Titanium and zirconium benzofuranoxides. Crystal structures and catalytic properties†

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Reactions of $Ti(O^iPr)_4$ or $Zr(OEt)_4$ with 4 equivalents of 2,3-dihydro-2,2-dimethyl-7-benzofuranol (ddbfoH) in toluene gave neutral complexes that in the solid state are dimers of $[Ti(\mu\text{-ddbfo})_2(ddbfo)_6]$ and $[Zr(ddbfo)_3(EtOH)(\mu\text{-EtO})]_2$ composition. The former could also be conveniently synthesized in a direct reaction of $TiCl_4$ with ddbfoH. This air-stable aryloxo compound was found to initiate living ring-opening polymerization of lactides affording polyesters with narrow molecular weight distribution. It also catalyzed addition of terminal acetylenes to aryl aldehydes.

Introduction

Transition metal aryloxides have been the subject of intense research since the early 1950's. Interest first focused on the π bonding abilities of aryloxo ligands as well as on a correlation between their structure and resulting agglomeration of a complex compound.[1] The early applications of metal aryloxides in industry focused on their use as antioxidants inhibiting decomposition of mineral oils, varnishes and lacquers.

More up to date chemistry turns the attention to the use of metal aryloxides in synthetic organic chemistry. Especially interesting is their use in enantioselective synthesis and catalysis. For instance, titanium aryloxides catalyze the alkene/alkyne cross coupling reactions that yield functionalized cyclic dienes.[2] They were successfully used for the cyclization of 1,6- and 1,7-dienes,[3] addition of acetylenes to aromatic aldehydes,[4] and enantioselective reduction of ketones with boranes.[5] Instead, zirconium aryloxide was utilized as a catalyst in the first enantioselective Mannich type reaction of aldimines with silyl enolates.[6] This and some other uses of zirconium aryloxides were nicely described by Yudin and co-workers in their review on modified BINOLates in asymmetric catalysis.[7]

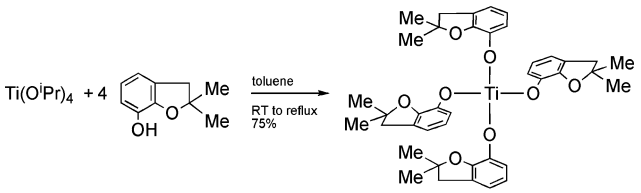
Besides their utilization in synthetic organic chemistry, titanium and zirconium aryloxides constitute a base for covalent metal–organic networks.[8] In host–guest chemistry, they form interesting metallocalixarenes.[9] Moreover, they are valuable precursors and initiators for different polymerization processes. They are extensively exploited in homogeneous ethylene and α-olefin polymerization.[10] There has also been extensive recent interest in their utilization in the polymerization of lactides and lactones.[11] Such high molecular weight polyesters are becoming more and more essential as biodegradable and environmentally friendly alternatives for many of the current commodity polymers.

In this paper we report the synthesis, structural characterization and reactivity of titanium and zirconium 7-benzofuranoxides. This two-coordinating ligand that is derived from 7-benzofuranol, an inexpensive substrate for the synthesis of pesticides, proved useful as a chelating agent for different transition metals. It is also able to mediate mixed metal aryloxides,[12] that are potential "single-source" precursors to technologically important ceramic oxides.

Results and discussion

Syntheses

Preparation of benzofuranoxide $Ti(ddbfo)_4$ (**1**, ddbfoH = 2,3-dihydro-2,2-dimethyl-7-benzofuranol) paralleled a common procedure for the preparation of metal aryloxides *via* ligand exchange.[1,13] As shown in Scheme 1 the direct reaction of $Ti(O^iPr)_4$ with 4 equivalents of 2,3-dihydro-2,2-dimethyl-7-benzofuranol in toluene gave red **1** in 75% yield after workup. Compound **1** can also be obtained with comparable yield (72%) in the direct reaction of 4 equivalents of ddbfoH with $TiCl_4$.



1
(proposed structure in solution)

Scheme 1 Synthesis of **1**.

The compound was characterized by ^1H NMR. It showed one set of signals of coordinated ddbfo ligands in expected positions proving complete exchange of the O^iPr groups. Also the elemental analysis was correct for the $Ti(ddbfo)_4$ formulation. The data suggested monomeric species, although rapid exchange of the bridging/terminal aryloxo ligand with Ti–O bond cleavage could not be ruled out. The possible agglomeration of **1** in solution was further studied with variable-temperature ^1H NMR. The spectra were collected to −65 °C showing no substantial changes compared to the RT data and supporting the assumption of **1** being a monomer in solution.

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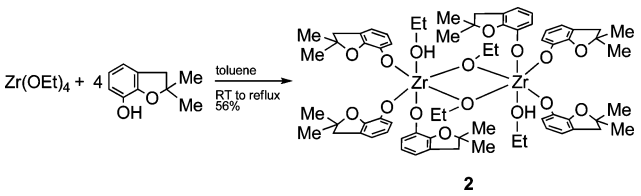
Although metal aryloxides are claimed to be highly susceptible to hydrolysis,[13] compound **1** appeared to be quite stable in air. Similar stability was underlined for heteroleptic titanium catecholates[10f] and mentioned for homoleptic Ti(2,6-$^{i}Pr_2C_6H_3O)_4$.[14] The ^{1}H NMR of **1** after four weeks of exposure to the air and moisture remained unchanged. The compound is soluble in halogenated organic solvents and fairly soluble in hexanes and toluene. It melts with decomposition at 140 °C (TGA analysis revealed a substantial mass loss that starts around that temperature).

Although agglomeration of **1** was not unambiguously excluded, the spectroscopic and analytical data suggested a low coordinated metal center. Based on that, the coordination abilities of **1** were tested. The reaction with an excess of PPh_3 in toluene gave a red phosphine adduct in 38% yield. The ^{1}H NMR data clearly suggested coordination of two molecules of PPh_3 that was further confirmed by elemental analysis.

In contrast to titanium, homoleptic monomeric zirconium aryloxides have proven to be much more elusive. The literature mentions two examples, but for one of them no crystallographic data were published.[15] Lately the homoleptic ionic $[NH_2(CH_3)_2]_2[Zr(OC_6H_4\text{-}2\text{-}Cl)_6]\cdot 2THF$ was presented by Giolando and co-workers.[16] In an attempt to obtain a homoleptic zirconium analog of **1** a reaction of $Zr(OEt)_4$ with 4 equivalents of ddbfoH was carried out as shown in Scheme 2.

Workup gave somewhat expected analytically pure heteroleptic **2** in 56% yield as colorless crystals. Longer reaction times, different stoichiometries as well as higher temperatures invariably lead to the same product. Complex **2** was characterized by ^{1}H NMR spectroscopy, elemental analysis and X-ray crystallography. It is soluble in toluene and dichloromethane and can be stored under dinitrogen for extended periods but tolerate only brief exposure to moisture. It melts with decomposition at 143–145 °C.



2

Scheme 2 Synthesis of **2**.

Crystal structures of 1 and 2

Complexity of the structures of the metal aryloxides depends greatly on the substituents on the aryl ring. For instance $Ti(OPh)_4\cdot HOPh$ in the solid state is a dimer,[17] while more bulky 2,6-$Me_2C_6H_3OH$,[18–19] 2,6-$^{i}Pr_2C_6H_3OH$,[20] 2-$^{t}BuC_6H_4OH$[14] or 2,3,5,6-Me_4C_6HOH[14] form monomeric $Ti(OAr)_4$ species.

The crystal structure of **1** was determined as outlined in Table 1 and described in the Experimental section. In the solid state complex **1** is a centrosymmetric dimer as shown in Fig. 1.

A discrete molecule of **1** contains two pentacoordinated titanium atoms in an arrangement that is between trigonal bypiramid and square pyramid (see O–Ti–O bond angles in Table 2) with a τ parameter of 0.3.[21] The TiO_5 core has five different Ti–$O_{aryloxo}$ distances of 1.7599(14), 1.8105(14), 1.8305(13), 1.9992(13) and 2.0783(13) Å. The last two values that characterize the aryloxo bridge show the magnitude of the rhombohedron asymmetry, which, due to the centrosymmetry of **1**, is ideally flat.

The terminal Ti–O distances are similar to that found in monomeric $Ti(2,6\text{-}Me_2C_6H_3O)_4$ (1.7853(17), 1.7841(18),

Table 1 Crystallographic data for **1** and **2**

Complex	**1**	**2**
Space group	$P\bar{1}$	$P\bar{1}$
Crystal system	Triclinic	Triclinic
Chemical formula	$C_{80}H_{88}O_{16}Ti_2$	$C_{68}H_{88}O_{16}Zr_2$
M	1401.30	1343.82
a/Å	12.1696(7)	11.1465(5)
b/Å	12.8552(6)	12.1096(7)
c/Å	13.0040(7)	13.1966(8)
α/°	73.920(4)	93.782(5)
β/°	81.944(4)	111.460(5)
γ/°	64.201(5)	92.187(4)
V/Å^3	1759.50(16)	1650.45(16)
Z	1	1
ρ_{calc}/g cm^{-3}	1.322	1.352
μ/mm^{-1}	0.296	0.382
T/K	100(2)	100(2)
F(000)	740	704
Crystal size/mm	0.3 × 0.3 × 0.3	0.4 × 0.3 × 0.04
Range for data collection/°	3.09 to 28.47	3.18 to 28.50
Index ranges (h, k, l)	−15 to 16; −16 to 16; −17 to 17	−14 to 14; −16 to 15; −17 to 16
Reflections collected	21 465	19 807
Independent reflections	8172	7632
R_{int}	0.0406	0.0447
Reflections [$I > 2\sigma(I)$]	6059	6169
Parameters	442	411
R indices (all data)	R1 = 0.0519 (0.0836) wR2 = 0.0994 (0.1067)	R1 = 0.0457 (0.0686) wR2 = 0.0843 (0.0900)
GOF	1.175	1.081
$\Delta\sigma$ (max.; min.)/e Å^3	0.324; −0.457	0.418, −0.365

Table 2 Bond lengths [Å] and angles [°] for **1**

Ti(1)–O(11)	1.9992(13)	Ti(1)–O(31)	1.8105(14)
Ti(1)–O(11′)	2.0783(13)	Ti(1)–O(41)	1.7599(14)
Ti(1)–O(21)	1.8305(13)		
O(11)–Ti(1)–O(21)	136.46(6)	O(31)–Ti(1)–O(11′)	154.25(6)
O(11)–Ti(1)–O(31)	90.63(6)	O(41)–Ti(1)–O(11′)	95.92(6)
O(11)–Ti(1)–O(41)	108.02(6)	Ti(1)–O(11)–C(11)	126.74(11)
O(11)–Ti(1)–O(11′)	68.96(6)	Ti(1)–O(21)–C(21)	151.95(13)
O(21)–Ti(1)–O(31)	98.10(6)	Ti(1)–O(31)–C(31)	159.32(13)
O(21)–Ti(1)–O(41)	110.40(6)	Ti(1)–O(41)–C(41)	167.77(13)
O(21)–Ti(1)–O(11′)	87.31(6)	Ti(1)–O(11′)–C(11′)	121.96(11)
O(31)–Ti(1)–O(41)	105.54(6)	Ti(1)–O(11)–Ti(1′)	111.04(6)

Symmetry transformations used to generate primed atoms: $-x + 2, -y + 1, -z$.

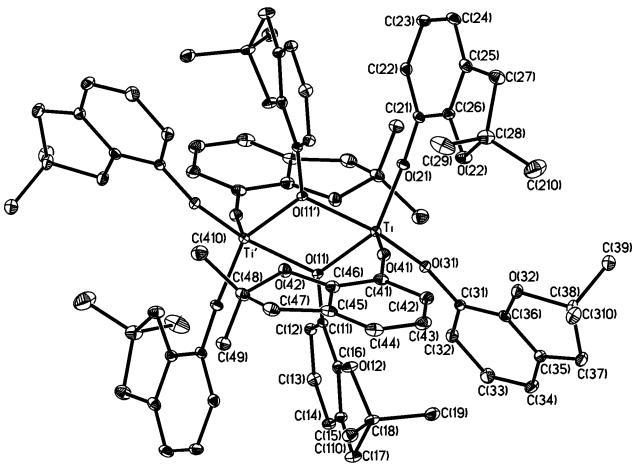


Fig. 1 View of **1** (hydrogen atoms were omitted for clarity). Symmetry operation for related atoms: $-x + 2, -y + 1, -z$.

1.7979(18) and 1.7990(18) Å),[18–19] Ti(2,6-^{i}Pr$_2$C$_6$H$_3$O)$_4$ (1.781(3) and 1.780(3) Å),[20a] Ti(2-^{t}BuC$_6$H$_4$O)$_4$ (1.779(3) Å)[14] or Ti(2,3,5,6-Me$_4$C$_6$HOH)$_4$ (1.78(2), 1.76(2), 1.76(2), and 1.79(2) Å).[14] Also the bridging Ti–O distances are similar to that found in Ti(OC$_6$H$_5$)$_4$·HOC$_6$H$_5$ (2.045(11) Å).[17] Interestingly, no ether oxygen from the furan rings is involved in coordination to the metal center. The Ti–O–C bond angles for terminal aryloxo ligands are within 151.95(13) to 167.77(13)° suggesting substantial π bonding character of the Ti–O$_{terminal}$ bonds. There is a nice correlation between the Ti–O bond lengths and the Ti–O–C bond angles (see Table 2). The longer bridging Ti–O distances are also characterized by much smaller Ti–O–C bond lengths.

The neutral heteroleptic **2** also possesses a dimeric nature as presented in Fig. 2. This centrosymmetric molecule exhibits two identically coordinated ZrO$_6$ cores.

The key bond lengths and angles are summarized in Table 3 and they are similar to those found in Zr(O-2,6-C$_6$H$_3$Me$_2$)$_2$(Me$_2$calix)·CH$_2$Cl$_2$,[9c] and in ionic {Me$_2$NH$_2$}{[(O-2,6-C$_6$H$_3$Me$_2$)Zr]$_2$(μ-OCH$_2$CH=CH$_2$)$_3$}.[22] Similar to **1** there is a nice correlation between the Zr–O$_{terminal}$ bond lengths and bond angles that evidences the π character of the Zr–O bond. The longest Zr–O(21) bond length is *trans* to the terminal EtOH molecule that results from the protonation of the ethoxo ligand by acidic benzofuranol in the reaction course. The ethoxo bridge is much more symmetric compared to the bridge in **1** with Zr–O(41) and

Table 3 Bond lengths [Å] and angles [°] for **2**

Zr–O(11)	1.9685(15)	Zr–O(41)	2.1310(15)
Zr–O(21)	2.0086(16)	Zr–O(41′)	2.1785(16)
Zr–O(31)	1.9637(16)	Zr–O(51)	2.2774(19)
Zr–Zr′	3.4734(5)		
O(11)–Zr–O(21)	99.13(7)	O(21)–Zr–O(51)	168.91(7)
O(11)–Zr–O(31)	97.11(7)	O(31)–Zr–O(41)	95.66(6)
O(11)–Zr–O(41)	160.08(6)	O(31)–Zr–O(41)′	166.46(6)
O(11)–Zr–O(41′)	92.59(6)	O(31)–Zr–O(51)	88.03(7)
O(11)–Zr–O(51)	86.86(7)	O(41)–Zr–O(41′)	72.59(7)
O(21)–Zr–O(31)	100.38(7)	O(41)–Zr–O(51)	78.35(7)
O(21)–Zr–O(41)	93.53(7)	O(41)′–Zr–O(51)	83.07(7)
O(21)–Zr–O(41)′	87.32(7)		
Zr–O(11)–C(11)	160.0(15)	Zr–O(41′)–C(41′)	122.91(13)
Zr–O(21)–C(21)	139.91(15)	Zr–O(51)–C(511)–Zr	129.8(6)
Zr–O(31)–C(31)	160.79(15)	Zr–O(51)–C(512)–Zr	129.5(7)
Zr–O(41)–C(41)	127.26(14)	Zr–O(41)–Zr′	107.41(7)

Symmetry transformations used to generate primed atoms: $-x + 1, -y + 1, -z + 2$.

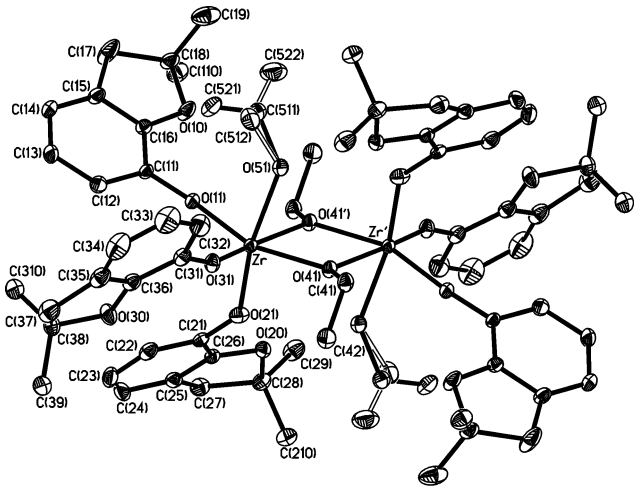


Fig. 2 View of **2** (hydrogen atoms were omitted for clarity; both positions of disordered terminal EtOH are shown). Symmetry operation for related atoms: $-x + 1, -y + 1, -z + 2$.

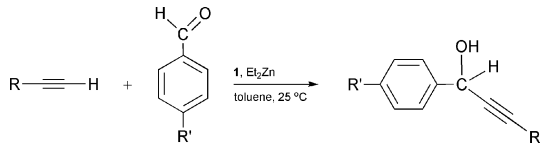
Zr–O(41)′ of 2.1310(15) and 2.1785(16) Å, respectively. Due to the symmetry it is also ideally flat.

Catalytic properties of 1

Addition of acetylenes to aldehydes. Stability of **1** against moisture seemed very attractive for its use as a potential reagent in different catalytic processes. For instance, the most widely used catalyst precursor Ti(O^{i}Pr)$_4$ has to be distilled prior to use in order to remove oxohomopolymetallic products of its degradation. It should also be standardized for having trustworthy results. Complex **1** would appear a very attractive substitute for Ti(O^{i}Pr)$_4$ if it has similar activity. To reveal its potential it was tested as a catalyst in the addition of terminal acetylenes to aldehydes and as an initiator of lactide ring-opening polymerization.

Addition of terminal acetylenes to aldehydes is one of the very important methods of C–C bond formation. By this method secondary propargyl alcohols are obtained that are very important building blocks for numerous organic compounds. Addition of chiral ancillary ligands enables this process to run enantioselectively.[23] They are often added along with titanium species that, *via*

Table 4 Addition of phenylacetylene to benzaldehyde with **1** as catalyst[a]



Entry	**1**/mol%	T/°C	Yield[b] (%)
1	60	25	85
2	60	60	68
3	60	100	42
4	10	25	86
5	30	25	100

[a] Acetylene/Et_2Zn/aldehyde/**1** = 10 : 10 : 3 : 1. [b] Isolated yield.

coordination, activate carbonyl groups and significantly improves the final yield.

First the reaction of the addition of phenylacetylene to benzaldehyde in toluene with **1** as the catalyst was tried and the process was optimized. Results are presented in Table 4 showing the optimum conditions to be 25 °C and 30 mol% catalyst concentration. The reaction time after which no further conversion was observed was 4 h.

Under these optimized reaction conditions **1** was employed to induce addition of terminal acetylenes to different aryl aldehydes. As shown in Table 5 with one exception they all gave rise to the desired products with moderate to very good yields.

Lactide polymerization. The catalytic behavior of **1** in the ring-opening polymerization of L- and *rac*-lactide (L-LA, *rac*-LA) was studied. As noted above, **1** in solution is most likely a monomeric species and is able to easily form adducts with electron donors. Treatment of **1** in toluene with two equivalents of L-LA readily generated monomeric complex Ti(ddbfo)$_4$(L-LA)$_2$ as evidenced by ^{1}H NMR. The spectrum showed characteristic resonances at δ = 3.87 and 2.72 ppm assigned to methine (C*H*) protons of lactide and methylene protons (CH_2) of ddbfo ligands in a 1 : 2 ratio. Next the polymerization of L-LA was tried with a monomer to initiator ratio ([M]$_0$/[I]$_0$) of 20, 100 and 200. At room temperature **1** displayed poor reactivity with only 10% conversion being observed after 6 d. Instead, at 70 °C, complex **1** initiated polymerization of L-LA (with ([M]$_0$/[I]$_0$) = 200) in 90% conversion within 20 h to afford PLA with M_n of 13 600 and PDI of 1.10. Interestingly, the degree of polymerization was almost a half of the monomer to initiator ratio suggesting the formation of two polymer chains from each molecule of **1**. Additionally the ^{1}H NMR spectrum of the living polymer obtained with [M]$_0$/[I]$_0$ = 20 showed resonances from

Table 5 Addition of terminal acetylenes to aromatic aldehydes promoted by **1**

Entry	Aldehyde	Acetylene	Yield (%)
1	Benzaldehyde	PhC≡CH	100
2	4-Bromobenzaldehyde	PhC≡CH	91
3	4-Chlorobenzaldehyde	PhC≡CH	85
4	4-(TMSC≡C)benzaldehyde	PhC≡CH	28
5	3,5-Dimethoxybenzaldehyde	PhC≡CH	66
6	2-Nitrobenzaldehyde	PhC≡CH	43
7	Benzaldehyde	4-MeC_6H_4C≡CH	57
8	Benzaldehyde	TMSC≡CH	67

ester end groups of the growing polymer chains and ddbfo ligands coordinated to titanium in equimolar ratio (Fig. 3).

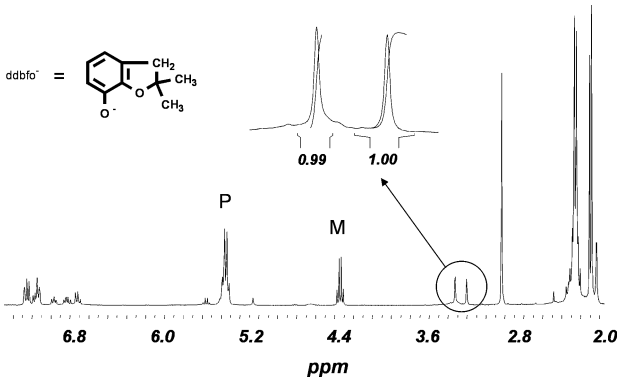


Fig. 3 ^{1}H NMR spectrum of the living polymer obtained with initiator **1** ([M]$_0$/[I]$_0$ = 20) in toluene at 70 °C.

The polymerization process was monitored by ^{1}H NMR. The molecular weight of the polymer increased linearly with respect to the conversion of monomer indicating the living nature of the polymerization system Fig. 4.

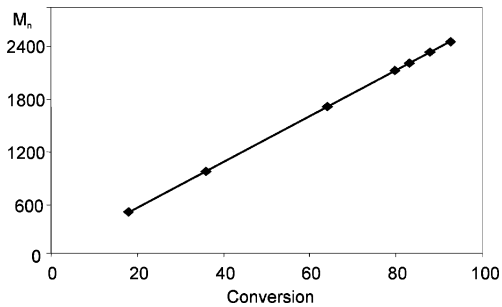


Fig. 4 Plot of M_n *vs.* conversion at 70 °C in toluene with [M]$_0$/[I]$_0$] = 35 using **1** as the initiator.

The parameters of PLA obtained with initiator **1** and equimolar amounts of ethanol as an initiating group were similar (M_n = 28 000, PDI = 1.18) but the polymerization reaction proceeded faster to reach 100% conversion within 12 h. Examination of the ^{1}H NMR spectrum of the obtained PLA shows resonances attributed to ethyl ester as well as the hydroxyl chain ends and exactly one polymer chain was formed. These results suggest a coordination–insertion mechanism occurring through the insertion of L-LA into aryloxo titanium.

The polymerization of *rac*-LA was next investigated. It has been reported that carbonyl and methine carbon atoms are the stereo-sensitive groups leading respectively to hexad and tetrad sequences.[24] Fig. 5 shows the ^{13}C NMR spectra of carbonyl and methine groups in PLA prepared using **1** as initiator. The intensities of the corresponding hexad and tetrad stereo sequences were calculated according to the literature.[25] These values suggested that the ROP of *rac*-LA initiated by **1** show a preference for heterotactic addition.

In conclusion, the efficient syntheses of homoleptic **1** and heteroleptic **2** were developed. Both compounds were characterized by X-ray analysis to show dimeric structures. Complex **1**

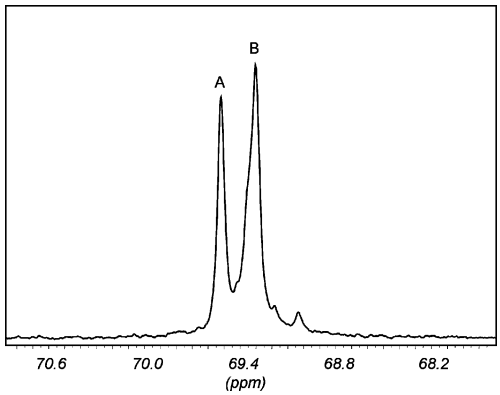


Fig. 5 Expanded region of methine atoms in ^{13}C NMR of poly(*rac*-LA) obtained with **1** as initiator; (A) isi and (B) iii + iis/sii + sis.

survives extended periods in air and appears to be a good initiator for controlled ring-opening polymerization of L-LA and *rac*-LA providing monodisperse PLA with higher degrees of heterotactic addition. The reaction showed a first-order dependence on [LA] consisted with a coordination–insertion mechanism. Complex **1** also catalyzes the addition of terminal acetylenes to aryl aldehydes to give propargyl alcohol derivatives in good yields.

Experimental

General data

All reactions were conducted under a N_2 atmosphere. Chemicals were treated as follows: toluene, distilled from Na/benzophenone; hexanes, distilled from P_2O_5; MeOH, distilled from Mg; Et_2O, distilled from Na/benzophenone; 2,3-dihydro-2,2-dimethyl-7-benzofuran alcohol (ddbfoH, Aldrich), distilled prior to use; (3*S*)-*cis*-3,6-dimethyl-1,4-dioxane-2,5-dione (L-LA; 98% Aldrich) and 3,6-dimethyl-1,4-dioxane-2,5-dione (*rac*-LA; Aldrich) sublimed prior to use; benzaldehyde, 4-bromobenzaldehyde, 4-chlorobenzaldehyde, 3,5- and 2,4-dimethoxybenzaldehyde, 2-nitrobenzaldehyde (6 × POCh), used as received; 4-(TMSC≡C)benzaldehyde;[26] PhC≡CH (Aldrich), distilled prior to use; 4-MeC_6H_4C≡CH, TMSC≡CH (2 × Aldrich) used as received; Ti(O^{i}Pr)$_4$ (1.0 M solution in hexane), $ZnEt_2$ (1.0 M solution in hexane), $TiCl_4$, $Zr(OEt)_4$ (4 × Aldrich), PPh_3 (Fluka), Na_2SO_4, NaCl, aqueous HCl (3 × POCh), and C_6D_6 (Cambridge Isotope Laboratories), used as received.

NMR spectra were obtained on a BRUKER ESP 300E spectrometer. The weights and number-average molecular weights of the PLAs were determined by gel permeation chromatography (GPC; HPLC-HP 1090 II with DAD-UV/vis and RI detector HP 1047A) using polystyrene calibration. Microanalyses were conducted using a Vario EL III instrument (in-house).

Syntheses

Ti(ddbfo)$_4$ (1). *Method (A).* A 250 mL Schlenk flask was charged with Ti(O^{i}Pr)$_4$ (1.20 g; 4.22 mmol) and toluene (30 mL) and 2.50 mL (2.77 g; 16.88 mmol) of ddbfoH was added. The colorless solution immediately turned red-orange. It was slowly warmed to 100 °C and after 2 h it was refluxed for an additional 4 h. After that time it was cooled and the solvent containing HO^{i}Pr was removed under vacuum. 30 mL of toluene was added and the clear solution was refluxed for 6 h. The solution was then cooled and the solvent was removed under vacuum. Hexanes (20 mL) were added and the suspension was placed in a freezer overnight. The red powder containing portions of crystalline material was then filtered off, washed with cold hexanes (3 × 5 mL) and dried under vacuum to give pure **1** in 75% yield (2.23 g; 3.18 mmol).

Method B. A 250 mL Schlenk flask was charged with $TiCl_4$ (0.55 mL; 0.95 g; 5.03 mmol) and toluene (30 mL) and 3.00 mL (3.30 g; 20.11 mmol) of ddbfoH was added. The colorless solution immediately turned red-orange and the evolution of HCl started. The solution was stirred at room temperature for 24 h and then the temperature was raised to 60 °C and stirring was continued until the evolution of gas had ceased. The solution was cooled, concentrated under vacuum and left at room temperature. After 12 h a red crystalline material had deposited which was filtered off and the filtrate was placed in the refrigerator to give after overnight standing another portion of **1**. Overall yield 72% (2.53 g; 3.62 mmol). Elemental analysis calcd for $C_{40}H_{44}O_8Ti$ (monomer: 700.66) (%): C, 68.57; H, 6.33. Found: C, 66.71 (66.67); H, 6.48 (6.66). ^1H NMR (δ, C_6D_6, 297 K): 1.32 (s, 24H, CH_3), 2.76 (s, 8H, CH_2), 6.67–7.00 (m, 18H, Ph of ddbfo). ^{13}C NMR (δ, C_6D_6): 27.9 (8CH_3), 43.9 (4CH_2), 89.9 (4C(CH_3)$_2$), 116.9, 117.1, 121.1, 126.3, 148.3, 151.6 (24C of Ph).

Ti(ddbfo)$_4$(PPh_3)$_2$ (1·2PPh_3). A 100 mL Schlenk flask was charged with **1** (0.10 g; 0.14 mmol) and toluene (20 mL) and PPh_3 (0.74 g; 2.82 mmol) was added. The solution was stirred for 3 h and the solvent was evaporated. The residue was dissolved in warm hexanes and the clear solution was placed in a fridge. Overnight a red powder precipitated to give **1**·2PPh_3 in 38% yield (0.07 g; 0.05 mmol) Elemental analysis calcd for $C_{76}H_{74}O_8P_2Ti$ (1225.25) (%): C, 74.50; H, 6.09. Found: C, 74.38; H, 6.12. ^1H NMR (δ, C_6D_6, 297 K): 1.26 (s, 24H, CH_3), 2.71 (s, 8H, CH_2), 6.72–6.95 (m, 12H, Ph of ddbfo), 7.15–7.17 and 7.48–7.54 (m, 30H, Ph_3 of PPh_3).

Zr_2(μ-OEt)$_2$(HOEt)$_2$(ddbfo)$_6$ (2). $Zr(OEt)_4$ (1.86 g; 6.85 mmol), ddbfoH 2.04 mL (2.25 g; 13.70 mmol), and toluene (30 mL) were combined in a procedure analogous to that for **1**. After being refluxed for the second time the cloudy solution was filtered, concentrated to one third and left at room temperature overnight. White crystals of **2** precipitated. They were filtered off, washed with a small amount of cold hexanes (~5 mL) and dried under vacuum. Yield 2.58 g (1.92 mmol; 56%). Elemental analysis calcd for [$C_{34}H_{44}O_8Zr$]$_2$ (dimer: 1343.82) (%): C, 60.81; H, 6.46. Found: C, 60.20 (59.97); H, 6.40 (6.26). ^1H NMR (δ, C_6D_6, 297 K): 1.26 (s, 36H, CH_3), 2.71 (s, 12H, CH_2), 3.49 (br s, 8H, OCH_2CH_3), 4.68 (br s, 12H, OCH_2CH_3), 6.52–7.05 (m, 18H, Ph of ddbfo); ^{13}C {^1H} NMR (partial: C_6D_6, 297 K): δ = 28.0 (2C, CH_3), 43.8 (1C, CH_2), 90.00 (1C, C(CH_3)$_2$), 115.2, 115.9, 117.0, 117.1.

Addition procedure

1 (usually around 0.05 g; 0.07 mmol) was placed in a Schlenk flask and toluene (10 mL) was added. $ZnEt_2$ (1.0 M solution in hexanes; 10 equivalents) was introduced and the mixture was stirred at room temperature for 2 h. Next acetylene (10 equivalents) was added and

the stirring continued for 1 h. The orange-red solution was cooled to 0 °C and treated with aldehyde (3 equivalents). The mixture was allowed to warm to room temperature and stirred for 24 h. After the reaction was complete (TLC monitored), it was cooled to 0 °C and quenched with aqueous HCl (5%). The mixture was extracted with diethyl ether. The organic layer was washed with brine, dried over Na_2SO_4, concentrated and purified by flash chromatography. The residue was analyzed by GC-MS.

Catalytic polymerization

In a typical experiment the monomer of lactide was placed in a Schlenk flask and a solution of **1** in toluene was added. The reaction mixture was warmed to 70 °C with stirring. At 6 h time intervals *ca*. 1 mL aliquots were taken out, the solvent was removed under vacuum and the conversion was determined using ^{1}H NMR. After the reaction was finished it was terminated with methanol and the sample was evaporated to dryness. The remaining residues were redissolved in CH_2Cl_2 and the polymer was precipitated with an excess of cold methanol. Filtration and drying under vacuum yielded a white polymer.

X-Ray crystallography

Crystal data collection and refinement are summarized in Table 1. Preliminary examination and intensity data collections were carried out on a KUMA KM4 κ-axis diffractometer with graphite-monochromated Mo-Kα radiation and with scintillation counter or CCD camera. All data were corrected for Lorentz and polarization effects. Data reduction and analysis were carried out with the Kuma Diffraction programs.[27,28] The structures were solved by direct methods[29] and refined by the full-matrix least-squares method on all F^2 data using the SHELXL97 software.[30] Hydrogen atoms were included in calculated positions and refined in the riding mode using SHELXL97 default parameters. All non-hydrogen atoms were refined with anisotropic displacement parameters. The terminal EtOH molecules in **2** are disordered. The occupancy factor for the more represented EtOH (C511 and C521) is 0.52.

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