J|A|C|S
ARTICLES
Published on Web 06/04/2005

Single-Component Catalyst/Initiators for the Organocatalytic Ring-Opening Polymerization of Lactide

Szilárd Csihony,[†] Darcy A. Culkin,[†] Alan C. Sentman,[‡] Andrew P. Dove,[‡] Robert M. Waymouth,*[,†] and James L. Hedrick*[,‡]

Contribution from the Center for Polymeric Interfaces and Macromolecular Assemblies, Department of Chemistry, Stanford University, Stanford, California 94305, and IBM Almaden Research Center, 650 Harry Road, San Jose, California 95120

Received February 11, 2005; E-mail: waymouth@stanford.edu; hedrick@almaden.ibm.com

Abstract: The synthesis and characterization of a series of primary and secondary alcohol adducts of 1,3-dimesitylimidazolin-2-ylidene is described. These adducts are stable as solids at room temperature, but readily release alcohol and the free carbene in solution. These alcohol adducts function as excellent single-component catalyst/initiators for the ring-opening polymerization of lactide under mild conditions, providing polymers with controlled molecular weights and narrow polydispersities. Multifunctional adducts were used to prepare poly(lactide)s of more complex architectures.

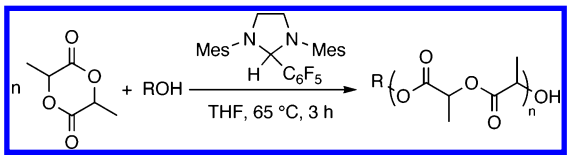
Introduction

N-Heterocyclic carbenes (NHCs) are versatile ligands for transition metals[1−3] and have emerged as potent nucleophilic organic catalysts.[4−24] These stabilized carbenes have been used recently as catalysts for Stetter reactions,[6−9] benzoin condensations,[10−14] and transesterification reactions.[15−21] We have recently demonstrated that NHCs catalyze the ring-opening polymerization of cyclic esters to polyesters,[25,26] an important class of biocompatible and biodegradable polymers derived from renewable resources.[27−30] The activity of the NHC catalysts for the ring-opening polymerization of cyclic esters depends sensitively on the steric and electronic properties of the carbene;[26] the high reactivity of these carbenes as well as their sensitivity to moisture has prompted us to develop strategies for generating these reactive compounds in situ under controlled conditions. To that end, we reported that both unsaturated imidazolylidene and saturated imidazolinylidene NHCs could be generated in situ by treatment of the corresponding imidazolium salts with *tert*-butoxide and used for the ROP of cyclic esters in the presence of an alcohol initiator.[26] This strategy provided a convenient means of screening a variety of imidazolium salts, but requires the addition of a strong base, which, if not completely consumed, could also initiate ring opening. To avoid this issue, we recently described an alternate strategy for generating saturated imidazolinylidene carbenes by thermolysis of stable chloroform and pentafluorobenzene adducts at elevated temperatures.[31] In the presence of lactide and an alcohol initiator, these adducts were excellent catalysts for controlled ring-opening polymerization to generate polylactides of narrow polydispersity (Scheme 1).[31] Nevertheless, this strategy requires elevated temperatures to liberate the carbene catalysts, and thus we sought other stable precatalysts that could liberate the reactive carbene at lower temperatures in a controlled manner.

[†] Stanford University.
[‡] IBM Almaden Research Center.

(1) Jafarpour, L.; Nolan, S. P. *Adv. Organomet. Chem.* **2001**, *46*, 181−222.
(2) Herrmann, W. A. *Angew. Chem., Int. Ed.* **2002**, *41*, 1290−1309.
(3) Perry, M. C.; Burgess, K. *Tetrahedron: Asymmetry* **2003**, *14*, 951−961.
(4) Nair, V.; Bindu, S.; Sreekumar, V. *Angew. Chem., Int. Ed.* **2004**, *43*, 5130−5135.
(5) Enders, D.; Balensiefer, T. *Acc. Chem. Res.* **2004**, *37*, 534−541.
(6) Enders, D.; Breuer, K.; Runsink, J.; Teles, J. H. *Helv. Chim. Acta* **1996**, *79*, 1899−1902.
(7) Kerr, M. S.; Read de Alaniz, J.; Rovis, T. *J. Am. Chem. Soc.* **2002**, 124, 10298−10299.
(8) Kerr, M. S.; Rovis, T. *Synlett* **2003**, 1934−1936.
(9) Kerr, M. S.; Rovis, T. *J. Am. Chem. Soc.* **2004**, *126*, 8876−8877.
(10) Enders, D.; Breuer, K.; Teles, J. H. *Helv. Chim. Acta* **1996**, *79*, 1217−1221.
(11) Dvorak, C. A.; Rawal, V. H. *Tetrahedron Lett.* **1998**, *39*, 2925−2928.
(12) Knight, R. L.; Leeper, F. J. *J. Chem. Soc., Perkin Trans. 1* **1998**, 1891−1893.
(13) Enders, D.; Kallfass, U. *Angew. Chem., Int. Ed.* **2002**, *41*, 1743−1745.
(14) Hachisu, Y.; Bode, J. W.; Suzuki, K. *J. Am. Chem. Soc.* **2003**, *125*, 8432−8433.
(15) Nyce, G. W.; Lamboy, J. A.; Connor, E. F.; Waymouth, R. M.; Hedrick, J. L. *Org. Lett.* **2002**, *4*, 3587−3590.
(16) Grasa, G.; Kissling, R. M.; Nolan, S. P. *Org. Lett.* **2002**, *4*, 3583−3586.
(17) Grasa, G. A.; Guveli, T.; Singh, R.; Nolan, S. P. *J. Org. Chem.* **2003**, *68*, 2812−2819.
(18) Singh, R.; Kissling, R. M.; Letellier, M. A.; Nolan, S. P. *J. Org. Chem.* **2004**, *69*, 209−212.
(19) Chow, K. Y. K.; Bode, J. W. *J. Am. Chem. Soc.* **2004**, *126*, 8126−8127.
(20) Reynolds, N. T.; de Alaniz, J. R.; Rovis, T. *J. Am. Chem. Soc.* **2004**, *126*, 9518−9519.
(21) Sohn, S. S.; Rosen, E. L.; Bode, J. W. *J. Am. Chem. Soc.* **2004**, *126*, 14370−14371.
(22) Duong, H. A.; Cross, M. J.; Louie, J. *Org. Lett.* **2004**, *6*, 4679−4681.
(23) Bourissou, D.; Guerret, O.; Gabbai, F. P.; Bertrand, G. *Chem. Rev.* **2000**, *100*, 39−91.
(24) Canac, Y.; Soleilhavoup, M.; Conejero, S.; Bertrand, G. J. *Organomet. Chem.* **2004**, *689*, 3857−3865.
(25) Connor, E. F.; Nyce, G. W.; Myers, M.; Möck, A.; Hedrick, J. L. *J. Am. Chem. Soc.* **2002**, *124*, 914−915.
(26) Nyce, G. W.; Glauser, T.; Connor, E. F.; Mock, A.; Waymouth, R. M.; Hedrick, J. L. *J. Am. Chem. Soc.* **2003**, *125*, 3046−3056.
(27) Dechy-Cabaret, O.; Martin-Vaca, B.; Bourissou, D. *Chem. Rev.* **2004**, *104*, 6147−6176.
(28) Lofgren, A.; Albertsson, A. C.; DuBois, P.; Jerome, R. *J. Macromol. Sci. Rev.* **1995**, *C35*, 379−418.
(29) Nouvel, C.; Dubois, P.; Dellacherie, E.; Six, J. L. *J. Polym. Sci., Part A: Polym. Chem.* **2004**, *42*, 2577−2588.
(30) Penczek, S.; Biela, T.; Duda, A. *Macromol. Rapid Commun.* **2000**, *21*, 941−950.
(31) Nyce, G. W.; Csihony, S.; Waymouth, R. M.; Hedrick, J. L. *Chem.-Eur. J.* **2004**, *10*, 4073−4079.

Scheme 1. ROP with Adducts of Saturated NHCs



To this end, we were attracted to alcohol adducts of saturated carbenes. Wanzlick generated the methanol adduct of 1,3-diphenylimidazolin-2-ylidene from the dimer of the carbene and methanol.[32] Thermolysis of this adduct in refluxing xylene regenerated the carbene dimer and methanol. Alcohol adducts of triazolylidene carbenes were prepared by Enders by reaction of the triazolium salt with methoxide[33] or by reaction of the free triazolylidene with methanol.[34] Thermolysis of this adduct at 80 °C liberated the free triazolylidene. More recently, Grubbs,[35−37] Blechert,[38] and Herrmann[39] have used alcohol adducts of imidazolin-2-ylidines to generate metal complexes with NHC ligands. The *tert*-butanol adduct of the saturated mesityl-substituted carbene SIMes(H)(O-*t*-Bu) was reported to decompose at room temperature, presumably to the free carbene.[37] These results suggested that the liberation of carbenes from the alcohol adducts might provide a suitable source of carbenes at lower temperatures.

Here we report the synthesis and characterization of a series of alcohol adducts of imidazolin-2-ylidene carbenes, including the first X-ray crystal structure of an alkoxyimidazole. These compounds function as single-component catalyst/initiators for the ring-opening polymerization of lactide to give polylactides of controlled molecular weight.

Results and Discussion

Synthesis and Characterization of Alcohol Adducts. To isolate alcohol adducts of saturated carbenes, reaction of the imidazolinium salt with an alkoxide salt seemed to be the most obvious pathway.[37] We found that simply mixing primary or

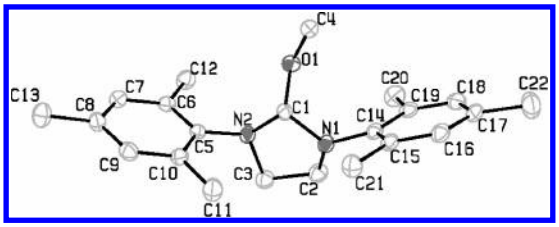


Figure 1. ORTEP diagram of **2**. Selected bond lengths (Å) and angles (deg): O(1)−C(1) 1.437, N(1)−C(1) 1.443, N(1)−C(2) 1.461, N(2)−C(1) 1.428, N(2)−C(3) 1.464, C(2)−C(3) 1.505, C(1)−N(1)−C(2) 109.4, C(1)−N(2)−C(3) 111.4, N(2)−C(1)−O(1) 107.9, N(2)−C(1)−N(1) 103.7, O(1)−C(1)−N(1) 114.7, N(1)−C(2)−C(3) 101.9, N(2)−C(3)−C(2) 102.4.

secondary alcohols with the isolated 1,3-dimesitylimidazolin-2-ylidene carbene[40] (SIMes, **1**) provided an expedient route to a broad family of these adducts (Scheme 2, method A). In addition, we developed two in situ procedures for the preparation of adducts that eliminate the need for the isolation of the free carbene. Adducts can be prepared and isolated from a THF suspension of the imidazolium salt, potassium hydride, and the appropriate alcohol (Scheme 2, method B). Multifunctional adducts **7** and **8** were easily prepared using this method by addition of 2 and 3 equiv, respectively, of the imidazolium salt relative to the di- or triol. Alternatively, we have prepared the ethanol adduct directly from the diamine in one pot by condensation with triethylorthoformate at elevated temperature, followed by subsequent addition of potassium hydride (Scheme 2, method C).[41] These procedures provided for the syntheses of a variety of alcohol adducts in 20−86% isolated yield.

Formation of the adducts was confirmed by ^{1}H and ^{13}C NMR spectroscopy in combination with X-ray crystallography. For example, in the ^{13}C NMR spectrum of methanol adduct **2**, a singlet resonance for carbon C(1) (Figure 1) was located at 104 ppm, significantly upfield from that observed for the carbene carbon in the free SIMes carbene (244 ppm).[40] The ^{1}H NMR spectrum of **2** displayed a singlet at 5.48 ppm for the C(1) proton and multiplets at 3.10 and 3.65 ppm for the inequivalent

Scheme 2. Preparation of Alcohol Adducts

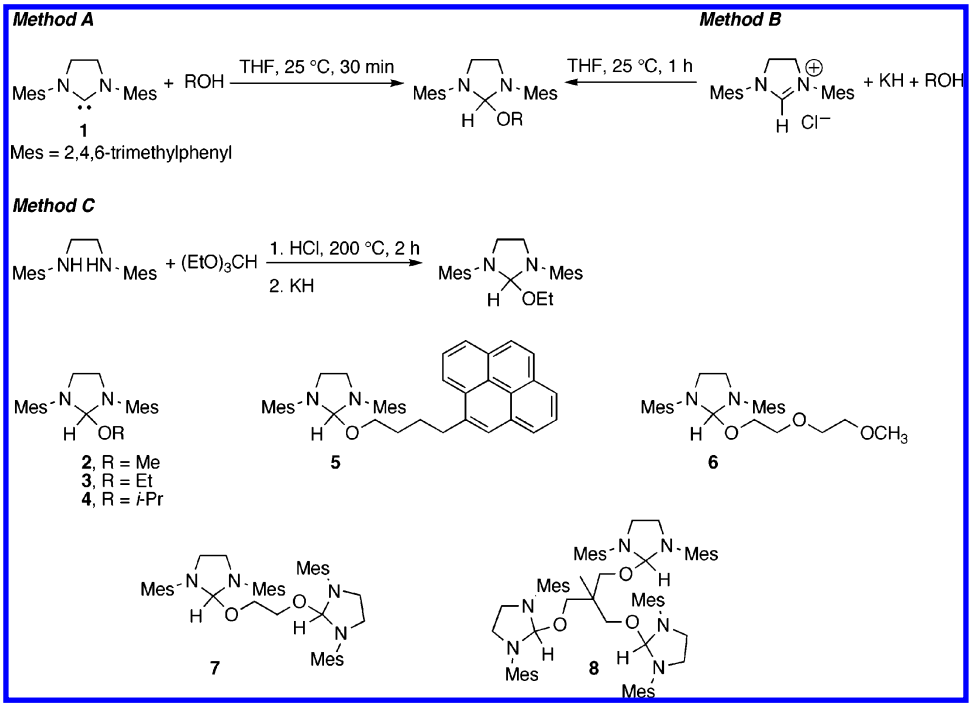
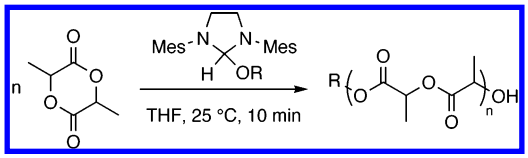


Table 1. Selected Data for the Polymerization of Lactide with Alcohol Adducts of Saturated Carbenes



entry	cat.	M/cat.[a]	conv[b]	DP[c]	PDI[d]
1	**2** (OMe)	100	89	89	1.18
2	**3** (OEt)	100	94	94	1.28
3	**5** (OPyr)	100	99	99	1.27
4	**6** (ODEG)	100	98	98	1.34
5	**7** (OEGO)	100	84	84	1.21
6	**8** (triol)	157	99	156	1.16
7	**1** (SIMes)[e]	100	87	87	1.30

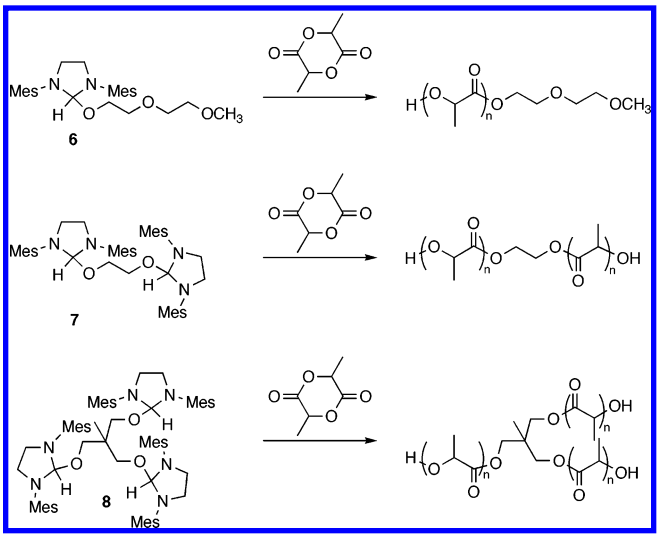
[a] Monomer to catalyst ratio. [b] Conversion determined by ^{1}H NMR spectropscopy. [c] Degree of polymerization; determined by end group analysis from ^{1}H NMR spectroscopy. [d] Polydispersity index; determined by gel permeation chromatography, calibrated with polystyrene standards. [e] Reaction conducted with methanol; lactide:**1**:MeOH, 100:1:1.

methylene resonances. However, the *ortho*-Me groups of **2** appear as magnetically equivalent resonances at 2.77 ppm, indicating that at room temperature the mesityl groups undergo facile rotation about the N−C bonds; similar behavior is observed for adducts **5**−**8** at room temperature. The ^{1}H NMR spectrum of ethanol adduct **3** displayed a single broad resonance for the *ortho*-Me groups, while the *ortho*-Me groups of secondary alcohol adduct **4** are magnetically inequivalent at room temperature.

Crystallization of **2** from pentane afforded crystals suitable for X-ray diffraction (Figure 1). Analysis of the structure reveals a tetrahedral geometry at C(1) with a C(1)−O(1) bond distance of 1.437 Å. The N(1)−C(1)−N(2) angle in **2** is smaller than that in the free carbene[40] (103.7° for **2** vs 104.7° for **1**), while the C(1)−N(1) and C(1)−N(2) bond distances are longer (1.443, 1.428 Å, respectively, for **2** vs 1.352, 1.345 Å, for **1**). Both N(1) and N(2) are pyramidal: the N(1) center lies 0.213 Å below the plane of its three attached C substituents (sum of the valence angles is 353.6°), and N(2) is displaced 0.278 Å above the plane of its attached C atoms (sum of the valence angles is 349.1°). The O(1)−C(1)−N(2)−C(5) and the O(1)−C(1)−N(1)−C(14) torsion angles are 91.9° and −54.3°, respectively, consistent with pyramidal nitrogen atoms. The methanol adduct of a related triazolium carbene reported by Enders also displays pyramidalization of the corresponding N atoms (sums of the valence angles are 356.9° and 358.2°).[33]

Ring-Opening Polymerization Activity. These alcohol adducts are potent organocatalysts for the ROP of lactide in THF at room temperature (Table 1). Polylactide was obtained within minutes in high yield with narrow polydispersity and predictable molecular weight based on the monomer-to-initiator ratio, and the α-chain end of the polymer contained the ester functionality of the alkoxy group of the catalyst. Slight increases in polydispersity were observed with increased reaction times (for polymerizations catalyzed by **2**, PDI = 1.18, 1.30, for 10, 60 min, respectively), suggesting that these compounds catalyze transesterification after consumption of the lactide monomer. Poly(lactide)s with simple alkyl ester end groups were obtained using **2** or **3** (entries 1, 2). In the electrospray ionization mass spectrum of oligomers formed from **2** and lactide ([lactide]/[**2**] = 10), only methoxy end groups are observed.[42] When the adduct **5**, derived from 1-pyrenebutanol, was used (entry 3),

Scheme 3. Polymerizations Using **6** or Multifunctional Adducts **7** or **8**

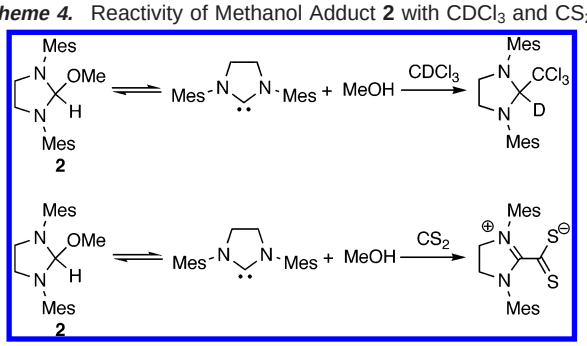


GPC traces for the resulting polylactide using both the refractive index and UV detectors (410 and 350 nm, respectively) showed the distribution of pyrene throughout the sample and corroborate ^{1}H NMR spectroscopy studies that indicate the presence of one initiator per polymer chain. Polymerizations of lactide using alcohol adducts of SIMes yielded results similar to those using the isolated carbene in the presence of methanol (entry 7) under the same conditions, indicating that these stable adducts can be used in place of the moisture-sensitive free saturated NHC. For these alcohol adducts, the polymerizations were well-controlled for degrees of polymerization ≤ 100 (Table 1); attempts to generate higher molecular weight polymers were less successful than those with the unsaturated imidazolylidenes,[26] which we attribute to the 1:1 stoichoimetry of the carbene and the initiating alcohol generated from the alcohol adducts. Further studies are underway to optimize these catalyst systems for the formation of higher molecular weight polymers.

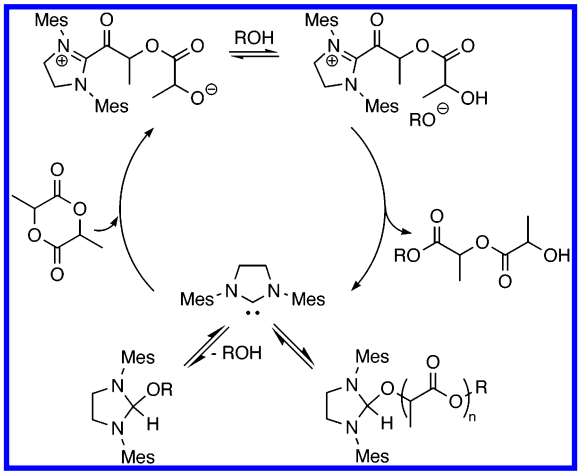
Polymerizations using adduct **6** or multifunctional adducts **7** or **8** highlight the use of this novel catalyst system for the synthesis of more complex polymer architectures (Scheme 3). Polymerizations of lactide using **6** and **7** illustrate the potential of these systems to generate diblock and triblock polymers of lactide and a polymer containing an alcohol end group. Polymerization of lactide with **8** generates telechelic and star polyesters in a single step.

(32) (a) Lachmann, B.; Wanzlick, H. W. *Liebigs Ann. Chem.* **1969**, *729*, 27−32. (b) Hoffmann, R. W.; Hagenbruch, B.; Smith, D. M. *Chem. Ber.* **1977**, *110*, 23−36. (c) Csihony, S.; Beaudette, T. T.; Sentman, A. C.; Nyce, G.; Waymouth, R. M.; Hedrick, J. L. *Adv. Synth. Catal.* **2004**, *346*, 1081−1086.
(33) Enders, D.; Breuer, K.; Raabe, G.; Runsink, J.; Teles, J. H.; Melder, J. P.; Ebel, K.; Brode, S. *Angew. Chem., Int. Ed.* **1995**, *34*, 1021−1023.
(34) Enders, D.; Breuer, K.; Runsink, J.; Teles, J. H. *Liebigs Ann. Chem.* **1996**, 2019−2028.
(35) Scholl, M.; Ding, S.; Lee, C. W.; Grubbs, R. H. *Org. Lett.* **1999**, *1*, 953−956.
(36) Morgan, J. P.; Grubbs, R. H. *Org. Lett.* **2000**, *2*, 3153−3155.
(37) Trnka, T. M.; Morgan, J. P.; Sanford, M. S.; Wilhelm, T. E.; Scholl, M.; Choi, T. L.; Ding, S.; Day, M. W.; Grubbs, R. H. *J. Am. Chem. Soc.* **2003**, *125*, 2546−2558.
(38) Schürer, S. C.; Gessler, S.; Buschmann, N.; Blechert, S. *Angew. Chem., Int. Ed.* **2000**, *39*, 3898−3901.
(39) Denk, K.; Sirsch, P.; Herrmann, W. A. *J. Organomet. Chem.* **2002**, *649*, 219−224.
(40) Arduengo, A. J., III; Goerlich, J. R.; Marshall, W. J. *J. Am. Chem. Soc.* **1995**, *117*, 11027−11028.
(41) Wanzlick, H. W.; Lachmann, B.; Schikora, E. *Chem. Ber.* **1965**, *98*, 3170.
(42) See Supporting Information.

Scheme 4. Reactivity of Methanol Adduct **2** with $CDCl_3$ and CS_2



Scheme 5. Proposed Mechanism for the ROP of Lactide with Alcohol Adducts



Several experiments were carried out to provide evidence for the generation of the carbene in solution at room temperature. Treatment of **2** with a 10-fold excess of $CDCl_3$ led to the quantitative formation of methanol and the chloroform adduct[43] within 10 min at room temperature (Scheme 4). Addition of CS_2 to a benzene solution of **2** immediately generated methanol and the zwitterionic CS_2 adduct,[44−46] which precipitated from solution.[31] These results are consistent with the elimination of the alcohol to generate the carbene, by either a concerted or stepwise heterolytic mechanism.[32] The observation of the CS_2 adduct provides strong evidence for the intermediacy of the free carbene. In contrast, elimination of methanol from the analogous triazolium carbene was reported to be endothermic and required heating to 80 °C at 0.1 mbar.[33] These results suggest that the thermal stabilities of alcohol adducts of N-heterocyclic carbenes are sensitive to the nature of the carbene.

We propose a nucleophilic, monomer-activated mechanism for the ring-opening polymerization of lactide catalyzed by alcohol adducts of NHCs (Scheme 5). Elimination of alcohol from the NHC adduct generates the carbene, which attacks the monomer, generating a zwitterionic intermediate. Proton exchange, followed by nucleophilic attack of the alkoxide on the activated acyl imidazolium intermediate, liberates the carbene and a new alcohol derived from lactide. As we have shown that saturated carbenes reversibly form alcohol adducts, the reaction of the saturated carbene with alcohol would generate a dormant alcohol adduct, providing a means of reversibly deactivating the carbene. The reversible formation of dormant and active species is a characteristic of controlled radical polymerization reactions[47−49] and may contribute to the exceptional control we observe for ring-opening polymerization in the presence of alcohol adducts of saturated carbenes.

Conclusions

Several methods for the synthesis and isolation of new alcohol adducts of saturated N-heterocyclic carbenes are reported. The structure and reactivity of these alcohol adducts reveal that they reversibly eliminate alcohol rapidly at room temperature. This behavior was exploited to generate effective single-component catalyst/initiators for the ring-opening polymerization of lactide. The ease of preparation and stability of these compounds in their isolated form, in combination with their ability to release the free carbene in solution, suggest that alcohol adducts of saturated NHCs will have broad applications as both organocatalysts and ligand delivery agents for transition metals.

Experimental Section

General Considerations. All syntheses and polymerizations were performed in a drybox or with Schlenk techniques under nitrogen. Solvents were dried and degassed by standard procedures. Methanol, ethanol, and 2-propanol were purchased from Fisher Chemicals and distilled twice from calcium hydride. 1-Pyrenebutanol, di(ethylene glycol) methyl ether, and ethylene glycol were purchased from Aldrich and used as received. Potassium hydride was freed from oil before use by washing three times with pentane and drying under vacuum. L- and D,L-lactide were obtained from Purac and used without further purification (water content < 0.02%). Deuterated chloroform was purchased from Cambridge Isotope Laboratories, Inc. and distilled from calcium hydride. 1,3-Bis(2,4,6-trimethylphenyl)imidazolinium chloride and 1,3-bis(2,4,6-trimethylphenyl)imidazolin-2-ylidene (SIMes, **1**) were prepared according to literature procedures.[50] ^1H and ^{13}C NMR spectra were recorded at room temperature on 300 or 400 MHz spectrometers, with shifts reported in parts per million downfield from tetramethylsilane and referenced to the residual solvent peak. Gel permeation chromatography was performed in tetrahydrofuran on a Waters chromatograph equipped with four 5 μm Waters columns (300 mm × 7.7 mm) connected in series with increasing pore size (10, 100, 1000, 10^5, 10^6 Å). A Waters 410 differential refractometer and 996 photodiode array detector were employed. Elemental analysis was performed by Robertson Microlit Laboratories, Inc., Madison, NJ 07940.

Synthesis of SIMes(H)(OMe) (2) using Method A. In a 25 mL Schlenk flask equipped with a stir bar, 1,3-bis(2,4,6-trimethylphenyl)-imidazolin-2-ylidene (200 mg, 0.65 mmol) was dissolved in 5 mL of dry THF. Methyl alcohol (0.072 mL, 2.0 mmol) was injected via syringe under nitrogen. The mixture was stirred for 30 min, and the volatiles were evaporated. The resulting white solid was dried under vacuum and crystallized from pentane (150 mg, 68%). ^1H NMR (C_6D_6, 400 MHz): δ 2.15 (s, 6H), 2.50 (s, 12H), 2.77 (s, 3H), 3.10 (m, 2H), 3.65 (m, 2H), 5.48 (s, 1H), 6.83 (s, 4H). ^{13}C NMR (C_6D_6, 400 MHz): δ 19.37, 20.89, 49.28, 54.07, 104.57, 129.78, 135.45, 138.64, 139.39. Anal. Calcd for $C_{22}H_{30}N_2O$: C, 78.06; H, 8.93; N, 8.28. Found: C, 77.92; H, 8.90; N, 8.12.

(43) Arduengo, A. J.; Calabrese, J. C.; Davidson, F.; Dias, H. V. R.; Goerlich, J. R.; Krafczyk, R.; Marshall, W. J.; Tamm, M.; Schmutzler, R. *Helv. Chim. Acta* **1999**, *82*, 2348−2364.
(44) Kuhn, N.; Bohnen, H.; Henkel, G. Z. *Naturforsch., B: Chem. Sci.* **1994**, *49*, 1473−1480.
(45) Schössler, W.; Regitz, G. *Chem. Ber.* **1974**, *107*, 1931−1948.
(46) Duong, H. A.; Tekavec, T. N.; Arif, A. M.; Louie, J. *Chem. Commun.* **2004**, 112−113.
(47) Matyjaszewski, K. *Macromol. Symp.* **2001**, *174*, 51−67.
(48) Matyjaszewski, K., Ed. *Controlled Radical Polymerization*; American Chemical Society: Washington, DC, 1998; Vol. 685.
(49) Hawker, C. J.; Bosman, A. W.; Harth, E. *Chem. Rev.* **2001**, *101*, 3661−3688.
(50) Arduengo, A. J.; Krafczyk, R.; Schmutzler, R.; Craig, H. A.; Goerlich, J. R.; Marshall, W. J.; Unverzagt, M. *Tetrahedron* **1999**, *55*, 14523−14534.

Synthesis of 2 using Method B. In an inert atmosphere, 1,3-bis-(2,4,6-trimethylphenyl)imidazolinium chloride (250 mg, 0.729 mmol) was suspended in THF (7 mL). Potassium hydride (38 mg, 0.95 mmol) was suspended in THF (2 mL) and added to the imidazolinium chloride suspension. Methanol (27 μL, 0.67 mmol) was added to the resulting suspension, and the mixture was stirred for 1 h. The mixture was then filtered to remove residual salts, and the solvent removed under vacuum to give 107 mg (47.2%) of the pure product as a white solid.

X-ray Crystal Structure of SIMes(H)(OMe) (2). Full details are contained in the Supporting Information. X-ray quality crystals of SImMesHOMe were grown by cooling a saturated pentane solution of **2**. A colorless rhombic crystal of $C_{22}H_{30}N_2O$ having approximate dimensions of 0.30 × 0.21 × 0.17 mm was mounted on a quartz fiber using Paratone N hydrocarbon oil. All measurements were made on a Bruker-Siemens SMART CCD area detector with monochromatic radiation of wavelength 0.71073 Å.

Synthesis of SIMes(H)(OEt) (3). In a drybox under N_2, a suspension of KH (68 mg, 1.7 mmol) in dry THF (5 mL) was added to a stirred suspension of 1,3-bis(2,4,6-trimethylphenyl)imidazolinium chloride (386 mg, 1.13 mmol) in dry THF (10 mL) in a 20 mL vial. Ethanol (69 μL, 1.2 mmol) was added to the resulting cloudy white suspension via microsyringe. The mixture was stirred at room temperature for 40 min and then filtered to remove residual salts. The resulting clear, colorless solution was concentrated under vacuum to yield 325 mg (81.9%) of the product as a colorless sticky solid. ^{1}H NMR (C_6D_6, 400 MHz): δ 0.72 (t, 6.8 Hz, 2H), 2.15 (s, 6H), 2.51 (br s, 12H), 2.92 (q, 6.8 Hz, 2H), 3.14 (m, 2H), 3.67 (m, 2H), 5.52 (s, 1H), 6.85 (s, 4H). ^{13}C NMR (C_6D_6, 400 MHz): δ 15.94, 19.40, 20.94, 49.19, 62.38, 103.52, 129.73, 135.45, 138.64, 139.27.

Synthesis of 3 using Method C. *N*,*N*′-(2,4,6-Trimethylphenyl)-ethylenediamine (0.31 g, 1.0 mmol) was dissolved in 3 mL of dry triethylorthoformate. A 1 M solution of hydrogen chloride in diethyl ether (1.0 mL, 1.0 mmol) was added by syringe. The suspension was heated to 200 °C for 2 h. After cooling to room temperature, potassium hydride (0.05 g, 1.0 mmol) was added and the suspension was stirred for 30 min before being filtered and concentrated under vacuum to yield **3** as an orange solid (0.16 g, 0.45 mmol, 45%).

Synthesis of SIMes(H)(O^{i}Pr) (4). In a 25 mL Schlenk flask equipped with a stir bar, 1,3-bis(2,4,6-trimethylphenyl)imidazolin-2-ylidene (50 mg, 0.163 mmol) was dissolved in 5 mL of dry THF, and isopropyl alcohol (0.062 mL, 0.817 mmol) was injected via syringe under nitrogen. The mixture was stirred for 30 min, the volatiles were evaporated, and the resulting white sticky solid was dried under vacuum (50 mg, 86%). ^{1}H NMR (400 MHz, C_6D_6): δ (d, 6.0 Hz, 6H), 2.15 (s, 6H), 2.43 (br s, 6H), 2.57 (br s, 6H), 2.99 (sept, 6.0 Hz, 1H), 3.15 (m, 2H), 3.67 (m, 2H), 5.54 (s, 1H), 6.85 (s, 4H). ^{13}C NMR (C_6D_6, 400 MHz): δ 18.87 (br s), 20.01 (br s), 20.99, 23.08, 48.95, 69.32, 102.70, 129.47 (br s), 129.84 (br s), 135.41, 137.51 (br s), 139.94, 140.05 (br s).

Synthesis of SIMes(H)(OPyr) (5). In a 25 mL Schlenk flask equipped with a stir bar, 1,3-bis(2,4,6-trimethylphenyl)imidazolin-2-ylidene (50 mg, 0.163 mmol) and 1-pyrenebutanol (45 mg, 0.163 mmol) were dissolved in 0.5 mL of dry THF under nitrogen. The mixture was stirred for 30 min, and the volatiles were evaporated. A yellow solid formed, which was dried under vacuum (80 mg, 84%). ^{1}H NMR (400 MHz, C_6D_6): δ 1.27 (m, 2H), 1.50 (m, 2H), 2.07 (s, 6H), 2.50 (br s, 12H), 2.88 (t, 8.0 Hz, 2H), 2.98 (t, 6.0 Hz, 2H), 3.11 (m, 2H), 3.65 (m, 2H), 5.56 (s, 1H), 6.79 (s, 4H), 7.52 (d, 7.6 Hz, 1H), 7.75−8.01 (m, 8H). ^{13}C NMR (C_6D_6, 400 MHz): δ 19.41, 20.88, 28.25, 30.86, 33.14, 49.16, 66.81, 103.95, 123.92, 124.88, 125.04, 125.07, 125.63, 125.69, 125.94, 126.76, 127.26, 127.28, 127.90, 129.06, 129.73, 130.11, 131.47, 131.96, 135.49, 137.40, 139.21. Anal. Calcd for $C_{41}H_{44}N_2O$: C, 84.79; H, 7.64; N, 4.82. Found: C, 84.20; H, 7.74; N, 4.71.

Synthesis of SIMes(H)($OCH_2CH_2OCH_2CH_2OMe$) (6). In a drybox under N_2, di(ethylene glycol) methyl ether (78 μL, 0.65 mmol) was added via microsyringe to a solution of SIMes (200 mg, 0.653 mmol) in dry THF (4 mL) in a 25 mL Schlenk flask. The resulting clear, yellow solution was stirred at room temperature for 20 min and then concentrated under vacuum. The resulting yellow solid was washed with pentane and dried under vacuum to yield 146 mg (52.5%) of the product as a pale yellow solid. ^{1}H NMR (C_6D_6, 400 MHz): δ 2.15 (s, 6H), 2.49 (br s, 12H), 3.03 (m, 2H), 3.06 (s, 3H), 3.08 (m, 2H), 3.12 (m, 4H), 3.16 (m, 2H), 3.66 (m, 2H), 5.58 (s, 1H), 6.83 (s, 4H). ^{13}C NMR (C_6D_6, 400 MHz): δ 19.76, 21.32, 49.55, 58.97, 66.96, 70.93, 71.95, 72.54, 104.55, 130.12, 135.83, 138.98, 139.50.

Synthesis of [SIMes(H)O]$_2$(CH_2CH_2) (7). In an inert atmosphere, 1,3-bis(2,4,6-trimethylphenyl)imidazolinium chloride (230 mg, 0.671 mmol) was suspended in THF (5 mL). Potassium hydride (40 mg, 1.0 mmol) was suspended in THF (1 mL) and added to the imidazolinium chloride suspension. Ethylene glycol (21 mg, 0.34 mmol) was added to the combined suspension, and the mixture stirred for 1 h. The mixture was then filtered via syringe filter, and the solvent removed under vacuum to give the crude product as a yellow solid. The product was purified by washing with a small amount of pentane (0.5 mL) to yield 44 mg (20%) of the pure product as a colorless crystalline solid. ^{1}H NMR (C_6D_6, 400 MHz): δ 2.18 (s, 12H), 2.34 (s, 24H), 2.72 (s, 4H), 3.03 (dd, 4H), 3.56 (dd, 4H), 5.22 (s, 2H), 6.78 (s, 8H). ^{13}C NMR (C_6D_6, 400 MHz): δ 19.64, 21.36, 49.47, 66.68, 104.25, 130.05, 135.55, 139.37.

Synthesis of [SIMes(H)OCH_2]$_3CCH_3$ (8). In an inert atmosphere, 1,3-bis(2,4,6-trimethylphenyl)imidazolinium chloride (289 mg, 0.842 mmol) was suspended in THF (5 mL). Potassium hydride (51 mg, 1.3 mmol) was suspended in THF (1 mL) and added to the imidazolinium chloride suspension. 2-(Hydroxymethyl)-2-methylpropane-1,3-diol (32 mg, 0.27 mmol) was added to the combined suspension, and the mixture stirred 1 h. The mixture was then filtered via syringe filter, and the solvent removed under vacuum to give the product as a white solid (75 mg, 27%). ^{1}H NMR (C_6D_6): δ 2.7 (s, 18H), 2.31 (s, 36H), 2.46 (s, 6H), 3.02 (dd, 6H), 3.27 (s, 3H), 3.52 (dd, 6H), 5.13 (s, 3H), 6.81 (s, 12H). ^{13}C NMR (C_6D_6, 400 MHz): δ 18.61, 19.66, 21.47, 41.42, 49.53, 68.15, 71.70, 104.21, 129.92, 135.34, 139.71.

Reaction of 2 with $CDCl_3$. In an NMR tube, SIMes(H)(OMe) (41 mg, 0.134 mmol) was dissolved in dry benzene and $CDCl_3$ (0.107 mL, 1.34 mmol) was injected via syringe. The ^{1}H NMR spectrum was recorded after 10 min. Formation of 1,3-dimesityl-2-deutero-2-trichloromethylimidazolidine[43] and methanol was observed in quantitative yield. At longer times an increase in the chloroform peak was also observed, indicative of a slower proton exchange between the MeOH and $CDCl_3$.

Reaction of 2 with CS_2. In an NMR tube equipped with J-young valve, SIMes(H)(OMe) **2** (10 mg, 0.03 mmol) was dissolved in 0.300 mL of dry benzene-d_6 and carbon disulfide (0.018 mL, 0.30 mmol) was injected via syringe under nitrogen. A red precipitate formed immediately, and methanol was observed by ^{1}H NMR spectroscopy. The solvent was decanted, and the red solid was identified as $SIMesCS_2$ by comparison of its ^{1}H NMR spectrum to that reported in the literature.[31] ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.23 (s, 6H), 2.54 (s, 12H), 4.20 (s, 4H), 6.87 (s, 4H).

Typical Method for Polymerization of Lactide. A 25 mL Schlenk flask, equipped with a stir bar, was charged with L-lactide (100 mg, 0.69 mmol) and dissolved in 1 mL of anhydrous THF. To this solution was added SIMes(H)(OMe) (2.3 mg, 6.9 μmol). The reaction mixture was stirred for 10 min, and the reaction was quenched with a drop of acetic acid. The conversion was determined by ^{1}H NMR spectroscopy. The polymer was precipitated in methanol and dried to a constant weight (89 mg, 89%, PDI = 1.18, M_n = 16500), and the degree of polymerization was analyzed by ^{1}H NMR spectroscopy (DP = 89). ^{1}H NMR (acetone-d_6): δ 1.46−1.56 (d, 3H, $-CH_3$), 5.05−5.25 (q, H, −CH−).

Acknowledgment. We gratefully acknowledge support from the NSF Center on Polymeric Interfaces and Macromolecular Assemblies (CPIMA: NSF-DMR-0213618) and an NSF-GOALI grant (NSF-CHE-0313993). D.A.C. thanks the NIH for a postdoctoral fellowship (GM070181-01A1). We thank Purac for a generous donation of lactide.

Supporting Information Available: X-ray diffraction data for **2**, CIF files, and electrospray MS of polylactide. This material is available free of charge via the Internet at http://pubs.acs.org.

JA050909N