

2,3-DIMETHYL-1-ETHYL-1,2,3-ALUMINADICARBADODECABORANE; A VERSATILE CARBOLLYL TRANSFER REAGENT

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Summary

2,3-Dimethyl-1-ethyl-1,2,3-aluminadecarbadodecaborane, prepared from triethyl-aluminum and 7,8-dimethyl-7,8-dicarbadodecaborane, has been shown to be a useful precursor for the synthesis of icosahedral main-group carboranes. The electrophilicity of the aluminum atom, which is illustrated by the formation of adducts with diethyl ether and tetrahydrofuran, enables the compound to undergo substitution reactions with nucleophiles. Whereas conversion with methylboron dibromide, germanium diiodide, or tin dichloride yielded the corresponding methylboron-, germanium- and tin-substituted icosahedrons, treatment with trimethyltin chloride or dimethyltin dichloride gave 1,1,2,3-tetramethyl-1,2,3-stannadecarbadodecaborane, apparently the first metalladecarbadodecaborane containing tetravalent tin.

Introduction

The carboride dianion, $7,8-C_2B_9H_{11}^{2-}$, and its derivatives are increasingly used as ligands for transition metals [1] and main-group elements [2], forming *closo*-heterocarboranes by incorporating non-boron fragments at the missing vertex of an icosahedron.

In addition to the hydrocarborane $C_2B_9H_{13}$, the disodium and the dithallium compounds have been used as sources of the carbolyl moiety. Both species are mainly ionic in character; the thallium carborane was formulated as $Tl[TiC_2B_9H_{11}]$ [3], illustrating the presence of an ionic icosahedral heterocarborane fragment. The insolubility of ionic compounds, which often results in a very low rate of conversion, as well as the non-specific reactivity of a "naked" $C_2B_9H_{11}^{2-}$ dianion which could be responsible for side-reactions, argue against use of such compounds as starting materials for new main-group carboranes. A particularly suitable reagent for carbolyl transfer appears to be an already complete heterocarborane cluster which is reactive enough to lead to a smooth synthesis involving substitution of the apical

hetero element in the manner reported for the cluster cation $\text{Me}_5\text{C}_5\text{Sn}^+$, the tin atom of which is replaced by the iodoboron fragment upon treatment with boron triiodide [4]. Assuming that heterocarboranes of electropositive main-group elements would be able to transfer the carbollyl moiety, we prepared the aluminacarborane 2,3-dimethyl-1-ethyl-1,2,3-aluminadecarbadodecaborane(9) (**3**), and its reactions with methylboron dibromide, germanium diiodide, tin dichloride, dimethyltin dichloride, and trimethyltin chloride are described here.

Results and discussion

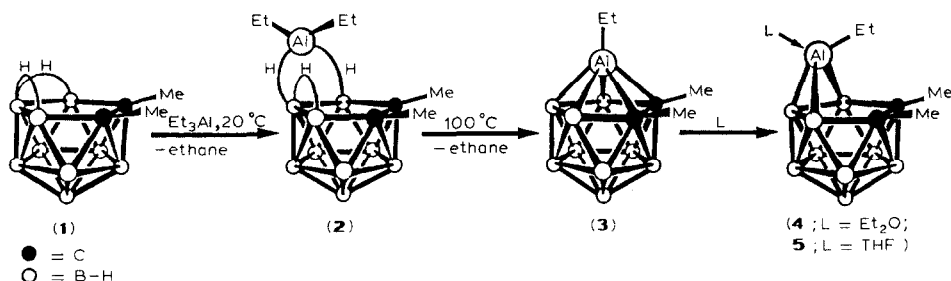
Following the procedure described by Hawthorne and his co-workers [5], 2,3-dimethyl-1-ethyl-1,2,3-aluminadecarbadodecaborane(9) (**3**) was prepared from 7,8-dimethyl-7,8-dicarbaundecaborane(11) (**1**), and triethylaluminum via the hydrogen-bridged species μ -9,10-diethylalumino-7,8-dimethyl-7,8-dicarbaundecaborane(10) (**2**) (Scheme 1). These compounds were identified and characterized by NMR spectroscopy, and, in the case of **1** and **3**, also by elemental analysis.

The electrophilic character of the apical aluminum atom in **3** is apparent from the formation of the adducts **4** and **5** with diethyl ether and tetrahydrofuran, respectively (see Scheme 1). The identity of compound **4** was confirmed by NMR spectroscopy and elemental analysis, but in the case of compound **5** NMR spectroscopy could not be used because of its very low solubility. Lewis bases stronger than diethyl ether and tetrahydrofuran, e.g. 2,2'-bipyridine, evidently remove the aluminum fragment from the carbollide unit, yielding the dianion 7,8-dimethylnonahydrido-7,8-dicarba-nido-undecaboranate($2-$), which was detected spectroscopically.

The synthetic utility of **3** is illustrated in Scheme 2, in which its reactions with some main group halides are summarized.

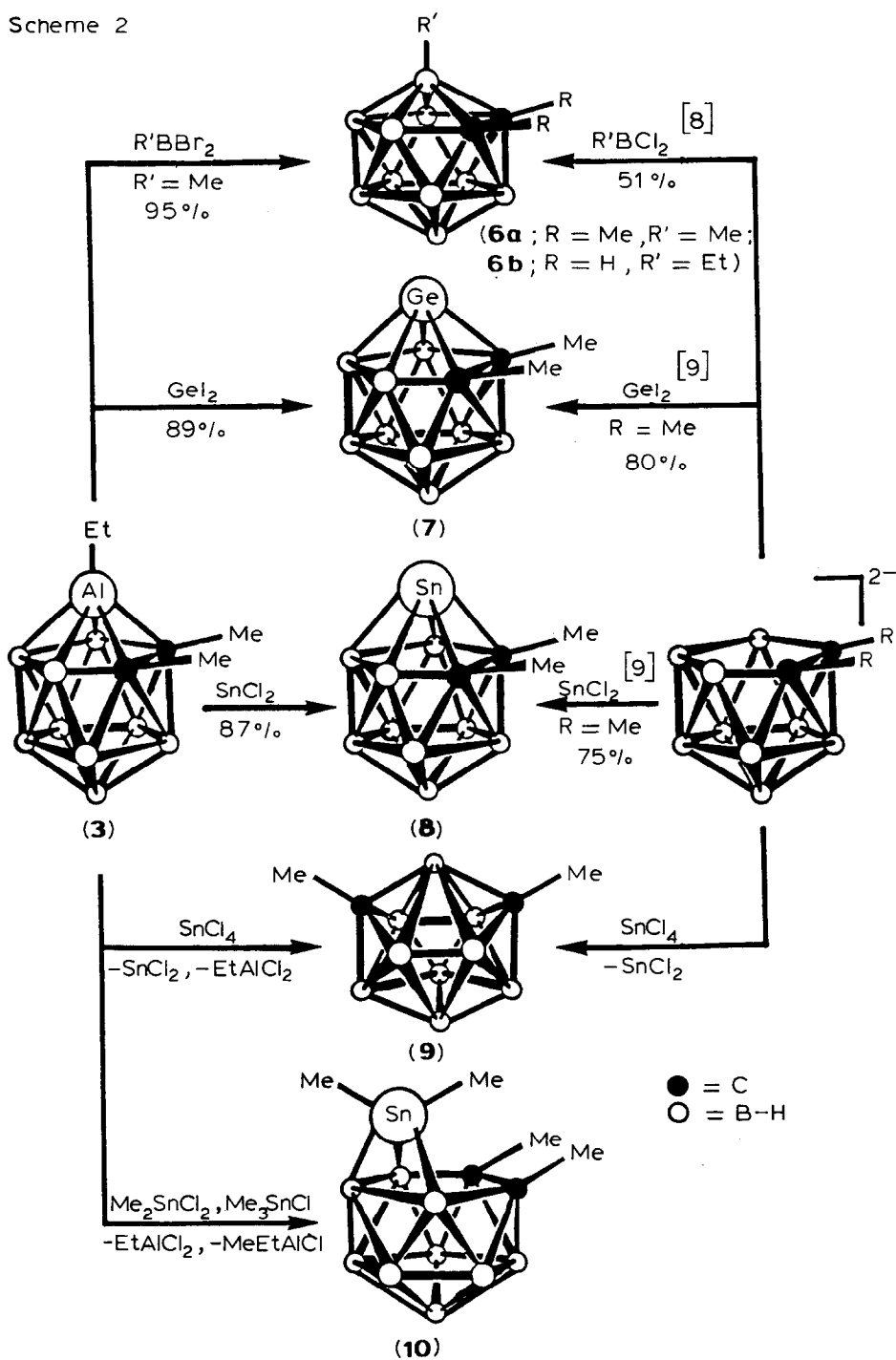
The conversions of **3** with methylboron dibromide, germanium diiodide, and tin dichloride proceed smoothly, affording high yields of 1,2,3-trimethyl-1,2-dicarbadodecaborane(9) (**6a**), 2,3-dimethyl-1,2,3-germadecarbadodecaborane(9) (**7**), and 2,3-dimethyl-1,2,3-stannadecarbadodecaborane(9) (**8**), respectively. In comparison, the preparation of these compounds from disodium 7,8-dimethyl-nonahydrido-7,8-dicarba-nido-undecaboranate, or from 7,8-disodium-undecahydrido-7,8-dicarba-nido-undecaboranate for the synthesis of compound **6b**, requires more severe reaction conditions owing to the heterogeneous nature of the mixture, and furthermore

Scheme 1



SCHEME 1. Preparation and adduct formation of the aluminacarborane **3**.

Scheme 2

SCHEME 2. Reactions of 3 and $R_2C_2B_9H_9^{2-}$ with main-group halides.

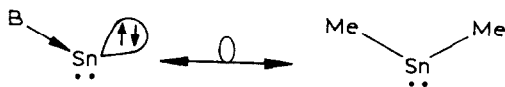
gives lower yields (see Scheme 2) [8,9]. Attempts to complete the series of 4B-element-dicarba-*closo*-dodecaboranes by treating lead(II) acetate with the aluminacarborane **3** did not give the expected product, nor did the reaction with disodium 7,8-dimethyl-nona-hydrido-7,8-dicarbaundecaboranate(2-).

The reaction of **3** with tin tetrachloride involves an oxidation-reduction reaction rather than a metal exchange, and instead of a tin(IV)-containing heterocarborane the *closo*-species 2,3-dimethyl-2,3-dicarbaundecaborane(9) (**9**) is formed. The reaction mixture was investigated spectroscopically; tin(II) chloride and ethylaluminum dichloride were detected by ^{119}Sn NMR and ^{27}Al NMR spectroscopy and the presence of the carborane **9** was confirmed by ^1H , ^{11}B and ^{13}C NMR spectroscopy. The carborane **9** is also formed in the reaction of disodium 7,8-dimethyl-nona-hydrido-7,8-dicarba-undecaboranate with tin tetrachloride (see Experimental). The aluminacarborane **3** reacts with dimethyltin dichloride to give the 1,1,2,3-tetramethyl-1,2,3-stanna-dicarbado-dodecaborane (**10**), the first heterocarborane containing tetravalent tin in a vertex position. Surprisingly, compound **10** is also formed from **3** and trimethyltin chloride.

The structure of the tin(IV) carborane **10** is mainly deduced from the ^{11}B NMR data. The sensitivity of the ^{11}B NMR patterns for carborane cages provides a reliable indicator for even slight structural alterations from the ideal *closo*-configuration to slipped distortions up to a *nido*-type configuration. Examination of the ^{11}B NMR line spectra reveals that the apical dimethyltin(IV) fragment of **10** seems to be connected to the open face of the C_2B_9 -carborane cage in the same way as the tin(II) fragment in stannacarborane adducts [9].

In Scheme 3 are shown the ^{11}B NMR line spectra for the stannacarboranes **8** and **10**, for the tetrahydrofuran and the pyridine adducts of **8**, and for the carbollid-dianion.

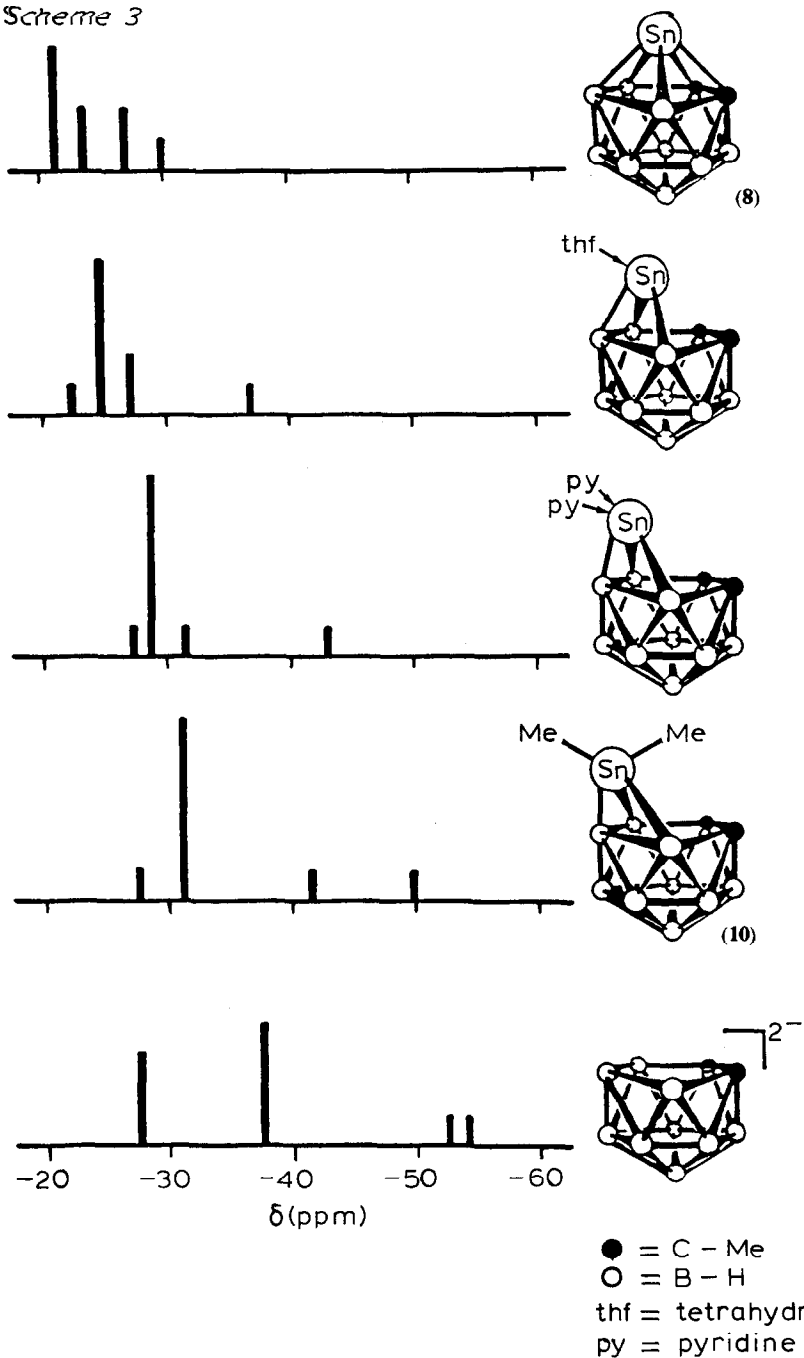
It has been established by X-ray crystallographic investigation of compound **8** that electron donation to the apical tin atom by various Lewis-bases is accompanied by a decrease of hapticity from h^5 to h^3 of the carbollid moiety. A relationship between a base coordinated tin(II) fragment and a dimethyltin(IV) fragment can be defined in terms of the isolobal concept which predicts identical structures for these stannacarboranes as shown below:



The ^{119}Sn NMR spectrum of compound **10** shows a signal in the usual range for Sn^{IV} species but the signal is significantly broadened, presumably under the influence of the neighboring quadrupolar ^{11}B nuclei.

No change in the characteristic ^{11}B NMR pattern of compound **10** was observed on cooling a sample from ambient temperature to -40°C . This indicates the presence of a rigid structure, and rules out fluxional behavior such as was reported for the aluminacarborane **2** [5]. Thus, the bonding between the dimethyltin fragment and the carbollid moiety in **10** is judged to be that of a slipped h^3 -type structure. The two ^1H NMR and ^{13}C NMR resonances shown by the methyl groups on the tin atom are due to an *exo-endo* arrangement.

Scheme 3



SCHEME 3. ^{11}B NMR line spectra for the stannacarboranes **8** and **10**, the thf- and pyridine adducts of **8** and the carbollid-dianion.

Conclusion

Exchange of the apical aluminum fragment in 2,3-dimethyl-1-ethyl-1,2,3-aluminadecarbadodecaborane(9) (**3**), as illustrated by its reactions with methylboron dibromide, germanium diiodide and tin dichloride, provides a good route to heterocarboranes. This methodology has been used for the preparation of the first tin(IV)-containing heterocarborane, for which the conventional method using disodium 7,8-dimethyl-nonahydrido-7,8-dicarbaundecaboranate(2 -) failed.

Experimental

All manipulations were carried out under dry nitrogen with Schlenk-type glassware; solvents and reagents were dried and purified by standard methods. Melting-points: Büchi 510 capillary melting-point apparatus (samples in sealed tubes; temperature uncorrected). NMR spectra: Bruker AM 300 ^1H (300.1 MHz; ext.-TMS; terminal hydrogen atoms of the carbollid cage omitted); ^{11}B (96.3 MHz; ext.- $\text{B}(\text{OMe})_3$); ^{13}C , $^{13}\text{C}\{^1\text{H}\}$ (75.4 MHz; ext.-TMS); $^{27}\text{Al}\{^1\text{H}\}$ (78.2 MHz; ext.- $\text{Al}(\text{H}_2\text{O})_6^{3+}$); $^{119}\text{Sn}\{^1\text{H}\}$ (111.9 MHz; ext.- Me_4Sn). Mass spectra: Varian 311 A (70 eV, 300 μA emission; only characteristic fragments are listed). CH-analyses: Mikroanalytisches Laboratorium Beller (Göttingen) or analytical laboratory of the University Bielefeld.

7,8-Dimethyl-undecahydrido-7,8-dicarbaundecaborane(11) (1)

Following the procedure described by Hawthorne [6], a suspension of disodium-7,8-dimethyl-7,8-dicarbaundecaborane (19.26 g, 93.32 mmol) in 350 ml of benzene was treated with anhydrous phosphoric acid (37.0 ml, 709.8 mmol) to give 14.63 g (95%) of **1**.

^1H NMR (C_6D_6) δ -0.80 (br. s, 2H, H_{br}), 1.36 (s, 6H, $\text{B}_9\text{C}_2\text{Me}_2$); ^{11}B NMR (CDCl_3) δ -43.2 (dd, $^1J(\text{BH}_1)$ 141, $^1J(\text{BH}_{\text{br}})$ 50 Hz, 3B), -34.7 (d, $^1J(\text{BH})$ 149 Hz; 1B), -28.4 (d, $^1J(\text{BH})$ 171 Hz; 1B), -26.5 (d, $^1J(\text{BH})$ 151 Hz; 2B), -11.8 (d, $^1J(\text{BH})$ 161 Hz; 2B); ^{13}C NMR (CDCl_3) δ 22.8 (q, $^1J(\text{CH})$ 130 Hz; $\text{B}_9\text{C}_2\text{Me}_2$), 83.3 (br. s; B_9C_2). Anal. Found: C, 29.45; H, 9.89. $\text{C}_4\text{H}_{17}\text{B}_9$ (162.47) calc: C, 29.57; H, 10.55%.

9,10- μ -Diethylalumino-7,8-dimethyl-7,8-dicarbaundecaborane(10) (2)

Following the procedure described by Hawthorne [5], a solution of triethylaluminum (3.76 g, 32.93 mmol) in 100 ml of benzene was added to a solution of **1** (5.40 g, 33.24 mmol) in 150 ml of benzene during 72 h, during which 6.50 ml (87% of the theoretical amount) of ethylene were evolved. The solution obtained was used for further reactions.

^1H NMR (C_6D_6) δ 0.14 (q, $^3J(\text{HH})$ 8.1 Hz; 4H, AlCH_2CH_3), 0.90 (t, $^3J(\text{HH})$ 8.1 Hz; 6H, AlCH_2CH_3), 1.39 (s, 6H, $\text{B}_9\text{C}_2\text{Me}_2$); ^{11}B NMR (C_6D_6) δ -50.6 (d, $^1J(\text{BH})$ 146 Hz, 1B), -48.5 (dd, 1B), -37.1 (d, $^1J(\text{BH})$ 115 Hz; 2B), -29.6 (d, $^1J(\text{BH})$ 137 Hz; 2B), -25.9 (d, $^1J(\text{BH})$ 171 Hz; 1B), -23.7 (d, $^1J(\text{BH})$ 158 Hz; 2B); $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6) δ 1.9 (AlCH_2), 8.6 (AlCH_2CH_3), 21.6 ($\text{B}_9\text{C}_2\text{Me}_2$), 68.3 (B_9C_2); $^{27}\text{Al}\{^1\text{H}\}$ NMR (C_6D_6) δ 203 ($\nu_{1/2}$ 8100 Hz).

2,3-Dimethyl-1-ethyl-1,2,3-aluminadecaborane(9) (3)

Following the procedure described by Hawthorne [5], a solution of **2** (7.08 g, 28.65 mmol) in 150 ml of benzene was heated under reflux; the reaction was monitored by ^{11}B NMR spectroscopy and the disappearance of **2** was found to complete within 15 d. Removal of the solvent in vacuo, followed by sublimation of the residue (70°C/0.01 mbar), gave 4.92 g (84%) of **3**, m.p. 84–86°C.

^1H NMR (C_6D_6) δ -0.34 (q, $^3J(\text{HH})$ 8.2 Hz; 2H, AlCH_2CH_3), 0.78 (t, $^3J(\text{HH})$ 8.2 Hz; 3H, AlCH_2CH_3), 1.19 (s; 6H, $\text{B}_9\text{C}_2\text{Me}_2$); ^{11}B NMR (C_6D_6) δ -42.4 (d, $^1J(\text{BH})$ 147 Hz; 1B), -35.3 (d, $^1J(\text{BH})$ 130 Hz; 1B), -33.3 (d, $^1J(\text{BH})$ 140 Hz; 2B), -29.8 (d, $^1J(\text{BH})$ 158 Hz; 2B), -27.8 (d, $^1J(\text{BH})$ 148 Hz; 2B), -23.5 (d, $^1J(\text{BH})$ 170 Hz; 1B); $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6) δ -3.8 (AlCH_2), 6.8 (AlCH_2CH_3), 20.8 ($\text{B}_9\text{C}_2\text{Me}_2$), 63.8 (B_9C_2); $^{27}\text{Al}\{^1\text{H}\}$ NMR (C_6D_6) δ 131 ($\nu_{1/2}$ 6800 Hz). Anal. Found: C, 34.54; H, 9.35. $\text{C}_6\text{H}_{20}\text{AlB}_9$ (216.49) calc: C, 33.29; H, 9.31%.

1-Diethylether-2,3-dimethyl-1-ethyl-1,2,3-aluminadecaborane(9) (4)

Upon addition of diethyl ether (2.0 ml, 19.25 mmol) to a solution of **3** (0.82 g, 3.79 mmol) in 30 ml of benzene, the title compound separated out as colorless needles, which were filtered off and dried in vacuo; yield 0.67 g (61%), decomp. above 330°C.

^1H NMR (CDCl_3 , 50°C) δ 0.35 (q, $^3J(\text{HH})$ 8.0 Hz; 2H, AlCH_2CH_3), 1.18 (t, $^3J(\text{HH})$ 8.0 Hz; 3H, AlCH_2CH_3), 1.40 (t, $^3J(\text{HH})$ 7.1 Hz; 6H, OCH_2CH_3), 1.54 (s; 6H, $\text{B}_9\text{C}_2\text{Me}_2$), 4.03 (br. s, $\nu_{1/2}$ 22 Hz; 4H, OCH_2CH_3); ^{11}B NMR (CDCl_3 , 50°C) δ -47.5 (d, $^1J(\text{BH})$ 130 Hz; 1B), -31.3 (d, $^1J(\text{BH})$ 113 Hz; 3B), -30.3 (d, $^1J(\text{BH})$ 162 Hz; 1B), -25.5 (d, $^1J(\text{BH})$ 160 Hz; 1B); ^{13}C NMR (CDCl_3 , 50°C) δ 1.7 (t, $^1J(\text{CH})$ 118 Hz; AlCH_2), 8.9 (q, $^1J(\text{CH})$ 126 Hz; AlCH_2CH_3), 13.7 (q, $^1J(\text{CH})$ 127 Hz; OCH_2CH_3), 23.1 (q, $^1J(\text{CH})$ 129 Hz; $\text{B}_9\text{C}_2\text{Me}_2$), 61.9 (s; B_9C_2), 67.9 (t, $^1J(\text{CH})$ 147 Hz; OCH_2); $^{27}\text{Al}\{^1\text{H}\}$ NMR (CDCl_3 , 50°C) δ 120. Anal. Found: C, 42.83; H, 10.25. $\text{C}_{10}\text{H}_{30}\text{AlB}_9\text{O}$ (290.86) calc: C, 41.29; H, 10.49%.

2,3-Dimethyl-1-ethyl-1-tetrahydrofuran-1,2,3-aluminadecaborane(9) (5)

Upon addition of tetrahydrofuran (1.0 ml, 12.33 mmol) to a solution of **3** (0.21 g, 0.97 mmol) in 30 ml of benzene, colorless needles of **5** separated out, and were filtered off and dried in vacuo; yield 0.18 g (64%), dec. above 308°C.

Anal. Found: C, 41.84; H, 9.64. $\text{C}_{10}\text{H}_{28}\text{AlB}_9\text{O}$ (288.61) calc: C, 41.62; H, 9.78%.

1,2,3-Trimethyl-1,2-dicarbodecaborane(9) (6)

A solution of methylboron dibromide (1.04 g, 5.58 mmol) in 10 ml of benzene was added dropwise to a solution of **3** (1.10 g, 5.08 mmol) in 40 ml of benzene. When the mixture was warmed, a colorless solid precipitated. The mixture was then refluxed for 2 h and the insoluble material then filtered off and extracted with 10 ml of hexane. Evaporation of the combined filtrate and hexane extract in vacuo, followed by recrystallization of the residue from 10 ml of ethanol yielded 0.90 g (95%) of **6** as colorless prisms, m.p. 205–206°C.

^1H NMR (C_6D_6) δ 0.19 (s; 3H, BMe), 1.18 (s; 6H, CMe); ^{11}B NMR (C_6D_6) δ -30.9 (d, $^1J(\text{BH})$ 159 Hz; 1B), -28.7 (d, $^1J(\text{BH})$ 174 Hz; 2B), -27.3 (d, $^1J(\text{BH})$ 143 Hz; 3B), -26.2 (d, 1B), -23.8 (d, $^1J(\text{BH})$ 152 Hz; 2B), -21.5 (s; 1B); $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6) δ -1.2 (BMe), 20.1 (CMe), 72.9 (B_9C_2). Anal. Found: C, 32.51; H, 9.75. $\text{C}_5\text{H}_{18}\text{B}_{10}$ (186.31) calc: C, 32.23; H, 9.74%.

2,3-Dimethyl-1,2,3-germadicarbododecaborane(9) (7)

Germanium diiodide (0.49 g, 1.50 mmol) was added to a solution of **3** (0.29 g, 1.34 mmol) in 20 ml of benzene. The mixture was stirred for 20 d and the solvent then removed in vacuo. Fractional sublimation of the residue (100°C/0.01 mbar) yielded 0.28 g (89%) of colorless crystals of **7**, m.p. 190°C (dec.).

^1H NMR (C_6D_6) δ 1.39 (s; 6H, Me); ^{11}B NMR (C_6D_6) δ -24.2 (d, $^1J(\text{BH})$ 134 Hz; 3B), -22.2 (d, overlapping doublet, 2B), -21.4 (d, overlapping doublet, 2B), -20.1 (d, $^1J(\text{BH})$ 147 Hz; 2B); $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6) δ 25.5 (q; Me), 77.7 (s; B_9C_2). Anal. Found: C, 20.76; H, 6.59. $\text{C}_4\text{H}_{15}\text{B}_9\text{Ge}$ (233.05) calc: C, 20.61; H, 6.49%.

2,3-Dimethyl-1,2,3-stannadicarbododecaborane(9) (8)

Addition of anhydrous tin dichloride (0.28 g, 1.47 mmol) to a solution of **3** (0.31 g, 1.43 mmol) in 20 ml of benzene produced a colorless precipitate, which was filtered off. The filtrate was concentrated in vacuo then cooled to give colorless crystals of **8**, 0.35 g (87%), m.p. 190°C (dec.).

^1H NMR (C_6D_6) δ 1.67 (s; 6H, Me); ^{11}B NMR (C_6D_6) δ -30.1 ($^1J(\text{BH})$ 143 Hz; 1B), -26.4 (d, $^1J(\text{BH})$ 140 Hz; 2B), -23.9 (d, $^1J(\text{BH})$ 172 Hz; 2B), -21.8 (d, $^1J(\text{BH})$ 132 Hz; 4B); $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6) δ 26.5 (Me), 69.2 (B_9C_2); $^{119}\text{Sn}\{^1\text{H}\}$ NMR (C_6D_6) δ -379 (br. s). Anal. Found: C, 17.08; H, 5.43. $\text{C}_4\text{H}_{15}\text{B}_9\text{Sn}$ (279.15) calc: C, 17.21; H, 5.42%.

2,3-Dimethyl-2,3-dicarbaundecaborane(9), (9), from $\text{EtAlMe}_2\text{C}_2\text{B}_9\text{H}_9$ and SnCl_4

Addition of tin tetrachloride (0.42 g, 1.60 mmol) to a solution of **3** (0.70 g, 3.20 mmol) in 20 ml of benzene produced a colorless precipitate. Stirring was continued for 12 h then the insoluble material was filtered off. The solution was shown spectroscopically to contain carborane **9** [7].

^1H NMR (CDCl_3) δ 1.90 (s; 6H); ^{11}B NMR (C_6D_6) δ -30.0 (d, $^1J(\text{BH})$ 166 Hz, $\nu_{1/2}$ 13 Hz; 1B), -28.8 (d, $^1J(\text{BH})$ 144 Hz, $\nu_{1/2}$ 84 Hz; 2B), -25.3 (d, $^1J(\text{BH})$ 162 Hz, $\nu_{1/2}$ 70 Hz; 2B), -21.5 (d, $^1J(\text{BH})$ 167 Hz, $\nu_{1/2}$ 56 Hz; 4B); $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6) δ 24.5 (CMe), 102.4 (B_9C_2).

*1,1,2,3-Tetramethyl-1,2,3-stannadicarbododecaborane (10) from **3** and trimethyltin chloride*

Addition of a solution of trimethyltin chloride (1.14 g, 5.72 mmol) in 40 ml of hexane to one of **3** (1.13 g, 5.22 mmol) in 80 ml of hexane produced a colorless precipitate, which was filtered off, washed with 10 ml of hexane, and dried in vacuo. Recrystallization from trichloromethane yielded 0.82 g (51%) of **10** as colorless crystals, which slowly softened above 80°C, m.p. 198–203°C (dec.).

^1H NMR ($\text{THF}-d_8$) δ 0.77 (s, $^2J(\text{SnH})$ 31 Hz; 3H, SnMe), 0.81 (s, $^2J(\text{SnH})$ 31 Hz; 3H, SnMe), 1.85 (s; 6H, $\text{B}_9\text{C}_2\text{Me}$); ^{11}B NMR (THF) δ -50.0 (d, $^1J(\text{BH})$ 143 Hz; 1B), -42.3 (d, $^1J(\text{BH})$ 121 Hz; 1B), -32.4 (d, $^1J(\text{BH})$ 139 Hz; 6B), -26.3 (d, $^1J(\text{BH})$ 156 Hz; 1B); $^{13}\text{C}\{^1\text{H}\}$ NMR ($\text{THF}-d_8$) δ -2.5 (s, $^1J(\text{SnC})$ 207 Hz, SnCH_3), -1.4 (s, $^1J(\text{SnC})$ 220 Hz, SnCH_3), 23.3 (s, CCH_3), 63.4 (br. s, B_9C_2); $^{119}\text{Sn}\{^1\text{H}\}$ NMR (C_6D_6) δ -2 (br. s). MS m/e (rel. int.) 120 (Sn^+ , 48), 135 (MeSn^+ , 59), 150 (Me_2Sn^+ , 20), 159 ($\text{Me}_2\text{C}_2\text{B}_9\text{H}_9^+ - 2\text{H}$, 100). Anal. Found: C, 23.46; H, 6.90. $\text{C}_6\text{H}_{21}\text{B}_9\text{Sn}$ (309.21) calc: C, 23.31; H, 6.85%.

1,1,2,3-Tetramethyl-1,2,3-stannadecaborane (10) from 3 and dimethyltin dichloride

A solution of dimethyltin dichloride (0.23 g, 1.05 mmol) in 5 ml of benzene was added to one of **3** (0.22 g, 1.02 mmol) in 10 ml of benzene. The colorless precipitate was filtered off, washed with 10 ml of hexane, and dried in vacuo to give 0.18 g (57%) of colorless crystals, which slowly softened above 80°C and melted at 199–202°C (dec.).

^1H NMR (THF- d_8) δ 0.77 (s, 3H, SnMe), 0.81 (s, 3H, SnMe), 1.85 (s, 6H, $\text{B}_9\text{C}_2\text{Me}_2$); ^{11}B NMR (THF) δ –49.9 (d, $^1J(\text{BH})$ 139 Hz; 1B), –42.4 (d, $^1J(\text{BH})$ 120 Hz, 1B), –32.6 (d, $^1J(\text{BH})$ 130 Hz; 6B), –26.8 (d, $^1J(\text{BH})$ 152 Hz; 1B).

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