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Authors
Dombrowski, James P
Ziegler, Micah S
Phadke, Neelay M
et al.

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Siloxyaluminate and Siloxygallate Complexes as Models for Framework and Partially-Hydrolyzed Framework Sites in Zeolites and Zeotypes

James P. Dombrowski,[a,b] Micah S. Ziegler,[a,b] Neelay Phadke,[c] Erum Mansoor,[c,d] Daniel S. Levine,[b,d] Martin Head-Gordon,[b,d] Alexis T. Bell,[b,c]* and T. Don Tilley[a,b]*

[a] Dr. J. P. Dombrowski, Dr. M. S. Ziegler, Prof. Dr. T. D. Tilley
Department of Chemistry
University of California, Berkeley
Berkeley, CA, USA
E-mails: tdtilley@berkeley.edu

[b] Dr. J. P. Dombrowski, Dr. M. S. Ziegler, Dr. D. S. Levine, Prof. Dr. M. Head-Gordon, Prof. Dr. A. T. Bell, Prof. Dr. T. D. Tilley
Chemical Sciences Division
Lawrence Berkeley National Laboratory
1 Cyclotron Road, Berkeley, CA, USA

[c] Dr. N. Phadke, E. Mansoor, Prof. Dr. A. T. Bell
Department of Chemical and Biomolecular Engineering
University of California, Berkeley
Berkeley, CA, USA

[d] Dr. D. S. Levine, Prof. Dr. M. Head-Gordon
Kenneth S. Pitzer Center for Theoretical Chemistry
Department of Chemistry
University of California, Berkeley
Berkeley, CA, USA

Supporting information for this article including experimental details, vibrational spectra and computational details, EXAFS modelling and figures, ESI-MS data, Crystal structure of Al(OSi(OBu)₃)₃·Et₂O, Crystal structure data tables and NMR spectra is given via a link at the end of the document.
Abstract: Anionic molecular models for non-hydrolyzed and partially hydrolyzed aluminum and gallium framework sites on silica, M(OSi(O′Bu))₃⁻ and HOM(OSi(O′Bu))₃⁻ (where M = Al or Ga), were synthesized from anionic chlorides Li[M(OSi(O′Bu))₃Cl] via salt metathesis reactions. Sequestration of lithium cations with 12-crown-4 allowed synthesis of charge-separated ion pairs composed of monomeric anions M(OSi(O′Bu))₃⁻ with outer-sphere [(12-crown-4)Li]⁺ cations, and hydroxides (HOM(OSi(O′Bu))₃) with pendant [(12-crown-4)Li]⁺ cations. These molecular models were characterized by single crystal X-ray diffraction, vibrational spectroscopy, mass spectrometry and NMR spectroscopy. Upon treatment of monomeric [(12-crown-4)Li]HOM(OSi(O′Bu))₃ complexes with benzyl alcohol, benzyloxide complexes were formed, modeling a possible pathway for the formation of active sites for Meerwin-Ponndorf-Verley (MPV) transfer-hydrogenations with Al/Ga-doped silica catalysts.

Introduction

Zeolites and zeotype materials are widely used in heterogeneous catalysis as their properties can be readily modified by incorporation of heteroatoms via cation exchange with surface protons or by site-exchange at lattice silicon sites. A subset of these materials containing group-13 atoms are prototypical solid-acid catalysts with highly acidic surface-bound protons that offset charge imbalance generated upon incorporation of M³⁺ atoms, especially aluminum, into four-coordinate tetrahedral Si⁴⁺ positions. Isomorphic substitution at Si⁴⁺ positions as described above generates heteroatom “framework sites” (a and b, Figure 1). In addition to heteroatom framework sites, various defect sites that can contain heteroatoms may also form, and these sites are often implicated in catalysis. For example, a three coordinate Lewis acid site can be associated with surface M³⁺ centers (c, Figure 1). Moreover, partial hydrolysis of a framework site can generate a defect site comprising a heteroatom bound in a tripodal arrangement and possessing a terminal hydroxide group (d, Figure 1). These sites are distinct from traditional extra-framework aluminium (EFAL) species in that they remain partially connected to the silica framework rather than fully extruded. However, they do not display the fourfold connectivity to the silica network of a framework site. Therefore, these defects could be viewed as intermediate between the two extremes.

Investigating the chemistry of such defect sites is challenging due to low defect concentrations and structural inhomogeneity of the defect sites. The targeted generation or enrichment of specific defect sites within a given material is a substantial synthetic challenge. Nevertheless, the reactivity of metal-doped zeolite and zeotype materials can be greatly influenced by the presence of these defects generating great interest in their study. One approach to addressing this issue is the creation of well-defined models containing silicates, to the best of our knowledge, well-defined models of monomeric anionic aluminum- or gallium-centered framework sites bearing four M–O–SiO₃ linkages have not been fully characterized. Similarly, monomeric molecular analogs of the aforementioned partially-hydrolyzed framework sites bearing three M–O–SiO₃ linkages have, to our knowledge, not yet been reported.

Recent reports describe the synthesis and characterization of aluminum and gallium siloxides Al(OSi(O′Bu))₃•THF, and Ga(OSi(O′Bu))₃•THF, which contain M–O–SiO₃ covalent linkages and can serve as models for neutral Lewis-acidic sites in silica materials. Some of these compounds were utilized as thermolytic molecular precursors (TMPs) to generate metal-containing silicas by thermolysis. Such precursors may also be employed to generate single-site species on a supporting oxide material by surface grafting of the precursor followed by thermolysis. Notably, this approach makes extensive use of the molecular precursors as spectroscopic models in the characterization of surface sites formed following thermolysis.

Herein we report the preparation of anionic gallate and aluminolate complexes that contain {M(OSi(O′Bu))₃}⁻ and {HOM(OSiO₃)}⁻ cores corresponding to framework and partially-hydrolyzed framework sites, respectively. We provide spectroscopic characterization that should assist in identification of similar sites in related heteroatom-containing silicates. In addition, reactivity studies of the partially-hydrolyzed framework site models reveal examples of proposed initiation steps in heterogeneous Meerwin-Ponndorf-Verley (MPV) catalysis using group-13 metals.

Results and Discussion

Molecular models are particularly relevant for understanding low-abundance or defect surface sites due to their ability to mimic such sites in a pure, uniform sample. Despite extensive reports of molecular models for heteroatom-containing silicates, to the best of our knowledge, well-defined models of monomeric anionic aluminum- or gallium-centered framework sites bearing four M–O–SiO₃ linkages have not been fully characterized. Similarly, monomeric molecular analogs of the aforementioned partially-hydrolyzed framework sites bearing three M–O–SiO₃ linkages have, to our knowledge, not yet been reported.

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Synthesis and single crystal X-ray diffraction studies of siloxyaluminate and siloxygallate complexes

The synthesis of model complexes designed to mimic the connectivity of framework sites and partially-hydrolyzed framework sites proceeded from initial syntheses of the "ate" metal chlorides, Li[Al(OSi(O\text{Et}Bu)\text{t}_{3})_3]\text{Cl} (1-Li) and Li[Ga(OSi(O\text{Et}Bu)\text{t}_{3})_3]\text{Cl} (2-Li), as starting materials (Scheme 1). Complex 1-Li was obtained in pure form by treatment of base-free Al[OSi(O\text{Et}Bu)\text{t}_{3}], recently reported by Valla et al., with lithium chloride in pentane and was isolated in 70% yield (Scheme 1). Complex 2-Li was synthesized by treatment of gallium trichloride with three equivalents of LiOSi(O\text{Et}Bu)\text{t}_{3} in diethyl ether (Scheme 1) and isolated in 74% yield. A similar synthetic approach using sodium tris(tert-butoxy)silanolate afforded the sodium analog 2-Na. Analogous treatment of aluminum trichloride with LiOSi(O\text{Bu})\text{t}_{3} led to a mixture of products including 1-Li and the diethyl ether adduct Al(OSi(O\text{Bu})\text{t}_{3})_2\text{Cl}_2\text{Et}_2\text{O} (3), which was confirmed by independent synthesis (see ESI).

Single-crystal X-ray diffraction studies of 1-Li and 2-Na revealed zwitterionic structures with alkali cations coordinated to oxygen atoms present in the silicate ligands. Chloride ions are bound terminally to the group-13 metal centers, and the M–Cl (M = Al or Ga) bond lengths are typical for Al/Ga in oxide environments (2.153(5) Å and 2.1540(5) Å for 1-Li and 2-Na, respectively; Figure 2).

The observed zwitterions with cation coordination to the ligand backbone are reminiscent of crystallographically-characterized chloroaluminate and chlorogallate structures previously reported by Bourissou and Evans, as well as a non-zwitterionic gallium silsesquioxane complex reported by Feher and coworkers.

Figure 2. (Left to right) Single-crystal X-ray diffraction structures of Li[Al(OSi(O\text{Bu})\text{t}_{3})_3]\text{Cl} (1-Li) and Na[Ga(OSi(O\text{Bu})\text{t}_{3})_3]\text{Cl} (2-Na). All ellipsoids shown at 50% probability. Hydrogen atoms omitted for clarity.
From complexes 1-Li and 2-Li, tetrasiloxyaluminate and gallate molecular models of framework aluminum and gallium sites were synthesized by addition of LiOSi(OCtBu)₃. Treatment of 1-Li with LiOSi(OCtBu)₃ afforded Li[Al(OSi(OCtBu)₃)]₄ (4), in 63% isolated yield (Scheme 2). It was found that treatment of GaCl₃ with four equivalents of LiOSi(OCtBu)₃ in diethyl ether afforded Li[Ga(OSi(OCtBu)₃)]₄ (5) in one step in 49% yield, presumably with 2-Li as an intermediate. These complexes all display high solubilities in aliphatic, aromatic, and polar aprotic solvents.

Cooling concentrated diethyl ether solutions of 4 and 5 to nearly 30 °C afforded crystals suitable for X-ray diffraction. The solid-state structures identified by single crystal X-ray diffraction revealed the presence of contact-ion pairs, with τδ values of nearly tetrahedral (τδ defined as a function of the largest (α) and second largest (β) angles about the four-coordinate metal center) [Eq. 1].

\[
\frac{360 - (\alpha + \beta)}{\alpha} = \frac{141}{\alpha}
\]

A saw-horse geometry is indicated by τδ = 0.54 for the Li cation in 4, whereas pseudo-tetrahedral coordination of the lithium cation in 5 is indicated by a value of 0.77 for the τδ geometric parameter.

The difference in geometries about the lithium cations in 4 and 5 likely reflects different degrees of steric congestion for the Al⁴⁺ and Ga³⁺ centers (T₄ ionic radii: Al⁴⁺, 0.53 Å; Ga³⁺, 0.61 Å). This difference in congestion resulting from non-bonded contacts is reflected in a greater linearization of the Al–O–Si linkages (Si–O–Al angles: 149.5(2), 150.3(2), 166.0(2), 171.5(2)°, as compared to the Si–O–Ga angles: 144.4(1), 148.9(1), 134.9(1), 133.1(1)°).

Upon addition of 12-crown-4 (3.5 equivalents) to pentane solutions of 4 and 5, colorless powders rapidly precipitated. These powders were identified as [(12-crown-4)Li][Al(OSi(OCtBu)₃)]₄ (6) and [(12-crown-4)Li][Ga(OSi(OCtBu)₃)]₄ (7), isolated in 74% and 71% yields, respectively (Scheme 3). The complexes display low solubility in nonpolar aliphatic and aromatic solvents, but good solubility in diethyl ether, tetrahydrofuran, and dichloromethane, consistent with formation of a polar charge-separated structure. Unfortunately, crystals of 6 and 7 from a variety of solvents (Et₂O, THF, o-difluorobenzene) gave poor diffraction beyond 1.0 Å, precluding structural assignments by X-ray crystallography.

Complexes 4 and 5 represent, to the best of our knowledge, the first analytically pure and structurally characterized monomeric tetrasiloxyaluminate and gallate structures bearing only M–O–SiO₃ linkages. A single crystal X-ray structure of a related gallate, Li[Ga(SSi(OCtBu)₃)]₄, was reported as a side-product of the reaction between gallium(I) bromide and LiSSi(OCtBu)₃, although no yield or additional characterization data was provided. In addition, two aluminate complexes containing only M–O–SiO₃ linkages, M[Al(OSi(OEt)₃)]₄ (M = Na, K) were claimed on the basis of elemental analysis and vibrational spectroscopy. Compounds 6 and 7 appear to represent the first examples of the component “free” anions, as supported by NMR spectroscopy and elemental analysis, which suggest the presence of separated ion pairs involving the [Li(12-crown-4)]⁺ cation. Related tetrasiloxyaluminates and gallates with Si–C bonds have been described, such as –OSiPh₃ and –OSiBuMe₂ complexes reported by Limberg and coworkers; however, these species lack SiO₃ units.
Salt metathesis reactions of complex 1-Li with anhydrous lithium hydroxide provided molecular models of partially-hydrolyzed framework sites \( \text{Li[Al(OSi(OtBu)3)]}_2\text{Cl} \) (8) (Scheme 4), in a mixture with free silanol, lithium silanolate, and 4, tentatively identified by \(^1\)H NMR spectroscopy as singlets with the reported NMR shifts. Similarly, treatment of 2-Li with LiOH afforded \( \text{Li[Ga(OSi(OtBu)3)]}_2\text{Cl} \) (9), in a mixture with silanol, lithium silanolate, and 5. Compounds 8 and 9 were purified by crystallization from toluene in approximately 50-60% yield. The X-ray structures of 8 and 9 show that in the solid state both complexes are composed of two \( [\text{tBuO}_3\text{SiO}]-\text{MOH}^- \) units bridged by a T-shaped \( \text{Li}_3\text{Cl} \) fragment (Figure 4). In each structure, both hydroxyl groups interact with a single central lithium atom while oxygen donors in the silanolate ligands bind to the remaining lithium cations. The Al–O(H) distances in 8 of ~1.76 Å and the Ga–O(H) distances in 9 of ~1.83 Å, along with similar Li–O(H) distances for both (~1.84-1.85 Å), reflect the smaller ionic radius of Al\(^{3+}\) versus Ga\(^{3+}\).

Addition of 12-crown-4 (6 equivalents) to pentane

Figure 4. (Top to bottom; left to right) Single-crystal X-ray diffraction structures of: \( \text{Li[Al(OSi(OtBu)3)]}_2\text{Cl} \) (8), \( \text{Li[Ga(OSi(OtBu)3)]}_2\text{Cl} \) (9), \( \text{Li[12-crown-4][Al(OSi(OtBu)3)]OH} \) (10), and \( \text{Li[12-crown-4][Ga(OSi(OtBu)3)]OH} \) (11). All ellipsoids shown at 50% probability. Tert-butoxy groups were truncated to their oxygen atoms for clarity, excluding those involved in donation to lithium cations. Hydrogen atoms and solvent molecules omitted for clarity with the exception of hydroxyl hydrogen atoms that were located in the difference electron density map and refined independently.
solutions of 8 and 9 induced loss of lithium chloride and cleavage of the dimers into monometallic fragments, [Li(12-crown-4)][Al(OSi(OtBu)3)2OH] (10) and [Li(12-crown-4)][Ga(OSi(OtBu)3)2OH] (11), which were isolated in ~50-55% yield after crystallization (Scheme 5). The resulting complexes serve as molecular models of partially-hydrolyzed framework sites with interacting cations.


Single crystals grown from concentrated pentane solutions at ~30 °C provided solid-state structures for 10 and 11 (Figure 4). The Ga–O(H) bond length of 1.8448(15) Å and the Li–O(H) bond length of 1.815(4) Å in 11 are comparable to Ga–O(H)–Li linkages observed previously. For example, Murugavel and coworkers compared the long Li–O(H) distances (av. 2.023(8) Å) found in the dimeric Ga–O(H)–Li core of the complex ion Li2[Li(THF)2][Ph2SiO2GaMe2][Ph2SiO2GaMe(OH)]2•2THF to those reported for (LiOH)2H2O (1.95 Å) in order to differentiate between structures having more lithium-versus gallium-hydroxide character.59 While 11 has shorter Li–OH contacts than (LiOH)2H2O, the corresponding Ga–OH bond lengths are also slightly shortened relative to the previously reported gallate structure (1.8448(15) vs. 1.880(3) Å). Comparison of 11 to the solid-state structure of Mes2GaOH Li(THF)3 (Li–OH = 1.83(2) Å; Ga–OH = 1.936(9) Å) suggests a similar Li–OH interaction in both cases, with the longer Ga–OH bond likely resulting from a more electron-rich Mes2Ga fragment.59 In the case of 10, a shorter Al–OH (vs. Ga–OH) distance combined with a longer Li–OH interaction is consistent with either a stronger interaction of the hydroxy fragment to the smaller, harder aluminum center and/or steric crowding associated with the smaller [SiO2]3–Al(OH)–Li core.

Complexes 8, 9, 10, and 11 represent novel examples of simple aluminate and gallate complexes bearing three M–O–Si O2 linkage and a terminal hydroxide ligand. While structures with identical oxide cores have not been reported, related examples of hydroxyl-gallium and hydroxy-aluminum siloxide complexes have been reported in the literature.60–73 In related work, Witter et al. reported the synthesis of [(Ph2SiO2)2Al(OH)(HNEt2)3 via hydrolysis of the [(Ph2SiO)2Al] anion or deprotonation of the aquo complex [(Ph2SiO2)Al(H2O)];74

1H NMR spectra of 8, 9, and 11 in benzene-d6 display singlets tentatively assigned to hydroxyl protons at 1.95, 2.43 and 2.07 ppm, respectively (See ESI). The 1H NMR spectrum of 10 in benzene-d6 did not contain a peak readily identifiable as the hydroxyl proton. The observed hydroxyl resonances are close to those calculated or measured for extra-framework HOAl(OSiO3)2 fragments in zeolites (~1.6 ppm),18 silanols and other weak acid sites in ZSM-5 (~1.4–2.2 ppm),75 acid sites of five-coordinate aluminum hydroxide surface species (1.9 ppm),76,77 weakly acidic Al–OH groups in related molecular aluminates (~1.4–2.0 ppm),82,73 and extra-framework aluminum species formed upon dealumination of HZSM-5 (~2.5–2.8 ppm).77,78 Interestingly, these results are consistent with a very recent report by Chen et al. of catalytically-relevant partially-hydrolyzed aluminum framework sites in HZSM-5.78 In general, these proton shifts suggest that the hydroxyl groups are less acidic than the Brensted acid bridging sites found in group-13-doped HZSM-5 zeolites (~4 ppm).77

Vibrational spectroscopic analysis of complexes 6, 7, 10, 11

Complexes 6, 7, 10, and 11 are structurally analogous to framework and partially-hydrolyzed framework sites in aluminosilicates and gallosilicates and were therefore additionally characterized using attenuated total reflectance Fourier-transform infrared spectroscopy (ATR-FITR), Nujol mull FTIR, and Raman spectroscopy (See ESI). Spectral assignments were supported by comparison to vibrational spectra computed using ab initio optimized structures of the anions for 6 and 7 and structures optimized from the crystal data of the whole contact-ion pairs of 10 and 11, as steric congestion was expected to influence coordination geometries and vibrational modes.

Perhaps most relevant to the chemistry of complexes 10 and 11 are the vibrations associated with O–H stretches; these are predicted to be located at 3786 cm–1 for 11 and 3757 cm–1 for 10 (3596 and 3569 cm–1, respectively, when an approximate scaling correction of 0.9575 is applied) which is consistent with expected differences in stretching frequencies for Ga–OH and Al–OH units.4,60–83 The unscaled and scaled computed frequencies straddle those reported for extra-framework Al–OH and Ga–OH in zeolites at ~3650-3680 cm–1 and for charge-compensating strong Brensted acid sites (Figure 1b) interacting with aluminum extra-framework species at ~3600 cm–1.84–88 Experimentally, multiple OH stretches are observed in the ~3550-3650 cm–1 range by FTIR spectroscopy of Nujol mulls and between ~3310 and 3580 cm–1 for ATR-FITR measurements under ambient conditions (See ESI). The shift to lower frequencies observed for ATR measurements is attributed to hydration during sample measurement, further supported by weak features around ~1650 cm–1 potentially due to H2O deformation modes, so the ATR spectra will not be discussed further.85,86 For the Nujol mull spectra, hydrogen bonding of M–O–H moieties with neighboring SiO2 units could lead to the observed frequencies (closest OH...O distances based on crystal structures: 11, H17...O12 = 2.193 cm–1).
Å; 10, H17–O16 = 2.247 Å, noting the high inherent error in hydrogen atom placement by XRD).\cite{81,82} It should be noted that these frequencies are similar to those reported for lithium hydroxide and lithium hydroxide monohydrate at ~3665-3680 and ~3565-3570, respectively, with the monohydrate crystal structure showing strong hydrogen-bonding from water to the hydroxyl oxygen but weak or no hydrogen bonding from the hydroxyl hydrogen itself, in contrast to the above proposal.\cite{85-87}

The high solubilities of 10 and 11 in non-polar aliphatic solvents may lead to partial dissolution of the sample in Nujol mineral oil allowing for the formation of hydrogen bonding interactions not observed in the crystal structures. Alternatively, adventitious water could allow for hydrogen-bonding interactions similar to those observed in lithium hydroxide monohydrate.

Significant differences are observed in the Si–O and OH stretching regions of FTIR spectra for 6, 7, 10, 11. Differences in the wavenumbers of bands tentatively assigned as M–O–Si and M–OH stretches for the Al/Ga pairs 6/7 and 10/11 were observed. The ATR-FTIR spectra of the aluminum complexes 6 and 10 exhibit bands at 1084 and 1080 cm\(^{-1}\), respectively, which are tentatively assigned to M–O–Si asymmetric stretches. For the gallium analogues, a lower-frequency shoulder band at 1059 cm\(^{-1}\) for 7 was apparent while no isolated unique band was identifiable for 11. As discussed below; however, the ATR-FTIR measurements of 10 and 11 should be interpreted with caution due to evidence of significant sample hydration during measurement.

Raman spectra collected for the pair of framework site models 6 and 7, and the partially-hydrolyzed site models 10 and 11, are similar for Al and Ga analogs (See ESI). There are relatively few Raman spectroscopic studies of zeolites, in comparison to IR studies.\cite{88,89} However, both visible and UV-resonance Raman spectra have been measured for a variety of zeolites and zeotypes and provide points of comparison.\cite{88-92}

Complexes 6, 7, 10, 11 exhibit bands in the ~650-750 and ~800-860 cm\(^{-1}\) regions, generally consistent with assignments for T-O/T-O-Si deformation and symmetric stretches of framework tetrahedra and bands at ~900-950 and ~1000-1100 cm\(^{-1}\), respectively, with asymmetric stretches.\cite{93-95} The observed bands are also in line with prior reports of Raman spectra for complexes containing the –OSi(O’Bu)\(_3\) fragment.\cite{96}

**EXAFS predictions based on single-crystal XRD of complexes 6, 7, 10, 11**

From the single-crystal XRD data of 10 and 11 and the computed geometries of 6 and 7, extended X-ray absorption fine structure (EXAFS) patterns were generated as references for zeotype materials. EXAFS patterns are commonly used in materials science to generate an average local geometry and set of statistical nearest/next-nearest neighbors for an absorbing atom in a material – information readily provided by the crystal structures.\cite{94}

The Fourier-transformed magnitude images and untransformed images are provided in the supplementary information for convenience (See ESI). Previously, isolated molecular complexes have served as models for the identification of structurally complex species on silica surfaces, so this data should be of general use to the zeolite community.\cite{20,29,95-99}

**Reactivity of complexes 10 and 11 with relevance for Meerwin-Pondorf-Verley transfer hydrogenation over supported group-13 metal catalysts**

In addition to serving as spectroscopic models of partially-hydrolyzed framework sites, complexes 10 and 11 were investigated as functional models of reactivity. Partially-hydrolyzed framework sites of group-13 metals have been proposed as pre-catalysts for MPV transfer-hydrogenation of ketones and aldehydes using alcohols as sacrificial reductants.\cite{17,18,100-102} It has been established that isolated group-13 alkoxide surface species are active for MPV transfer-hydrogenation catalysis; however, the structures and mechanisms for generation of such surface sites are debated.\cite{93,103} The isolation of 10 and 11, which mimic defective framework sites that have been partially hydrolyzed, provides an opportunity to investigate proposed pre-catalyst initiation steps starting from a HOM[OSiO\(_2\)]\(_{13}\) partially-hydrolyzed surface site. Specifically, alcoholsysis of the M–OH bond to form a metal alkoxide and water (Figure 5) is a proposed initiation step for group-13 and various other Lewis-acidic heteroatom sites in zeotypes.\cite{101}

Exposure of 10 or 11 to one equivalent of benzyl alcohol in benzene or toluene led to a mixture of products by \(^1\)H NMR spectroscopy including new, unidentified species, free silanol, lithium silanolate, and 4 (from 10) or 5 (from 11). Removal of the volatile components in vacuo gave white solids. Analysis of the solid from the reaction of 10 by electrospray ionization mass spectrometry (ESI-MS) in negative mode indicated formation of the expected benzyloxide complex (BnOAl[OSi(O’Bu)\(_3\)])\(_2\) as well as (BnO)\(_2\)Al[OSi(O’Bu)\(_3\)]\(_2\). Similarly, ESI-MS indicated that 11 had reacted with benzyl alcohol to give {BnOGa[OSi(O’Bu)\(_3\)])\(_2\} and {(BnO)\(_2\)Ga[OSi(O’Bu)\(_3\)]\(_2\)} (See ESI). p-Nitrobenzaldehyde, included in the probe reaction for 10 as a potential reactant for transfer hydrogenation, did not appear to generate new aluminate products identifiable by ESI-MS beyond the analogous benzyloxide anions formed from 11. Dimeric products were also observed by ESI-MS, although these could have formed during ionization of the relatively concentrated solution.\cite{104,105}
In order to confirm the presence of benzyloxide-ligated metallates in the product mixture prior to ionization during ESI–MS analysis, isolation of a benzyloxide-substituted gallate directly from the product mixture was pursued. Exposure of 11 to two equivalents of benzyl alcohol in toluene for 24 h followed by evaporation to dryness gave a white residue that, by $^1$H NMR spectroscopy (benzene-$d_6$ solvent), is composed of a mixture of products similar to that observed previously. No precipitate formation was observed during the reaction. Following removal of the solvent in vacuo, extraction of the solid residue with pentane left a white deposit, indicating the formation of a new product, as all identified components of the product mixture are readily soluble in pentane. The deposit was dissolved in a minimum amount of toluene and cooled to –30 °C for 24 h which afforded single, plate-like crystals that were identified by X-ray crystallography as [(12-crown-4)$_2$Li][[(BnO)Ga(OSi(O$^t$Bu)$_3$)$_3$] (12; Figure 6). An independently prepared sample of 12 was synthesized by treatment of 2 with lithium benzyloxide in 27% yield (see ESI). This isolation of 12 from the mixture formed by treating 11 with benzyl alcohol (2 equiv) indicates that formation of (benzyloxide)gallate anions occurred prior to ESI-MS measurements and are not purely an artifact of ionization.

The reactivity observed for 10 and 11 suggests that, upon exposure to alcohols, partially-hydrolyzed framework group-13 sites readily form alkoxides. However, in this model system, significant ligand exchange of both benzyl oxide and silanolate ligands appeared to have...
occurred. It is unclear what, if any, role the lithium cation plays in this reaction. While consistent with prior hypotheses, the observations made using these molecular models do not definitively assign partially hydrolyzed sites on group-13-containing silicon materials as the pre-catalyst sites for MPV-transfer hydrogenation – only direct observation of the active catalyst can make such an assignment. However, the chemistry described above provides a model of the behavior of isolated defect site structures and supports the assertion that partially-hydrolyzed sites can readily generate alkoxides upon exposure to alcohols, a necessary step in proposed mechanisms for MPV active site formation.

Conclusions
The aluminum and gallium silanlates 1–12, featuring M-O(SiO)_3, silicate cores, were synthesized and employed as new molecular models for important active sites in group-13 metal-containing silicate materials. The zwitterionic metal chlorides 1 and 2 allow for ready synthetic access to analogous pairs of aluminum- and gallium-containing complexes via salt metathesis reactions with halide moieties. The synthesized metal silanolate complexes can serve as models for defective or intact zeotype framework sites as demonstrated herein with the synthesis of tris(siloxy)(hydroxy)-aluminate and -gallate models for partially-hydrolyzed framework sites in zeotypes, as well as homoligated tetrasiroyxaluminates and gallates to model framework sites, all of which contain SiO_2 units analogous to a silicate framework. Complexes 10 and 11 are shown to undergo facile reaction with benzyl alcohol to form metal alkoxides, providing support for proposed initiation steps in MPV transfer hydrogenations over group-13-doped silica materials.

Conflicts of interest
There are no conflicts to declare.

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Keywords: Zeolite • Molecular Modelling • Hydrogen Transfer

References
The synthesis and characterization of anionic molecular models for aluminum and gallium framework sites and partially-hydrolyzed framework sites on silica with $\text{M}\left[\text{OSi(O}^\text{Et}_2\text{Bu)}_3\right]^-$ and $\text{HOM}\left[\text{OSi(O}^\text{Et}_2\text{Bu)}_3\right]^-$ cores are reported. Upon treatment of partially-hydrolyzed framework-site models with alcohols, alkoxide complexes were formed, reminiscent of proposed pre-catalyst activation for transfer-hydrogenations.