endo-σ-Bonded Group 14 Heterodicarboranes: Synthesis of [Ph₃MC₂B₉H₁₁]⁻ [M = Germanium(iv), Tin(iv)] and Structure of [10-endo-(SnPh₃)-10-µ-H-7,8-nido-C₂B₉H₁₀][trans-Ir(CO)(PPh₃)₂(MeCN)]

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Reaction of equimolar amounts of thallium(I) salts of monoanionic group 14 heterodicarboranes [Ph₃MC₂B₉H₁₁]⁻, generated *in situ* by treating Tl₂C₂B₉H₁₁ with Ph₃MCl in MeCN, and *trans*-Ir(CO)(PPh₃)₂Cl afforded [10-*endo*-(MPh₃)-10-µ-*H*-7,8-*nido*-C₂B₉H₁₀][*trans*-Ir(CO)(PPh₃)₂(MeCN)] (M = Geᴵⱽ, Snᴵⱽ) in which the Ph₃M 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 Alᴵᴵᴵ and Siᴵⱽ.[3] The paucity of recent work on the σ-coordination dicarborane chemistry and the recent demonstration on the use of [10-*endo*-(AuPPh₃)-7,8-*nido*-C₂B₉H₉Me₂]⁻ anion[5] as a carborane cage transfer reagent[6] prompted a synthetic search for σ-bonded heterodicarboranes of heavier group 14 atoms in the formal +4 state.

The Tlᴵ salt of [Ph₃SnC₂B₉H₁₁]⁻ **1** was prepared by allowing an equimolar (0.5 mmol) slurry of Tl₂C₂B₉H₁₁ and Ph₃SnCl 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 [*trans*-Ir(CO)(PPh₃)₂-(MeCN)]·1 in *ca.* 68% yield.† The lighter congener of **1**, [Ph₃GeC₂B₉H₁₁]⁻ **2**, was also isolated as a yellow salt of [*trans*-Ir(CO)(PPh₃)₂(MeCN)]⁺ cation in 54% yield from the equimolar reaction mixture of Tl₂C₂B₉H₁₁–Ph₃GeCl and *trans*-Ir(CO)(PPh₃)₂ Cl 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 C₅ symmetrical nature of these group 14 heterodicarborane anions in solution and greater structural similarity among the foregoing three anions. Recent establishment[7] of the *endo*-σ-bonding nature of the 12th hydrogen in [7,8-*nido*-C₂B₉H₁₂]⁻ and the isolobal analogy[8] between H⁺ and [Ph₃M]⁺ (M = Ge, Sn) suggest that the species **1** and **2** might be expected to contain an *endo*-σ-M–B bonding interaction. The molecular structure of [*trans*-Ir(CO)(PPh₃)₂(MeCN)]·1, established by X-ray diffraction,‡ is consistent with these expectations.

The crystal structure consists of well separated anion **1** and [*trans*-Ir(CO)(PPh₃)₂(MeCN)]⁺ cation. In the anion **1** whose molecular structure is displayed in Fig. 2, an *endo*-(Ph₃Sn)⁺

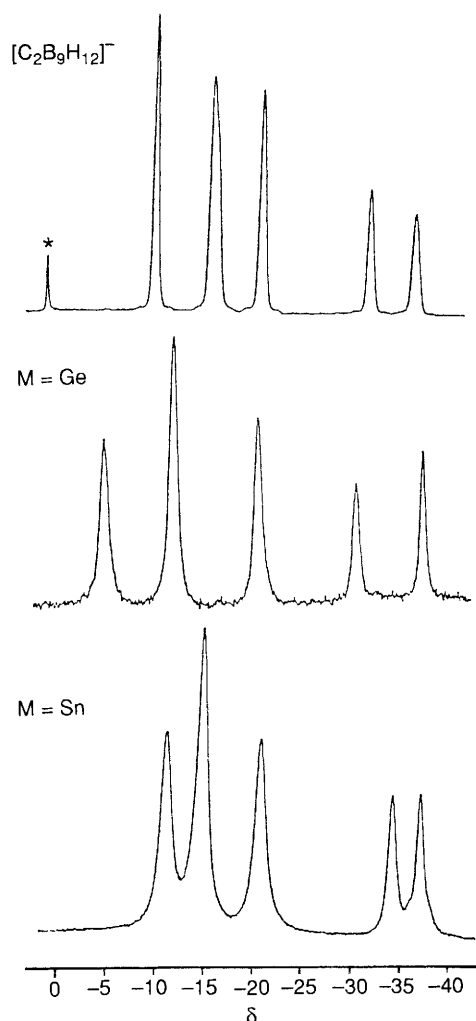**Fig. 1** ¹¹B{¹H} NMR spectra of [Ph₃MC₂B₉H₁₁]⁻ (M = Ge, Sn) in MeCN–10% CD₃CN. The top spectrum is that of [10-*endo*-*H*-7,8-C₂B₉H₁₁]⁻ in the same medium with internal BF₃·OEt₂.

Fig. 2 Molecular structure of [10-*endo*-SnPh$_3$-10-μ-*H*-7,8-*nido*-C$_2$B$_9$H$_{10}$]$^-$ **1**. Dimensions: Sn–B(10) 2.324(16), Sn$\cdots$B(9) 2.761, Sn$\cdots$B(11) 2.764, Sn$\cdots$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*-C$_2$B$_9$ 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 Δ^9 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 MC$_2$B$_9$H$_{11}$ 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*-

C$_2$B$_9$H$_{11}$]$^-$ (L = H[7] and Ph$_3$PAu[5]) and [10-*endo*-(Ph$_3$PHg)-7,8-*nido*-C$_2$B$_9$H$_{11}$],[10] respectively. The pentagonal C$_2$B$_3$ face is slightly nonplanar and fold angles[9] are θ = 1.51 and ϕ = 2.66°. It is interesting to note that one phenyl ring is situated on top of the C$_2$B$_3$ 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[Ph$_3$MC$_2$B$_9$H$_{11}$] (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(PPh$_3$)$_3$Cl, Tl salts of **1** and **2** seem to take different reaction route whose nature and the X-ray structure of [*trans*-Ir(CO)(PPh$_3$)$_2$(MeCN)]·**2** are under investigation.

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