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## Controlled hydrolysis of AlMe<sub>3</sub> 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 AlMe<sub>3</sub> in the presence of pyridine. The AlMe<sub>3</sub>(pyr) hydrolysis by 0.5 and 1 equiv. of H<sub>2</sub>O has been followed with real-time <sup>1</sup>H 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.<sup>1,2</sup> The chemistry of alumoxanes has a rich history; initial studies trace back to the end of the 1950s.<sup>1</sup> They have attracted attention as highly active catalysts in the polymerisation of a wide range of organic monomers.<sup>2,3</sup> In particular, methylalumoxane (MAO) is an effective cocatalyst in olefin polymerisation.<sup>4–6</sup> Interestingly, many structural models have been proposed for MAO,<sup>7–15</sup> and only very recently, its molecular structure was crystallographically documented as a discrete sheet cluster.<sup>16</sup>

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.<sup>1,17</sup> Although various methods of introducing water have been used to lower the rate of the hydrolysis reaction (*e.g.*, using hydrated salts<sup>18</sup> or the dropwise addition of water at low temperatures<sup>18,19</sup>), 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 <sup>1</sup>H NMR spectroscopy,<sup>18–21</sup> mass spectrometry,<sup>22,23</sup> and the identity of intermediates has been supported by quantum-chemical calculations.<sup>22–27</sup> Simultaneously, various alternative non-hydrolytic approaches to alumoxanes have also been used, such as the decomposition of aluminium alkoxides,<sup>28</sup> reactions of AlR<sub>3</sub> compounds with carboxylic acids<sup>11,29–31</sup> or R<sub>2</sub>BOH,<sup>32–35</sup> and other methods.<sup>36–40</sup> Strikingly, only the phthalic acid alkylation has paved the way for isolating the tetramethylalumoxane moieties arranged as nodes in the bipyridine-linked polymeric chains.<sup>30</sup> 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, [Bu<sub>2</sub>AlOAl<sup>t</sup>Bu<sub>2</sub>]<sub>2</sub>, its adduct with pyridine (py), and a series of *tert*-butylaluminium hydroxides, (oxide)hydroxides and [(<sup>t</sup>BuAlO)<sub>n</sub>] cages.<sup>41–46</sup>

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,<sup>47–50</sup> herein we present an efficient route to a well-defined tetramethylalumoxane by the controlled hydrolysis of AlMe<sub>3</sub> in the presence of pyridine derivatives as strong coordinating ligands. To gain additional insight into the AlMe<sub>3</sub> hydrolysis, we have examined the reaction system by variable-temperature <sup>1</sup>H NMR spectroscopy along with theoretical calculations of the incipient AlMe<sub>3</sub>·H<sub>2</sub>O 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.<sup>51</sup> Thus, we chose a series of [AlMe<sub>3</sub>L] adducts as model precursors, where L = THF, pyrrolidine, pyridine (py) and *p*-dimethylaminopyridine (dmap). The controlled hydrolysis of [AlMe<sub>3</sub>(L)] (1, L = py, dmap) by 0.5 equiv. of H<sub>2</sub>O 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>





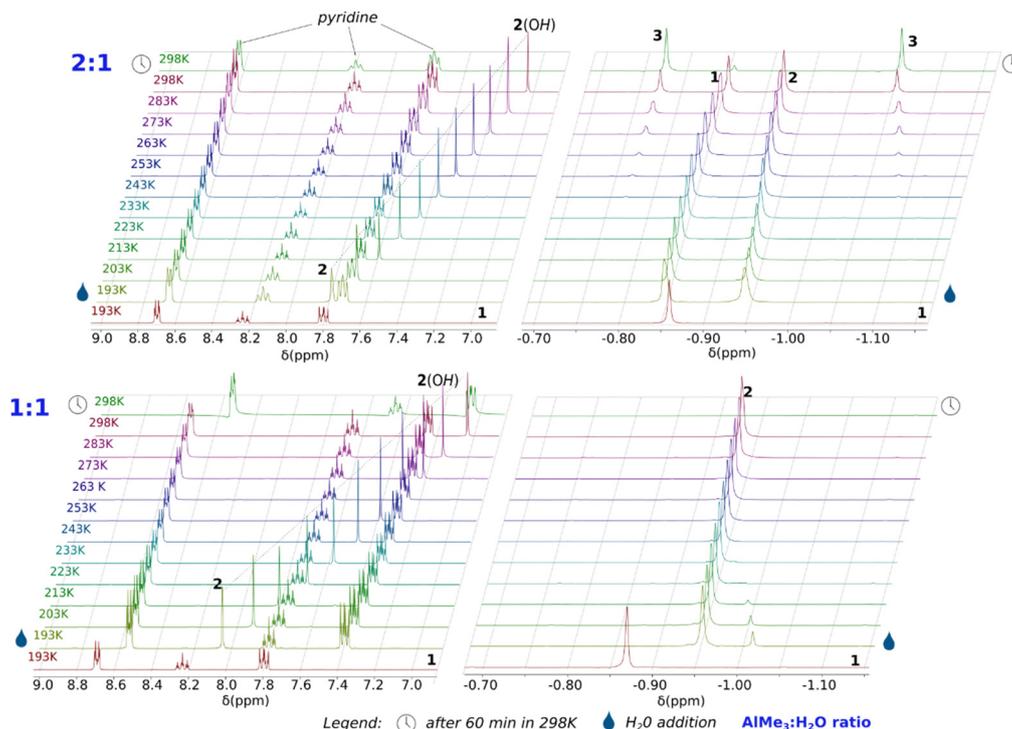


Fig. 3 Variable-temperature NMR spectra for the reaction of **1** with H<sub>2</sub>O in 2 : 1 (top) and 1 : 1 (down) stoichiometries.

While our results corroborate to some degree with previous experimental<sup>1,20,21</sup> and computational<sup>23–29</sup> investigations of the initial steps of AlMe<sub>3</sub> hydrolysis that the character of an initial AlMe<sub>3</sub>/H<sub>2</sub>O 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,<sup>51,53</sup> 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))<sup>54–56</sup> and include estimates for complete PNO space,<sup>57</sup> complete basis set,<sup>58</sup> zero-point energy, and solvent effects (THF). Details of calculations can be found in the ESI,<sup>†</sup> 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 AlMe<sub>3</sub>. Here, the energies of  $-16.8$ ,  $-23.3$ , and  $-26.5$  kcal mol<sup>-1</sup> have been found (Table S7, ESI<sup>†</sup>). According to our expectation, the four-coordinate AlMe<sub>3</sub>-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 H<sub>2</sub>O molecule remains outside the first coordination sphere (structure **A** in Fig. 4; see also Fig. S24, ESI<sup>†</sup>), 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<sup>-1</sup>), which corresponds to an equilibrium constant of  $8.5 \times 10^{-4}$  at 195 K (Tables S8 and S9, ESI<sup>†</sup>), and the process has a negligible activation energy of 3.3 kcal mol<sup>-1</sup> (Table S8, ESI<sup>†</sup>). Interestingly, a van der Waals complex **B** remains in equilibrium with a hypervalent complex **C** involving H<sub>2</sub>O in the first coordination sphere (the Al–O distance equals 2.34 Å, see Fig. S24, ESI<sup>†</sup>). The energy difference between the van der Waals complex **B** and the five-coordinate complex **C** is small enough (0.9 kcal mol<sup>-1</sup>) to result in a relatively large equilibrium constant of  $1.1 \times 10^{-1}$  (as shown in several works,<sup>13,22–27</sup> the quantum-chemical modelling of AlMe<sub>3</sub> 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<sup>-1</sup>. 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 AlMe<sub>3</sub> in the presence of pyridines as strong coordinating ligands. Moreover, using both high-level quantum-chemical calculations and

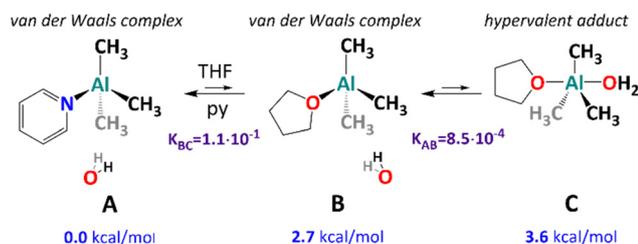


Fig. 4 Computationally modelled incipient complexes of AlMe<sub>3</sub> with H<sub>2</sub>O in the presence of neutral donor ligands.



variable temperature  $^1\text{H}$  NMR studies, we provided a new look at incipient complexes of  $\text{AlMe}_3$  with  $\text{H}_2\text{O}$  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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