Isolation and structure of a silicocationic species with 1,3-aryl bridging between silicon atoms: a bis-silylated benzenium ion or a bridging Ph group?†

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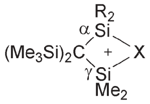
Hydride abstraction from $(Me_3Si)_3CSiMePhH$ by Ph_3C^+ affords the cation $[(Me_3Si)_2CSiMe_2–Ph–SiMe_2]^+$, which is shown by X-ray crystallography to contain the first structurally characterised example of a Ph group bridging between two silicon atoms.

The synthetic pursuit and computational characterisation of silylium ions (R_3Si^+ species) in condensed phases has intensified greatly in the last ten years.[1–3] Along with the search for structural characterisation of silylium ions, there have been many studies undertaken to demonstrate the intermediacy of silylium-like ions in various reactions.[1] The most detailed studies have been directed towards understanding the reaction mechanisms of tetrasilylmethanes such as $(Me_3Si)_3CSiRR^1Z$ (where R and R^1 = alkyl, aryl, vinyl *etc.*, and Z = halide or pseudohalide).[4] This work has shown, for example, that for reactions of $(Me_3Si)_3CSiR_2I$ (where R = CD_3, Et, Ph, *etc.*) with AgY (where Y = O_2CCF_3, OSO_2CF_3, *etc.*), there are two main products, one, $(Me_3Si)_3CSiR_2Y$, resulting from simple substitution, the other, a rearranged product $(Me_3Si)_2C(SiMe_2Y)(SiR_2Me)$, resulting from a 1,3-Si-to-Si methyl migration.[4] The amount of rearranged product formed varies widely and depends on both steric and electronic factors of the R groups, the solvent and the nature of the incoming group Y.[4] The rearranged product is thought to be formed *via* a bridged cationic intermediate of type **1** (X = Me).[5]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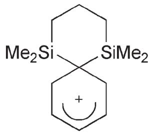
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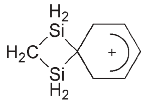
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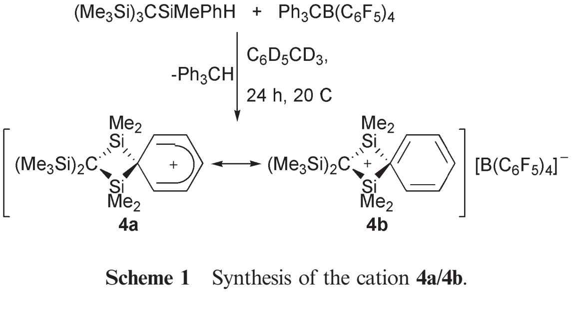
Such a cation can be attacked by Y^- at either end of the bridge to give either the unrearranged $(Me_3Si)_3CSiR_2Y$ for attack at the α-silicon, or $(Me_3Si)_2C(SiMe_2Y)(SiR_2Me)$ for attack at the γ-silicon. Other studies showed that the bridging group X in **1** need not only be methyl, but other groups such as Ph or OMe could also give rise to rearranged products *via* ions analogous to **1**.[4] (A related 1,2-methyl shift in $[(^tBu_2MeSi)_3Si]^+$ has been reported.[6]) Müller and co-workers have characterised a three-centre Si–H–Si bridged species[7] and a three-centre Si–Ph–Si bridged species (cation **2**) in solution,[8] while Sekiguchi *et al.* have characterised Si–X–Si (X = Cl or Br) bonding by X-ray crystallography.[9]

The synthesis of a cation analogous to **1** in the presence of a poorly coordinating anion was attempted in the hope that the cation could be fully characterised. Thus, reactions between $(Me_3Si)_3CSiMePhH$ and $Ph_3CB(C_6F_5)_4$ in $C_6D_5CD_3$ or $C_6D_5CD_3$/PhCl were monitored by ^{1}H NMR spectroscopy (Scheme 1). This showed slow loss of the Si–H quartet at 4.77 ppm and the growth of a signal due to $Ph_3C\underline{H}$ at 5.33 ppm as the hydride abstraction proceeded (all NMR data are given for $C_6D_5CD_3$/PhCl solutions). The Si–Me region of the spectrum showed loss of the SiMePhH doublet at 0.48 ppm, and after 24 h at room temperature there were only two singlets in this region, one at 0.24 ppm attributable to $(Me_3Si)_4C$ (which was isolated and compared with an authentic sample), and a second signal of *ca.* five times greater intensity at 0.06 ppm. This is inconsistent with either $[(Me_3Si)_3CSiMePh]^+$ or **4a/4b**, but instead suggests that methyl group site exchange is occurring and that the signal at 0.06 ppm is attributable to a rapidly equilibrating mixture of ions of type **1**, **4a/4b** and $[(Me_3Si)_3CSiMePh]^+$. Attempts to record low temperature ^{1}H NMR spectra were hampered by the formation of precipitates. The ^{29}Si NMR spectrum of the reaction mixture at room temperature showed many signals: several sharp peaks between *ca.* −1 and 10 ppm, a broad signal between *ca.* 17 and 22 ppm and a sharp one at 61 ppm. These signals coalesce on raising the temperature, and a single sharp resonance at 17.8 ppm is observed at 60 °C (see ESI for pictures of the spectra†). This is similar in chemical shift to that found for **2** (26.9 ppm), and shows similar changes in shift from the precursor $(Me_3Si)_3CSiMePhH$ (in $CDCl_3$) to the equilibrating cationic species: $\Delta\delta$ ^{29}Si (Si-aryl) of 29.3 and $\Delta\delta$ ^{29}Si ($SiMe_3/SiMe_2$) of 18.9, compared with that of 31.0 for $\Delta\delta$ ^{29}Si (Si-aryl) and 41.4 for $\Delta\delta$ ^{29}Si (Si–H) for **2** and its



Scheme 1 Synthesis of the cation **4a/4b**.

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precursor $HMe_2Si(CH_2)_3SiMe_2Ph$.[8] This significant downfield shift is indicative of a build up of positive charge at silicon.

The ^{13}C NMR spectrum after 24 hours reaction showed an absence of signals for $(Me_3Si)_3CSiMePhH$ and the formation of signals characteristic of Ph_3CH (*e.g.* 57.0 ppm due to the methine $Ph_3C\underline{H}$). The upfield region of the spectrum showed an intense sharp signal due to Si–Me groups at 5.2 ppm and a small quaternary signal at 8.5 ppm. The aryl region of the spectrum was complicated but a DEPT-135 experiment revealed at least thirteen new C–H signals ranging from 125.0 to 140.0 ppm, presumably due to the presence of several new Si–Ph environments. There were also at least five new quaternary signals at 144.0, 143.9, 136.8, 124.8 and 124.5 ppm. These resonances are tentatively assigned to the presence of five new Si–Ph environments that would require fifteen C–H signals (some C–H signals could easily be overlapped by the other signals present) and five quaternaries. None of these signals is consistent with the values found for the aryl ring in **2**, which have C_{ipso} and C_{ortho} values of 102.4 and 162.9 ppm respectively.[8] This suggests that either the bridged structure has little benzenium ion character, **4a** (see below), or that it has no significant concentration at room temperature in solution. Equilibrating structures such as $[(Me_3Si)_3CSiMePh]^+$ or $[(Me_3Si)_2(PhMe_2Si)CSiMe_2]^+$ (which are both inconsistent with the lack of very downfield ^{29}Si chemical shifts), in which the Ph groups are terminal, and a bridged isomer of **4a/4b**, with a methyl group in the bridge and a terminal Ph group, are also possible structures in an equilibrium. Non-planar four-membered ring structures such as **4a/4b** may also lead to more inequivalence of NMR signals than might be expected. Additional Ph resonances are presumably attributable to arylsilanes formed in reactions leading to the production of $(Me_3Si)_4C$, but it is not yet clear what these are. The simple Si–Me but complicated Si–Ph regions of the ^{13}C NMR spectrum are presumably a result of the different rates at which Me and Ph exchange occurs, due to their different steric requirements. (A more detailed variable temperature NMR study is being carried out.)

The formation of $(Me_3Si)_4C$ as a by-product from the reaction in Scheme 1 is surprising, and is indicative of intermolecular Me and Ph exchange processes occurring as well as the intramolecular migrations. The amount of $(Me_3Si)_4C$ formed increases to a maximum of about 20% of the total integrated Me signal. Related intermolecular exchanges are also observed in the reaction of $(Me_3Si)_3CSiMe_2H$ with Ph_3C^+, which, if treated with Et_3SiH, gives rise to products containing both Me and Et groups such as Et_2Me_2Si and $(Me_3Si)_2C(SiMe_2Et)_2$.[10] Intermolecular Si-to-Si methyl group exchange has also been found to occur in the gas phase,[11] and cations Me_3M^+ (where M = Ge, Sn or Pb) have recently been shown to interact with the methyl groups in $CB_{11}Me_{12}^-$.[12] Addition of dry pentane to the toluene reaction solution under an inert atmosphere caused the slow growth of small, yellow-orange crystals that were suitable for X-ray diffraction studies.§ The crystalline material was found to be the $[B(C_6F_5)_4]^-$ salt of the cation **4a/4b** shown in Scheme 1, analogous in structure to the bridged cation **1**. Preliminary reports on the preparation of **1** have already appeared.[13]

The aryl group in **4a/4b** forms an almost symmetrical bridge, C(1)–Si(1) and C(1)–Si(2) distances being 2.104(8) and 2.021(7) Å, respectively (Fig. 1). These bonds are longer than normally observed for terminal Si–Ph bonds, *cf.* 1.903(7) Å in $(Me_3Si)_3CSiMe_2Ph$,[14] while the mean $SiMe_2$–C(0) bond length of 1.860(5) Å is shorter than this and the mean $SiMe_3$–C(0) distance of 1.918(5) Å is slightly longer. The Si–CH_3 bond lengths range from 1.831(5) to 1.856(6) Å for the $SiMe_2$ groups and 1.857(6) to 1.890(5) for the $SiMe_3$ groups. The four-membered ring is folded about the Si(1)···Si(2) vector with a dihedral angle of 13.5° (Fig. 2), similar to the 14° fold along the Al···Al vector in one of the two independent molecules (the other is planar) in the crystal of $[AlMe_2Ph]_2$.[15] The Si(1)···Si(2) distance across the ring is 2.617(2) Å, close to the value of 2.603 Å calculated for the less hindered ring in **3**, which is also calculated to have slightly shorter Si–Ph bonds of 2.025 Å and a much larger dihedral angle of 28.9°.[16]

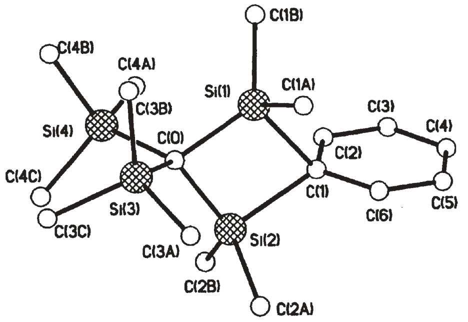

Fig. 1 Molecular structure of the cation **4a/4b**.

Calculations on cation **2**, indicate an Si–C_{ipso} distance of 2.049 Å,[8] *i.e.* intermediate between the values found for **4a/4b**. Calculations on **2** also show the C_{ortho}–C_{ipso}–C_{ortho} angle to be 115.5° and the bond lengths within the carbocycle to have the trend long C_{ipso}–C_{ortho}, short C_{ortho}–C_{meta} and long C_{meta}–C_{para} (*ca.* 1.440, 1.386 and 1.402 Å, respectively), attributable to a cyclohexadienyl resonance structure.[8] This trend in bond lengths is found in several other arenium ions[17–19] and in **3**,[16] but not in the triethylsilyltoluenium ion[20] or in **4a/4b**, in which the C_{ipso}–C_{ortho} (1.408(9), 1.400(8) Å), C_{ortho}–C_{meta} (1.372(9), 1.363(9) Å) and C_{meta}–C_{para} (1.358(9), 1.365(9) Å) lengths show small differences of very low significance and are closely similar to those found in the neutral species $(Me_3Si)_3CSiMe_2Ph$[14] (corresponding distances:

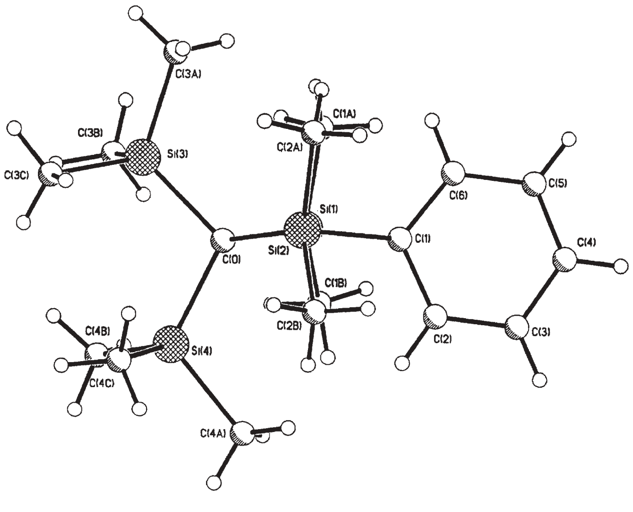

Fig. 2 Structure of **4a/4b** viewed along the Si···Si vector.

1.39(1), 1.40(1); 1.37(1), 1.37(1); 1.33(2), 1.38(1) Å) and $[AlMe_2Ph]_2$[15] (corresponding distances: 1.415(9), 1.401(9); 1.398(10), 1.418(12); 1.370(12), 1.391(13) Å for one of the Ph groups). Thus, the aryl group has little **4a** character but is better represented by **4b**, similar to a σ-bonded Si–Ph group.

The degree to which an electrophile has a σ or π interaction with an arene ring has been rationalised in terms of the angles α and β subtended by each of the two substituents at C_{ipso} and the plane of the arene ring; a σ complex such as pentamethylbenzenium having α and β values each of 50° and arene/nitrosonium π complexes having values $\alpha \geqslant 90^\circ$ and $\beta = 0^\circ$.[19,21] The triethylsilyltoluenium ion[20] has a value $\alpha = 76^\circ$ for the Et_3Si substituent, and calculations[22] on the interactions of MeH_2Si^+ and Me_2HSi^+ with benzene also show the interaction to be predominantly of π character. In cation **4a/4b**, the constraining of the two silyl substituents within a four-membered ring means that the sum of the angles $\alpha + \beta$ (*i.e.* Si(2)–C(1)–Si(1)) is only 78.5(2)°, *i.e.* significantly smaller than other σ arenium ions, and perhaps the reason for the more aromatic nature of the aryl ring. The constraining of the two silyl substituents in a ring is reminiscent of the well known spirocyclopropyl phenonium ions originally proposed by Cram[23] and calculated to have a long–short–long series of bond lengths in the six-membered ring.[24] The spirocyclobutyl benzenium ion is structurally more similar to **4a** than the spirocyclopropyl analogues but it is much less well studied.[25,26]

Calculations[27] at the B3LYP/6-31G(d) level on **4a/4b** provide a NICS(1) value of −9.1 ppm (*cf.* −11.3 ppm for benzene), *i.e.* consistent with an aromatic rather than a cyclohexadienyl ring. The Wiberg bond index for the Si–C_{ipso} bond is 0.52 and the positive charge is predominantly in the C_2Si_2 ring rather than the aryl ring, again consistent with structure **4b**. It should also be noted that although $C_6H_7^+$ has a cyclohexadienyl structure, calculations show that the positive charge is delocalised onto the H atoms and not the *para* carbon atom.[19] The nature of the charge distribution in **4a/4b** is being further investigated.

In conclusion, although the solid state structure of cation **4a/4b** appears to resemble a bis-silylated benzenium ion **4a**, the C_6H_5 ring seems little perturbed by its unusual environment, and 1,3-Si-Si-Ph bridge **4b** is a better description of the structure. Thus, cation **4b** can be seen as the first structurally characterised Ph-bridged silicon compound, providing a fascinating example of a structure not fitting with the conventional view of benzenium ions but being closer to that for neutral main group compounds containing a bridging Ph group. Cation **4b** crystallizes from a solution containing a complicated mixture of equilibrating species, the nature of which are under further study.

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Notes and references

§ All manipulations were carried out under an atmosphere of dry nitrogen. An NMR tube was charged with $(Me_3Si)_3CSiMePhH$[28] (100 mg, 0.283 mmol) and $Ph_3CB(C_6F_5)_4$ (261 mg, 0.283 mmol), and dry d_8-toluene (0.5 ml) then added. The progress of the reaction was monitored by ^1H NMR spectroscopy and showed the disappearance of the starting material after 24 h at room temperature. Dry pentane was added to the solution, and this caused small yellow-orange crystals to form. The yield (*ca.* 25%) was difficult to determine exactly as the crystals were coated with a heavy orange oil of the sort often found when working with $Ph_3CB(C_6F_5)_4$ in toluene. The same problem prevented elemental analysis from being carried out.

Crystal data: $C_{41}H_{35}BF_{20}Si_4$, M = 1030.86, triclinic, space group $P\bar{1}$, a = 12.4299(13), b = 12.7886(10), c = 15.7132(10) Å, α = 69.726(5), β = 69.678(7), γ = 83.481(7)°, V = 2197.1(3) Å^3, Z = 2, D_c = 1.558 g cm^{-3}, absorption coefficient = 0.252 mm^{-1}. Data collection 1.84 to 25.0° performed on a Bruker P4 four-circle diffractometer at 223(2) K (Mo-Kα = 0.71073 Å). The structure was refined by full-matrix least-squares on F^2 using 7627 independent reflections and 605 parameters, and converged to $R1 = 0.0584$ [$I > 2\sigma(I)$] and $wR2 = 0.1492$. CCDC 284611. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b513203g

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