# **ORGANOMETALLICS**

### Novel N,O,N-Supported Tetracoordinate Aluminum Complexes for the Highly Controlled and Immortal ROP of Trimethylene Carbonate (TMC) under Mild Conditions: Access to Narrowly Disperse poly-TMC and Derived Copolymers

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Supporting Information

**ABSTRACT:** The novel N,O,N-supported tetracoordinate amidoaluminum complexes { $\eta^3(N,O,N)$ -(C<sub>5</sub>H<sub>9</sub>)N-C<sub>6</sub>H<sub>4</sub>}<sub>2</sub>O-AlNMe<sub>2</sub> (**2a**, R = C<sub>5</sub>H<sub>9</sub>; **2b**, R = C<sub>6</sub>H<sub>11</sub>) have been synthesized and structurally characterized. In the solid state, as determined from X-ray crystallographic studies, complex **2a** consists of a four-coordinate Al species in which the Al center adopts a distorted-trigonal-monopyramidal (tmp) geometry with the nitrogens of the three amido groups (defining the pyramidal base) being nearly coplanar with Al. Such Al species, when



combined with an alcohol source such as benzyl alcohol, effectively polymerize trimethylene carbonate (TMC) at room temperature in a highly controlled manner to yield narrowly disperse poly(trimethylene carbonate), as deduced from polymer characterizations with various kinetic studies. The high degree of molecular chain length control of the present system was further exploited to access narrowly dispersed PEG-functionalized amphiphilic copolymers. The attractive features of the system lie in the combination of an excellent activity, a high level of chain length control, and mild reaction conditions.

Biodegradable aliphatic polyesters and polycarbonates such as poly(lactic acid) (PLA) and poly(trimethylene carbonate) (PTMC) have received increased interest in recent years due to their important biomedical and pharmaceutical applications as well as their being viable alternatives to petrochemical-based plastics.<sup>1</sup> In this area, the ring-opening polymerization (ROP) of cyclic esters (lactide,  $\varepsilon$ -caprolactone for example) by discrete metal-based initiators has undoubtedly established itself as the method of choice to access well-defined and narrowly disperse polyesters through precise chain length control.<sup>2</sup> In contrast, despite interest in the resulting polymer, the ROP of cyclic carbonates such as trimethylene carbonate (TMC), a monomer that may be readily prepared from glycerol, by well-defined metal species has been relatively less studied and the reported systems thus far, some of which display high catalytic activity, typically require heating and yield poly(trimethylene carbonate) (PTMC) with moderately narrow polydispersity (PDI > 1.5) whether in bulk or solution polymerization.<sup>3</sup> In general, apart from their intrinsic specific properties, narrowly disperse polymers are also of interest as well-defined building blocks for their subsequent incorporation in, for instance, copolymer block structures to produce various tailor-made materials with precise chain length, featuring improved mechanical properties versus their ill-defined counterparts. In this regard, PTMC appears as an interesting candidate for subsequent access to well-defined biomaterials of current interest such as copolymer PTMC-PLA, a material more

Chart 1



flexible and acid resistant than PLA, and PTMC-PEG, an amphiphilic polymer that may be used as a drug-delivery agent.<sup>1,4,5</sup>

Albeit little studied, constrained tetracoordinate Al(III) complexes supported by an appropriately designed  $LX_2$ -dianionic ligand forcing the Al center into a trigonal-pyramidal coordination geometry (versus its classically preferred tetrahedral geometry) have been shown to be effective Lewis acid catalysts for the mediation of various asymmetric transformations (**B**, Chart 1).<sup>6</sup> On one occasion, such Al complexes (**A**, Chart 1) were also shown to initiate the ROP of *rac*-lactide and propene oxide, yet with low activity and control. The increased reactivity of such Al

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complexes (vs tetrahedral Al systems) arises from a destabilizing ligand-defined geometry distortion, resulting in a more Lewis acidic Al metal center.<sup>6c</sup> Yet, in comparison to usually reactive Al systems, which typically require a low-coordinate metal center (<4) for Lewis acid activation and whose limited stability and tendency to aggregate is frequently problematic,<sup>7</sup> distorted tetra-coordinate aluminum chelates may be readily accessible (in a mononuclear form) and provide a superior steric protection of the Lewis acidic metal center and, hence, an increased stability. Such entities may thus well represent a reasonable reactivity/ stability balance, which is of interest in catalysis.

On these basis and within the above context, we are interested in the development of novel families of tetracoordinate group 13 Lewis acids in order to probe their potential in the polymerization catalysis of polar monomers. As part of this work, we report here on the synthesis and structural characterization of novel N,O,Nsupported tetracoordinate aluminum species (2a,b; Scheme 1) and their subsequent use as initiators (in the presence of an alcohol source) for the highly controlled and immortal ROP of TMC. Also, as shown below, the attractive features of the described system, which combines an excellent activity, a high level of chain length control, and mild reaction conditions, were further exploited to access PTMC-PEG amphiphilic polymers in a well-defined manner.



#### RESULTS AND DISCUSSION

As an entry to novel constrained tetracoordinate Al species, the diamino ether proligands 1a,b (Scheme 1) were picked as supporting ligands for their backbone structure, thought to be susceptible for imposing the desired trigonal-monopyramidal geometry (tmp) to the coordinated Al center; also, compounds 1a,b are readily available in good yield via a one-step procedure from commercially available 2,2'-oxidianiline and have already been shown to be suitable for coordination to oxophilic metals.<sup>8</sup> As illustrated in Scheme 1, the derived N,O,N-supported Al amido species { $\eta^3(N,O,N)$ -RN-C<sub>6</sub>H<sub>4</sub>}<sub>2</sub>OAlNMe<sub>2</sub> ( $2a, R = C_5H_9$ ; **2b**,  $R = C_6H_{11}$ ; Scheme 1) may be directly prepared in good yield via an amine elimination route by reaction of ligands 1a, with 1 equiv of Al(NMe<sub>2</sub>)<sub>3</sub>. Compounds **2a,b** were isolated as highly air- and moisture-sensitive colorless solids, and their molecular structures were confirmed by X-ray crystallography analysis.

As depicted in Figure 1, complex **2a** indeed consists of a fourcoordinate Al species effectively  $\eta^3(N,O,N)$ -chelated by the dianionic diamido amino  $[\{(C_5H_9)N-C_6H_4\}_2O]^{2-}$  ligand, forcing the Al center to adopt a distorted-tmp geometry. The nitrogens of the three amido groups (defining the pyramidal base) are thus nearly coplanar with Al (sum of N-Al-N angles 356.83°). All bond lengths in **2a** are rather as expected with, in particular, all Al-N amido bond distances (see Figure 1) lying within the typical range (1.78–1.86 Å) for terminal Al-amido bonds.<sup>10</sup> Importantly, these solid-state data for **2a** indicate the presence of an apical vacant site ideally disposed for coordination to the Lewis acid Al center. NMR solution data for **2a,b** are consistent with a  $C_s$ -symmetric structure for both complexes under the studied conditions (room temperature,  $C_6D_6$ ), in agreement with solid-state structural data.

Compounds **2a**,**b** were then tested as ROP initiators of TMC in both the absence and presence of an alcohol source such as BnOH. As expected, species **2a**,**b** exhibit very similar ROP activities and control; thus, these will be discussed only for **2a**.



**Figure 1.** Molecular structure of the Al complex **2a**: (a) front view; (b) side view. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Al(1)–N(1) = 1.834(1), Al(1)–N(2) = 1.828(1), Al(1)–N(3) = 1.784(1), Al(1)–O(1) = 1.964(1); N(1)–Al(1)–N(2) = 125.00(6), N(1)–Al(1)–N(3) = 116.11(6), N(3)–Al(1)–N(2) = 115.73(7), N(3)–Al(1)–O(1) = 115.72(6).

 Table 1. ROP of Trimethylene Carbonate by the Al Complex

 2a in the Presence/Absence of  $BnOH^a$ 

entry	$\mathrm{TMC}^{b}$	$BnOH^b$	$t  (\min)^c$	conversn $(\%)^d$	$M_{\rm n,theor}^{e}$	$M_{\rm n,corr}^{~~f}$	$M_{\rm w}/M_{\rm n}^{\ g}$
1	100	0	$10^h$	100	10 200	23 521	2.29
2	100	5	5	90	1 940	1 514	1.12
3	300	3	$30^h$	100	10 200	9 492	1.18
4	600	3	$30^h$	100	20 400	20 678	1.12
5	1100	10	$30^h$	100	11 220	11 973	1.04
6	3000 <sup>i</sup>	30	30	70	7 140	8 1 2 0	1.08

<sup>*a*</sup> Polymerization conditions:  $[TMC]_0 = 1 \text{ M}$ , CH<sub>2</sub>Cl<sub>2</sub>, room temperature. <sup>*b*</sup> Amount in equiv versus Al initiator **2a**. <sup>*c*</sup> Reaction time. <sup>*d*</sup> Monomer conversion. <sup>*e*</sup> Calculated using  $M_{n,\text{theor}} = [TMC]_0/[BnOH]_0 \times M_{TMC} \times$ conversn. <sup>*f*</sup> Measured by GPC in THF (30 °C) using PS standards and corrected by applying the appropriate correcting factor (0.57 for entry 1, 0.88 for entries 2–5).<sup>3c</sup> <sup>*g*</sup> Measured by GPC in THF (30 °C). <sup>*h*</sup> The reaction time is not optimized. <sup>*i*</sup> [TMC]\_0 = 2 M.



**Figure 2.** Plot of the molecular weight number  $(M_n)$  of the formed PTMC as a function of TMC conversion in the ROP of TMC by a 2a/ BnOH initiating system. Conditions: 100 equiv of TMC (vs 2a), 5 equiv of BnOH (vs 2a), [TMC]<sub>0</sub> = 1 M, CH<sub>2</sub>Cl<sub>2</sub>, room temperature.

As a starting point, the Al amido species 2a was found to readily mediate the ROP of TMC with the quantitative conversion of 100 equiv of TMC within a few minutes at room temperature to PTMC (entry 1, Table 1), yet the resulting polymer features a broad polydispersity, indicative of a likely poorly controlled polymerization reaction. In contrast, the ROP of TMC initiated by a 2a/BnOH mixture was much more successful (entries 2-5, Table 1). Thus, using various amounts of BnOH and monomers, the 2a/BnOH system may quantitatively polymerize from 100 up to 1100 equiv of TMC at room temperature within 30 min to yield narrowly disperse PTMC, as deduced from NMR and GPC data (see the Supporting Information, Figures S2 and S3). Carrying out the ROP catalysis using 3000 equiv of TMC in the presence of 30 equiv of BnOH (vs species 2a) yields a 70% conversion to PTMC after 30 min at room temperature (corresponding to a TON of 4200  $h^{-1}$ ), thereby showing the excellent activity of the present 2a/BnOH system. All data support that the ROP polymerization by 2a/BnOH proceeds in an immortal manner, with BnOH acting as a chain transfer agent.<sup>9</sup> In particular, as shown in Table 1, all observed  $M_n$  values (after correction) closely match the initial  $[TMC]_0/[BnOH]_0$ ratio with, for instance, up to 30 polymer chains being generated per Al center (entry 6, Table 1). The controlled character of the





**Figure 3.** Plot of the molecular weight number  $(M_n)$  of the formed PTMC as a function of  $[2a]_0/[BnOH]_0$  in the ROP of TMC by a 2a/BnOH initiating system. Conditions: 1100 equiv of TMC (vs 2a),  $[TMC]_0 = 1 \text{ M}$ ,  $CH_2Cl_2$ , room temperature.

present ROP system is further substantiated by the linear correlation between the  $M_n$ (corrected) value of the formed PTMC and monomer conversion during the polymerization reaction (Figure 2). Also, as depicted in Figure 3, varying the initial Al initiator/BnOH ratio (for a given amount of monomer) was found to be linearly related to the molecular weight number  $(M_n)$  of the resulting polymers, this being consistent with the alcohol-mediated chain transfer reactions proceeding in a controlled manner during these polymerization reactions.

Whether it be with regard to catalytic performance or polymer chain length control, the ROP activity of initiators **2a**,**b** compares very favorably with that of higher coordinate Al(III) complexes such as, for instance, salen-supported Al alkoxides; at best, the latter have been reported to quantitatively polymerize 350 equiv of TMC within 2 h at 95 °C to yield PTMC with moderately narrow polydispersity (PDI = 1.6).<sup>3b</sup>

End-group analysis of the obtained PTMCs (entries 2-5, Table 1) by <sup>1</sup>H NMR and MALDI-TOF spectrometry (see the Supporting Information, Figure S1) unambiguously establish the presence of a OBn moiety at the ester end and the absence of amido-capped PTMCs, suggesting that the Al-amido group in 2a may not act as an initiating moiety at all in these polymerization reactions as might have been thought. This, along with control experiments showing that 2a does not readily convert to the corresponding Al-OBn derivative in the presence of BnOH at room temperature, disfavor a coordination-insertion mechanism proposal similar to that taking place in the ROP of TMC by salen-bearing Al alkoxide complexes.<sup>3a</sup> Rather, it appears likely that the present polymerization may occur through a sequential Lewis acid monomer activation/alcohol nucleophilic attack and subsequent chain transfer reactions,<sup>3g</sup> in which complex 2a would act as a well-defined Lewis acid component (Scheme 2).

The apparent attractive features of the **2a**/ROH initiating system prompted us to further exploit its possibilities to access various well-defined biomaterials, such as PTMC-PEG amphiphilic polymers, through the use of a monocapped methoxy ether PEG-OH(5000) polymer as an alcohol source. Remarkably, the ROP of TMC (from 100 to 600 equiv) initiated by a **2a**/mPEG-OH (5000) two-component initiator was found to proceed at room temperature with efficiency and high level of chain length control similar to that observed with **2a**/BnOH (Table 2, Scheme 3). In all cases, the ROP reactions were complete within 30 min to yield narrowly disperse PTMC-PEG block copolymers

Scheme 2



## Table 2. ROP of Trimethylene Carbonate by the Al Complex 2a in the Presence of mPEG-OH $(5000)^a$

entry	$\mathrm{TMC}^{b}$	mPEG-OH <sup>b</sup>	$M_{ m n,theor}{}^c$	$M_{n,obs}(GPC)^d$	$M_{\rm n,corr}^{\ \ e}$	$M_{\rm w}/M_{\rm n}^{f}$
1	100	5	7040	10979	6627	1.08
2	200	5	9080	11739	9278	1.20
3	400	5	13160	15328	13525	1.09
4	600	5	17240	25418	19020	1.11

<sup>*a*</sup> Polymerization conditions:  $[TMC]_0 = 1M$ ,  $CH_2Cl_2$ , room temperature, 30 min. All conversions are quantitative after 30 min (the reaction time is not optimized). <sup>*b*</sup> Amount in equiv versus initiator **2a**. <sup>*c*</sup> Measured by GPC using standard PS calibration in THF (30 °C). <sup>*d*</sup> Calculated using  $M_{n,theo}$  r=  $[TMC]_0/[mPEG-OH]_0 \times M_{TMC} + 5000$ . <sup>*e*</sup> Measured by GPC in THF (30 °C) using PS standards. <sup>*f*</sup> Measured by GPC in THF (30 °C) using PS standards and corrected by applying the appropriate correcting factors  $X (X_1 = 0.61 \text{ for mPEG}(5000) \text{ and } X_2 = 0.57 \text{ or } 0.88 \text{ for PTMC}$  using  $M_{n,corr} = M_{n,obs}(GPC) \times X_1 \times (mPEG \text{ fraction in PTMC-PEG based on <sup>1</sup>H NMR) + <math>M_{n,obs}(GPC) \times X_2 \times (PTMC \text{ fraction in PTMC-PEG based on <sup>1</sup>H NMR). <sup>11</sup>$ 

Scheme 3



with molecular weight numbers in agreement with the initial  $[TMC]_0/[mPEG-OH]_0$  ratio, as deduced from <sup>1</sup>H NMR and GPC data (see the Supporting Information, Figures S4–S6). Also, indicative of their amphiphilic nature, the <sup>1</sup>H NMR spectrum in D<sub>2</sub>O of all prepared PTMC-PEG copolymers only contains the PEG resonances, which is consistent with a biphasic medium under the conditions studied.<sup>4</sup> Notably, as a comparison, PTMC-PEG copolymers (with moderate to broad molecular distributions) are typically prepared via the ROP of TMC at 130 °C using a Sn(Oct)<sub>2</sub>/mPEG-OH initiator.<sup>5a</sup> For the ROP of TMC by **2a**/mPEG-OH, it appears likely that the mild reaction conditions account for the precise molecular control of the resulting copolymers; in that regard, higher ROP temperatures are, for instance, known to favor polymer chain transfer reactions,

frequently resulting in a broadening of the material's molecular distribution. The present 2a/ROH initiating systems might well apply to the synthesis of various well-defined PTMC-containing block copolymers via the use of appropriate polymer monoblocks as alcohol sources.

In conclusion, novel constrained tetracoordinate aluminum complexes **2a,b** supporting a N,O,N diamido-amino dianionic ligand have been prepared in a two-step procedure from simple reagents. When they are combined with an alcohol source, such Al entities afford a highly effective two-component initiator for the ROP of TMC. Importantly, the reported **2a,b**/ROH systems combine catalytic efficiency, a high level of molecular weight control for the resulting homo-/copolymers, and mild polymerization conditions, allowing a straightforward access to welldefined PTMC and associated block copolymers such as PTMC-PEG. Such Al-based initiators may well be useful for the ready preparation of various tailor-made and narrowly disperse copolymeric biomaterials.

#### EXPERIMENTAL SECTION

General Procedures. All experiments were carried out under N<sub>2</sub> using standard Schlenk techniques or in a Mbraun Unilab glovebox. Toluene and pentane were collected after being passed through drying columns (SPS apparatus, MBraun) and stored over activated molecular sieves (4 Å) for 24 h in a glovebox prior to use. Tetrahydrofuran was distilled over Na/benzophenone and stored over activated molecular sieves (4 Å) for 24 h in a glovebox prior to use. CH2Cl2, CD2Cl2, and C<sub>6</sub>D<sub>6</sub> were distilled from CaH<sub>2</sub>, degassed under a N<sub>2</sub> flow, and stored over activated molecular sieves (4 Å) in a glovebox prior to use. All deuterated solvents were obtained from Eurisotop (CEA, Saclay, France). All other chemicals were purchased from Aldrich and were used as received, with the exception of trimethylene carbonate, purchased from either TCI Europe Corp. or Boehringer: it was recrystallized twice from dry Et<sub>2</sub>O prior to use. The NMR spectra were recorded on Bruker AC 300 and 400 MHz NMR spectrometers in Teflon-valved J. Young NMR tubes at ambient temperature. <sup>1</sup>H and <sup>13</sup>C chemical shifts are reported vs SiMe<sub>4</sub> and were determined by reference to the residual <sup>1</sup>H and <sup>13</sup>C solvent peaks. Elemental analyses for all compounds were performed at the Service de Microanalyse of the Université de Strasbourg (Strasbourg, France). GPC analyses were performed on a system equipped with a Shimadzu RID10A refractometer detector using HPLC-grade THF as an eluant. Molecular weights and polydispersity indices (PDIs) were calculated using polystyrene standards. In the case of molecular weight number  $(M_n)$ , these were corrected with appropriate correcting factors for the  $M_n$  values. MALDI-TOF mass spectroscopic analyses were performed at the Service de Spectrométrie de Masse de l'Institut de Chimie de Strasbourg and run in a positive mode: samples were prepared by mixing a solution of the polymers in  $CH_2Cl_2$  with a 0.5 mg/100 mL concentration, and 2,5-dihydroxybenzoic acid (DHB) was used as the matrix in a 5/1 volume ratio. Al(NMe<sub>2</sub>)<sub>3</sub> was prepared according to a literature procedure.<sup>12</sup>

 $(RNH-C_6H_4)_2O$  (1a, R = C<sub>5</sub>H<sub>9</sub>; 1b, R = C<sub>6</sub>H<sub>1</sub>). The bis-aminoether ligands were synthesized in good yields via a one-step procedure from 2,2'-oxidianiline,  $(H_2N-C_6H_4)_2O$ , according to a literature procedure.<sup>8</sup>

 $\{\eta^{3}(N,O,N)-(C_{5}H_{9})N-C_{6}H_{4}\}_{2}OAINMe_{2}$  (2a). In a nitrogen-filled glovebox, the ligand 1a (4.26 mmol) was charged in a Schlenk flask and a toluene solution (10 mL) of Al(NMe<sub>2</sub>)<sub>3</sub> (677 mg, 4.26 mmol) was added to yield a colorless solution. The reaction mixture was then heated for 24 h at 90 °C in an oil bath to yield a pale yellow solution that was subsequently cooled to room temperature and evaporated to dryness in vacuo, affording an off-white solid residue. The latter was washed with pentane and further dried under vacuum to afford the Al complex 2a as an analytically pure colorless solid (1.02 g, 60% yield). <sup>1</sup>H NMR (300 MHz,  $CD_2Cl_2$ :  $\delta$  7.47 (dd,  ${}^{3}J_{HH}$  = 8.1 Hz,  ${}^{4}J_{HH}$  = 1.5 Hz, 2H), 7.10 (dt,  ${}^{3}J_{HH}$  = 8.1 Hz,  ${}^{4}J_{HH} = 1.5$  Hz, 2H), 6.73 (dd,  ${}^{3}J_{HH} = 8.1$  Hz,  ${}^{4}J_{HH} = 1.5$  Hz, 2H), 6.50 (dt,  ${}^{3}J_{HH} = 8.1$  Hz,  ${}^{4}J_{HH} = 1.5$  Hz, 2H), 3.83 (q,  ${}^{3}J_{HH} = 7.5$  Hz, 2H), 2.56 (s, 6H, Al–NMe<sub>2</sub>), 1.40–2.40 (m, 16H).  ${}^{13}$ C NMR (300 MHz,  $CD_2Cl_2$ ):  $\delta$  146.4 ( $C_{ipso}$ ), 146.3 ( $C_{ipso}$ ), 127.9 (Ar), 117.5 (Ar), 113.0 (Ar), 56.6 (CH-C<sub>5</sub>H<sub>9</sub>), 40.2 (Al-NMe<sub>2</sub>), 34.2 (C<sub>5</sub>H<sub>9</sub>), 34.1 (C<sub>5</sub>H<sub>9</sub>), 25.1 (C5H9), 24.9 (C5H9). Anal. Calcd for C24H32AlN3O: C, 71.08; H, 7.95; N, 10.36. Found: C, 70.96; H, 8.07; N, 9.57.

{ $\eta^{3}$ (*N*,*O*,*N*)-(C<sub>6</sub>H<sub>11</sub>)N-C<sub>6</sub>H<sub>4</sub>}<sub>2</sub>OAINMe<sub>2</sub> (2b). The Al amido complex 2b was synthesized by following a procedure identical with that used for compound 2a using equimolar amounts of ligand 1b (550 mg, 1.51 mmol) and Al(NMe<sub>2</sub>)<sub>3</sub> (240 mg) to afford the Al complex 2b in a pure form as a colorless solid (445 mg, 68% yield). <sup>1</sup>H NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  7.43 (dd, <sup>3</sup>*J*<sub>HH</sub> = 8.1 Hz, <sup>4</sup>*J*<sub>HH</sub> = 1.5 Hz, 2H), 7.05 (dt, <sup>3</sup>*J*<sub>HH</sub> = 8.1 Hz, <sup>4</sup>*J*<sub>HH</sub> = 1.5 Hz, 2H), 6.70 (dd, <sup>3</sup>*J*<sub>HH</sub> = 8.1 Hz, <sup>4</sup>*H*<sub>HH</sub> = 1.5 Hz, 2H), 6.49 (dt, <sup>3</sup>*J*<sub>HH</sub> = 8.1 Hz, <sup>4</sup>*J*<sub>HH</sub> = 1.5 Hz, 2H), 3.26 (g, <sup>3</sup>*J*<sub>HH</sub> = 7.5 Hz, 2H), 2.56 (s, 6H), 1.10–2.30 (m, 20H). <sup>13</sup>C NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  146.4 (C<sub>ipso</sub>), 145.5 (C<sub>ipso</sub>), 127.9 (Ar), 117.9 (Ar), 112.9 (Ar), 112.6 (Ar), 54.1 (CH-Cy), 40.7 (Al-NMe<sub>2</sub>), 34.2 (Cy), 34.0 (Cy), 26.7 (Cy), 26.5 (Cy), 26.1 (Cy). Anal. Calcd for C<sub>24</sub>H<sub>32</sub>AlN<sub>3</sub>O: C, 72.03; H, 8.37; N, 9.69. Found: C, 71.85; H, 8.14; N, 9.04.

Typical Procedure for Trimethylene Carbonate Polymerization by Al Complexes 2a,b. In a glovebox, an appropriate amount of species 2a,b was charged in a vial equipped with a Teflontight screw cap and a TMC/ROH dichloromethane solution (prepared in such a way that  $[TMC]_0 = 1 \text{ M}$ ) was quickly added via a syringe all at once. The resulting colorless solution was vigorously stirred at room temperature for 30 min. The reaction mixture was then quenched with MeOH, provoking the precipitation of the polymer. After filtration through a glass frit, the latter material was washed several times with MeOH, dried in vacuo to constant weight, and subsequently analyzed by <sup>1</sup>H NMR, SEC, and MALDI-TOF spectrometry.

Determination of the Correcting Factor X for m-PEG(5000) Correlating  $M_{n'obs}$ (GPC) (using PS Standards Calibration) with the Real  $M_{n'}$ . This was performed according to a well-established literature procedure,<sup>3c,11a,11b</sup> as follows: the real molecular weight number for the monocapped methoxy ether PEG-OH(5000) (m-PEG-(5000)) was determined via MALDI-TOF spectrometry ( $M_n = 5030$ ), while GPC (PS standards) analysis of m-PEG(5000) yielded  $M_n = 8225$ along with PDI = 1.04. The factor was thus determined to be 0.61 (i.e., 5030/8225).

#### ASSOCIATED CONTENT

**Supporting Information.** Figures, tables, and a CIF file giving the MALDI-TOF spectrum of PTMC, representative

SEC chromatograms of PTMC and PTMC-PEG polymers, and crystal data and refinement details for complex 2a. This material is available free of charge via the Internet at http:// pubs.acs.org.

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