Novel weak coordination to silylium ions: formation of nearly linear Si–H–Si bonds†

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The weakly coordinating carborane anion in ion-like trialkylsilyl species $R_3Si(CHB_{11}Cl_{11})$ can be displaced by nucleophiles as weak as *ortho*-dichlorobenzene, SO_2 and trialkylsilanes, the latter forming nearly linear hydride bridges in $R_3Si–H–SiR_3^+$ cations.

Proof of the existence of a trialkylsilylium ion (R_3Si^+) in condensed media is an unsolved problem because unsaturation in three-coordinate silicon cations is thwarted by the coordination of anions, solvent molecules or other nucleophiles to the silicon centre.[1] Even the least coordinating anions presently known, such as perfluorinated tetraphenylborate or carboranes, form four-coordinate species of the type $R_3Si^{\delta+}$ (anion)$^{\delta-}$, which, although ion-like, nevertheless retain some degree of covalence. Weakly basic solvents such as acetonitrile[2] or toluene[3] have been shown to displace these anions, forming isolable four-coordinate species of the type $R_3Si(solvent)^+$, and there is calculational evidence that even argon can be a significant ligand to Me_3Si^+.[4] Only with bulky aryl groups attached to the silicon (*e.g.* mesityl) can nucleophiles be excluded from coordination to it and *bone fide* three-coordinate silyl cations be isolated.[5] This chemistry reflects the extraordinary electrophilicity of three-coordinate silyl cations, a property that has recently been exploited to catalytically activate C–F bonds[6] and to prepare the strongest known Brønsted acid.[7] In the present communication, we show that solvents as weakly coordinating as *ortho*-dichlorobenzene (ODCB) and SO_2 also form stable adducts with trialkylsilylium ions, and that trialkylsilanes themselves are sufficiently nucleophilic to react with silylium ion-like species. Nearly linear, hydride-bridged $[R_3Si–H–SiR_3]^+$ cations with 3-centre-2-electron bonds are formed.

Carborane anions based on the CB_{11} icosahedral cluster are amongst the least coordinating, least basic and most chemically inert anions presently known.[8,9] Of these, the anion with eleven chloro substituents, $CHB_{11}Cl_{11}^-$,[10,7] has optimized properties for silylium ion chemistry. Its salts are more soluble in chlorocarbon solvents than the corresponding salts with hexachloro[11] or pentamethyl-hexachloro carborane anions.[12] This follows the principle that "like dissolves like". The conjugate acid of this anion, $H(CHB_{11}Cl_{11})$, is stronger and more thermally stable than its hexa-chloro counterpart,[7,9] so we expected that the undeca-chloro anion would be less coordinating and more chemically inert towards silylium ions than the hexa-chloro anion.

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While neutral $R_3Si(carborane)$ species such as $^iPr_3Si(CHB_{11}H_5Cl_6)$ can typically be recrystallized intact from ODCB solution, attempts to grow crystals of $^iPr_3Si(CHB_{11}Cl_{11})$ under these conditions resulted in the isolation of the solvent-coordinated ionic species $[^iPr_3Si(ODCB)][CHB_{11}Cl_{11}]$ (**1**).‡ The crystal structure is shown in Fig. 1, and is apparently the first example of a σ Cl-coordinated ODCB. A search of the Cambridge Structural Database produced only 2 examples of a coordinated ODCB, both in π-mode to a transition metal (Fe). The angle at Cl is 109.7(7)° (average of two conformers), which is large relative to the VSEPR expectation of *ca.* 90° for two bonding pairs to a heavy atom.[13] The Si–Cl bond length (average 2.33(3) Å) is *ca.* 0.25 Å longer than a typical Si–Cl covalent bond, indicative of weaker, dative bonding.

Reflecting the delicate balance between anion and solvent coordination, the same experiment with ethyl rather than *iso*-propyl substituents on the silicon leads to crystals of the anion-coordinated species $Et_3Si(CHB_{11}Cl_{11})$ (**2**), free of ODCB solvation. As shown in Fig. 2, the carborane anion is coordinated to silicon *via* a chloro substituent from the 7-position with a Si–Cl bond length of 2.334(3) Å. This bond length is within experimental error of that in **1**, reflecting that the coordinating ability of the chlorocarborane anion is comparable to that of a chloroarene solvent.

When neutral $R_3Si(carborane)$ species are recrystallized from liquid SO_2 as solvent, ionic species with coordinated SO_2 can be isolated for certain R and carborane anion combinations. Single crystals suitable for X-ray structural characterization were formed for $[Et_3Si(SO_2)][CHB_{11}Me_5Br_6]$ (**3**). As shown in Fig. 3, the SO_2 ligand is coordinated in O-bound mode with Si–O = 1.820(5) Å. This is at the longer end of the range for Si–O bonds and is longer than that in the water-coordinated silyl cation (*i.e.* a protonated
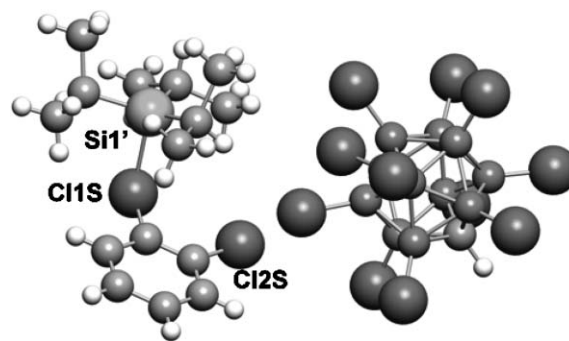

Fig. 1 X-Ray structure of the major conformer of $[^iPr_3Si(ODCB)][CHB_{11}Cl_{11}]$ (**1**) showing coordination of *ortho*-dichlorobenzene; C–Si–C$_{ave}$ = 116.7°.
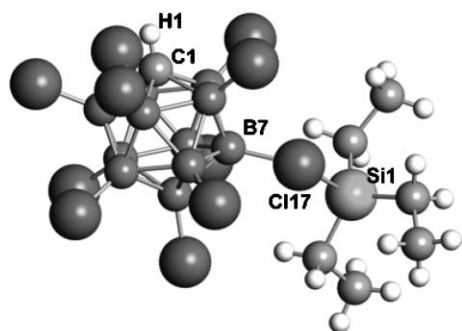
Fig. 2 X-Ray structure of Et₃Si(CHB₁₁Cl₁₁) (**2**); C–Si–C$_{ave}$ = 116.5°.
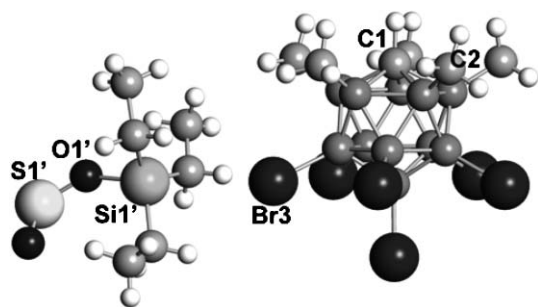
Fig. 3 X-Ray structure of [Et₃Si(SO₂)][CHB₁₁Me₅Br₆] (**3**); C–Si–C$_{ave}$ = 115.7°, Si–O = 1.820(5) Å.

silanol) [^{t}Bu₃Si(OH₂)][CHB₁₁H₅Br₆], 1.779(9) Å.[14] SO₂ is a common ligand of transition metals but, with the exception of SO₂·SbF₅, is virtually undocumented with main group elements.[15]

When Et₃SiH is present in the preparation of **2**, the silane competes with ODCB and the anion for coordination to the silicon and crystals of a silane-coordinated species [Et₃Si–H–SiEt₃][CHB₁₁Cl₁₁] (**4**) are produced along with **2**. The X-ray structure of **4** showed disorder but nevertheless had sufficient resolution to indicate a nearly linear, symmetrical, hydride-bridged structure for the [Et₃Si–H–SiEt₃]⁺ cation. Disorder-free single crystals were obtained with the corresponding methyl derivative, prepared by reaction of [Ph₃C][CHB₁₁Cl₁₁] with excess trimethylsilane in ODCB at reduced temperatures. In this case, only the silane adduct [Me₃Si–H–SiMe₃][CHB₁₁Cl₁₁] (**5**) crystallized. The X-ray structure is shown in Fig. 4, confirming an essentially symmetrical, hydride-bridged cation that is well separated from the
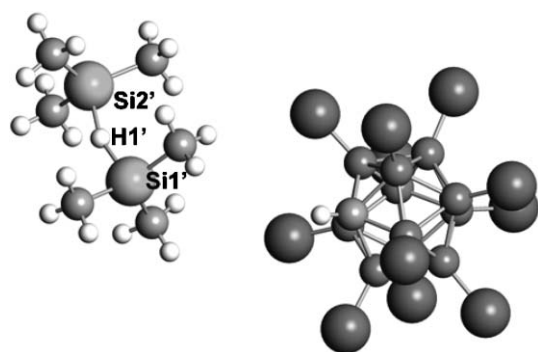

Fig. 4 X-Ray structure of [Me₃Si–H–SiMe₃][CHB₁₁Cl₁₁] (**5**); C–Si–C$_{ave}$ = 116.7°.

carborane anion. The bridge H atom in **5** was located and its position refined. The key metrical parameters are Si–H = 1.60(2) and 1.62(2) Å, Si···Si = 3.1732(4) Å, ∠Si–H–Si = 160(1)° and ∠C–Si–C$_{ave}$ = 116.7°. The structure is quite different from transition metal complexes of silanes, which, when structurally characterized, have been shown to be σ complexes with "side-on" rather than "end-on" binding of the Si–H bond.[16]

The only precedent for the Si–H–Si structural motif in the cations of **4** and **5** is the NMR characterization of intramolecular hydride bridge formation in **I**[17] and a related 5-membered ring compound.[18]
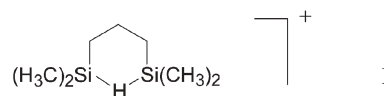
The NMR data for **I** are consistent with a symmetrical structure, and DFT calculations indicate a Si–H–Si bridge angle of *ca.* 140°. The cations in **4** and **5** differ in that they are formed without the entropic assistance of six-membered ring formation in **I**, and the geometry is free to relax towards linearity. Indeed, a DFT calculation for the [Me₃Si–H–SiMe₃]⁺ cation at the B3LYP/6-311+G(d,p) level using int(grid = ultrafine) yields a linear structure with ∠Si–H–Si = 179.7°, Si···Si = 3.28 Å and ∠C–Si–C$_{ave}$ = 116.0°. The small differences between the calculated and experimental structures can be ascribed to the absence of the counterion and crystal packing effects in the calculated structure.

Because of rapid chemical equilibration between the three energetically similar species, *i.e.* the solvent-, anion- and silane-coordinated species, little useful data can be obtained from ¹H NMR spectroscopy, and no reliably interpretable information can be obtained from ²⁹Si NMR spectroscopy in solution. However, in the case of **5**, which has a proton directly attached to the silicon atom giving rapid nuclear relaxation, it was possible to obtain a ²⁹Si NMR signal in the solid state. Two peaks were observed, consistent with the crystallographic site asymmetry of the cation in **5**. The chemical shifts are 85.4 and 82.2 ppm, in fair agreement with the DFT/GIAO calculated value (107 ppm). The corresponding resonance in cation **I** appears at 77 ppm (J_{SiH} = 39 Hz).[17]

The IR spectra of **4** and **5** show broad, intense bands at *ca.* 1900 and 1950 cm⁻¹, respectively, which are readily assigned to v_{as}(Si–H–Si). The DFT calculated values are 1902 and 1982 cm⁻¹, respectively. Sharp bands near 2100 cm⁻¹ due to v(Si–H) of free silane are absent from the experimental spectrum.

It is of interest to compare the degree of silylium ion character developed in each of these species with that in closely related silyl species. The extent of downfield shift of the ²⁹Si NMR resonances and the approach of the R₃Si$^{δ+}$ moiety towards planarity, as measured by the average C–Si–C angle (∠C–Si–C$_{ave}$), are often taken as useful measures of silylium ion character.[1] Selected data are gathered in Table 1.

It is apparent from the data in Table 1 that ²⁹Si chemical shifts in carborane anion-coordinated species tend to be slightly further downfield than in weakly ligated cations but the average C–Si–C bond angles are sufficiently close that reliable trends in experimental data cannot be discerned. All species have roughly the same degree of silylium ion character. This is consistent with the observation that equilibria between them are delicately balanced and crystallization is biased by subtle changes in solvent,

Table 1 Comparison of silylium ion character in selected compounds by ^{29}Si NMR and bond angle criteria

Species	^{29}Si/ppm	$\angle$C–Si–C$_{ave}$/°
^{i}Pr$_3$Si(CHB$_{11}$H$_5$Cl$_6$)	103 (benzene)	117.3
Et$_3$Si(CHB$_{11}$Me$_5$Br$_6$)	103 (benzene)	Unavailable
Et$_3$Si(CHB$_{11}$Cl$_{11}$) (**2**)	Unavailable	116.5
[^{i}Pr$_3$Si(ODCB)][CHB$_{11}$Cl$_{11}$] (**1**)	Unavailable	116.7
[Et$_3$Si(SO$_2$)][CHB$_{11}$Me$_5$Br$_6$] (**3**)	85 (SO$_2$)	115.7
[^{i}Pr$_3$Si(SO$_2$)][CHB$_{11}$H$_5$Br$_6$]	85 (SO$_2$)	Unavailable
[Me$_3$Si–H–SiMe$_3$][CHB$_{11}$Cl$_{11}$] (**5**)	85.4 and 82.2 (solid)	116.7
[Et$_3$Si(toluene)][F$_{20}$-BPh$_4$]	94 (solid)[a]	114.2[a]

[a] Ref. 3.

alkyl substituents on silicon and halogen substituents on the carborane anions.

Trialkylsilylium ion chemistry is an area where there is presently no such thing as a non-coordinating anion or a non-nucleophilic solvent. The prospects for characterizing a three-coordinate trialkylsilylium ion in condensed media appear rather slim unless groups bulkier than *tert*-butyl[19] can be employed. On the other hand, as anions become less and less coordinating, the prospects for demonstrating the coordination of ligands even weaker than *ortho*-dichlorobenzene, benzene, SO$_2$ and silanes improve.

Notes and references

‡ All reactions were carried out with carefully dried solvents and reagents within an inert atmosphere glove box (H$_2$O, O$_2$ < 0.5 ppm). Synthesis of **1**: [(C$_6$H$_5$)$_3$C][HCB$_{11}$Cl$_{11}$]·(toluene) (100 mg) was covered with 1,2-dichlorobenzene (0.5 mL). To this suspension, ^{i}Pr$_3$SiH (15 drops, *ca.* 0.3 mL) was added and stirred for 15 min until all orange colouration had vanished. Pentane (*ca.* 2 mL) was added while stirring. The resulting precipitate was filtered and washed with pentane (2 mL). The product was recrystallized by dissolving in ODCB (0.5 mL) and layering with pentane (3 mL) (85 mg, 85%). ^{1}H NMR (500 MHz, d_4-ODCB) (/ppm): ~0.95 (m, 18 H, ((CH$_3$)$_2$CH)$_3$–Si), ~1.3 (b, 3 H, (H–C(CH$_3$)$_2$)$_3$–Si) and ~3.0 (s, 1 H, C–H). X-Ray crystal data for **1** (CCDC 280853): C$_{16}$H$_{26}$B$_{11}$Cl$_{13}$Si, M = 826.2, monoclinic $P2(1)/c$, a = 14.9219(10), b = 13.6733(9), c = 18.5433(13) Å, α = 90, β = 110.906(2), γ = 90°. V = 3534.3(4) Å^3, T = 223(2) K, Z = 4, μ = 1.063 mm^{-1}, independent reflections = 8766 [R_{int} = 0.0365], R [$I > 2\sigma$ (I)] = 3.20%. The synthesis of **2** was carried out in the same manner as **1** using Et$_3$SiH instead of ^{i}Pr$_3$SiH. X-Ray crystal data for **2** (CCDC 280854): C$_7$H$_{16}$B$_{11}$Cl$_{11}$Si, M = 637.15, monoclinic $P2(1)/c$, a = 16.3058(6), b = 10.2062(4), c = 17.5343(6) Å, α = 90, β = 117.6017(14), γ = 90°. V = 2593.09(17) Å^3, T = 100(2) K, Z = 4, μ = 1.223 mm^{-1}, independent reflections = 16251 [R_{int} = TWIN n/a], R [$I > 2\sigma$ (I)] = 2.52%. Compound **3** was crystallized by slow cooling of a saturated solution of Et$_3$Si(CHB$_{11}$Me$_5$Br$_6$)[12] in SO$_2$ from room temperature to −18 °C. X-Ray crystal data for **3** (CCDC 261758): C$_{12}$H$_{31}$B$_{11}$Br$_6$O$_2$SSi, M = 865.89, monoclinic $P2(1)/c$, a = 15.0241(15), b = 14.16348(14), c = 16.2817(16) Å, α = 90, β = 116.708(2), γ = 90°. V = 3095.3(5) Å^3, T = 218(2) K, Z = 4, μ = 7.901 mm^{-1}, independent reflections = 6321 [R_{int} = 0.0423], R [$I > 2\sigma$ (I)] = 4.02%. Synthesis of **5**: [(C$_6$H$_5$)$_3$C][HCB$_{11}$Cl$_{11}$]·(toluene) (114 mg) was dissolved in ODCB (6 mL) in an 8 mL vial fitted with a teflon-lined screw cap with syringe access. After cooling to dry ice temperature, a similarly cooled solution of Me$_3$SiH was added (*ca.* 0.25 mL) *via* syringe. Upon shaking and warming to room temperature, the colourless product precipitated out (74 mg, 75%). ^{1}H NMR (d_4-ODCB) (/ppm): 2.93 (B$_{11}$CH, s, 1) and 0.48 (Me$_5$, MeSi, br s, 18). ^{29}Si CPMAS (/ppm): 85.4 and 82.2. IR v_{as}(Si–H–Si) (/cm^{-1}) = 1950br. Single crystals were grown by layering the cold solution with pentane. X-Ray crystal data for **5** (CCDC 280855): C$_7$H$_{20}$B$_{11}$Cl$_{11}$Si$_2$, M = 669.27, triclinic P-1, a = 9.2823(2), b = 12.3891(2), c = 12.5827(2) Å, α = 80.4810(10), β = 86.0780(10), γ = 85.6450(10)°. V = 1420.66(4) Å^3, T = 100(2) K, Z = 2, μ = 1.161 mm^{-1}, independent reflections 13696 [R_{int} = 0.0447], R [$I > 2\sigma$ (I)] = 3.20%. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b511344j

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