 20·5; Na, 4·4%). The yields of the products (A) and (B) could be varied by altering the mol ratios of reactants and the volume of the solvents: *e.g.* when $[Ph_4As]Br$ and $Na_2[B_{10}H_{12}]$,2thf were reacted in 1 : 1 mol ratio in a 2 : 1 mixture of CH_2Cl_2–thf the yields were $[Ph_4As]_2[B_{10}H_{12}]$ (4%) and $[Ph_4As]Na[B_{10}H_{12}]$ (64%). The detailed i.r. spectra of these salts and of $[Ph_3MeP]_2[B_{10}H_{12}]$ were recorded in the range 4 000—20 cm^{-1} and the ^{11}B n.m.r. spectra (relative to Et_2O,BF_3) were also obtained.[5] For $[Ph_4As]_2[B_{10}H_{12}]$ the ^{11}B spectrum comprised (*a*) a low-field doublet of area 1 centred at δ +1·44 p.p.m. [*J*(B–H) 162 Hz], (*b*) a doublet of area 2 at 6·65 p.p.m. [*J*(B–H) 132 Hz], (*c*) asymmetric peaks of total area 5 centred at 19·7, 25·9, and 31·3 p.p.m., (*d*) a doublet of area 1 at 36·2 p.p.m. [*J*(B–H) 134 Hz], and (*e*) a high-field doublet of area 1 at 40·60 p.p.m. [*J*(B–H) 132 Hz].

Analytical data (%) for stannadecaborates

Compound		C	H	As/P	B	Cl	Sn
$[Ph_4As]_2[B_{10}H_{12}SnCl_2]$	Found	51·8	5·6	14·2	10·7	6·8	11·1
	Calc.	53·6	4·9	13·9	10·1	6·6	11·0
$[Ph_3MeP]_2[B_{10}H_{12}SnCl_2]$	Found			7·5	11·9	8·7	15·1
	Calc.			7·2	12·5	8·2	13·7
$[Ph_4As]_2[B_{10}H_{12}Me_2SnCl_2]$	Found	55·2	5·6	12·9	10·1	6·2	10·2
	Calc.	54·3	5·3	13·5	9·8	6·4	10·7
$[Ph_4As]_2[B_{10}H_{12}Et_2SnCl_2]$	Found	57·3	5·9	12·6	9·4	6·3	11·2
	Calc.	55·0	5·5	13·2	9·5	6·3	10·5
$[Ph_3MeP]_2[B_{10}H_{12}Et_2SnCl_2]$	Found				12·0	7·6	13·7
	Calc.				11·7	7·7	12·9

Bis(*methyltriphenylphosphonium*) *dodecahydro*-nido-*decaborate*(2—). A solution of $[Ph_3MeP]Br$ (3·99 g) in CH_2Cl_2 (15 cm^3) was added to $Na_2[B_{10}H_{12}]$,2thf (2·08 g) in thf (mol ratio of reactants 1 : 2). Orange-yellow $[Ph_3MeP]_2[B_{10}H_{12}]$ (0·93 g) and NaBr (1·25 g) were precipitated and a further 0·21 g of $[Ph_3MeP]_2[B_{10}H_{12}]$ was obtained on adding more thf (total yield 50%). The remaining solution was evaporated to 15 cm^3 and diethyl ether was added, but no pale yellow solid was precipitated on further addition of diethyl ether or benzene.

Reactions.—$[Ph_4As]_2[B_{10}H_{12}]$ *and* $SnCl_2$. A solution of $[Ph_4As]_2[B_{10}H_{12}]$ (1·44 g, 1·63 mmol) in CH_2Cl_2 (25 cm^3) was added to a solution of anhydrous $SnCl_2$ (0·17 g, 0·92 mmol) in thf (30 cm^3). There was an immediate red colouration, followed at once by precipitation of metallic tin and a white solid, $[Ph_4As]_2[B_{10}H_{10}]$. The solids were filtered, extracted with CH_2Cl_2, and $[Ph_4As]_2[B_{10}H_{10}]$ reprecipitated with thf (yield 0·32 g, 0·36 mmol) (Found: B, 12·4. Calc.: B, 12·2%). ^{11}B N.m.r. spectrum: two doublets of relative intensity 1 : 4 at δ 0·69 [*J*(B–H) 142] and 28·4 p.p.m. [*J*(B–H) 124 Hz] as expected.

The reaction solution, after filtration, was concentrated to 15 cm^3 and *ca.* 5 cm^3 of diethyl ether was added to yield pale yellow *crystals* of $[Ph_4As]_2[B_{10}H_{12}SnCl_2]$. The compound was recrystallized by addition of Et_2O to a thf solution (yield 0·61 g, 40%). Analytical data are in the Table, and the ^{11}B n.m.r. spectrum is in Figure 1: the low-field doublet at −6·30 p.p.m. has *J*(B–H) 148 Hz and a relative area 4; the high-field doublet of area 1 has δ +37·4 p.p.m. and *J*(B–H) 150 Hz; and the intense asymmetric central resonance of area 5 has peaks at +2·14 and 6·58 p.p.m. (separation 128 Hz).

$[Ph_3MeP]_2[B_{10}H_{12}]$ *and* $SnCl_2$. The reaction was carried out in essentially the same way, precipitation of metallic tin and $[Ph_3MeP]_2[B_{10}H_{10}]$ (0·41 g) following the momentary red colouration which appeared on first mixing the solutions containing $[Ph_3MeP]_2[B_{10}H_{12}]$ (0·93 g) and $SnCl_2$ (0·25 g). $[Ph_3MeP]_2[B_{10}H_{10}]$ Was identified by its i.r. and ^{11}B n.m.r. spectrum and by analysis (Found: B, 16·3. Calc.: B, 16·0%). The filtrate was concentrated and diethyl ether added to precipitate an orange oil; the oil partially crystallized on standing to yield well formed pale yellow crystals and a red oil. The mixture was filtered and a little benzene and light petroleum were added to the resulting solution. A pale yellow crystalline *precipitate* of $[Ph_3MeP]_2[B_{10}H_{12}SnCl_2]$ was obtained (0·27 g). Analytical data are in the Table and the ^{11}B n.m.r. spectrum was identical with that of the tetraphenylarsonium salt shown in Figure 1.

$[Ph_4As]_2[B_{10}H_{12}]$ *and* Me_2SnCl_2. A solution of $[Ph_4As]_2[B_{10}H_{12}]$ (1·99 g, 2·25 mmol) in CH_2Cl_2 (25 cm^3) was added to a solution of Me_2SnCl_2 (0·47 g, 2·14 mmol) in CH_2Cl_2 (30 cm^3). A white crystalline solid $[Ph_4As]_2[B_{10}H_{10}]$ (0·58 mmol) started to deposit almost immediately and precipitation continued for *ca.* 5 min. The filtrate was concentrated to 20 cm^3 and diethyl ether added until a pale yellow crystalline material deposited (0·65 g). The mixture was then separated by a sequence of fractional crystallizations using a range of thf–diethyl ether mixtures to give pale yellow *crystals* of $[Ph_4As]_2[B_{10}H_{12}Me_2SnCl_2]$ (0·17 g) (see Table for analytical data) and white *crystals* of $[Ph_4As]_2[Me_2SnCl_2]$ (0·04 g) (Found: Cl, 7·4. Calc.: Cl, 7·2%). In an experiment to determine whether substantial quantities of hydrogen or methane were evolved during the reaction, $[Ph_4As]_2[B_{10}H_{12}]$ (1·25 g, 1·41 mmol) in CH_2Cl_2 reacted with Me_2SnCl_2 (0·30 g, 1·36 mmol) in thf on a vacuum line during 30 min at room temperature and the volume of permanent gas evolved was determined by use of a Töpler pump after the reaction mixture had been repeatedly cycled between room and liquid-nitrogen temperature. The total amount of gas evolved was 0·02 mmol and was predominantly hydrogen with a trace of methane (1·6%) as determined by mass spectroscopy. As 0·35 mmol of $[Ph_4As]_2[B_{10}H_{10}]$ was produced in this experiment it is clear that elimination of HCl rather than hydrogen was a major step in the reaction. The i.r. spectrum of $[Ph_4As]_2[B_{10}H_{12}Me_2SnCl_2]$ has been recorded in detail [5] and the Mössbauer spectrum is discussed above. The ^{11}B n.m.r. spectrum in thf is shown in Figure 1 and comprises the following features: (*a*) a low-field doublet of area 2 at −6·06 p.p.m. relative to Et_2O,BF_3 and with *J*(B–H) 152 Hz; (*b*) an asymmetric doublet of area 4 at +5·19 p.p.m. [*J*(B–H) 136 Hz]; (*c*) a doublet of area 1 partly overlapping (*b*) and having δ *ca.* 9·7 p.p.m. and *J*(B–H) *ca.* 140 Hz; (*d*) a doublet of area 2 at 20·2 p.p.m. [*J*(B–H) 124 Hz]; and (*e*) a high-field doublet of area 2 centred at 37·4 p.p.m. and having *J*(B–H) 136 Hz.

$[Ph_4As]_2[B_{10}H_{12}]$ *with* Et_2SnCl_2. A solution of $[Ph_4As]_2[B_{10}H_{12}]$ (1·69 g, 1·91 mmol) in CH_2Cl_2 (25 cm^3) was added to a solution of Et_2SnCl_2 (0·49 g, 1·98 mmol) in thf (30 cm^3) at room temperature. There was immediate deposition of a white crystalline solid which was filtered off after 10 min and identified as $[Ph_4As]_2[B_{10}H_{10}]$ by its ^{11}B n.m.r. spectrum. The filtrate was concentrated to 20 cm^3 during which more $[Ph_4As]_2[B_{10}H_{10}]$ deposited from solution. On addition of Et_2O a sticky yellow solid (0·11 g) was precipitated and removed by filtration. Further addition of Et_2O precipitated a pale yellow crystalline *solid* which, on recrystallization, gave 0·50 g of $[Ph_4As]_2[B_{10}H_{12}Et_2SnCl_2]$ (see Table for analytical data). The filtrate was further concentrated to 15 cm^3 and benzene and a little cyclohexane were added; a sticky yellow solid formed but resisted attempts to recrystallize it and no diethyl analogue of $[Me_2SnCl_2]^{2-}$ was isolated. The ^{11}B n.m.r. spectrum of $[B_{10}H_{12}Et_2SnCl_2]^{2-}$ in thf is shown in Figure 1; it is similar to that of the dimethyl analogue, though the relative intensities of the lines are somewhat different.

Reactions of $[Ph_3MeP]_2[B_{10}H_{12}]$ with Me_2SnCl_2 and Et_2SnCl_2 were analogous to the above reactions using the tetraphenylarsonium salt, but solubility relations made the isolation of pure products more difficult.

We thank the S.R.C. for financial support and for the award of a maintenance grant (to B. Y.).

[4/1482 *Received*, 19*th July*, 1974]