

## Alternating Copolymerization of CO<sub>2</sub> and Cyclohexene Oxide by New Pyridylamido Zn(II) catalysts

Ilaria D'Auria,<sup>a</sup> Massimo Christian D'Alterio,<sup>a,b</sup> Giovanni Talarico<sup>b</sup> and Claudio Pellecchia<sup>a\*</sup>

<sup>a</sup> Dipartimento di Chimica e Biologia "A. Zambelli", Università di Salerno, via Giovanni Paolo II 132, 84084 Fisciano (SA), Italy.

<sup>b</sup> Dipartimento di Scienze Chimiche, Università "Federico II" di Napoli, Complesso Monte Sant'Angelo, via Cintia 21, 80126 Napoli, Italy.

### ABSTRACT

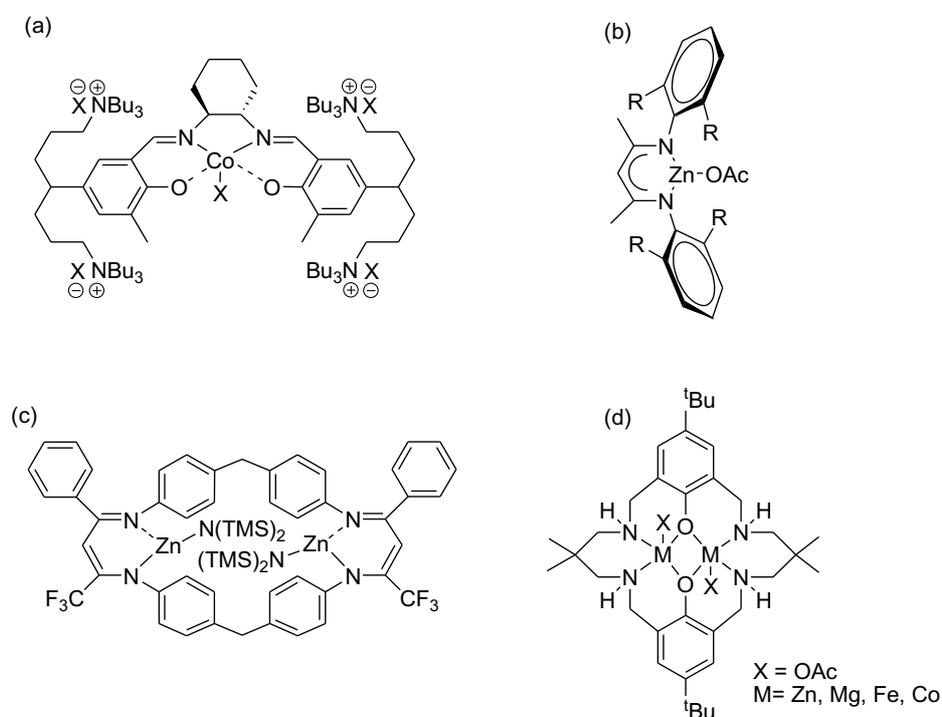
Five new Zn(II) complexes bearing pyridylamido ligands with different substituents at the pyridine and at the amido moieties were synthesized and evaluated as catalysts for the alternating copolymerization of carbon dioxide and cyclohexene oxide. Polymers with carbonate linkages ranging between 86-98% and a slightly isotactic-enriched structure were selectively obtained under a variety of reaction conditions, including 1 atm of CO<sub>2</sub> pressure, without any co-catalyst. Some experimental and theoretical evidence support the hypothesis that the active species involved in the catalytic cycle are dimeric  $[(L_x)Zn(\mu-OR)]_2$  and  $[(L_x)Zn(\mu-O_2COR)]_2$  complexes similar to those involved in the classical  $\beta$ -diiminate Zn(II) catalysts.

## INTRODUCTION

The production of synthetic polymers has increased exponentially in the last century, currently resulting in volumes higher than 300 million tons/year, a number which is expected to increase monotonically. Two major environmentally related issues have emerged concerning the continuous growth of polymers: (i) they are essentially manufactured from non-renewable resources, consuming about 8% of oil produced annually, and (ii) they are not biodegradable and only partially recycled, constituting more than 10% by weight (and a much larger fraction in volume) in the municipal solid waste and over 80% of waste that accumulates in shorelines and eventually in the ocean, where microplastic pollution can persist indefinitely and enter the trophic chain.<sup>1</sup> In this framework, the development of biodegradable polymeric materials derived from renewable resources has gained increasing interest both in the industry and in the research community, also on the basis of political pressure from the main international funding agencies and, more recently, from legislation restricting the use of non-degradable plastics for packaging.<sup>2</sup> On the other hand, the global concern for the increase in CO<sub>2</sub> concentration in the atmosphere has boosted research efforts toward CO<sub>2</sub> utilization as an abundant and renewable carbon source for chemical production, although it is clear that even extensive incorporation of CO<sub>2</sub> feedstock in industrial chemical processes would have only a very limited impact on the *greenhouse effect* problem.<sup>3</sup> The Ring Opening CoPolymerization (ROCOP) of CO<sub>2</sub> with energy-rich substrates such as epoxides dimeric  $[(L_x)Zn(\eta^2-OR)]_2$  and  $[(L_x)Zn(\eta^2-O_2COR)]_2$  is a rare example of catalytic process with the potential to deliver large-scale quantities of products from carbon dioxide. The most commonly studied epoxides are cyclohexene oxide (CHO) and propylene oxide (PO). At present, the reaction is applied industrially in relatively large scale to produce low-molecular-weight, dihydroxy-terminated "polycarbonate diols" which are intermediates or additives in the polyurethane industry.<sup>2</sup> A variety of catalytic systems for the ROCOP of CO<sub>2</sub> and epoxides have been reported in the last two decades, most notable examples being [salen]MX type complexes (where M = Cr(III), Co(III), Al(III)), usually requiring an ionic compound or a Lewis base as a cocatalyst, possibly covalently bonded to the

*salen* ligand (scheme 1a).<sup>4</sup> A second class involves high-performing  $\beta$ -diiminate (BDI) Zn(II) catalysts (scheme 1b) disclosed by Coates,<sup>5,6</sup> not requiring any cocatalyst owing to a bimetallic mechanism being in operation.<sup>7</sup> The latter discovery triggered the development of catalysts featuring bi-nucleating ligands: e. g., Rieger reported Zn(II) catalysts with ligands obtained by tethering two BDI moieties (scheme 1c), resulting in the highest TOFs ever measured in the ROCOP of CO<sub>2</sub> and CHO;<sup>8,9</sup> homo- and hetero-binuclear complexes of Robson-type macrocyclic tetraamine-diphenolate ligands with Zn(II), Mg(II), Fe(III), and Co(III) (Scheme 1d) were also shown to be highly efficient ROCOP catalysts.<sup>10 11</sup>

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Scheme 1

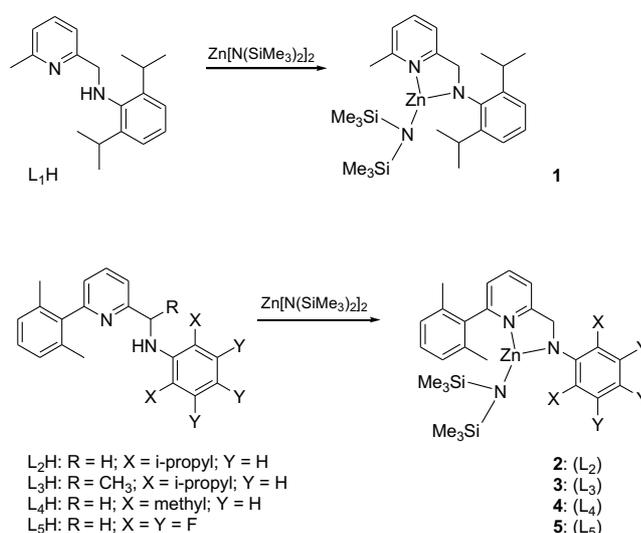
Considering the high efficiency of catalysts based on BDI ligands, it is somehow surprising that other classes of chelating monoanionic [N,N] ligands have not been investigated for the synthesis of potential ROCOP catalysts. In previous studies we reported properly designed pyridylamido<sup>13</sup> or pyridylimino<sup>14</sup> complexes of Groups 2, 3, 4, 10 and 13 metals as catalysts for the polymerization of olefins,<sup>15,16,17,18</sup> dienes,<sup>19</sup> and cyclic esters.<sup>20</sup> In this paper we report the synthesis of some new Zn(II) complexes bearing pyridylamido ligands (see

Scheme 2) and their performance as catalysts for the ROCOP of CHO and carbon dioxide.

## Results and discussion

### *Synthesis and characterization of the pyridylamido complexes*

The pyridylamino proligands  $L_xH$  ( $x=1-5$ ) were synthesized following previously reported procedures (see the Supporting information).<sup>21</sup> Complexes **1-4** were cleanly obtained in yields ranging between 90-95%, following a typical synthetic approach, i. e. the reaction of  $L_xH$  and  $Zn[(NSiMe_3)_2]_2$  in 1:1 ratio (Scheme 2) in toluene, at 25 °C for complex **1** and at 80°C for complexes **2-4**. Complexes **1-4** were characterized by multinuclear NMR spectroscopy, confirming heteroleptic monomeric structures (see the Supporting information for details). Complex **5** was obtained following a similar procedure, but a lower reaction temperature (0 °C) was required, since a Schlenk-type equilibrium between the heteroleptic and the homoleptic bis(chelate) complex was observed at room temperature in benzene- $d_6$  solution (see the Supporting information).



**Scheme 2.** Synthesis of the Zn(II) complexes **1-5**

### *Alternating copolymerization of cyclohexene oxide and carbon dioxide.*

$L_xZnN(SiMe_3)_2$  complexes **1-5** were tested as catalysts for the ROCOP of cyclohexene oxide (CHO) and carbon dioxide. Initially, complex **1**, bearing a methyl substituent in the *ortho* position of the pyridine moiety and a 2,6-diisopropylphenyl substituent at the amido N, was tested under a variety of

reaction conditions. Representative copolymerization runs are reported in Table 1 and discussed in the following. Some runs were carried out using 0.05 mmol of **1**, 4 mL CHO (monomer/catalyst mole ratio = 800) without solvent, for 17 h at 80 °C and increasing CO<sub>2</sub> pressures (see Table 1). Notably, the catalyst promoted the copolymerization even at 1 atm of CO<sub>2</sub> pressure, and the polymerization rate increased at increasing CO<sub>2</sub> pressure<sup>7a</sup> (cf. runs 1-3). The catalyst seems stable over extended reaction times, resulting in > 70% CHO conversion in 62 h (cf. runs 3-5). High selectivities were observed in all runs, with carbonate linkages ranging between 86-98% (see Table 1). Reducing the temperature to 50 °C resulted in a lower productivity (see run 6). Since the fraction of ether linkages seems higher for shorter runs (cf. runs 3, 4 and 5), we suspected that some CHO homopolymerization can occur at the beginning of the reaction: as a matter of fact, run 7, carried out with CHO only, indicated that **1** is able to homopolymerize CHO in the absence of CO<sub>2</sub>. Also in agreement with the above hypothesis, carrying the copolymerization using 2 mL of toluene solvent and 2 mL of CHO resulted in carbonate selectivity >99% , although at the expense of the polymer productivity, as expected if the copolymerization rate depends on CHO concentration (cf. run 8 vs. run 3). Addition of 1 equiv of bis-(triphenylphosphorylidene)ammonium chloride (PPNCl, a typical cocatalyst used for mononuclear catalysts) resulted in switching the chemoselectivity of the reaction towards the prevailing formation of *cis*-cyclohexenecarbonate and in a reduction of the catalytic activity (see run 9).

As originally addressed by Coates for BDI catalysts,<sup>22</sup> even subtle modifications of the coordination environment can result in dramatic changes of catalytic activity. In this preliminary exploration of the title class of complexes, we devised some ligand variations aimed at addressing the importance of both steric and electronic substituent effects. Thus, catalyst **2**, bearing a much more sterically encumbered 2,6-dimethylphenyl substituent in the *ortho* pyridine position, was tested under similar conditions at 80 °C and 8 atm CO<sub>2</sub> pressure, also affording polycyclohexene carbonate with good selectivity (85% carbonate linkages), although at a lower rate with respect to **1** (cf. runs 2 and 10). A higher productivity was achieved under higher CO<sub>2</sub> pressure (cf. runs 10 and 11) as well as at higher temperature (run 12).

Introduction of a methyl substituent on the carbon bridging the pyridine and the aniline moieties in catalyst **3** resulted in further reduction of the productivity, while maintaining a good selectivity (cf. run 13 vs. run 10).

Subsequently, we tested catalyst **4**, maintaining the bulky *ortho* 2,6-dimethylphenyl substituent at the pyridine moiety like in **2** (and **3**), but carrying a less hindered 2,6-dimethylphenyl substituent also at the N-amido atom. Catalyst **4** tested at 80 °C and under 25 atm CO<sub>2</sub> pressure resulted significantly more active than **2** under identical conditions (cf. run 14 vs. run 11)

Finally, catalyst **5**, featuring the same structure of **2-4** at the pyridine moiety and a strong electron-withdrawing (and less hindered) pentafluorophenyl substituent at the N-amido atom, showed the highest activity when tested under identical conditions (see run 15).

The isolated polymer samples were analyzed by <sup>13</sup>C NMR: interestingly, inspection of the carbonyl region of the spectra (see e. g. Figure 1) indicated a prevailing content of m-centered tetrads with respect to r-centered tetrads, with P<sub>m</sub> ranging between 0.60 and 0.67.

**Table 1.** Copolymerization of cyclohexene oxide and CO<sub>2</sub> using pyridylamido Zn(II) catalysts **1-5**.<sup>a</sup>

Run	Cat.	p CO <sub>2</sub> (atm)	T (°C)	t (h)	yield (g)	carbonate linkages <sup>b</sup> (%)
1	<b>1</b>	1	80	17	0.45	88
2	<b>1</b>	8	80	17	1.7	87
3	<b>1</b>	25	80	17	2.3	96
4	<b>1</b>	25	80	4	0.9	86
5	<b>1</b>	25	80	62	4.0	98
6	<b>1</b>	25	50	17	0.85	90
7	<b>1</b>	-	80	4	0,35 <sup>c</sup>	c
8 <sup>d</sup>	<b>1</b>	25	80	17	1.4	>99
9 <sup>e</sup>	<b>1</b>	25	80	17	0.35 <sup>f</sup>	f
10	<b>2</b>	8	80	17	1.1	85
11	<b>2</b>	25	80	17	1.7	98
12	<b>2</b>	25	100	17	2.3	98
13	<b>3</b>	8	80	17	0.75	87
14	<b>4</b>	25	80	17	2.8	95
15	<b>5</b>	25	80	17	3.3	98

<sup>a</sup>) Excepting where differently specified, the runs were performed in neat CHO (4.0 ml) using 5.0 x 10<sup>-5</sup> mol of Zn complex ( [CHO] / [Zn] ratio = 800 : 1.) <sup>b</sup>) determined by integration of the methine resonances in the <sup>1</sup>H NMR spectrum of

polymer <sup>c)</sup> The product was poly(cyclohexene oxide). <sup>d)</sup> Like in <sup>a)</sup> but CHO = 2.0 ml; toluene = 2.0 ml. <sup>e)</sup> Like in <sup>a)</sup> but 1 equiv of PPNCI was added. <sup>f)</sup> Main product was *cis*-cyclohexenecarbonate.

### **Mechanism of the copolymerization.**

Seminal and elegant studies by Coates showed that the active species involved in (BDI)Zn catalysts for the alternating copolymerization of epoxides and carbon dioxide are dimeric [(BDI)Zn( $\mu$ -OR)]<sub>2</sub> species which are converted to the corresponding dimeric [(BDI)Zn( $\mu$ -O<sub>2</sub>COR)]<sub>2</sub> species upon CO<sub>2</sub> insertion.<sup>7</sup> A cooperative bimetallic mechanism was suggested on the basis of kinetic studies and investigation of the elementary steps using model complexes. A key element for high catalytic activity was shown to be related to the dimer association equilibrium constant, with monomeric species and tightly bound dimers being poorly reactive or unreactive, while loosely bound fluxional dimers are highly reactive.<sup>7</sup> As mentioned in the introduction, the peculiarity of (BDI)Zn<sup>6</sup> and other dinuclear catalysts<sup>8-12</sup> is the fact that they do not require any cocatalyst. Considering (i) the similarities between the structures of the pyridylamido Zn catalysts reported here and those of the (BDI)Zn catalysts and (ii) that also for the pyridylamido Zn catalysts no cocatalyst is required for the copolymerization activity (but on the contrary the addition of a typical cocatalyst used for ROCOP is detrimental to both activity and chemoselectivity) we hypothesized that dimeric [(L<sub>x</sub>)Zn( $\mu$ -OR)]<sub>2</sub> and [(L<sub>x</sub>)Zn( $\mu$ -O<sub>2</sub>COR)]<sub>2</sub> active species are involved in our systems, too. Interestingly, also in the case of (BDI)ZnN(SiMe<sub>3</sub>)<sub>2</sub> the active species were shown to be [(BDI)Zn( $\mu$ -OSiMe<sub>3</sub>)]<sub>2</sub> dimers, deriving from CO<sub>2</sub> insertion and subsequent elimination of trimethylsilyl isocyanate.<sup>7</sup> Thus, we monitored by <sup>1</sup>H NMR the reaction of complex **1** and a few equivalents of CO<sub>2</sub> in an NMR tube in toluene-*d*<sub>8</sub>: after 5 min at 80°C, the resonances of complex **1** disappeared, while the resonance of Me<sub>3</sub>SiN=C=O appeared at  $\delta$  = 0,21 ppm<sup>23</sup> together with new resonances attributable to a [L<sub>1</sub>Zn(-OSiMe<sub>3</sub>)] species (see Figure 2). Comparative diffusion NMR experiments performed on complex **1** and on the newly formed [L<sub>1</sub>Zn(-OSiMe<sub>3</sub>)] species provided an estimation of their molecular masses, confirming the monomeric structure of **1** and suggesting a

dimeric structure for the new species, i. e.  $[(L_1)Zn(\mu-O\text{SiMe}_3)]_2$  (see the Experimental Section for details).

A low molecular weight polymer sample prepared with catalyst **1** at a lower temperature (50 °C) and low CHO conversion was analyzed by MALDI-ToF high resolution MS, clearly showing the presence of two major distributions (see Figure 3) separated by 142.16 m.u., which is the mass of the polymer repeating unit: both series correspond to linear polymer chains with a hydroxyl end group, but in the former one the other end group is an  $-O\text{SiMe}_3$ , while in the latter it is a  $-N(\text{SiMe}_3)_2$ . This finding confirms that initiation occurs after  $\text{CO}_2$  insertion into  $Zn-N(\text{SiMe}_3)_2$  bonds and subsequent formation of  $Zn-O\text{SiMe}_3$  by trimethylsilyl isocyanate elimination (as observed for (BDI)Zn catalysts), but suggests that insertion of CHO can also occur into the  $Zn-N(\text{SiMe}_3)_2$  bond, at least when trimethylsilyl isocyanate elimination is slow, i. e. at lower temperatures. In fact, when a toluene solution of **1** was aged 2 h under 8 atm of  $\text{CO}_2$  at 80 °C before adding CHO, the MS spectrum of the obtained polymer indicated the formation only of macromolecules having a hydroxyl and an  $-O\text{SiMe}_3$  end groups or  $\alpha,\omega$ -dihydroxyl-terminated chains, the latter probably originated by adventitious traces of water. These findings are in agreement with the hypothesis that the active species involved in the ROCOP by our pyridylamido Zn(II) catalysts are dimeric  $[(L_x)Zn(\mu-OR)]_2$  and  $[(L_x)Zn(\mu-O_2COR)]_2$  complexes analogous to those involved in (BDI) Zn(II) systems.

Unfortunately, several attempts to isolate model compounds such as  $[(L_x)Zn(\mu-OR)]_2$  by alcoholysis of either  $(L_x)Zn(N\text{SiMe}_3)_2$  or  $(L_x)Zn\text{Et}$  resulted invariably in complex degradation *via* ligand dissociation. Similarly, attempts to obtain  $[(L_x)Zn(\mu,\kappa^2-OAc)]_2$  species *via* either the reaction of  $L_x$  and  $Zn(\text{OAc})_2$  or the reaction of  $(L_x)Zn\text{Et}$  and  $\text{AcOH}$  met with failure.

To validate our hypothesis, we performed DFT calculations (computational details are reported in the Experimental Section) to estimate the free energy equilibria between monomeric  $[(L_x)Zn(-O\text{SiMe}_3)]$  and dimeric  $[(L_x)Zn(\mu-O_2\text{SiMe}_3)]_2$  species in solution. The comparison was extended also to (BDI)Zn( $-O\text{SiMe}_3$ ) complexes where the active species were shown to be  $[(\text{BDI})Zn(\mu-O\text{SiMe}_3)]_2$  dimers, deriving from  $\text{CO}_2$  insertion and subsequent elimination of trimethylsilyl isocyanate.<sup>7</sup> The geometries of dimeric complexes deriving from **1**,

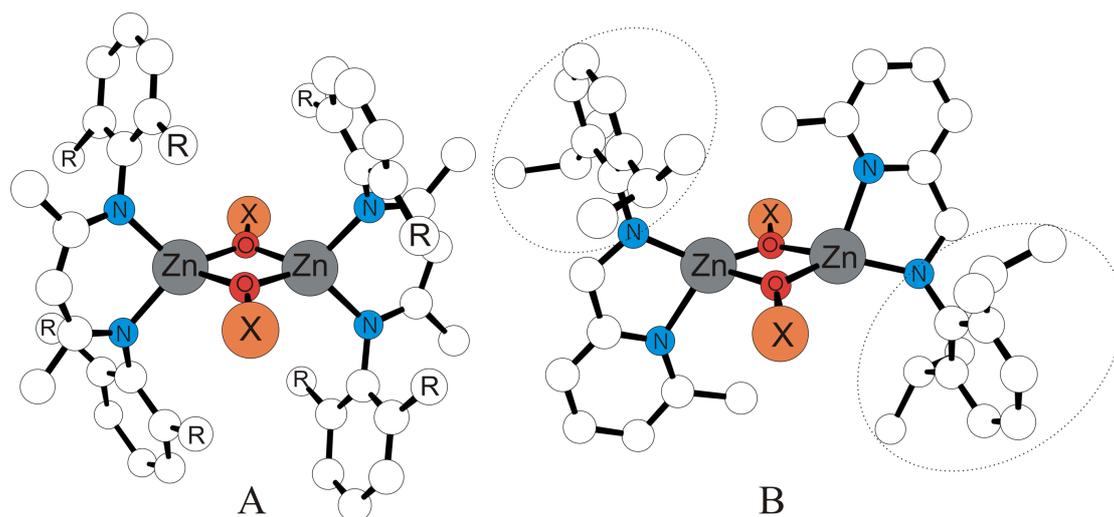
**2**, **3**, **4** and **5** are all referred to the most stable trans configuration ( $C_2$  symmetry). For the dimeric complex deriving from **3**, which shows an asymmetric carbon, we evaluated also the energy for *R,R* and *R,S* isomers.

**Table 2.** Free energies comparison between dimeric and monomeric species  $\Delta G_{\text{dim}} = (G_{\text{dim}} - 2G_{\text{mon}})$  for selected (BDI) Zn(II) systems<sup>7</sup> and the  $[(L_x)\text{Zn}(-\text{OSiMe}_3)]$  (with  $x = 1-5$ ) species. Negative  $\Delta G_{\text{dim}}$  means that dimeric species are favored with respect to the monomeric ones.

$[(L)\text{Zn}(-\text{OSiMe}_3)]$	$\Delta G_{\text{dim}}$ (kcal/mol)
L=BDI with R =Et	-25.9
L=BDI with R =Me	-22.6
L <sub>1</sub>	-22.2
L <sub>2</sub>	-9.2
L <sub>3</sub> ( <i>R,R</i> )	-1.0
L <sub>3</sub> ( <i>R,S</i> )	+3.8
L <sub>4</sub>	-21.5
L <sub>5</sub>	-20.5

The results, reported in Table 2, clearly show that  $[(L_1)\text{Zn}(-\text{OSiMe}_3)]$ ,  $[(L_4)\text{Zn}(-\text{OSiMe}_3)]$  and  $[(L_5)\text{Zn}(-\text{OSiMe}_3)]$ , deriving from the more active complexes **1**, **4**, **5**, present higher  $\Delta G_{\text{dim}}$  values with respect to  $[(L_2)\text{Zn}(-\text{OSiMe}_3)]$  and  $[(L_3)\text{Zn}(-\text{OSiMe}_3)]$ , deriving from the less active complexes **2** and **3**. Moreover, the  $\Delta G_{\text{dim}}$  values found for the former complexes are similar to those calculated for the BDI Zn(II) complexes. These findings are in agreement with the hypothesis that the active species involved in the ROCOP by our pyridylamido Zn(II) catalysts are dimeric  $[(L_x)\text{Zn}(\text{O}^-\text{OR})]_2$  and  $[(L_x)\text{Zn}(\text{O}^-\text{O}_2\text{COR})]_2$  complexes analogous to those involved in (BDI) Zn(II) systems.

Additional considerations can be sorted out by comparing the geometries of dimeric species obtained for (BDI) Zn(II) complexes (see Figure 4-A) and our Zn(II) systems (see Figure 4-B). Despite the clear analogy between Figure 4-A and Figure 4-B, it may be worth to stress that a larger tuning variation (and hence  $\Delta G_{\text{dim}}$ ) can be obtained by suitable modification of substituents at the N amido atoms (with a dot circle in Figure 4-B) with respect to the R substituents of the BDI systems (see Figure 4-A).



**Figure 2.** DFT optimized geometries for  $[(\text{BDI})\text{Zn}(\mu\text{-OSiMe}_3)]_2$  dimers with  $\text{R} = \text{Et}$  (A) and  $[(\text{L}_1)\text{Zn}(\mu\text{-O}_2\text{SiMe}_3)]_2$  (B). Hydrogen atoms omitted for clarity and  $\text{X} = \text{SiMe}_3$ .

## Conclusions

Several new pyridylamido Zn(II) complexes were synthesized and successfully tested as "single component" catalysts for the alternating copolymerization of carbon dioxide and cyclohexene oxide also under rather mild conditions. A preliminary screening of some substituent variation in the coordination environment of the Zn catalyst addressed the potential tuning flexibility of steric and electronic features of this class of complexes. Both experimental and theoretical evidence supported the hypothesis that the active species involved in the catalytic cycle are dimeric  $[(\text{L}_x)\text{Zn}(\mu\text{-OR})]_2$  and  $[(\text{L}_x)\text{Zn}(\mu\text{-O}_2\text{COR})]_2$  complexes similar to those involved in benchmark (BDI) Zn(II) systems. Future work will be aimed at optimizing the catalyst structure to increase the copolymerization performance also using High Throughput Screening techniques and computational models.

## EXPERIMENTAL SECTION

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