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Accepted Article

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To be cited as: *Eur. J. Inorg. Chem.* 10.1002/ejic.201800564

Link to VoR: http://dx.doi.org/10.1002/ejic.201800564

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European Journal of Inorganic Chemistry 10.1002/ejic.201800564

Reactivity of Cp*Al Towards Silanols: Formation and Hydrolysis of Alumosiloxanes

Philipp Wittwer,[a] Adrian Stelzer,[a] and Thomas Braun*[a]

Abstract: Treatment of $[Cp^*Al]_4$ (**1**) (Cp* = pentamethylcyclopentadienyl) with various silanols gave access to the compounds $[Al\{OSi(OtBu)_3\}_3(DMAP)]$ (**3**) (DMAP = 4-dimethylaminopyridine), $[HNEt_3][Al(OSiPh_3)_4]$ (**4**), and $[Al_7(OH)_9\{(OSiiPr_2)_2O\}_6]$ (**6**). ESI mass spectrometry revealed that **6** exchanges its outer hydroxyl groups in the presence of $H_2{}^{18}O$ water. Hydrolysis of **4** led to the formation of $[HNEt_3][Al(OH)(OSiPh_3)_3]$ (**5**), but only in the presence of additional NEt_3. The structures in the solid state of **6**·toluene, **6**·$(THF)_3$, **6**·$(H_2O{\cdot}2THF)_3$, and **5** were determined by X-ray crystallography.

Introduction

Alumosilicates play a crucial part as catalysts in fundamental industrial processes,[1] e.g. crude oil cracking.[1h] A mechanistic understanding of their formation is needed in order to design catalysts without laborious screening processes. One step towards this goal comprises the synthesis of molecular alumosiloxanes, as they can be regarded as model structures for early steps in zeolite formation.

Considerable contributions were reported by Veith and coworkers.[2] For example, the alumosiloxane $[Al_4(OH)_4(OSiPh_2OSiPh_2O)_4]$ consists of a ring of four $[AlO_4]^-$ tetrahedra which are linked by OH groups, and four siloxanediol ligands arranged around this core.[2c] Deprotonation of the bridging aluminum hydroxyl groups is possible on using amine bases. More recently, Limberg *et al.* reported the synthesis of $[Al_3(\mu_2\text{-}OH)_3(THF)_3\{PhSi(OSiPh_2O)_3\}]$ which is characterized by three OH-linked tetrahedral coordinated aluminum atoms in its core.[3] The hydrolysis of both compounds led to larger clusters with a core featuring octahedral coordinated aluminum atoms, which are linked by bridging hydroxide ligands. Barron *et al.* reported on the synthesis of the cluster $[Al_{10}(OH)_{16}(OSiEt_3)_{14}]$ that shows a motif which resembles moieties found in boehmite or diaspore.[4] A comparable structural motif was also established in two different clusters obtained by hydrolysis of $[\{(tBuO)_3SiO\}AlO]_4$.[5] The latter compound has a heterocubane structure and was prepared by the reaction of $[Cp^*Al]_4$ (**1**) (Cp* = pentamethylcyclopentadienyl) with O_2 or N_2O to yield $[Cp^*AlO]_4$, which was treated with $HOSi(OtBu)_3$. Note that subvalent aluminum compounds, such as $[Cp^*Al]_4$ (**1**), can be valuable tools to access unusual binding motifs and complexes of aluminum.[6] Thus, H. W. Roesky *et al.* showed that **1** inserts into the Si-F bond of SiF_2Ph_2 to give $[\{(Cp^*AlF)_2SiPh_2\}_2]$.[7] Later, the synthesis of the molecular alumoxane $[\{(NacNac)^{Dipp}Al\}_2O]$ by oxygenation of $[(NacNac)^{Dipp}Al]$ ($NacNac^{Dipp}$ = $CH\{(CMe)(2,6\text{-}iPr_2C_6H_3N)\}_2$) with O_2 was reported.[8] Additionally, $[(NacNac)^{Dipp}Al]$ undergoes an oxidative addition reaction when treated with a broad scope of E-H compounds, thus as in the reaction with HO*i*Pr giving $[(NacNac)^{Dipp}Al(H)OiPr]$.[9] Although Al–O–Si linkages are accessible from Al(III) compounds and silanols,[10] Al(I) complexes might lead to different structural motifs.

To the best of our knowledge, no reports on the reactivity of $[Cp^*Al]_4$ (**1**) towards compounds containing hydroxyl groups have been published, except for the slow decomposition in the presence of water.[11] In this contribution we present studies on the reactivity of $[Cp^*Al]_4$ (**1**) towards various silanols to give alumosiloxanes. The compounds were studied with regard to their reactivity towards water.

Results and Discussion

Treatment of $HOSi(OtBu)_3$ with $[Cp^*Al]_4$ (**1**) at 80°C led to gas evolution and after ten minutes to the formation of a colorless gel (Scheme 1). ^1H NMR measurements of the gel showed signals corresponding to *iso*-butene, Cp*H and H_2. Similar decomposition reactions were reported in the past for Al compounds containing $-OSi(OtBu)_3$ moieties yielding an alumosilicate gel of an unknown structure, although in the present case, the gelation occurs faster.[6g] When the reaction solution was heated for only five minutes and then immediately cooled down to room temperature, or when the reaction was followed *in situ* at 80 °C via ^1H NMR spectroscopy, additional signals were detected. The ^1H NMR spectrum of the reaction mixture after being stirred at 80°C for five minutes shows signals at room temperature for $[Cp^*Al]_4$ (**1**), $HOSi(OtBu)_3$, Cp*H, H_2 and for an additional Cp* species at $\delta = 1.92$ ppm, as well as resonances for *t*Bu groups in the region of $\delta = 1.62–1.45$ ppm. The ratio of **1** : unknown species : Cp*H is approximately 4 : 12 : 84. The $^1H,^{29}Si$ HMBC NMR spectrum shows signals that can be assigned to $HOSi(OtBu)_3$ and $[Al(OSi(OtBu_3)_3]$.[6g] However, in the ^{27}Al NMR spectrum of the reaction solution a broad singlet at $\delta = -58$ ppm ($\omega_{1/2} \approx 340$ Hz) for an unknown aluminum species was observed in addition to the signal for unreacted $[Cp^*Al]_4$ (**1**) at $\delta = -80$ ppm. A resonance which could

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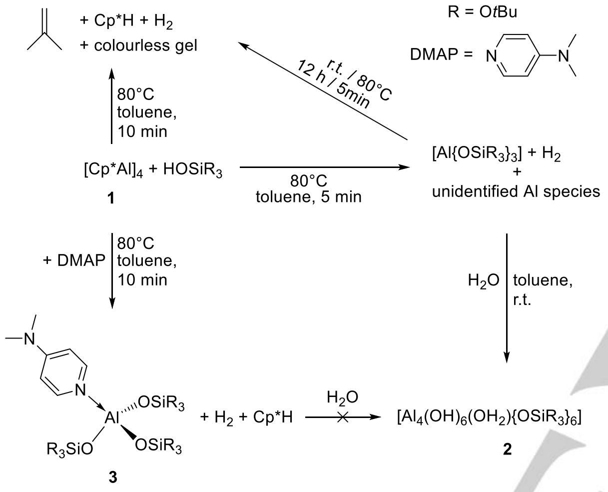
be assigned to [Al(OSi(OtBu$_3$)$_3$] was not observed. It appears plausible, that the resonances at $\delta = 1.92$ ppm in the ^{1}H NMR spectrum and the resonance at $\delta = -80$ ppm in the ^{27}Al NMR spectrum are caused by the same unidentified compound, the identity of which remains unclear. Comparable ^{27}Al shifts to the unknown aluminum species were reported for the aluminum halides [Cp*AlX$_2$]$_2$ (X = Br, Cl) at $\delta = -45.5$ ppm and -53 ppm, respectively.[12] Thus the unknown species likely posseses a Cp* ligand and might be a dimeric Cp*Al(III) compound. When adventitious water is present in the reaction mixture, after two days crystals of the literature known cluster [Al$_4$(OH)$_6$(H$_2$O)$_2$(OSi(O*t*Bu)$_3$)$_6$][5] (**2**) were identified by X-ray crystallography.

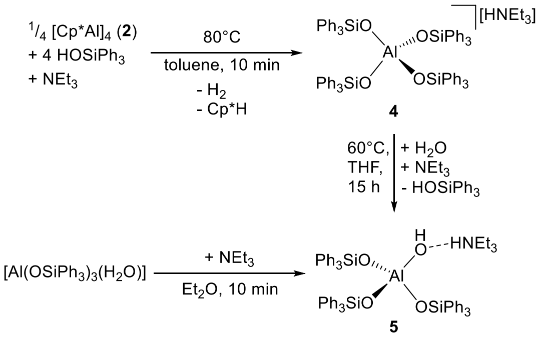


Scheme 1. Reactivity of [Cp*Al] (**1**) towards HOSi(O*t*Bu)$_3$.

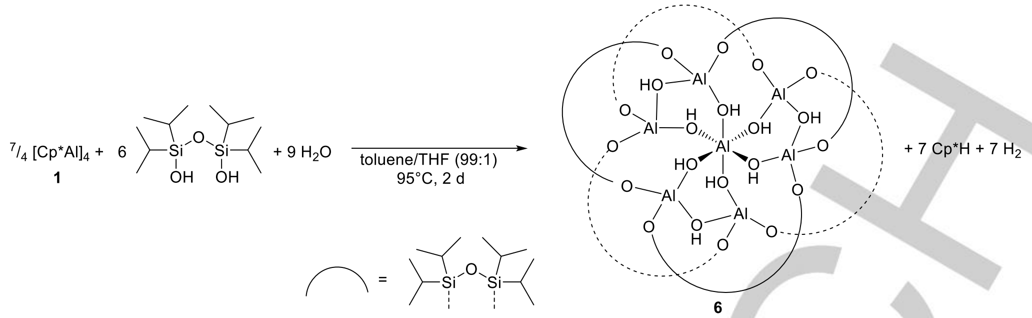
Treatment of [Cp*Al]$_4$ (**1**) with HOSi(O*t*Bu)$_3$ at 80°C in the presence of 4-dimethylaminopyridine (DMAP) gave the mononuclear compound [Al{OSi(O*t*Bu)$_3$}$_3$(DMAP)] (**3**), Cp*H and H$_2$ (Scheme 1). The ^{1}H NMR spectrum shows two resonances in the aliphatic region, one for the butoxy groups at $\delta = 1.59$ ppm and one for the amine-bound methyl groups at $\delta = 1.88$ ppm, whereas the two resonances at $\delta = 6.20$ ppm and $\delta = 9.00$ ppm can be attributed to the *meta* and *ortho* bound hydrogen atoms at the DMAP ring, respectively. The ^{1}H,^{29}Si HMBC NMR spectrum shows a correlation between the signals caused by the butoxy groups and a resonance in the ^{29}Si domain at $\delta = -97$ ppm. No signal could be detected in the ^{27}Al NMR spectrum. However, a signal for **3** in the ^{27}Al MAS NMR spectrum was detected at $\delta_{iso} = 55.0$ ppm, compatible with a tetracoordinated Al center.[12a, 13] This signal shows a nearly axial electric field gradient ($\eta_Q = 0.05$) and strong quadrupolar coupling ($\nu_Q = 1.669$ MHz), which is consistent with the suggested structure for **3** in Scheme 1. The geometry is also supported by X-ray single crystallography, however, strong disorder of a majority of the butoxy groups impair the quality factors of the refinement. ESI-MS studies of **3** in THF showed a signal at m/z = 961.56 for the cation [NaAl{OSi(O*t*Bu)$_3$}$_3$(DMAP)]$^+$. [Al{OSi(O*t*Bu)$_3$}$_3$(DMAP)] (**3**) was also characterized by IR-ATR spectroscopy. The spectrum shows an absorption band at 1630 cm^{-1}. A ring breathing mode of pyridine adsorbed at Lewis acidic centers are reported in this region.[14] Bands at comparable energies are also reported for other pyridine-derivatives coordinated at an aluminum centre,[15] such as for [(Cl)$_2$Al(η^2-O$_2$CPh)(4-Me-C$_5$NH$_4$)$_2$] (1627 cm^{-1})[15a] or [Et$_2$Al(η-O$_2$CC$_6$H$_4$-2-NH)AlEt$_2$(4-Me-C$_5$NH$_4$)] (1616 cm^{-1}).[15d] The coordinated Lewis base strongly enhances the thermal stability of compound **3,** as it shows no sign of decomposition at 90°C. The stability towards hydrolysis is also increased, as there is no indication of decomposition upon direct exposure to H$_2$O at room temperature.

In order to gain more information about the aforementioned unidentified aluminum species, DMAP was added after five minutes to a reaction mixture of HOSi(O*t*Bu)$_3$ and [Cp*Al]$_4$ (**1**) which was heated at 80°C. Comparison of the NMR spectra at room temperature before and after the DMAP addition showed that the signals corresponding to the unknown compound were still present after the addition of the Lewis base. The NMR data for **3** were also observed. Hence, DMAP did not react with the unknown aluminum compound, whereas the formation of **3** is likely due to a reaction of [Al(OSi(OtBu$_3$)$_3$] with DMAP.

Treatment of [Cp*Al]$_4$ (**1**) with HOSiPh$_3$ at 80°C in the presence of NEt$_3$ led to the precipitation of [HNEt$_3$][Al(OSiPh$_3$)$_4$] (**4**) and release of H$_2$ from the reaction solution. The conversion is complete after 10 minutes (Scheme 2). A stoichiometric amount of the amine with regard to the silanol is needed to avoid side reactions. Hydrolysis of **4** with water in THF occurred only in the presence of NEt$_3$ after heating to 60 °C for 15 hours yielding [HNEt$_3$][Al(OH)(OSiPh$_3$)$_3$] (**5**). This observation is in contrast to the reactivity reported for [Li(THF)$_4$][Al(OSiPh$_3$)$_4$],[16] which hydrolyses immediately upon treatment with H$_2$O to furnish [Al(OSiPh$_3$)$_3$(H$_2$O)]. In principle, the anion in **5** can also be regarded as the deprotonated form of the known compound [Al(OSiPh$_3$)$_3$(H$_2$O)].[17] Indeed, **5** can also be synthesized by addition of NEt$_3$ to [Al(OSiPh$_3$)$_3$(H$_2$O)] (Scheme 2).



Scheme 2. Synthesis of [HNEt$_3$][Al(OSiPh$_3$)$_4$] (**4**) and formation of [HNEt$_3$][Al(OH)(OSiPh$_3$)$_3$] (**5**).



Scheme 3. Formation of $[Al_7(OH)_9\{(OSi\mathit{i}Pr_2)_2O\}_6]$ (**6**).

ESI-MS studies of the alumosiloxanes **4** and **5** revealed signals for the cation (m/z = 102.13) and the anions $[Al(OSiPh_3)_4]^-$ (m/z = 1127.33) and $[Al(OH)(OSiPh_3)_3]^-$ (m/z = 869.26). No signal in the ^{1}H NMR spectrum could be detected for the ammonium protons or OH group in **4** or **5**. The ATR-IR spectrum of **5** shows weak broadened absorption bands at 3140 cm^{-1} and 3673 cm^{-1}, which can be attributed to the N–H and O–H units of separated ions, respectively,[18] and furthermore two broad absorption bands in the regions of 2000-2550 cm^{-1} and 2550-2760 cm^{-1} for the hydrogen bonding.[19] Since no such interaction occurs in **4**, its IR-ATR spectrum shows a more intense and less broadened absorption band corresponding to the N–H vibration at 3144 cm^{-1} and none of the other discussed features. The ^{27}Al NMR spectra of **4** (δ = 54.8 ppm) and **5** (δ = 59.8 ppm) each show a signal in the typical range for an Al center with tetrahedral coordination of oxygen atoms.[12a] Both signals differ in shape, and the spectrum of **4** shows a sharp signal with a line width of $\omega_{1/2} \approx 10$ Hz, while in contrast a broad singlet is detected for **5** ($\omega_{1/2} \approx 270$ Hz).[13] For comparison the ^{27}Al NMR spectrum of $[Li(THF)_4][Al(OSiPh_3)_4]$ was also measured and it exhibits a signal at δ = 54.9 ppm with a comparable line width to the resonance for **4**.[16] The structure of $[HNEt_3][Al(OH)(OSiPh_3)_3]$ (**5**) was determined by X-ray crystallography (Figure 1), whereas measurements of single crystals of $[HNEt_3][Al(OSiPh_3)_4]$ (**4**) revealed a severe disorder of the cations. The cation in **5** is hydrogen bonded to the oxygen atom of the hydroxyl group at the anion. The Al–OH bond (Al1–O4 1.772(1) Å) is elongated when compared to the distances of the three Al–OSi bonds (averaged 1.728(1) Å), which are close to the corresponding bond lengths in $[Li(THF)_4][Al(OSiPh_3)_4]$ (averaged 1.729(1) Å).[16] Such a difference in distances between Al–OSi and terminal Al–OH bonds at AlO_4 tetrahedra was also found for $[NMe_4]_4[Al_4O_{12}Si_4(OH)_8]$ (1.78(3) Å vs averaged 1.70(2) Å), but the latter compound does not exhibit an interaction between the cations and the hydroxyl groups.[20] Literature reveals only four published compounds characterized by X-ray crystallography which exhibit a terminal O_3Al–OH moiety.[21] The geometry index[22] derived from the bond angles for the aluminum atom of **5** (τ_4' = 0.96) is comparable to the one in the $[Al(OSiPh_3)_4]^-$ anion in $[Li(THF)_4][Al(OSiPh_3)_4]$ (τ_4' = 0.98), and the structure is close to an ideal tetrahedral one (τ_4' = 1).

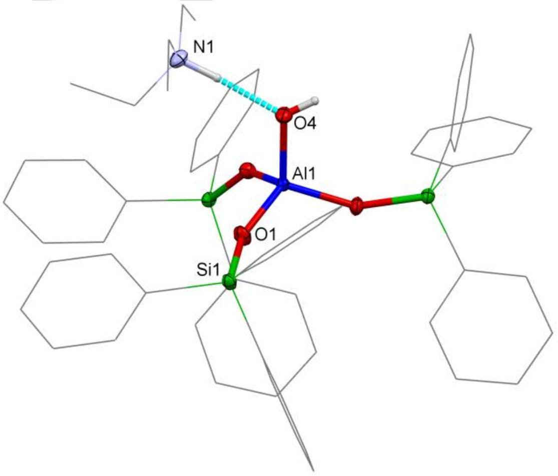


Figure 1. Structure of $[HNEt_3][Al(OH)(OSiPh_3)_3]$ (**5**). Thermal ellipsoids are drawn at 50% probability level, the hydrogen bond is depicted as a dashed line, and hydrogen atoms except for the oxygen and nitrogen bound ones were omitted for clarity. Selected distances [Å] and angles [°]: Al1–O1 1.7250(9); Al1–O4 1.7719(10); Si1–O1 1.6002(9); N1···O4 2.661(2); O1–Al1–O4 108.34(5).

We also investigated the reaction of [Cp*Al]$_4$ (**1**) with the disiloxanediol $\mathit{i}Pr_2Si(OH)(\mu\text{-}O)Si(OH)\mathit{i}Pr_2$ in the presence of water, which yielded the cluster $[Al_7(OH)_9\{(OSi\mathit{i}Pr_2)_2O\}_6]$ (**6**) after stirring at 95°C for two days (Scheme 3). The formation of H_2 and Cp*H was also detected via NMR spectroscopy. Crystals of **6**·toluene suitable for X-ray diffraction studies were obtained by slow cooling of a hot saturated toluene solution (Figure 2a). A representation of the oxygen coordinating polyhedra of the Al_7 core is shown in Figures 2b and 2c (for an animated rotating representation of the inner core, see the GIF file in the SI). The structure consists of an inner octahedral $Al(OH)_6$ core which is linked to three pairs of corner-shared AlO_4 tetrahedra via its hydroxyl groups. Additional OH groups link the six AlO_4 units to form the three pairs. The polyhedral view in Figure 2b reveals the C_3 symmetry of the aluminum core in **6**. The AlO_4 tetrahedra pairs can be transformed into each other by C_3 rotation.

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Furthermore, the AlO_4 pairs are connected *via* siloxanediolate ligands in such a way that three AlO_4 and three siloxanediolates form one moiety bound to a face of the inner $Al(OH)_6$ core. The six inner hydroxyl groups form hydrogen bonds to the oxygen atoms of six of the twelve Al–O–Si units in the cluster. The structure of **6** does formally not obey Loewensteins rule, which states that Al–O–Al linkages in zeolitic frameworks (i.e. between tetrahedral AlO_4 units) are avoided.[23] To the best of our knowledge there is only one comparable compound to **6** reported in the literature.[2b, 2d] $[Al_7(OH)_9\{(OSiPh_2)_2O\}_6]$ was characterized by X-ray crystallography and exhibits a similar Al–O–Si framework and three diethyl ether molecules hydrogen bonded to the outer hydroxyl groups, but no other analytical data were presented.

Single crystals of **6**·(3 THF·H_2O)$_{1.5}$ suitable for X-ray crystallography were formed by dissolving compound **6** in wet THF and subsequent slow evaporation of the solvent. The obtained structure is comparable to the one obtained from a toluene solution, but additionally the three outer hydroxyl groups form hydrogen bonds either to THF or alternatively to water molecules, which are additionally bound to two THF molecules via hydrogen bridges (Figure 2d and 2e). Refinement set the ratio of the independent moieties **6**·(THF)$_3$ and **6**·(H_2O·2THF)$_3$ to 55 : 45. Table 1 summarizes selected bond lengths of **6**·(3 THF·H_2O)$_{1.5}$ and **6**·toluene. While the central $Al(OH)_6$ part of both structures is virtually identical, certain bonds of the outer framework differ. A small but significant difference is observed for the Al–OH and Si–OAl bonds at the outer hydroxyl groups (Figure 2a: Al2–O7/Si6–O18; Figure2d/e: Al2–O2/Si1–O3, Table 1, entries 1-3). These bond lengths are shorter when the hydroxyl groups are involved in an intermolecular hydrogen bond in **6**·(3 THF·H_2O)$_{1.5}$ compared to **6**·toluene.

Table 1. *Selected bond lengths of **6**·toluene[a] and **6**·(3 THF·H_2O)$_{1.5}$.*

	***6**·toluene*	***6**·(3 THF·H_2O)$_{1.5}$*
*O_3**Al–O**(H)AlO_3 [Å]*	*1.823(1)*	*1.796(2)*
***Si–O**Al [Å]*	*1.620(1)*	*1.605(3)*
*[b]**Si–O**Al [Å]*	*1.634(1)*	*1.616(3)*
***Al1–O**(H)AlO_3 [Å]*	*1.893(1)*	*1.896(2)*
*O_3**Al–O**(H)Al1 [Å]*	*1.771(1)*	*1.769(2)*
***Al–O**Si [Å]*	*1.698(1)*	*1.699(3)*
*[b]**Al–O**Si [Å]*	*1.717(1)*	*1.722(3)*

[a] averaged bond length of chemically equivalent bonds, [b] with intramolecular hydrogen bond at the oxygen atom

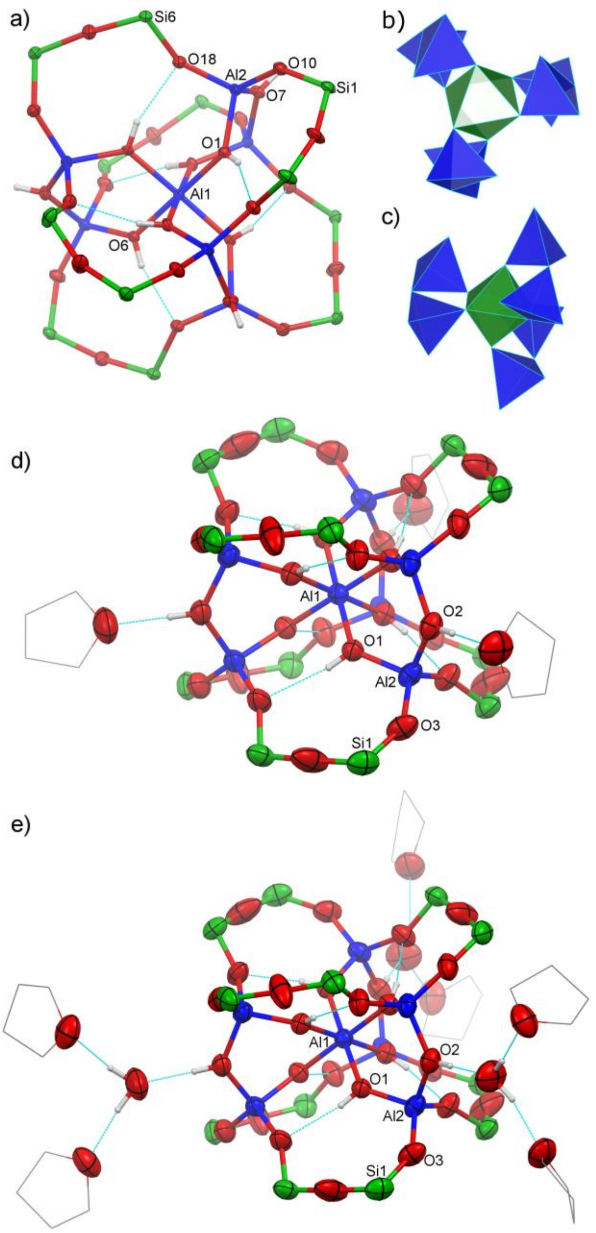

Figure 2. a) Structure of **6**·toluene, b) & c) polyhedral view of the AlO_4 (blue) and AlO_6 (green) units of **6,** d) Structures of **6**·(THF)$_3$ and e) **6**·(H_2O·2THF)$_3$. Thermal ellipsoids are set at 50% probability level, hydrogen bonds are depicted as lightblue dashed lines, the *i*Pr groups and hydrogen atoms except for those bound to an O atom were omitted for clarity. Selected bond lengths [Å] and angles [°]: **6**·toluene: Al1-O1 1.8912(18); Al2-O1 1.7748(18); Al2-O7 1.8249(19); Al2-O10 1.7002(18); Si1-O10 1.6229(19); O1-Al1-O6179.61(10); O1-Al2-O7 98.50(9); O1-Al2-O10 112.26(9); 6·(THF/H2O)3: Al1-O1 1.896(2); Al2-O1 1.769(2); Al2-O2 1.796(2); Al2-O3 1.699 (3); Si1-O3 1.605(3); O1-Al1-O1' 179.12(14); O1-Al2-O2 101.31(13); O1-Al2-O3 111.52(14).

The ATR-IR spectrum of compound **6** shows a broad absorption band between 3560 to 2850 cm^{-1}, which is assigned to OH bonds involved in hydrogen bonding.[18] The ^{29}Si NMR spectrum of $[Al_7(OH)_9\{(OSi\textit{i}Pr_2)_2O\}_6]$ (**6**) displays resonances for two chemically inequivalent silicon atoms at δ = -23.1 and -24.8 ppm. This is consistent with the presence of intramolecular hydrogen bonding of the inner hydroxyl groups, which only affects half of the silicon atoms. Likewise, the ^{1}H and ^{13}C NMR data for compound **6** show more than only one set of signals for the *i*Pr groups. The methyl groups at the *i*Pr moieties show eight signals at δ = 20–18 ppm, because of prochirality and the lower symmetry due to the hydrogen bonds. Similarly, the CH groups display four signals at δ = 17–15 ppm. The ^{1}H NMR spectrum reveals two signals at δ = 7.87 and 5.55 ppm with an integral ratio of 3:6 corresponding to the outer and inner hydroxyl groups, respectively. In the ^{27}Al NMR spectrum a signal at δ = 5.2 ppm of **6** was detected, which is a typical chemical shift for octahedral coordinated AlO_6 nuclei.[12a] No signals for the six outer AlO_4 units were identified in solution. However, in the ^{27}Al MAS NMR spectrum a good agreement of measured and fitted data for cluster **6** is achieved by fitting one signal at δ_{iso} = 5.32 ppm with a Gaussian line (linewidth ~500 Hz, i.e. almost negligible quadrupolar distortion) and one signal with a chemical shift of δ_{iso} = 61.7 ppm, a quadrupolar coupling of ν_Q = 1.175 MHz and a non-axial electric field gradient (η_Q = 1.00). The former signal is again caused by the octahedral coordinated aluminum atom, while the latter one corresponds to the AlO_4 units and its isotropic chemical shift appears in the expected range for fourfold oxygen coordinated aluminum atoms.[12a]

ESI-MS measurements of **6** reveal peaks at m/z = 1999.85 for the $[M\text{-}H]^{-}$ ion with the expected isotopic pattern (Figure 4 bottom). The formation of **6** was also monitored by ESI-MS and data were collected after solutions being stirred at 95°C for 12, 24, 36 and 48 hours (Figure 3). Negatively charged clusters with differing intensities at given reaction times were detected. The data after 12 hours revealed signals of smaller clusters such as $[Al(L)_2]^{-}$ or $[Al(LH)_2(L)]^{-}$ (L = $i\text{Pr}_2\text{Si(O)}(\mu\text{-O})\text{Si(O)}i\text{Pr}_2$), whereas after 24 and 36 hours the intensity of signals with larger m/z ($[Al_2(LH)_2(L)_2(OH)]^{-}$, $[Al_3(L)_4(OH)_2]^{-}$, $[Al_6(OH)_6(L)_6\text{-H}]^{-}$) increased. After a reaction time of 48 hours, the most intense signal corresponds to $[Al_7(OH)_9\{(OSi\textit{i}Pr_2)_2O\}_6\text{–H}]^{-}$ (**6**–H^{+}). Of special interest is the signal at m/z = 1921.84. The mass and isotopic pattern fits to $[Al_6(OH)_5(O)\{(OSi(\textit{i}Pr)_2)_2O\}_6]^{-}$ and differs to $[Al_7(OH)_9\{(OSi\textit{i}Pr_2)_2O\}_6]$ (**6**) by the mass of one $Al(OH)_3$ unit and one proton. The signal is already observed after 12 hours reaction time and increases in intensity over time, until its corresponding anion presumably gets consumed, forming **6**. When the reaction solution was analyzed by ^{1}H NMR spectroscopy after 24 hours, several singlets in the region of δ = 10–4 ppm were detected. These signals are likely caused by aluminum hydroxyl groups of various intermediate clusters, but they could not be assigned further.

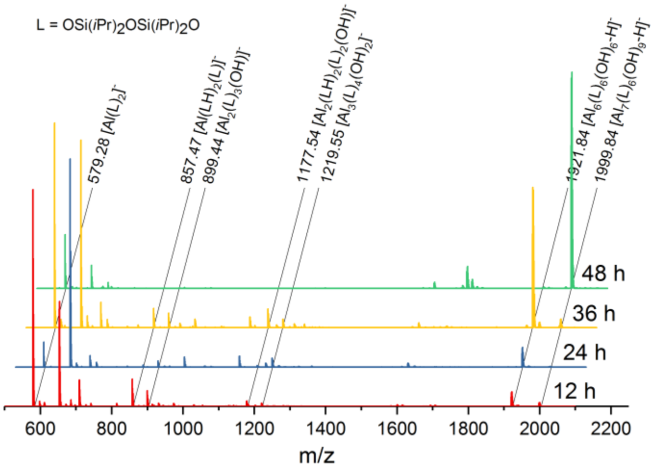

Figure 3. ESI-MS data of reaction solutions for the synthesis of **6** after different reaction times (see Figure S4 in ESI for bigger picture).

To investigate how cluster **6** interacts with water, **6** was dissolved in THF and an excess of ^{18}O enriched water was added to the solution. The ESI-MS data measured after one week at room temperature show peaks at m/z = 1999.84, 2001.84, 2003.84 and 2005.84 for $[Al_7(OH)_{9\text{-}x}(^{18}OH)_x\{(OSi\textit{i}Pr_2)_2O\}_6]$ (x = 0-3) (Figure 4), which revealed the incorporation of up to three ^{18}O atoms, presumably by exchange of hydroxyl groups. The reaction solution was then exposed to air. Subsequent ESI-MS measurements after roughly one and three weeks showed a decrease of peak intensity for clusters with labeled oxygen atoms (Table 2). Obviously, the ambient conditions led to exchange reaction with unlabeled air moisture. When D_2O was added to a [D$_8$]THF solution of **6**, ^{1}H NMR measurements showed a decrease in intensity of the signal in the ^{1}H NMR spectrum for the outer hydroxyl groups (see SI). The experimental data therefore suggest, that only the outer hydroxyl groups are exchanged in the presence of water. In a separate experiment, **6** was exposed to an excess of water in [D$_8$]THF and the reaction solution was monitored by ^{1}H NMR spectroscopy, revealing partial decomposition over the course of ten days.

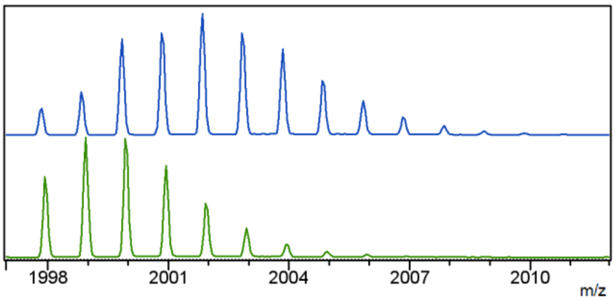

Figure 4. ESI-MS spectra of **6** before (bottom, green) and one week after treatment with $H_2{}^{18}O$ (top, blue).

Table 2. Percentage of incorporated ^{18}O atoms of a THF solution of **6** after different times.

Nr. of ^{18}O	1 week, inert	5 days later, air	21 days later, air
0	26 %	87 %	93 %
1	45 %	13 %	7 %
2	24 %	–	–
3	5%	–	–

Calculations on the exchange mechanism of OH bridges between two AlO_6 moieties with solvent water were performed for the Al_{13}-ε-Keggin-ion by Rustad and Casey.[24] According to those calculations, the first step involves a cleavage of the Al–O bonds of both aluminum atoms to the bulk structure, which results in five-fold coordinated aluminum atoms. This is followed by the coordination of solvent water at both Al atoms. Since compound **6** shows tetrahedral geometry at the six outer aluminum atoms, such a mechanism is unlikely, because it would lead to at least one intermediate AlO_3 moiety. Therefore, an associative-type mechanism appears more plausible instead.

Addition of 20 Eq. NEt_3 to a solution of cluster **6** in [D$_8$]THF led exclusively to the deprotonation of the outer hydroxyl groups, as revealed by the disappearance of their corresponding peak in the ^1H NMR spectrum. The $[HNEt_3]^+$ cation is likely hydrogen bound to the now deprotonated hydroxyl-bridge, in a similar manner as in compound **5**. An increase of the temperature to 60 °C for three days did not lead to any deprotonation of the inner hydroxyl groups nor to decomposition. Removal of all volatiles *in vacuo* restored the cluster **6** by reprotonation.

When 1,8-bis(dimethylamino)naphthalene (‘proton-sponge’) was used, no deprotonation was detected in [D$_8$]THF after one day at room temperature. However, when deuterated benzene was used as solvent, deprotonation of the outer hydroxyl groups was detected over the course of one day at room temperature. When compound **6** was exposed to KOH, $LiOH\cdot H_2O$, or acetic acid, decomposition takes place, and the ^1H NMR spectra revealed the formation of $i\mathrm{Pr_2Si(OH)(\mu\text{-}O)Si(OH)}i\mathrm{Pr_2}$. As mentioned above, the cluster **6** showed partial decomposition upon exposure to an excess of water in [D$_8$]THF over the course of ten days. This decomposition was considerably faster when six equivalents of NEt_3 (relating to **6**) were added and in that case the decomposition was nearly completed after ten days (see SI). Decomposition reactions outside of a certain pH range are not surprising, considering also the amphoteric nature of $Al(OH)_3$. Accordingly, other aluminum hydroxide clusters are also only stable in certain pH regions.[25]

Conclusions

The reaction of $[Cp^*Al]_4$ (**1**) towards various silanols revealed that the subvalent Al atom is able to react with the OH moiety of silanols. This led to the generation of $[\mathrm{Al\{OSi(O}t\mathrm{Bu)_3\}_3(DMAP)}]$ (**3**), $[HNEt_3][Al(OSiPh_3)_4]$ (**4**) and to $[\mathrm{Al_7(OH)_9\{(OSi}i\mathrm{Pr_2)_2O\}_6}]$ (**6**), when for the latter a siloxanediol was used. The reaction of **1** towards silanols gave, therefore, products which are accessible from Al(III) staring compounds. Use of less than three equivalents of silanols per aluminum atom did not change the type of product, only its yield. This is in contrast to the known reactivity of $[(\mathrm{NacNac})^{\mathrm{Dipp}}\mathrm{Al}]$.[10] Hydrolysis of **4** yielded $[HNEt_3][Al(OH)(OSiPh_3)_3]$ (**5**), which exhibits a rare example of a terminal hydroxyl group at a molecular aluminum compound. The compound is stabilized by a hydrogen bond. The cluster $[\mathrm{Al_7(OH)_9\{(OSi}i\mathrm{Pr_2)_2O\}_6}]$ (**6**) features formally a Loewenstein-forbidden framework. NMR and MS data reveal an exchange of its outer hydroxyl groups in the presence of water, which is remarkable and unprecedented.

Experimental Section

General Procedures

The SI contains the reports for the tested reactions with **6**, as well as selected spectra (^1H, ^{27}Al NMR, IR, ESI-MS) and tables (XRD, ESI-MS).

All manipulations were carried out under an atmosphere of argon using standard Schlenk techniques or in an argon-filled glovebox (MBRAUN). THF, toluene, pentane and benzene were dried over Solvona® and then distilled, degassed three times by freeze-pump-thaw procedure and stored over activated 3 Å molecular sieve. $[Cp^*Al]_4$[26] (**1**) and $i\mathrm{Pr_2Si(OH)(\mu\text{-}O)Si(OH)}i\mathrm{Pr_2}$[27] were prepared according to literature procedure. Deionized water was degassed three times by freeze-pump-thaw procedure. The NMR spectra were recorded at a Bruker AVANCE II 400, AVANCE II 500 NMR or a Bruker DPX 300 spectrometer, all at 25 °C, except if otherwise noted. The ^1H NMR chemical shifts were referenced to residual [D$_7$]THF at $\delta = 1.72$ ppm or C_6D_5H at $\delta = 7.16$ ppm and the ^{13}C NMR chemical shifts were referenced to [D$_8$]THF at $\delta = 25.31$ ppm or C_6D_6 at $\delta = 128.06$ ppm. The ^{29}Si NMR spectra were referenced externally to TMS at $\delta = 0.0$ ppm. $^{27}Al\{^1H\}$ NMR spectra were referenced externally to $AlCl_3$ in D_2O at $\delta = 0.00$ ppm. ^{27}Al MAS NMR spectra have been recorded on a Bruker AVANCE400 spectrometer using a 2.5 mm MAS probe. The resonance frequency has been 104.6MHz for ^{27}Al. The MAS NMR spectra have been fitted by the program DMFit.[28] Microanalyses were performed with a HEKAtech Euro EA Elemental Analyzer. Infrared spectra were recorded at a Bruker Vertex 70 spectrometer that was equipped with an ATR unit (diamond).

Crystal Structure Determination

Diffraction data were collected on a Bruker D8 Venture spectrometer at -173 °C using Mo-K$_\alpha$ (λ = 0.71073 Å) radiation. Multi-scan absorption corrections using SADABS[29] were applied on the data. The structures were solved by intrinsic phasing (SHELXT-2013)[30] and refined with the full matrix least squares method on F² (SHELXL-2014, via ShelXle[31]). The hydrogen atoms were placed at calculated positions and refined by using a riding model, except for the protons on the hydroxyl groups in **5** and **6** as well as the amine bound proton in **5**. These were found in the electron density difference fourier map and refined freely for **5** or refined with DFIX

10.1002/ejic.201800564

restraints for **6**·toluene and **6**·(3 THF·H_2O)$_{1.5}$. Due to strong disorder of the iso-propyl groups in the solid structure of **6**, the data resolution quality was limited and in **6**·(3 THF·H_2O)$_{1.5}$ one carbon atom could not be refined anisotropically, while in **6**·toluene one carbon atom has an elongated ADP shape, but could not be better modelled. Similar behavior was also observed in the outer residues of the only published comparable structure $[Al_7(OH)_9\{(OSiPh_2)_2O\}_6]$ (CCDC 971744). As these problems occur in the outer sphere of the molecule, it is only a minor influence on the central Al–O–Si framework. The crystallographic data are summarized in Table S1 in the SI. Supplementary crystallographic data for this paper have been uploaded to the CCDC with the access numbers 1825941 for **6**·(3 THF·H_2O)$_{1.5}$, 1825942 for **6**·toluene and 1825943 for **5**.

Reaction of $[Cp^*Al]_4$ (1) and $HOSi(OtBu)_3$

$[Cp^*Al]_4$ (**1**) (5.2 mg, 0.0080 mmol) was dissolved in 0.4 mL C_6D_6 and in a second Schlenk tube $HOSi(OtBu)_3$ (16.6 mg, 0.0628 mmol) was dissolved in 0.6 mL C_6D_6. Both solutions were heated to 80 °C and after stirring for 2 minutes, the hot $HOSi(O\textit{t}Bu)_3$ solution was quickly transferred into the solution of $[Cp^*Al]_4$ (**1**) via a cannula, upon which a gas evolution occured. After stirring for 5 minutes, the flask was immediately cooled down to room temperature with a cold water bath and the solution was transferred into a NMR tube. Signals are assigned to $[Al(OSi(O\textit{t}Bu)_3)_3]$ (*A*), $HOSi(O\textit{t}Bu)_3$ (*S*), Cp*H (*C*) or $[Cp^*Al]_4$ (**1**) or belong to yet unidentified species (*X*).

^1H NMR (500.1 MHz, C_6D_6, 25 °C): δ = 4.47 (s, H_2), 2.42 (q, $^3J(H,H)$ = 8 Hz, *C*), 1.92 (s, *X*), 1.90 (s, ***1***), 1.81 (s, *C*), 1.75 (s, *C*), 1.50 (s, tBu, *A*), 1.39 (s, *S*), 1.00 (d, $^3J(H,H)$ = 8 Hz, *C*); ^{13}C NMR (125.8 MHz, C_6D_6, 25 °C): δ = 137.7 (*C*), 134.6 (*C*), 114.1 (*X*), 72.8 (*A*), 72.7 (*X*), 72.5 (*X*), 72.1 (*X*), 52.0 (*C*), 32.3 (*X*), 32.2 (*X*), 32.1 (*X*), 32.0 (*A*), 31.6 (*S*), 14.3 (*C*), 11.8 (*C*), 11.3 (*C*), 10.9 (Cp*, *X*) ppm; $^{27}Al\{^1H\}$ NMR (130.3 MHz, C_6D_6, 25 °C): δ = -58.2 ($\omega \approx$ 340 Hz, *X*), -79.4 ($\omega \approx$ 110 Hz, ***1***) ppm; ^1H, ^{29}Si HMBC (500.1/99.4 MHz, C_6D_6, 25 °C): δ = 1.50/-95 (*A*), 1.39/-90 (*S*) ppm.

Synthesis of $[Al\{OSi(OtBu)_3\}_3(DMAP)]$ (3)

$[Cp^*Al]_4$ (**1**) (100 mg, 0.154 mmol), $HOSi(OtBu)_3$ (490 mg, 1.85 mmol) and 4-dimethylaminopyridine (DMAP) (75 mg, 0.61 mmol) were dissolved in 10 mL toluene. The mixture was heated to 80 °C and after stirring for 5 minutes, gas evolution stopped and decolorization of the solution had occured. After stirring for 10 minutes, heating was stopped and the solution was brought to room temperature. All volatiles were removed in vacuo and the resulting colorless solid was dissolved in 0.5 mL pentane. After filtration, the solution was stored at − 40 °C for 3 days to obtain colorless crystals of $(DMAP)Al(OSi(O\textit{t}Bu)_3)_3$ (**3**) (249 mg, 265 mmol, 43%). The compound is highly soluble in apolar solvents like benzene and pentane, poorly soluble in ethers like diethyl ether and THF, but is insoluble in water.

^1H NMR (300.1 MHz, C_6D_6, 25 °C): δ = 9.00 (d, $^3J(H,H)$ = 7 Hz, 2 H, *o*-DMAP), 6.20 (d, $^3J(H,H)$ = 7 Hz, 2H, *m*-DMAP), 1.88 (s, 6H, $N(CH_3)_2$), 1.59 (s, 81 H, *t*Bu) ppm; ^{13}C NMR (75.5 MHz, C_6D_6, 25 °C): δ = 155.7 (DMAP), 148.6 (DMAP), 105.6 (DMAP), 71.7 ($OC(CH_3)_3$, 38.0 ($N(CH_3)_2$), 32.3 ($OC(CH_3)_3$) ppm; ^{27}Al MAS NMR (104.3 MHz, neat, 25 °C, ν_{rot} = 20 kHz): δ = 55.0 (ν_Q = 1.669 MHz, η_Q = 0.05) ppm; ^1H, ^{29}Si NMR HMBC)(500.1/99.4 MHz, C_6D_6, 25 °C): δ = 1.59/-97 ppm; IR (neat, ATR/Diamond): $\tilde{\nu}$ = 405 (w), 430 (w), 472 (m), 480 (w), 507 (w), 514 (w), 569 (w), 583 (w), 659 (w), 698 (m), 769 (w), 826 (m), 1021 (s), 1042 (s), 1072 (m), 1134 (w), 1193 (m), 1238 (m), 1361 (m), 1386 (w), 1459 (w), 1473 (w), 1551 (w), 1630 (m), 2871 (w), 2906 (w), 2929 (w), 2971 (m) cm^{-1}; ESI-MS: *m/z* (%) = 961.56 (100) [*M+Na*$^+$], 839.47 (47) [$M-(C_7H_{10}N_2)+Na^+$].

Synthesis of $[HNEt_3][Al(OSiPh_3)_4]$ (4)

NEt_3 (0.25 mL, 1.8 mmol) and 8 mL toluene were added to a mixture of $[Cp^*Al]_4$ (65 mg, 0.10 mmol) and $HOSiPh_3$ (446 mg, 1.61 mmol). A bubbler was connected and the solution stirred at 80 °C for 10 minutes. After filtration, the residue was washed two times with 2 mL toluene. After dissolving the residue in 5 mL THF and filtration, 7 mL of pentane were added to the solution, whereby a colorless solid precipitated. The solvent was then removed by filtration and the precipitate dried *in vacuo*, yielding $[HNEt_3][Al(OSiPh_3)_4]$ (**4**) as a colorless solid (354 mg, 0.284 mmol, 71% yield).

^1H NMR (400.1 MHz, $[D_8]$THF, 25 °C): δ = 7.57 (d, $^3J(H,H)$ = 8 Hz, 24 H, *o*-Ar), 7.04 (t, $^3J(H,H)$ = 8 Hz, 12 H, *p*-Ar), 6.80 (t, $^3J(H,H)$ = 8 Hz, 24 H, *m*-Ar), 2.80 (q, $^3J(H,H)$ = 7 Hz, 6 H, NCH_2), 0.96 (t, $^3J(H,H)$ = 7 Hz, 9 H, NCH_2CH_3) ppm; ^{13}C NMR (100.6 MHz, $[D_8]$THF, 25 °C): δ = 142.4, 136.4, 128.0, 127.5, 47.6, 9.4 ppm; $^{27}Al\{^1H\}$ NMR (104.3 MHz, $[D_8]$THF, 25 °C): δ = 54.8 ($\omega \approx$ 10 Hz) ppm; ^1H, ^{29}Si HMBC (400.1/79.5 MHz, $[D_8]$THF, 25 °C): δ = 7.57/-30 ppm; IR (neat, ATR/Diamond): $\tilde{\nu}$ = 430 (m), 443 (m), 465 (m), 516 (s), 613 (w), 631 (w), 698 (s), 997 (w), 1024 (m), 1061 (m), 1108 (s), 1427 (w), 2996 (w), 3044 (w), 3063 (w), 3144 (w) cm^{-1}; ESI-MS: *m/z* (%) = 1127.33 (100) [$Al(OSi(C_6H_5)_3)_4^-$] (negative mode), 102.13 (100) [$HN(C_2H_5)_3^+$] (positive mode).

Synthesis of $[HNEt_3][Al(OH)(OSiPh_3)_3]$ (5)

a) H_2O (1.2 µL, 0.067 mmol), NEt_3 (0.02 mL, 0.1 mmol), and 2.5 mL THF were added to $[HNEt_3][Al(OSiPh_3)_4]$ (**4**) (77 mg, 0.063 mmol) in a Schlenk tube. The suspension was stirred at 60 °C for 15 hours. After removal of the solvent in vacuo, the colorless sticky residue was extracted with 15 mL diethyl ether. The solution was then concentrated to about 2 mL and cooled down with an ice bath, which lead to a colorless precipitate. The supernatant solution was filtered off, the residue was washed two times with 0.5 mL cold diethyl ether and dissolved in 1 mL THF. Storing the solution in the freezer at -26 °C for 3 days yielded $[HNEt_3][Al(OH)(OSiPh_3)_3]$ (**5**) as colorless crystals (81 mg, 0.040 mmol, 43% yield). Crystals suitable for XRD measurements were obtained by evaporation of a concentrated THF solution exposed to air.

b) After dissolving $[Al(OSiPh_3)_3(H_2O)]$ (176 mg, 0.202 mmol) in 4 mL diethyl ether, NEt_3 (0.04 mL, 0.3 mmol) was added, and the mixture was afterwards stirred for two hours. The flask was cooled with an ice bath and the reaction mixture after 20 minutes filtered. The filtrate was dried *in vacuo*. $[HNEt_3][Al(OH)(OSiPh_3)_3]$ (**5**) (143 mg, 0.147 mmol, 73%) was obtained as a colorless powder.

^1H NMR (300.1 MHz, $[D_8]$THF, 25 °C): δ = 7.59 (d, $^3J(H,H)$ = 7 Hz, 18 H, *o*-Ar), 7.16 (t, $^3J(H,H)$ = 7 Hz, 9 H, *p*-Ar), 7.00 (t, $^3J(H,H)$ = 7 Hz, 18 H, *m*-Ar), 2.49 (q, $^3J(H,H)$ = 7 Hz, 6 H, NCH_2), 0.83 (t, $^3J(H,H)$ = 7 Hz, 9 H, NCH_2CH_3) ppm; ^{13}C NMR (75.5 MHz, $[D_8]$THF, 25 °C): δ = 141.3, 136.2, 128.9, 127.8, 45.7, 8.9 ppm; $^{27}Al\{^1H\}$ NMR (104.3 MHz, $[D_8]$THF, 25 °C): δ = 59.2 ($\omega \approx$ 270 Hz) ppm; ^1H, ^{29}Si HMBC (400.1/79.5 MHz, $[D_8]$THF, 25 °C): δ = 7.59/-27.6 ppm; IR (neat, ATR/Diamond) $\tilde{\nu}$ = 430 (m), 445 (m), 473 (m), 507 (s), 514 (s), 617 (w), 636 (w), 669 (m), 698 (s), 743 (m), 997 (w), 1023 (m), 1045 (m), 1107 (m), 1427 (m), 2000-2550 (br), 2550-2760 (br), 2997 (w), 3020 (w), 3045 (w), 3064 (w), 3140 (w), 3673 (w) cm^{-1}; ESI-MS: *m/z* (%) = 869.26 (100) [$Al(OH)(OSi(C_6H_5)_3)_3^-$] (negative mode), 102.13 (100) [$HN(C_2H_5)_3^+$] (positive mode).

Synthesis of [$Al_7(OH)_9\{(OSi\mathit{i}Pr_2)_2O\}_6$] (6)

10mL toluene and 0.1 mL THF were added to a mixture of [Cp^*Al]$_4$ (65 mg, 0.10 mmol) and *i*$Pr_2Si(OH)(\mu\text{-}O)Si(OH)$*i*$Pr_2$ (96 mg, 0.34 mmol) in a Schlenk flask. Then H_2O (10 µL, 0.56 mmol) was added and the reaction solution was stirred at 95 °C for 48 hours. Afterwards all volatiles were removed *in vacuo* and the colorless solid was washed two times with 2 mL of cold pentane. After drying *in vacuo*, [$Al_7(OH)_9\{(OSi\mathit{i}Pr_2)_2O\}_6$] (**6**) was obtained as a colorless solid (81 mg, 0.040 mmol, 71% yield). Colorless crystals of **6**·toluene suitable for XRD were obtained by storing a saturated toluene solution of **6** in the freezer (-26 °C) for 3 days. Colorless crystals of **6**·(H_2O· THF)$_{1.5}$ suitable for XRD were obtained by dissolving **6** in a wet THF solution and slow evaporation at ambient conditions.

^1H NMR (400.1 MHz, [D_8]THF, 25 °C): δ = 7.87 (s, 3 H, OH), 5.55 (s, 6 H, OH), 1.21-0.79 (m, *i*Pr) ppm; ^{13}C NMR (75.5 MHz, [D_8]THF, 25 °C): δ = 19.6, 19.4, 19.1, 19.0, 18.9, 18.6, 18.6, 18.4, 16.6, 16.4, 15.7, 15.3 ppm; $^{27}Al\{^1H\}$ NMR (104.3 MHz, [D_8]THF, 25 °C): δ = 5.2 ($\omega \approx$ 15 Hz, central $Al(OH)_6$ unit) ppm; ^{29}Si NMR (79.5 MHz, [D_8]THF, 50 °C): δ = -23.0, -24.6 ppm; ^{27}Al MAS NMR (104.3 MHz, neat, 25 °C, ν_{rot} = 25 kHz): δ = 61.7 (ν_Q = 1.175 MHz, η_Q = 1.00), 5.3 ppm; IR (neat, ATR/Diamond) $\tilde{\nu}$ = 3560-2850 (br, OH), 2943 (m), 2891 (m), 2865 (m), 1463 (m), 1385 (w), 1365 (w), 1245 (w), 1162 (w), 1085 (m), 1033 (s), 985 (s), 884 (s), 717 (m), 692 (s), 642 (m), 609 (m), 502 (m), 462 (m), 441 (m), 405 (m) cm^{-1}; ESI-MS: *m/z* (%) = 1999.85 (100) [$M\text{-}H^+$]; elemental analysis calcd (%) for $C_{72}H_{177}Al_7O_{27}Si_{12}$: C 43.22, H 8.92; found: C 43.88, H 8.95.

Acknowledgements

We thank Dr. I. Pryjomska-Ray for ESI-MS measurements and Dr. G. Scholz for MAS NMR measurements and helpful discussions. We gratefully acknowledge the Collaborative Research Centre SFB 1109 funded by the Deutsche Forschungsgemeinschaft (DFG) for financial support.

Keywords: aluminates • Cp*Al • hydrolysis • alumosiloxanes • silanols •

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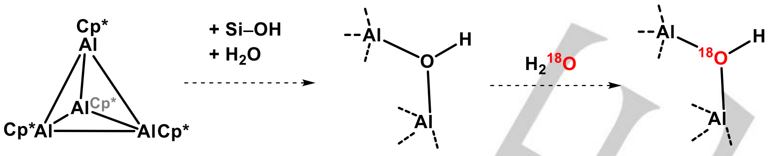

The reaction of [Cp*Al]$_4$ with various silanols was studied. Treatment with a siloxanediol gave [Al$_7$(OH)$_9${(OSi*i*Pr$_2$)$_2$O}$_6$] (**6**), which exhibits OH exchange reactions of the outer hydroxide groups in the presence of $H_2{}^{18}O$.

*Philipp Wittwer, Adrian Stelzer, Thomas Braun**

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Reactivity of Cp*Al Towards Silanols: Formation and Hydrolysis of Alumosiloxanes