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Synthesis and X-ray Structures of New Titanium(IV) Aryloxides and Their Exploitation for the Ring Opening Polymerization of ϵ-Caprolactone

Matthew G. Davidson,*,† Matthew D. Jones,† Matthew D. Lunn,‡ and Mary F. Mahon§

Department of Chemistry, University of Bath, Claverton Down, Bath, BA2 7AY, U.K., Johnson Matthey Catalysts, P.O. Box 1, Belasis Avenue, Billingham, Cleveland, TS23 1LB, U.K., and Bath Chemical Crystallography Unit, Department of Chemistry, University of Bath, Claverton Down, Bath, BA2 7AY, U.K.

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A series of titanium catecholates have been prepared and characterized by single-crystal X-ray diffraction studies. Complexes **1a**–**7a** were synthesized by the reaction of 1 equiv of ligand with $Ti(O^iPr)_4$. All are dimers in the solid-state, in which a catechol bridges between two titanium centers. Electronic (nitro and methoxy groups) and steric (*tert*-butyl groups) effects of the ligand have been investigated. Complex **1b** was synthesized by reaction of 2 equiv of ligand with $Ti(O^iPr)_4$. A dimer is again observed with the same bridging ligand together with a terminal catechol moiety. All complexes contain a coordinated 2-propanol ligand on each titanium center forming pseudo-octahedral metal centers. All complexes were tested for the ring-opening-polymerization of ϵ-caprolactone to afford polycaprolactone (PCL). Reasonable yields (up to 79%) were obtained at room temperature, and narrow molecular weight distributions (1.13–1.27) were observed for the PCL produced. The most active complex was found to be complex **1a**, containing unsubsituted catechol ligands.

Introduction

Catechol (1,2-dihydroxybenzene, **1**) is a potent bidentate ligand with a high affinity for metals that possess a high oxidation state.[1,2] In nature, catechol functional groups are common; they are found, for example, in certain sideophores.[3] In catalysis, titanium alkyloxides and aryloxides are extensively used as precatalysts for olefin polymerization,[4] oxidation,[5] epoxidation,[6] and enantioselective carbon−carbon bond formation.[7] Structurally, titanium aryloxides are able to stabilize unusual coordination polyhedra,[8] and in supramolecular chemistry, titanium catecholates self-assemble into helicate compounds and, in recent years, efforts have focused on synthesizing catechol imine complexes and studying their supramolecular properties.[9] Titanium aryloxides have also been used to synthesize covalent 2-D and 3-D metal−organic frameworks.[10] A tremendous effort has focused on the potential exploitation of titanium aryloxides for the ring-opening polymerization (ROP) of ϵ-caprolactone to afford polycaprolactone (PCL).[11] PCLs have attracted interest due to their potential application as biodegradable polymers.[11b] Consequently, it is pertinent to design novel titanium aryloxide catalysts for such applications, particularly those

* To whom correspondence should be addressed. Fax: +44 (0)1225 386231. Tel: +44 (0)1225 384467. E-mail: m.g.davidson@bath.ac.uk.
† Department of Chemistry, University of Bath.
‡ Johnson Matthew Catalysts.
§ Bath Chemical Crystallography Unit, Department of Chemistry, University of Bath.

(1) Borgias, B. A.; Cooper, S. R.; Koh, Y. B.; Raymond, K. N. *Inorg. Chem.* **1984**, *23*, 1009.
(2) Dahl, G. H.; Block, B. P. *Inorg. Chem.* **1966**, *5* (8), 1394.
(3) Raymond, K. N.; Carrano, C. J. *Acc. Chem. Res.* **1979**, *12*, 183.
(4) (a) Oakes, D. C. H.; Kimberley B. S.; Gibson V. C.; Jones D. J.; White, A. J. P.; Williams D. J. *Chem. Commun.* **2004**, 2174. (b) Kretschmer, W. P.; Dijkhuis, C.; Meetsma, A.; Hessen, B.; Teuben, J. H. *Chem. Commun.* **2002**, 608. (c) Chen, E. Y. X.; Marks, T. J. *Chem. Rev.* **2000**, *100* (4), 1391. (d) Coates, G. W. *Chem. Rev.* **2000**, *100 (4)*, 1223.
(5) Fujiwara, M.; Xu, Q.; Souma, Y.; Kobayashi, T. *J. Mol. Catal. A-Chem.* **1999**, *142* (1), 77.
(6) Perez, Y.; Del Hierro, I.; Fajardo, M.; Otero, A. *J. Organomet. Chem.* **2003**, *679* (2), 220.
(7) Chen, Y.; Yekta, S.; Yudin, A. K. *Chem. Rev*, **2003**, *103* (8), 3155.
(8) (a) Gigant, K.; Rammal, A.; Henry, M. *J. Am. Chem. Soc.* **2001**, *123*, 11632. (b) Lei, X.; Shang, M.; Fehlner, T. P. *Organometallics* **1996**, *15*, 3779.
(9) Albrecht, M.; Ingo, J. A.; Frohlich, R. *Chem. Commun.* **2005**, 157.
(10) (a) Tanski, J. M.; Wolczanski, P. T. *Inorg. Chem.* **2001**, *40*, 2026. (b) Tanski, J. M.; Vaid, T. P.; Lobkovsky, E. B.; Wolczanski, P. T. *Inorg. Chem.* **2000**, *39*, 4756. (c) Vaid, T. P.; Tanski, J. M.; Pette, J. M.; Lobkovsky, E. B.; Wolczanski, P. T. *Inorg. Chem.* **1999**, *38*, 3394.

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Table 1. Crystal Data for the Structures **1a**−**6a**

ligand	**1** (1:1)	**1** (1:2)	**2**	**3**	**4**	**5**	**6**
formula	$C_{30}H_{52}O_{10}Ti_2$	$C_{30}H_{32}O_{10}Ti_2$,2(C_3H_8O), 2(CH_2Cl_2)	$C_{32}H_{56}O_{10}Ti_2$	$C_{38}H_{68}O_{10}Ti_2$	$C_{46}H_{84}O_{10}Ti_2$	$C_{32}H_{56}O_{12}Ti_2$ 2(CH_2Cl_2)	$C_{30}H_{50}N_2O_{14}Ti_2$
fw	668.46	938.40	696.57	780.66	892.87	898.42	758.52
crystal system	triclinic	triclinic	monoclinic	triclinic	monoclinic	triclinic	monoclinic
space group	$P\bar{1}$	$P\bar{1}$	$P2_1/c$	$P\bar{1}$	$P2_1/n$	$P\bar{1}$	$P2_1/c$
temp/K	150(2)	150(2)	170(2)	150(2)	150(2)	150(2)	193(2)
a (Å)	10.819(3)	8.513(1)	8.199(6)	7.995(2)	11.520(1)	8.828(2)	8.1770(1)
b (Å)	12.807(4)	12.481(2)	17.901(1)	11.661(3)	17.579(1)	10.598(2)	11.3900(2)
c (Å)	13.713(5)	12.627(2)	12.565(1)	12.223(3)	12.660(2)	13.265(3)	20.8130(4)
α (°)	97.73(1)	116.68(1)	90	81.75(2)	90	111.26(1)	90
β (°)	108.17(2)	98.59(1)	95.88(3)	72.73(1)	96.00(1)	93.12(1)	101.152(1)
γ (°)	102.29(2)	102.94(1)	90	75.64(1)	90	102.40(1)	90
V (Å^3)	1722.01(10)	1119.02(3)	1834.5(2)	1051.22(5)	2549.70(5)	1117.58(4)	1901.84(5)
Z	2	1	2	1	2	1	2
D_{calc} (g cm^{-3})	1.289	1.393	1.261	1.230	1.163	1.335	1.325
reflns collected	10 843	12 809	7987	9010	40 046	16 606	21 387
indep. reflns(R_{int})	5964(0.0625)	3921(0.0432)	2302(0.0549)	3714(0.0389)	4475(0.0651)	5021(0.0364)	4340(0.0460)
GOF	1.033	1.085	1.056	1.158	1.061	1.057	1.027
R1,wR2 [$I > 2\sigma(I)$][a]	0.0471, 0.1196	0.0327, 0.0861	0.0524, 0.1250	0.0635, 0.1502	0.0380, 0.0852	0.0313, 0.0787	0.0507, 0.1275
R1, wR2 (all data)[a]	0.0814, 0.1344	0.0383, 0.0891	0.0717, 0.1410	0.0723, 0.1540	0.0506, 0.0904	0.0386, 0.0832	0.0667, 0.1390

[a] $R1 = \sum|F_0| - |F_c|/\sum|F_0|$, $wR2 = [\sum(F_0^2 - F_c^2)^2/\sum w(F_0^2)^2]^{1/2}$

with readily available ligands that form air-stable complexes. Catechol ligands are very cheap and easy to handle; thus, they should be ideal for industrial applications. In this paper, we report the synthesis and structural characterization of seven new titanium catechol-based complexes. Unusually, in all the structures, a coordinated 2-propanol ligand is observed, which is involved in hydrogen bonding to one of the isopropoxide ligands. The complexes have also been screened for the ROP of ϵ-caprolactone at room temperature.

Experimental Section

For the preparation and characterization of complexes, all reactions and manipulations were performed under an inert atmosphere of argon using standard Schlenk or glovebox techniques and all solvents were freshly distilled over suitable drying agents and degassed prior to use. All ligands were purchased from Aldrich or Lancaster and used as received. Ti(O^iPr)$_4$ was purchased from Aldrich and purified by vacuum distillation prior to use. ^{1}H NMR spectra were recorded on a Bruker Advance 300 MHz spectrometer, using internal references. Coupling constants are given in hertz. For **5a**, ^{1}H NMR spectra were consistently too broad to allow meaningful assignment of resonances. Similarly, ^{13}C NMR spectra of all complexes gave broad resonances that preclude meaningful assignment. Elemental analysis was performed by Mr. A. K. Carver at the Department of Chemistry, University of Bath. Deviations in analyses from theoretical values are common for similar species and are attributed to the presence of "trapped" solvent.[12] Crystallographic data were collected on a Nonius KappaCCD area detector diffractometer using Mo Kα radiation (λ = 0.71073 Å), and all structures were solved by direct methods and refined on all F^2 data using SHELXL-97 suite of programs,[13] with hydrogen atoms not involved in hydrogen-bonding networks included in idealized positions and refined using the riding model. Hydrogen atoms involved in hydrogen bonding were located in difference electron density maps and freely refined. Absorption corrections were applied where appropriate, see Table 1 for crystallographic parameters. FT-IR measurements were recorded in Nujol using a Nicolet Nexus spectrometer. UV−vis measurements were carried out in quartz cells using CH_2Cl_2 as the solvent on a Perkin-Elmer Lambda 650 UV−vis spectrometer.

Complex 1a. Ti(O^iPr)$_4$ (1.04 mL, 3.5 mmol) was added to dichloromethane (10 mL). To this, catechol (0.387 g, 3.5 mmol) was added and the solution immediately turned red. The solution was stirred for 1 h. The solution was slightly concentrated in vacuo and placed in the freezer (−10 °C) overnight, crystals suitable for X-ray diffraction were obtained. The mother liquor was removed, and the resultant crystals dried to remove the solvent and 2-propanol and washed with cold hexane (20 mL) to form the de-alcoholated **1a** in near quantitative yield. Anal. Calcd for $C_{24}H_{36}O_8Ti_2$ C, 52.55; H, 6.57; Found C, 51.5; H, 6.68. ^{1}H NMR ($CDCl_3$) 1.16 (d J = 6 Hz, 24H, CH(CH_3)$_2$), 4.23 (sept J = 6 Hz, 4H CH(CH$_3$)$_2$), 6.0−6.7 (broad multiplet, 8H, Ar). FT-IR 2920(s), 1700(w), 1653(s), 1466(s), 1378(s), 1326(w), 1253(s), 1204(w), 1163(s), 1130(s), 1017(s), 952(w), 817(m), 739(m), 654(m), 564(w). λ_{max} = 355 nm, ϵ_0 = 37 000 L mol^{-1}cm^{-1}.

Complex 1b. A similar method was employed as that for complex **1a**, with the exception of using 2 mol equiv of catechol. In this case, the bound 2-propanol was not removed when the complex was dried. Anal. Calcd for $C_{30}H_{32}O_{10}Ti_2$ C, 55.55; H, 4.94; Found C, 55.8; H, 4.80.^{1}H NMR ($CDCl_3$) 1.11 (d J = 6 Hz, 12H, CH(CH_3)$_2$), 2.5−3.5 (broad singlet, 2H, OH), 3.92 (sept J = 6 Hz, 2H CH(CH$_3$)$_2$), 6.0−7.0 (broad multiplet, 16H, Ar). FT-IR 3066(s), 2938(s), 2854(s), 1716(w), 1562(s), 1469(s), 1378(s), 1315(w), 1270(s), 1249(s), 1193(s), 1097(m), 1071(s), 920(m), 876(m), 821-(m), 668(m), 628(m), 604(w). λ_{max} = 360 nm, ϵ_0 = 60 000 L mol^{-1} cm^{-1}.

Complex 2a. A similar method was employed as that for complex **1a**. Anal. Calcd for $C_{26}H_{40}O_8Ti_2$ C, 54.17; H, 6.94; Found C, 54.9; H, 6.07. ^{1}H NMR ($CDCl_3$) 1.16 (d J = 6 Hz, 24H, CH-

(11) (a) Takeuchi, D.; Nakumura, T.; Aida, T. *Macromolecules* **2000**, *33*, 725. (b) Albertsson, A. C.; Varma, I. K. *Biomacromolecules* **2003**, *4*, 1466. (c) Kim, Y.; Jnaneshwara, G. K.; Verkade, J. G. *Inorg. Chem.* **2003**, *42*, 1437. (d) Takashima, Y.; Nakayama, Y.; Watanabe, K.; Itono, T.; Ueyama, N.; Nakamura, A.; Yasuda, H.; Harada, A.; Okuda, A. *Macromolecules* **2002**, *35*, 7538. (e) Takashima, Y.; Nakayama, Y.; Hirao, T.; Yasuda, H.; Harada, A. *J. Organomet. Chem.* **2004**, *689*, 612. (f) Asandei, A. D.; Saha G. *Macromol. Rapid Commun.* **2005**, *26*, 626.

(12) (a) Boyle, T. J.; Tribby, L. J.; Alam, T. M.; Bunge, S. D.; Holland, G. P. *Polyhedron* **2005**, *24*, 1143. (b) Boyle, T. J.; Andrews, N. L.; Rodriguez, M. A.; Campana, C.; Yiu, T. *Inorg. Chem*, **2002**, *42*, 5357.

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

(CH_3)$_2$), 2.21 (s, 6H, $-CH_3$), 4.35 (sept J = 6 Hz, 4H CH(CH_3)$_2$), 6.2−6.6 (broad multiplet, 6H, Ar). FT-IR 2952(s), 2870(s), 1652(s), 1577(w), 1463(s), 1377(s), 1320(w), 1269(s), 1248(w), 1216(w), 1169(w), 1123(m), 1076(w), 1021(m), 859(w), 769(w) 734(m), 665-(m), 624(m), 607(m). λ_{max} = 358 nm, ϵ_0 = 26 000 L mol^{-1} cm^{-1}.

Complex 3a. A similar method was employed as that for complex **1a**. Anal. Calcd for $C_{32}H_{52}O_8Ti_2$ C, 58.18; H, 7.88; Found C, 57.2; H, 7.89. ^{1}H NMR ($CDCl_3$) 1.20 (d J = 6 Hz, 24H, CH-(CH_3)$_2$), 1.25 (s, 18H, $-CH_3$), 4.51 (sept J = 6 Hz, 4H CH(CH_3)$_2$), 6.0−7.1 (broad multiplet, 6H, Ar). 2921(s), 2854(s), 1660(s), 1456(s), 1418(s), 1400(m), 1377(s), 1282(w), 1262(s), 1200(w), 1124(m), 1020(m), 942(m), 861(w), 812(w), 712(m), 647(m). λ_{max} = 354 nm, ϵ_0 = 33 000 L mol^{-1} cm^{-1}.

Complex 4a. A similar method was employed as that for complex **1a**. Anal. Calcd for $C_{40}H_{68}O_8Ti_2$ C, 62.18; H, 8.81. Found C, 62.2; H, 9.31. ^{1}H NMR ($CDCl_3$) 1.19 (d J = 6 Hz, 24H, CH-(CH_3)$_2$), 1.26 (s, 18H, $-CH_3$), 1.35 (s, 18H, $-CH_3$), 4.41 (sept J = 6 Hz, 4H CH(CH_3)$_2$), 6.81 (d J = 2 Hz, 2H, Ar), 7.06 (d J = 2 Hz, 2H, Ar). FT-IR 2936(s), 1700(w), 1650(s), 1560(w). 1460(s), 1416(w), 1377(s), 1318(w), 1277(w), 1202(w), 1162(m), 1130(w), 1023(m), 984(m), 837(m), 753(w), 722(w), 611(w). λ_{max} = 370 nm, ϵ_0 = 35 000 L mol^{-1} cm^{-1}.

Complex 5a. A similar method was employed as that for complex **1a**. Anal. Calcd for $C_{26}H_{40}O_{10}Ti_2$ C, 51.32; H, 6.58. Found C, 50.50; H, 6.85. FT-IR 2936(s), 1652(s), 1589(s), 1540(w), 1463(s), 1377(s), 1325(w), 1294(m), 1269(w), 1244(m), 1163(br), 1019(m), 855(m), 767(m), 626(m). λ_{max} = 365 nm, ϵ_0 = 40 000 L mol^{-1} cm^{-1}.

Complex 6a. A similar method was employed as that for complex **1a**. Anal. Calcd for $C_{24}H_{34}N_2O_{12}Ti_2$ C, 45.14; H, 5.33; N, 4.39. Found C, 46.2; H, 5.79; N, 4.10. ^{1}H NMR ($CDCl_3$) 1.20 (d J = 6 Hz, 24H, CH(CH_3)$_2$), 4.52 (sept J = 6 Hz, 4H CH(CH_3)$_2$), 6.4−6.6 (broad multiplet, 2H, Ar), 7.6−7.8 (br multiplet 4H, Ar). FT-IR 2924(s), 2852(s), 1624(s), 1578(s), 1463(s), 1377(s), 1332(s), 1276(s), 1219(m), 1163(m), 1123(m), 1070(m), 1017(m), 948(w), 875(w), 816(w), 749(w), 684(w), 659(w), 624(w). λ_{max} = 323 nm, ϵ_0 = 53 000 L mol^{-1} cm^{-1}.

Complex 7a. A similar method was employed as that for complex **1a**. Anal. Calcd for $C_{26}H_{40}O_8Ti_2$ C, 54.17; H, 6.94; Found C, 54.7; H, 6.52. ^{1}H NMR ($CDCl_3$) 1.22 (d J = 6 Hz, 24H, CH-(CH_3)$_2$), 2.27 (s, 6H, $-CH_3$), 4.44 (sept J = 6 Hz, 4H CH(CH_3)$_2$), 6.3−6.9 (broad multiplet, 6H, Ar). FT-IR 2961(s), 2872(s), 1652(s), 1578(w), 1459(s), 1377(s), 1315(w), 1270(s), 1250(w), 1235(w), 1218(w), 1169(w), 1125(m), 1079(w), 1023(m), 860(w), 737(m), 665(m), 607(m). λ_{max} = 358 nm, ϵ_0 = 28 000 L mol^{-1} cm^{-1}.

Catalysis. In a typical run, the catalyst (0.1 mmol) was dissolved in toluene (10 mL) to which ϵ-caprolactone (10.0 mmol, 1.11 mL) was added. This was left to stir at room temperature for 24 h during which time the viscosity of the solution significantly increased. The catalysis was then quenched using 30% acetic acid and water solution, and the polymer was precipitated using hexane, filtered, washed with copious amount of hexane, and dried in vacuo. ^{1}H NMR spectroscopy ($CDCl_3$) and GPC (THF, referenced to polystyrene) were used to determine conversions and molecular weights (M_n and M_w) of the polymers produced. Typical ^{1}H NMR analysis of PCL: 1.15 (d J = 6 Hz CH(CH_3)$_2$ end group), 1.3 (m 2H, CH_2 backbone), 1.6 (m 4H, CH_2 backbone), 2.2 (m 2H, CH_2 backbone), 3,6 (t $-$CH_2OH end group), 4.0 (m 2H, OCH_2 backbone), 4.9 (sept J = 6 Hz CH(CH_3)$_2$ end group).

Results and Discussion

Initial attempts focused on unsubstituted catechol **1**, which was reacted with Ti(O^{i}Pr)$_4$ in stiochiometries of 1:1 and 2:1 (catechol/Ti). In the former case (complex **1a**), the catecholate ligand bridges between the two titanium centers, forming a dimeric species. In contrast to previous reports, our attempts to form single crystals under anhydrous conditions proved successful.[8a] In the latter instance (complex **1b**), the same bridging mode for the ligand is observed, in addition to each titanium being capped by a catecholate moiety. To the best of our knowledge, **1b** is only the second example of a neutral titanium catecholate with a catechol/Ti ratio greater than 1.[12a] Boyle et al. have synthesized a related and interesting Ti$_3$-(cat)$_6$$\mu_3$-O complex; however, for charge balancing, either catechol or pyridine solvent of crystallization, must be protonated. Previous reports have attempted to form complexes with a ratio greater than 1 have been unsuccessful.[8a] Complex **1b** is also the first example showing both a bridging and capping dianionic catechol ligand in the same structure with a titanium metal center.

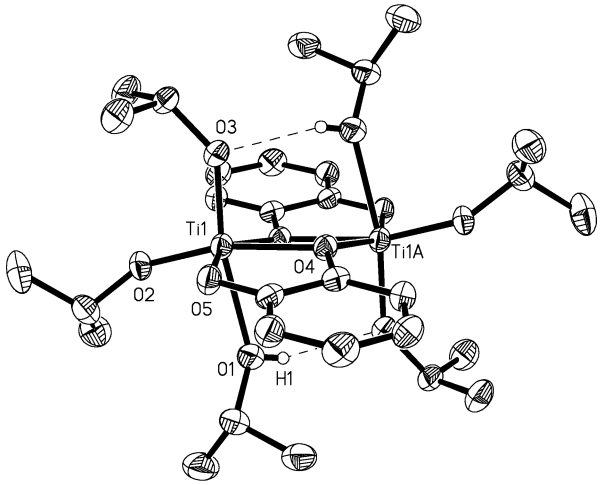


Figure 1. Molecular structure of complex **1a**, showing the numbering scheme employed. The ellipsoids are shown at the 50% probability level and all hydrogens with the exception of those involved in hydrogen bonding have been omitted for clarity, as have lattice solvent molecules.

In both **1a** and **1b**, the Ti centers are six-coordinate and pseudo-octahedral with the coordination sphere being completed by the incorporation of one 2-propanol ligand bound in a *transoid* configuration to each metal center of the dimeric Ti_2O_2 ring, Figures 1 and 3. In both cases, the coordinated alcohol ligand is stabilized via O−H···O hydrogen bonding. In **1a**, the intramolecular hydrogen bond acceptor is a Ti-bound isopropoxide ligand, whereas in **1b**, in the absence of isopropoxide, a further, noncoordinated alcohol acts as an intermolecular hydrogen bond acceptor and in turn donates a hydrogen bond to a Ti-bound catecholate ligand. This difference presumably reflects a lower flexibility within the coordination sphere of **1b** imposed by the additional bidentate ligands which disfavors the intramolecular hydrogen bonding found in **1a**. The high-quality, low-temperature (150 K) X-ray data allow unambiguous location of hydrogen atoms and also precludes any significant disorder of the OH groups in the solid state, as highlighted by the difference electron density map for the hydrogen-bonded region of **1b** shown

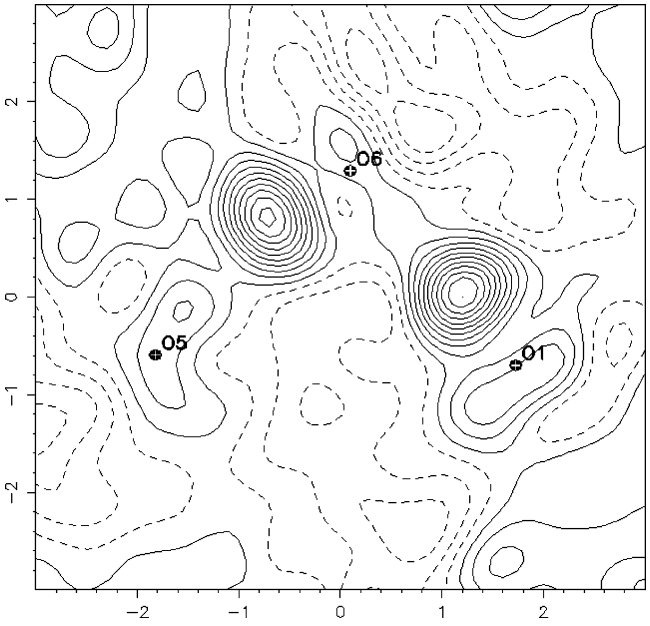


Figure 2. Difference electron density map for the hydrogen-bond region of **1b** (min. and max. electron density, −0.24 and +0.64 eÅ^{-3}, respectively). Dashed (negative) and solid (positive) contour lines are shown at intervals of 0.1 eÅ^{-3}.

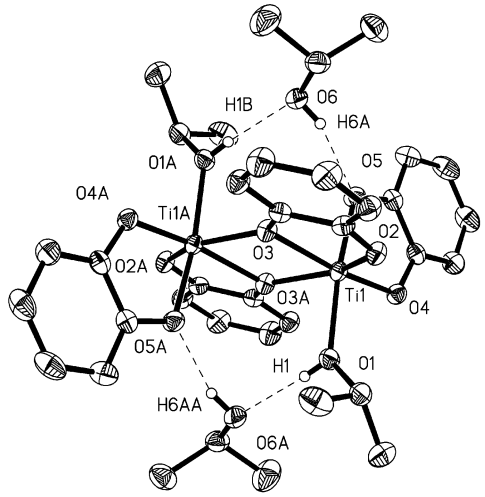


Figure 3. Molecular structure of complex **1b**, showing the hydrogen-bonded network. O5−H6A = 1.94(3) Å, H1B−O6 = 1.87(2) Å. The ellipsoids are shown at the 50% probability level, and all hydrogens with the exception of those involved in hydrogen bonding have been omitted for clarity, as have lattice solvent molecules.

in Figure 2.[14] While the Ti−O(R)−H···O(R)−Ti motif of **1a** has been observed previously for Ti[10,15] and other group 4 metals,[16] to our knowledge, the Ti−O(R)−H···O(R)−H···O(R)−Ti scheme found for **1b** is unique.

(14) We are grateful to one of the referees for highlighting that a bond valence sum (bvs) analysis [Brown, I. D.; Altermatt, D. *Acta Crystallogr.* **1985**, *B41*, 244] of **1b** can be interpreted in favor of an alternative hydrogen-bonded scheme in which the titanium-bound 2-propanol ligand (O1) is deprotonated and the catecholate oxygen atom (O5) is protonated. However, such an analysis requires accurate positional parameters for the hydrogen atoms and, while the X-ray data is consistent with our model (as highlighted by the difference electron density map, Figure 2), further confirmation would require a single-crystal neutron diffraction study for which suitable crystals are not available.

Table 2. Selected Bond Distances (Å) and Angles (deg) for Complexes **1a** and **1b**

	1a		**1b**
Ti1−O1	2.301(2)	Ti1−O1	2.0416(14)
Ti1−O2	1.7674(18)	Ti1−O4	1.8761(12)
Ti1−O3	1.822(2)	Ti1−O3	2.0931(12)
Ti1−O4	2.1078(2)	Ti1−O2	1.8712(12)
Ti1−O4A	2.003(2)	Ti1−O5	1.9401(12)
Ti1−O5	1.907(2)	Ti1−O3A	1.9967(12)
O3A−H1	2.19(3)		
		O4−Ti1−O5	80.67(5)
O4−Ti1−O5	78.56(1)	O2−Ti1−O3	78.32(5)
O1−Ti1−O3	167.69(9)	O3A−Ti1−O2	147.60(5)
Ti1−O4−TiA	107.21(8)	O3A−Ti1−O3	71.29(5)
O4−Ti1−O4A	72.18(8)	O1−Ti1−O5	168.95(5)
		Ti1−O3−Ti1A	108.71(5)

The structure of **1a** consists of two crystallographically independent but chemically similar centrosymmetric dimers, whereas that of **1b** consists of a single centrosymmetric dimer. The bond lengths and angles are in agreement with similar reported crystal structures and are given in Table 2.[1,17] In both cases, one of the oxygen centers of the catechol bridges the two titanium centers. As a consequence of this, it has a longer Ti−O^{bridging} compared to the Ti−O^{terminal} bond length. The average Ti−O^{bridging} bond length for **1a** is 2.06 Å, slightly greater than that for **1b** at 2.04 Å. For the bridging catechol, the Ti−O^{terminal} bond lengths are 1.907(2) and 1.904(2) Å for **1a** (for the two crystallographically unique Ti centers), these are slightly longer than the corresponding distance for **1b** (Ti1−O2, 1.8712(12) Å), suggesting that this bridging ligand is held more tightly in complex **1b** than **1a**. Also noteworthy for complex **1a** is that the Ti−O^{i}Pr trans to the Ti−O(H)^{i}Pr is significantly longer than that of the cis Ti−O^{i}Pr. A similar trait is observed in complex **1b** with the Ti−O for the terminal catechol trans (O5) to the coordinated 2-propanol longer than that of the cis terminal catechol ligand (O4).

A significant difference between **1a** and **1b** is the length of the Ti−O(H) bond, which is shorter for the disubstituted complex (by ca. 0.2 Å). Presumably, this is simply as a result of one chelating catecholate ligand being a weaker donor than two isopropoxide ligands, resulting in a more electron deficient titanium center which can be relieved by tighter coordination of the 2-propanol moiety. This point is further supported by the fact that the Ti−O bonds for the isopropoxide in **1a** are much shorter than those of the capping catechol in **1b**.

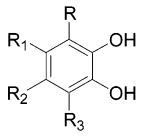
The solid-state structures described above were obtained on crystalline samples mounted directly from solution. On isolation of **1a**, the 2-propanol ligand is removed in vacuo,

(15) (a) Wu, Y. T.; Ho, Y. C.; Lin, C. C.; Gau, H. M. *Inorg. Chem.* **1996**, *35*, 5948 (b) Pandey, A.; Gupta, V. D.; Noth, H. *Eur. J. Inorg. Chem.* **2000**, 1351. (c) Svetich, G. W.; Voge, A. A. *Acta Crystallogr. Sec. C.* **1972**, *28*, 1760. (d) Zechmann, C. A.; Huffman, J. C.; Folting, K.; Caulton, K. G. *Inorg. Chem.* **1998**, *37*, 5856

(16) (a) Vaartstra, B. A.; Huffman, J. C.; Gradeff, P. S.; Hubert-Pfulzgraf, L. G.; Daran, J. C.; Parraud, S.; Yunlu, K.; Caulton, K. G. *Inorg. Chem.* **1990**, *29*, 3126. (b) Veith, M.; Mathur, S.; Mathur, C.; Huch, V. *J. Chem. Soc., Dalton Trans.* **1997**, 2101.

(17) (a) Albrecht, M.; Schneider, M.; Frohlich, R. *New J. Chem.* **1998**, *22*, 753 (b) Chi, Y.; Hsu, P. F.; Lan, J. W.; Chen, C. L.; Peng, S. M.; Lee, G. H. *J. Phys. Chem. Solids* **2001**, *62*, 1871. (c) Albrecht, M.; Frohlich, R. *J. Am. Chem. Soc.* **1997**, *119*, 1656.

Scheme 1 Ligands Used in This Study



1 R=R$_1$=R$_2$=R$_3$ = H

2 R=R$_2$=R$_3$ = H, R$_1$ = Me

3 R=R$_2$=R$_3$ = H, R$_1$ = tBu

4 R=R$_2$ = tBu, R$_1$=R$_3$ = H

5 R = OMe, R$_1$=R$_2$=R$_3$ = H

6 R=R$_2$=R$_3$ = H, R$_1$ = NO$_2$

7 R = Me, R$_1$=R$_2$=R$_3$ = H

Table 3. Selected Bond Distances (Å) and Angles (deg) for Complexes **2a**−**6a**

	2a	**3a**	**4a**	**5a**	**6a**
Ti1−O1	2.245(3)	2.250(3)	2.2389(14)	2.1906(11)	2.2216(18)
Ti1−O2	1.767(3)	1.774(3)	1.7748(12)	1.7654(10)	1.7532(17)
Ti1−O3	1.829(3)	1.834(3)	1.8544(12)	1.8447(10)	1.8213(18)
Ti1−O4	1.997(3)	2.119(3)	1.9871(12)	2.0043(10)	2.0023(14)
Ti1−O4A	2.106(3)	2.004(3)	2.1019(12)	2.0920(9)	2.1235(15)
Ti1−O5A	1.903(3)	1.907(3)	1.8951(12)	1.9142(10)	1.9288(15)
O3A−H1	2.05(4)	2.03(5)	2.04(2)	2.10(2)	2.06(3)
Ti1−O4−Ti1A	107.28(11)	107.07(11)	106.65(5)	106.93(4)	107.39(6)
O4A−Ti1−O5A	78.60(12)	79.00(10)	78.16(5)	79.01(4)	77.98(6)
O1−Ti1−O3	165.44(14)	165.18(12)	166.80(5)	166.60(5)	166.70(8)
O4−Ti1−O4A	72.72(11)	72.93(11)	73.35(5)	73.07(4)	72.61(6)

implying that this ligand is weakly coordinated to the titanium center, and ^{1}H spectra are consistent with the 2-propanol-free complex maintaining a similar structure to that observed in the solid state. However, these data do not preclude aggregation of dimeric units or additional bridging of terminal catecholate oxygen atoms in order to maintain six-coordinate titanium centers. In contrast, for complex **1b**, the coordinated alcohol is retained following isolation (as indicated by NMR, FTIR, and elemental analysis) although the noncoordinated alcohol is lost. However, NMR data are consistent with the molecular unit observed in the solid-state being maintained in solution.

Having established the synthetic methodology and structural features of these complexes using the parent ligand, a number of derivatives were investigated (4-methylcatechol, **2**; 4-^{t}Bu-catechol, **3**; 3,5-^{t}Bu-catechol, **4**; 3-methoxycatechol, **5**; 4-nitrocatechol, **6**; and 3-methylcatechol, **7**, see Scheme 1) in order to assess electronic and steric effects on both structure and reactivity.

All ligands were reacted with Ti(O^{i}Pr)$_4$ in a 1:1 ratio to form the desired complexes **2a**−**7a**. The molecular structures of complexes **2a**−**6a** are very similar to that described above for **1a**. Selected bond distances and angles are given in Table 3, and complex **5a** is shown in Figure 4. In addition to the X-ray data, solution and solid-state analytical data for complexes **2a** to **7a** are consistent with those described above for **1a**, suggesting that all catecholate ligands used in this study form structurally similar titanium complexes both in the solid state and in solution. Attempts to grow crystals suitable for X-ray diffraction for catechol/Ti ratios greater than 1 were unsuccessful, and only powders were obtained.

All complexes described above were screened for the polymerization of ϵ-caprolactone, following prior removal of the coordinated alcohol in vacuo (except in the case of **1b** for which the coordinated alcohol remains and acts as the initiator for the polymerization). The polymerization was carried out at room temperature in toluene solution. After 24 h, the polymer was precipitated with hexane following quenching with acetic acid. All complexes afford PCL with narrow polydispersities indicating controlled polymerization (Table 4). These results are comparable with previous reports of titanium alkoxide catalyzed polymerization of ϵ-caprolactone.[11] For example, a series of titanium bis(phenolate) systems were reported to achieve 100% conversion at room temperature in CH_2Cl_2 in times ranging from 5 to 75 h[11a] whereas polymerization in toluene (70 °C for 24 h) gave isolated yields of 52%, 77%, and 89% PCL for titanium alkoxide-based catalysts.[11c]

In all cases, isopropoxide end groups were observed by ^{1}H NMR spectroscopic analysis of the isolated PCL, which suggests initiation of polymerization proceeds via insertion into a titanium isopropoxide bond. These observations are consistent with the accepted coordination−insertion mechanism for metal alkoxide-catalyzed ROP,[18] including previous studies with titanium alkoxides.[11c] Furthermore, since the titanium-bound 2-propanol ligands found by X-ray crystallography are removed on isolation of complexes the titanium centers of **1a** to **7a** are coordinatively unsaturated in the dimeric state, which facilitates precomplexation of the caprolactone monomer to the metal center. In the case of

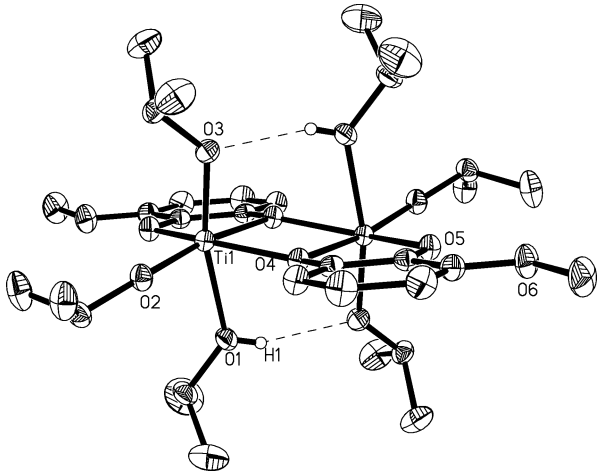


Figure 4. Molecular structure of complex **5a**, showing the numbering scheme employed The ellipsoids are shown at the 50% probability level, and all hydrogens with the exception of those involved in hydrogen bonding have been omitted for clarity, as have lattice solvent molecules.

Table 4. Results for the Polymerization of ϵ-Caprolactone[a]

entry	ligand	% yield[b]	M_w[c]	M_n[c]	PDI[c]	M_n (NMR)[d]
1	**1** (1:1 with Ti)	79	4900	4100	1.19	2400
2	**1** (2:1 with Ti)	25	2600	2100	1.22	1300
3	**2**	61	5300	4400	1.20	2600
4	**3**	5	1900	1700	1.13	1200
5	**4**	71	5800	4600	1.27	3500
6	**5**	4	2700	2200	1.24	1300
7	**6**	29	3300	2800	1.18	1500
8	**7**	45	4200	3600	1.17	2050

[a] Conditions [CL]/[Ti] = 100:1, 10 mL toluene, time 24 h, room temperature (20 °C). [b] Isolated yield. [c] Determined from GPC using polystyrene as the reference. [d] Calculated from ^{1}H NMR ($CDCl_3$) analysis.

(18) O'Keefe, B. J.; Hillmyer, M. A.; Tolman, W. B. *J. Chem. Soc., Dalton Trans.* **2001**, 2215.

1b, which contains a coordinated 2-propanol ligand and two dianionic catecholate ligands per titanium center, the presence of an isopropoxide end group in the isolated polymer suggests that initiation is preceded by proton transfer from 2-propanol to a catecholate ligand, thereby generating a catalytically active titanium isopropoxide species in situ. It is noteworthy that a number of monoprotic catecholate titanium species have been reported previously.[12a] Although alcohol initiators are commonly added to precatalysts in ROP, to our knowledge, this is the first example of a well-defined precoordinated precatalyst system. Such a strategy may have advantages in that the initiator−metal stoichiometery is controlled precisely at the molecular level.

Polymers were analyzed by MALDI-TOF mass spectrometry; in all cases, a single series of peaks was observed with the appropriate end groups (see Supporting Information). Substitution of the catecholate ring with either nitro (entry 7) or methoxy (entry 6) groups reduces the catalyst activity, as seen with the lower conversions. This suggests that steric factors predominate over electronic considerations in influencing catalytic activity. This is further supported by the contrast seen in 4-methyl and 4-^{t}butyl systems (entries 3 and 4, respectively). Addition of alkyl groups on the aromatic ring also do not increase the activity of catalysts compared to the unsubstituted catechol moiety. In contrast to the bisphenolate systems reported by Aida et al[11a] where steric bulk was required to induce activity, the least sterically demanding ligands in the catecholate series are among the most active.

In conclusion, seven new titanium aryloxides have been characterized by X-ray diffraction. For the 1:1 complexes, the structural moiety described is very robust and persistent as it is observed in all cases. Unusually, in all the complexes, a coordinated 2-propanol ligand is observed, which is bound significantly more tightly to the metal in complex **1b**. We also report a structure showing two bonding motifis (capping and bridging) of the catecholate ligand. The complexes catalyze the ROP of ϵ-caprolactone at rates comparable to previously reported systems affording polyester with narrow molecular weight distributions: To our knowledge, these are the first examples of well-defined metal−catecholate systems applied to the ROP of ϵ-caprolactone.

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Supporting Information Available: X-ray crystallographic data in cif format; selected MALDI-TOF mass spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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