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$(RO)_2Ta$[tris(2-oxy-3,5-dimethylbenzyl)amine]: Structure and Lactide Polymerization Activities

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The novel atrane-like six-coordinate $(RO)_2TaL$ complexes [where R = Me or Et and L = tris(2-oxy-3,5-dimethylbenzyl)amine] containing three six-membered rings have been synthesized and characterized. The R = Me complex is the first group 5 representative of this class of compounds structurally characterized by X-ray means. Somewhat surprisingly, these compounds failed to function as single-site initiators for the polymerization of *l*-LA to isotactic PLA and *rac*-LA to atactic PLA, whereas $Ta(OEt)_5$ and two titanium analogues ROTiL (where R = 2,6-di-*i*-PrC_6H_3 and *i*-Pr) as well as Ti(O-*i*-$Pr)_4$ were effective catalysts for both polymerizations.

The tripodal trialkoxy amine ligands made by deprotonating tris(2-hydroxy-3,5-dimethylbenzyl)amine (**1**) or other 3,5-dialkyl derivatives of **1** have recently been used to make silicon[1] and phosphorus[2] complexes resembling the corresponding atranes (made from triethanolamine) except that the three chelating rings are six- instead of five-membered. The silicon complexes made from deprotonated **1**, and some of its derivatives, are more structurally flexible than silatranes themselves, thus allowing for changes in their Si−N bond lengths and ^{29}Si NMR chemical shifts that are roughly correlated to the electron donating effects of their axial substituents.[2] Recently it was also shown that analogous titanium(IV) complexes of deprotonated **1** and some of its derivatives are catalysts for the syndiospecific polymerization of styrene[3] and in the bulk polymerization of lactide (LA).[4] Although it is commonly accepted that the polymerization rate of polar or functionalized monomers is generally relatively slow with titanium compounds, ROTiL [L here and throughout this paper = tris(2-oxy-3,5-dimethylbenzyl)amine] recently reported from our laboratories[4] where R = *i*-Pr or 2,6-di-*i*-PrC_6H_3 are noteworthy for their good catalytic activity in the polymerization of LA in the absence of any co-initiator such as an alcohol, and despite the considerable bulkiness of the tripodal ligand. This polymerization presumably proceeds via a coordination−insertion mechanism, which was substantiated by end-group NMR analysis of the polylactide.[5]

In view of the assumption that the reactive intermediate in the aforementioned LA polymerization is a six-coordinate titanium complex,[4] we were curious to determine if an $(RO)_2TaL$ complex would be five-coordinate (owing to a lack of transannulation) or six-coordinate (because of its presence), and whether this complex (regardless of its coordination number) could catalyze the polymerization of LA. We describe here the synthesis and characterization of $(EtO)_2TaL$ (**2**) and its dimethoxy analogue **3**, and the X-ray structural analysis of **3**. In addition, comparisons of the activities for LA polymerization are made among $Ta(OEt)_5$, Ti(O-*i*-$Pr)_4$, **2**, **3**, and its titanium analogue ROTiL where R = *i*-Pr or 2,6-di-*i*-Pr-phenyl.

Experimental Section

All reactions were carried out under argon with standard Schlenk and glovebox techniques.[6] All chemicals were purchased from Aldrich and were used as supplied unless otherwise indicated. THF

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and toluene (Fischer HPLC grade) were dried and purified under nitrogen in a Grubbs-type nonhazardous two-column solvent purification system[7] (Innovative Technologies) and were stored over activated 3 Å molecular sieves. All deuterium solvents were dried over activated molecular sieves (3 Å) and were used after vacuum transfer to a Schlenk tube equipped with a J. Young valve. *l*-LA and *rac*-LA were purified twice by sublimation at 70 °C under 7 μm Hg pressure before use. ^{1}H and ^{13}C{^{1}H} spectra were recorded at ambient temperature on a Varian VXR-400 NMR spectrometer, using standard parameters. The chemical shifts are referenced to the residual peaks of $CDCl_3$ (7.24 ppm, ^{1}H NMR; 77.0 ppm, ^{13}C{^{1}H} NMR) and C_6D_6 (7.15 ppm, ^{1}H NMR; 128 ppm, ^{13}C{^{1}H} NMR). Elemental analyses were performed by Desert Analytics Laboratory. Molecular weights of polymers were determined by gel permeation chromatography (GPC) at room temperature with THF as the eluent (1 mL/min), using a Waters 510 pump, a Waters 717 Plus Autosampler, four Polymer Laboratories PLgel columns (100, 500, 10^4, 10^5 Å) in series, and a Wyatt Optilab DSP interferometric refractometer as a detector. The columns were calibrated with polystyrene standards. Compound **1**[1] (the precursor to L) and ROTiL (R = *i*-Pr or 2,6-di-*i*-Pr-phenyl)[4,8] were synthesized by literature procedures.

Synthesis of (EtO)$_2$TaL (2). A solution of $Ta(OEt)_5$ (2.0 mmol, 0.81 g) in toluene (30 mL) was added dropwise via a cannula to a solution of **1** (2.0 mmol, 0.84 g) in toluene (40 mL) with stirring at room temperature over a period of 10 min. The solution was refluxed for 14 h and then the solvent was removed in vacuo. A yellowish spongy solid **2** (1.20 g) was obtained after drying under vacuum (yield, 87.3%). ^{1}H NMR (400.147 MHz, C_6D_6, ppm) δ 6.84 (s, 2H, aryl-*H*), 6.79 (s, 1H, aryl-*H*), 6.58 (s, 2H, aryl-*H*), 6.31 (s, 1H, aryl-*H*), 4.98 (q, $J = 7.0$ Hz, 2H, OCH_2CH_3), 4.04 (d, $J = 13$ Hz, 2H, CH_2N), 3.95 (q, $J = 7.0$ Hz, 2H, OCH_2CH_3), 3.47 (s, 1H, CH_2N), 3.22 (d, $J = 13$ Hz, 2H, CH_2N), 2.40 (s, 3H, aryl-*Me*), 2.31 (s, 6H, aryl-*Me*), 2.21 (s, 6H, aryl-*Me*), 2.11 (s, 3H, aryl-*Me*), 1.51 (t, $J = 7.0$ Hz, 3H, OCH_2CH_3), 0.92 (t, $J = 7.0$ Hz, 3H, OCH_2CH_3). ^{13}C{^{1}H} NMR (C_6D_6, 100.626 MHz) δ 156.2, 155.8, 132.0, 131.4, 128.0, 127.0, 126.3, 125.2, 124.1 (aryl), 71.03 (OCH_2CH_3), 67.23 (OCH_2CH_3), 63.50 (NCH_2), 60.83 (NCH_2), 21.09 (aryl-*Me*), 21.00 (aryl-*Me*), 19.37 (OCH_2CH_3), 19.29 (OCH_2CH_3), 17.10 (aryl-*Me*), 16.77 (aryl-*Me*). Three aromatic carbon peaks overlapped those of the C_6D_6 solvent. Elemental Anal. Calcd for $C_{31}H_{40}NO_5Ta$: C, 54.15; H, 5.86; N, 2.04. Found: C, 53.13; H, 6.06; N, 2.16.

Synthesis (MeO)$_2$TaL (3). MeOH (30 mL) was added to a solution of **2** (1.00 g, 1.45 mmol) in THF (10 mL) at room temperature. The solution was refluxed overnight and all volatiles were removed under vacuum, leaving a colorless solid, to which was added 15 mL of toluene. The clear solution was filtered and the desired product **3** was isolated as colorless needlelike crystals after the solution remained at −15 °C in a refrigerator for a few days (0.88 g, 92% yield). ^{1}H NMR (400.147 MHz, C_6D_6, ppm) δ 6.80 (s, 2H, aryl-*H*), 6.71 (s, 1H, aryl-*H*), 6.54 (s, 2H, aryl-*H*), 6.18 (s, 1H, aryl-*H*), 4.67 (3H, s, O*Me*), 4.02 (d, $J = 10$ Hz, 2H, CH_2N), 3.75 (3H, s, O*Me*), 3.41 (s, 2H, CH_2N), 3.13 (d, $J = 10$ Hz, 2H, CH_2N), 2.37 (s, 3H, aryl-*Me*), 2.30 (s, 6H, aryl-*Me*), 2.21 (s, 6H, aryl-*Me*), 2.09 (s, 3H, aryl-*Me*). ^{1}H NMR (400.147 MHz, $CDCl_3$, ppm) δ 6.80 (s, 2H, aryl-*H*), 6.67 (s, 2H, aryl-*H*), 6.61 (s, 1H, aryl-*H*), 6.17 (s, 1H, aryl-*H*), 4.70 (3H, s, O*Me*), 4.32 (d, $J = 13.2$ Hz, 2H, CH_2N), 3.93 (3H, s, O*Me*), 3.50 (s, 2H, CH_2N), 3.43 (d, $J = 13.2$ Hz, 2H, CH_2N), 2.19 (s, 3H, aryl-*Me*), 2.18 (s, 6H, aryl-*Me*), 2.14 (s, 6H, aryl-*Me*), 1.98 (s, 3H, aryl-*Me*). ^{13}C{^{1}H} NMR (C_6D_6, 100.626 MHz) δ 156.0, 155.6, 132.1, 131.4, 128.9, 126.9, 126.1, 125.2, 124.10 (aryl), 63.69 (NCH_2), 62.63 (OCH_3), 60.70 (NCH_2), 58.97 (OCH_3), 21.07 (aryl-*Me*), 20.95 (aryl-*Me*), 17.10 (aryl-*Me*), 16.64 (aryl-*Me*). Three aromatic carbon peaks overlapped those of C_6D_6. Elemental Anal. Calcd for $C_{29}H_{36}NO_5Ta$: C, 52.81; H, 5.50; N, 2.12. Found: C, 51.58; H, 5.82; N, 2.19.

Table 1. Crystallographic Data for Compound **3**

empirical formula	$C_{29}H_{36}NO_5Ta$
formula weight	659.54
temp (K)	298(2)
cryst syst	orthorhombic
space group	*Pbca*
a (Å)	22.771(5)
b (Å)	9.565(2)
c (Å)	26.204(5)
α (deg)	90
β (deg)	90
γ (deg)	90
V (Å^3)	5707(2)
Z	8
D_{calcd} (Mg/m^3)	1.535
abs coeff (mm^{-1})	3.888
F(000)	2640
θ range (deg)	2.37 to 24.71
reflns collected	23223
independent reflns	4847
no. of parameters refined	333
GOF	1.020
final *R* indices [$I > 2\sigma(I)$][a]	$R_1 = 0.0457$, $wR_2 = 0.1092$
largest diff. peak and hole (eÅ^{-3})	0.831 and −1.620

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$ and $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

X-ray Crystallography for 3. Crystallographic measurements were performed at 298 K with a Bruker CCD-1000 diffractometer with Mo Kα ($\lambda = 0.71073$ Å) radiation and a detector-to-crystal distance of 5.03 cm. A specimen of suitable quality and size (0.3 × 0.1 × 0.08 mm^3) was selected and mounted on a glass fiber with epoxy glue. The initial cell constants were obtained from three series of ω scans at different starting angles. Each series consisted of 30 frames collected at intervals of 0.3° in a 10° range about ω with an exposure time of 30 s per frame. Systematic absences in the diffraction data were consistent for the space group *Pbca* and yielded chemically reasonable and computationally stable refinement results. Positions of heavy atoms were found by the Patterson method. The remaining atoms were located in an alternating series of least-squares cycles and difference Fourier maps. All non-hydrogen atoms were refined in a full-matrix anisotropic approximation. All hydrogen atoms were placed at idealized positions in the structure factor calculation and were allowed to ride on the neighboring atoms with relative isotropic displacement coefficients. Final refinement based on the reflections ($I > 2.0\sigma(I)$) converged at $R_1 = 0.0457$, $wR_2 = 0.1092$, and GOF = 1.020. Further details are listed in Table 1.

Polymerization Procedure. LA polymerizations were carried out by charging 2.00 g of LA to a 25-mL Schlenk flask, followed by the appropriate amount of catalyst precursor. The flask was then immersed in an oil bath at 130 °C and after the time shown in Table 2, the reaction was terminated by the addition of 5 mL of methanol. No significant differences in yields and molecular weights were observed when 10% aqueous HCl/MeOH was substituted for MeOH, thus indicating that active catalyst was not left behind to cause transesterification. The polymer so obtained as a precipitate was dissolved in a minimum amount of methylene chloride and then excess methanol was added. The resulting reprecipitated polymer was collected, washed with 3 × 50 mL of methanol, and dried in vacuo at 50 °C for 12 h. The results of these experiments

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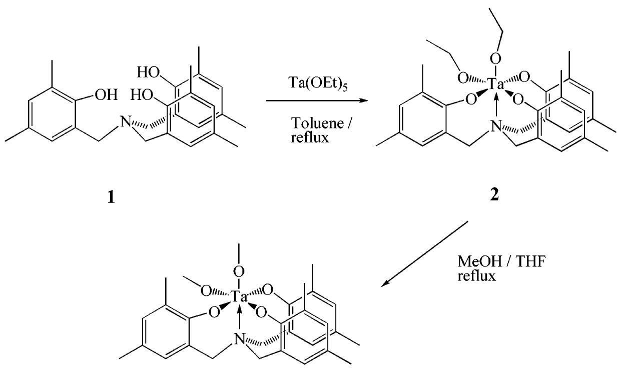
Table 2. Data for *l*- and *rac*-LA Bulk Polymerizations[a]

catalyst	type of LA	time (h)	*g* of polymer	yield (%)	MW[b]	M_n[b]	M_w/M_n[b]
Ti(O-*i*-Pr)$_4$	*l*-LA	2	1.49	75	35 700	16 000	2.24
	rac-LA	2	1.42	71	41 100	19 600	2.10
LTi(OR) (R = 2,6-di-*i*-PrC$_6$H$_3$)	*l*-LA	4	0.56	28	12 800	8 400	1.52
	rac-LA	4	0.50	25	9 100	6 300	1.45
LTi(OR) (R = *i*-Pr)	*l*-LA	4	1.10	55	76 100	52 000	1.46
	rac-LA	4	1.05	53	51 400	38 000	1.35
Ta(OEt)$_5$	*l*-LA	15	1.76	88	23 400	15 900	1.47
	rac-LA	15	1.74	87	14 000	10 400	1.35
2	*l*-LA	24	0	0			
	rac-LA	24	0	0			
3	*l*-LA	24	0	0			
	rac-LA	24	0	0			

[a] Polymerization conditions: 2 g of LA, oil bath temperature = 130 ± 3 °C, LA/M = 300 (M = Ti or Ta), no solvent used. [b] Measured by GPC.

Scheme 1



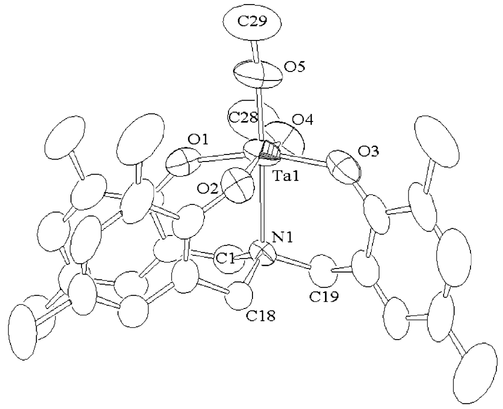


Figure 1. ORTEP drawing of LTa(OMe)$_2$ showing 50% probability thermal ellipsoids with H atoms and solvent omitted for clarity. Selected bond distances (Å): Ta1−O1 = 1.933(5), Ta1−O2 = 1.984(5), Ta1−O3 = 1.932(5), Ta1−O4 = 1.914(6), Ta1−O5 = 1.845(5), Ta1−N1 = 2.388(5). Selected bond angles (deg): C28O4Ta1 = 133.0(6), C29O5Ta1 = 161.7(7), O1Ta1N1 = 80.47(18), O2Ta1N1 = 79.87(17), O3Ta1N1 = 82.68(18), O4Ta1N1 = 86.9(2), O5Ta1N1 = 174.6(2).

are summarized in Table 2. Solution polymerization experiments failed with the tantalum compounds, giving only trace amounts of lactide polymers. Although such experiments were successful with the titanium compounds discussed here, those results will be published in due course along with others obtained with additional titanium catalysts.

Results and Discussion

Complex **2** was synthesized by transesterification of Ta(OEt)$_5$ with **1** in toluene while **3** was formed in an analogous reaction of **2** (generated in situ) with methanol/THF as shown in Scheme 1. Initially, we employed TaCl$_5$ in a reaction with **1**, and also with trilithiated **1** in methanol, toluene, and THF solutions. However, only mixtures were obtained under these conditions.

The NMR spectral data for **2** and **3** are consistent with the octahedral structure found for **3** by crystallographic means (see below) in which three six-membered rings are present (as is also the case for their titanium analogues[3,4,8]). The aryl proton resonances for **2** and **3** appear as singlets because of the presence of the two methyl substituents on each aryl ring. In addition, two sets of methyl proton resonances and two sets of arene hydrogen peaks are present in a 2:1 ratio, reflecting the fact that one of the six-membered rings is trans to an equatorial alkoxide group while two are cis, as is confirmed by the X-ray data which include a σ-plane through the four-membered Ta1−N1−C18−O2 square (Figure 1). Signals for the NCH_2C$_6$H$_2$ protons are also consistent with this geometry. The NCH_2C$_6$H$_2$ protons cis to the equatorial alkoxide group are diastereotopic and appear as two well-separated doublets while the NCH_2C$_6$H$_2$ protons trans to the equatorial alkoxide group are related by a mirror plane and appear as a singlet. These conclusions are further confirmed by the observation that **2** and **3** display 10 and 8 resonances for the aliphatic carbons in their ^{13}C{^{1}H} NMR spectra, respectively.

As seen in Figure 1, the metal in **3** possesses a slightly distorted octahedral geometry. In addition to five anionic oxygens, the tantalum atom is ligated by a transannular interaction from the bridgehead nitrogen in the tripodal ligand. The sum of the OTaO angles around the “equatorial” oxygens is 356.23(20)°. As a result, the acute O$_{eq}$TaN angles [av = 82.48(18)°] and the obtuse O$_{eq}$TaO$_{ax}$ angles [av = 97.5(3)°] reflect a 0.255(7) Å displacement of the tantalum atom toward the axial oxygen. Likewise, the angles for O1TaO3 [163.15(19)°] and O2TaO4 [166.8(2)°] deviate considerably from linearity while the N$_{ax}$TaO$_{ax}$ angle deviates only somewhat from linearity [5.4(2)°]. Interestingly, the transannular Ta−N bond distance in **3** [2.388(5) Å] falls near the long end of the range [2.264(3)−2.400(3) Å] found previously in titanatranes.[9] In addition, the Nb−N distance [2.369(7) Å] in the structurally characterized five-membered-ring group 5 atrane N(*o*-C$_6$H$_4$O)$_3$Nb-η^5-CpCl[3] is similar to the Ta−N transannular distance in **3**, which contains six-membered rings. Interestingly, the V−N transannular distance [2.269(3) Å] in the five-membered-ring vanadatrane $O{=}V[O{-}(R)\text{-}t\text{-}BuCHCH_2]_3N$[9e] is distinctly shorter than those in the aforementioned tantalum and niobium atranes. The Ta−O bond distances in **3** range from 1.845(5) to 1.984(5) Å, with the shortest (strongest) Ta−O5 bond length corresponding to the oxygen trans to the bridgehead N. This constitutes additional evidence for an exceptionally long (weak) transannular interaction in **3**.

Oxygen atoms can potentially engage in π donation to early transition metal centers.[10] The unusually large Ta1O5C29 bond angle [161.7(7)°] can be interpreted to indicate the presence of significant $p\pi{-}d\pi$ retrodative bonding by at least one p-housed oxygen lone pair and perhaps a significant fraction of a second with considerable p-character. The large Ta1O5C29 bond angle in **3**, which contrasts that for Ta1O4C28 [133.0(6)°] in this molecule, may reflect retrodative bonding sufficiently strong to account for the noticeably shortened Ta−O5 distance of 1.845(5) Å compared with the $Ta{-}O_{eq}$ lengths [av = 1.941(5) Å] whose $Ta{-}O_{eq}{-}C$ angles are much smaller [av = 134.3(5)°] than that for Ta1O5C29. Although the synthesis of η^5-CpTaClL was recently reported,[3] its structural characterization was limited to the interpretation of NMR and IR spectral analysis and cyclic voltammogram data. Thus **3** is the first group 5 atrane-type complex featuring six-membered rings that has been structurally characterized by X-ray means.

Our results on the use of titanium and tantalum alkoxide catalysts for the bulk polymerization of *l*-LA and *rac*-LA are summarized in Table 2. Polymerizations were performed at 130 °C with the [LA]/[M] ratio fixed at 300 for M = Ti and Ta. This table reveals that all the titanium compounds catalyze LA polymerization. Moreover, it appears that chelation of the tripodal tetradentate ligand significantly decreases the polydispersity index and polymer yield. The presence of the tripodal tetradentate ligand also increases MW in the case of R = *i*-Pr although it is decreased when R = 2,6-di-*i*-Pr-phenyl. When the axial bulky 2,6-di-*i*-Pr-phenoxide alkoxide was substituted by the smaller *i*-PrO substituent, the molecular weight, polydispersity, and yield of the polymer increased substantially. As shown earlier by ^1H NMR spectroscopy,[11] the end groups of PLA supplied by alkoxy titanium compounds were the corresponding alkoxy ester units. Thus, initiation undoubtedly occurs via the insertion of the alkoxy group from titanium catalyst into *l*-LA or *rac*-LA, which is consistent with a coordination−insertion polymerization mechanism.[5] Homonuclear decoupled ^1H NMR spectroscopy showed that PLA derived from *rac*-LA gave rise to five characteristic methine resonances, whereas such spectra of PLA derived from *l*-LA exhibit only one methine peak.[12]

On the basis of these polymerization data, we speculated on the possibility that similar results could be obtained with $Ta(OEt)_5$ and perhaps with **2** and/or **3** despite the fact that they are already six-coordinate. Thus the latter six-coordinate complexes could be expected to be too sterically crowded to allow expansion to seven-coordination although many examples of seven-coordinate tantalum complexes are known.[13] $Ta(OEt)_5$ did function as a catalyst for LA polymerization, producing a high polymer yield, a relatively low MW value, and a rather high polydispersity index over a comparatively long reaction time. It is worth noting that the ^1H NMR spectrum of the PLA obtained with $Ta(OEt)_5$ also shows an ethyl ester and an hydroxy chain end, suggesting that initiation occurs through the insertion of the OEt group from $Ta(OEt)_5$ into LA.

The homonuclear decoupled ^1H NMR spectra of these polymers displayed one and five resonances in the methine region for poly(*l*-LA) and poly(*rac*-LA), respectively.[12] Furthermore, epimerization of the chiral centers in poly(*l*-LA) apparently does not occur according to homonuclear decoupled ^1H NMR spectral studies of the methine region. However, some transesterification probably occurred during the polymerization reaction since the polydispersity indices of both PLA products were somewhat higher than expected for a controlled polymerization. Despite polymerization times of 24 h, compounds **2** and **3** show no observable catalytic activity for ROP of LA under our bulk polymerization conditions. Although the atomic radii of titanium (147 pm) and tantalum (146 pm) are about the same, the effective ionic radius of six-coordinate Ti(IV) (60.5 pm[14]) is smaller than that of seven-coordinate Ta(V). Although such a value does not appear to be available, it would be expected to lie between that for six- (64 pm[14]) and eight-coordinate (74 pm[14]). Thus if five-coordinate Ti(IV) analogues of **2** or **3** can become six-coordinate in the coordination−insertion pathway for lactide polymerization in which they participate,[4] it should be sterically possible for six-coordinate **2** and **3** to accommodate a seven-coordinate geometry in a coordination−insertion mechanism, provided that the covalent radii of these metals parallel their ionic radii. It may be that the positive charge density on such a coordinatively expanded Ta(V) species is not sufficient to ligate effectively to the

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lactide carbonyl oxygen, whereas this ligation is possible when five-coordinate $Ta(OEt)_5$ becomes six-coordinate in the coordination−insertion mechanism.

In summary, we have synthesized and characterized the novel tantalum(V) atrane-like compounds **2** and **3** containing the tris(2-oxy-3,5-dimethylbenzyl)amine tripodal ligand. These complexes do not catalyze to any observable degree the polymerization of *l*-LA or *rac*-LA whereas $Ta(OEt)_5$ does so, as does Ti(O-*i*-Pr)$_4$ and the titanium analogues of **2** and **3**.

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Supporting Information Available: Data collection and structure solution and refinement details, tables of crystal data, atomic coordinates, thermal parameters, bond distances, and bond angles, and ORTEP diagrams for **3**, as well as X-ray cryatallographic data (CIF). This material is available free of charge via the Internet at http://pubs.acs.org..

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