New facets of an old ligand: titanium and zirconium complexes of phenylenediamine bis(phenolate) in lactide polymerisation catalysis

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General

All reactions with air- and/or water sensitive compounds were carried out under dry nitrogen atmosphere in a glovebox. Ether was purified by distillation under dry argon atmosphere from purple Na/benzophenone solution. Pentane was washed with HNO₃/H₂SO₄ prior to distillation from Na/benzophenone/tetraglyme. Toluene was refluxed over Na and distilled. 1,2-Phenylenediamine, 3,5-di-*tert*-butylcatechol, *rac*-Lactide, *L*-Lactide, Zr(O-*tert*-butoxide)₄, Zr(O-isopropoxide)₄(isopropanol), and Ti(O-isopropoxide)₄ were purchased from Aldrich and used as received. Triethylamine was purchased from Merck, *n*-heptane was purchased from Riedel-de Haen and used as received. *N*,*N*²-bis(3,5-di-*tert*-butyl-2-hydroxyphenyl)-1,2-phenylenediamine ({ONNO}H₂) was synthesized according to a published procedure.¹ Ti(O-*tert*-Bu)₄ was prepared in quantitative yield by repeated additions of excess of *t*-BuOH to a solution of Ti(O-*i*-Pr)₄ in diethyl ether at room temperature and removal of the volatiles. ¹H NMR (200 MHz, C₆D₆), δ 1.36 (s).

All NMR data were recorded on a Bruker Avance-400 spectrometer. C₆D₆ (impurities in benzene-d₆ at δ 7.15, and ¹³C chemical shift of benzene at δ 128.70 were used as reference) and C_7D_8 (impurities in toluene-d₈ at δ 2.09, 6.98, 7.00, 7.09) were used as NMR solvents for the metal complexes. CDCl₃ was used as NMR solvent for the PLA samples (chemical shift of TMS at δ 0.00, and ¹³C chemical shift of the solvent at δ 77.16 were used as reference). Elemental analyses were performed in the microanalytical laboratory at the Hebrew University of Jerusalem. X-ray diffraction measurements were performed on a Nonius Kappa CCD diffractometer system, using MoK α ($\lambda = 0.7107$ Å) radiation. The analyzed crystals were embedded within a drop of viscous oil and freeze-cooled to ca. 110 K. The structures were solved by a combination of direct methods and Fourier techniques using SIR-97 software,² and were refined by full-matrix least squares with SHELXL-97.³ PLA molecular weights were determined by gel permeation chromatography (GPC) using TSKgel GMHHR-M and TSKgel G 3000 HHR columns set on a Jasco instrument equipped with a refractive index detector. Molecular weight determination was carried out relative to polystyrene standards using THF (high-performance liquid chromatography grade, distilled and filtered under vacuum prior to use) as the eluting solvent.

[{ONNO}Ti(O-*i*-Pr)₂]. A solution of {ONNO}H₂ (40 mg, 0.08 mmol) in *ca.* 2 mL of ether was added dropwise to a solution of Ti(O-*i*-Pr)₄ (22 mg, 0.08 mmol) in *ca.* 2 mL of ether. The color changed immediately from colorless to dark red. The reaction was stirred at room temperature for 30 minutes after which the volatiles were removed under reduced pressure. The crude

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product was washed with pentane to give [{ONNO}Ti(O-*i*-Pr)₂] as a white solid in a final yield of 78%. ¹H NMR (400 MHz, C₆D₆), δ 7.32 (d, *J* = 2.0 Hz, 2H), 6.82 (m, 2H), 6.70 (d, *J* = 2.0 Hz, 2H), 6.60 (m, 2H), 5.25 (s, 2H), 4.76 (sept, *J* = 5.8 Hz, 2H), 1.67 (s, 18H), 1.34 (s, 18H), 1.16 (d, *J* = 6.2 Hz, 12H); ¹³C NMR (400 MHz, C₆D₆), δ 159.8 (*C*), 141.9 (*C*), 138.2 (*C*), 135.6 (*C*), 134.9 (*C*), 131.7 (*C*H), 117.7 (*C*H), 77.7 (*C*H), 35.0 (*C*), 34.1 (*C*), 31.7 (*C*H₃), 29.4 (*C*H₃), 24.6 (*C*H₃). Repeated elemental analysis measurement attempts gave incorrect values probably due to impurities caused by formation of the dinuclear complex. Anal. Calcd. for C₄₀H₆₀N₂O₄Ti: C, 70.57; H, 8.88; N, 4.11. Found: C, 70.03; H, 8.71; N, 4.14.

[{ μ -ONNO}(Ti(μ -O-i-Pr)(O-i-Pr)₂)₂]. A solution of {ONNO}H₂ (58 mg, 0.11 mmol) in *ca.* 2 mL of ether was added dropwise to a solution of Ti(O-i-Pr)₄ (64 mg, 0.22 mmol) in *ca.* 2 mL of ether. The reaction mixture turned brown-red immediately and was stirred at room temperature for 60 minutes, and the volatiles were removed under vacuum. Crystallization from pentane at - 35 °C gave red crystals of [{ μ -ONNO}(Ti(μ -O-i-Pr)(O-i-Pr)₂)₂] suitable for X-ray structure determination (116 mg, 92% yield). ¹H NMR (400 MHz, C₆D₆) was not informative due to overlapping broad peaks in chemical shifts typical of the {ONNO} and isopropoxo groups (See Figure 1). Anal. Calcd. for C₅₂H₈₈N₂O₄Ti₂: C, 64.72; H, 9.19; N, 2.90. Found: C, 65.81; H, 9.30; N, 2.80.

[{ONNO}Ti(O-*t*-Bu)₂]. A solution of {ONNO}H₂ (49 mg, 0.095 mmol) in *ca*. 2 mL of ether was added dropwise to a solution of Ti(O-*t*-Bu)₄ (32 mg, 0.094 mmol) in *ca*. 2 mL of ether. The reaction was stirred at room temperature for 40 minutes during which time a white precipitate had formed. The volatiles were removed under vacuum and the crude product was washed with pentane to give {ONNO}Ti(O-*t*-Bu)₂ as a white solid in a final yield of 80%. ¹H NMR (400 MHz, C₆D₆) δ 7.31 (d, *J*= 2.4 Hz, 2H), 6.81 (m, 4H), 6.61 (m, 2H), 5.26 (s, 2H), 1.65(s, 18H), 1.36 (s, 18H), 1.29 (s, 18H); ¹³C NMR (400 MHz, C₆D₆), δ 160.3 (*C*), 141.9 (*C*), 137.9 (*C*), 135.9 (*C*), 134.6 (*C*), 121.5 (*C*H), 117.6 (*CH*), 82.6 (*C*), 35.0 (*C*), 34.0 (*C*), 31.7 (*C*H₃), 31.5 (*CH*₃), 29.4 (*C*H₃). Anal. Calcd. for C₄₂H₆₄N₂O₄Ti: C, 70.63; H, 9.12; N, 4.00. Found: C, 71.17; H, 9.10; N, 3.95.

[{ONNO}Zr(O-*t*-Bu)₂]. A solution of {ONNO}H₂ (39 mg, 0.076 mmol) in *ca*. 2 mL of ether was added dropwise to a solution of $Zr(O-t-Bu)_4$ (29 mg, 0.076 mmol) in *ca*. 2 mL of ether. The reaction was stirred at room temperature for 50 minutes during which time a white precipitate had formed. The volatiles were removed under reduced pressure and the crude product was washed with pentane to give [{ONNO}Zr(O-*t*-Bu)₂] as a white solid in a final yield of 98%. ¹H NMR (400 MHz, C₆D₆) δ 7.36 (d, *J* = 2.4 Hz, 2H), 6.81 (m, 2H), 6.74 (d, *J* = 2.3 Hz, 2H), 6.60

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(m, 2H), 5.00 (s, 2H), 1.67 (s, 18H), 1.34 (s, 181H), 1.25 (s, 18H); ¹³C NMR (400 MHz, C₆D₆), δ 157.6 (*C*), 141.3 (*C*), 138.2 (*C*), 137.0 (*C*), 134.6 (*C*), 122.3 (*C*H), 118.5 (*CH*), 75.6 (*C*), 35.2 (*C*), 34.0 (*C*), 32.3 (*C*H₃), 31.7 (*CH*₃), 29.4 (*C*H₃). Anal. Calcd. for C₄₂H₆₄N₂O₄Zr: C, 66.77; H, 8.59; N, 3.71. Found: C, 67.06; H, 8.54; N, 3.72.

[{ μ -ONNO}(Zr(μ -O-i-Pr)(O-i-Pr)₂)₂]. A solution of {ONNO}H₂ (66 mg, 0.13 mmol) in 2 mL of ether was added dropwise to a solution of Zr(O-i-Pr)₄·(i-Pr-OH)₂ (66 mg, 0.13 mmol in 2 mL of ether. The reaction mixture turned to light purple color and was stirred at room temperature for 60 minutes. The volatiles were removed under vacuum. Crystallization from pentane at -35 °C gave light purple crystals of [{ μ -ONNO}(Zr(μ -O-i-Pr)(O-i-Pr)₂)₂] suitable for X-ray structure determination (111 mg, 98% yield). ¹H NMR (400 MHz, C₆D₆) was not informative due to overlapping broad peaks in chemical shifts typical of the {ONNO} and isopropoxo groups See Figures 2 and 3).

[{ONNO}Hf(O-t-Bu)₂]. A solution of {ONNO}H₂ (28 mg, 0.05 mmol) in *ca.* 2 mL of ether was added dropwise to a solution of Hf(O-t-Bu)₄ (25 mg, 0.05 mmol) in *ca.* 2 mL of ether. The reaction was stirred at room temperature for 60 minutes during which time a white precipitate had formed. The volatiles were removed under reduced pressure and the crude product was washed with pentane to give [{ONNO}Hf(O-t-Bu)₂] as a white solid in a final yield of 94%.

¹H NMR (400 MHz, C₆D₆) δ 7.37 (d, J = 2.4 Hz, 2H), 6.78 (m, 2H), 6.73 (d, J = 2.2 Hz, 2H), 6.59 (m, 2H), 5.00 (s, 2H), 1.67 (s, 18H), 1.34 (s, 181H), 1.26 (s, 18H); ¹³C NMR (400 MHz, C₆D₆), δ 157.6 (*C*), 141.2 (*C*), 138.2 (*C*), 137.6 (*C*), 134.5 (*C*), 122.4 (*C*H), 118.4 (*CH*), 75.3 (*C*), 35.1 (*C*), 34.0 (*C*), 32.5 (*C*H₃), 31.7 (*CH*₃), 29.4 (*C*H₃). Anal. Calcd. for C₄₂H₆₄N₂O₄Hf: C, 60.09; H, 7.68; N, 3.34. Found: C, 60.40; H, 7.95; N, 3.21.

General Polymerisation Procedure.

Purified Lactide obtained by crystallization from toluene followed by two sublimations, led to polymers of similar characteristics to those obtained from unpurified lactide. Therefore the unpurified lactide was employed in all polymerisations. Bulk polymerisations of *L*-Lactide and *rac*-Lactide were carried out by heating the monomer and the catalyst in a closed glass vessel to 130°C for a period of time by which the melt became viscous. 10 mg of catalyst and a 300:1 molar ratio were employed for all polymerisations. In addition, molar ratios of 1000:1 and 2000:1 were employed with [{ONNO}(O-*t*-Bu)₂] as catalyst. The polymerisation runs were terminated by the addition of 1 mL of methanol. The reaction mixture was dissolved in dichloromethane, followed by removal of the volatiles under reduced pressure. The resulting polymer was washed with excess of methanol to remove any unreacted monomer, filtered and

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dried under vacuum for 2 hours. ¹H NMR analysis of the PLA samples obtained by polymerisation of *L*-Lactide (400 MHz, CDCl₃) indicated that no epimerization occurred during the polymerisation, and that the polymer was isotactic, as was evident from a quartet (5.16 ppm) and a doublet (1.58 ppm) in a ratio of 1:3.

Solution polymerisation runs (of *rac*-Lactide) in 5 mL of toluene were carried out in the same manner described for the bulk polymerisations at various temperatures. After a given period of time the reaction was terminated by the addition of 1 mL of methanol and the volatiles were removed under vacuum. The resulting polymer was washed with excess of methanol to remove any unreacted monomer and dried under vacuum for 2 hours. The homonuclear decoupled ¹H NMR spectrum of the PLA samples (400 MHz, CDCl₃) of the methine region was consistent with the formation of chains that are most predominantly heterotactic, estimated from relative intensity of the *rmr* (δ 5.23 ppm) and *mrm* (δ 5.16 ppm) tetrads *vs* other tetrads (*rmm/mmr*, δ 5.22 ppm and 5.18 ppm; *mmm*, δ 5.17 ppm).⁴ For typical NMR spectra of these polymers see Figures 4 and 5. Molecular weight determination and PDI analysis were done by GPC. Representative polymerisation data using *L*-Lactide and *rac*-Lactide as monomers are summarized in Table 1 and 2, respectively. Monitoring the polymerization process by conducting an NMR tube experiment in Toluene-D₈ at 75 °C indicated that only the formed polymer and the un-reacted monomer existed.

Entry	Initiator ^a	L-lactide	Time (h)	PLA obtained	Conv.	M_w^{b}	$M_{n, calc}$	PDI
		(g)		(g)	(%)	$(g mol^{-1})$	$(g mol^{-1})$	
1	$\{ONNO\}Zr(O-t-Bu)_2$	0.57	23	0.20	35	3,000	14,500	1.28
2	{ONNO}Ti(O- <i>i</i> -Pr) ₂	0.61	1.25	0.42	69	5,000	30,000	1.30
3	$\{ONNO\}Ti(O-t-Bu)_2$	0.67	1	0.32	48	4,000	21,000	1.13

Table 1ROP of L-lactide at 130 °C.

^a10 mg of catalyst was employed. ^bcorrection parameter 0.58 x M_w polystyrene standards. ^ccalculated from 144.13 x (LA/I) x conversion of monomer.

Supplementary Material (ESI) for Chemical Communications This journal is (c) The Royal Society of Chemistry 2009 **Table 2** ROP of *rac*-lactide.

	Initiator ^a	rac-	Temp.	Tol.	P_r^{b}	Time	PLA	Conv.	M_w^{c}	$M_{n, calc_1}^{d}$	PDI
		lactide (g)	(°C)	(ml)		(h)	(g)	(%)	(g mol ⁻¹)	$(g \text{ mol}^{-1})$	
1	$\{ONNO\}Zr(O-t-Bu)_2$	0.58	130	-	0.72	0.25	0.38	65	14,000	28,000	1.65
2	{ONNO}Ti(O- <i>i</i> -Pr) ₂	0.68	130	-	0.62	0.03	0.64	94	28,000	41,500	1.48
3	$\{ONNO\}Zr(O-t-Bu)_2$	0.61	130	5	0.69	2	0.44	72	33,000	32,000	1.66
4	$\{ONNO\}Zr(O-t-Bu)_2$	0.68	75	5	0.87	2	0.08	12	8,700	4,900	1.29
5	$ONNOZr(O-t-Bu)_2$	0.59	75	5	0.87	24	0.21	35	15,000	17,000	1.65
6	$\{ONNO\}Zr(O-t-Bu)_2$	0.59	75	5	0.87	48	0.55	93	49,000	40,000	1.50
7	{ONNO}Ti(O- <i>i</i> -Pr) ₂	0.65	75	5	0.61	1	0.65	100	14,000	43,000	1.13
8	{ONNO}Ti(O- <i>i</i> -Pr) ₂	0.67	50	5	0.68	24	0.67	1.00	32,000	41,500	1.59
9	{ONNO}Ti (O-t-Bu) ₂	0.45	130	-	0.61	0.01	0.34	75	22,500	32,500	1.56
10	$\{ONNO\}Ti(O-t-Bu)_2$	0.63	75	5	0.62	1	0.59	93	18,000	39,000	1.20
11 ^e	$\{ONNO\}Ti(O-t-Bu)_2$	2.01	75	5	0.62	3	2.01	100	61,800	144,000	1.13
12 ^f	{ONNO}Ti(O-t-Bu) ₂	4.47	75	10	0.57	6.5	4.00	89	69,000	260,000	1.18
13 ^f	$\{ONNO\}Ti(O-t-Bu)_2$	3.93	75	10	0.57	24	3.93	100	110,500	300,000	1.30
14	{ONNO}Hf(O-t-Bu) ₂	0.54	130	-	0.55	0.25	0.46	0.85	18,000	37,000	1.38
15	${ONNO}Hf(O-t-Bu)_2$	0.51	75	5	0.82	26	0.50	0.98	16,000	42,000	1.59

^a10 mg of catalyst and *ca*. 300:1 molar ratio of LA/I was employed. ^b P_r is the probability of racemic enchainment between monomer units and is determined from the methine region of the homonuclear ¹H NMR.⁵ ^c correction parameter 0.58 x M_w polystyrene standards. ^d calculated from 144.13 x (LA/I) x conversion of monomer. ^e1000:1 molar ratio of LA/I was employed. ^f2000:1 molar ratio of LA/I was employed.



Figure 1. ¹H NMR of complex [{µ-ONNO}(Ti(µ-O-i-Pr)(O-i-Pr)₂)₂], 298K, Tol-D₈



Figure 2. ¹H NMR of complex [$\{\mu$ -ONNO $\}(Zr(\mu$ -O-i-Pr)(O-i-Pr)_2)_2], 298K, Tol-D8



Figure 3. ¹H NMR of complex [{μ-ONNO}(Zr(μ-O-i-Pr)(O-i-Pr)₂)₂], 258K, Tol-D₈



Figure 4. PLA obtained with {ONNO}Ti(O-i-Pr)₂ at 50 °C, Entry 8, Table 2



Figure 5. PLA obtained with {ONNO}Zr(O-t-Bu)2 at 75 °C, Entry 6, Table 2

- 1. P. Chaudhuri, M. Hess, J. Müller, K. Hildenbrand, E. Bill, T. Weyhermüller, K. Wieghardt, J. *Am. Chem. Soc.*, 1999, **121**, 9599.
- 2. A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M. C. Burla, G. Polidori, M. Camali, *J. Appl. Cryst.*, 1994, **27**, 435.
- 3. G. M. Sheldrick, SHELXL-97 Program; University of Göttingen, Germany, 1996.

4. (a) K.A.M. Thakur, R. T. Kean, M. T. Zell, B. E. Padden, E. J. Munson, Chem. Commun.,

1998, 1913. (b) K. A. M. Thakur, R. T. Kean, E. S. Hall, J. J. Kolstad, T. A. Lindgren, M. A.

Doscotch, J. I. Siepmann, E. J. Munson, Macromolecules, 1997, 30, 2422.

5. B. M. Chamberlain, M. Cheng, D. R. Moore, T. M. Ovitt, E. B. Lobkovsky, G. W. Coates, J. Am. Chem. Soc., 2001, **123**, 3229.