Electronic Supplementary Material

for

Novel weak coordination to silylium ions. Formation of nearly linear Si-H-Si bonds.

Stephan P. Hoffmann, Tsuyoshi Kato, Fook S. Tham, Christopher A. Reed[*]

10 pages (including colour versions of Figs. 1-4 from the main communication)

X-ray data for [(C$_3$H$_7$)$_3$Si(ODCB)][CHB$_{11}$Cl$_{11}$], 1.

A colorless fragment of a prism (0.44 x 0.33 x 0.14 mm^3) was used for the single crystal x-ray diffraction study of [(C$_3$H$_7$)$_3$Si(C$_6$H$_4$Cl$_2$)][CHB$_{11}$Cl$_{11}$], **1,** (sample code cr421m; iPrSiCl11). The crystal was coated with paratone oil and mounted on to a glass fiber. X-ray intensity data were collected at 223(2) K on a Bruker SMART 1000 (ref. 1) platform-CCD x-ray diffractometer system (Mo-radiation, λ = 0.71073 Å, 50KV/40mA power). The CCD detector was placed at a distance of 3.9540 cm from the crystal.

A total of 1868 frames were collected for a hemisphere of reflections (with scan width of 0.3^o in ω and ϕ angles of 0°, 90°, 180°, and 0° for every 606, 606, 606, and 50 frames, respectively, 20sec/frame exposure time). The frames were integrated using the Bruker SAINTPLUS software package (ref. 2) and using a narrow-frame integration algorithm. Based on a monoclinic crystal system, the integrated frames yielded a total of 38098 reflections at a maximum 2θ angle of 56.56^o (0.75 Å resolution), of which 8766 were independent reflections (R$_{int}$ = 0.0365, R$_{sig}$ = 0.0279, redundancy = 4.3, completeness = 100%) and 7027 (80.2%) reflections were greater than 2σ(I). The unit cell parameters were, a = 14.9219(10) Å, b = 13.6733(9) Å, c = 18.5433(13) Å, β = 110.906(2)^o, V = 3534.3(4) Å^3, Z = 4, calculated density D$_c$ = 1.553 g/cm^3. Absorption corrections were applied (absorption coefficient μ = 1.063 mm^{-1}; max/min transmission = 0.8654/0.6519) to the raw intensity data using the SADABS program in the SAINTPLUS software (ref. 2).

The Bruker SHELXTL (Version 6.10) software package (ref. 3) was used for phase determination and structure refinement. The distribution of intensities (E^2-1 = 0.978) and systematic absent reflections indicated one possible space group; P2(1)/c. The space group P2(1)/c was later determined to be correct. Direct methods of phase determination followed by two Fourier cycles of refinement led to an electron density map from which most of the non-hydrogen atoms were identified in the asymmetry unit of the unit cell. With subsequent isotropic refinement, all of the non-hydrogen atoms were identified. There were one cation [C$_3$H$_7$]$_3$Si$^+$, one anion CHB$_{11}$Cl$_{11}^-$, and one solvent molecule of ODCB (orthodichlorobenzene) present in the asymmetry unit of the unit cell. The ODCB was disordered (disordered site occupancy ratio was 92%/8%). One of the two Cl-atoms of ODCB was coordinated to the Si-atom.

Atomic coordinates, isotropic and anisotropic displacement parameters of all the non-hydrogen atoms were refined by means of a full matrix least-squares procedure on F^2. The H-atoms were included in the refinement in calculated positions riding on the atoms to which they were attached. The refinement converged at R1 = 0.0320, wR2 = 0.0789, with intensity, I>2σ(I). The largest peak/hole in the final difference map was 0.460/-0.251 e/Å^3.

REFERENCES

1. SMART Software Reference Manual, Version 5.054, Bruker Analytical X-Ray System, Inc., Madison, WI 1997-1998.

2. SAINTPLUS Software Reference Manual, Version 6.02A, Bruker Analytical X-Ray System, Inc., Madison, WI 1997-1998.

3. SHELXTL Software Reference Manual, Version 6.10, Dec. 5th, 2000, Bruker Analytical X-Ray System, Inc., Madison, WI.

Figure S1. Atom numbering scheme for $[(C_3H_7)_3Si(C_6H_4Cl_2)][CHB_{11}Cl_{11}]$, **1,** showing the two orientations of the coordinated ODCB molecules.
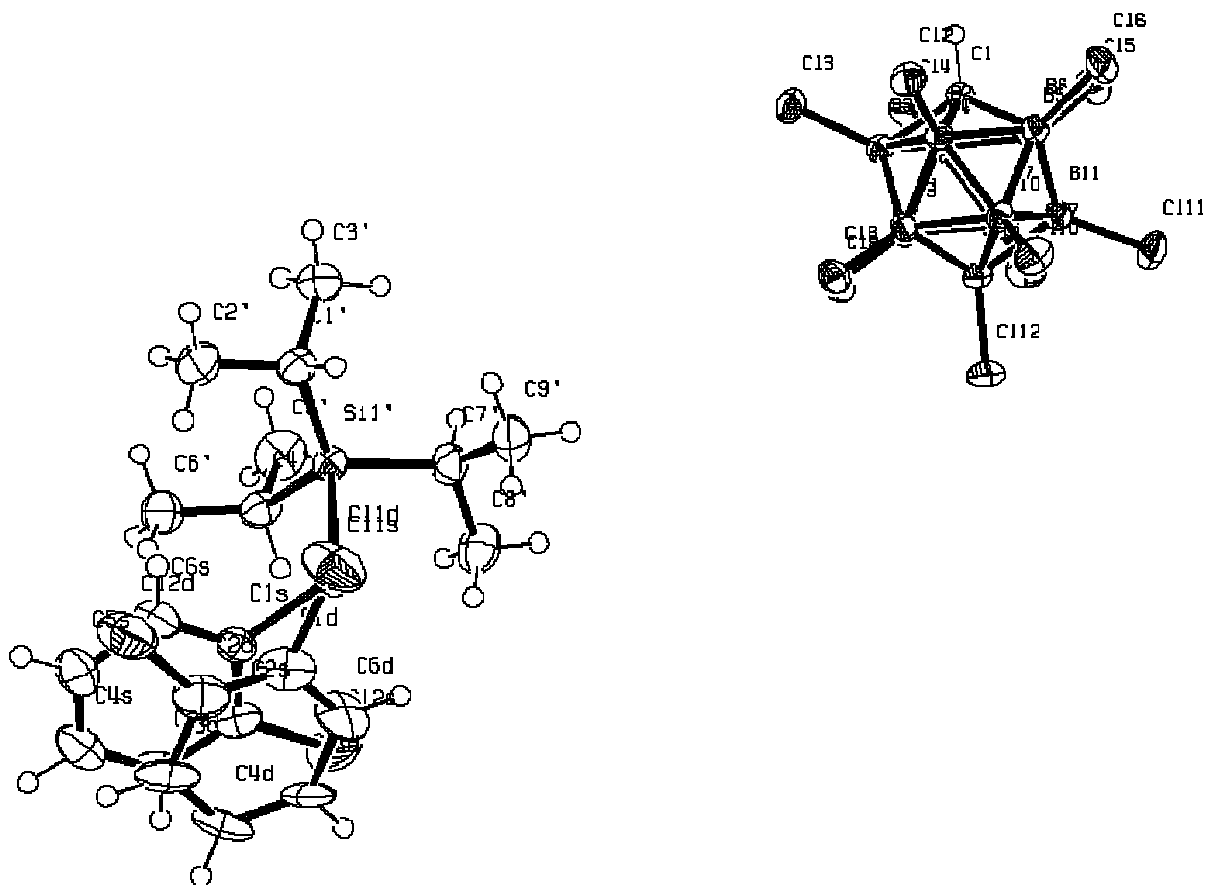
X-ray data for Et$_3$Si(CHB$_{11}$Cl$_{11}$), 2.

A colorless fragment of a prism (0.45 x 0.24 x 0.22 mm^3) was used for the single crystal x-ray diffraction study of (C$_2$H$_5$)$_3$Si(CHB$_{11}$Cl$_{11}$) (sample cr84_gm_2_m5). The crystal was coated with perfluoropolyethers (PFPE) oil and mounted on to a glass fiber. X-ray intensity data were collected at 100(2) K on a Bruker APEX2 (version 1.0-22, ref. 1) platform-CCD x-ray diffractometer system (Mo-radiation, λ = 0.71073 Å, 50KV/40mA power). The CCD detector was placed at a distance of 5.0450 cm from the crystal.

A total of 4800 frames were collected for a hemisphere of reflections (with scan width of 0.3^o in ω, starting 2θ angles of –30° and –60°, and ϕ angles of 0°, 90°, 180°, and 270° for every 600 frames, 20 sec/frame exposure time). The Bruker Cell_Now program (version 12-31-03, ref. 2) was used to obtain the two different matrices of the rotational twin components (180° rotation about the 1 0 1 real axis). Using the Bruker SAINT software package (version V7.06A, ref. 3) and using a narrow-frame integration algorithm, the frames were first integrated using the first twin domain matrix and then with the second twin domain matrix. Absorption corrections were applied (absorption coefficient μ = 1.223 mm^{-1}; max/min transmission = 0.7763/0.6078) to the raw intensity data using the TWINABS program (version 1.05, ref. 4). A total of 16251 independent reflections at a maximum 2θ angle of 80.50^o (0.55 Å resolution) were collected (completeness = 99.7%) and 15792 (97.2%) reflections were greater than 2σ(I). The unit cell parameters were, a = 16.3508(6) Å, b = 10.2062(4) Å, c = 17.5343(6) Å, β = 117.6017(14)^o, V = 2593.09(17) Å^3, Z = 4, calculated density D$_c$ = 1.632 g/cm^3.

The Bruker SHELXTL software package (Version 6.14, ref. 5) was used for phase determination and structure refinement. Using the first domain HKL intensity data, the distribution of intensities (E^2-1 = 0.892) and systematic absent reflections indicated one possible space group; P2(1)/n. The space group P2(1)/n was later determined to be correct. Direct methods of phase determination followed by two Fourier cycles of refinement led to an electron density map from which most of the non-hydrogen atoms were identified in the asymmetry unit of the unit cell. With subsequent isotropic refinement, all of the non-hydrogen atoms were identified. The combined (major and minor components) HKL intensity data was used in the final structure refinement. There was one cation of [C$_2$H$_5$]$_3$Si$^+$ and one anion of CHB$_{11}$Cl$_{11}^-$ present in the asymmetry unit of the unit cell. The sample was a rotational twin crystal (180° rotation about the 1 0 1 real axis; major/minor component ratio = 63%/37%).

Atomic coordinates, isotropic and anisotropic displacement parameters of all the non-hydrogen atoms were refined by means of a full matrix least-squares procedure on F^2. The H-atoms were included in the refinement in calculated positions riding on the atoms to which they were attached. The refinement converged at R1 = 0.0252, wR2 = 0.0626, with intensity, I>2σ(I). The largest peak/hole in the final difference map was 0.568/-0.338 e/Å^3.

REFERENCES

1.   **APEX 2**, version 1.0-22, Bruker (2004), Bruker AXS Inc., Madison, Wisconsin, USA.

2.   **CELL_NOW**, version 12-31-03, Bruker (2003), Bruker AXS Inc., Madison, Wisconsin, USA.

3.   **SAINT**, version V7.06A, Bruker (2003), Bruker AXS Inc., Madison, Wisconsin, USA.

4.   **TWINABS**, version 1.05, Bruker (2004), Bruker AXS Inc., Madison, Wisconsin, USA.

5.   **SHELXTL**, version 6.14, Bruker (2003), Bruker AXS Inc., Madison, Wisconsin, USA.

Figure S2. Atom numbering scheme for $Et_3Si(CHB_{11}Cl_{11})$, **2.**
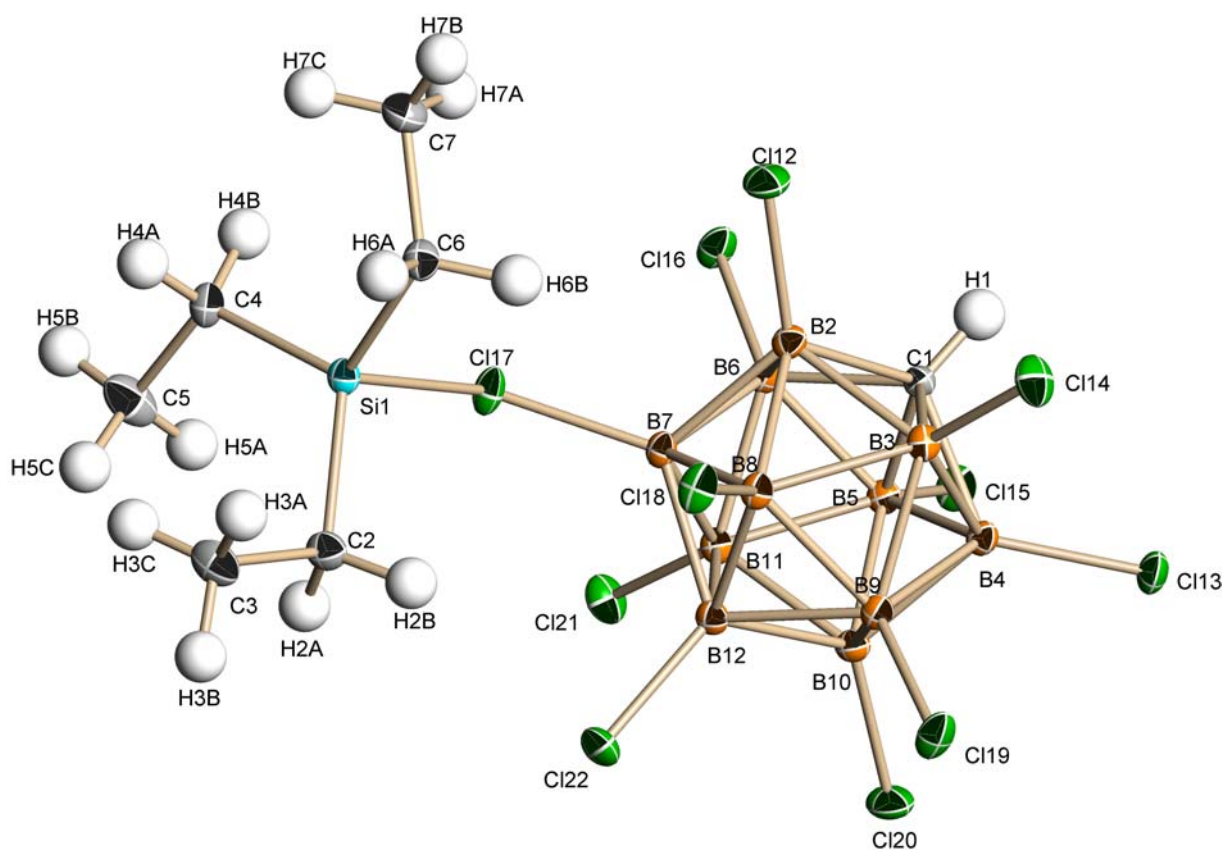
X-ray data for [Et$_3$Si(SO$_2$)][CHB$_{11}$Me$_5$Br$_6$], 3.

A yellow fragment of a prism (0.38 x 0.25 x 0.15 mm^3) was used for the single crystal x-ray diffraction study of C$_{12}$H$_{31}$B$_{11}$Br$_6$O$_2$SSi (sample code cr381m; EtSiMeBr). The crystal was coated with paratone oil and mounted on to a glass fiber. X-ray intensity data were collected at 218(2) K on a Bruker SMART 1000 (ref. 1) platform-CCD x-ray diffractometer system (Mo-radiation, λ = 0.71073 Å, 50KV/40mA power). The CCD detector was placed at a distance of 5.0180 cm from the crystal.

A total of 1800 frames were collected for a hemisphere of reflections (with scan width of 0.3^o in ω and ϕ angles of 0°, 90°, and 180° for every 606, 606, and 606 frames, respectively, 30 sec/frame exposure time). The frames were integrated using the Bruker SAINT software package (ref. 2) and using a narrow-frame integration algorithm. Based on a monoclinic crystal system, the integrated frames yielded a total of 24715 reflections at a maximum 2θ angle of 52.74^o (0.80 Å resolution), of which 6321 were independent reflections (R$_{int}$ = 0.0423, R$_{sig}$ = 0.0388, redundancy = 3.9, completeness = 99.9%) and 4554 (72.0%) reflections were greater than 2σ(I). The unit cell parameters were, a = 15.0241(15) Å, b = 14.1648(14) Å, c = 16.2817(16) Å, β = 116.708(2)^o, V = 3095.3(5) Å^3, Z = 4, calculated density D$_c$ = 1.858 g/cm^3. Absorption corrections were applied (absorption coefficient μ = 7.901 mm^{-1}; max/min transmission = 0.3836/0.1532) to the raw intensity data using the SADABS program in the SAINT software (ref. 2).

The Bruker SHELXTL (Version 6.10) software package (ref. 3) was used for phase determination and structure refinement. The distribution of intensities (E^2-1 = 0.940) and systematic absent reflections indicated one possible space group; P2(1)/c. The space group P2(1)/c was later determined to be correct. Direct methods of phase determination followed by two Fourier cycles of refinement led to an electron density map from which most of the non-hydrogen atoms were identified in the asymmetry unit of the unit cell. With subsequent isotropic refinement, all of the non-hydrogen atoms were identified. There was one cation of [C$_2$H$_5$]$_3$SiSO$_2^+$ and one anion of CHB$_{11}$[CH$_3$]$_5$Br$_6^-$ present in the asymmetry unit of the unit cell. The [C$_2$H$_5$]$_3$SiSO$_2^+$ cation was disordered (disordered site occupancy ratio was 71%/29%).
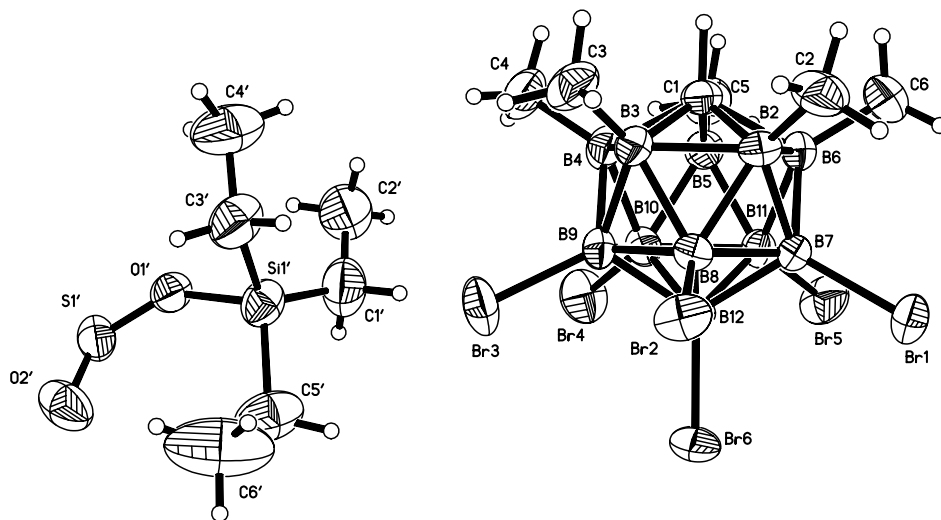
Atomic coordinates, isotropic and anisotropic displacement parameters of all the non-hydrogen atoms were refined by means of a full matrix least-squares procedure on F^2. The H-atoms were included in the refinement in calculated positions riding on the atoms to which they were attached. The refinement converged at R1 = 0.0402, wR2 = 0.0951, with intensity, I>2σ(I). The largest peak/hole in the final difference map was 0.901/-0.512 e/Å^3.

REFERENCES

1.   SMART Software Reference Manual, Version 5.054, Bruker Analytical X-Ray System, Inc., Madison, WI 1997-1998.

2.   SAINTPLUS Software Reference Manual, Version 6.02A, Bruker Analytical X-Ray System, Inc., Madison, WI 1997-1998.

3.   SHELXTL Software Reference Manual, Version 6.10, Dec. 5th, 2000, Bruker Analytical X-Ray System, Inc., Madison, WI.

Figure S3. Atom numbering scheme for [Et$_3$Si(SO$_2$)][CHB$_{11}$Me$_5$Br$_6$], **3,** (50% thermal ellipsoid representation); disordered positions are removed for clarity in *A*; disordered positions are shown in *B*.
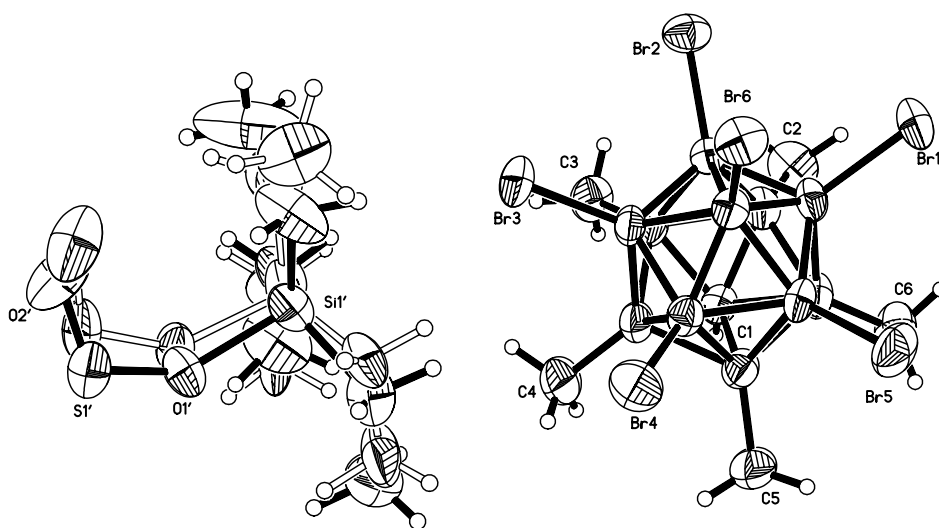
X-ray data for [Me$_3$Si-H-SiMe$_3$][CHB$_{11}$Cl$_{11}$], 5.

A colorless fragment of a prism (0.25 x 0.13 x 0.08 mm^3) was used for the single crystal x-ray diffraction study of [(CH$_3$)$_3$SiHSi(CH$_3$)$_3$][CHB$_{11}$Cl$_{11}$], **4**. (sample cr109_0m; Trimethyl silylium dimer). The crystal was coated with perfluoropolyethers (PFPE) oil and mounted on to a glass fiber. X-ray intensity data were collected at 100(2) K on a Bruker APEX2 (version 1.0-22, ref. 1) platform-CCD x-ray diffractometer system (Mo-radiation, λ = 0.71073 Å, 50KV/40mA power). The CCD detector was placed at a distance of 5.0450 cm from the crystal.

A total of 7200 frames were collected for a sphere of reflections (with scan width of 0.3^o in ω, starting 2θ angles of –30° and –60°, and ϕ angles of 0°, 90°, 120°, 180°, 240°, and 270° for every 600 frames, 10 sec/frame exposure time). The frames were integrated using the Bruker SAINT software package (version V7.06A, ref. 2) and using a narrow-frame integration algorithm. Based on a triclinic crystal system, the integrated frames yielded a total of 73069 reflections at a maximum 2θ angle of 62.64^o (0.60 Å resolution), of which 13696 were independent reflections (R$_{int}$ = 0.0447, R$_{sig}$ = 0.0450, redundancy = 5.3, completeness = 99.5%) and 10281 (75.1%) reflections were greater than 2σ(I). The unit cell parameters were, a = 9.2823(2) Å, b = 12.3891(2) Å, c = 12.5827(2) Å, α = 80.481(1)^o, β = 86.078(1)^o, γ = 85.645(1)^o, V = 1420.66(4) Å^3, Z = 2, calculated density D$_c$ = 1.565 g/cm^3. Absorption corrections were applied (absorption coefficient μ = 1.161 mm^{-1}; max/min transmission = 0.9129/0.7570) to the raw intensity data using the SADABS program (version 2004/1, ref. 3).

The Bruker SHELXTL software package (Version 6.14, ref. 4) was used for phase determination and structure refinement. The distribution of intensities (E^2-1 = 1.016) and no systematic absent reflections indicated two possible space groups; P-1 and P1. The space group P-1 was later determined to be correct. Direct methods of phase determination followed by two Fourier cycles of refinement led to an electron density map from which most of the non-hydrogen atoms were identified in the asymmetry unit of the unit cell. With subsequent isotropic refinement, all of the non-hydrogen atoms were identified. There was one cation of [(CH$_3$)$_3$SiHSi(CH$_3$)$_3$]$^+$ and one anion of [CHB$_{11}$Cl$_{11}$]$^-$ present in the asymmetry unit of the unit cell. The H-atom between the two Si-atoms was located from the difference map and was refined unrestrained. Their bond distances and angle were given in Table 7.

Atomic coordinates, isotropic and anisotropic displacement parameters of all the non-hydrogen atoms were refined by means of a full matrix least-squares procedure on F^2. The H-atoms were included in the refinement in calculated positions riding on the atoms to which they were attached. The refinement converged at R1 = 0.0320, wR2 = 0.0722, with intensity, I>2σ(I). The largest peak/hole in the final difference map was 0.637/-0.480 e/Å^3.

REFERENCES

1. *APEX 2,* version 1.0-22, Bruker (2004), Bruker AXS Inc., Madison, Wisconsin, USA.

2. *SAINT,* version V7.06A, Bruker (2003), Bruker AXS Inc., Madison, Wisconsin, USA.

3. *SADABS,* version 2004/1, Bruker (2004), Bruker AXS Inc., Madison, Wisconsin, USA.

4. *SHELXTL,* version 6.14, Bruker (2003), Bruker AXS Inc., Madison, Wisconsin, USA.

Figure S4. Atom numbering scheme for [(CH$_3$)$_3$Si-H-Si(CH$_3$)$_3$][CHB$_{11}$Cl$_{11}$], **5**.
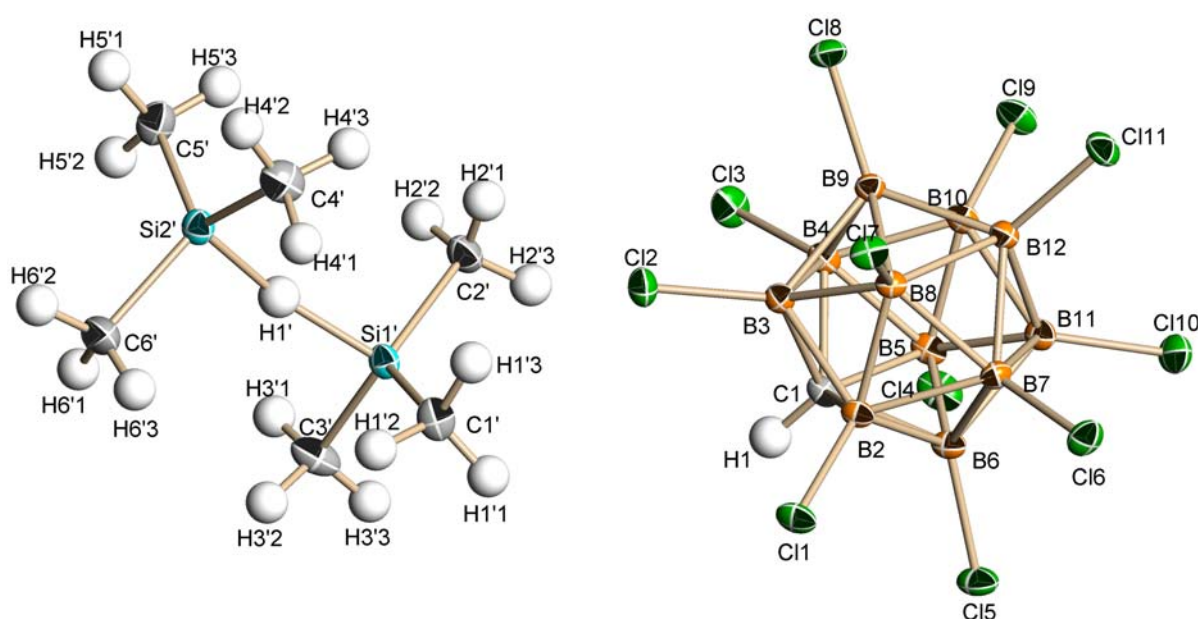
Colour versions of Figs. 1-4 from the main communication

Fig. 1. X-ray structure of the major conformer of [*i*-Pr$_3$Si(ODCB)][CHB$_{11}$Cl$_{11}$], **1**, showing coordination of *o*-dichlorobenzene; C-Si-C$_{ave}$ = 116.7°.
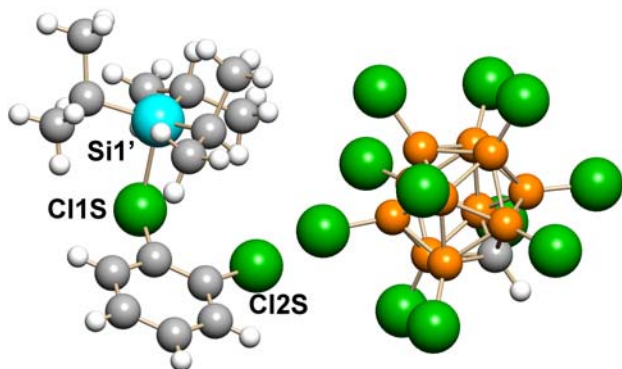
Fig. 2. X-ray structure of $Et_3Si(CHB_{11}Cl_{11})$, **2**; $C-Si-C_{ave}$ = 116.5°.
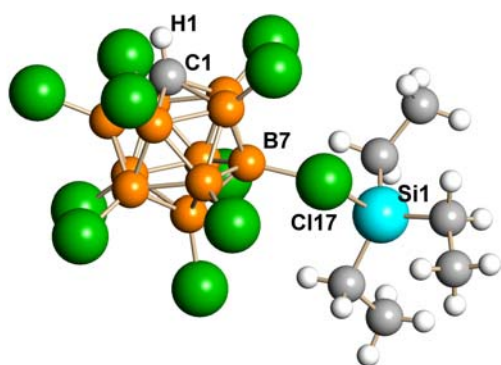
Fig. 3. X-ray structure of $[Et_3Si(SO_2)][CHB_{11}Me_5Br_6]$, **3**; $C-Si-C_{ave}$ = 115.7°, Si-O = 1.820(5);
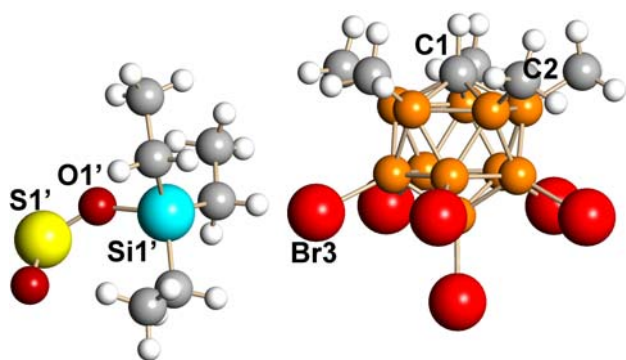
Fig. 4. X-ray structure of $[Me_3Si-H-SiMe_3][CHB_{11}Cl_{11}]$, **5**; $C-Si-C_{ave}$ = 116.7°.