Dimethylindium(III), Dimethylthallium(III), and Methylmercury(II) Derivatives of the Dodecahydro-*nido*-decaborate(2−) Ion

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Deprotonation of decaborane(14) by trimethylindium yields two derivatives, $[Me_2In]^+[B_{10}H_{12}InMe_2]^-$ and $[B_{10}H_{12}InMe]$. The analogous reaction with trimethylthallium produces $[Me_2Tl]^+[B_{10}H_{12}TlMe_2]^-$ and $[Me_2Tl]^+[B_{10}H_{13}]^-$. The presence of two distinct dimethylmetal groups in the compounds $[Me_2M]^+[B_{10}H_{12}MMe_2]^-$, one of which is co-ordinated by the dodecahydro-*nido*-decaborate(2−) anion, is based on analytical data, electrical conductivity, i.r. and n.m.r. spectra, and chemical reactions of the compounds. Metathetical reactions of $[Me_2Tl]^+[B_{10}H_{12}TlMe_2]^-$ lead to $[Ph_3PMe]^+[B_{10}H_{12}TlMe_2]^-$ and to the new organomercury complex $[Ph_3PMe]^+[B_{10}H_{12}HgMe]^-$ for which physical data are also presented.

REACTIONS of decaborane(14) with derivatives of Group IIIB elements other than boron have received little attention,[1] despite the current interest in Group IIIB derivatives of boron hydrides and carbaboranes in general.[2-5] Indeed, the only examples are the reaction of decaborane with trimethylamine–alane to give the extremely reactive compound $[Me_3NH]^+[B_{10}H_{12}AlH_2]^-$ as an etherate [2]

$$B_{10}H_{14} + Me_3N{\cdot}AlH_3 \xrightarrow{Et_2O} [Me_3NH]^+[B_{10}H_{12}AlH_2]^-{\cdot}2Et_2O + H_2$$

and the corresponding reaction with trimethylamine–gallane to produce the more stable unsolvated complex $[Me_3NH]^+[B_{10}H_{16}Ga]^-$ without loss of hydrogen.[2]

$$B_{10}H_{14} + Me_3N{\cdot}GaH_3 \xrightarrow{Et_2O} [Me_3NH]^+[B_{10}H_{16}Ga]^-$$

In view of the known reactivity of heavy-metal alkyls with decaborane and the existence of numerous complexes in which the dianion $[B_{10}H_{12}]^{2-}$ acts as a *tetrahapto*-ligand,[1] the reactions of decaborane with trimethylindium and trimethylthallium were investigated in an attempt to extend the range of known metalloborane derivatives. A preliminary report of some of this work has been published.[6]

RESULTS AND DISCUSSION

Deprotonation of decaborane by trimethylindium in 1 : 2 molar ratio in benzene at room temperature yields the complex $[Me_2In]^+[B_{10}H_{12}InMe_2]^-$. The analogous thallium compound can be isolated from the corresponding reaction in diethyl ether:

$$2Me_3M + B_{10}H_{14} \xrightarrow{\text{solv.}} [Me_2M]^+[B_{10}H_{12}MMe_2]^- + 2MeH$$

Both compounds are pale yellow, air-sensitive, solids which crystallise from solution during the reaction, and in each case two equivalents of methane were evolved. $[Me_2Tl]^+[B_{10}H_{12}TlMe_2]^-$ is soluble in polar solvents such as acetone, tetrahydrofuran, and acetonitrile, while the indium analogue is soluble in acetone but rapidly decomposes in the latter two solvents with deposition of indium metal.

Reaction of $[Me_2Tl]^+[B_{10}H_{12}TlMe_2]^-$ with an equimolar quantity of triphenylmethylphosphonium bromide in dichloromethane–tetrahydrofuran at room temperature results in the precipitation of dimethylthallium bromide and yields the yellow crystalline salt $[Ph_3PMe]^+[B_{10}H_{12}TlMe_2]^-$. Use of 2 mole equivalents of $[Ph_3PMe]Br$ in this reaction does not result in the replacement of the second dimethylthallium group. However, reaction of $[Me_2Tl]^+[B_{10}H_{12}TlMe_2]^-$ with methylmercury chloride in tetrahydrofuran at room temperature, followed by addition of a solution of $[Ph_3PMe]Br$ in dichloromethane, yields $[Ph_3PMe]^+[B_{10}H_{12}HgMe]^-$, as an air-stable orange crystalline solid which is soluble in chloroform, dichloromethane, tetrahydrofuran, acetone, and acetonitrile but insoluble in hexane and ether.

In contrast to its behaviour in non-aqueous polar solvents, $[Me_2Tl]^+[B_{10}H_{12}TlMe_2]^-$ dissolves in water to form $[Me_2Tl]^+$ (as shown by ^1H n.m.r.) and $[B_{10}H_{12}]^{2-}$ ions; from such aqueous solutions Me_2TlBr and $[Ph_3PMe]^+{}_2[B_{10}H_{12}]^{2-}$ can be obtained in almost quantitative yield by reaction firstly with sodium bromide and then with $[Ph_3PMe]Br$.

All attempts to carry out metathetical reactions of $[Me_2In]^+[B_{10}H_{12}InMe_2]^-$ were unsuccessful, presumably because of the high solubility of dimethylindium(III) halides in the solvents employed.

When trimethylindium was treated with an equimolar amount of decaborane(14) in benzene solution $[Me_2In]^+[B_{10}H_{12}InMe_2]^-$ was again formed, but a second product, $[B_{10}H_{12}InMe]$, remained in solution, and could be isolated as a pale yellow solid. The second product from the corresponding thallium reaction was $[Me_2Tl]^+[B_{10}H_{13}]^-$, which also remained in solution. Evidently the inherent stability of the dimethylthallium cation precludes further elimination of methane from $[Me_2Tl]^+[B_{10}H_{13}]^-$ to give the thallium analogue of $[B_{10}H_{12}InMe]$ and attack by a second molecule of trimethylthallium is necessary for the reaction to proceed further.

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

[2] N. N. Greenwood and J. A. McGinnety, *Chem. Comm.*, 1965, 331; *J. Chem. Soc.* (*A*), 1966, 1090.

[3] B. M. Mikhailov and T. V. Potapova, *Izvest. Akad. Nauk S.S.S.R., Ser. khim.*, 1968, **5**, 1153; M. R. Churchill, A. H. Reis, D. A. T. Young, G. R. Willey, and M. F. Hawthorne, *J. Amer. Chem. Soc.*, 1970, **92**, 6663; *Chem. Comm.*, 1971, 298.

[4] R. N. Grimes and W. J. Rademaker, *J. Amer. Chem. Soc.*, 1969, **91**, 6498; R. N. Grimes, W. J. Rademaker, M. L. Denniston, R. F. Bryan, and P. T. Greene, *ibid.*, 1972, **94**, 1865.

[5] J. L. Spencer, M. Green, and F. G. A. Stone, *J.C.S. Chem. Comm.*, 1972, 1178.

[6] N. N. Greenwood, N. F. Travers, and D. W. Waite, *Chem. Comm.*, 1971, 1027.

Physical Properties of $[Me_2In]^+[B_{10}H_{12}InMe_2]^-$, $[Me_2Tl]^+[B_{10}H_{12}TlMe_2]^-$, *and* $[Ph_3PMe]^+[B_{10}H_{12}TlMe_2]^-$.—Conductivity measurements for these three compounds (Table 1) clearly show that, in solution, the compounds exist as 1 : 1 electrolytes whereas $[B_{10}H_{12}InMe]$ is essentially a non-electrolyte.

TABLE 1

Molar conductivity of $[B_{10}H_{12}]^{2-}$ complexes in acetone

Compound	Concentration/ mmol l^{-1}	Λ_M/ Ω^{-1} cm^2 mol^{-1}
$[Me_2In]^+[B_{10}H_{12}InMe_2]^-$	1·00	136
$[Me_2Tl]^+[B_{10}H_{12}TlMe_2]^-$	1·01	138
$[Ph_3PMe]^+[B_{10}H_{12}TlMe_2]^-$	0·97	140
$[B_{10}H_{12}InMe]$	1·05	27
$Cs^+[B_9H_{12}S]^-$	0·99	136

The 90 MHz ^1H n.m.r. spectra of $[^2H_6]$acetone solutions of $[Me_2In]^+[B_{10}H_{12}InMe_2]^-$ and $[Me_2Tl]^+[B_{10}H_{12}TlMe_2]^-$, which are shown in Figure 1, indicate the presence of two distinct dimethylmetal groups in each case. The spectrum of the indium compound consists of three sharp singlets of relative intensities 6 : 3 : 3 and a broad hump of intensity 2 to high field. The most intense singlet is assigned to $[Me_2In]^+$ and the existence of *two* singlets of equal intensity for the covalently bound Me_2In group suggests that the two methyl groups are in different environments and that $[B_{10}H_{12}InMe_2]^-$ may have a structure such as that in Figure 2, where the dodecahydro-*nido*-decaborate(2−) ion, $[B_{10}H_{12}]^{2-}$, acts as a formal bidentate four-electron, *tetrahapto*-ligand towards $[Me_2In]^+$. Single-crystal *X*-ray studies have shown that the $[B_{10}H_{12}]^{2-}$ ligand behaves in an analogous manner towards Zn^{2+} and Ni^{2+} in the complex ions $[Zn(B_{10}H_{12})_2]^{2-}$ [7] and $[Ni(B_{10}H_{12})_2]^{2-}$.[8] The broad hump at high field in the proton n.m.r. spectrum is most reasonably assigned to the two bridging hydrogen atoms between B(6)–B(7) and B(8)–B(9) in the proposed structure. Broad-band ^{11}B-decoupling of the spectrum resulted in considerable sharpening of this signal. The signals for the remaining ten protons attached as terminal hydrogens to boron are seen only at high r.f. power and remain unresolved under the conditions employed.

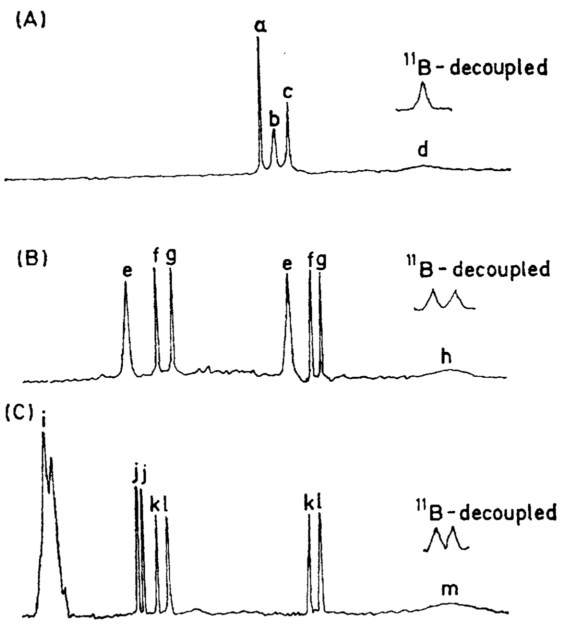

FIGURE 1 The 90 MHz ^1H n.m.r. spectra of some Group IIIB derivatives of $[B_{10}H_{12}]^{2-}$ (assignment of coupling constants verified by spectra obtained at 60 MHz) τ (relative to tetramethylsilane)/p.p.m. (*J*/Hz). (A) $[Me_2In]^+[B_{10}H_{12}InMe_2]^-$ in $[^2H_6]$acetone: a, 9·93; b, 10·40; c, 10·73; d, 15·3. (B) $[Me_2Tl]^+[B_{10}H_{12}TlMe_2]^-$ in $[^2H_6]$acetone: e, 8·54 (404); f, 9·31 (354); g, 9·67 (338); h, 15·8 (66?). (C) $[Ph_3PMe]^+$-$[B_{10}H_{12}TlMe_2]^-$ in $[^2H_1]$chloroform: i, 2·00; j, 7·15 (16); k, 9·35 (346); l, 9·68 (328); m, 15·8 (66?)

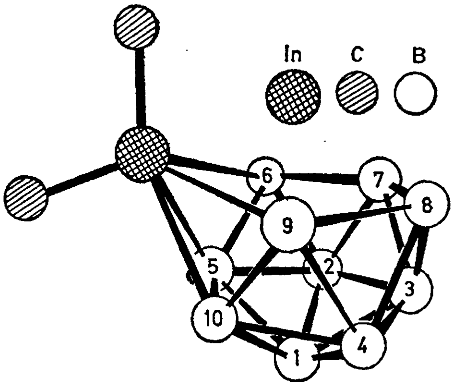

FIGURE 2 Proposed heavy-atom structure of the $[B_{10}H_{12}InMe]^-$ ion; numbering as in decaborane(14). Each boron atom carries one external hydrogen atom and there are bridging hydrogen atoms between B(6)–B(7) and between B(8)–B(9)

The pattern of the 90 MHz ^1H n.m.r. spectrum of $[Me_2Tl]^+[B_{10}H_{12}TlMe_2]^-$ is similar (see Figure 1) except that Tl–H coupling causes each signal to split into a doublet. (Separate splitting of the proton signals by ^{203}Tl, abundance 30%, and ^{205}Tl, abundance 70%, was not observed since these nuclei have similar gyromagnetic ratios.) The ^1H n.m.r. spectrum of $[Ph_3PMe]^+[B_{10}H_{12}TlMe_2]^-$ shows no resonances corresponding to the cation $[Me_2Tl]^+$ and indicates the presence of only the covalently bound Me_2Tl group; as in $[Me_2Tl]^+[B_{10}H_{12}TlMe_2]^-$ the two doublets are assigned to two non-equivalent methyl groups bound to the co-ordinated thallium. The unresolved multiplet and sharp doublet in the low-field portion of the spectrum are assigned respectively to the phenyl groups and methyl group attached to phosphorus in the cation.

The signal for the bridging protons in both spectra is again a broad hump at high field but broad-band ^{11}B-decoupling results in the resolution of the signal into two sharper resonances separated by *ca.* 66 Hz. Either the bridging protons in the $[B_{10}H_{12}TlMe_2]^-$ ion are in different environments or they are coupled to thallium with *J*(Tl–H) = 66 Hz. Unfortunately, facilities for broad-band ^{11}B-decoupling of the 60 MHz spectra, which would have resolved the problem, were not available.

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[7] N. N. Greenwood, J. A. McGinnety, and J. D. Owen, *J. Chem. Soc.* (*A*), 1971, 809.

[8] L. J. Guggenberger, *J. Amer. Chem. Soc.*, 1972, **94**, 114.

The 28·87 MHz ^{11}B n.m.r. spectrum of $[Me_2In]^+[B_{10}H_{12}InMe_2]^-$ in acetone, which is shown in Figure 3, is entirely consistent with the structure proposed for the complex ion. The undecoupled spectrum yields little useful information but broad-band ^1H-decoupling clearly resolves the spectrum into five singlets of relative intensities 2 : 1 : 3 : 2 : 2 in order of increasing field. The predicted spectrum of the complex ion with the proposed structure would consist of six resonances of relative intensities (in arbitrary sequence) of 2 : 1 : 2 : 1 : 2 : 2, but accidental coincidence of the central two peaks of intensities 2 and 1 would result in the spectrum observed. Such accidental coincidences of component peaks is well known in ^{11}B n.m.r. spectroscopy even at higher frequencies.[9,10]

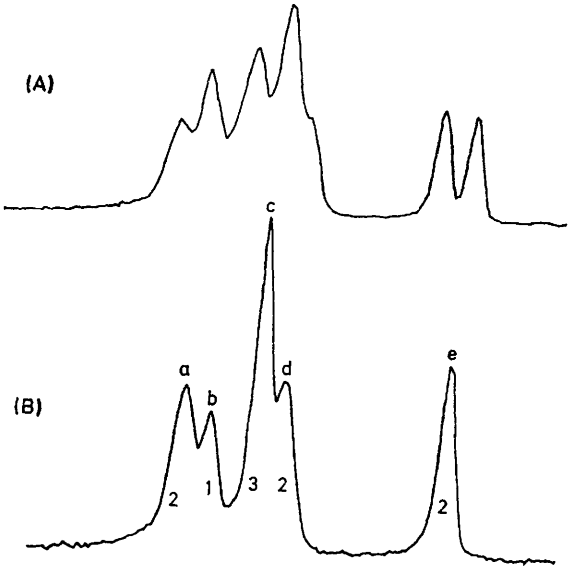

FIGURE 3 The 28·87 MHz ^{11}B n.m.r. spectrum of $[Me_2In]^+[B_{10}H_{12}InMe_2]^-$ in $[^2H_6]$acetone (BF_3·Et_2O = 0). A, Normal spectrum. B, ^1H-decoupled spectrum. Relative integrated areas are indicated beneath the peaks. δ/p.p.m. (*J*/Hz): a, −7·6; b, −3·8; c, 3·5; d, 7·2; e, 32·0 (140)

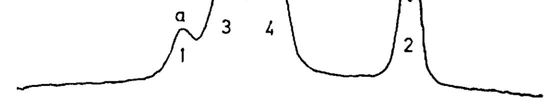

FIGURE 4 The 28·87 MHz ^{11}B n.m.r. spectrum of $[Me_2Tl]^+[B_{10}H_{12}TlMe_2]^-$ in $[^2H_6]$acetone (BF_3·Et_2O = 0). (A) Normal spectrum. (B) ^1H-decoupled spectrum. Relative integrated areas are indicated beneath the peaks. δ/p.p.m.: a, −7·8; b, −0·8; c, 1·1; d, 6·5; e, *ca.* 8; f, 32·3; *J*(B–H) 134 Hz, *J*(B–Tl) 70 Hz

The 28·87 MHz ^{11}B n.m.r. spectrum of $[Me_2Tl]^+[B_{10}H_{12}TlMe_2]^-$, in acetone which is shown in Figure 4 and which is virtually identical to that of $[Ph_3PMe]^+[B_{10}H_{12}TlMe_2]^-$, is less readily interpreted. In particular, the high-field portion of the spectrum consists of a non-binomial quartet which on broad-band ^1H-decoupling reduces to a doublet of relative intensity 2, while the low-field portion of the spectrum becomes a series of overlapping resonances of relative intensities 1 : 3 : 4. The 80·53 MHz ^{11}B n.m.r. spectrum of $[Me_2Tl]^+[B_{10}H_{12}TlMe_2]^-$ in tetrahydrofuran (Figure 5) confirms the assignment of the high-field portion of the spectrum as a doublet of doublets due, presumably, to the coupling of two equivalent boron atoms to both ^1H (J = 134 Hz) and to Tl (J = 70 Hz). However, the rest of the spectrum, which consists of two partially overlapping doublets of intensity 1, one triplet of intensity 1, and a partially resolved resonance of intensity 5 (probably formed by the overlapping of two doublets of intensity 2 and one doublet of intensity 1), suggests that the structure of the $[B_{10}H_{12}TlMe_2]^-$ ion is of lower symmetry than that proposed for the indium analogue, for which only two unique boron atoms are possible. The most reasonable structure is shown in Figure 6 and involves *dihapto*-coordination of the metal atom by B(5) and B(6); this implies that all boron atoms are inequivalent but, once again, accidental overlap of some of the signals in the spectrum would result in the observed apparent equivalence of three pairs of boron atoms. The only feature of the spectrum inconsistent with this interpretation is the triplet (J = 98 Hz) of relative intensity 1 in the low-field portion. One obvious explanation is that the $[B_{10}H_{12}TlMe_2]^-$ ion contains a BH_2 group, but

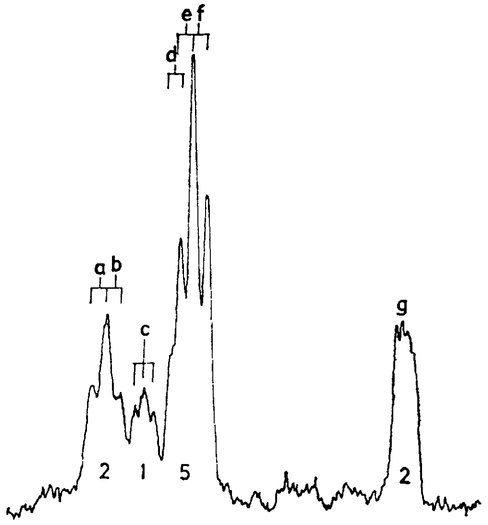

FIGURE 5 The 80·53 MHz ^{11}B n.m.r. spectrum of $[Me_2Tl]^+[B_{10}H_{12}TlMe_2]^-$ in tetrahydrofuran (BF_3·Et_2O = 0). Relative integrated areas are indicated beneath the peaks. δ/p.p.m. (*J*/Hz): a, −11·2 (165); b, −9·2 (165); c, −5·5 (98); d, −1·0 (165); e, 0·2 (165); f, 2·1 (165); g, 29·2

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[9] F. Klanberg, P. A. Wegner, G. W. Parshall, and E. L. Muetterties, *Inorg. Chem.*, 1968, **7**, 2072.

[10] A. R. Siedle, G. M. Bodner, and L. J. Todd, *J. Inorg. Nuclear Chem.*, 1971, **33**, 3671.

since integration of the ^1H n.m.r. spectrum of the ion shows that there are two bridging hydrogen atoms this would leave one boron atom which was not attached to any terminal hydrogen atoms, a situation which is clearly unsatisfactory in the absence of a singlet in the 80·53 MHz ^{11}B n.m.r. spectrum. A complete interpretation of the ^{11}B n.m.r. spectrum of the $[B_{10}H_{12}TlMe_2]^-$ ion must await the possibility of proton decoupling of the ^{11}B spectrum at 80·53 MHz.

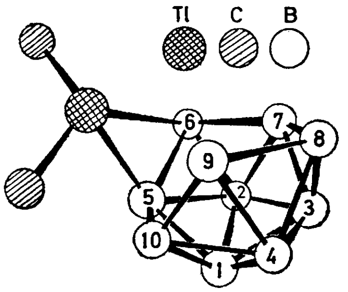

FIGURE 6 Proposed heavy-atom structure of the $[B_{10}H_{12}TlMe_2]^-$ ion; numbering as in Figure 2. Each boron atom carries one external hydrogen atom and there are bridging hydrogen atoms between B(6)–B(7) and between B(8)–B(9)

TABLE 2

I.r. data for ionic and co-ordinated dimethylindium(III) and dimethylthallium(III) groups

$[Me_2In]^+$-$[B_{10}H_{12}InMe_2]^-$ ν/cm^{-1}	$[Me_2Tl]^+$-$[B_{10}H_{12}TlMe_2]^-$ ν/cm^{-1}	Assignment
570	554	ν_{asym} in $[Me_2M]^+$
519	494	ν_{asym} in $[B_{10}H_{12}MMe_2]^-$
490	461	ν_{sym} in $[B_{10}H_{12}MMe_2]^-$

The i.r. spectral data for $[Me_2In]^+[B_{10}H_{12}InMe_2]^-$ and $[Me_2Tl]^+[B_{10}H_{12}TlMe_2]^-$ are given in the Experimental section. Within the range 4000—600 cm^{-1}, the spectra (obtained from Nujol mulls) are very similar, as might be expected for compounds with closely related structures. Within the range 600—400 cm^{-1}, however, each compound exhibits three strong absorptions which can be assigned to the vibrational modes involving the dimethylmetal moieties. The positions of these bands are listed in Table 2 together with the tentative assignments based on previous work of other authors,[11] which has shown that the asymmetric C–M–C stretching frequency in the linear $[Me_2M]^+$ cations (where M = In, Tl) falls within narrow limits,[11-13] whereas the symmetric and asymmetric M–C stretching frequencies observed when the metal is in a four-co-ordinate tetrahedral environment occur at lower wavenumbers.[13-15] Although the i.r. spectrum of $[Ph_3PMe]^+[B_{10}H_{12}TlMe_2]^-$ is obscured in the region 500—450 cm^{-1} by bands due to the cation, the absence of a band around 550 cm^{-1} attributable to $[Me_2Tl]^+$ lends support to the above assignments.

TABLE 3

90 MHz ^1H n.m.r. data for $[Ph_3PMe]^+[B_{10}H_{12}HgMe]^-$, $[Me_2Tl]^+[B_{10}H_{13}]^-$, and $[B_{10}H_{12}InMe]$

Compound	Solvent	τ/^{a} p.p.m.	J/^{b} Hz	Relative area	Assignment
$[Ph_3PMe]^+[B_{10}H_{12}HgMe]^-$	[$^2H_1$]Chloroform	2·17		15	Ph–P
		7·17	12	3	Me–P
		9·55		3	Me–Hg
		15·6 ^{c}		2	B–H–B
$[Me_2Tl]^+[B_{10}H_{13}]^-$	[$^2H_6$]Acetone	8·60	401		Me_2Tl^+
$[B_{10}H_{12}InMe]$	[$^2H_6$]Acetone	9·90			Me–In
	[$^2H_6$]Benzene	9·91			Me–In

^{a} Chemical shifts relative to $\tau_{Me_4Si} = 10·00$. ^{b} Coupling constants verified by spectra obtained at 60 MHz. ^{c} Broad hump which sharpens to singlet with broad-band ^{11}B decoupling.

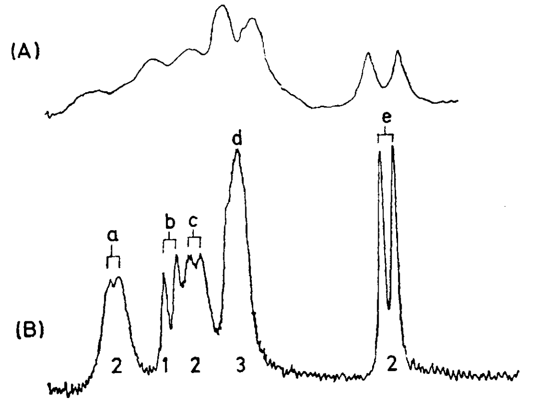

FIGURE 7 The ^{11}B n.m.r. spectrum of $[Ph_3PMe]^+[B_{10}H_{12}HgMe]^-$ in [$^2H_1$]chloroform ($BF_3·Et_2O$ = 0). (A) 28·87 MHz spectrum; (B), 80·53 MHz spectrum. Relative areas are indicated beneath the peaks. δ/p.p.m. (J/Hz): a, −8·1 (131); b, −0·4 (131); c, 2·8 (131); d, 9·0; e, 28·8 (137)

Physical Properties of $[Ph_3PMe]^+[B_{10}H_{12}HgMe]^-$.—The 90 MHz ^1H n.m.r. data for $[Ph_3PMe]^+[B_{10}H_{12}HgMe]^-$ are in Table 3 and are consistent with the proposed formulation of the compound. The 28·87 MHz ^{11}B n.m.r. spectrum shown in Figure 7 yields little information on the structure of the $[B_{10}H_{12}HgMe]^-$ ion. However, the 80·53 MHz spectrum (Figure 7) is better resolved and supports the proposal that the structure of the ion is analogous to that of $[B_{10}H_{12}InMe_2]^-$, with the methylmercury group chelated by the *tetrahapto*-$[B_{10}H_{12}]^{2-}$ ion. The spectrum consists of a series of doublets of relative intensities 2, 1, and 2, an unresolved resonance of intensity 3, and a doublet of intensity 2, in

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[11] J. S. Poland and D. G. Tuck, *J. Organometallic Chem.*, 1972, **42**, 315.

[12] C. W. Hobbs and R. S. Tobias, *Inorg. Chem.*, 1970, **9**, 1998.

[13] G. D. Shier and R. S. Drago, *J. Organometallic Chem.*, 1966, **5**, 330.

[14] H. C. Clark and A. L. Pickard, *J. Organometallic Chem.*, 1967, **8**, 427.

[15] H. C. Clark and A. L. Pickard, *J. Organometallic Chem.*, 1968, **13**, 61.

order of increasing field. Once again, if the most intense resonance consists of overlapping doublets of intensities 1 and 2, the spectrum is consistent with the proposed structure.

The i.r. spectral data for $[Ph_3PMe]^+[B_{10}H_{12}HgMe]^-$ are given in the Experimental section.

Physical Properties of $[Me_2Tl]^+[B_{10}H_{13}]^-$ *and* $[B_{10}H_{12}InMe]$.—The 90 MHz ^1H n.m.r. data for $[Me_2Tl]^+[B_{10}H_{13}]^-$ are in Table 3, the only prominent feature being a sharp doublet characteristic of the dimethylthallium cation.[13] Similarly the 28·87 MHz ^{11}B n.m.r. spectrum of the compound (Figure 8) is virtually identical with that reported for $[B_{10}H_{13}]^-$ by Norman,[16] and the i.r. data given in the Experimental section are also consistent with the formulation of the compound as $[Me_2Tl]^+[B_{10}H_{13}]^-$.

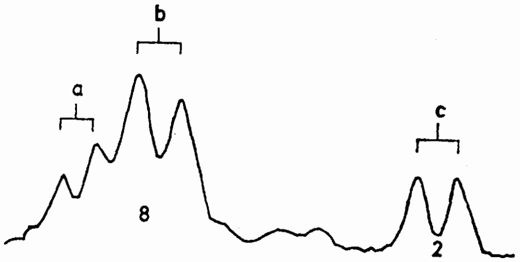

FIGURE 8 The 28·87 MHz ^{11}B spectrum of $[Me_2Tl]^+[B_{10}H_{13}]^-$ in $[^2H_6]$acetone ($BF_3{\cdot}Et_2O$ = 0). Relative integrated areas are indicated beneath the peaks. δ/p.p.m. (*J*/Hz): a, −6·4 (148); b, 4·5 (132); c, 35·0 (136)

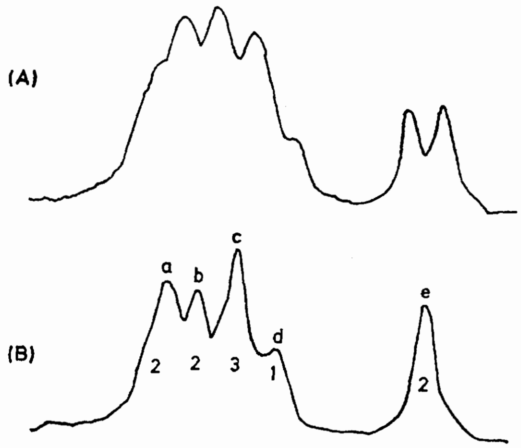

FIGURE 9 The 28·87 MHz ^{11}B n.m.r. spectrum of $[B_{10}H_{12}InMe]$ in $[^2H_6]$acetone ($BF_3{\cdot}Et_2O$ = 0). (A) Normal spectrum; (B) ^1H-decoupled spectrum. Relative integrated areas are indicated beneath the peaks. δ/p.p.m. (*J*/Hz): a, −5·5; b, −1·3; c, 4·2; d, 11·2; e, 31·9 (140)

The 90 MHz ^1H n.m.r. spectrum of $[B_{10}H_{12}InMe]$ (see Table 3) consists of a singlet due to the methyl protons, the broad resonances due to the B–H protons remaining unresolved under the conditions employed. The 28·87 MHz ^{11}B n.m.r. spectrum of the compound is shown in Figure 9, together with the broad-band ^1H-decoupled spectrum which consists of a series of heavily overlapped singlets of relative intensities 2 : 2 : 3 : 1 and a high-field singlet of area 2, the now familiar pattern for this structural type of compound. The low conductivity of $[B_{10}H_{12}InMe]$ in acetone (Table 1) and its solubility in benzene show that the compound is a non-electrolyte. Since it is formally isoelectronic with $[B_{10}H_{12}HgMe]^-$ it is not surprising that the two species are apparently isostructural.

EXPERIMENTAL

Materials were handled in a conventional high-vacuum line or in an atmosphere of pure dry nitrogen. Solvents were thoroughly dried and distilled from $LiAlH_4$ or CaH_2 before use, except for $[^2H_6]$acetone, $[^2H_6]$benzene, and $[^2H_1]$chloroform (Fluorochem Ltd.) which were used without further purification.

Decaborane was sublimed *in vacuo* before use. Trimethylindium was prepared by heating dimethylmercury with a slight excess of indium in a sealed thick-walled glass tube at 410 K for several days. The product was purified by sublimation *in vacuo*. Trimethylthallium was prepared by the method of Gilman and Jones [17] and stored in the absence of light.

Routine i.r. spectra were recorded on Nujol mulls using a Perkin-Elmer 457 spectrometer (4000—250 cm^{-1}). ^1H N.m.r. spectra were recorded at 60 MHz using a Perkin-Elmer R12 spectrometer and at 90 MHz using a Bruker HFX4 spectrometer. Chemical shifts were measured relative to the solvent employed and are quoted as τ values relative to τ(Me_4Si) = 10·00 p.p.m. The 28·87 MHz ^{11}B n.m.r. spectra were recorded using the Bruker spectrometer. Chemical shifts were measured relative to external boron trifluoride–diethyl ether. The 80·53 MHz ^{11}B n.m.r. spectra were obtained for us at the Department of Chemistry, University of California, Los Angeles, by Dr. R. J. Wiersema, on an instrument built by Mr. Craig Bradley and Professor F. A. L. Anet of that Department.

Conductances of solutions of the compounds were measured at 298 K, using a Wayne–Kerr Universal Bridge B221.

Metal–boron hydride compounds were degraded for elemental analysis by the Parr procedure; [18] boron was determined by the fixed pH method.[19] Indium and thallium (which were present in the Parr filtrate) were determined by ethylenediaminetetra-acetic acid (EDTA) titration.[20] Mercury, phosphorus, carbon, and hydrogen analyses were carried out by the Schwarzkopf Microanalytical Laboratory, U.S.A. Results are in Table 4.

Reaction of Trimethylindium with Decaborane in Benzene.—A solution of trimethylindium (1·11 g, 6·94 mmol) in benzene (10 ml) was added to a solution of decaborane (0·40 g, 3·30 mmol) in the same solvent. During several hours at room temperature a slow evolution of methane occurred and a pale yellow crystalline *solid*, $[Me_2In]^+[B_{10}H_{12}InMe_2]^-$, was deposited. The solid was filtered off, washed with a further portion of benzene (10 ml), and dried *in vacuo* (wt. 1·30 g; yield 96%).

The position (in cm^{-1}) of the bands in the i.r. spectrum of $[Me_2In]^+[B_{10}H_{12}InMe_2]^-$ and a partial assignment are

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[16] J. Q. Chambers, A. D. Norman, M. R. Bickell, and S. H. Cadle, *J. Amer. Chem. Soc.*, 1968, **90**, 6056.

[17] H. Gilman and R. G. Jones, *J. Amer. Chem. Soc.*, 1946, **68**, 517.

[18] Parr Manual No. 121, Parr Instrument Co., Moline, Illinois, U.S.A.

[19] R. C. Rittner and R. Culmo, *Analyt. Chem.*, 1963, **35**, 1268.

[20] J. Kinnunen and B. Wennerstrand, *Chemist-Analyst*, 1957, **46**, 92.

as follows: 2540sh (terminal B–H), 2511vs (terminal B–H), 2505sh (terminal B–H), 2360vs,br (terminal B–H), 1880w (bridge B–H–B), 1150s, 1084ms, 1055s, 1008s, 997s, 931w, 915w, 897w, 870w, 850w, 821w, 789sh, 760sh 730vs,br (In–CH_3 rock), 635w, 570s (Me_2In^+ asym. stretch), 519vs (co-ordinated Me_2In asym. stretch), 490s (co-ordinated Me_2In sym. stretch).

TABLE 4

Analytical data (weight %)

Compound		C	H	B	In/Tl/ Hg	P
$[Me_2In][B_{10}H_{12}InMe_2]$	Obs.	11·2	5·90	25·9	56·0	
	Calc.	11·9	5·87	26·4	56·0	
$[B_{10}H_{12}InMe]$	Obs.	4·5	5·40	42·0	46·1	
	Calc.	4·8	6·00	43·2	46·2	
$[Me_2Tl][B_{10}H_{12}TlMe_2]$	Obs.	8·0	4·10	18·5	69·4	
	Calc.	8·2	4·11	18·4	69·4	
$[Me_2Tl][B_{10}H_{13}]$	Obs.	6·95	4·95	28·4	56·9	
	Calc.	6·8	5·35	30·4	57·5	
$[Ph_3PMe][B_{10}H_{12}TlMe_2]$	Obs.	39·4	5·95	17·1	39·1	4·8
	Calc.	39·9	5·74	17·1	32·3	4·9
$[Ph_3PMe][B_{10}H_{12}HgMe]$	Obs.	39·05	5·55	17·8	31·7	5·0
	Calc.	39·2	5·42	17·6	32·7	5·05

When the reaction of trimethylindium with decaborane was carried out in approximately 1 : 1 molar ratio a second product, $[B_{10}H_{12}InMe]$, remained in solution. This was isolated by removal of benzene and the excess of decaborane from the filtrate *in vacuo* leaving a pale yellow *solid* (yield 9%).

The position (in cm^{-1}) of the bands in the i.r. spectrum of $[B_{10}H_{12}InMe]$ and a partial assignment are as follows: 2520s,br (terminal B–H), 1890vw (bridge B–H–B), 1009m, 885w, 721s,br (In–Me rock), 528w (In–Me stretch).

Reaction of Trimethylthallium with Decaborane in Diethyl Ether.—In a typical reaction trimethylthallium (6·89 g, 27·6 mmol) was condensed onto a solution of decaborane (1·69 g, 13·8 mmol) in diethyl ether (50 ml) in a break-seal vessel at 76 K. The mixture was allowed to warm to room temperature during one day and left for a further seven days during which time large waxy yellow plates were deposited and the supernatent liquid became bright yellow. After this time the vessel was opened and the quantity of methane measured (594 ml, 26·5 mmol). The yellow *solid*, $[Me_2Tl]^+[B_{10}H_{12}TlMe_2]^-$, was removed from the bomb, washed with diethyl ether, and dried *in vacuo* (wt. 6·93 g; yield 85%).

The position (in cm^{-1}) of the bands in the i.r. spectrum of $[Me_2Tl]^+[B_{10}H_{12}TlMe_2]^-$ and a partial assignment are as follows: 2530sh (terminal B–H), 2510vs (terminal B–H), 2476sh (terminal B–H), 2370vs,br (terminal B–H), 1900w,br (bridge B–H–B), 1158m, 1148m, 1079m, 1054s, 1020s, 995m, 914m, 820s, 790s,br, 755s, 738s, 720s, 700sh, 670m,sh, 635s, 587w, 554s (Me_2Tl^+ asym. stretch), 494 (co-ordinated Me_2Tl asym. stretch), 461 (co-ordinated Me_2Tl sym. stretch).

Evaporation of the ethereal filtrate from the above reaction, followed by washing with n-hexane, gave $[Me_2Tl]^+$-$[B_{10}H_{13}]^-$, a pale yellow *solid* (wt. 0·99 g; yield 20%).

The position (in cm^{-1}) of the bands in the i.r. spectrum of $[Me_2Tl]^+[B_{10}H_{13}]^-$ and a partial assignment are as follows: 2580s (terminal B–H), 2520s (terminal B–H), 2430s (terminal B–H), 2360sh (terminal B–H), 1900w,br (bridge B–H–B), 1150w, 1090m, 1060m, 1009s, 960w, 932m, 920m, 900sh, 820s, 810s, 770m, 720s, 550m (Me_2Tl^+ asym. stretch).

Preparation of $[Ph_3PMe]^+[B_{10}H_{12}TlMe_2]^-$.—A solution of $[Ph_3PMe]Br$ (1·45 g, 4·03 mmol) in dichloromethane (10 ml) was added to a stirred solution of $[Me_2Tl]^+[B_{10}H_{12}TlMe_2]^-$ (2·38 g, 4·03 mmol) in tetrahydrofuran (40 ml) at room temperature. After 20 min the precipitate of Me_2TlBr (1·28 g, 4·03 mmol) was filtered off and evaporation of the filtrate *in vacuo* produced $[Ph_3PMe]^+[B_{10}H_{12}TlMe_2]^-$, a yellow *solid* (wt. 2·51 g, yield 97%). The complex was recrystallised from dichloromethane–diethyl ether at 277 K.

The position (in cm^{-1}) of the bands in the i.r. spectrum of $[Ph_3PMe]^+[B_{10}H_{12}TlMe_2]^-$ and a partial assignment are as follows: 2530sh (terminal B–H), 2492s (terminal B–H), 2475s (terminal B–H), 2448sh (terminal B–H), 2360sh (terminal B–H), 1915w,br (bridge B–H–B), 1800vw,br (bridge B–H–B), 1337m, 1320sh, 1300w, 1187w, 1163m, 1148m, 1140w, 1113s, 1083m, 1054m, 1012m, 997m, 920m, 900s, 890s, 880m, 855sh, 837w, 788m, 754m, 737s, 718s, 683s, 630m, 515s, 500s, 480s, 450m, 440m.

Preparation of $[Ph_3PMe]^+[B_{10}H_{12}HgMe]^-$.—A solution of methylmercury(II) chloride (0·62 g, 2·5 mmol) in tetrahydrofuran (10 ml) was added to a stirred solution of $[Me_2Tl]^+[B_{10}H_{12}TlMe_2]^-$ (1·51 g, 2·5 mmol) in the same solvent (15 ml) at room temperature. The mixture was stirred for a further 30 min and then filtered into a solution of $[Ph_3PMe]Br$ (0·91 g, 2·5 mmol) in dichloromethane (10 ml). Precipitates of Me_2TlCl (0·74 g, 2·7 mmol) and Me_2TlBr (0·74 g, 2·4 mmol) were produced at the first and second stages respectively. Evaporation of the final filtrate *in vacuo* produced $[Ph_3PMe]^+[B_{10}H_{12}HgMe]^-$, an orange crystalline *solid* (wt. 1·54 g, yield 98%). The complex was recrystallised from dichloromethane–diethyl ether at 277 K.

The position (in cm^{-1}) of the bands in the i.r. spectrum of $[Ph_3PMe^+][B_{10}H_{12}HgMe]^-$ and a partial assignment are as follows: 2533s (terminal B–H), 2508s (terminal B–H), 2495s (terminal B–H), 2480s (terminal B–H), 2447s (terminal B–H), 2350sh (terminal B–H), 1900w,br (bridge B–H–B), 1317w, 1300w, 1260w, 1190w, 1171w, 1163w, 1115s, 1080w, 1050w, 1012m, 1000m, 970w, 900m, 890s, 850m, 820m, 800w, 787w, 750s, 745m, 720s, 687s, 627w, 605w, 530w, 507s, 493w, 450w.

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