

Heteroleptic Aluminum Allyls as Initiators for Lactide Polymerization

Lauren E. Wenger, Nicholas M. Shawver, William W. Brennessel, Brian K. Long, and Timothy P. Hanusa*



Cite This: <https://doi.org/10.1021/acs.organomet.2c00482>



Read Online

ACCESS |



Metrics & More

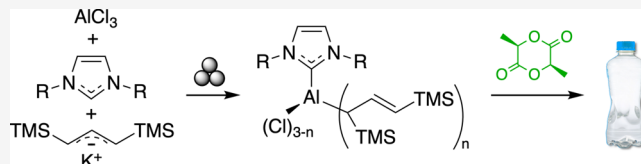


Article Recommendations



Supporting Information

ABSTRACT: Organoaluminum complexes with the formula $[(\text{NHC})\text{AlCl}_{3-n}\text{A}'_n]$ ($\text{NHC} = \text{IMes}$ ($\text{IMes} = 1,3\text{-bis}(2,4,6\text{-trimethylphenyl})\text{imidazol-2-ylidene}$) or IDipp ($\text{IDipp} = 1,3\text{-bis}(2,6\text{-diisopropylphenyl})\text{imidazol-2-ylidene}$); $\text{A}' = [1,3\text{-(SiMe}_3)_2\text{C}_3\text{H}_3]^-$; $n = 0\text{--}2$) were synthesized either through solution or mechanochemical methods. Although an NHC adduct with $[\text{AlA}'_3]$ did not form, $[(\text{IDipp})\text{AlCl}_2\text{A}']$ and $[(\text{IMes})\text{AlClA}'_2]$ were obtained and X-ray crystallography confirmed their construction around Al in a distorted tetrahedral environment. The $[(\text{NHC})\text{AlCl}_{3-n}\text{A}'_n]$ complexes, $[\text{AlA}'_3]$, and $[\text{Al}(\text{O}^i\text{Pr})_3]$ (as a reference) were examined for their ability to polymerize L-lactide via ring-opening polymerization to produce polylactide. All of them did so with varying degrees of effectiveness. Of the organoaluminum species, the $[(\text{NHC})\text{AlCl}_3]$ complexes were very weak initiators, and $[\text{AlA}'_3]$ the most effective, producing polymer molecular weights up to 49 kDa (M_w), with the mixed chloro/allyl complexes in between. All initiators were slower than $[\text{Al}(\text{O}^i\text{Pr})_3]$.



INTRODUCTION

Despite a millennia-long history,¹ mechanochemistry has only recently emerged as an increasingly applicable tool for organometallic synthesis under solvent-free conditions.² Initiated by the absorption of mechanical energy, often by grinding and ball milling,³ mechanochemical reactions represent “green chemistry” techniques by reducing solvent waste and offering shorter reaction times, enhanced yields, and improved selectivity when compared to analogous solution-based approaches.⁴ One of the greatest benefits of mechanochemically based synthesis is the potential access it provides to new types of molecular structures, including low-coordinate metal complexes.⁵

Unsolvated organometallics constitute one class of such low-coordinate complexes. For example, the parent tri(allyl) aluminum complex exists only in the form of solvent adducts $[\text{Al}(\text{C}_3\text{H}_5)_3\cdot\text{S}]$ ($\text{S} = \text{THF}$, pyridine, OPPh_3).⁶ Attempts to form the potentially more reactive unsolvated complex with either the unsubstituted or substituted allyl ligand, $[1,3\text{-(SiMe}_3)_2\text{C}_3\text{H}_3]^-$ ($= [\text{A}']^-$), with solution-based syntheses have not been successful.^{2b,7} In contrast, a mechanochemical approach, in which the reagents are ground without a solvent, is effective and leads to the isolation of $[\text{AlA}'_3]$ in high yield.^{2b} As an additional benefit, the mechanochemically produced complex displays greater reactivity in a stoichiometric context than the solvated counterpart, a feature that could potentially contribute to higher reactivity in catalytic reactions.⁴

To this aim, we sought to prepare new initiators for lactide polymerization. Polylactide (PLA) is a biodegradable plastic alternative (Figure 1a) that is sourced from renewable sources

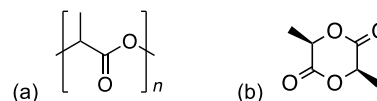


Figure 1. (a) Repeating unit of polylactide (PLA) and (b) L-lactide.

including corn and sugar beets.⁸ PLA can be used for packaging, drug delivery, and biomedical applications,⁹ and has steadily grown in popularity in recent decades. Despite its increasing adoption, there are still issues with PLA's physical properties and processing characteristics that are highly sensitive to the polymerization conditions. Such issues have kept its cost relatively high and prevented PLA from becoming a commodity polymer.¹⁰

Although low-molecular-weight PLA can be generated by direct polycondensation of lactic acid,⁹ higher-molecular-weight PLA is routinely accessed via a milder alternative route employing the ring-opening polymerization (ROP) of lactide (Figure 1b).¹¹ Since the first report of aluminum isopropoxide as an initiator of ROP in 1991,¹² aluminum complexes have played a major role in the development of this initiator class.^{12,13} Investigations have examined the effect of steric bulk at the aluminum center and the strength of metal–

Received: September 21, 2022



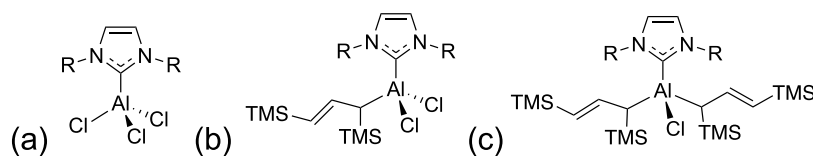


Figure 2. Structures of NHC adducts $R = 2,6$ -diisopropylphenyl or $2,4,6$ -trimethylphenyl: (a) $[(\text{NHC})\text{AlCl}_3]$; (b) $[(\text{NHC})\text{AlCl}_2\text{A}']$; and (c) $[(\text{NHC})\text{AlClA}'_2]$.

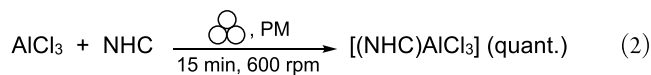
ligand bonds, and considerable work has been conducted with polydentate N- or O-donor ligands, with both aluminum and other early main-group metals.¹⁴ In contrast, organoaluminum initiators are much less explored, comprising mainly β -diketiminate-aluminum species with methyl or ethyl ligands, sometimes including mixed chloro/alkyl species. Several homoleptic organoaluminums $[\text{AlR}_3]$ ($R = \text{Me}$, Et , $i\text{Bu}$, and octyl) have been examined as potential ROP initiators and their reactivity compared with $[\text{Al}(\text{O}^i\text{Pr})_3]$. Although conversion of L-lactide is slower with $[\text{AlR}_3]$ species than with isopropoxide, molecular weights can be higher by almost a factor of two.¹³ As a complement to this work, we here report the result of generating and employing bulky allyl aluminum complexes as ROP initiators.

RESULTS AND DISCUSSION

Synthesis of Aluminum Allyl NHC Adducts. Heteroleptic aluminum complexes $[(\text{NHC})\text{AlCl}_{3-n}\text{A}'_n]$ ($\text{NHC} = \text{N}$ -heterocyclic carbene) were prepared by various solution and mechanochemical methods, although not all methods worked for every combination of ligands. For the trichloro species $[(\text{NHC})\text{AlCl}_3]$ (Figure 2a), the solution route described by Schödel¹⁵ was adapted for the present work (eq 1; $\text{NHC} = \text{IDipp}$ (1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene) or IMes (1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene))



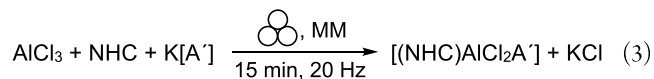
An analogous preparation involved grinding the reagents in a planetary mill (PM) (eq 2). The reactions gave quantitative yields and were complete in shorter times than the solution-based routes, which is a commonly encountered benefit of mechanochemically initiated reactions^{2c}



Preparation of the mono(allyl) $[(\text{NHC})\text{AlCl}_2\text{A}']$ (Figure 2b) complexes could be performed with either solution or mechanochemical methods. For the solution route, the NHC was dissolved in toluene, and then AlCl_3 was added. After allowing the solution to stir for 15 min, $\text{K[A}']$ was added, and the combined mixture was allowed to stir for an additional 3 h. The mixture was then filtered to remove KCl and the filtrate evaporated to give a dark orange oil that solidified on standing over several days, providing $[(\text{NHC})\text{AlCl}_2\text{A}']$ in high yield (96% to quant.).

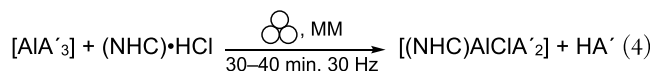
The mechanochemical equivalent could be done in one step, combining NHC , AlCl_3 , and $\text{K[A}']$ and then grinding the mixture for 15 min in a mixer mill (MM) (or 5 min in a planetary mill at 300 rpm) (eq 3). The ground mixture was extracted with a minimal amount of toluene, the extract filtered, and dried. This approach generated more byproducts than the solution route, although their formation could be suppressed to some extent by prechilling the grinding jar in

liquid nitrogen before milling. A cleaner product in roughly 56–80% yield was obtained in this way

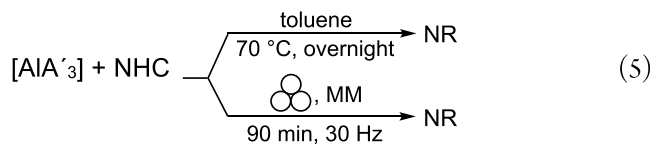


Under certain conditions, and only when using the solution route to form $[(\text{IMes})\text{AlCl}_2\text{A}']$, small crystals of the mesitylaminium salt N -(2-(mesitylamino)-3,5-bis(trimethylsilyl)pent-4-en-1-yl)-mesitylaminium chloride were obtained. It was identified through its single-crystal X-ray structure (see Figure S7), which, although definitive as to composition, is of connectivity only quality. Its formation apparently involves attack of the $[\text{A}']^-$ ion on the $\text{C}=\text{C}$ double bond of IMes , but we have not been able to reproduce it consistently, and so cannot more precisely describe the exact conditions required for its formation.

Attempts to form bis(allyl) complexes $[(\text{NHC})\text{AlClA}'_2]$ (Figure 2c) by extension of the previously used methods, i.e., mixing NHC , AlCl_3 , and 2 equiv. of $\text{K[A}']$ under either solution or mechanochemical conditions (including variations in time, temperature, solvent, and milling conditions), produced only the mono(allyl) aluminum species and the protonated allyl ligand (i.e., the propene HA'). Instead, these complexes had to be accessed by combining $(\text{NHC})\cdot\text{HCl}$ with the mechanochemically generated $[\text{AlA}'_3]$,^{2b} producing HA' as a byproduct (eq 4). Removal of the HA' under vacuum gave $[(\text{NHC})\text{AlClA}'_2]$ complexes in moderate yield, ca. 35–40%



To complete the series of complexes, synthesis of $[(\text{NHC})\text{AlA}'_3]$ adducts was attempted by combining $[\text{AlA}'_3]$ with NHCs (eq 5). Even under forcing conditions that were more energetic than those used for the other adducts, the attempted reactions yielded only starting material



We hypothesized that steric crowding may be responsible for the failure to form $[(\text{NHC})\text{AlA}'_3]$ adducts. To examine this possibility, an estimate of the congestion in the coordination sphere of aluminum was generated with the Solid-G program¹⁶ on DFT-optimized models of $[\text{AlA}'_3]$ and $[(\text{IMes})\text{AlA}'_3]$. The G_{complex} value represents the net coverage so that regions of the coordination sphere where the projections of the ligands overlap are counted only once; for $[\text{AlA}'_3]$, the G_{complex} value is 79.7% (see Figure S8 for an illustration of this). Although IMes coordinates to $[\text{AlA}'_3]$ in the gas-phase approximation, the G_{complex} value is pushed to 97.8%. There is no absolute cut-off value for stable structures, but the very high amount of steric congestion that would be encountered in such an adduct

would likely discourage stable adduct formation, particularly in the condensed phase. Note also that the calculated Al–C_{allyl} distances have lengthened by 0.06 Å in the hypothetical [(IMes)AlA'₃] complex, and the Al–C_{carbene} distance is 2.157 Å, which is longer (and presumably weaker) than the comparable 2.07–2.10 Å distances found for the other NHC–Al complexes described here.

The NMR spectra for the [(NHC)AlCl_{3-n}A'_n] (*n* = 1,2) complexes display resonances consistent with η¹-bound A' ligands, indicating that the molecules are not fluxional (see Figures S3 and S6). This is in contrast to the [AlA'₃] complex, which although displaying η¹-bound ligands in the solid state, is highly fluxional in solution, with the A' ligands giving the appearance of being π-bound down to –70 °C (e.g., only one signal is observed for the otherwise inequivalent trimethylsilyl groups).^{2b}

Crystallographic Results. The IDipp version of [(NHC)–AlCl₂A'] was highly crystalline, forming crystals with little effort. In contrast, the IMes analogue was amorphous, and X-ray quality crystals were not obtained. Interestingly, the situation was reversed in the [(NHC)AlClA'₂] case, and suitable crystals of [(IMes)AlClA'₂] were obtained, as discussed below.

Solid-State Structure of [(IDipp)AlCl₂A']. Colorless crystals of [(IDipp)AlCl₂A'] were grown from toluene over several days. The asymmetric unit contains one molecule in a general position. One isopropyl group was modeled as disordered over two sites (0.51:0.49) (Figure 3). The aluminum lies in the center of a distorted tetrahedron, coordinated by the two chlorines, the IDipp carbene, and an η¹-bonded A' ligand.

The Al–C_{carbene} bond length of 2.069(3) Å is within the typical range of 2.008–2.118 Å found for similar compounds,¹⁷ and is slightly elongated from that found in [(IDipp)AlCl₃] (2.018(2) Å).¹⁸ Compared to the [AlA'₃] complex, the Al–C_{allyl} bond is barely longer (1.989(3) vs 1.964(2) Å), despite the higher coordination number in [(IDipp)AlCl₂A'].^{2b} The average Al–C_{allyl} bonds are slightly lengthened from those in [(IDipp)AlCl₃] (2.154 and 2.128 Å, respectively).¹⁸

Solid-State Structure of [(IMes)AlClA'₂]. Colorless crystals of [(IMes)AlClA'₂] were grown from hexanes over several weeks (Figure 4). As in the structure of [(IDipp)–AlCl₂A'], the Al in [(IMes)AlClA'₂] is in a distorted tetrahedral environment. Probably reflecting the increased steric bulk of the ligands, the distances of aluminum to the ligands are slightly longer than those in [(IDipp)AlCl₂A']. For example, the aluminum–carbene distance (2.105 Å) is longer than in [(IDipp)AlCl₂A'] (2.069 Å) by 0.036 Å. Similarly, the Al–Cl bond (2.197(1) Å) has increased by 0.043 Å from the Al–Cl distance in [(IDipp)AlCl₂A'] (2.154 Å, ave.).

Polymerization Results. Polymerization results are presented in Table 1 and Figure 5. As a summary of the data, [AlA'₃] was the most active allyl initiator of L-lactide. Among the [(NHC)AlCl_{3-n}A'_n] complexes, reactivity dropped with increasing number of chloride ligands. Even when only chlorides were present, which do not usually initiate lactide polymerization, low (3–4%) conversion was observed. The most likely source of initiation in these cases may be from small amounts of adventitious water that acts as an external initiating species; however, we were unable to conclusively show this (attempts to analyze the end-groups were not definitive).¹⁹

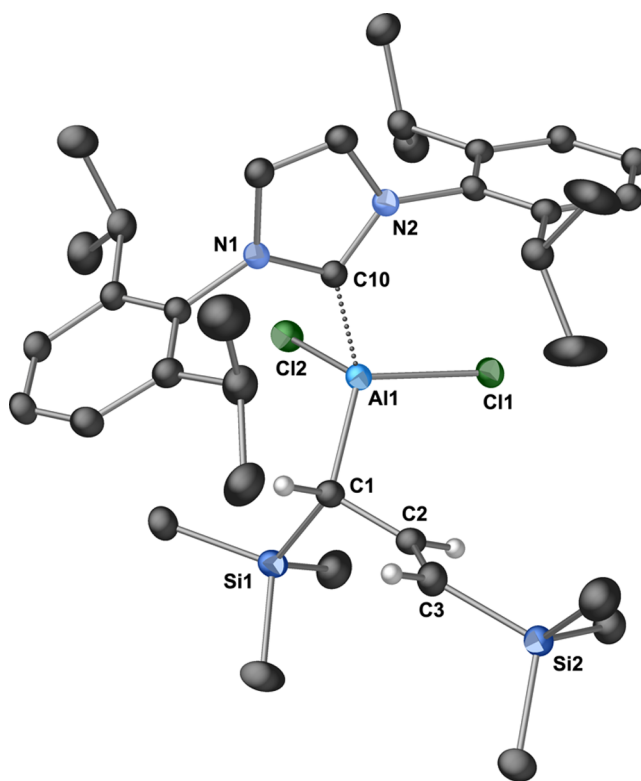


Figure 3. Thermal ellipsoid plot (50% level) of [(IDipp)AlCl₂A']. For clarity, one conformation of the disordered isopropyl group is omitted, as are all hydrogens except those on the C₃ section of the A' ligand. Selected bond distances (Å) and angles (deg): Al1–Cl1, 2.1533(9); Al1–Cl2, 2.1544(9); Al1–C1, 1.989(3); Al1–C10, 2.069(3); C1–C2, 1.492(4); C2–C3, 1.337(4); Cl1–Al1–Cl2, 106.02(4); Cl1–Al1–C1, 110.01(8); Cl2–Al1–C1, 116.44(9); C1–Al1–C10, 114.79(10); Cl1–Al1–C10, 109.06(7); and Cl2–Al1–C10, 99.74(7).

The identity of the NHC was not consistently associated with the more active (highest % conversion) initiator; e.g., in the monochloro species [(NHC)AlClA'₂], the IMes complex was more reactive, whereas with the dichloro compounds [(NHC)AlCl₂A'], the IDipp variant displayed higher conversion. A similar flip was found with polydispersity values (*D*) in which the IMes complex of the monochloro species [(NHC)AlClA'₂] provided PLA with a slightly lower dispersity (*D* = 1.6 vs 2.0), whereas with the dichloro [(NHC)AlCl₂A'] compounds, the IDipp variant displayed substantially better control (*D* = 2.1 vs 5.4). All polymerizations were generally slow, most were not complete at 120 h, and there was moderate to poor dispersity control (1.6 ≤ *D* ≤ 5.4) that is comparable to that found using [Al(O^{*i*}Pr)₃]₃ under our conditions (*D* = 3.4). Despite this, high-molecular-weight PLAs were obtained when using some of the organoaluminum initiators (e.g., *M_w* = 49 kDa with [AlA'₃]).

It was found that the polymers produced via the initiators [(IDipp)AlCl₃], [(IMes)AlClA'₂], and [Al(O^{*i*}Pr)₃] (Table 1 and Figures S14, S18, and S20) each displayed a bimodal molecular weight distribution. While this observation may suggest the presence of two or more propagating species, which could result due to differential ligation of active species or the presence of aggregates, additional experimentation will be required to confirm this.

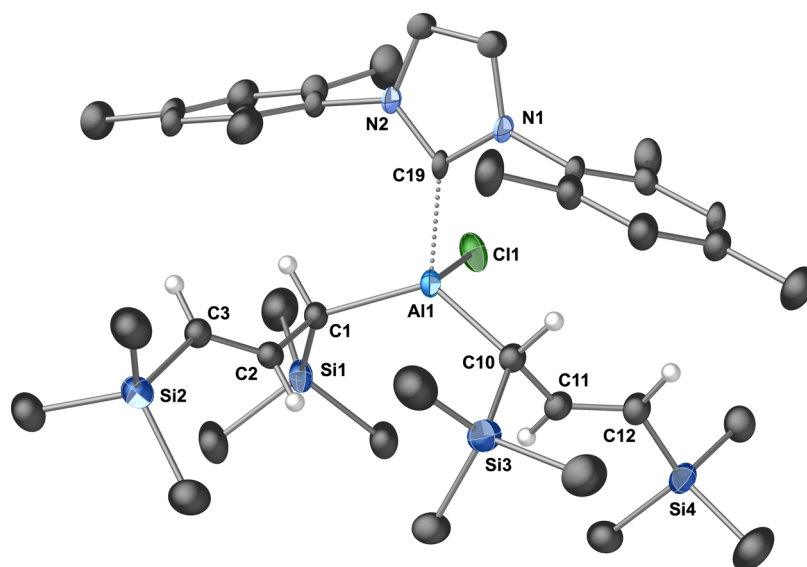


Figure 4. Thermal ellipsoid plot (50% level) of $[(\text{IMes})\text{AlClA}'_2]$. For clarity, all hydrogens except those on the C_3 section of the A' ligands are omitted. Selected bond distances (Å) and angles (deg): $\text{Al1}-\text{Cl1}$, 2.197(1); $\text{Al1}-\text{C1}$, 1.992(3); $\text{Al1}-\text{C10}$, 1.996(3); $\text{Al1}-\text{C19}$, 2.105(4); $\text{C1}-\text{C2}$, 1.489(5); $\text{C2}-\text{C3}$, 1.325(5); $\text{C10}-\text{C11}$, 1.505(6); $\text{C11}-\text{C12}$, 1.324(4); $\text{Cl1}-\text{Al1}-\text{C1}$, 104.4(1); $\text{Cl1}-\text{Al1}-\text{C10}$, 108.6(1); $\text{Cl1}-\text{Al1}-\text{C19}$, 96.2(1); $\text{C1}-\text{Al1}-\text{C10}$, 112.6(2); $\text{C1}-\text{Al1}-\text{C19}$, 112.0(1); and $\text{C10}-\text{Al1}-\text{C19}$, 109.6(2).

Table 1. Results of Polymerization with L-Lactide^a

initiator	conv. (%)	M_n (kDa)	M_w (kDa)	\bar{D} (M_w/M_n)
$[\text{AlA}'_3]$	80.5	22.8	48.8	2.1
$[(\text{IMes})\text{AlClA}'_2]$	47.3	9.3	50.1	5.4
$[(\text{IDipp})\text{AlClA}'_2]$	35.9	7.9	16.3	2.1
$[(\text{IDipp})\text{AlCl}_2\text{A}']$	17.7	7.4	27.7	3.7
$[(\text{IMes})\text{AlCl}_2\text{A}']$	6.0	10.2	16.6	1.6
$[(\text{IDipp})\text{AlCl}_3]$	4.0	7.4	27.7	3.7
$[(\text{IMes})\text{AlCl}_3]$	3.4	8.8	18.4	2.1
$[\text{Al}(\text{O}^i\text{Pr})_3]^b$	96.7	18.7	66.0	3.4

^a $[\text{L-lactide}] = 1.0 \text{ M}$, benzene- d_6 , 90 °C, 100:1 $[\text{LA}]/[\text{Al}]$, 0.007 mmol $[\text{Al}]$, 119 or 120 h. ^bSame conditions as above but for 27 h.

The coordination number (CN) of aluminum may play a role in the polymerization rate in that a highly coordinated

metal center would have to displace ligands to become active. For example, aluminum isopropoxide forms clusters of trimers and tetramers in solution, in which the aluminum has a CN of 4 or 5 in the trimer and 4 or 6 in the tetramer.²⁰ Penczek and co-workers have observed that trimeric $[\text{Al}(\text{O}^i\text{Pr})_3]_3$ is much faster than tetrameric $[\text{Al}(\text{O}^i\text{Pr})_3]_4$ in the ROP of L-lactide, at least partially reflecting the lower metal CN in the trimer.²¹ Analogously, a structural element of $[\text{AlA}'_3]$ that may contribute to its activity is its 3-coordinate metal center. This is a relatively uncommon feature in “ $[\text{AlR}_3]$ ” complexes (many such complexes are found as dimers in the solid state, with CN for the metal of four).²² The low CN for aluminum may help accelerate the catalytic ROP process, much as it assists in its stoichiometric reactivity.

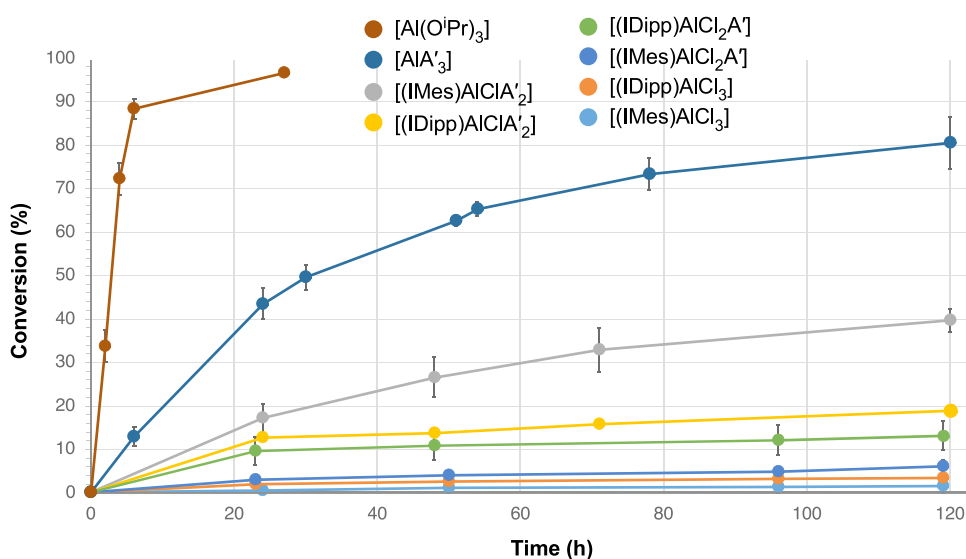


Figure 5. Conversion as a function of time for various $[(\text{NHC})\text{AlCl}_{3-n}\text{A}'_n]$ complexes, $[\text{AlA}'_3]$, and $[\text{Al}(\text{O}^i\text{Pr})_3]$.

CONCLUSIONS

A series of heteroleptic organoaluminum complexes were prepared using a variety of mechanochemical and solution routes. All complexes displayed some ability to polymerize L-lactide without the use of external initiating species, such as alcohols, with activity increasing as the number of allyl ligands increases. The initiation was slow compared to aluminum isopropoxide, but high-molecular-weight PLA could be obtained, especially when using $[\text{AlA}'_3]$, with lower dispersity than when using aluminum isopropoxide under identical conditions.

While comparisons across lactide polymerization studies are difficult to make, as reaction conditions greatly affect the resulting polymer, the reactivities of both heteroleptic and homoleptic aluminum alkyl complexes have been compared to that of aluminum isopropoxide complexes. The general trend observed is that aluminum alkoxide complexes usually result in faster polymerization, but aluminum alkyl complexes lead to comparable, if not higher, molecular-weight polymers.^{13,23} These conclusions are consistent with the findings discussed here and suggest that continued development of low-coordinate initiators may provide valuable advances in lactide polymerization.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.organomet.2c00482>.

Optimized coordinates of structures (XYZ)

Experimental and computational details (PDF)

Accession Codes

CCDC 2142729–2142730 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

AUTHOR INFORMATION

Corresponding Author

Timothy P. Hanusa – Department of Chemistry, Vanderbilt University, Nashville, Tennessee 37235, United States; orcid.org/0000-0002-7935-5968; Email: t.hanusa@vanderbilt.edu

Authors

Lauren E. Wenger – Department of Chemistry, Vanderbilt University, Nashville, Tennessee 37235, United States

Nicholas M. Shawver – Department of Chemistry, University of Tennessee, Knoxville, Tennessee 37996-1600, United States

William W. Brennessel – X-ray Crystallographic Facility, Department of Chemistry, University of Rochester, Rochester, New York 14627, United States; orcid.org/0000-0001-5461-1825

Brian K. Long – Department of Chemistry, University of Tennessee, Knoxville, Tennessee 37996-1600, United States; orcid.org/0000-0002-2691-6194

Complete contact information is available at:

<https://pubs.acs.org/doi/10.1021/acs.organomet.2c00482>

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

Financial support by the National Science Foundation (CHE-1665327 and CHE-2155144) is gratefully acknowledged. The authors thank Prof. Nathan D. Schley for collecting and solving the crystallographic data for $[(\text{IMes})\text{AlClA}'_2]$.

REFERENCES

- (1) Takacs, L. Quicksilver from cinnabar: The first documented mechanochemical reaction? *JOM* **2000**, *52*, 12–13.
- (2) (a) James, S. L.; Adams, C. J.; Bolm, C.; Braga, D.; Collier, P.; Friščić, T.; Grepioni, F.; Harris, K. D. M.; Hyett, G.; Jones, W.; Krebs, A.; Mack, J.; Maini, L.; Orpen, A. G.; Parkin, I. P.; Shearouse, W. C.; Steed, J. W.; Waddell, D. C. Mechanochemistry: Opportunities for New and Cleaner Synthesis. *Chem. Soc. Rev.* **2012**, *41*, 413–447. (b) Rightmire, N. R.; Hanusa, T. P.; Rheingold, A. L. Mechanochemical Synthesis of $[1,3-(\text{SiMe}_3)_2\text{C}_3\text{H}_3]_3(\text{Al}, \text{Sc})$, a Base-Free Tris(allyl)aluminum Complex and Its Scandium Analogue. *Organometallics* **2014**, *33*, 5952–5955. (c) Do, J.-L.; Friščić, T. Mechanochemistry: A Force of Synthesis. *ACS Cent. Sci.* **2017**, *3*, 13–19.
- (3) McNaught, A. A.; Wilkinson, A. *IUPAC Compendium of Chemical Technology (the Gold Book)*, 2nd ed.; Blackwell Scientific: Oxford, 1997.
- (4) Tan, D.; García, F. Main group mechanochemistry: from curiosity to established protocols. *Chem. Soc. Rev.* **2019**, *48*, 2274–2292.
- (5) Hernández, J. G.; Bolm, C. Altering Product Selectivity by Mechanochemistry. *J. Org. Chem.* **2017**, *82*, 4007–4019.
- (6) Lichtenberg, C.; Robert, D.; Spaniol, T. P.; Okuda, J. Bis(allyl)aluminum Cation, Tris(allyl)aluminum, and Tetrakis(allyl)aluminate: Synthesis, Characterization, and Reactivity†. *Organometallics* **2010**, *29*, 5714–5721.
- (7) (a) Grignard, V.; Jenkins, R. L. The Organoaluminium Compounds: Ethyl Diodide and Diethyl Iodide of Aluminium. *Bull. Soc. Chim. Fr.* **1925**, *37*, 1376–1385. (b) Rainier, J. D.; Cox, J. M. Aluminum- and Boron-Mediated C-Glycoside Synthesis from 1,2-Anhydroglycosides. *Org. Lett.* **2000**, *2*, 2707–2709. (c) Majumder, U.; Cox, J. M.; Johnson, H. W. B.; Rainier, J. D. Total Synthesis of Gambierol: The Generation of the A–C and F–H Subunits by Using a C-Glycoside Centered Strategy. *Chem. - Eur. J.* **2006**, *12*, 1736–1746. (d) Picotin, G.; Miginiac, P. Reaction of allylic aluminum reagents with 1,3-dithienium tetrafluoroborate and with 2-chloro-1,3-dithiane: preparation of 2-substituted 1,3-dithianes. *J. Org. Chem.* **1985**, *50*, 1299–1301. (e) Shen, K.-H.; Yao, C.-F. Novel and Efficient Method for the Allylation of Carbonyl Compounds and Imines Using Triallylaluminum. *J. Org. Chem.* **2006**, *71*, 3980–3983. (f) Shen, K. H.; Liu, J. T.; Wu, Y. R.; Yao, C. F. Conjugate Addition of Triallylaluminum to α,β -Unsaturated Nitroalkenes to Produce 4,5-Unsaturated Nitroalkenes. *Synth. Commun.* **2007**, *37*, 3677–3687. (g) Shen, K.-H.; Kuo, C.-W.; Yao, C.-F. An efficient of Grignard-type procedure for the preparation of gem-diallylated compound. *Tetrahedron Lett.* **2007**, *48*, 6348–6351. (h) Kulkarni, N. A.; Yao, C.-F.; Chen, K. On the scope of diastereoselective allylation of various chiral glyoxylic oxime ethers with allyltributylstannane in the presence of a Lewis acid and triallylaluminum. *Tetrahedron* **2007**, *63*, 7816–7822.
- (8) Puaux, J.-P.; Banu, I.; Nagy, I.; Bozga, G. A Study of L-Lactide Ring-Opening Polymerization Kinetics. *Macromol. Symp.* **2007**, *259*, 318–326.
- (9) Masutani, K.; Kimura, Y. PLA Synthesis. From the Monomer to the Polymer. In *Poly(lactic acid) Science and Technology: Processing, Properties, Additives and Applications*; Jiménez, A.; Peltzer, M.; Ruseckaite, R., Eds.; Royal Society of Chemistry: Cambridge, 2014; pp 1–36.

- (10) Balaji, A. B.; Pakalapati, H.; Khalid, M.; Walvekar, R.; Siddiqui, H. Natural and synthetic biocompatible and biodegradable polymers. In *Biodegradable and Biocompatible Polymer Composites*; Shimi, N. G., Ed.; Elsevier: Duxford, CB22 4QH, UK, 2018; pp 3–32.
- (11) (a) Dechy-Cabaret, O.; Martin-Vaca, B.; Bourissou, D. Controlled Ring-Opening Polymerization of Lactide and Glycolide. *Chem. Rev.* **2004**, *104*, 6147–6176. (b) Kamber, N. E.; Jeong, W.; Waymouth, R. M.; Pratt, R. C.; Lohmeijer, B. G. G.; Hedrick, J. L. Organocatalytic Ring-Opening Polymerization. *Chem. Rev.* **2007**, *107*, 5813–5840.
- (12) Dubois, P.; Jacobs, C.; Jerome, R.; Teyssie, P. Macromolecular engineering of polylactones and polylactides. 4. Mechanism and kinetics of lactide homopolymerization by aluminum isopropoxide. *Macromolecules* **1991**, *24*, 2266–2270.
- (13) Yoo, J. Y.; Kim, Y.; Ko, Y. S. Ring-opening polymerization behavior of L-lactide catalyzed by aluminum alkyl catalysts. *J. Ind. Eng. Chem.* **2013**, *19*, 1137–1143.
- (14) Gao, J.; Zhu, D.; Zhang, W.; Solan, G. A.; Ma, Y.; Sun, W.-H. Recent progress in the application of group 1, 2 & 13 metal complexes as catalysts for the ring opening polymerization of cyclic esters. *Inorg. Chem. Front.* **2019**, *6*, 2619–2652.
- (15) Schödel, F.; Bolte, M.; Wagner, M.; Lerner, H.-W. NHC Supersilyl Silver Complex [Ag(IPr)Si^tBu₃] as a Promising Agent for Substitution Reactions. *Z. Anorg. Allg. Chem.* **2020**, *646*, 264–267.
- (16) Guzei, I. A.; Wendt, M. An improved method for the computation of ligand steric effects based on solid angles. *Dalton Trans.* **2006**, 3991–3999.
- (17) Romain, C.; Flidel, C.; Bellemin-Laponnaz, S.; Dagorne, S. NHC Bis-Phenolate Aluminum Chelates: Synthesis, Structure, and Use in Lactide and Trimethylene Carbonate Polymerization. *Organometallics* **2014**, *33*, 5730–5739.
- (18) Mikhaylov, V. N.; Kazakov, I. V.; Parfeniuk, T. N.; Khoroshilova, O. V.; Scheer, M.; Timoshkin, A. Y.; Balova, I. A. The carbene transfer to strong Lewis acids: copper is better than silver. *Dalton Trans.* **2021**, *50*, 2872–2879.
- (19) It is not uncommon for metal alkyls to be activated with an alcohol to achieve better initiation for ROP, since alkoxides are more active for lactide polymerization than alkyls or chlorides. However, bulky alcohols, such as Ph₃COH, react sluggishly, if at all, with [AlA'₃] (see ref 2b.), and (iPr)OH rapidly converts it into [Al(OiPr)₃]_n (N. Rightmire, T. Hanusa, unpublished results). At that point, one is measuring the reactivity of the alkoxide, not the allyl complex.
- (20) Turova, N. Y.; Kozunov, V. A.; Yanovskii, A. I.; Bokii, N. G.; Struchkov, Y. T.; Tarnopol'skii, B. L. Physico-chemical and structural investigation of aluminium isopropoxide. *J. Inorg. Nucl. Chem.* **1979**, *41*, 5–11.
- (21) Kowalski, A.; Duda, A.; Penczek, S. Polymerization of L,L-Lactide Initiated by Aluminum Isopropoxide Trimer or Tetramer. *Macromolecules* **1998**, *31*, 2114–2122.
- (22) Cowley, A. R.; Downs, A. J.; Marchant, S.; Macrae, V. A.; Taylor, R. A.; Parsons, S. Crystal Structures of Tris(tert-butyl)boron, -aluminum, -gallium, and -indium: Nonplanarity of the AlC₃ Skeleton and Evidence of Inter- and Intramolecular “Agostic” or Hyperconjugative Interactions. *Organometallics* **2005**, *24*, 5702–5709.
- (23) (a) Kan, C.; Ge, J.; Ma, H. Aluminum methyl, alkoxide and α -alkoxy ester complexes supported by 6,6'-dimethylbiphenyl-bridged salen ligands: synthesis, characterization and catalysis for rac-lactide polymerization. *Dalton Trans.* **2016**, *45*, 6682–6695. (b) Wei, Y.; Song, L.; Jiang, L.; Huang, Z.; Wang, S.; Yuan, Q.; Mu, X.; Zhu, X.; Zhou, S. Aluminum complexes with Schiff base bridged bis(indolyl) ligands: synthesis, structure, and catalytic activity for polymerization of rac-lactide. *Dalton Trans.* **2019**, *48*, 15290–15299.