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Controlled hydrolysis of AlMe₃ to tetramethylalumoxane and a new look at incipient adducts with water†‡

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We present an efficient route to tetramethylalumoxane by the controlled hydrolysis of AlMe₃ in the presence of pyridine. The AlMe₃(pyr) hydrolysis by 0.5 and 1 equiv. of H₂O has been followed with real-time ¹H NMR. Based on high-level quantum-chemical calculations, we conclude that hypervalent, pentacoordinate aluminium species are critical in the first steps of hydrolysis.

Alumoxanes belong to the family of organometallics comprising an Al–O–Al unit with pendant organic substituents.^{1,2} The chemistry of alumoxanes has a rich history; initial studies trace back to the end of the 1950s.¹ They have attracted attention as highly active catalysts in the polymerisation of a wide range of organic monomers.^{2,3} In particular, methylalumoxane (MAO) is an effective cocatalyst in olefin polymerisation.^{4–6} Interestingly, many structural models have been proposed for MAO,^{7–15} and only very recently, its molecular structure was crystallographically documented as a discrete sheet cluster.¹⁶

The hydrolytic approach seems conceptually the simplest way to alumoxanes. However, all attempts for the initial three decades have focused on hydrolysis reactions involving homoleptic short-chain-alkyl aluminates.^{1,17} Although various methods of introducing water have been used to lower the rate of the hydrolysis reaction (e.g., using hydrated salts¹⁸ or the dropwise addition of water at low temperatures^{18,19}), complexity and limited stability of the resulting species have prevented their detailed structural investigations. Moreover, the hydrolysis of short-chain-alkyl homoleptic aluminates has been monitored using

variable-temperature ¹H NMR spectroscopy,^{18–21} mass spectrometry,^{22,23} and the identity of intermediates has been supported by quantum-chemical calculations.^{22–27} Simultaneously, various alternative non-hydrolytic approaches to alumoxanes have also been used, such as the decomposition of aluminium alkoxides,²⁸ reactions of AlR₃ compounds with carboxylic acids^{11,29–31} or R₂BOH,^{32–35} and other methods.^{36–40} Strikingly, only the phthalic acid alkylation has paved the way for isolating the tetramethylalumoxane moieties arranged as nodes in the bipyridine-linked polymeric chains.³⁰ A milestone in the hydrolytic synthesis of molecular alkylalumoxanes has been achieved by Barron *et al.*, employing sterically demanding *tert*-butylaluminium compounds. The authors have isolated and structurally characterised the first tetraalkylalumoxane, [Bu₂AlOAlBu₂]₂, its adduct with pyridine (py), and a series of *tert*-butylaluminium hydroxides, (oxide)hydroxides and [(^tBuAlO)_n] cages.^{41–46}

Further studies on the controlled hydrolysis of alkylaluminium compounds are highly desired and may lead to the accelerated development of well-defined alumoxanes. In the course of our systematic studies on the controlled hydrolysis of various organometallics to desired molecular complexes and functional materials,^{47–50} herein we present an efficient route to a well-defined tetramethylalumoxane by the controlled hydrolysis of AlMe₃ in the presence of pyridine derivatives as strong coordinating ligands. To gain additional insight into the AlMe₃ hydrolysis, we have examined the reaction system by variable-temperature ¹H NMR spectroscopy along with theoretical calculations of the incipient AlMe₃·H₂O adducts in the presence of donor molecules.

Homoleptic aluminium alkyls readily form four-coordinate Lewis acid–base adducts with neutral donor ligands, which reduces their reactivity.⁵¹ Thus, we chose a series of [AlMe₃L] adducts as model precursors, where L = THF, pyrrolidine, pyridine (py) and *p*-dimethylaminopyridine (dmap). The controlled hydrolysis of [AlMe₃(L)] (1, L = py, dmap) by 0.5 equiv. of H₂O was performed in a THF/hexane mixture, starting at –78 °C to ambient temperature (Fig. 1). Subsequent crystallisation led to

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‡ Electronic supplementary information (ESI) available: Experimental section, XRD, NMR, IR, data, computational details. CCDC 2352082 and 2369858. For ESI and crystallographic data in CIF or other electronic format see DOI: <https://doi.org/10.1039/d4cc03672g>



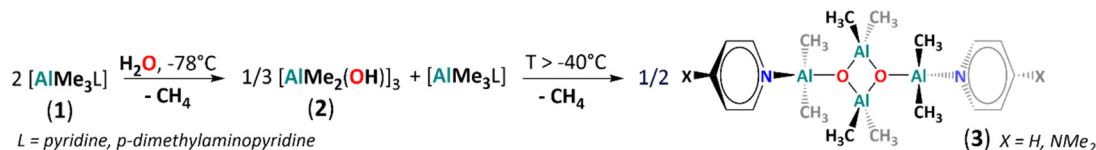


Fig. 1 Synthesis of $[\text{AlMe}_2(\text{pyr})(\mu_3\text{-O})\text{AlMe}_2]_2$ (3) and $[\text{AlMe}_2(\text{dmap})(\mu_3\text{-O})\text{AlMe}_2]_2$ (4).

the colourless crystals of tetramethylalumoxane adducts $[\text{AlMe}_2(\text{L})(\mu_3\text{-O})\text{AlMe}_2]_2$ with py (3) and dmap (4), isolated in high yields. In contrast, using THF or pyrrolidine as donor ligands, analogous reactions were unselective and led to viscous mixtures of products according to ^1H NMR spectra (Fig. S10 and S11, ESI†). Compounds 3 and 4 are isostructural and crystallise as a dimer with C_i symmetry based on an essentially planar $[\text{Al}_4(\mu_3\text{-O})_2]$ core (Fig. 2 and Fig. S23, ESI†). The Al centres are four-coordinate, adopting distorted tetrahedral geometries, and the py/dmap ligands are coordinated to the exocyclic Al1 centres. Similarly to other reported $[\text{Al}_4(\mu_3\text{-O})_2]$ cores,^{30,41} the exocyclic Al–O bonds are slightly shorter than the endocyclic ones (by *ca.* 0.05–0.1 Å). Both compounds are essentially isostructural to the asymmetric unit of a tetramethylalumoxane-based coordination polymer $[\text{AlMe}_2(\mu_3\text{-O})\text{AlMe}_2(1,2\text{-bis}(4\text{-pyridyl})\text{ethane})]_n$.³⁰ The ^1H NMR spectra of 3 and 4 confirm the presence of two distinct methyl groups and py/dmap moiety in the 2 : 2 : 1 ratio (Fig. S6 and S8, ESI†). Using 1D transient NOE and $^1\text{H}/^{13}\text{C}$ HSQC experiments for 3, we assigned the $^1\text{H}/^{13}\text{C}$ NMR chemical shifts at $-0.79/-9.8$ ppm to the exocyclic Al-bonded methyl groups and the resonances at $-1.05/-7.6$ ppm to the endocyclic Al-bonded methyl moieties (Fig. S6, S7, S11 and S12 and Table S2, ESI†). Despite two independent Al centres in 3 and 4, we have observed only one broad resonance in the ^{27}Al spectrum at *ca.* 150 ppm, typical for the four-coordinate Al centres.⁵² The dimeric form of 3 and 4 in THF solution was proved by DOSY (Table S1 and Fig. S14 and S15, ESI†) and ESI-MS (Fig. S18 and S19, ESI†).

To gain a deeper understanding of the AlMe_3 hydrolysis, we examined the title reaction system (with py) by variable-temperature ^1H NMR experiments. The ^1H NMR-tracked hydrolysis of 1 was carried out with one and two equiv. of H_2O . (Fig. 3) The reaction progress was monitored from 193 K to 298 K with a temperature interval of 10 K. The parent solution

of 1 in $\text{THF-}d_8$ exhibits a single resonance of the Al–Me protons at -0.87 ppm, and its chemical shift is only slightly different from that for a solution of AlMe_3 in $\text{THF-}d_8$ (-0.95 ppm, Fig. S1 and S2, ESI†), suggesting a dynamic equilibrium between 1 and a $[\text{AlMe}_3(\text{THF-}d_8)]$ adduct. For the reaction at 0.5 equiv. of H_2O per 1, new signals characteristic of Al–Me protons (-0.95 ppm) and an Al–OH proton (7.98 ppm) immediately appeared in the spectrum after the addition of H_2O at 193 K. Their integrals ratio of 6 : 1 indicates the formation of a $[\text{AlMe}_2\text{OH}]$ (2) species with concomitant liberation of methane (signal at 0.18 ppm). At this temperature, the formed hydroxide compound 2 does not interact with the excessive amount of 1, which chemical shift remains intact. Notably, no signals indicating the presence of a labile $\text{AlMe}_3\text{-OH}_2$ adduct were observed. In the temperature range of 193–233 K, the reaction system is intact, and only the $-\text{OH}$ proton resonance gradually shifts to 7.50 ppm at 233 K. Above 233 K, the resonances of the final product 3 appear and gradually grow with temperature gain to 298 K with simultaneous expiring of the signals from 1 and 3. Notably, the Al–Me resonance of 2 vanishes faster than that from 1, suggesting a side reaction of 2 at 298 K.

In the case of the equimolar $\text{AlMe}_3/\text{H}_2\text{O}/\text{py}$ reaction system, the ^1H NMR spectra demonstrate that the addition of H_2O to a $\text{THF-}d_8$ solution of 1 at 193 K affords effectively the hydroxide compound 2 with concomitant disappearance of 1. Interestingly, initially, the low-intensity resonance at -1.03 was observed at 193 K, which could be related to the formation of an unstable adduct of AlMe_3 with H_2O ; this signal relatively quickly dissipates as a result of leaving the sample at this temperature (for detailed discussion *vide infra*). Notably, no new signals were observed with the temperature gain. Instead, a gradual expiration of the resonances of 2 takes place at 298 K due to an oligomerisation of the hydroxide species to an amorphous solid (Fig. S12, ESI†).

In order to determine the nature of the hydroxide, DOSY NMR experiments were performed. The estimated molecular weight indicates values corresponding to the formation of OH-bridged trimer solvated by three molecules of $\text{THF-}d_8$ or pyridine ($M \approx 460 \text{ g mol}^{-1}$, Table S1, ESI†). In turn, the ^{27}Al NMR spectrum of 2 shows a signal at 146 ppm, suggesting the four-coordinate Al centre.⁵² Thus, the neutral donor molecules are outside the first coordination sphere and likely solvate the trimer *via* hydrogen bonding. The formation of trimeric dialkylaluminium hydroxide species solvated by neutral donor molecules was previously anticipated by Pasynkiewicz.¹ Moreover, such type of adducts featuring the bulky ^tBu groups have been isolated in crystal form and structurally characterised by Barron for $[\text{Al}(^t\text{Bu})_2(\mu\text{-OH})]_3 \cdot 2\text{L}$ ($\text{L} = \text{THF}, \text{MeCN}$).⁴¹

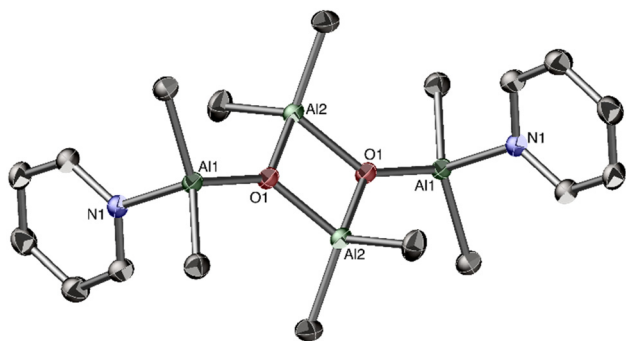


Fig. 2 The molecular structure of $[\text{AlMe}_2(\text{pyr})(\mu_3\text{-O})\text{AlMe}_2]_2$ (3). Hydrogen atoms were omitted for clarity.



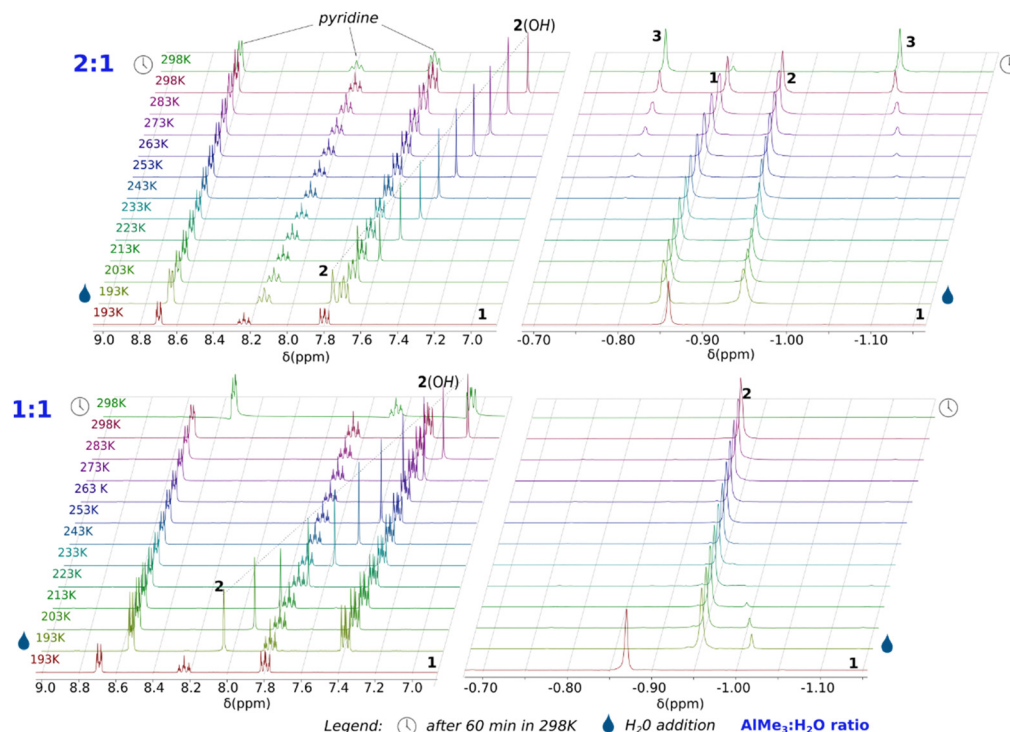


Fig. 3 Variable-temperature NMR spectra for the reaction of **1** with H₂O in 2:1 (top) and 1:1 (down) stoichiometries.

While our results corroborate to some degree with previous experimental^{1,20,21} and computational^{23–29} investigations of the initial steps of AlMe₃ hydrolysis that the character of an initial AlMe₃/H₂O adduct is unclear as the presence of both donor solvent molecules and pyridine (as a strong Lewis base) in the first coordination sphere should be considered. To determine the character of this unstable intermediate state, we performed state-of-the-art quantum-chemical calculations, including the possibility of the formation of hypervalent five-coordinate adducts,^{51,53} which have not been considered before. The energies reported below have been obtained at the domain-based local pair natural orbital coupled cluster method with singles, doubles, and iterative triples (DLPNO-CCSD(T1))^{54–56} and include estimates for complete PNO space,⁵⁷ complete basis set,⁵⁸ zero-point energy, and solvent effects (THF). Details of calculations can be found in the ESI,[†] where the comparison with density functional theory results is provided for completeness. First, we have considered the binding energies of water,

THF, and pyridine to AlMe₃. Here, the energies of -16.8 , -23.3 , and -26.5 kcal mol⁻¹ have been found (Table S7, ESI[†]). According to our expectation, the four-coordinate AlMe₃-py adduct is the most stable, and in the presence of THF and water, one can consider an equilibrium presented in Fig. 4.

For the py adduct, the H₂O molecule remains outside the first coordination sphere (structure **A** in Fig. 4; see also Fig. S24, ESI[†]), and no stable hypervalent minimum has been located. The replacement of py with a THF molecule (structure **B**) leads to slight energy elevation (2.7 kcal mol⁻¹), which corresponds to an equilibrium constant of 8.5×10^{-4} at 195 K (Tables S8 and S9, ESI[†]), and the process has a negligible activation energy of 3.3 kcal mol⁻¹ (Table S8, ESI[†]). Interestingly, a van der Waals complex **B** remains in equilibrium with a hypervalent complex **C** involving H₂O in the first coordination sphere (the Al–O distance equals 2.34 Å, see Fig. S24, ESI[†]). The energy difference between the van der Waals complex **B** and the five-coordinate complex **C** is small enough (0.9 kcal mol⁻¹) to result in a relatively large equilibrium constant of 1.1×10^{-1} (as shown in several works,^{13,22–27} the quantum-chemical modelling of AlMe₃ hydrolysis is highly challenging, and further steps of the hydrolysis process deserve advanced calculations and will be published due course). It is worth noting that similarly to the **A** → **B** step, the **B** → **C** step features rather a small activation barrier of 6.3 kcal mol⁻¹. Therefore, the whole reaction process **A** → **B** → **C** is under thermodynamic control.

In summary, we developed the efficient synthesis of tetramethylalumoxane by the controlled hydrolysis of AlMe₃ in the presence of pyridines as strong coordinating ligands. Moreover, using both high-level quantum-chemical calculations and

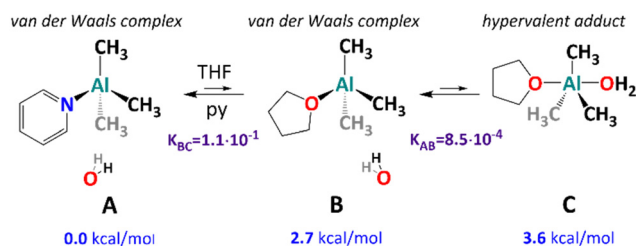


Fig. 4 Computationally modelled incipient complexes of AlMe₃ with H₂O in the presence of neutral donor ligands.

variable temperature ^1H NMR studies, we provided a new look at incipient complexes of AlMe_3 with H_2O in the presence of neutral donor ligands and revealed the immediate formation of the quasi-stable trimeric dimethylaluminium hydroxide species, respectively. Our studies contribute to extensive research on the organoaluminium compounds' hydrolysis and should be helpful in a rational design of studies on alumoxanes reactivity and their further stepwise transformations.

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Data availability

The data supporting this article was included as part of the ESI.†

Conflicts of interest

There are no conflicts to declare.

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