

endo- σ -Bonded Group 14 Heterodiboranes: Synthesis of $[\text{Ph}_3\text{MC}_2\text{B}_9\text{H}_{11}]^-$ [$\text{M} = \text{Germanium(IV), Tin(IV)}$] and Structure of $[\text{10-endo-(SnPh}_3\text{)-10-}\mu\text{-H-7,8-nido-C}_2\text{B}_9\text{H}_{10}][\text{trans-Ir(CO)(PPh}_3\text{)}_2(\text{MeCN})]$

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Reaction of equimolar amounts of thallium(I) salts of monoanionic group 14 heterodiboranes $[\text{Ph}_3\text{MC}_2\text{B}_9\text{H}_{11}]^-$, generated *in situ* by treating $\text{Tl}_2\text{C}_2\text{B}_9\text{H}_{11}$ with Ph_3MCl in MeCN, and *trans*-Ir(CO)(PPh₃)₂Cl afforded $[\text{10-endo-(MPh}_3\text{)-10-}\mu\text{-H-7,8-nido-C}_2\text{B}_9\text{H}_{10}][\text{trans-Ir(CO)(PPh}_3\text{)}_2(\text{MeCN})]$ ($\text{M} = \text{Ge}^{\text{IV}}, \text{Sn}^{\text{IV}}$) in which the Ph_3M moiety interacts with the unique boron atom of the *nido*-C₂B₉ cage *via* *endo*- σ -M-B bond as well as weak M-H-B bridge bond.

The heterocarborane chemistry of the main group elements has been developed largely in the form of π -complexes.¹⁻⁴ In contrast to a wealth of π -coordination carborane chemistry of *p*-block elements, examples of σ -bonded heterocarboranes are scarce and limited to C₂B₉H₁₁²⁻ complexes of Al^{III} and Si^{IV}.³ The paucity of recent work on the σ -coordination dicarborane chemistry and the recent demonstration on the use of $[\text{10-endo-(AuPPh}_3\text{)-7,8-nido-C}_2\text{B}_9\text{H}_9\text{Me}_2]^-$ anion⁵ as a carborane cage transfer reagent⁶ prompted a synthetic search for σ -bonded heterodiboranes of heavier group 14 atoms in the formal +4 state.

The Tl^I salt of $[\text{Ph}_3\text{SnC}_2\text{B}_9\text{H}_{11}]^-$ **1** was prepared by allowing an equimolar (0.5 mmol) slurry of $\text{Tl}_2\text{C}_2\text{B}_9\text{H}_{11}$ and Ph_3SnCl in

20 ml tetrahydrofuran (THF) to react anaerobically at ambient temperature for 5 h, followed by treatment of the concentrated colourless reaction filtrate with Et₂O. Recrystallization from THF-Et₂O afforded analytically pure white Tl-**1** solids in 77% yield.[†] In MeCN, the compound Tl-**1**, as isolated or generated *in situ*, reacts with *trans*-Ir(CO)(PPh₃)₂-Cl to afford yellow crystalline $[\text{trans-Ir(CO)(PPh}_3\text{)}_2(\text{MeCN})]\cdot\mathbf{1}$ in *ca.* 68% yield.[†] The lighter congener of **1**, $[\text{Ph}_3\text{GeC}_2\text{B}_9\text{H}_{11}]^-$ **2**, was also isolated as a yellow salt of $[\text{trans-Ir(CO)(PPh}_3\text{)}_2(\text{MeCN})]^+$ cation in 54% yield from the equimolar reaction mixture of $\text{Tl}_2\text{C}_2\text{B}_9\text{H}_{11}$ -Ph₃GeCl and *trans*-Ir(CO)(PPh₃)₂Cl in MeCN.[†]

The ¹¹B{¹H} NMR spectra of **1** and **2** in MeCN, displayed in Fig. 1 along with that of the C₂B₉H₁₂⁻ monoanion, indicate the C_v symmetrical nature of these group 14 heterodiborane anions in solution and greater structural similarity among the foregoing three anions. Recent establishment⁷ of the *endo*- σ -bonding nature of the 12th hydrogen in $[\text{7,8-nido-C}_2\text{B}_9\text{H}_{12}]^-$ and the isolobal analogy⁸ between H⁺ and $[\text{Ph}_3\text{M}]^+$ ($\text{M} = \text{Ge}, \text{Sn}$) suggest that the species **1** and **2** might be expected to contain an *endo*- σ -M-B bonding interaction. The molecular structure of $[\text{trans-Ir(CO)(PPh}_3\text{)}_2(\text{MeCN})]\cdot\mathbf{1}$, established by X-ray diffraction,[‡] is consistent with these expectations.

The crystal structure consists of well separated anion **1** and $[\text{trans-Ir(CO)(PPh}_3\text{)}_2(\text{MeCN})]^+$ cation. In the anion **1** whose molecular structure is displayed in Fig. 2, an *endo*-(Ph₃Sn)⁺

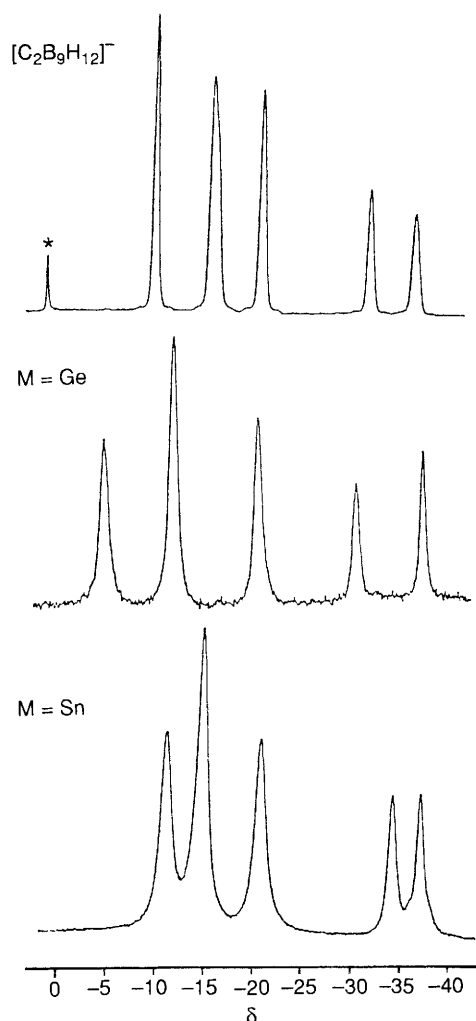


Fig. 1 ¹¹B{¹H} NMR spectra of $[\text{Ph}_3\text{MC}_2\text{B}_9\text{H}_{11}]^-$ ($\text{M} = \text{Ge}, \text{Sn}$) in MeCN-10% CD₃CN. The top spectrum is that of $[\text{10-endo-H-7,8-nido-C}_2\text{B}_9\text{H}_{11}]^-$ in the same medium with internal BF₃·OEt₂.

[†] All NMR spectra but ¹H NMR were taken in MeCN-10% CD₃CN. Data for Tl-**1**: IR(KBr), $\nu_{\text{BH}}/\text{cm}^{-1}$ 2566, 2510, 2474 and 2422; ¹¹B{¹H} NMR (referenced to external BF₃·OEt₂) δ -11.0, -14.8, -20.7, -34.2 and -37.1; ¹¹⁹Sn NMR (referenced to external SnMe₄) δ -21 ($\Delta_{1/2}$ 660 Hz). Data for $[\text{trans-Ir(CO)(PPh}_3\text{)}_2(\text{MeCN})]\cdot\mathbf{1}$: IR(KBr) $\nu_{\text{BH}}/\text{cm}^{-1}$ 2521, ν_{BHSn} 2398, ν_{CN} 2289, ν_{CO} 1997 and 1981; ¹H NMR(CD₃CN), δ 7.69-7.27 (m, Ph-H), 2.18 (s, Me-H) and 1.16 (s, carboranyl CH); ¹¹B{¹H} NMR δ -11.1, -15.1, -21.1, -34.6 and -37.3; ³¹P{¹H} NMR (referenced to external 85% H₃PO₄) δ 25.2. Data for $[\text{trans-Ir(CO)(PPh}_3\text{)}_2(\text{MeCN})]\cdot\mathbf{2}$: IR(KBr) $\nu_{\text{BH}}/\text{cm}^{-1}$ 2519, ν_{BHGe} 2397, ν_{CN} 2288 and ν_{CO} 1998; ¹¹B{¹H} NMR δ -5.0, -12.3, -21.0, -31.2 and -38.1. Satisfactory elemental analyses were obtained for all three compounds.

[‡] Crystallographic data for $[\text{trans-Ir(CO)(PPh}_3\text{)}_2(\text{MeCN})]\cdot\mathbf{1}$: C₅₉H₅₉B₉IrNOP₆Sn, $M = 1268.3$, monoclinic, space group $P2_1/n$, $a = 11.552(2)$, $b = 45.568(10)$, $c = 11.852(3)$ Å, $\beta = 92.56(1)^\circ$, $V = 5822.6$, $Z = 4$, $D_c = 1.45$ g cm⁻³, $R(R_w) = 0.052(0.057)$ for 4081 observed data [$F > 6\sigma(F)$]. The diffraction data of a yellow needle crystal growth from an MeCN-Et₂O-pentane solution by layer diffusion were collected at 298 K in the ω scan mode on an Enraf-Nonius CAD4 diffractometer using Mo-K α radiation to a maximum 2θ value of 40° . The structure was solved with use of statistical method (SHELXS 86) and full-matrix least-squares procedures (SHELX 76) on the CRAY-2S/4-128 supercomputer. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

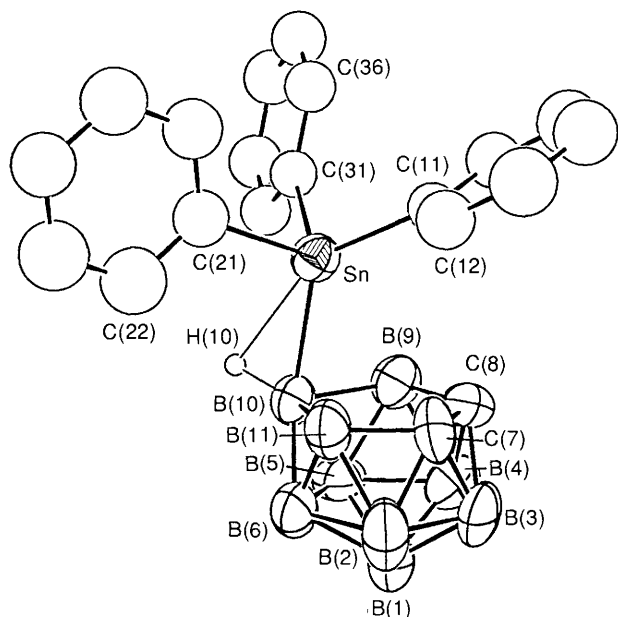


Fig. 2 Molecular structure of [10-endo-SnPh₃-10-μ-H-7,8-nido-C₂B₉H₁₀]⁻ **1**. Dimensions: Sn–B(10) 2.324(16), Sn···B(9) 2.761, Sn···B(11) 2.764, Sn···H(10) 2.349, C(7)–C(8) 1.524(19), <B–B_{facial}> 1.836, <B–C_{facial}> 1.606 Å; Sn–B(10)–H(10) 77.3(8), Sn–B(10)–B(9) 82.4(8), Sn–B(10)–B(11) 82.2(8), C(11)–Sn–B(10) 125.6(4), C(21)–Sn–B(10) 107.9(4), C(31)–Sn–B(10) 107.3(4), C(11)–Sn–C(21) 107.0(3), C(11)–Sn–C(31) 106.5(3), C(21)–Sn–C(31) 99.5(3)°. The atom H(10) was located in a difference map but its position was not refined.

moiety interacts with the unique boron atom of the *nido*-C₂B₉ cage via a σ-Sn–B(10) bond [2.324(16) Å] and a weak Sn–H(10)–B(10) bridge bond. The observation of an IR band at 2398 cm⁻¹ is indicative of the presence of a weak Sn–H–B bridge interaction.[†] The slipping parameter Δ⁹ which reflects the extent of the *nido* nature of the tin unit is calculated as 1.257 Å. This is the largest value among the structurally characterised *endo*-σ bonded MC₂B₉H₁₁ species and might be partially ascribed to the bridge bond. Previously, Δ values of 0.91, 0.87 and 0.92 Å were reported for [10-endo-L-7,8-nido-

C₂B₉H₁₁]⁻ (L = H⁷ and Ph₃PAu⁵) and [10-endo-(Ph₃PHg)-7,8-nido-C₂B₉H₁₁]⁻,¹⁰ respectively. The pentagonal C₂B₃ face is slightly nonplanar and fold angles⁹ are θ = 1.51 and φ = 2.66°. It is interesting to note that one phenyl ring is situated on top of the C₂B₃ plane like a visor such that a dihedral angle of 31.0° and a C(11)–Sn–B(10) angle of 125.6(4)° result.

The discrete nature between the iridium cation and the anion **1** or **2** clearly indicates that Tl[Ph₃MC₂B₉H₁₁] (M = Ge or Sn) does not act as either a carborane cage transfer agent or a synthon for preparing polynuclear metal compound toward Vaska's complex. With Cu(PPh₃)₃Cl, Tl salts of **1** and **2** seem to take different reaction route whose nature and the X-ray structure of [*trans*-Ir(CO)(PPh₃)₂(MeCN)]·**2** are under investigation.

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