reactivity might be enhanced.[12] In addition, the beneficial impact of microwave irradiation can be attributed to the instant, internal heat-transfer mode, as opposed to conventional heat transfer from the walls that is characteristic of traditional heating devices.[13] However, the origin of the increased efficiency in performing metal-catalyzed asymmetric high-temperature alkylations with focused microwave heating requires further investigation.

In conclusion, we have demonstrated a synthetically useful and easily handled microwave protocol for fast and selective molybdenum(0)-catalyzed allylic alkylation. The former sensitive reaction procedure has been transformed into a robust, air-stable, one-step procedure employing the inexpensive and stable precatalyst [Mo(CO)$_6$] in low concentration.

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A Novel Borosilicate Cage Compound with an Incomplete B_4Si_4 Cube Structure: $[(t\text{BuSi})_4(\text{CH}_2{=}\text{CHC}_6\text{H}_4\text{B})_4\text{O}_{10}]$**

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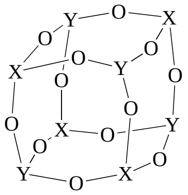
George Ferguson

Recently there has been a proliferation of cube-based cages in which a variety of main group elements occupy corner sites and oxygen atoms bridge the main group atoms. Many "cubic" sections of the cages have the general formula $X_4Y_4O_{12}$ and adopt the double four-ring (D4R) (4-4) structure **1**. The positioning of the X and Y atoms at alternate corners is noteworthy and has been observed with various combinations of Group 13, 14, and 15 elements including those with X = Si and Y = Al,[1] Ga,[2] or In[2b, 3] and those with X = P and Y = B,[4] Al,[5] or Ga.[6] These compounds are related to silsesquioxanes (X = Y = Si in **1**) which have been studied extensively.[7] One aim in developing the chemistry of these compounds is to use them as building blocks in the construction of more complex materials, possibly zeolites or catalyst supports. Another aim is to develop their applications in microelectronics as interlevel low *k* dielectrics. In the latter respect, silsesquioxanes have already attracted the attention of several industries including microelectronics manufacturers.[8]



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Relatively little work has been done on the chemistry of molecular borosilicates. Established borosilicate cages which have been reported are $[t\text{BuSi}\{\text{O}(\text{BC}_6\text{H}_4\text{Br})\text{O}\}_3\text{Si}t\text{Bu}]$ (**2**)[9] with a $\{B_3Si_2O_6\}$ cage, $[\text{B}(\text{OSiPh}_2\text{OSiPh}_2\text{O})_3\text{B}]$ (**3**)[10] with a $\{B_2Si_6O_9\}$ cage, and the silsesquioxane-based borosilicates $[\{(cyclo\text{-}\text{C}_6\text{H}_{11}\text{Si})_7\text{BO}_{12}\}_2]$[11] and $[\{(cyclo\text{-}\text{C}_6\text{H}_{11}\text{Si})_8\text{O}_{13}(\text{B}n\text{-Bu})]$,[12] and anionic silsesquioxane-borato complexes of the types $[\text{R}_7\text{Si}_8\text{O}_{12}\{\text{OB}(\text{C}_6\text{F}_5)_3\}]^-$ and $[\text{R}_7\text{Si}_7\text{O}_9(\text{OH})_2\{\text{OB}(\text{C}_6\text{F}_5)_3\}]^-$.[13] Whereas all the silsesquioxane-based compounds were synthesized from preformed silsesquioxane fragments and single boron-containing reagents, compounds **2** and **3** were synthesized from reagents containing only single silicon and boron. In the case of **2**, the reagents were $t\text{BuSi(OH)}_3$ and a boronic acid, and for **3** the reagents were $\text{Ph}_2\text{Si(OH)}_2$ and boric acid. We have now used single boron- and silicon-containing reagents to synthesize a new type of cube-based compound with both three- and four-coordinate corner sites. The compound $[(t\text{BuSi})_4(\text{CH}_2{=}\text{CHC}_6\text{H}_4\text{B})_4\text{O}_{10}]$

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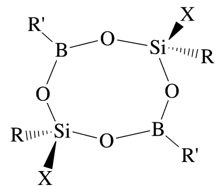
(**4**) (see Figure 1) has an incomplete cage with a pair of $B_2Si_2O_4$ faces held together by two Si-O-Si bridges. The construction of a cube-based cage with two X or two Y atoms at adjacent corners has not previously been realized.

Compound **4** was synthesized in 19% yield from the reaction between *t*BuSiCl$_3$, 4-vinylphenylboronic acid, aniline, and water in refluxing toluene. An alternative synthesis from the reaction between *t*BuSi(OH)$_3$ and 4-vinyl-phenylboronic acid in refluxing toluene also afforded **4** but in less reproducible yields. The constitution of **4** as a molecular borosilicate with a 1:1 ratio of B:Si was confirmed by IR and ^{1}H, ^{11}B, and ^{29}Si NMR spectra. The former showed intense absorptions due to B-O-Si and Si-O-Si units. The ^{1}H spectrum contained signals due to *t*Bu and $C_6H_4CH{=}CH_2$ substituents in a 9:7 ratio. The single singlet resonance signals in the ^{11}B and ^{29}Si NMR spectra were typical of three-coordinate boron and {*t*BuSiO$_3$} units, respectively. The exact configuration of the molecule in the solid state was determined by an X-ray crystal structure analysis (Figure 1). The molecule lies about a crystallographic inversion center and the borosilicate cage can be described as being formed from two inversion-related eight-membered {B-O-Si-O-B-O-Si-O} "rings" joined confacially through two Si-O-Si bridges. Since there is no bonding between opposite boron atoms, the cube structure is incomplete. In each $\{B_2Si_2O_4\}$ face, one silicon, both borons, and all oxygen atoms are essentially coplanar but the other silicon atom clearly lies out of this plane. Thus, the atoms Si1, B3, B7, O2, O4, O6, and O8 lie in a plane with a root mean square deviation of 0.053 and maximum deviations from the mean plane of −0.062 (0.001) Å (for Si1) and 0.081 (0.002) Å (for O8). However, one silicon atom, Si5, is 0.705 (0.002) Å from the mean plane. This contrasts with the configurations found in the $\{B_2Si_2O_4\}$ rings in $(PhBO)_2(Ph_2SiO)_2$[14] and $(PhBO)_2$-$(tBu_2SiO)_2$.[15] In the former compound the $\{B_2Si_2O_4\}$ ring is essentially planar with maximum deviations from the mean plane of 0.137 Å for O2 and −0.025 Å for B1.[14] In the latter compound the $\{B_2Si_2O_4\}$ ring lies about an inversion center. Six of the atoms, that is both boron and all oxygen atoms, are essentially coplanar with deviations from the six-atom plane of ±0.010 to 0.014 Å. The silicon atoms are ±0.303 Å from the six-atom plane. These observations clearly illustrate the flexibility of borosilicate rings.

The mean B−O interatomic distance in the symmetry-related borosilicate rings in **4** is 1.366(3) Å, typical of distances between three-coordinate boron centers and oxygen atoms (compare mean values in **2**[9] and **3**[10] of 1.362 and 1.356 Å, respectively). The mean Si−O distance in **4** is 1.616(4) Å (compare mean values in **2** and **3** of 1.621 and 1.631 Å, respectively) and the Si−O distances in the Si-O-Si bridges average 1.607(4) Å. In **4**, the Si-O-Si angle is 154.14(14)°; large variations in Si-O-Si angles are well established with values from 89.4° to 180°.[16] The individual B-O-Si angles vary significantly from 137.5(2)° to 154.4(2)°. This is not surprising, since B-O-Si angles show considerable flexibility in borosilicate rings containing trigonal-planar boron atoms; reported values range from 129.89(14)° in $(PhBO)(Ph_2SiO)_2$[17] to 160.9(3)° in $(PhBO)_2(Ph_2SiO)_2$.[14] This feature of borosilicate chemistry has been discussed in detail elsewhere.[18] The mean values of the angles at boron and silicon are close to those expected for trigonal-planar boron and tetrahedral silicon centers at 120.8° and 109.10°, respectively, but it is noteworthy that the O-Si-O angles in the borosilicate rings of **4** are significantly larger (110.23 and 112.51°) than those involving the Si-O-Si bridging oxygen atoms (from 107.02 to 108.88°). These values are typical of those reported in the structures of the cages of **2** and **3**.

A notable feature of **4** is the parallel nature of both the phenyl and vinyl units in the vinylphenyl groups (Figure 1). The torsion angles C12-C13-C14-C17 and C22-C23-C24-C27 are 178.6(4)° and 175.6(4)°, respectively. Values of the various C−C dimensions are in accord with accepted values, except for those of the terminal vinyl moieties whose atoms (C18, C28) show marked anisotropy; attempts to model this with slightly disordered vinyl groups led to no improvement in the *R* factor and had no effect at all on the Si cage geometry.

The formation of the $\{B_4Si_4O_{10}\}$ cage of **4** most probably proceeds through the condensation reaction of two cyclic borosilicate intermediates which have structure **5** with X = OH and which have



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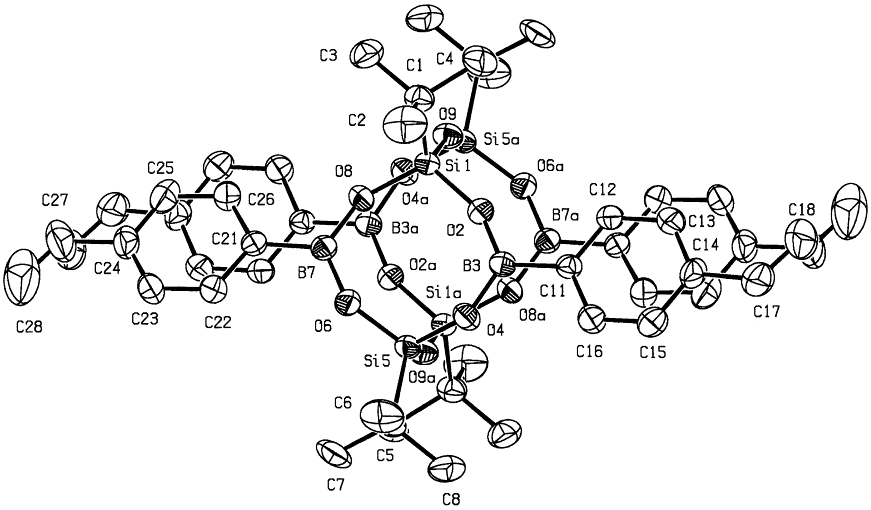
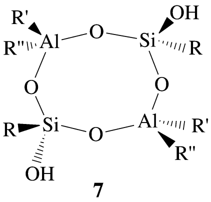


Figure 1. Molecular structure of **4** in the crystal (ORTEP plot). Thermal elipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Si1-O2 1.609(2), Si1-O8 1.620(2), Si1-O9 1.603(2), Si1-C1 1.843(3), B3-O2 1.361(4), B3-O4 1.367(4), B3-C11 1.541(4), Si5-O4 1.619(2), Si5-O6 1.616(2), Si5-O9a 1.611(2) [atom O9a is at equivalent position −*x*, −*y*, −*z*], Si5-C5 1.847(3), B7-O6 1.369(4), B7-O8 1.366(4), B7-C21 1.536(5); O2-Si1-O8 112.51(12), O2-Si1-O9 107.02(12), O2-Si1-C1 110.08(15), O8-Si1-O9 107.42(12), O8-Si1-C1 109.85(14), O9-Si1-C1 109.87(13), Si1-O2-B3 154.4(2), O2-B3-O4 120.7(3), O2-B3-C11 120.6(3), O4-B3-C11 118.7(3), B3-O4-Si5 137.5(2), O4-Si5-O6 110.23(12), O4-Si5-C5 108.59(14), O6-Si5-C5 109.11(14), O4-Si5-O9 108.51(12), O6-Si5-O9 108.88(11), O9-Si5-C5 111.52(13), Si5-O6-B7 139.4(2), O6-B7-O8 120.9(3), O8-B7-C21 120.2(3), O6-B7-C21 118.9(3), Si1-O8-B7 147.9(2), Si1-O9-Si5a 154.14(14) [atom Si5a is at equivalent position −*x*, −*y*, −*z*].

the {*t*BuSiX} moieties configured in a *cis* arrangement across the borosilicate ring. The condensation of two such rings would clearly lead to a structure with parallel "eclipsed" {$B_2Si_2O_4$} faces. This intermediate could be formed from the chlorosilane precursor (X = Cl) by hydrolysis or, in the reaction with *t*BuSi(OH)$_3$ directly. We have previously shown that, under the conditions used in the present study, that is in refluxing toluene, dehydration reactions of mixtures of B–OH and Si–OH reagents form B-O-Si linkages in preference to either Si-O-Si or B-O-B linkages.[18] Hence an alternating B-O-Si motif shown in **5** would be expected initially. Furthermore, structural studies of silesquioxane-based polyhydroxy derivatives[19] demonstrate the importance of intermolecular hydrogen bonding in stabilizing the solid-state structures of these compounds. The recently reported compound tetrahydroxy *cis,cis,cis*-[$Ph_4Si_4O_4(OH)_4$] (**6**) is of particular importance to the present study.[19c] Compound **6** was isolated from the hydrolytic condensation of $PhSiCl_3$ in aqueous acetone. It was found to be a single isomer both in the solid state and in solution. The crystalline state contains pairs of molecules linked by intermolecular hydrogen bonds. When catalytic hydrogenation of **6** was attempted, the major product identified was the condensed cubic silesquioxane [(*cyclo*-hexyl)$_8$Si$_8$O$_{12}$] (15 %).[19c] It is also noteworthy that the more sterically hindered aluminosilicate {$Al_2Si_2O_4$} ring compound which has tetrahedrally coordinated aluminum and silicon atoms (**7**) with R = (2,6-*i*Pr$_2$C$_6$H$_3$)N(SiMe$_3$), R′ = *i*Bu, R″ = thf, was only isolated as the all *trans* isomer.[20] Moreover, no cubic cage compound with structure **1** was isolated during the study.



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We have no direct evidence concerning the sterochemistry of the intermediates that lead to **4**, but it is possible that both *cis* and *trans* isomers of **5** could be formed. The low yield of **4** (19 %) may be due in part to the inability of the *trans* isomer of **5** to produce the {$B_4Si_4O_{10}$} cage. Although the construction of the {$B_4Si_4O_{10}$} cage is understandable in the light of the foregoing comments, the possible role of the vinylphenyl groups in the formation of **4** is unclear and requires further work.

Experimental Section

The synthesis was carried out in an inert atmosphere: isolation of the product was in air.

4: A mixture of *tert*-butylsilane trichloride (0.6 g, 3.1 mmol) and 4-vinylphenylboronic acid (0.46 g, 3.1 mmol) was dissolved in toluene (50 mL). A mixture of aniline (0.87 g, 9.4 mmol) and water (0.06 g, 3.1 mmol) in toluene (10 mL) were added to this mixture through an addition funnel over a period of 10 min. The reaction mixture was heated at reflux temperature for 16 h. After cooling, a colorless precipitate of [$PhNH_3$]Cl was filtered off. Removal of solvent from the filtrate and crystallization of the resulting residue from CH_2Cl_2/heptane solution (1:2) afforded **4** (0.124 g, 18.6 %). Compound **4** does not melt below 370°C. ^{1}H NMR (270 MHz, $CDCl_3$, TMS): $\delta = 7.46$ (d, 2 H; C_6H_4), 7.11 (d, 2 H; C_6H_4), 6.61 (m, 1 H; $CHCH_2$), 5.74 (d, 1 H; $CHCH_2$), 5.26 (d, 1 H; $CHCH_2$), 1.22 (s, 9 H; $C(CH_3)_3$); ^{13}C NMR (67.9 MHz, $CDCl_3$, TMS): $\delta = 140.76$, 136.93, 135.69, 133.77 (all C_6H_4), 125.47 ($CHCH_2$), 114.58 ($CHCH_2$), 25.52 ($C(CH_3)_3$), 17.07 ($C(CH_3)_3$); ^{11}B NMR (128 MHz, $CDCl_3$, F_3BOEt_2): $\delta = 25.5$ (s); ^{29}Si NMR (99 MHz, $CDCl_3$, TMS): $\delta = -66.0$ (s); FTIR (KBr disc): $\tilde{\nu}_{max} =$ 2959 m, 2862 w, 1608 m, 1307 vs (B-O-Si), 1262 w, 1097 s (Si-O-Si), 991 w, 908 w, 908 w, 665 m cm^{-1}; elemental analysis calcd for $C_{48}H_{64}B_4O_{10}Si_4$ (%): C 60.3, H 6.7; found: C 60.3, H 6.5.

Crystal structure data for **4**: $C_{48}H_{64}B_4O_{10}Si_4$, $M_r = 956.59$, monoclinic, space group $P2_1/n$, $a = 10.4526(13)$, $b = 18.6540(16)$, $c = 14.6121(15)$ Å, $\beta = 106.936(8)°$, $V = 2725.5(5)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.166$ g cm^{-3}, $F(000) = 1016$, $\lambda = 0.71073$ Å, $T = 294(1)$ K, $\mu(Mo_{K\alpha}) = 0.160$ mm^{-1}. Intensity data were measured on an Enraf-Nonius CAD4 diffractometer for a colorless needle crystal of dimensions $0.42 \times 0.24 \times 0.22$ mm^3 in the range $4° < 2\theta < 50°$ using $\theta/2\theta$ scans and graphite-monochromated radiation. The data were corrected for Lorentz, polarization, and absorption effects (Gaussian correction,[21] transmission coefficients 0.960–0.971). From the 5203 measured reflections, 4762 were independent ($R_{int} = 0.016$) and 2113 had $I > 2\sigma(I)$. The structure was solved by direct methods (SHELXS-97)[22] and refined by using all measured F^2 data using SHELXL-97.[23] In the full-matrix least-squares refinement (299 parameters) all non-hydrogen atoms were refined anisotropically and hydrogen atoms were allowed for as riding atoms. Max./min. residual electron density +0.342/−0.214 e Å^{-3}. $R1(F > 4\sigma(F)) = 0.0461$ and $wR2 = 0.1266$ (all data) with $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $wR2 = (\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2)^{0.5}$. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-118471. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Hydrogen Bonding Interactions in Amorphous Salicyl Salicylate[**]

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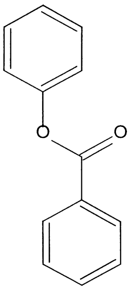
Michael Hodkinson

The macroscopic physical properties of a chemical substance are determined by the intra- and intermolecular interactions of each individual molecule comprising it. Presently, reliable prediction of the three-dimensional structure of a multiple-atom chemical species from only its structural formula is not possible,[1] thus the ab initio prediction of bulk physical properties is likewise not currently attainable. To circumvent this obstacle, empirical studies of systematic chemical series have been pursued, and experimentally derived properties, such as crystal structure[2] and melting point,[3] have been correlated with structural formula.

Our research is concerned with the production of supramolecular materials, a field that has promised much.[4] Recent work in the field of supramolecular materials assembly has focused upon the synthesis of molecules containing multiple hydrogen bonding motifs at chain termini[5] and inner-chain sites.[6] We wished to make a departure from this approach to understand the macroscopic physical effect of systematic changes in the chemical structure of simple species. We aimed to maximize the observed change in physical attributes while minimizing the structural change at the molecular level. We studied the molecular series: phenyl benzoate (**1**), phenyl salicylate (**2**), and salicyl salicylate (**3**).



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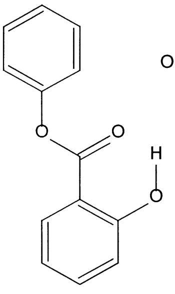

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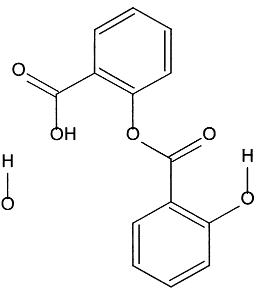

3

Each compound was melted and allowed to cool at ambient temperature. Compound **1** melted at 342 K and recrystallized at this temperature upon cooling; **2** melted at 317 K and undercooled to ambient temperature without crystallization, the low viscosity undercooled liquid could be maintained in this state for several weeks without difficulty; **3** melted over the range 412–424 K and undercooled to a high viscosity liquid that could be moulded and stress-fractured: a potentially useful material (crystallization in **3** could not be induced by any means, including crystal seeding and holding at the crystallization temperature for several hours. Recrystallization could be achieved only by dissolution and reprecipitation.). Thus we observed gross physical changes with small molecular alterations in the series **1**–**3**.

To elucidate the molecular interactions giving rise to these physical manifestations we reviewed the single-crystal structures of **1**[7] and **2**,[8] and determined the structure of **3**. In addition, **3** was studied extensively by NMR and IR spectroscopy.

The low viscosity of the amorphous **3** at temperatures in the range 373–423 K allowed study by ^{13}C NMR spectroscopy. The spectrum recorded at 423 K is shown in Figure 1, and was assigned by 2D NMR experiments,[9] and comparison with reference spectra.[10] Multiple resonances were observed for many peaks, most notably those carbon atoms lying along the functional backbone: C14, C9, C1, C3, and C4. The acid carbonyl, C2, gave a single resonance signal. The ester carbonyl resonance, C1, was composed of at least five discrete signals, indicating that at least this many environments were stable on the NMR time scale. This multiple-resonance effect persisted, without diminuition, across the observable temperature range. Peak shifting within the multiple-resonance sets was observed over the temperature range, in all cases peaks moved, at various rates, to lower field with cooling (increased hydrogen bonding[11]).

To assess potential structural similarities between the amorphous and crystalline phases of **3**, solid-state ^{13}C NMR spectra of both were recorded at ambient temperature (Figure 1).[12] There was a good correlation between the liquid and solid-state NMR spectra of amorphous **3** and the solid-state NMR spectra of crystalline **3**. The lack of significant chemical shifting of resonances in any of the spectra suggests

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