Al(ORF)$_3$ ($R^F = C(CF_3)_3$) activated silica: a well-defined weakly coordinating surface anion†

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Weakly Coordinating Anions (WCAs) containing electron deficient delocalized anionic fragments that are reasonably inert allow for the isolation of strong electrophiles. Perfluorinated borates, perfluorinated aluminum alkoxides, and halogenated carborane anions are a few families of WCAs that are commonly used in synthesis. Application of similar design strategies to oxide surfaces is challenging. This paper describes the reaction of Al(ORF)$_3$*PhF ($R^F = C(CF_3)_3$) with silica partially dehydroxylated at 700 °C (SiO$_2$-700) to form the bridging silanol $^=\text{Si–O–H}$–Al(ORF)$_3$ (1). DFT calculations using small clusters to model 1 show that the gas phase acidity (GPA) of the bridging silanol is 43.2 kcal mol$^{-1}$ lower than the GPA of H$_2$SO$_4$, but higher than the strongest carborane acids, suggesting that deprotonated 1 would be a WCA.

Reactions of 1 with NOct$_3$ show that 1 forms weaker ion-pairs than classical WCAs, but stronger ion-pairs than carborane or borate anions. Though 1 forms stronger ion-pairs than these state-of-the-art WCAs, 1 reacts with alkylsilanes to form silylium type surface species. To the best of our knowledge, this is the first example of a silylium supported on derivatized silica.

**Introduction**

The development of inert Weakly Coordinating Anions (WCAs) was critical to isolate very reactive electrophilic species.† Studies of superacid media resulted in the first generation of WCAs (CF$_3$SO$_3^-$, PF$_6^-$, SbF$_6^-$, etc., Fig. 1).‡ The first generation WCAs continue to find broad applications in the synthetic community, but these anions are too reactive or coordinating to stabilize highly reactive cations. For example, organometallic Zr(ν) cations, key 14-electron intermediates in the synthesis of polyolefins, are incompatible with first generation WCAs.¶ These anions are also not sufficiently weakly coordinating to form R$_3$Si$^+$ cations.

Fluorinated borates (e.g. $^\text{5B(C}_6\text{F}_5\text{)}$$_3$, $^\text{5B(3,5-(CF}_3\text{)}$_2$C_6\text{H}_3\text{)}$$_3$),§ aluminates (e.g. $^\text{Al[OC(CF}_3\text{)}$_3$]_3$),¶ or carborane anions (e.g. $^\text{CHB}_1\text{H}_x\text{X}_y$, $^\text{CHB}_1\text{X}_z\text{X}_y; X =$ halide),¶ shown in Fig. 1, stabilize organometallic Zr(ν) cations or R$_3$Si$^+$. The anions are designed to delocalize charge throughout the structure of the WCA, which results in low basicity. The conjugate acids of the WCAs shown in Fig. 1, when isolable, are the strongest known Bronsted acids.¶ The strong C–F or B–X bonds in these WCAs also provide some degree of chemical inertness, which is important in reactions involving the strong electrophiles mentioned above.

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† Electronic supplementary information (ESI) available. See DOI: 10.1039/c9sc05904k

**Fig. 1.** Structures of first generation WCAs (a) and bulky inert WCAs (b); very strong electrophiles that are too reactive to form with first generation WCAs (c).
Direct translation of these concepts to well-defined heterogeneous catalysts is more challenging. Well-defined heterogeneous catalysts are desirable because the molecular structure of a catalytically active site can be determined using spectroscopic methods,9–11 which provides opportunities to optimize the properties of these catalysts based on the structure of the active site. The largest class of well-defined heterogeneous catalysts are supported on SiO2 partially dehydroxylated at 700 °C. Well-defined sites supported on SiO2 generally do not form ion-pairs but rather 31Si Cross Polarization Magic Angle Spinning (CPMAS) NMR spectrum of alkylsilane functionalized silica (31Si–SiMe3, Fig. 2a) contains a signal at 14 ppm for the alkylsilane fragment, which is inconsistent with formation of a Me3Si+ species on the silica surface.12–15 Similarly, Cp*ZrMe2 (Cp* = pentamethyleclopentadienyl) reacts with partially dehydroxylated SiO2 to form 31Si–Zr(Cp*)Me2 (Fig. 2a),16 which is inactive in the polymerization of ethylene. However, 31Si–Zr(Cp*)Me2 does react with B(C6F5)3 to form electrophilic ion-pairs that are active in the polymerization of ethylene.17 Silica surfaces can also form strong ion-pairs with between surface siloxane anions and tetraethylphosphonium groups.18,19

Partially dehydroxylated Al2O3 contains a very small quantity of tri-coordinate Al Lewis-acid sites20 that react with organometallic complexes to form electrophilic ion-pairs, Fig. 2b.21,22 However, the surface coverage of the –OH sites is much higher than the surface coverage of Lewis sites, resulting in low active site loadings in these well-defined catalysts.23

The trends in WCAs described above suggest that oxides containing more acidic –OH sites may be more weakly coordinating. Zeolites contain –OH sites that are more acidic than –OH sites on SiO2, and can support organometallic species.24 Studies of well-defined organometallics are limited to small molecules because SiO2/Al2O3 zeolite materials have small pore sizes. Oxides treated with sulfuric acid, sulfated oxides, were claimed to contain superacid Brønsted acid sites.25 This relates sulfated oxides to first generation WCAs, and several studies showed that sulfated oxides form electrophilic ion pairs with organometallics (Fig. 2c).26–31 However, titrations of the –OH sites on sulfated oxides with phosphines are inconsistent with superacid –OH sites.32 This data is consistent with DFT calculations showing that sulfated oxides are weaker acids than zeolites.33 Detailed studies showed that sulfated oxides also contain significant amounts of oxidative pyrosulfate sites, which can result in undesirable side reactions with organometallic substrates.34

The reaction of a strong Lewis acid and a 31Si–OH on partially dehydroxylated silica should form a strong Brønsted acid site (Fig. 3a).35 Deprotonation of the strong Brønsted acid should result in a weakly coordinating anion that may stabilize electrophilic surface species that would not typically form on SiO2 surfaces, and also translate solution WCA concepts to heterogeneous supports. Contacting dehydroxylated silica with AlCl3 forms strong Brønsted acid sites, but also results in various side reactions leading to strong Lewis sites on the silica surface,36 which is common in this class of functionalized oxides.37 Redox inactive strong Lewis acids, such as B(C6F5)3, are not sufficiently Lewis acidic to form stable bridging silanols with silica (Fig. 3b).38 However, B(C6F5)3 reacts with silica and aniline bases to form ion-pairs that are capable of activating organometallic species,39,40 or with exogenous H2O to form grafted species on the SiO2 surface.41 This paper describes the reaction of Al(OR)3)*PhF (R = C(CF3)3)42 with silica partially dehydroxylated at 700 °C (SiO2, 700°) to generate 31Si–OH…Al(OR)3 (1, Fig. 3c). Calculated gas phase acidity (GPA) of 1 shows that the activated silanols are very strong Brønsted acids. Reactions of 1 with silane reagents result in the formation of [R3Si][31Si–O…Al(OR)3], a rare example of a silylum supported on SiO2.

## Results and discussion

### Reaction of Al(OR)3)*PhF with partially dehydroxylated SiO2

A perfluoroheptane slurry of SiO2-700 (0.26 mmol OH g–1) reacts with Al(OR)3)*PhF to form 31Si–OH…Al(OR)3 (1, Fig. 4a). ICP-

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OES analysis shows that 0.24 mmol g\(^{-1}\) is present in 1, indicating that most of the silanols in SiO\(_2\)-700 are coordinated to Al(OR\(_3\))\(_3\). The FTIR spectrum of 1, shown in Fig. 4b, contains a new red-shifted \(\nu_{\text{OH}}\) at 3542 cm\(^{-1}\) that is typical of bridging silanols in silica-alumina materials. This spectrum also contains an \(\nu_{\text{OH}}\) corresponding to silanols that do not form adducts with Al(OR\(_3\))\(_3\). Weak sp\(^2\)-CH and \(\text{sp}^3\)-CH are also present, suggesting that some fluorobenzene remains adsorbed to 1.

Consistent with this observation, \(^1\text{H}\){\(^{27}\text{Al}\)} NMR measurements of 1 suspended in CD\(_3\)CN show that 0.045 \(\pm\) 0.004 mmol g\(^{-1}\) of PhF leaches off the silica surface (Fig. S19†).

The static \(^{27}\text{Al}\) NMR spectrum of 1 contains a typical quadrupolar powder pattern that can be simulated with a single site (Fig. 5a).\(^{41}\) The isotropic chemical shift (\(\delta_{\text{iso}} = 43\) ppm) and large quadrupolar coupling constant (\(C_Q = 14.6\) MHz) is consistent with a highly distorted tetrahedral Al coordination environment. These values are in agreement with those obtained from \(^{27}\text{Al}\) MAS measurements of 1 (Fig. S4†). The \(^1\text{H}\) magic angle spinning (MAS) NMR spectrum of 1 contains signals at 7.1 (adsorbed PhF), 5.0 (\(\equiv\text{Si–OH}–\text{Al(OR}^3\text{)}\)\(_3\)), and 2.3 (\(\equiv\text{Si–OH}\)) ppm (Fig. 5b, top trace). A \(^1\text{H}\) dipolar double-quantum single-quantum (DQ-SQ) spectrum does not show crosspeaks between adsorbed PhF and the bridging silanol (see the ESI, Fig. S5†), suggesting that adsorbed PhF is distant from the acidic silanol in 1. A 2D \(^1\text{H}\)(\(^{27}\text{Al}\)) D-RINEPT spectrum shows that the \(^{27}\text{Al}\) signal in 1 correlates to the acidic silanol (\(\equiv\text{Si–OH}–\text{Al(OR}^3\text{)}\)\(_3\)) signal at 5.0 ppm (Fig. S7†), supporting these assignments.

The \(^1\text{H}\)(\(^{27}\text{Al}\)) Resonance-Echo Saturation-Pulse Double-Resonance (RESPDOR)\(^{44,45}\) NMR experiment allows measurement of the dipolar coupling constant for \(^1\text{H}\) and \(^{27}\text{Al}\) spins. The \(^1\text{H}\)–\(^{27}\text{Al}\) dipolar coupling constant is inversely proportional to the cube of the inter-atomic distance, so only \(^1\text{H}\) and \(^{27}\text{Al}\) spins that are in close spatial proximity (<3 Å) will be affected in this experiment. The \(^1\text{H}\)(\(^{27}\text{Al}\))-RESPDOR difference NMR spectrum of 1 (Fig. 5b, bottom trace) shows a single \(^1\text{H}\) NMR signal that the bridging silanol is close to the aluminum in Al(OR\(_3\))\(_3\), and that the signals at 7.1 ppm (PhF) and 2.3 ppm (\(\equiv\text{Si–OH}\)) are from protons distant from aluminum, as expected. Variation of recoupling times in the \(^1\text{H}\)(\(^{27}\text{Al}\))-RESPDOR pulse sequence, and numerical simulation of the RESPDOR dipolar dephasing curve allows the \(^1\text{H}\)–\(^{27}\text{Al}\) dipolar coupling constant to be determined. These data are given in Fig. 5c, and show that the \(^1\text{H}\)–\(^{27}\text{Al}\) dipolar coupling is \(2.0–2.3\) kHz, which corresponds to Al–OH distances in the range of 2.4–2.5 Å. This distance is in good agreement with structural models predicted by DFT (see below).

DFT studies of small cluster models of 1

1 was modeled using Al(OR\(_3\))\(_3\) and the -SiH\(_3\) capped poly-sesquisiloxane cluster\(^{46}\) at the B3LYP/6-31G(d,p) level of theory.
The cluster 1-DFT is shown in Fig. 6. Al(ORF)₃ in 1-DFT coordinates to the isolated silanol in the cluster and not Si–O–Si bridges. The aluminum fragment in 1-DFT adopts a distorted tetrahedral geometry, and the Al–OH distance in 1-DFT is 1.91 Å. The terminal Si–O distance is 1.70 Å, slightly longer than the average Si–O distances (1.62 Å) in the cluster. These observations are similar to those obtained for alcohol adducts of Al(ORF)₃.²⁷ The predicted Al–OH distance is 2.46 Å, and is in good agreement with an estimated Al–OH distances determined with the ¹H[²⁷Al] RESP DOR experiment.

The calculated IR spectrum of 1-DFT predicts a νOH at 3550 cm⁻¹ (expt. νOH = 3542 cm⁻¹). NMR calculations at the M06L/Al[6–311G(d,p)], 6–31G(d,p) level of theory predict that the acidic proton appears at 5.1 ppm, and that the ²⁷Al CQ is 15.3 MHz. These values agree well with those obtained experimentally for 1, and are similar to those obtained for molecular H[Al(O CF₃)₃] (299.5 ppm, 305.9 MHz). Quantitative measurement of Brønsted acidity on oxides is challenging.³⁹–⁴⁸ Gas-phase acidity (GPA) can be calculated using DFT methods, and is reasonably accurate for small molecules. Table 1 gives the GPA of various mineral acids at BP86/def2-TZVP to calibrate the accuracy of this level of theory. The GPA of HCl is 334.5 kcal mol⁻¹, which is very close to the experimental value (333.6 kcal mol⁻¹). In general, we find good agreement between experimental and calculated values. The calculated deprotonation energy of 1-DFT is 262.7 kcal mol⁻¹. For comparison, small clusters of Si–OH···Al(OME)₃, simplified models for bridging silanols in SiO₂/Al₂O₃, were also calculated at this level of theory and have deprotonation energy of 279–299 kcal mol⁻¹ (see the ESI for details). These values are similar to those calculated for more complex models of zeolites,³¹–³⁴ indicating that 1-DFT is more acidic than bridging silanols in silica/aluminas. However, 1-DFT is clearly a weaker acid than H[Al(O CF₃)₃] (GPA = 262.7 kcal mol⁻¹) or the H[CHB₁₁Cl₁₁] carborane acid (GPA = 239.0 kcal mol⁻¹). The strong Bronsted acidity of 1 suggests that the conjugate base of the bridging silanol may behave as a weakly coordinating anion.

### Table 1: Calculated gas-phase acidity (GPA) in kcal mol⁻¹ at BP86/def2-TZVP level of theory

<table>
<thead>
<tr>
<th>Acid</th>
<th>Expt. GPA (kcal mol⁻¹)</th>
<th>Calc’d GPA (kcal mol⁻¹)</th>
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<tr>
<td>HCl</td>
<td>336.2</td>
<td>334.5</td>
</tr>
<tr>
<td>HBr</td>
<td>318.3</td>
<td>321.6</td>
</tr>
<tr>
<td>HI</td>
<td>309.2</td>
<td>305.9</td>
</tr>
<tr>
<td>H₂SO₄</td>
<td>302.2</td>
<td>305.9</td>
</tr>
<tr>
<td>HSO₃F</td>
<td>299.8</td>
<td>294.6</td>
</tr>
<tr>
<td>Zeolite</td>
<td>—</td>
<td>279–299</td>
</tr>
<tr>
<td>HSO₃CF₃</td>
<td>299.5</td>
<td>293.3</td>
</tr>
<tr>
<td>1-DFT</td>
<td>—</td>
<td>262.7</td>
</tr>
<tr>
<td>H[Al(O CF₃)₃]</td>
<td>—</td>
<td>248.8 (ref. 47)</td>
</tr>
<tr>
<td>H[CHB₁₁Cl₁₁]</td>
<td>—</td>
<td>239.1</td>
</tr>
</tbody>
</table>

The reaction of 1 with 0.95 equiv NOct₃ in C₆H₁₂ at room temperature results in the formation of [Oct₃NH][R₄PO₅]·Al–Oₛᵢ sesión (2, eqn (1)). Solution ¹⁹F NMR spectra of this mixture indicates that desorption of Al(ORF)₃ or decomposition of 1 does not occur under these conditions. 2 was characterized by multinuclear solid-state NMR spectroscopy (see the ESI for details).

### Table 2: ℏOH stretching frequencies for [Oct₃NH][X]

<table>
<thead>
<tr>
<th>Anion</th>
<th>ℏOH (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B(C₆F₅)₄</td>
<td>3223</td>
</tr>
<tr>
<td>[CHB₁₁Cl₁₁]</td>
<td>3163</td>
</tr>
<tr>
<td>[CH₃B₃Cl₃]</td>
<td>3148</td>
</tr>
<tr>
<td>[CH₃B₃Br₃]</td>
<td>3125</td>
</tr>
<tr>
<td>[CH₃B₁₁I₁₁]</td>
<td>3097</td>
</tr>
<tr>
<td>2</td>
<td>3070</td>
</tr>
<tr>
<td>ClO₄</td>
<td>3049</td>
</tr>
<tr>
<td>FSO₄</td>
<td>2953</td>
</tr>
<tr>
<td>CF₃SO₄</td>
<td>2939</td>
</tr>
</tbody>
</table>

²⁷ Values from ref. 54. ⁶ This work.

Formation of ion-pairs with 1

The most common experimental method to assess the ion-pairing on a solid involves adsorption of a probe molecule to the solid and measuring the change in a spectroscopic observable, usually Δν by FTIR or Δδ by NMR spectroscopy. However, solution ¹⁹F[¹H] NMR studies indicate adsorption of common probes (pyridine or triethylphosphine oxide) or heteroatom containing solvents (CD₃CN, Et₂O or CH₂Cl₂) to 1 results in desorption of solvated Al(ORF)₃ from the silica surface.

Reed and co-workers described the properties of [Oct₃NH][X] contact ion pairs in CCl₄ solution.²⁵ The νOH stretch from FTIR measurements provides information about ion-pairing in [Oct₃NH][X]. In a H-bonded contact ion-pair, weaker NH···X interactions will result in higher νOH stretching frequencies. The νOH values for selected [Oct₃NH][X] contact ion pairs in CCl₄ solution are given in Table 2.

The reaction of 1 with 0.95 equiv NOct₃ in C₆H₁₂ at room temperature results in the formation of [Oct₃NH][R₄PO₅]·Al–Oₛᵢ sesión (2, eqn (1)). Solution ¹⁹F NMR spectra of this mixture indicates that desorption of Al(ORF)₃ or decomposition of 1 does not occur under these conditions. 2 was characterized by multinuclear solid-state NMR spectroscopy (see the ESI for details).
The FTIR spectrum of 2 shows $\nu_{\text{NH}}$ at 3070 cm$^{-1}$. This result indicates 2 forms a weaker ion pair than [Oct$_3$NH][SO$_2$CF$_3$] ($\nu_{\text{NH}}$ = 2939 cm$^{-1}$) or [Oct$_3$NH][ClO$_4$] ($\nu_{\text{NH}}$ = 3049 cm$^{-1}$), common first generation WCAs. This experimental data is consistent with the calculated GPA showing that 2 is a very strong Brønsted acid because strong acids form weak ion pairs. However, 2 forms stronger ion-pairs with [Oct$_3$NH] than carborane or [B(C$_6$F$_5$)$_4$] anions.

**Formation of [iPr$_3$Si][RFO$_3$Al–OSi=] (3)**

As mentioned above, R$_3$Si$^+$ ions are not stable in the presence of first generation WCAs due to strong binding to silanol. The characteristics of 1 suggest that R$_3$Si$^+$ species may be stable on this surface. The reaction of allyltetrasiloxanes and 1 results in the formation of [Pr$_3$Si][RFO$_3$Al–OSi=] and small amounts of $\equiv$SiOSi$^3$Pr$_3$ (3, Fig. 7a). The FTIR of 3 lacks the strong $\nu_{\text{OH}}$ for the bridging silanol observed in 1 (Fig. 7b). The $^{29}$Si CPMAS NMR spectrum of 3 contains a minor signal at 4.0 ppm, which is commonly observed in allylsilane functionalized silica, and is consistent with the formation of $\equiv$SiOSi$^3$Pr$_3$. The major signal in the $^{29}$Si CPMAS NMR spectrum is at 70 ppm (Fig. 7c), and is assigned to 3. This chemical shift is typical of R$_3$Si$^+$ fragments interacting with weak ligands. The $^{29}$Si chemical shift of [Pr$_3$Si(SO$_2$)][CH$_4$B$_4$B$_4$Br]$_3$ appears at 85 ppm, and [Et$_3$Si(toluene)]$\equiv$B(C$_6$F$_5$)$_3$ appears at 94 ppm. Solvents that form stronger complexes with R$_3$Si$^+$ fragments appear at lower chemical shift values. For example, the $^{29}$Si chemical shift of [Bu$_3$Si(OH$_3$)][CH$_4$B$_4$B$_4$Br]$_3$ is 46.7 ppm, and [Pr$_3$Si(NCCH$_3$)][CH$_4$B$_4$B$_4$Br]$_3$ appears at 37.2 ppm. These results suggest that the Pr$_3$Si$^+$ fragment in 3 is bound to a weaker ligand than MeCN or H$_2$O, but a stronger ligand than toluene or SO$_2$.

The structure of 3 was studied using DFT methods. The optimized structure of the [Pr$_3$Si][RFO$_3$Al–OSi==] ion pair (3-DFT) at the B3LYP/6-31G(d,p) level of theory is shown in Fig. 8. The calculated $^{29}$Si NMR chemical shift of 3-DFT at the M06L/Al[6-311G(d,p),6-31G(d,p)] level of theory is 67 ppm, in good agreement with experimental data. The Pr$_3$Si$^+$ fragment coordinates to the most sterically open $\equiv$Si–O–Si$\equiv$ bridge in the polysesquisiloxane model, and does not interact with the C-F bonds on the anionic (RFO$_3$Al–OSi==) fragment. The Si–O distance in 3-DFT is 1.86 Å, which is ~0.1 Å longer than the Si–O bond in [Bu$_3$Si(OH$_3$)][CH$_4$B$_4$B$_4$Br]$_3$. The Si is displaced from the plane defined by the three carbon atoms by 0.57 Å, a larger value than typically observed for silylum ions containing carborane anions (~0.3–0.4 Å).

Pr$_3$Si$^+$ salts contain $\sigma_{c\cdot\cdot\cdot3p}$ hyperconjugation interactions between the methine C–H group of an isopropyl group and the empty 3p$_z$ hybrid orbital on Si.$^{29}$ The presence of hyperconjugation results in bond angles that deviate from those expected for $sp^3$ geometries. A Newman projection showing the Pr$_3$Si$^+$ fragment in 3 is shown in Fig. 8b. The Si–C–H bond angles in two of the ‘pr units are 96.4° and 99.0°, respectively. These values are lower than the expected 109.5° expected for $sp^3$ carbon, and is suggestive of $\sigma_{c\cdot\cdot\cdot3p}$ hyperconjugative interactions in 3-DFT. The sum of bond angles around these isopropyl carbons ($\Sigma_{c\cdot\cdot\cdot3p}$X = C or Si) are 345.4° and 343.9°, respectively. Similar trends in bond angles were observed in the solid-state structure of [Pr$_3$Si][CH$_4$B$_4$B$_4$Br]$_3$. The third isopropyl has bond angles closer to those expected for $sp^3$ carbon (Si–C–H = 103.4°; $\Sigma_{c\cdot\cdot\cdot3p}$X = 339°).
A scale of $^{29}$Si NMR chemical shift for selected $^3$Pr$_3$Si-X species is shown in Fig. 9. The $^{29}$Si NMR chemical shift of triisopropylsilane is 11 ppm, while triisopropylsilyltriflate has a chemical shift of 41 ppm. R$_3$Si$^+$ salts containing carborane anions are more deshielded with respect to these species, appearing between 97 ppm for [Pr$_3$Si][CH$_6$B$_{11}$Cl$_6$] and 115 ppm for [Pr$_3$Si][CH$_6$B$_{11}$Cl$_6$].$^{60}$ [Me$_3$Si][EtCB$_{11}$F$_{11}$] contains a more weakly coordinating carborane anion and has a $^{29}$Si NMR chemical shift of 138 ppm,$^{61}$ similar to silylum zwitterions.$^{62}$

Typical $^{29}$Si NMR chemical shifts for alkylsilanes on oxides are also included in Fig. 9. The $^{29}$Si CPMAS NMR spectrum of partially dehydroxylated silica containing −OSiMe$_3$ groups contains a $^{29}$Si NMR signal at 14 ppm.$^{12-15}$ The $^{29}$Si NMR chemical shift of trimethylsilyl functionalized zeolites appear at 17 ppm.$^{61}$ These results are consistent with a silylum character in these materials. To the best of our knowledge, the only $[R_3Si][oxide]$ type species is $^3$Pr$_3$Si$^+$ supported on sulfated zirconia (δ$^{29}$Si = 53 ppm).$^{64}$ The $^{29}$Si NMR chemical shift of 3 is 17 ppm more downfield than that of [Pr$_3$Si][sulfated zirconia].

The data in Fig. 9 indicates that the isotropic $^{29}$Si NMR chemical shift of R$_3$Si–X relate to the electronics at silicon.$^{60}$ A clear comparison is $^3$Pr$_3$Si–OTf (δ$^{29}$Si = 41 ppm) and [Pr$_3$Si][CH$_6$B$_{11}$Cl$_6$] (δ$^{29}$Si = 115 ppm). Triflate anions bind to Pr$_3$Si fragments stronger than electron deficient carborane anions, which modulates the Lewis acidity of the Pr$_3$Si-fragment in these compounds because silicon is more positively charged in carborane salts than triflates. This is also reflected in the geometry of the Pr$_3$Si-fragment, which becomes more planar in carborane salts than typical sp$^3$ organosilanes. Less clear was if this trend would also apply to alkylsilanes supported on oxides. The available $^{29}$Si chemical shift values for R$_3$Si-supported on silica and silica–alumina suggested that alkylsilanes do not form R$_3$Si$^+$ sites.$^{12-15,61}$ This is a result of formation of ≡SiO–SiR$_3$ sites on these material surfaces.

Sulfated zirconium oxide and 1 are more acidic than silica or silica alumina based on proton affinity calculations.$^{31}$ This suggests that these $^3$Pr$_3$Si-functionalized materials would contain $^{29}$Si NMR chemical shifts more downfield than R$_3$Si-functionalized silica or silica alumina. The $^{29}$Si chemical shift of [Pr$_3$Si][sulfated zirconia] (δ$^{29}$Si = 53 ppm) and 3 (δ$^{29}$Si = 70 ppm) are consistent with formation of species with R$_3$Si$^+$ character. However, these chemical shifts are far from those of $^3$Pr$_3$Si$^+$ carborane salts. These data indicate that $^{29}$Si NMR chemical shift trends for molecular R$_3$Si–X also apply to surface species. This implies that the $^{29}$Si NMR chemical shift on R$_3$Si-functionalized surfaces gives information about ion-pairing on surfaces sites, which could be important in designing catalytic sites on these weakly coordinating surfaces.

Silylum ions are strong Lewis acids that catalyze or mediate numerous chemical reactions.$^{65-67}$ Silylum ions activate C–F bonds to form R$_3$Si–F and carbocation intermediates,$^{68-72}$ which are rapidly quenched in the presence of excess silane to form C–H bonds. 3 activates C–F bonds in 1-adamantylfluoride in the presence of Et$_3$SiH at 0 °C to give adamantane (TON = 18). This reactivity is consistent with silylum character in the $^3$Pr$_3$Si$^+$ fragment in 3. However, 3 is less stable than $^3$Pr$_3$Si$^+$ sites supported on sulfated zirconia, which gives 160 turnovers in this reaction.$^{64}$ Solution $^{19}$F NMR spectra monitored during the C–F

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**Fig. 8** 3-DFT with hydrogens hidden for clarity (a); Newman projection of the $^3$Pr$_3$Si$^+$ fragment in 3 (b). Selected angles (deg) are given in red and referred to in the text.

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**Fig. 9** A scale relating buildup of positive charge on silicon to $^{29}$Si NMR chemical shift for various WCAs and oxides.
bond activation reaction contain signals for Al(OR^3)_3 and HOC(CF_3)_3, indicating that the low stability of 3 is probably related to decomposition reactions of the surface aluminium anion under these conditions (Fig. S20†).

Conclusions

This study shows that design strategies for WCAs in solution can be applied to generate well-defined surface WCAs. The reaction of SiO_2-700 with Al(OR^3)_3·PhF in perfluorohexane forms $\equiv$Si—OH·····Al(OR^3)_3 (1) and contains strong Brønsted acid sites based on GPA calculations. Experimental evaluation of the $r_{NH}$ stretch in [Oct_3NH][R^3O]_3Al(OSi)] (2) shows that this material forms weaker ion-pairs than typical first generation WCAs. 1 reacts with allyltriisopropylsilane to generate [Pr_3Si][R^3O]_3Al(OSt)] (3), a rare example of a silylium-like Lewis acid supported on an oxide, and to the best of our knowledge the only example supported on derivatized silica. Though the $r_{NH}$ stretch of 2 and $^{25}$Si NMR chemical shift of 3 show that 1 does fulfill the prerequisites to form WCAs, these data also suggest that ion-pairing on these surface sites is stronger than carborane or [B(C_6F_5)_4] anions. Neutral Lewis acids stronger than Al(OR^3)_3 are necessary to form strong Brønsted acids with partially dehydroxylated silica to form weaker coordinating anions than 1.

Conflicts of interest

There are no conflicts to declare.

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