


 Cite this: *Chem. Commun.*, 2024, 60, 9392

 Received 22nd July 2024,
 Accepted 5th August 2024

DOI: 10.1039/d4cc03672g

rsc.li/chemcomm

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

 Krzesimir Korona,^a Iwona Justyniak,^b James Pogrebetsky,^b Marta Lemieszka,^a Piotr Bernatowicz,^b Antoni Pietrzykowski,^a Adam Kubas^b and Janusz Lewiński^{†‡*}

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, [Bu₂AlOAl^tBu₂]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

^a Faculty of Chemistry, Warsaw University of Technology, Noakowskiego 3, 00-664 Warsaw, Poland. E-mail: janusz.lewinski@pw.edu.pl

^b Institute of Physical Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, 01-224 Warsaw, Poland. E-mail: ijustyniak@ichf.edu.pl, akubas@ichf.edu.pl

† Dedicated to the memory of Prof. Stanislaw Pasynekiewicz and his invaluable contribution to organoaluminium chemistry.

‡ 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>



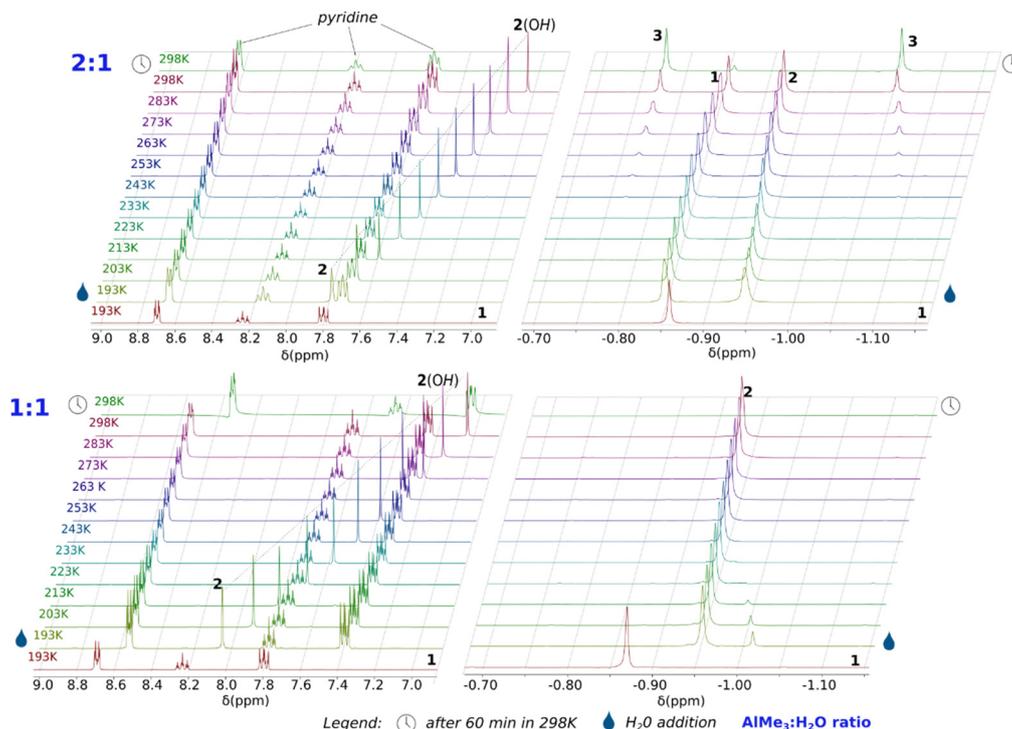


Fig. 3 Variable-temperature NMR spectra for the reaction of **1** with H₂O in 2 : 1 (top) and 1 : 1 (down) stoichiometries.

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

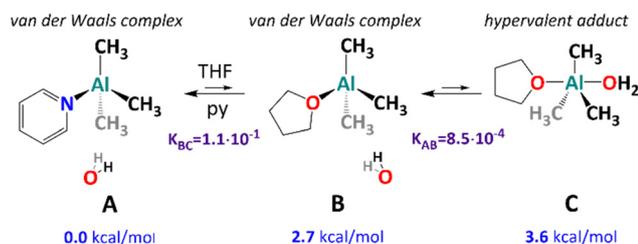


Fig. 4 Computationally modelled incipient complexes of AlMe₃ with H₂O in the presence of neutral donor ligands.



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.

We acknowledge financial support from the National Science Centre, Poland, grant OPUS 2020/37/B/ST4/03310.

Data availability

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

Conflicts of interest

There are no conflicts to declare.

Notes and references

- S. Pasynkiewicz, *Polyhedron*, 1990, **9**, 429–453.
- B. Wu, C. J. Harlan, R. W. Lenz and A. R. Barron, *Macromolecules*, 1997, **30**, 316–318.
- Z. Florjańczyk, A. Plichta and M. Sobczak, *Polymer*, 2006, **47**, 1081–1090.
- E. Zurek and T. Ziegler, *Prog. Polym. Sci.*, 2004, **29**, 107–148.
- M. Bochmann, *Organometallics*, 2010, **29**, 4711–4740.
- W. Kaminsky, *Macromolecules*, 2012, **45**, 3289–3297.
- H. Sinn, *Macromol. Symp.*, 1995, **97**, 27–52.
- E. Zurek, T. K. Woo, T. K. Firman and T. Ziegler, *Inorg. Chem.*, 2001, **40**, 361–370.
- Z. Boudene, T. De Bruin, H. Toulhoat and P. Raybaud, *Organometallics*, 2012, **31**, 8312–8322.
- Z. Falls, N. Tyminska and E. Zurek, *Macromolecules*, 2014, **47**, 8556–8569.
- A. F. R. Kilpatrick, J.-C. Buffet, P. Nørby, N. H. Rees, N. P. Funnell, S. Sripathongnak and D. O'Hare, *Chem. Mater.*, 2016, **28**, 7444–7450.
- M. Linnolahti and S. Collins, *ChemPhysChem*, 2017, **18**, 3369–3374.
- S. Collins, G. Hasan, A. Joshi, J. S. McIndoe and M. Linnolahti, *ChemPhysChem*, 2021, **22**, 1326–1335.
- A. Joshi, S. Collins, M. Linnolahti, H. S. Zijlstra, E. Liles and J. S. McIndoe, *Chem. – Eur. J.*, 2021, **27**, 8753–8763.
- S. Collins and M. Linnolahti, *ChemPhysChem*, 2023, **24**, e202300342.
- L. Luo, J. M. Younker and A. V. Zabula, *Science*, 2024, **384**, 1424–1428.
- H. S. Zijlstra and S. Harder, *Eur. J. Inorg. Chem.*, 2015, 19–43.
- A. Storr, K. Jones and A. W. Laubengayer, *J. Am. Chem. Soc.*, 1968, **90**, 3173–3177.
- M. Bolesławski and J. Serwatowski, *J. Organomet. Chem.*, 1983, **254**, 159–166.
- M. Bolesławski and J. Serwatowski, *J. Organomet. Chem.*, 1983, **255**, 269–278.
- S. Pasynkiewicz, A. Sadownik and A. Kunicki, *J. Organomet. Chem.*, 1977, **124**, 265–269.
- A. Joshi, H. S. Zijlstra, E. Liles, C. Concepcion, M. Linnolahti and J. S. McIndoe, *Chem. Sci.*, 2021, **12**, 546–551.
- S. Collins, A. Joshi and M. Linnolahti, *Chem. – Eur. J.*, 2021, **27**, 15460–15471.
- L. Negureanu, R. W. Hall, L. G. Butler and L. A. Simeral, *J. Am. Chem. Soc.*, 2006, **128**, 16816–16826.
- R. Glaser and X. Sun, *J. Am. Chem. Soc.*, 2011, **133**, 13323–13336.
- M. Linnolahti, A. Laine and T. A. Pakkanen, *Chem. – Eur. J.*, 2013, **19**, 7133–7142.
- J. T. Hirvi, M. Bochmann, J. R. Severn and M. Linnolahti, *ChemPhysChem*, 2014, **15**, 2732–2742.
- S. J. Obrey, S. G. Bott and A. R. Barron, *Organometallics*, 2001, **20**, 5162–5170.
- J. Lewiński, I. Justyniak, J. Zachara and E. Tratkiewicz, *Organometallics*, 2003, **22**, 4151–4157.
- J. Lewiński, W. Bury, I. Justyniak and J. Lipkowski, *Angew. Chem., Int. Ed.*, 2006, **45**, 2872–2875.
- A. Pietrzykowski, I. Justyniak, V. Szejko, T. Skrok, T. Radzymiński, K. Suwińska and J. Lewiński, *Chem. – Eur. J.*, 2024, e202402021.
- L. Synoradzki, M. Bolesławski and J. Lewiński, *J. Organomet. Chem.*, 1985, **284**, 1–4.
- R. Anulewicz-Ostrowska, S. Luliński, J. Serwatowski and K. Suwińska, *Inorg. Chem.*, 2000, **39**, 5763–5767.
- V. C. Gibson, S. Mastroianni, A. J. P. White and D. J. Williams, *Inorg. Chem.*, 2001, **40**, 826–827.
- R. Tanaka, T. Hirose, Y. Nakayama and T. Shiono, *Polym. J.*, 2016, **48**, 67–71.
- R. J. Wehmschulte and P. P. Power, *J. Am. Chem. Soc.*, 1997, **119**, 8387–8388.
- Y. V. Kissin and A. J. Brandolini, *Macromolecules*, 2003, **36**, 18–26.
- F.-J. Wu, L. S. Simeral, A. A. Mrse, J. L. Eilertsen, L. Negureanu, Z. Gan, F. R. Fronczek, R. W. Hall and L. G. Butler, *Inorg. Chem.*, 2007, **46**, 44–47.
- Y. Yang, H. Zhu, H. W. Roesky, Z. Yang, G. Tan, H. Li, M. John and R. Herbst-Irmer, *Chem. – Eur. J.*, 2010, **16**, 12530–12533.
- Y. Yang, H. Li, C. Wang and H. W. Roesky, *Inorg. Chem.*, 2012, **51**, 2204–2211.
- M. R. Mason, J. M. Smith, S. G. Bott and A. R. Barron, *J. Am. Chem. Soc.*, 1993, **115**, 4971–4984.
- C. J. Harlan, M. R. Mason and A. R. Barron, *Organometallics*, 1994, **13**, 2957–2969.
- C. C. Landry, C. J. Harlan, S. G. Bott and A. R. Barron, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 1201–1202.
- C. J. Harlan, E. G. Gillan, S. G. Bott and A. R. Barron, *Organometallics*, 1996, **15**, 5479–5488.
- C. J. Harlan, S. G. Bott, B. Wu, R. W. Lenz and A. R. Barron, *Chem. Commun.*, 1997, **22**, 2183–2184.
- C. N. McMahon and A. R. Barron, *J. Chem. Soc., Dalton Trans.*, 1998, 3703–3704.
- W. Bury, E. Krajewska, M. Dutkiewicz, K. Sokołowski, I. Justyniak, Z. Kaszkur, K. J. Kurzydłowski, T. Płociński and J. Lewiński, *Chem. Commun.*, 2011, **47**, 5467–5469.
- W. Bury, E. Chwojnowska, I. Justyniak, J. Lewiński, A. Affek, E. Zygadło-Monikowska, J. Bąk and Z. Florjańczyk, *Inorg. Chem.*, 2012, **51**, 737–745.
- M. Terlecki, S. Badoni, M. K. Leszczyński, S. Gierlotka, I. Justyniak, H. Okuno, M. Wolska-Pietkiewicz, D. Lee, G. De Paëpe and J. Lewiński, *Adv. Funct. Mater.*, 2021, **31**, 2105318.
- V. Gupta, I. Justyniak, E. Chwojnowska, V. Szejko and J. Lewiński, *Inorg. Chem.*, 2023, **62**, 16274–16279.
- J. Lewiński and A. E. H. Wheatley, in *Modern Organoaluminum Reagents*, ed. S. Woodward and S. Dagorne, Springer Berlin Heidelberg, Berlin, Heidelberg, 2012, vol. 41, pp. 1–58.
- J. Lewiński and D. Kubicki, *Encyclopedia of Spectroscopy and Spectrometry*, Elsevier, 2017, pp. 318–329.
- G. A. Papoian and R. Hoffmann, *Angew. Chem., Int. Ed.*, 2000, **39**, 2408–2448.
- C. Riplinger and F. Neese, *J. Chem. Phys.*, 2013, **138**, 034106.
- C. Riplinger, B. Sandhoefer, A. Hansen and F. Neese, *J. Chem. Phys.*, 2013, **139**, 134101.
- Y. Guo, C. Riplinger, D. G. Liakos, U. Becker, M. Saitow and F. Neese, *J. Chem. Phys.*, 2020, **152**, 024116.
- J. Pogrebetsky, A. Siklitskaya and A. Kubas, *J. Chem. Theory Comput.*, 2023, **19**, 4023–4032.
- J. Šponer and P. Hobza, *J. Phys. Chem. A*, 2000, **104**, 4592–4597.

