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Four- and five-coordinate titanium (IV) complexes supported by the dpp-bian ligand in ROP of *L*-lactide

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Abstract: A titanium (IV) alkoxido complex, (dpp-bian)Ti(OBn)₂ (2), chlorido complexes as well as alkoxido (dppbian)TiCl(OCH₂CH₂OMe) (3) and (dpp-bian)TiCl₂OBn (4), were synthesized from the titanium (IV) dichloride precursor [(dppbian)TiCl2]2 (1) by exchange with corresponding sodium salts (comps. 2 and 3) or by the alcoholysis with BnOH (comp. 4). The compounds 2-4 were fully characterized by elemental analysis, NMR or EPR, and IR spectroscopies. Molecular structures of the metal complexes in the solid state have been determined by singlecrystal XRD analysis. Compounds 2-4 were tested as catalysts in the ROP of L-lactide in a toluene medium. Whereas complexes 2 and 3 produce cyclic PLAs with broad dispersities and unpredictable molecular weights, complex 4 acts as an efficient ROP catalyst which polymerizes the monomer in a highly controllable manner. It produces BnO-capped PLAs with narrow molecular weight distributions as well as linear dependence of Mns on monomer conversion.

Introduction

Poly(α-hydroxy acids) are aliphatic polyesters of biomedical interest, owing to their biocompatible and biodegradable properties. In particular, poly(lactic acid), otherwise known as polylactide (PLA), produced by catalytic ring-opening polymerization (ROP) of cyclic di-ester derivatives, or lactides^[1], has been widely used in surgeryor, as a component of copolymers, in various medical devices, such as dental implants, stents, resorbable sutures, and erodible polymer vehicles for controlled drug delivery^[2]. A wide range of metal complex-based catalysts for controllable ROP of lactides has been studied extensively over the last three decades. Coordination compounds of tin^[3], aluminum^[4], or zinc^[5] together with rareearth elements^[6], were found to be efficient catalysts for the ROP of cyclic esters via a coordination-insertion mechanism. However, harmful metallic remnants which cannot be entirely removed from the resulting polymers constrain their further utilization as implant materials in medicine. Catalyst-induced

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toxicity of polyesters is avoided by using catalytic systems based on alkaline-earth metals^[7], or group 4 metals^[8a] including titanium and zirconium alkoxides, stabilized primarily by various Schiff base ligands^[8b-i]. Recently^[9], multidentate we demonstrated that the chelate ene-bisamide form of the ligand dpp-bian (=1,2-bis[(2,6-diisopropylphenyl)imino]acenaphthene) readily stabilizes the a^0 configuration of the titanium atom with the formation of the chlorido complex [(dpp-bian)TiCl2]2, which appears to be an easy-to-use precursor for further dpp-biansupported titanium derivatives. It should be noted that magnesium and calcium complexes of dpp-bian have proved to be robust catalysts for the ROP of *L*- and *rac*-lactides^[10], forming PLAs^[11] which are non-toxic toward human fibroblasts, while the binuclear aluminum compound [(dpp-bian)Al]2 was found to be an extremely active initiator of the controlled ROP of εcaprolactone at room temperature.^[12] In an effort to expand the scope of non-toxic catalytic systems based on dpp-bian for the polymerization of cyclic esters, we report on the synthesis and catalytic activity of titanium alcoholates stabilized with dianionic and radical anionic forms of dpp-bian, in the ROP of L-lactide (LA).

Results and Discussion

Synthesis of $(dpp-bian)Ti(OBn)_2$ (2), $(dpp-bian)Ti(OCH_2CH_2-OMe)CI$ (3) and $(dpp-bian)Ti(OBn)CI_2$ (4)

The compounds **2** and **3** were prepared by exchange reactions between the titanium complex $[(dpp-bian)TiCl_2]_2$ (**1**), generated *in situ*, and the sodium salts of benzyl alcohol and 2-methoxyethanol, respectively (Scheme 1). A deep orange-red color of the solutions of the complexes indicates the presence of four-coordinate titanium.^[9]



Scheme 1. Synthesis of 2 and 3. i) 2 eq. BnONa, toluene, 25 °C; ii) 1 eq. MeOCH_2CH_2ONa, toluene, 25 °C; iii) hexane, 25 °C

Complexes 2 and 3 were isolated by crystallization from hexane. Another synthetic route to titanium alkoxides is the treatment of appropriate chlorides with alcohols. For instance, adding 2 eq. of BnOH to the solution of 1 causes an immediate color change from green-brown to blue-violet (Scheme 2). We assume that formation of 4 proceeds through hydrolysis of Ti–Cl bonds, with subsequent binding of the liberated HCl, to give dpp-bianH₂ and the titanium(III) alkoxy chloride. Quenching of the reaction mixture with heptane allows one to isolate the blue crystalline product 4, albeit in quite low yield (48 %).



Scheme 2. Synthesis of 4. i) 2 eq. BnOH, toluene, 25 °C; ii) heptane, 25 °C.

Compounds 2–4 have been characterized by elemental analysis, IR spectroscopy, and single-crystal X-ray analysis. The solution structures of 2 and 3 were investigated by NMR spectroscopy, while paramagnetic complex 4 was examined using X-band EPR spectroscopy. Compounds 2–4 efficiently initiate the ring-opening polymerization of *L*-lactide, with complex 4 carrying out the process in a highly controllable manner to give a linear poly-*L*-lactide.

Solution Spectroscopy Studies of Complexes 2–4

Compounds 2 and 3 are diamagnetic and thus amenable to straightforward NMR spectroscopic characterization. ¹H-NMR spectra of their toluene solutions (Fig. 1) reveal similar sets of signals from the ligand isopropyl groups, which represent four methyl doublets at $\overline{0}$ 1.30, 1.15, 1.10, 1.01 ppm for 2 and $\overline{0}$ 1.51, 1.31, 1.12, 0.91 ppm for 3, respectively, as well as two methine septets at $\overline{0}$ 3.62 and 3.15 ppm for 2 and at $\overline{0}$ 3.92 and 2.86 ppm for 3. This spectral pattern is typical for {dpp-bian²⁻}-containing metal complexes that have one mirror plane of symmetry.



Figure 1. ¹H NMR spectra of 2 (top) and 3 (bottom) in toluene-d₈ (298 K).

The aliphatic protons of the alkoxido ligands in 2 appear as two singlets, at δ 5.32 and 4.68 ppm, originating from the methylene groups of two different benzylato ligands, whereas complex 3 reveals two triplets, at δ 4.41 and 3.24 ppm, arising from the two non-equivalent methylene groups of the methoxyethylato moiety. Furthermore, both complexes show the downfield set of resonances characteristic of aromatic protons, of the naphthalene backbone of dpp-bian and the phenyl substituents of the benzylato ligands, respectively, at δ 7.5...6.5 ppm. In contrast to 2 and 3, complex 4 proved to be paramagnetic. Figure 2 shows the EPR spectrum of 4 at 330 K (upper spectra experimental; lower spectra - simulated using EasySpin software^[13], RMSD 3.26 %). Variable-temperature EPR (Fig. S4, SI) show the formation of another experiments paramagnetic species at low temperature (260 K and below) which is in equilibrium with 4. The nature of this phenomenon will be discussed elsewhere, as it is of no immediate interest to the research reported here.



Figure 2. X-band EPR spectrum of 4 in toluene at 330 K.

On the whole, in a toluene solution, compound 4 reveals a complicated EPR signal, due to the coupling of the unpaired electron to the titanium nucleus (⁴⁷Ti: I = 5/2, natural abundance 7.44 %; 49 Ti: I = 7/2, natural abundance 5.41 %), two chlorine nuclei (35 Cl: I = 3/2, natural abundance 75.78 %; 37 Cl: I = 3/2, natural abundance 24.22 %), and two nitrogen nuclei (14 N: I = 1, natural abundance 99.63 %). The spectral parameters of the given signal, in particular, $g_i = 1.997$, $a_i(^{47, 49}Ti) = 0.556$, $a_i(2 \times {}^{35, 37}CI) = 0.129$ and $a_i({}^{14}N) = 0.071 \text{ mT}$, are essentially independent of temperature and can be referred to the system where the spin density is localized either on the ligand (form A), or the metal center (form **B**, Scheme 3). Kaim^[14] reported on a series of titanium isopropoxido complexes with m-acceptor substrates, including α-diimines, where paramagnetic

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compounds were described as Ti^{III} or Ti^{IV} /radical species,^[15] depending on the reduction potential of the ligand.



Scheme 3. Probable structures of compound 4 in toluene solution.

The ligand dpp-bian, which is a π -acceptor of reasonable strength, has a first reduction potential of $-1.0 V^{[16]}$, and is expected to be present as a radical anion. The relatively low value of the ^{47,49}Ti hyperfine coupling (HFC) constant, accompanied by a g-factor very close to 2, lead us to suggest that the structure of the metal complex **4** in toluene solution is **A**. An unusually low ¹⁴N HFC constant^[17] indicates that the unpaired electron is localized to a lesser extent on the dpp-bian ligand than on the titanium atom.

Molecular Structures of 2-4

Crystals of the complexes **2** and **3** suitable for x-ray diffraction analysis were obtained at room temperature from hexane solutions while **4** was recrystallized from toluene. Selected bond lengths and angles for complexes **2–4** are listed in Table 1.

Table	 Selected 	bond lengths	and angles	for complex	(es 2-4.
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	2	3	4
Ti–O(1)	1.806(3)	1.755(4)	1.741(2)
Ti–O(2)	1.784(3)	-	-
Ti–N(1)	1.951(6)	1.926(3)	2.178(2)
Ti–N(2)/N(1') ^[a]	1.938(3)	1.926(3)	2.068(2)
Ti–Cl(1)	-	2.286(2)	2.288(1)
Ti–Cl(2)	-	-	2.240(1)
Ti–C(1)	2.373(3)	2.401(4)	2.940(3)
Ti–C(2)/C(1') ^[a]	2.381(4)	2.401(4)	2.905(3)
C(1)–C(2)/C(1') ^[a]	1.411(4)	1.472(5)	1.439(4)
N(1)–C(1)	1.382(3)	1.378(5)	1.308(4)
N(2)/N(1') ^[a] –C(2)/C(1') ^[a]	1.382(3)	1.378(5)	1.325(3)
N(1)–Ti–O(1)	115.50(7)	113.11(10)	153.03(10)
N(1)–Ti–O(2)	112.47(7)	-	-
N(1)–Ti–Cl(1)	-	112.26(9)	86.22(7)
N(1)–Ti–Cl(2)	+	-	98.87(7)
N(2)/N(1') ^[a] -Ti-O(1)	116.38(6)	113.11(10)	90.76(11)
N(2)–Ti–O(2)	106.93(7)	-	-
N(2)/N(1') ^[a] -Ti-Cl(1)	-	112.26(9)	148.90(7)
N(2)–Ti–Cl(2)	-	-	101.34(7)
O(1)–Ti–Cl(1)	-	112.42(12)	94.00(9)
O(1)–Ti–Cl(2)	-	-	106.84(9)
Cl(1)–Ti–Cl(2)	-	-	106.58(4)
O(1)–Ti–O(2)	112.17(7)	-	-
Ti–O(1)–C(37)/C(20) ^[a]	170.96(14)	172.27(40)	160.18(22)
Ti–O(2)–C(44)	154.56(16)	-	-

[a] Alternative atom numbering is given for compound 3.

Complex 2 (Fig. 3) crystallizes in the triclinic space group $P\overline{1}$, with two molecules in the unit cell. The Ti atom has a distorted tetrahedral environment formed by N(1), N(2), O(1) and O(2) atoms (geometry index τ'_4 is equal to 0.54). The lengths of the Ti-N(av.) and Ti-O(av.) bonds are 1.942(5) and 1.795(3) Å, respectively, which is very close to those in similar titanium alcoholates (tBuNC(CH₂Ph)=C(CH₂Ph)NC₆H₃Me₂)Ti(OC₆H₃iPr₂)₂ (Ti-N(av.) 1.393(10) and Ti–O(av.) 1.818(13) Å), {PhNC(CH₂SiMe₃)=C(CH₂SiMe₃)=NPh}Ti(OC₆H₃Ph₂)₂ (Ti-N(av.) 1.902(15) and Ti-O(av.) 1.834(8) Å)^[18], Ti(OC₆H₃Ph₂-2,6)₂{N(xy)CMeCMeN(xy)}^[19] (Ti-N(av.) 1.926(5) and Ti-O(av.) 1.838(5) Å) and (dpp-bian)Ti(OtBu)2[9] (Ti-N(av.) 1.949(2) and Ti-O(av.) 1.798(2) Å). The deviation of the angles C(13)-N(1)-N(2) and C(25)-N(2)-N(1) (160.35(12)° and 161.51(12)°, respectively) from 180°, along with the non-orthogonal disposition of the N-aryl substituents toward the bisamidoacenaphthylene fragment (the dihedral angles between the described planes are 77.46(25)° and 102.81(21)°, respectively), reflect the mutual repulsion of the *i*Pr-groups of the dpp-bian and benzylato ligands.



Figure 3. Molecular structure of compound 2. Thermal ellipsoids are at 50% probability. Hydrogen atoms are omitted for clarity.

Complex 3 (Fig. 4), which crystallizes in the orthorhombic space group Pnma with four molecules in the unit cell, has almost regular tetrahedral coordination geometry at Ti (τ_4' = 0.95). A molecule of **3** has a mirror plane σ which is orthogonal to the acenaphthylene backbone and bisects the angle N(1)-Ti-N(1'), containing the atoms Ti, Cl(1), O(1), C(20), C(6) and C(7). The bond length Ti-N (1.926(3) Å) is close to those in 2 and other ene-bisamide-supported titanium complexes. Conversely, the Ti–O(1) bond (1.755(4) Å) in the alkoxido chlorido complex 3 appears slightly shorter than in the homo-alkoxido complexes mentioned above. The interatomic distance Ti...O(2), at 4.127(7) Å, is significantly longer than the sum of the related van der Waals radii, indicating a lack of auxiliary coordination of the alcoholato ligand to the metal center carrying the methoxy group. The Ti atoms in 2 and 3 are, respectively, 1.2729(3) Å and 1.1914(9) Å away from the bisamidoacenaphthylene plane that is caused by π -type interaction between the C=C fragment and

the metal center^[20]. The observed values are slightly higher than those in the starting complex **1** (1.0576(3) Å) as well as in the similar alkoxide (dpp-bian)Ti(O^tBu)₂ (1.1665(3) Å).^[9]



Figure 4. Molecular structure of compound 3. Thermal ellipsoids are at 50% probability. Hydrogen atoms are omitted for clarity.

By contrast, the titanium atom in **4** (Fig. 5), which has a square pyramidal environment ($\tau_5 = 0.07$), is nearly in the ligand plane (0.2737(5) Å away), which points to a considerable decrease of π -d interaction. The C(1)–C(2) bond in **4** is almost 0.03 Å longer than that in **2** and **3** (1.439(4) Å vs. 1.411(4) and 1.421(5) Å, respectively). Meanwhile, the C–N(av.) bonds are shorter by 0.06 Å when moving from **2** and **3** to **4** (1.382(3) and 1.378(5) Å vs. 1.317(4) Å, respectively). In this way, dpp-bian in compounds **2** and **3** constitutes a dianionic reduced form, whereas in **4** the ligand has a radical-anionic character as inferred from the diagnostic C–N and C–C bond lengths, which are intermediate between those in neutral dpp-bian (1.282(4) Å and 1.534(6) Å, respectively)^[21] and (dpp-bian)^{2–} in **2** and **3** and other similar compounds^[12, 15, 22].



Figure 5. Molecular structure of compound 4. Thermal ellipsoids are at 30% probability. Hydrogen atoms are omitted for clarity.

The Ti–N bond lengths in **4** (av. 2.123(2) Å) correspond to those in the tris(semiquinonate) complex $[Ti(dmp-BIANisq)_3]$

(2.0940(11) Å)^[23], where bian acts as a monoanionic ligand. Moreover, the bond lengths Ti–Nav. in **4** are intermediate between those in the compounds **2** and **3** described above and the Ar-bian⁰-supported metal complex (tmp-BIAN)TiCl₄ (Ti–Nav. 2.269(2) Å)^[24], which also confirms the radical anion state of dpp-bian in **4**.

ROP of L-lactide catalyzed by complexes 2-4

The compounds **2–4** were tested as ROP catalysts for *L*-lactide (LA) polymerization in toluene (Scheme 4).



Scheme 4. ROP of LA catalyzed by complexes 2-4.

As shown in Table 2, complex 2 reveals moderate catalytic activity, converting up to 300 eq. of LA within 24 hours, whereas compound 3 takes twice as long to convert only 25 eq. In both cases, the polydispersity index of the resulting PLAs varies from moderate (1.40, entry 3) to sufficiently high values (2.85, entry 4); along with unpredictable polymer molecular weights, this amounts to uncontrollable ROP. The lower experimental $M_{\rm n}$ (when compared with the calculated values) may originate from chain transfer reactions. According to the ¹H NMR data (Fig. S7, SI) the PLA obtained using complex 3 has a cyclic structure most likely due to intramolecular termination by way of a "backbiting" reaction. Compound 2 gives preferably linear BnO-capped polymer mixed with low molecular byproduct that was proved by the ¹H NMR spectroscopy (Fig. S6, SI) whereas the results of ESI mass spectrometry confirm the cyclic structure of a low-molecular fraction (Fig. S9, SI).

Table 2. ROP of *L*-lactide catalyzed by compounds 2-4.^[a]

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Entry	Cat.	LA ^[b] (equiv.)	Time ^[c] (h)	Conv ^[d] (%)	$\underset{[e]}{M}_{n, \ theor}$	M _{n, exp} ^[f]	Ð ^[g]
1	2	50	24 ^[h]	95	6840	8100	1.69
2	2	100	24 ^[h]	95	13680	4950	2.36
3	2	300	24 ^[h]	95	41040	17750	1.40
4	3	100	48	25	3600	3450	2.85
5	4	50	24 ^[h]	90	6480	8400	1.26
6	4	100	20	67	9650	11320	1.30
7	4	100	24	82	11810	14270	1.23
8	4	200	20	35	10080	12130	1.23
9	4	300	165 ^[h]	72	31100	33730	1.15

[a] Polymerization conditions: $[LA]_0 = 0.5 \text{ M}$, toluene, 70 °C. [b] Amount in equiv versus catalyst. [c] Reaction time. [d] Monomer conversion. [e] Calculated using $M_{n,\text{theor}} = [LA]_0/[\text{catalyst}]_0 \times M_{LA} \times \text{conversion}$. [f] Measured by GPC in THF (30 °C) using PS standards and corrected by applying the appropriate correcting factor (0.58). [g] Measured by GPC in THF (30 °C). [h] Time was not optimized.

By contrast, 4 readily polymerizes L-lactide in a controlled manner, reflected by narrow dispersities and a near-perfect match of the theoretical and experimental chain lengths of the desired polymers. Additional kinetic studies carried out for a 1:100 mixture of 4/LA showed a first-order dependence on LA concentration (Fig. 6, $k_{obs} = 0.0573 h^{-1}$) as well as a linear correlation between monomer conversion and the M_n values of the PLA produced (Fig. S10, SI). MALDI-TOF mass spectrometric data gathered for the polymer produced from a 50:1 LA/4 mixture is in good agreement with linear PLA capped with benzyloxy end groups (Figs. S11 and S 12, SI). Overall, the collected experimental data may suggest the mechanism of ROP of L-lactide in the system LA/4 to be of the coordinationinsertion type^[25] (Scheme S1, SI).



Figure 6. Plot of $\ln([M]_0/[M])$ as a function of time in the ROP of *L*-lactide using complex 4 as catalyst (M = LA, conditions: LA/4 in a 100:1 ratio, $[M]_0 = 0.5$ M, toluene, 70 °C).

Conclusions

We have obtained and characterized three new titanium(IV) alkoxides supported by non-innocent bis(arylimino)acenaphthene. In compounds **2** and **3**, the bisamide chelate ligand acts as a $\sigma^2 \pi$ -donor, whereas the monomeric five-coordinated complex **4** is stabilized by radical anionic dpp-bian. While all of the species demonstrate catalytic activity in the ROP of *L*-lactide, compound **4** carries out a living polymerization. It readily polymerizes *L*-lactide, at a relatively low rate (0.0573 h⁻¹) but in a highly controlled manner, producing BnO-capped polymer chains with predictable molecular weights and narrow dispersities. The weaker binding of the ligand to the metal center, due to decreasing π -d interaction, leads to enhanced catalytic activity of compound **4** in ROP of *L*-lactide through a coordination-insertion mechanism, in comparison with **2** and **3**.

Experimental Section

General Remarks. All manipulations were carried out under nitrogen using Schlenk techniques or in a nitrogen-filled MBraun Unilab glovebox. Toluene, n-hexane, and n-heptane were distilled from sodium/benzophenone and stored over 4 Å molecular sieves under nitrogen. [(dpp-bian)TiCl₂]₂ (1) was prepared according to a published procedure^[9]

and used in situ for the further syntheses. (3S)-cis-3,6-Dimethyl-1,4dioxane-2,5-dione (L-lactide, Purac, Netherlands) was purified by single vacuum sublimation (95°C, 5×10⁻² mbar) and stored under an inert atmosphere. C, H, N combustion analysis was conducted with a Flash 1112 Series (Thermo Finnigan) elemental analyzer. ¹H and ¹³C NMR spectra were recorded on Bruker Avance II 200 MHz and 400 MHz spectrometers using the deuterated solvent as an internal standard. Molecular weights of PLA samples were determined by gel permeation chromatography (GPC) on a chromatograph "Knauer Smartline" equipped with Phenogel Phenomenex Columns 5u (300×7.8 mm) 10⁴, 10⁵ and Security Guard Phenogel Column with RI and UV detectors (254 nm). The mobile phase was tetrahydrofuran, and the flow rate was 2 ml/min. Phenomenex Medium and High Molecular Weight Polystyrene Standard Kits with peak MW from 2700 to 2 570 000 Da were used for calibration, and the Mark-Houwink correction factor for PLA (0.58) was applied to account for the difference in hydrodynamic volumes between polystyrene and polylactide.^[26] Mass spectra of PLA samples were recorded on a Thermo Fisher Scientific LTQ Orbitrap XL equipped with ESI ion source and a Bruker Microflex LT mass spectrometer for MALDI TOF MS measurements which were performed in linear mode using (4hydroxybenzilydene)malonitrile as a matrix and THF as a solvent.

Sodium alcoholates. Sodium benzylate as well as sodium 2-methoxyethylate were synthesized by the reaction of 60 % sodium hydride (0.40 g, 10 mmol) with benzyl alcohol (1.11 g, 10.28 mmol) or 2-methoxyethanol (0.78 g, 10.26 mmol) correspondingly. The resulting mixture in n-hexane was stirred overnight at room temperature. The white precipitates were filtered off, washed with hexane and dried in vacuum at elevated temperature (100 °C) for two hours. The yield of BnONa: 1.10 g (85 %); ¹H NMR (400 MHz, toluene-d₈, 298 K), δ , ppm: 7.15 (d, J = 4.5 Hz, 4H); 7.08 (m, 1H); 4.37 (s, 2H). The yield of MeOCH₂CH₂ONa: 0.78 g (80 %); ¹H NMR (400 MHz, toluene-d₈, 298 K), δ , ppm: 4.43 (br. s, 2H); 3.63 (br. s, 2H); 3.39 (s, 3H).

(dpp-bian)Ti(OBn)₂ (2). To a toluene solution of 1, prepared from 0.5 g (1.0 mmol) of dpp-bian in 25 ml toluene, a suspension of 2.08 equiv. sodium benzylate (0.27 g, 2.08 mmol) in toluene (5 ml) was added at room temperature. After stirring of the mixture during 1 hour, the solvent was vaporized and n-hexane (25 ml) was added. The mixture was stirred within 15 min and the volatiles were evaporated in vacuo for complete disposal of toluene residues. The crude product was dissolved again in n-hexane (25 ml) and the precipitated was filtered off. The solution was concentrated to a volume of 10 ml. Complex 2 was isolated as plate dark red crystals. Total yield: 0.65 g (85 %). Anal. calc. for C₅₀H₅₄N₂O₂Ti: C, 78.72; H, 7.14; N, 3.67 %. Found: C, 78.33; H, 7.30; N, 3.54%. ¹H NMR (200 MHz, toluene-d_8, 298 K), $\delta,$ ppm: 7.29...7.12 (m, 11H); 6.97...6.87 (m, 4H), 6.80...6.57 (m, 7H); 5.32 (s, 2H), 4.68 (s, 2H), 3.62 (sept, J = 6.8 Hz, 2 H), 3.15 (sept, J = 6.8 Hz, 2 H), 1.30 (d, J = 6.8 Hz, 6H), 1.15 (d, J = 6.8 Hz, 6H), 1.11 (d, J = 6.8 Hz, 6H), 1.01 (d, J = 6.8 Hz, 6H). ¹³C NMR (50 MHz, toluene-d_8, 298 K), $\delta,$ ppm: 23.49, 23.99, 24.65, 25.77, 28.39, 28.47, 75.85, 78.00, 115.43, 122.22, 123.50, 124.19, 125.38, 126.14, 126.44, 126.61, 126.76, 127.12, 127.87, 127.98, 128.21, 128.35, 129.15, 134.18, 135.90, 141.72, 141.95, 142.57, 143.81, 146.18. IR (Nujol) v/cm⁻¹: 1330 (m, C–N), 1125 (s, C–O).

(dpp-bian)TiCl(OCH₂CH₂OMe) (3). Sodium 2-methoxyethylate (0.10 g, 1.02 mmol) as a suspension in toluene (5 ml) was added to a solution of 1, prepared from 0.5 g (1.0 mmol) of dpp-bian in 25 ml toluene. The mixture was stirred within 1 hour and the solvent was changed to n-hexane twice in an analogous manner to the synthesis of 2. The solids were filtered off and the n-hexane solution was concentrated to a volume of 5 ml. Complex 3 was isolated as needle-like red crystals. Total yield: 0.51 g (77 %). Anal. calc. for $C_{39}H_{47}ClN_2O_2Ti$: C, 71.07; H, 7.19; N, 4.25 %. Found: C, 70.41; H, 7.34; N, 4.12%. ¹H NMR (400 MHz,

Toluene- d_8 , 298 K) δ 7.27 (dd, J = 7.7, 1.9 Hz, 2H), 7.21 (t, J = 7.6 Hz, 2H), 7.17 (d, J = 8.2 Hz, 2H), 7.11 (dd, J = 7.7, 1.9 Hz, 2H), 6.89 (dd, J = 8.3, 7.0 Hz, 2H), 6.74 (d, J = 7.0 Hz, 2H), 4.40 (t, J = 5.0 Hz, 2H), 3.91 (hept, J = 6.8 Hz, 2H), 3.23 (t, J = 4.9 Hz, 2H), 2.84 (hept, J = 6.8 Hz, 2H), 2.76 (s, 3H), 1.50 (d, J = 6.8 Hz, 6H), 1.30 (d, J = 6.8 Hz, 6H), 1.11 (d, J = 6.8 Hz, 6H), 0.90 (d, J = 6.8 Hz, 6H). We could not obtain the appropriate ¹³C NMR data for alkoxy chloride complex **3** due to its insufficient solubility. IR (Nujol) v/cm⁻¹: 1324 (m, C–N), 1140 (s, C–O), 1110 (s, C–O).

(dpp-bian)TiOBnCl₂ (4). A solution of 0.98 equiv. benzyl alcohol (0.105 g, 0.98 mmol) in toluene (2 ml) was added dropwise to a toluene solution of 1, prepared from 0.5 g (1.0 mmol) of dpp-bian in 25 ml toluene, under constant stirring at room temperature. The color of the reaction mixture changed from green to blue-violet. The solvent was evaporated in *vacuo* and n-heptane (30 ml) was added. Within few minutes complex 4 precipitated as a dark-blue crystalline solid which was filtered off, washed with n-heptane and dried in *vacuo*. Total yield: 0.34 g (47 %). Anal. calc. for C₄₃H₄₇Cl₂N₂OTi: C, 71.08; H, 6.52; N, 3.86 %. Found: C, 70.92; H, 6.70; N, 3.67 %. IR (Nujol) v/cm⁻¹: 1506 (s, C–N), 1059 (s, C–O). EPR (330 K, toluene): g₁ = 1.997, $a_{1}^{(47,49}Ti) = 0.556$, $a_{1}(2 \times {}^{35,37}Cl) = 0.129$ and $a_{1}(2 \times {}^{14}N) = 0.071$ mT.

Typical Procedure for the Polymerization of *L***-Lactide**. A 20 ml vial equipped with Teflon screw cap and magnetic stirrer was loaded with 8 ml of a toluene solution which contains 5.0 mmol of *L*-lactide. An appropriate amount of a catalyst was added as a toluene solution (2 ml) under vigorous stirring. The vial was capped tightly and stirred at 70 °C within the required time. The monomer conversion was determined by ¹H NMR spectroscopy. For this purpose a solution aliquot was taken to the NMR tube, the solvent was removed in a vacuo, and the dry residue was dissolved in chloroform-d₁. PLA was isolated from the reaction mixture by quenching it with hexanes. The polymer as white nontransparent flakes was washed on the filter with hexanes and dried in vacuo. The product yield in all the experiments was 85–90%.

X-ray crystallography

The data of the single-crystal X-ray structure analysis were collected at 150 K (2 and 3) and 298 K (4) with an Agilent SuperNova diffractometer equipped with an Atlas CCD-detector Sapphire S, using graphitemonochromated Cu-K α radiation (λ = 1.54184 Å). Suitable crystals were attached to glass fibers using perfluoropolyalkylether oil (Supplier: ABCR) and transferred to a goniostat, where if necessary, they were cooled to 150 K for data collection. The software package used: CrysAlis Pro for data collection, cell refinement, and data reduction.^[27] The crystal structure was solved by direct methods with SHELXT^[28] and refined on F² using full-matrix least-squares with SHELXL^[29] as part of Olex2^[30]. All non-hydrogen atoms were refined anisotropically. Carbon-bonded hydrogen atoms were refined isotropically with riding models. Crystallographic details are given in the Supporting Information (Table S1, SI). CCDC 1936221 (2), 1936222 (3), and 1936223 (4) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

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Keywords: titanium • bis(arylimino)acenaphthenes • noninnocent ligands • ring-opening polymerization • *L*-lactide

- S. Dutta, W. C. Hung, B. H. Huang, C. C. Lin, in *Synthetic Biodegradable Polymers*, *Vol. 245* (Eds.: B. Rieger, A. Kunkel, G. W. Coates, R. Reichardt, E. Dinjus, T. A. Zevaco), Springer-Verlag Berlin, Berlin, **2012**, pp. 219-283.
- [2] A.-C. Albertsson, I. K. Varma, Biomacromolecules 2003, 4, 1466-1486.
- [3] a) E. J. Lee, K. M. Lee, J. Jang, E. Kim, J. S. Chung, Y. Do, S. C. Yoon, S. Y. Park, J. Mol. Catal. A: Chem. 2014, 385, 68-72; b) L. Wang, V. Poirier, F. Ghiotto, M. Bochmann, R. D. Cannon, J.-F. Carpentier, Y. Sarazin, Macromolecules 2014, 47, 2574-2584; c) L. Wang, S.-C. Rosca, V. Poirier, S. Sinbandhit, V. Dorcet, T. Roisnel, J.-F. Carpentier, Y. Sarazin, Dalton Trans. 2014, 43, 4268-4286.
- [4] a) C. Robert, T. E. Schmid, V. Richard, P. Haquette, S. K. Raman, M.-N. Rager, R. M. Gauvin, Y. Morin, X. Trivelli, V. Guerineau, I. del Rosal, L. Maron, C. M. Thomas, J. Am. Chem. Soc. 2017, 139, 6217-6225; b) E. Rufino-Felipe, N. Lopez, F. A. Vengoechea-Gomez, L.-G. Guerrero-Ramirez, M.-A. Munoz-Hernandez, Appl. Organometal. Chem. 2018, 32, https://doi.org/10.1002/aoc.4315; c) R. Zaremba, M. Dranka, B. Trzaskowski, L. Checinska, P. Horeglad, Organometallics 2018, 37, 4585-4598; d) D. Zhu, L. Guo, W. Zhang, X. Hu, K. Nomura, A. Vignesh, X. Hao, Q. Zhang, W.-H. Sun, Dalton Trans. 2019, 48, 4157-4167.
- [5] R. Petrus, P. Sobota, Coord. Chem. Rev. 2019, 396, 72-88.
- [6] J.-F. Carpentier, *Organometallics* **2015**, *34*, 4175-4189.
- [7] J.-F. Carpentier, Y. Sarazin, *Top. Organomet. Chem.* **2013**, 45, 141-189.
- [8] a) A. Sauer, A. Kapelski, C. Fliedel, S. Dagorne, M. Kol, J. Okuda, *Dalton Trans.* 2013, *42*, 9007-9023; b) F. Della Monica, E. Luciano, G. Roviello, A. Grassi, S. Milione, C. Capacchione, *Macromolecules* 2014, *47*, 2830-2841; c) C.-Y. Tsai, H.-C. Du, J.-C. Chang, B.-H. Huang, B.-T. Ko, C.-C. Lin, *RSC Adv.* 2014, *4*, 14527-14537; d) D. Chakraborty, D. Mandal, V. Ramkumar, V. Subramanian, J. Vijaya Sundar, *Polymer* 2015, *56*, 157-170; e) B. Rajashekhar, S. K. Roymuhury, D. Chakraborty, V. Ramkumar, *Dalton Trans.* 2015, *44*, 16280-16293; f) D. Mandal, D. Chakraborty, V. Ramkumar, D. K. Chand, *RSC Adv.* 2016, *6*, 21706-21718; g) M. Mandal, U. Monkowius, D. Chakraborty, *New J. Chem.* 2016, *40*, 9824-9839; h) S. Pappuru, D. Chakraborty, J. Vijaya Sundar, S. K. Roymuhury, V. Ramkumar, V. Subramanian, D. K. Chand, *Polymer* 2016, *102*, 231-247; i) S. Pappuru, D. Chakraborty, V. Ramkumar, D. K. Chand, *Polymer* 2017, *123*, 267-281.
- [9] A. G. Morozov, I. L. Fedushkin, E. Irran, A. Grohmann, *Inorg. Chem. Commun.* 2018, 95, 50-55.
- [10] a) I. L. Fedushkin, A. G. Morozov, M. Hummert, H. Schumann, *Eur. J. Inorg. Chem.* **2008**, 1584-1588; b) I. L. Fedushkin, A. G. Morozov, V. A. Chudakova, G. K. Fukin, V. K. Cherkasov, *Eur. J. Inorg. Chem.* **2009**, 4995-5003.
- [11] A. G. Morozov, I. L. Fedyushkin, D. Y. Aleinik, Russ. J. Appl. Chem. 2016, 89, 2095-2101.
- [12] O. V. Kazarina, C. Gourlaouen, L. Karmazin, A. G. Morozov, I. L. Fedushkin, S. Dagorne, *Dalton Trans.* 2018, 47, 13800-13808.
- [13] S. Stoll, A. Schweiger, J. Magn. Reson. 2006, 178, 42-55.
- [14] M. Moscherosch, W. Kaim, J. Chem. Soc., Perkin Trans. 2 1992, 1493-1496.
- [15] I. L. Fedushkin, O. V. Maslova, A. G. Morozov, S. Dechert, S. Demeshko, F. Meyer, *Angew. Chem. Int. Ed.* 2012, *51*, 10584-10587.

- [16] V. I. Baranovski, A. S. Denisova, L. I. Kuklo, J. Mol. Struct. (THEOCHEM) 2006, 759, 111-115.
- [17] I. L. Fedushkin, A. A. Skatova, V. A. Dodonov, V. A. Chudakova, N. L. Bazyakina, A. V. Piskunov, S. V. Demeshko, G. K. Fukin, *Inorg. Chem.* 2014, 53, 5159-5170.
- [18] L. R. Chamberlain, L. D. Durfee, P. E. Fanwick, L. M. Kobriger, S. L. Latesky, A. K. McMullen, B. D. Steffey, I. P. Rothwell, K. Foltin, J. C. Huffman, *J. Am. Chem. Soc.* **1987**, *109*, 6068-6076.
- [19] M. G. Thorn, P. E. Fanwick, I. P. Rothwell, Organometallics 1999, 18, 4442-4447.
- [20] S. Anga, K. Naktode, H. Adimulam, T. K. Panda, *Dalton Trans.* 2014, 43, 14876-14888.
- [21] I. L. Fedushkin, V. A. Chudakova, G. K. Fukin, S. Dechert, M. Hummert, H. Schumann, *Russ. Chem. Bull.* **2004**, *53*, 2744-2750.
- [22] a) I. L. Fedushkin, A. A. Skatova, V. A. Chudakova, G. K. Fukin, S. Dechert, H. Schumann, *Eur. J. Inorg. Chem.* 2003, 3336-3346; b) I. L. Fedushkin, A. G. Morozov, O. V. Rassadin, G. K. Fukin, *Chem.: Eur. J.* 2005, *11*, 5749-5757; c) A. N. Lukoyanov, I. L. Fedushkin, M. Hummert, H. Schumann, *Russ. Chem. Bull.* 2006, *55*, 422-428; d) I. L. Fedushkin, A. N. Lukoyanov, S. Y. Ketkov, M. Hummert, H. Schumann, *Chem.: Eur. J.* 2007, *13*, 7050-7056; e) I. L. Fedushkin, V. M. Makarov, V. G. Sokolov, G. K. Fukin, *Dalton Trans.* 2009, 8047-8053; f) I. L. Fedushkin,

O. V. Markina, A. N. Lukoyanov, A. G. Morozov, E. V. Baranov, M. O. Maslov, S. Y. Ketkov, *Dalton Trans.* 2013, *42*, 7952-7961; g) I. L. Fedushkin, V. M. Makarov, V. G. Sokolov, G. K. Fukin, M. O. Maslov, S. Y. Ketkov, *Russ. Chem. Bull.* 2014, *63*, 870-882; h) I. L. Fedushkin, A. A. Skatova, D. S. Yambulatov, A. V. Cherkasov, S. V. Demeshko, *Russ. Chem. Bull.* 2015, *64*, 38-43.

- [23] K. M. Clark, J. Bendix, A. F. Heyduk, J. W. Ziller, *Inorg. Chem.* 2012, 51, 7457-7459.
- [24] K. M. Clark, J. W. Ziller, A. F. Heyduk, Inorg. Chem. 2010, 49, 2222-2231.
- [25] O. Dechy-Cabaret, B. Martin-Vaca, D. Bourissou, Chem. Rev. 2004, 104, 6147-6176.
- [26] M. Save, M. Schappacher, A. Soum, *Macromol. Chem. Phys.* 2002, 203, 889-899.
- [27] CrysAlisPro Version 1.171.38.46 ed., Rigaku Oxford Diffraction, Abingdon, Oxfordshire, England, **2015**.
- [28] G. M. Sheldrick, Acta Cryst. 2015, A71, 3-8.
- [29] G. M. Sheldrick, Acta Cryst. 2015, C71, 3-8.
- [30] O.V. Dolomanov, L.J. Bourhis, R.J. Gildea, J.A.K. Howard, H. Puschmann, J. Appl. Cryst. 2009, 42, 339-341.

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FULL PAPER



Titanium (IV) alkoxido and alkoxido chlorido complexes supported by bis(arylimino)acenaphthene ligand dpp-bian in different reduced forms were obtained and fully characterized. Benzoxido dichlorido titanium derivative (dpp-bian)TiOBnCl₂ proved to be an efficient catalyst for the living ROP of *L*-lactide providing a PLA in a highly controlled manner.

Titanium catalysts for ROP

Dr. Alexander G. Morozov*, Tatyana V. Martemyanova, Dr. Vladimir A. Dodonov, Dr. Olga V. Kazarina, and Prof. Dr. Igor L. Fedushkin

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Four- and five-coordinate titanium (IV) complexes supported by the dppbian ligand in ROP of *L*-lactide