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Zinc(II) Silsesquioxane Complexes and Their Application for the Ring-Opening Polymerization of *rac*-Lactide

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In this Communication, we report the unprecedented solid-state structures for a series of zinc(II) silsesquioxane complexes. Initial catalytic data for the ring-opening polymerization of *rac*-lactide are also presented together with analogous heterogeneous species.

There are many elegant cases in the literature concerning the use of silsesquioxanes as soluble models for heterogeneous catalysts.[1] The vast majority of examples involve the reaction of an organometallic precursor directly with the silsesquioxane (typically in its silanol form).[1,2] Duchateau et al. have prepared zinc alkylsilsesquioxane complexes as model catalysts for the copolymerization of cyclohexene oxide and CO_2. Zirconium(IV) silsesquioxane complexes have been investigated as model catalysts for alkene polymerization, and the same research group has also prepared tin(II), aluminum(III), and gallium(III) complexes.[3] We have recently prepared titanium(IV), aluminum(III), and zinc(II) systems that are models for heterogeneous lactide polymerization initiators.[4] However, increasingly over the last 20 years, tremendous efforts have been made to progressively build ligand systems on silica surfaces.[5] A classic example is to first react the silica with $(MeO)_3Si(CH_2)_3NH_2$ and then use the pendent amine functionality to further derivatize the silica surface.[6] A rare example of a crystallographically tethered system is that of Maschmeyer et al., who have used silsesquioxanes as solution models for tethered osmium(IV) and rhodium(II) complexes.[6e,7] To the best of our knowledge, the work described herein represents one of the very few crystallographically characterized examples of a tethered silsesquioxane complex and is the first involving the ubiquitous *n*-propyl tethered system.

In this present work, we have prepared a series of zinc(II) silsesquioxane complexes and their corresponding heterogeneous analogues. These have been tested for the ring-opening polymerization (ROP) of *rac*-lactide under melt conditions to produce polylactide (PLA). PLA has many uses from commodity plastics to surgical sutures and tissue engineering.[8] Homogeneous Lewis acidic metal centers are well-known to act as initiators for this polymerization.[9] However, there are far fewer examples of the use of heterogeneous initiators.[10]

In this study, the ligands were prepared by the reaction of the triol **1**H_3 (1,3,5,7,9,11,14-heptaisobutyltricyclo$[7.3.3.1^{5,11}]$-heptasiloxane-*endo*-3,7,14-triol) in MeOH with $(MeO)_3Si(CH_2)_3NH_2$ to form **1**NH_2,[6e] followed by reaction with the appropriate aldehyde to form **1**aH, **1**bH, and **1**cH, as shown

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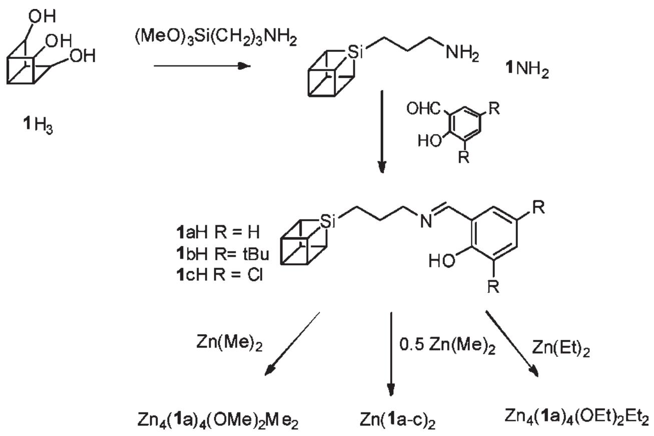
Scheme 1. Complexes Prepared in This Study



in Scheme 1. All species have been characterized via multinuclear NMR spectroscopy (^1H, $^{13}C\{^1H\}$, and $^{29}Si\{^1H\}$) and high-resolution mass spectrometry. These ligands were then reacted with either $ZnMe_2$ or $ZnEt_2$ in a 1:1 or 2:1 ratio. Either monometallic species or tetrametallic zinc(II) complexes were isolated from the reactions depending on the nature of the starting material. The solid-state structures of the reaction of **1**aH with either 1 or 0.5 equiv of $ZnMe_2$ are shown in Figure 1.

The monometallic species Zn(**1**a)$_2$ is the expected product based on analogous Schiff base species in the literature prepared by Darensbourg and Chisholm among others.[11] However, the tetrametallic species Zn_4(**1**a)$_4$(OMe)$_2$Me$_2$ was not similarly predicted. Species of this type (RZnOR) were hypothesized as far back as 1864. However, much more recently, this work has been pioneered by Lewinski and co-workers, who have structurally characterized such species.[12] In the last 10 years, there has been an increased interest in the reaction of alkyl zinc species and dioxygen.[12,13] The molecular structure of Zn_4(**1**a)$_4$(OMe)$_2$(Me)$_2$ (Figure 1) consists of a central $Zn_4O_6C_2$ core, which can be described as an inversion-related, corner-removed face-shared cube. There are two distinct Zn^{II} centers; Zn1 is in a pseudooctahedral environment bound to two imine N centers, two phenoxides, and the μ_3-methoxide. Zn2 is in a pseudotetrahedral environment and is bound to a methyl group, μ_3-methoxide, and two phenoxides. The solution-state ^1H NMR spectrum in C_6D_6 of Zn_4(**1**a)$_4$(OMe)$_2$(Me)$_2$ has a 6H resonance at 0.14 ppm for the Zn−Me group and a 6H resonance at 3.30 for the Zn−OMe group. The $^{29}Si\{^1H\}$ NMR spectrum has four resonances in a 3:1:3:1 ratio, implying that the solid-state structure is maintained in solution.

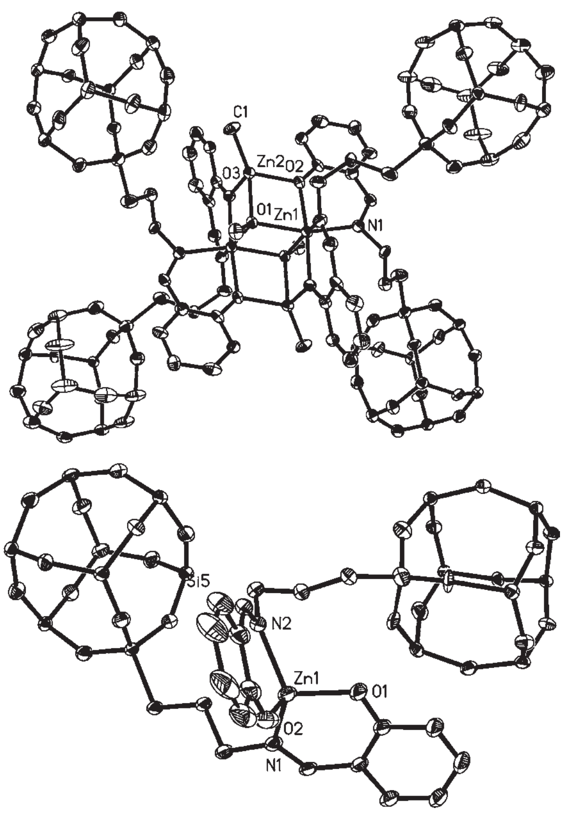


Figure 1. Top: Molecular structure of Zn_4(**1**a)$_4$(OMe)$_2$(Me)$_2$. Selected bond lengths (Å) and angles (deg): Zn1−N1 2.127(5), Zn1−N1A 2.133(5), Zn1−O2 2.091(4), Zn1−O1 2.117(4), Zn2−C1 1.957(7), Zn2−O1 2.021(4), Zn2−O2 2.033(4), Zn2−O3 2.028(4); O3−Zn2−C1 126.1(3), O3−Zn2−O2 96.10(17), O1−Zn1−N1 162.96(18). Bottom: Molecular structure of Zn(**1**a)$_2$. Selected bond lengths (Å): Zn1−O1 1.922(3), Zn1−O2 1.916(4), Zn1−N1 1.996(3), Zn1−N2 2.012(3). Ellipsoids are shown at the 30% probability level.

To confirm that it was serendipitous oxygen insertion into the Zn−alkyl bond and not from the solvent used in the ligand synthesis, the reaction was repeated with $ZnEt_2$. In this case, crystals suitable for X-ray diffraction were obtained (see the Supporting Information). From this analysis, it was clear that Zn_4(**1**a)$_4$(OEt)$_2$Et$_2$ had formed albeit in much lower yield than the previous example. Zn_4(**1**a)$_4$(OMe)$_2$Me$_2$ could be formed in good yields if the system was deliberately exposed to an atmosphere of air directly after the addition of $ZnMe_2$ to the ligand. When 0.5 equiv of $ZnMe_2$ was added to **1**aH, Zn(**1**a)$_2$ was then formed in good yield; again multinuclear NMR spectroscopy indicated that the solid-state structure is maintained in solution. The starting ligand was further varied to incorporate ^{t}Bu and Cl moieties. In these cases, only the 1:2 complexes Zn(**1**b)$_2$ (solid-state structure reported in the Supporting Information) and Zn(**1**c)$_2$ could be isolated regardless of the amount of $ZnMe_2$ added. Attempts to prepare the POSS−Zn−Me complexes under anaerobic conditions were unsuccessful; upon recrystallization, only Zn(**1**a−c)$_2$ were isolated.

The unanticipated inclusion of the methoxy moiety (which potentially could act as a polymerization initiator) prompted

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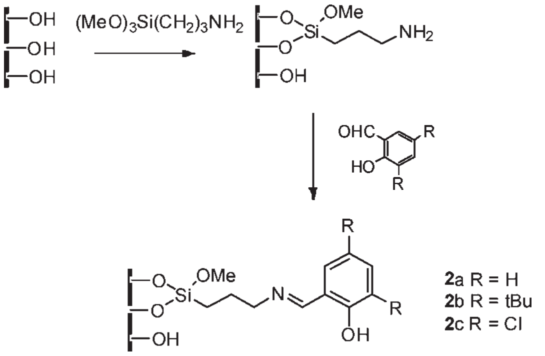
Scheme 2. Preparation of Heterogenized Ligands



us to investigate complexes for the ROP of *rac*-lactide under melt and solution conditions. Complex $Zn_4(\mathbf{1}a)_4(OMe)_2Me_2$ was active in the melt (130 °C in the absence of solvent) with a conversion of 70% after 10 min (M_n = 40 050; PDI = 1.79). This complex was also active in a toluene solution at room temperature with a 94% conversion after 96 h (M_n = 206 000; PDI = 1.42). All 1:2 complexes were inactive for the ROP of *rac*-lactide.

The immobilization of catalysts in small molecular catalysis is common place. However, the heterogenization of catalysts for the ROP of cyclic esters has only recently been demonstrated.[10c,14] One of the main driving forces is to remove any metal contaminant in the resultant polymer, which is important for biological applications.[10c] The ligands could be heterogenized on the surface using standard literature procedures (Scheme 2).[11c] The heterogeneous zinc(II) complexes were prepared by taking the heterogenized ligand systems and reacting them with 1 equiv of $ZnMe_2$. All heterogeneous systems were characterized by elemental analysis and inductively coupled plasma-atomic emission spectrometry for the zinc content; **2**a + $ZnMe_2$ was also analyzed via solid-state NMR spectroscopy and X-ray photoelectron spectroscopy (XPS). The results of all characterization methods are provided as Supporting Information. For comparison, unreacted silica heterogenized with $ZnMe_2$ was also tested. Under melt conditions, all heterogeneous systems were shown to be active initiators for the ROP of *rac*-lactide, affording high-molecular-weight atactic PLA (Table 1). The heterogeneous catalysts required significantly longer reaction times than the homogeneous initiators; this is presumably related to mass-transport effects in the solid-supported materials.

Table 1. Summary of the Melt Polymerization Data for the Heterogeneous Initiators

initiator	time/h	conversion/%	M_n	PDI
silica + $ZnMe_2$	24	40	18 550	1.47
2a + $ZnMe_2$	24	55	54 200	1.53
2b + $ZnMe_2$	24	60	81 800	1.61
2c + $ZnMe_2$	24	73	77 150	1.58

In conclusion, a series of tethered zinc(II) silsesquioxane complexes have been prepared and structurally characterized. These complexes and heterogeneous analogues have been shown to be efficient initiators for the ROP of lactide. Under melt conditions, the heterogeneous systems appeared to produce PLA with a higher M_n. Work is ongoing to fully understand this and to control the molecular weight and PDI to a greater extent. Further work to ascertain the polymerization mechanism and investigate the recyclability of these systems is underway.

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Supporting Information Available: Full synthetic procedures, X-ray analysis, CIF files, and synthesis and solid-state NMR spectroscopic, elemental analysis, and XPS data for heterogeneous systems. This material is available free of charge via the Internet at http://pubs.acs.org.

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