

REPORTS

reaction in S_1 (model A) or by a multi-stepwise recovery of the bR_{570} ground state within S_0 (model B). Indications for model A were given from the observation of a biphasic decay of the excited electronic state with time constants of 0.24 and 0.75 ps (5). These authors suggested a fast, reactive path leading to the isomerized state (J) and a slower, nonreactive path leading back to the educt. This model cannot be ruled out by the IR transients reported here, which rise within 0.5 ps or less; however, it is not supported by our own optical experiments (26).

The more likely model is model B, which could be realized by vibrational relaxation (for example, vibrational cooling) processes in S_0 that accompany the full recovery to the vibrational ground state of bR_{570} within 1.0 to 1.7 ps and the transformation from J to K in 3 ps. The J-K transition might take longer than the bR_{570} recovery because substantial conformational changes, including parts of the protein, are involved in the former. Vibrational cooling would be indicated by the decay of small shoulders on the low-energy side of the vibrational bands as the vibrational ground state recovers, an effect which is easily obscured by the 13-cis product bands. However, this view is also supported by time-resolved IR experiments on the isomerization reaction of protonated SB retinal in solution (29) and the observation of anti-Stokes RR bands of the chromophore in bR (20, 30).

A small negative shoulder at about 1660 cm^{-1} (Fig. 2, A to C) appears within 1 ps or less (the apparent rise time is again limited by the dephasing time). Because no chromophore vibrational band is expected in this spectral region, it is possibly a contribution of the protein amide I band or a result of the bending vibration of a protein-bound water molecule. The molecular structure of bR as determined from x-ray diffraction (31) indicates a water molecule close to the SB as part of the hydrogen bond network in the chromophore binding pocket. Photoexcitation, that is, an electric field jump, or isomerization of the chromophore, might affect the absorption cross section, orientation, or even location of this water molecule or of a protein constituent and may lead to the observed bleach signal. In this case, the observed signal would indicate a fast response not of the chromophore but of the environment, that is, the cofactor binding pocket.

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- Valuable discussions with M. Sheves and M. Ottolenghi are greatly acknowledged. We thank D. Stehlik for support, M. Heyn and I. Wallat for generous bR sample supply, and U. Alexiev for characterizing the ms kinetics of the bR films. Supported by Deutsche Forschungsgemeinschaft Sfb 450.

22 March 2002; accepted 5 June 2002

Crystallographic Evidence for a Free Silylium Ion

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Evidence for a three-coordinate silyl cation is provided by the crystal structure of $[(\text{Mes})_3\text{Si}][\text{H-CB}_{11}\text{Me}_5\text{Br}_6] \cdot \text{C}_6\text{H}_6$ (where Mes is 2,4,6-trimethylphenyl). Free $(\text{Mes})_3\text{Si}^+$ cations are well separated from the carborane anions and benzene solvate molecules. *Ortho*-methyl groups of the mesityl substituents shield the silicon atom from the close approach of nucleophiles, while remaining innocent as significant ligands themselves. The silicon center is three-coordinate and planar. The downfield ^{29}Si nuclear magnetic resonance chemical shift in the solid state (226.7 parts per million) is almost identical to that in benzene solution and in "gas phase" calculations, indicating that three-coordination can be preserved in all phases.

The silylium ion problem has exercised the minds of many (1–5). The essential debate concerns the existence of three-coordinate silicon cations, R_3Si^+ (where R is an alkyl or aryl group), unfettered by interactions with solvent, counterion, or neighboring groups. The fundamental question concerns how far the analogy to carbocations, R_3C^+ , known now for more than 100 years (6), extends down group 14 of the periodic table.

Despite ready mass spectrometric detection in the gas phase, there has been no convincing evidence for the existence of free R_3Si^+ ions in condensed phases when R is an alkyl group. The closest approach is found in

"ion-like" species, $\text{R}_3\text{Si}^{\delta+}\text{Y}^{\delta-}$, where R is *iso*-propyl and Y is a very weakly coordinating anion, such as the perfluorinated tetraphenylborate ion or a carborane (7). These species behave like silylium ions toward arenes (8) and in the production of superacidity (9), but they are not free silylium ions.

However, when R is a bulky aryl group, there is growing spectroscopic evidence and theoretical support for truly free, three-coordinate silyl cations. Species formulated as $[\text{Ar}_3\text{Si}][\text{Y}]$ have been reported for Ar = mesityl or duryl and Y = $\text{B}(\text{C}_6\text{F}_5)_4^-$ (10, 11). Silyl cation character is indicated by downfield shifted resonances in the ^{29}Si nuclear magnetic resonance (NMR) spectrum near 220 parts per million (ppm). The NMR shifts have been reproduced computationally in the calculated structures of these triarylsilylium ions (12, 13). An arylated silatropilium ion (14) and a *cyclo*-tetrasilylium ion with bulky substituents (15) provide convincing evidence for three-coordination in other sili-

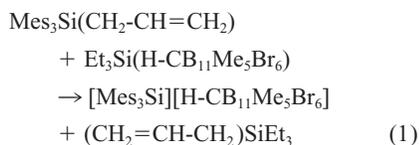
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con cations. None with a Si-C bond has been characterized by x-ray crystallography.

The definitive structural characterization of a triarylsilylium ion by x-ray crystallography has been hampered by the tendency of $B(C_6F_5)_4^-$ salts to form oils or liquid clathrates rather than crystallize. Fluorocarbon and hydrocarbon entities are not particularly compatible. In addition, the B-C₆F₅ bond in the anion is prone to electrophilic cleavage. These problems are overcome by carborane anions, whose properties can be optimized for applications with reactive cations (16). In particular, the icosahedral carborane anion, H-CB₁₁Me₅Br₆⁻, has 7,8,9,10,11,12-hexahalo substituents for inertness and 2,3,4,5,6-pentamethyl substituents for good solubility of its salts (17).

The synthesis of a triarylsilylium ion exploits remote attack of a strong electrophile on a triarylsilyl silane (10). Stoichiometric treatment of trimesitylsilyl silane (10.0 mg) with Et₃Si(H-CB₁₁Me₅Br₆) (17) (18.8 mg) in dry benzene (3 ml) gives yellow solutions of [Mes₃Si][H-CB₁₁Me₅Br₆].



Yellow crystals of the benzene solvate [Mes₃Si][H-CB₁₁Me₅Br₆] \cdot C₆H₆ suitable for x-ray crystallography were grown in 1 day at 5°C by vapor diffusion with hexanes. Higher temperatures led to cleavage of Si-Ar bonds from which crystals of protonated arenes (18) can be isolated.

The crystal structure was solved to high accuracy (R = 4.0%) by standard methods (19). It reveals well-separated cations, anions, and solvate molecules. No atoms of the carborane or benzene approach the Si atom closer than 6 Å (Fig. 1). The closest approaches to the Mes₃Si⁺ cation arise from methyl-methyl group nonbonded interactions rather than from the more electron rich bromine atoms of the carborane anion or the π system of benzene. This finding indicates that the crystal structure is primarily determined by packing efficiency considerations rather

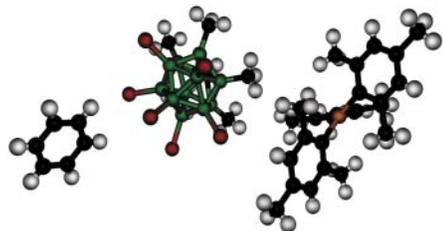


Fig. 1. Perspective view of the asymmetric unit in the crystal structure of [Mes₃Si][H-CB₁₁Me₅Br₆] \cdot C₆H₆ (green, B; red, Br; black, C; gray, H; brown, Si).

than specific electrostatic effects. The positive charge at the Si center is highly screened, and the negative charge on the carborane cluster is highly delocalized. The crystal packing can be described as alternating columns of cations and anions, with benzene filling space primarily in the anion columns.

As shown (Fig. 2), the silicon atom has the trigonal planar coordination geometry expected of an sp² silylium ion center. Planarity is indicated by summation of the three C-Si-C angles (120.5°, 121.7°, and 117.7°) to 359.9°, within experimental error (0.2°) of 360°. As expected, the Si-C bonds [1.808(5), 1.820(5), and 1.823(5) Å, where values in parentheses represent the estimated SD; average, 1.817 Å] are significantly shorter than those observed in the neutral sp³ trimesitylsilyl silane precursor (avg., 1.91 Å) (11).

A critical question regarding the truly three-coordinate nature of the Mes₃Si⁺ cation is whether the substituent *ortho*-methyl groups (*o*-Me) interact with the silicon center. The potential for Me to act as a ligand has been referred to as “internal solvation” or an “agostic” C-H interaction. The closest approach of an *o*-Me C atom to Si is 3.12 Å and that for the calculated position of an *o*-Me H atom is 2.73 Å. To be noninteracting, these distances should be greater than the sum of their respective van der Waals radii. Standard values of C = 1.6 Å, H = 1.2 Å, and Si = 2.1 Å and simple arithmetic suggests this condition is not met. However, van der Waals radii are situation-dependent and, therefore, are only a rough guide to nonbonded contacts. The van der Waals radius of cationic Si is unknown, but the positive charge should shrink it substantially from that of neutral Si. An alternative criterion is angular distortion of the Me groups. The C_{ipso}-C-*o*-methyl bond angles (range 120.8° to 123.1°; avg., 122.2°) differ by only 1° from those in the neutral sp³ trimesitylsilyl precursor (avg., 123.2°). This trivial difference suggests that the *o*-Me groups are neither pushed nor pulled significantly by Si. We conclude that the Mes₃Si⁺ is free and three-coordinate. The rigid *o*-Me groups on the Mes substituents are seen to have played a key role in blocking entry of nucleophiles to the Si center, while remaining essentially innocent as electron donors themselves.

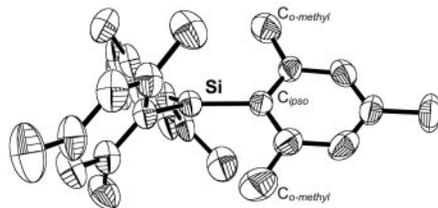


Fig. 2. Perspective drawing of the Mes₃Si⁺ cation. Thermal ellipsoids are shown at the 50% probability level.

As shown in Fig. 2, the Mes groups have a propeller-like arrangement around the Si center with twist angles $\tau = 51.3^\circ, 54.5^\circ,$ and 41.9° relative to the coordinate plane. The average value (49.2°) is very close to those computed for an isolated Mes₃Si⁺ ion, 47.3° to 49° depending on the calculation (12, 13). This result suggests that the conformation is intrinsic, a balance struck between minimizing nonbonded repulsions of the *o*-Me groups at high twist angles and maximizing conjugative 2p(Si) \rightarrow 3p(Si) π stabilization at low twist angles.

Further comparisons with theory are made in Fig. 3. The calculated bond angles agree extremely well with experiment. The calculated bond lengths involving the π system are mostly longer than experiment, suggesting that theory slightly underestimates conjugative stabilization. However, the differences are less than 1.2%. Theory has performed well in part because the large cation with its buried charge is probably insensitive to the surrounding environment.

The ²⁹Si NMR chemical shift of the Mes₃Si⁺ ion provides an excellent means to assess structural consistency between phases. In benzene solution with B(C₆F₅)₄⁻ as counterion, the value is 225.5 ppm (10). It is unperturbed by the addition of more basic bulky arenes such as toluene or xylene (20). The calculated (“gas phase”) value lies in the range 226 to 230 ppm, depending on the method used (12, 13). The solid state value obtained via magic angle spinning methods for the present species is 226.7 ppm. Such close congruence provides a powerful argument that the structure of the Mes₃Si⁺ ion is

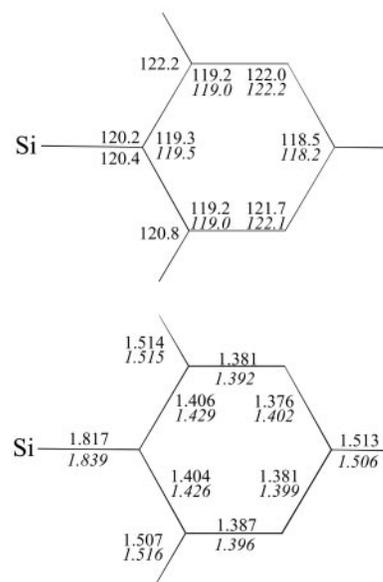


Fig. 3. Comparison of experimental and calculated (italics) average bond angles (in degrees, top) and bond lengths (in angstroms, bottom) in the Mes₃Si⁺ cation.

the same in all phases. If the twist angles were greater, significantly further downfield shifted values would be expected, up to 373.5 ppm for $\tau = 90^\circ$ (12). If electron donors such as solvent, anion, or the nearby Me groups closely approached the Si center, less downfield-shifted values would be expected. Similar shifts have been observed in related tin chemistry where the downfield ^{119}Sn chemical shift of the Bu_3Sn^+ cation is attenuated by axial interactions from Me groups of the counterion (21).

Additionally, the full ^{29}Si chemical shielding tensor can be determined in the solid state. The best fit to the slow magic-angle spinning spectrum (Fig. 4) gives 226.7 ppm for the isotropic shift, 185.5 ppm for the anisotropy (δ), and 0 for the asymmetry parameter (η). An axially symmetric tensor ($\eta = 0$) is required in the presence of a threefold rotational axis. On the basis of molecular symmetry, the equivalent δ_{xx} and δ_{yy} tensor components (319.5 ppm) lie within the coordination plane, whereas the δ_{zz} component (41.2 ppm) is aligned with the local C_3 axis. This distinctively large anisotropy under axial symmetry provides complementary structural characterization for the planar sp^2 -hybridized silylium center. Related large anisotropies are seen in disilenes (22).

These results bring the differences between carbon and silicon into sharp focus (3). Because of its small size and intermediate value of electronegativity, carbon readily sustains coordinative unsaturation. Positive charge is readily stabilized by π conjugative (and hyperconjugative) effects. Silicon and the remainder of the group 14 elements are significantly larger in size and considerably more electropositive, so unsaturation is less easily stabilized by conjugative effects. Charge is less easily delocalized, and longer bonds to substituents invite access by nucleo-

philes so higher coordination numbers prevail. Substituent bonds are more polar and thus more easily cleaved. These features have conspired over the years to create the "silylium ion problem" that now appears to be solved. The situation with gerymlium and stannylum ions is less resolved (20, 21, 23).

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- Supported by the National Science Foundation CHE 0095206 (to C.A.R.), CHE 0091162 (to J.B.L.), CHE-9982362 and ACS PRF Grant 35320-G6 (to L.J.M.), and Department of Education Graduate Fellowship (GAANN) P200A000208 (to D.W.E.).

2 May 2002; accepted 19 June 2002

Laminar Growth of Ultrathin Metal Films on Metal Oxides: Co on Hydroxylated $\alpha\text{-Al}_2\text{O}_3(0001)$

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Metals deposited in vacuum on metal oxides such as alumina normally grow as three-dimensional clusters because of weak adatom-substrate interactions. This tendency hinders our ability to form interfaces of ultrathin, laminar metal films on oxides for use in microelectronics and other technologies where nanostructural control is desired. We present experimental and theoretical results showing that room temperature Co deposition on fully hydroxylated clean sapphire ($\alpha\text{-Al}_2\text{O}_3$) produces a surface chemical reaction that leads to laminar growth, despite a large mismatch in lattice constants. This process should be applicable to a wide range of metals and metal oxides.

Durable interfaces between disparate materials, such as metals and metal oxides (1), are critical for nanotechnology [e.g., for the manufacture of microelectronics (2), seals, and sensors]. We lack the ability to form multilayer structures of metals and oxides in which the interface is strong and ultrathin layers grow in a laminar fashion. In contrast, nonlaminar island growth is often seen, because adatom-adatom interactions are stronger than adatom-substrate interactions. In this case, the surface-free energy change for film growth $[(\Delta\gamma) = (\gamma_{\text{film}} + \gamma_{\text{int}} - \gamma_{\text{sub}})]$ is greater than zero because the surface free energy of the film (γ_{film}) may be larger than

that of the substrate (γ_{sub}), and the interface free energy (γ_{int}) is small because of weak adsorbate-substrate interactions. In addition, metal/metal-oxide interfaces are of critical importance for understanding heterogeneous catalysis (3), corrosion, and adhesion.

Co on alumina is especially important because of a proposed use in magnetoresistive random access memory (2). A thin (~ 1 nm) alumina layer is sandwiched between two magnetic layers to form a tunnel junction. High-quality alumina films can be produced by plasma oxidation of Al films (2). However, it is problematic to grow a thin magnetic Co layer on top of the alumina film in a

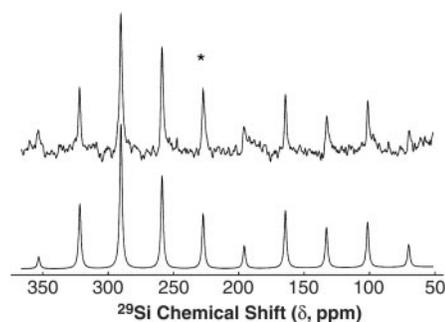


Fig. 4. The ^1H -decoupled ^{29}Si CPMAS (condensed phase magic angle spinning) NMR spectrum of $[\text{Mes}_3\text{Si}][\text{H-CB}_{11}\text{Me}_5\text{Br}_6]\cdot\text{C}_6\text{H}_6$ at a spinning rate of 2.5 kHz (top). The nonlinear least-squares fit of the sideband manifold (bottom) using the method of (24) gives an axially symmetric chemical shift tensor [$\sigma_{\text{iso}} = 226.7$ ppm (*); $\delta = 185.5$ ppm; $\eta = 0$].