Inorganic Chemistry

ARTICLE

pubs.acs.org/IC

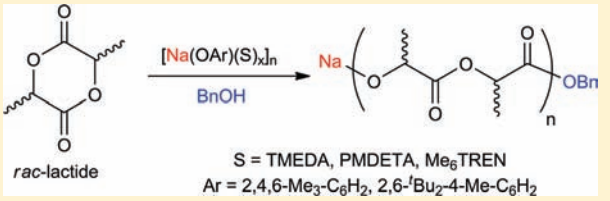
Polyamine-Stabilized Sodium Aryloxides: Simple Initiators for the Ring-Opening Polymerization of *rac*-Lactide

Beatriz Calvo, Matthew G. Davidson,* and Daniel García-Vivó*

Department of Chemistry, University of Bath, Claverton Down, Bath BA2 7AY, U.K.

Supporting Information

ABSTRACT: Metalation of 2,4,6-tri(methyl)phenol (^{Me}ArOH) and 2,6-di(*tert*-butyl)-4-methylphenol (^{Bu}ArOH) with NaN(SiMe$_3$)$_2$ in toluene and in the presence of stoichiometric amounts of the polydentate amines *N,N,N′,N′*-tetramethylethylenediamine (TMEDA) and *N,N,N′,N′′,N′′*-pentamethyldiethylenetriamine (PMDETA) affords three new sodium aryloxide complexes [Na(μ-OAr^{Bu})(TMEDA)]$_2$ (**3**), [Na(μ-OAr^{Me})(PMDETA)]$_2$ (**4**), and [Na(OAr^{Bu})(PMDETA)] (**5**). Complexes **3** to **5** have been isolated as crystalline materials in reasonable yields and characterized in the solid state by X-ray crystallography and in solution by NMR spectroscopy. Complexes **3** to **5** and the related [*tris*(2-dimethylaminoethyl)amine] (Me$_6$TREN) derivatives [Na(OAr^{Me})(HOAr^{Me})(Me$_6$TREN)] (**1**) and [Na(OAr^{Bu})(Me$_6$TREN)] (**2**), recently prepared in our group, are shown to be active as initiators for the ring-opening polymerization (ROP) of *rac*-lactide with benzyl alcohol as a co-initiator. However, during the course of the polymerization reactions intrachain and stereorandom transesterification side-reactions were observed under some of the experimental conditions tested.



INTRODUCTION

In recent years the ring-opening polymerization (ROP) of cyclic esters has received increasing attention from both academic and industrial points of view mainly because the resulting polymers have found use in high value biomedical applications because of their biodegradable, biocompatible, and permeable properties.[1] Doubtless, the most commonly studied cyclic ester is lactide which can be obtained from renewable resources such as corn starch, thus suggesting its derived polymer, polylactide (PLA), as a viable alternative to traditional petrochemical commodity polymers.[2] The industrial scale production of PLA relies on the use of Sn(II) initiators. However, these are difficult to remove[3] from the resultant polymer and there are concerns over the toxicity of tin.[1c] This drawback has prompted the development of "benign" polymerization initiators from which biomedical grade polymers could be obtained,[1,2] and numerous zinc,[4] magnesium,[4c,d,5] calcium,[6] and iron[7] complexes have been prepared and screened in ROP processes. Even more recently in this context the alkali metals have emerged as very attractive alternatives because of their low cost and low toxicity,[2d,8] and a range of Group 1 alkoxides have been prepared and shown to be active toward the ROP of cyclic esters.[2d] It is noteworthy that simple alkoxides (i.e., Li^{t}Bu[9] or K^{t}Bu[10]) exhibit useful activity in ROP of cyclic esters, but they suffer from undesirable backbiting and transesterification reactions. More recently, these side reactions have been minimized by using sterically demanding diols[11−13] which provide a steric barrier around the active metal center. For example, the lithium[11] and sodium[12] derivatives of 2,2′-ethylidene-*bis*(4,6-di-*tert*-butylphenol) (EDBPH$_2$) were proven to be very active initiators in the ROP of L-lactide, exhibiting a highly controlled polymerization with low molecular weight distributions in the resulting polymers. However, most of these systems exhibit a high structural complexity including the presence of various chemical environments for the metal centers and/or the coordination of hydrogen bonded alcohols and solvent molecules, which makes it difficult to extract information about the structural features responsible for the controlled polymerization observed.

In this context, we have recently reported the synthesis of a family of simple, well-defined Group 1 metal aryloxides supported by the *tris*(2-dimethylaminoethyl)amine (Me$_6$TREN) ligand.[14] In addition to a number of tetrameric complexes, use of bulky aryloxide anions led to the isolation of two sodium complexes exhibiting simple monomeric structural motifs. In spite of the possible advantages that this type of monomeric complexes can present for catalytic applications, well-characterized examples are still rare in the chemistry of Group 1 metal alkoxides or aryloxides.[15] Therefore, those new monomeric complexes, [Na(OAr^{Bu})(Me$_6$TREN)] (**1**) and [Na(OAr^{Me})(HOAr^{Me})(Me$_6$TREN)] (**2**) (HOAr^{Bu} = 2,6-di(*tert*-butyl)-4-methylphenol and HOAr^{Me} = 2,4,6trimethylphenol) (Figure 1), seemed ideal candidates to be tested as simple initiators in the ROP of *rac*-lactide. To extend the scope of our polymerization studies, herein we also report the preparation of three new well-defined sodium complexes of 2,6-substituted aryloxide anions, stabilized by the more commonly employed polydentate amines *N,N,N′,N′*-tetramethylethylenediamine (TMEDA)

Received: December 21, 2010
Published: March 16, 2011

and *N,N,N′,N″,N″*-pentamethyldiethylenetriamine (PMDETA) (Figure 1).

RESULTS AND DISCUSSION

Synthesis and Characterization of Sodium Aryloxide Complexes 3, 4, and 5. All the new complexes (**3**−**5**) have been synthesized by simple metalation reactions. Thus, upon addition of a 1:1 stoichiometric amount of the desired phenol to a toluene solution of $NaN(SiMe_3)_2$ and the appropriate Lewis base (Scheme 1) the new complexes were obtained cleanly in reasonable isolated yields, with the exception of a 1:1:1 reaction mixture of ^{Me}ArOH, $NaN(SiMe_3)_2$, and TMEDA (**A**) which did not result in a soluble complex. We have recently observed a similar situation for a related lithium aryloxide complex,[16] and suggest that such insolubility is attributed to the formation of high molecular weight oligomeric complexes because of the availability of only a bidentate donor ligand.[17]

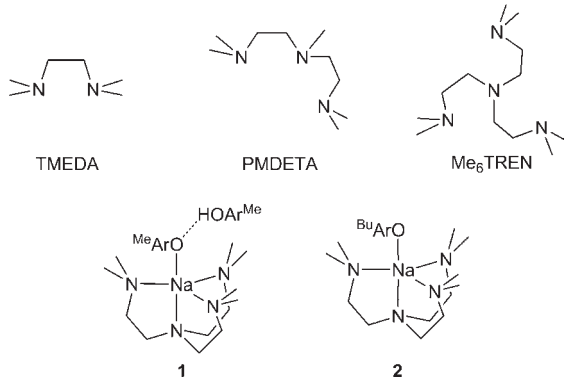
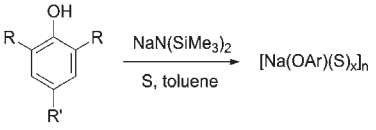


Figure 1. Ligands employed in this work (top), and schematic representations of the previously reported Me_6TREN complexes (bottom).

Scheme 1. Synthesis of New Complexes



R	R′	S	n	x	
Me	Me	TMEDA			**A**
^{t}Bu	Me	TMEDA	2	1	**3**
Me	Me	PMDETA	2	1	**4**
^{t}Bu	Me	PMDETA	1	1	**5**

The structural characterization of the new complexes has been carried out by a combination of X-ray crystallography and NMR spectroscopy. Complexes **3** and **4** are dimeric and crystallize in the centrosymmetric space group $P\bar{1}$ (see Figure 2 and Table 1). Although both complexes possess a similar and perfectly planar central Na_2O_2 ring [sum of endocyclic angles: 359.8° (**3**) and 360.0° (**4**)], the coordination geometry around the metal centers differs because of the different denticity of the N-donor ligands. Thus, in the TMEDA complex **3** the metal centers are four-coordinate exhibiting a distorted tetrahedral geometry [mean deviation from 109.5°: 26° for Na(1) and 25° for Na(2)], whereas the five-coordinate Na atoms in the PMDETA derivative **4** have a distorted trigonal bipyramidal geometry. In spite of these differences in coordination number and geometry the Na−O or Na−N bond distances remain similar for both complexes [average distances: Na−O 2.307 (**3**), 2.293 Å (**4**) and Na−N 2.692 (**3**), 2.646 Å (**4**)]. This observation probably reflects a balance between the electronic saturation of the metal centers, four (**3**) versus five-coordinated (**4**), and the steric hindrance generated by the *ortho* alkyl substituents of the phenolate bridges, ^{t}Bu (**3**) versus Me (**4**). The Na−O bond lengths found for the central rings in **3** and **4** are marginally longer than those previously found in the related dimers $[Na(\mu\text{-}OC_6H_3\text{-}2,6\text{-}^tBu_2)(THF)_2]_2$ (2.276 Å),[18] $[Na(\mu\text{-}OC_6H_3\text{-}2,4,6\text{-}^tBu_3)(Et_2O)]_2$ (2.226 Å),[19] and $[Na\{\mu\text{-}OC_6H_3\text{-}2,6\text{-}(CF_3)_2\}(THF)_2]_2$ (2.264 Å).[20] Another point of interest is the presence of short Na···C interactions in complex **3**. Thus, the aromatic rings are slightly bent toward the metal centers, facilitating Na−C(ipso) interactions

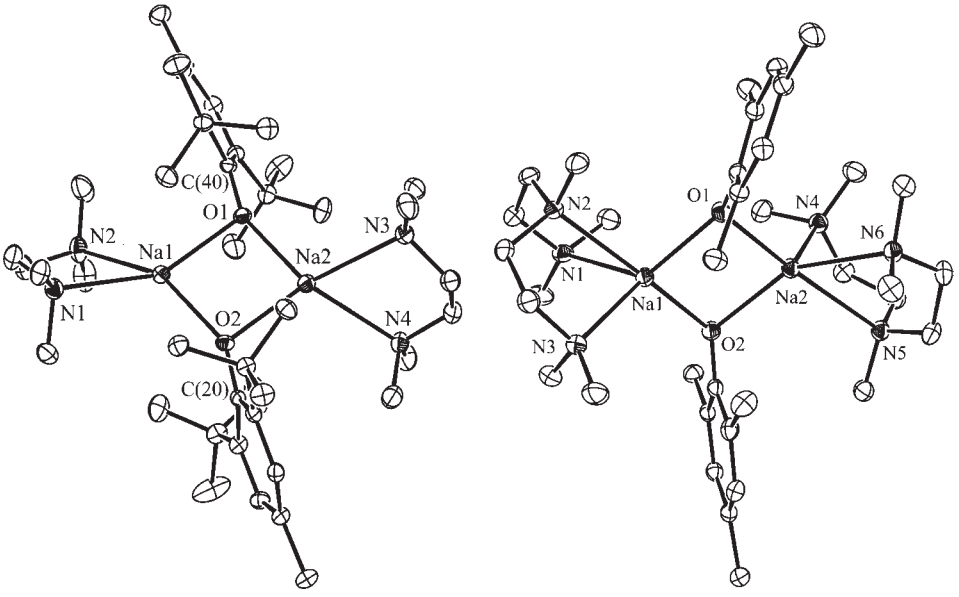


Figure 2. ORTEP diagrams of complexes **3** (left) and **4** (right), ellipsoid probability at 30% and hydrogen atoms omitted for clarity. Selected bond distances [Å]: **3** Na(1)−O(1) 2.364(2), Na(1)−O(2) 2.258(2), Na(2)−O(1) 2.254(2), Na(2)−O(2) 2.352(2), Na(1)−N(1) 2.745(3), Na(1)−N(2) 2.639(3), Na(2)−N(3) 2.701(3), Na(2)−N(4) 2.682(2); **4** Na(1)−O(1) 2.238(2), Na(1)−O(2) 2.300(2), Na(2)−O(1) 2.300(2), Na(2)−O(2) 2.333(2), Na(1)−N(1) 2.745(2), Na(1)−N(2) 2.564(2), Na(1)−N(3) 2.674(2), Na(2)−N(4) 2.568(2), Na(2)−N(5) 2.663(2), Na(2)−N(6) 2.662(2).

dx.doi.org/10.1021/ic102542q |*Inorg. Chem.* 2011, 50, 3589–3595

Table 1. Crystal Data for the Structures Reported

	3	4	5
mol formula	$C_{42}H_{78}N_4Na_2O_2$	$C_{36}H_{68}N_6Na_2O_2$	$C_{24}H_{46}N_3NaO$
mol wt	717.07	662.94	415.63
cryst syst	triclinic	triclinic	monoclinic
space group	$P\bar{1}$	$P\bar{1}$	$P2_1/n$
radiation (λ, Å)	0.71073	0.71073	0.71073
a (Å)	10.1610(4)	11.4470(2)	10.1480(4)
b (Å)	12.5230(4)	13.6090(3)	15.6060(6)
c (Å)	18.2140(6)	15.0490(3)	17.1010(7)
α (deg)	75.212(2)	94.0880(10)	90
β (deg)	82.060(2)	106.3490(10)	94.186(2)
γ (deg)	84.557(2)	114.6690(10)	90
V (Å^3)	2215.11(13)	1995.78(7)	2701.06(19)
Z	2	2	4
D_{calc} (g cm^{-3})	1.075	1.103	1.022
μ (mm^{-1})	0.082	0.087	0.076
temp, K	150(2)	150(2)	150(2)
θ range (deg)	3.513−27.485	4.19−27.52	5.31−27.47
index ranges (h, k, l)	−13,13; −16,16; −22,23	−14,14; −17,17; −18,19	−12,13; −20,20; −22,22
no. reflcns collected	29124	28124	38548
no. indep reflcns (R_{int})	10071 (0.1327)	9114 (0.0806)	6136
R_1, wR_2 [$I > 2\sigma(I)$][a]	0.0684, 0.1649[b]	0.0529, 0.1268[c]	0.062, 0.1434[d]
R_1, wR_2 (all data)[a]	0.1307, 0.2094[b]	0.0919, 0.151[c]	0.1344, 0.1938[d]
GOF	1.009	1.022	1.058
restraints/parameters	0/451	0/431	0/274
$\Delta\rho$(max,min), e Å^{-3}	0.324, −0.338	0.216, −0.265	0.229, −0.27

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR_2 = \{\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2\}^{1/2}$, $w = 1/[\sigma^2(F_o)^2 + (aP)^2 + bP]$, where $P = (F_o^2 + 2F_c^2)/3$. [b] $a = 0.0878$, $b = 1.1043$. [c] $a = 0.0680$, $b = 0.4427$. [d] $a = 0.0654$, $b = 1.4148$.

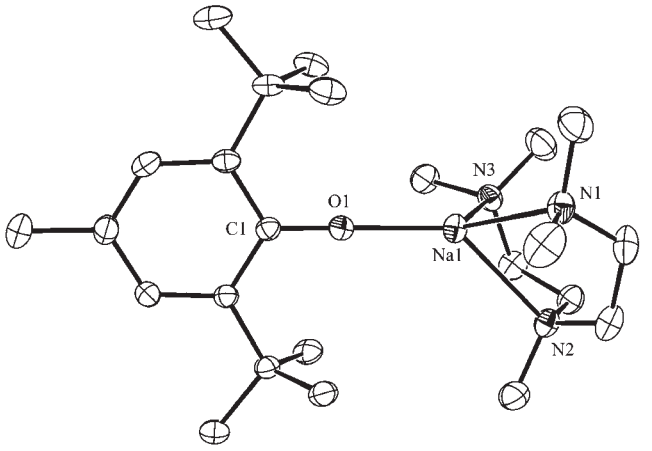


Figure 3. ORTEP diagram of complex **5**, ellipsoid probability at 30% and hydrogen atoms omitted for clarity. Selected bond distances [Å] and angles [deg]: Na(1)−O(1) 2.100(2), Na(1)−N(1) 2.431(3), Na(1)−N(2) 2.478(2), Na(1)−N(3) 2.438(2), O(1)−Na(1)−N(1) 123.91(9), O(1)−Na(1)−N(2) 135.81(9), O(1)−Na(1)−N(3) 120.16(9), N(1)−Na(1)−N(2) 75.37(8), N(1)−Na(1)−N(3) 111.22(8), N(2)−Na(1)−N(3) 76.22(8).

[Na(1)−C(40) 3.097(3) and Na(2)−C(20) 3.123(3) Å] comparable to those described as Na−C π-bonding interactions in the above-mentioned complex [Na(μ-OC$_6$H$_3$-2,4,6-^{t}Bu$_3$)(OEt$_2$)]$_2$ [3.004(2) Å].[19] In addition, the metal centers in **3** are further stabilized by intramolecular Na···CH$_3$ interactions, with the two shortest Na···C distances, Na(1)···C(50) 2.961(4) Å and Na(2)···C(29) 3.090(4) Å; values close to the range found for the sodium silanide complex [NaSi(SiMe$_3$)$_3$]$_2$ (2.85−3.05 Å).[21]

In contrast, compound **5** (Figure 3 and Table 1) exhibits a monomeric structural motif in the solid state crystallizing in the monoclinic space group $P2_1/n$. The coordination geometry around the sodium center is again far from ideal tetrahedral, with angles ranging from 135° to 75°. As expected for a terminal phenolate, the Na−O bond length [2.100(2) Å] is shorter than those above-discussed for complexes **3** and **4** with bridging aryloxides. It is also shorter than the values previously reported by us for the monomeric sodium aryloxides [Na(OAr^{Bu})(Me$_6$-TREN)] (**1**), 2.262(3) Å, and [Na(OAr^{Me})(HOAr^{Me})(Me$_6$-TREN)] (**2**), 2.270(2) Å,[14] this most likely being a consequence of the lower coordination number of the sodium center in complex **5** (four- vs five-coordinate). Consequently, the Na−N bond distances in **5** are also significantly shorter (ca. 0.2 Å) than those found for the dimeric complexes **3** and **4**, and similarly, slightly shorter than those found in the Me$_6$TREN complexes mentioned above.

In the solution state, crystalline samples of complexes **3**−**5** are soluble in C$_6$D$_6$; hence a NMR spectroscopic study of all complexes was possible. In all cases the available spectroscopic data are consistent with the solid state structure and in particular with the high pseudosymmetry of all these complexes. For example, ^{1}H NMR of complexes **3**−**4** displays only one set of

dx.doi.org/10.1021/ic102542q |*Inorg. Chem.* 2011, 50, 3589–3595

Table 2. Results for the ROP of *rac*-Lactide[a]

entry	initiator	$([Lact]_0/[Na]_0):[BnOH]_0$	t (min)	%conv.[b]	M_w[c]	$M_{n,theorethical}$	M_n[c]	PDI[c]	P_r[d]
1	**1**	100:0	5	99	57000	14391	37000	1.54	0.47
2	**2**	100:0	5	57*	9710	8427	7480	1.30	0.47
3	**3**	100:0	30	97	74400	14188	28400	2.61	0.47
4	**4**	100:0	30	99	44400	14391	26200	1.69	0.43
5	**5**	100:0	30	90	160700	13180	106000	1.51	0.45
6	**1**	100:1	5	99	16400	14363	11700	1.40	0.43
7	**2**	100:1	5	99	14400	14363	9810	1.46	0.43
8	**3**	100:1	5	99	25300	14363	15500	1.63	0.37
9	**4**	100:1	5	99	17800	14363	11900	1.50	0.40
10	**5**	100:1	5	98	21800	14220	14200	1.54	0.43
11	**1**	300:0	5	82*	21900	35560	13800	1.59	0.47
12	**1**	300:1	5	86	30900	37260	24100	1.28	0.44
13	**1**	300:1	10	85*	32400	36828	25700	1.26	0.45
14	**2**	300:1	5	99*	11500	42876	9210	1.25	0.41
15	**3**	300:1	15	80	36100	34668	28200	1.27	n.d.
16	**3**	300:1	30	81	35100	35100	27200	1.28	n.d.
17	**3**	300:1	45	81	37000	35100	30100	1.23	0.46
18	**4**	300:1	30	84*	31500	36396	26500	1.19	0.49
19	**4**	300:1	45	98*	29400	42336	21100	1.39	0.46
20	**5**	300:1	45	74*	26200	10584	21600	1.21	0.45
21[e]	**1**	100:1	5	99	21300	14363	25000	1.42	
22[e]	**3**	100:1	5	68	9560	9899	7130	1.34	
23[e]	**3**	100:1	10	71	14400	10331	9810	1.46	

[a] All the polymerizations were carried out in CH_2Cl_2 (5 mL) at 25 °C unless otherwise stated. [*rac*-lactide]$_0$ = 0.5 M. Reaction quenched by the addition of 1 mL of 0.35 M acetic acid solution in hexanes. [b] Determined by ^{1}H NMR analysis; those marked with an asterisk (*) contain cyclic oligomers in the final reaction mixtures. [c] Determined by GPC in THF, relative to polystyrene standards (uncorrected data). [d] P_r is the probability of racemic enchainment calculated by analysis of the homonuclear decoupled ^{1}H NMR spectra (according to ref 24). [e] Polymerizations using L-lactide.

resonances for each of the phenolate and N-donor ligands, in agreement with the presence of a (noncrystallographic) inversion center in the middle of the Na_2O_2 rhombi.

ROP of *rac*-Lactide. All sodium aryloxide complexes (**1**−**5**) were screened as initiators in the ROP of *rac*-lactide in dichloromethane solution at room temperature (Table 2). Experiments were carried out in both the absence and the presence of benzyl alcohol (BnOH) as a co-initiator and with a variety of monomer/initiator ratios.

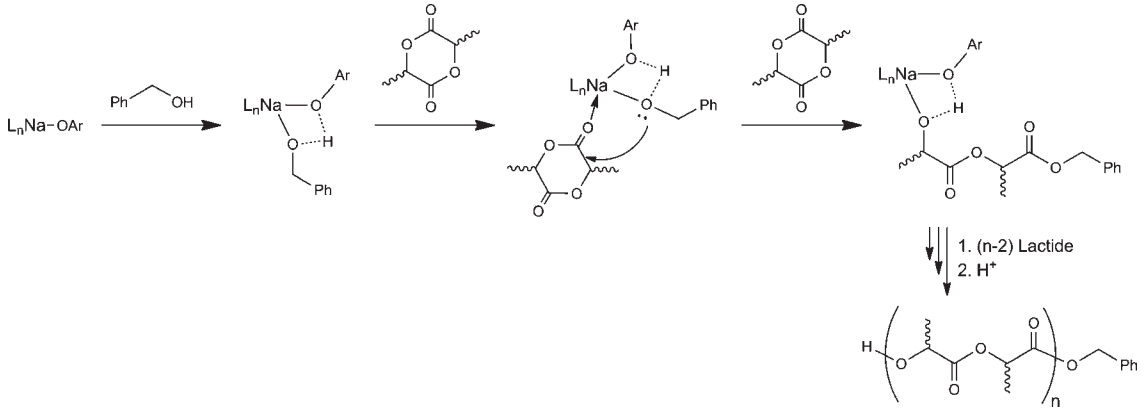
As anticipated, all the complexes were found to be very active in the ROP of *rac*-lactide, achieving almost complete conversions in relatively short reaction times when a 100:1 (monomer/initiator) ratio was used, and with the Me_6TREN complexes **1** and **2** being significantly faster than those based on the TMEDA and PMDETA supporting ligands. However, a particular comment is required for complex **2** (entry 2) which, apart from being comparatively slower than the other Me_6TREN derivative **1** (57% vs 99% conversion after 5 min), generates a final reaction mixture containing small amounts of cyclic oligomers,[22] pointing to the presence of intrachain transesterification side reactions which will be discussed later. It should be noted that for all initiators, only modest control was observed under these experimental conditions as can be inferred from the relatively high polydispersity indexes (PDI) and the slightly unpredictable molecular weights of the resulting polymers (entries 1−5 in Table 2).

For related Group 1 metal catalysts an improvement of the control over polymerization has been observed upon addition of benzyl alcohol as co-initiator,[11b,23] For the complexes **1**−**5**, when benzyl alcohol is added to the reaction media, before the addition of the monomer, a much faster reaction was observed with complete conversions achieved after only 5 min of reaction for all the initiators under evaluation. Most importantly, the resulting polymers exhibit much more predictable molecular weights and lower PDI's (entries 6−10 in Table 2). Also the formation of small cyclic oligomers previously observed for complex **2** in the absence of benzyl alcohol is suppressed. As observed previously,[11b,23] when benzyl alcohol is used as co-initiator, the ^{1}H NMR of the resulting polymers exhibit hydroxyl and benzyl ester ending group. An observation consistent with activation of the benzyl alcohol through hydrogen bond coordination to the phenolate oxygen atom, followed by insertion of the benzyl oxide group in to the lactide carbonyl as the first steps in the ROP mechanism (Scheme 2).

Another point of interest arises from the analysis of the methine region of the homonuclear decoupled ^{1}H NMR of these polymers, which can be used to obtain information about their microstructure.[24] In this study, the probability of racemic enchainment (P_r) for all polymers is within the range 0.37−0.43, which indicates a small isotactic bias (a value of 0.5 is expected for a perfectly atactic polymer). However, we must note that even when the *iii* tetrad, indicative of isotactic enchainment of lactide units (-RRRR- or -SSSS-), is almost always the most prominent signal there is an unusual enhancement of the *isi* tetrad (Figure 4, top). We[25] and others[5a,26] have found previously that this enhancement might be related to the presence of stereorandom transesterification during the course of the polymerization reaction (Scheme 3, top), which accounts for an increase of the intensity of the *iss*, *sss* and *ssi* tetrads, all of which have an

dx.doi.org/10.1021/ic102542q |*Inorg. Chem.* 2011, 50, 3589–3595

Scheme 2. Proposed Mechanism for the Polymerization of *rac*-Lactide Initiated by Complexes 1− 5 under Benzyl Alcohol Activation



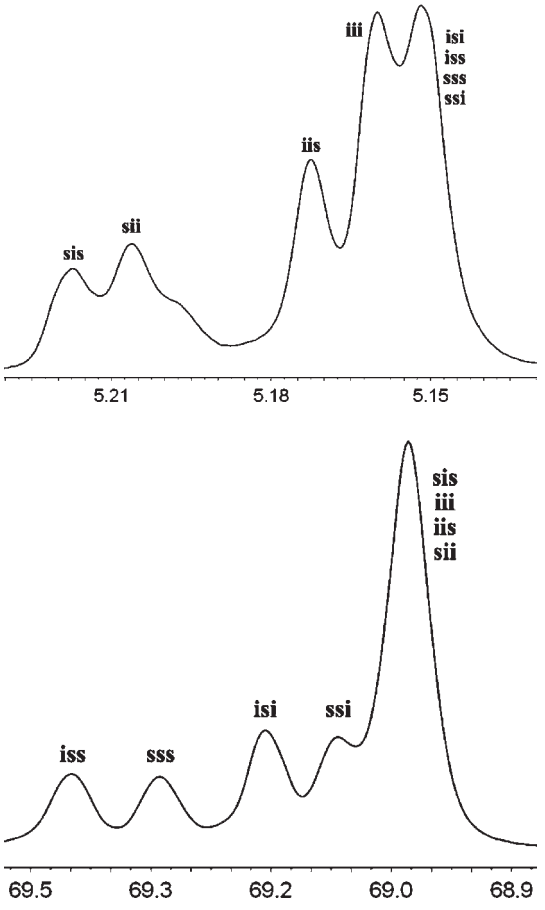


Figure 4. ^{1}H homonuclear decoupled NMR for the methine region of the polymer in entry 9 (top). $^{13}C\{^{1}H\}$ NMR region of the same polymer (bottom).

analogous chemical shift to the *isi* tetrad, but which should not be present in the ^{1}H NMR for the polymerization of *rac*-lactide in the absence of transesterification and/or epimerization side reactions during the polymerization. However, the latter can be excluded in our case as complexes **1** and **3** yielded perfectly isotactic polymers when enantiomerically pure L-lactide was used (entries 21−23 in Table 2). Unambiguous observation of *iss*, *sss*, and *ssi* tetrads come from the $^{13}C\{^{1}H\}$ NMR spectrum of these polymers (Figure 4, bottom) supporting the above argument.

Finally, complexes **1**−**5** were tested using a lower catalyst loading, 300:1:1 monomer/initiator/benzyl alcohol ratio (entries 11−20 in Table 2). The results obtained are much more difficult to interpret. In general the polymerization reaction progress rapidly initially. Typically conversions of about 80% were reached after about 15 min of reaction, then the polymerization progress is almost stopped and then for the vast majority of the complexes studied the formation of cyclic oligomers was observed. As was previously commented, an intrachain transesterification mechanism accounts for the formation of cyclic oligomers in the ROP of *rac*-lactide (Scheme 3, bottom).

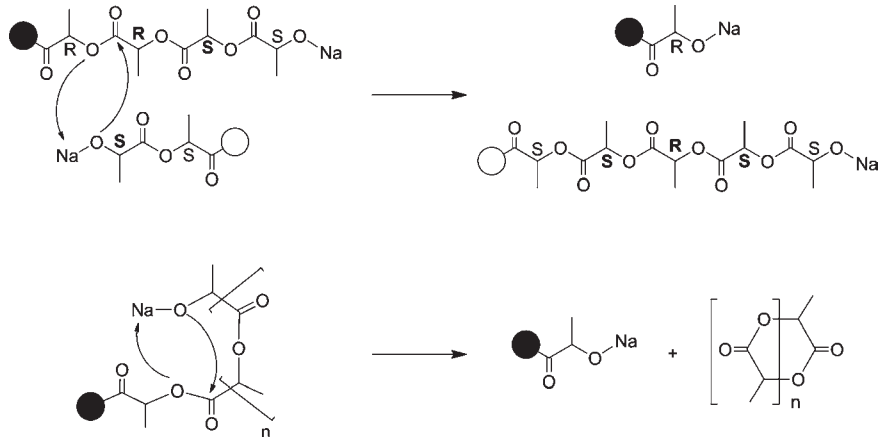
In conclusion, three new sodium aryloxide complexes stabilized by the polyamine ligands TMEDA and PMDETA have been prepared and characterized in both solution and the solid state. These new sodium complexes, together with two previously prepared in our group containing the tetradentate ligand Me_6TREN, were proven to be highly active in the ROP polymerization of *rac*-lactide although only moderate control over the polymerization was found. However, when benzyl alcohol is used as co-initiator in the polymerization reaction, complete conversions were achieved after only 5 min of reaction, and significantly better control was observed. In spite of this, the detailed study of the microstructure of the final polymers revealed the presence of stereorandom interchain transesterification side reactions during the course of the polymerization reaction. When lower catalysts loadings were employed, small cyclic oligomers indicative of intrachain transesterification were present in the final reaction mixtures.

EXPERIMENTAL SECTION

General Procedures. All experimental manipulations were performed under an atmosphere of dry, oxygen-free argon, using standard Schlenk and glovebox techniques. All solvents were degassed, eluted over activated alumina columns and stored under argon prior to use. Sodium hexamethyldisilazide [$NaN(SiMe_3)_2$], 2,4,6-trimethylphenol, and 2,6-di(*tert*-butyl)-4-methylphenol were bought from Aldrich and used without further purification. *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA) and *N*,*N*,*N*′,*N*′′,*N*′′-pentamethyldiethylenetriamine (PMDETA) were bought from Aldrich and stored over 4 Å molecular sieves prior to use. Complexes **1** and **2** have been prepared according to

dx.doi.org/10.1021/ic102542q |*Inorg. Chem.* 2011, 50, 3589–3595

Scheme 3. Inter- (top) and Intra-Chain (bottom) Transesterification Side Reactions Leading to the Presence of Disyndiotactic Tetrads and to the Formation of Cyclic Oligomers Respectively



literature procedures.[14] ^{1}H NMR spectra were recorded on a Bruker 300 MHz, 400 or 500 MHz spectrometers at room temperature and referenced to residual protio solvent peaks, unless otherwise stated. Benzene-d^6 and toluene-d^8 (Aldrich) were degassed and stored over 4 Å molecular sieves. Coupling constants J are given in hertz. Elemental analysis was performed by Mr. A. K. Carver at the Department of Chemistry, University of Bath, on an Exeter Analytical CE440 Elemental Analyzer. Analyses that were acceptable within the standard variances were not collected for complexes **3** and **5** even when rigorous exclusion of air was undertaken. This deviation has been previously observed for other Group 1 metal aryloxide complexes,[27] and might be attributed to several factors including excess "trapped" solvent or the imcomplete combustion of the samples. Gel Permeation Chromatography (GPC) analyses were performed on a Polymer Laboratories PL-GPC 50 integrated system using a PLgel 5 μm MIXED-D 300 × 7.5 mm column at 35 °C, tetrahydrofuran (THF) solvent (flow rate, 1.0 mL/min). The PDI was determined from M_w/M_n, where M_n is the number average molecular weight and M_w the weight average molecular weight. The polymers were referenced to 11 narrow molecular weight polystyrene standards with a range of M_w 615−5680000 Da.

Preparation of [Na(μ-OAr^{Bu})(TMEDA)]$_2$ (3). *N,N,N′,N′*-Tetramethylenediamine (0.136 mL, 0.908 mmol) was added to a solution of NaN(SiMe$_3$)$_2$ (0.136 mL, 0.908 mmol) and 2,6-di-*tert*-butyl-4-methylphenol (0.200 g, 0.908 mmol) in toluene (10 mL). The resulting solution was stirred for 15 min at room temperature to give a colorless solution with fine precipitate. The precipitate was redissolved by heating, and the resulting solution was then left to cool to room temperature to yield a crop of crystals which were isolated by filtration, washed with cold hexane (2 × 5 mL), and dried in vacuo (0.223 g, 68%). Anal. Calcd for $C_{42}H_{78}N_4Na_2O_2$: C, 70.33; H, 10.97; N 7.82. Found C, 68.70; H, 10.90; N, 7.64. ^{1}H NMR (C_6D_6): δ 7.22 [s, 2H, H(Ar)], 2.47 [s, 3H, Me(Ar)], 1.92 [s, 4H, NCH$_2$,], 1.88 [s, 12H, NMe$_2$], 1.61 [s, 18H, ^{t}Bu(Ar)] ppm.

Preparation of [Na(μ-OAr^{Me})(PMDETA)]$_2$ (4). 2,4,6-Trimethylphenol (0.200 g, 1.500 mmol) was added to a solution of NaN(SiMe$_3$)$_2$ (0.289 g, 1.500 mmol) and *N,N,N′,N″,N‴*-pentamethyldiethylenetriamine (0.305 mL, 1.500 mmol) in toluene (10 mL). The resulting solution was stirred for 15 min at room temperature, then the solution was gently concentrated (ca. 2 mL), a small amount of precipitate was redissolved by heating, and the resulting solution was then left to cool to 253 K to yield a crop of crystals which were isolated by filtration, washed with cold hexane (2 × 5 mL), and dried in vacuo (0.252 g, 52%.). Anal. Calcd for $C_{36}H_{68}N_6Na_2O_2$: C, 65.21; H, 10.34; N 12.68. Found C, 65.30; H, 10.50; N, 12.80. ^{1}H NMR (C_6D_6): δ 7.09 [s, 2H, H(Ar)], 2.44 [s, 3H, *p*-Me(Ar)], 2.43 [s, 6H, *o*-Me(Ar)], 2.02 [s, 12H, NMe$_2$], 1.93 [m, 8H, NCH$_2$], 1.75 [s, 3H, NMe] ppm.

Preparation of [Na(OAr^{Bu})(PMDETA)] (5). *N,N,N′,N″,N‴*-Pentamethyldiethylenetriamine (0.142 mL, 0.680 mmol) was added to a solution of NaN(SiMe$_3$)$_2$ (0.132 g, 0.680 mmol) and 2,6-di-*tert*butyl-4-methylphenol (0.150 g, 0.680 mmol) in toluene (10 mL). The resulting solution was stirred for 20 min at room temperature to give a colorless solution with fine precipitate. The precipitate was redissolved by heating, and the resulting solution was then left to cool to room to yield a crop of crystals which were isolated by filtration, washed with cold hexane (2 × 5 mL) and dried in vacuo (0.104 g, 34%). Anal. Calcd for $C_{24}H_{46}N_3NaO$: C, 69.34; H, 11.16; N 10.11. Found C, 67.20; H, 10.90; N, 9.80. ^{1}H NMR (C_6D_6): δ 7.38 [s, 2H, H(Ar)], 2.65 [s, 3H, Me(Ar)], 1.89 [s, 3H, NMe], 1.82 [s, 12H, NMe$_2$], 1.81 [s, 18H, ^{t}Bu(Ar)], 1.68 [s, 8H, NCH$_2$] ppm.

Solution Polymerization of *rac*-Lactide. In a typical run the initiator (0.025 mmol) was dissolved in dichloromethane (5 mL) to which *rac*-lactide (2.5 mmol, 0.36 g) was added, and the vessel left to stir at room temperature for the prescribed time. The mixture was then quenched by the addition of a solution of acetic acid in hexane (0.35 M, 1 mL), and the polymer was precipitated on pouring into *n*-hexane (50 mL) to give white solids. The solvents were removed and the resulting solid washed with methanol to remove any excess monomer and dried in vacuo. ^{1}H NMR spectroscopy ($CDCl_3$) and GPC (THF) were used to determine tacticity and molecular weights (M_n and M_w) of the polymers produced; P_r (the probability of heterotactic linkages) were determined by analysis of the methine region of the homonuclear decoupled ^{1}H NMR spectra according to literature procedures.[24]

General X-ray Crystal Structure Information. Suitable single crystals of compounds **3**−**5** were mounted on glass fibers using perfluoroether oil. Data collections were carried out on an Enraf Nonius Kappa CCD diffractometer, equipped with a Oxford Cryosystems cooling device, and graphite-monochromated Mo−Kα radiation (λ = 0.71069 Å). Data were corrected for Lorentz and polarization effects. The structures were solved by direct methods, and refined using full-matrix least-squares on F^2 with all non-hydrogen atoms assigned anisotropic displacement parameters. Hydrogen atoms were included at calculated positions throughout and refined using a riding model, with U_{iso} set to 1.2-times (1.5-times for methyl-H) U_{equiv} of the carrier carbon atom. In the final stages of refinement a weighting scheme was introduced and refinement continued until convergence was achieved. Programs used were SHELXL-97[28] as implemented in the WINGX[29]

package. Experimental data relating to all the structure determinations are presented in Table 1.

■ ASSOCIATED CONTENT

Supporting Information. Crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: m.g.davidson@bath.ac.uk (M.G.D.), d.garcia@bath.ac.uk (D.G.-V.).

■ ACKNOWLEDGMENT

We thank the University of Bath for funding, and D.G.-V. thanks the European Commission for financial aid under the Marie Curie Intra-European Postdoctoral Fellowship (PIEF-2009-235173) program.

■ REFERENCES

(1) For recent reviews on biomedical applications of polyesters, see: (a) Vert, M. *Biomacromolecules* **2005**, *6*, 538. (b) Albertsson, A. C.; Varma, I. K. *Biomacromolecules* **2003**, *4*, 1466. (c) Uhrich, K. E.; Cannizzaro, S. M.; Langer, R. S.; Shakesheff, K. M. *Chem. Rev.* **1999**, *99*, 3181.

(2) For recent reviews on ring-opening polymerization of lactones, see: (a) Wheaton, C. A.; Hayes, P. G.; Ireland, B. J. *Dalton Trans.* **2009**, 4832. (b) Platel, R. H.; Hodgson, L. M.; Williams, C. K. *Polym. Rev.* **2008**, *48*, 11. (c) Dove, A. P. *Chem. Commun.* **2008**, 6446. (d) Wu, J. C.; Yu, T. L.; Chen, C. T.; Lin, C. C. *Coord. Chem. Rev.* **2006**, *250*, 602. (e) Dechy-Cabaret, O.; Martin-Vaca, B.; Bourissou, D. *Chem. Rev.* **2004**, *104*, 6147. (f) O'Keefe, B. J.; Hillmyer, M. A.; Tolman, W. B. *J. Chem. Soc., Dalton Trans.* **2001**, 2215.

(3) Schwach, G.; Coudane, J.; Engel, R.; Vert, M. *Polym. Bull.* **1996**, *37*, 771.

(4) See for example: (a) Dittrich, W.; Schulz, R. C. *Angew. Makromol. Chem.* **1971**, *15*, 109. (b) Cheng, M.; Attygalle, A. B.; Lobkovsky, E. B.; Coates, G. W. *J. Am. Chem. Soc.* **1999**, *121*, 11583. (c) Chisholm, M. H.; Eilerts, N. W.; Huffman, J. C.; Iyer, S. S.; Pacold, M.; Phomphrai, K. *J. Am. Chem. Soc.* **2000**, *48*, 11845. (d) William, C. K.; Breyfogle, L. E.; Choi, S. K.; Nam, W.; Young, V. G., Jr.; Hillmyer, M. A.; Tolman, W. B. *J. Am. Chem. Soc.* **2003**, *125*, 11350.

(5) Some recent examples: (a) Kasperczyk, J.; Bero, M. *Polymer* **2000**, *41*, 391. (b) Shueh, M.-L.; Wang, Y.-S.; Huang, B.-H.; Kuo, C.-Y.; Lin, C.-C. *Macromolecules* **2004**, *37*, 5155. (c) Yu, T.-L.; Wu, C.-C.; Chen, C.-C.; Huang, B.-H.; Wu, J.; Lin, C.-C. *Polymer* **2005**, *46*, 5909.

(6) Some recent examples: (a) Li, S. M.; Rashkov, I.; Espartero, J. L.; Manolova, N.; Vert, M. *Macromolecules* **1996**, *29*, 57. (b) Dobrzynski, P.; Kasperczyk, J.; Bero, M. *Macromolecules* **1999**, *32*, 4735. (c) Chisholm, M. H.; Galluci, J.; Phomphrai, K. *Chem. Commun.* **2003**, 48. (d) Chisholm, M. H.; Galluci, J.; Phomphrai, K. *Inorg. Chem.* **2004**, *43*, 6717. (e) Chen, H.; Tang, H.; Lin, C. *Polymer* **2007**, *48*, 2257. (f) Darensbourg, D. J.; Choi, W.; Richers, C. P. *Macromolecules* **2007**, *40*, 3521.

(7) See for example: (a) Stolt, M.; Södergård, A. *Macromolecules* **1999**, *32*, 6412. (b) O'Keefe, B. J.; Breyfogle, L. E.; Hillmyer, M. A.; Tolman, W. B. *J. Am. Chem. Soc.* **2002**, *124*, 4384.

(8) For a recent review on ring-opening polymerizations catalysed by lithium compounds see: Sutar, A. K.; Maharana, T.; Dutta, S.; Chen, C.-T.; Lin, C.-C. *Chem. Soc. Rev.* **2010**, *39*, 1724.

(9) Kasperczyk, J. E. *Macromolecules* **1995**, *28*, 3937.

(10) (a) Kricheldorf, H. R.; Kreiser-Saunders, I. *Makromol. Chem.* **1990**, *191*, 1057. (b) Sipos, L.; Zsug, M.; Kelen, T. *Polym. Bull.* **1992**, *27*, 495.

(11) (a) Ko, B. T.; Lin, C.-C. *J. Am. Chem. Soc.* **2001**, *123*, 7973. (b) Hsueh, M.-L.; Huang, B.-H.; Wu, J.; Lin, C.-C. *Macromolecules* **2005**, *38*, 9482.

(12) Chen, H.-Y.; Zhang, J.; Lin, C.-C.; Reibenspies, J. H.; Miller, S. A. *Green Chem.* **2007**, *9*, 1038.

(13) Chisholm, M. H.; Lin, C.-C.; Gallucci, J. C.; Ko, B. T. *Dalton Trans.* **2003**, 406.

(14) Cousins, D. M.; Davidson, M. G.; Frankis, C. J.; García-Vivó, D.; Mahon, M. F. *Dalton Trans.* **2010**, *39*, 8278.

(15) (a) Collum, D. B. *Acc. Chem. Res.* **1992**, *25*, 448. (b) Gregory, K.; Schleyer, P. v. R.; Snaith, R. *Adv. Inorg. Chem.* **1991**, *37*, 47.

(16) Cousins, D. M.; Davidson, M. G.; García-Vivó, D.; Mahon, M. F. *Dalton Trans.* **2010**, *39*, 8203.

(17) (a) Kunert, M.; Dinjus, E.; Nauck, M.; Sieler, J. *Chem. Ber.* **1997**, *130*, 1461. (b) Dinnebier, R. E.; Pink, M.; Sieler, J.; Stephens, P. W. *Inorg. Chem.* **1997**, *36*, 3398.

(18) Klinga, M.; Matilainen, L.; Leskel, M. *Private Communication to the Cambridge Structural Database* 1999, deposition number 110183.

(19) Yuan, F.; Yang, J.; Xiong, L. *J. Organomet. Chem.* **2006**, *691*, 2534.

(20) Brooker, S.; Edelman, F. T.; Kottke, T.; Roesky, H. W.; Sheldrick, G. M.; Stalke, D.; Whitmire, K. H. *Chem. Commun.* **1991**, 144.

(21) Klinkhammer, K. W. *Chem.—Eur. J.* **1997**, *3*, 1418.

(22) The presence of small cyclic esters in the final reaction mixtures was initially observed in the ^{1}H NMR of reaction crudes, and unambiguously indentified by mass spectrometry (ESI-MS).

(23) (a) Huang, C.-A.; Chen, C.-T. *Dalton Trans.* **2007**, 5561. (b) Huang, C.-A.; Ho, C.-L.; Chen, C.-T. *Dalton Trans.* **2008**, 3502.

(24) (a) Chamberlain, B. M.; Cheng, M.; Moore, D. R.; Ovitt, T. M.; Lobkovsky, E. B.; Coates, G. W. *J. Am. Chem. Soc.* **2001**, *123*, 3229. (b) Thakur, K. A. M.; Kean, R. T.; Zell, M. T.; Padden, B. E.; Munson, E. J. *Chem. Commun.* **1998**, 1913. (c) Thakur, K. A. M.; Kean, R. T.; Hall, E. S.; Kolstad, J. J.; Lindgren, T. A.; Doscotch, M. A.; Siepmann, J. I.; Munson, E. J. *Macromolecules* **1997**, *30*, 2422. (d) Chisholm, M. H.; Iyer, S. S.; Matison, M. E.; McCollum, D. G.; Pagel, M. *Chem. Commun.* **1997**, 1999.

(25) Chmura, A. J.; Davidson, M. G.; Jones, M. D.; Lunn, M. D.; Mahon, M. F.; Johnson, A. F.; Khunkamchoo, P.; Roberts, S. L.; Wong, S. S. F. *Macromolecules* **2006**, *39*, 7250.

(26) Bero, M.; Kasperczyk, J.; Jedlinski, Z. J. *Makromol. Chem.* **1990**, *191*, 2287.

(27) Boyle, T. J.; Pedrotty, D. M.; Alam, T. M.; Vick, S. C.; Rodriguez, M. A. *Inorg. Chem.* **2000**, *39*, 5133.

(28) Sheldrick, G. M. *SHELXL-97*; University of Göttingen: Göttingen, Germany, 1997.

(29) Farrugia, L. J. *J. Appl. Crystallogr.* **1999**, *32*, 837.