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PAPER

Crystallographic characterisation of Ti(IV) piperazine complexes and their exploitation for the ring opening polymerisation of *rac*-lactide

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In this paper a series of eight Ti(IV) piperazine based complexes have been prepared and fully characterised in the solid-state by X-ray crystallography and in solution *via* NMR spectroscopy. In the solid-state either $\mathrm{Ti_2(\mathbf{L})(O^iPr)_6}$ or $\mathrm{Ti_2(\mathbf{L})_2(O^iPr)_4}$ were observed depending upon the nature of the starting ligand. For complexes with less sterically demanding ligands ($\mathbf{1}\mathrm{H_2}$ and $\mathbf{2}\mathrm{H_2}$) an equilibrium was observed: $2\ \mathrm{Ti_2(\mathbf{L})(O^iPr)_6} \Leftrightarrow \mathrm{Ti_2(\mathbf{L})_2(O^iPr)_4} + 2\ \mathrm{Ti(O^iPr)_4}$. The thermodynamic properties (ΔG, ΔH and ΔS) have been investigated *via* variable temperature NMR spectroscopy. With more sterically demanding ligands ($\mathbf{3–8}\mathrm{H_2}$) the $\mathrm{Ti_2(\mathbf{L})(O^iPr)_6}$ form was the most prevalent in the solid-state and in solution. These complexes have been tested for the production of polylactide under melt and solution conditions with high conversions being obtained.

Introduction

The preparation of homogeneous Lewis acidic complexes for the ring opening polymerisation (ROP) of cyclic esters (such as *rac*-lactide) has received considerable attention in recent years.[1] Examples of initiators for this process include groups 1–3,[2] Al(III),[3] In(III),[4] Zn(II),[2b,5] lanthanides[6] and pertinent to this study group 4 metal centres.[7] The polymers themselves have found many uses from commodity plastics to high value biomedical applications.[8] The use of amine bis(phenolate) ligands in such chemistry is ubiquitous and there are numerous examples of such initiators in the literature.[3c,7a,7d–7f] However, the use of the more conformationally strained piperazine derived ligands for this polymerisation remains limited. A notable example of work in this area is that by Yao and co-workers who have recently prepared a Yb–Li bimetallic piperazidine complex.[9] This was shown to act as a promising initiator for the ROP of L-lactide. The same group have also very recently prepared lanthanide complexes for L- and *rac*-lactide polymerisation based on piperazine ligands.[10] It has been found that *N*-substituted piperazine complexes are very versatile and can bind to either one or two metal centres.[9] Previous crystallographically characterised piperazine-phenolate complexes include Al(III),[11] Pd(II),[12] Zn(II)[13] and Cu(II).[14] For example, a series of Al(III) complexes with 1,4-bis(2-hydroxy-3,5-di-*tert*-butyl)piperazine have been prepared and in this case either monometallic or bimetallic complexes were formed in the solid-state.[11] With the same ligand Zn(II) bimetallic structures have been prepared.[13] To the best of our knowledge there are no reported examples of crystallographically characterised piperazine-phenolate complexes with Ti(IV), although the analogous 1,4-bis(2-aminobenzyl)piperazine ligand has been used by Mountford to prepare Ti(IV) imido complexes.[15] Also to the best of our knowledge there are no crystallographically characterised complexes of the methyl substituted piperazine ring systems. Crystallographically characterised complexes with the homopiperazine ligand (7 membered ring) remain limited to Fe(III),[16] Cu(II),[17] Ni(II)[17] and one example of a Ti(IV) oxo complex has been previously published.[18]

In this paper we report the preparation and characterisation of new piperazine and homopiperazine ligands. These ligands were complexed to Ti(IV) and either complexes of the form $\mathrm{Ti_2(\mathbf{L})(O^iPr)_6}$ or $\mathrm{Ti_2(\mathbf{L})_2(O^iPr)_4}$ have been isolated in the solid-state. Interestingly, in some cases a complex equilibrium was observed in solution between these two dimers and $\mathrm{Ti(O^iPr)_4}$. The complexes have been tested for the ROP of *rac*-lactide with high conversions.

Results and discussion

Synthesis of ligands and complexes

The ligands were prepared *via* a modified Mannich reaction as shown in Scheme 1.[11] All ligands were characterised *via* ^{1}H and ^{13}C{^{1}H} NMR spectroscopy and HR-MS, $\mathbf{1}\mathrm{H_2}$ was also characterised using single crystal X-ray diffraction. The complexes were prepared by the reaction of 1 equivalent of ligand with 2 equivalents of $\mathrm{Ti(O^iPr)_4}$ in $\mathrm{CH_2Cl_2}$.[7a,7d,7e] It was observed that the same products were also isolated in the solid-state with 1 equivalent of $\mathrm{Ti(O^iPr)_4}$. For complexes with ligands $\mathbf{1}\mathrm{H_2}$ and $\mathbf{2}\mathrm{H_2}$ the solid-state structures are shown in Fig. 1 and selected bond lengths and angles are in Table 1.

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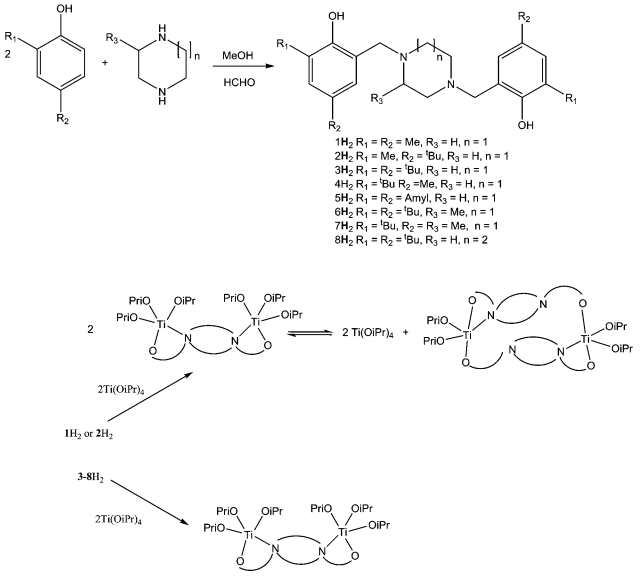
Table 1 Selected bond lengths (Å) and bond angles (°) for complexes $Ti_2(\mathbf{1})_2(O^iPr)_4$ and $Ti_2(\mathbf{2–8})(O^iPr)_6$

	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**
Ti1–O1	1.859(2)	1.7813(18)	1.7758(17)	1.7835(17)	1.7803(17)	1.790(3)	1.796(4)	1.7798(19)
Ti1–O2	1.857(2)	1.8080(18)	1.8131(17)	1.8001(17)	1.8127(17)	1.817(3)	1.809(3)	1.814(2)
Ti1–O3	1.817(2)	1.8360(18)	1.8317(17)	1.834(2)	1.8308(17)	1.817(3)	1.8334(18)	1.832(2)
Ti1–O4	1.775(2)	1.8883(17)	1.8735(17)	1.8809(18)	1.8649(16)	1.869(3)	1.8689(16	1.8624(19)
Ti1–N1	—	2.3499(18)	2.3547(19)	2.351(2)	2.3567(18)	2.357(3)	2.357218)	2.378(2)
Ti1–N3	2.353(3)	—	—	—	—	—	—	—
O1–Ti1–N1	—	175.03(9)	177.20(8)	173.01(8)	176.55(7)	177.19(13)	165.4(7)	173.78(9)
O4–Ti1–N1	—	79.86(7)	81.07(7)	79.27(7)	80.49(6)	81.68(11)	79.78(7)	80.26(7)
O1–Ti1–N3	81.87(9)	—	—	—	—	—	—	—
O4–Ti1–N3	178.59(10)	—	—	—	—	—	—	—
O1–Ti1–O2	117.50(10)	100.21(9)	99.64(8)	101.85(10)	100.54(8)	99.02(15)	107.(10)	100.53(10)



Scheme 1 Ligands and complexes prepared in this study.

For $\mathbf{1}H_2$ the observed solid-state product was the dimeric species $Ti_2(\mathbf{1})_2(O^iPr)_4$ with each Ti centre being trigonal pyramidal in geometry. This is exemplified by analysis of the N(2)–Ti(2)–O(8) angle of 177.15(12)° and N(2)–Ti(2)–O(5) of 81.29(9)°. This motif is similar to a structure recently reported by Tshuva and co-workers, in which 1,4-bis(2-hydroxy-3,5-di-*tert*-butyl-benzyl)-imidazolidine produced a dimer with Ti(IV).[19] Each metal centre is coordinated to the phenoxide oxygen and nitrogen of one ligand, a phenoxide centre from another ligand and two isopropoxide moieties complete the coordination sphere. This leaves one nitrogen per ligand uncoordinated. The metrics of each titanium centre are analogues to Ti(IV) bisphenolates reported in the literature.[7a,7d–7f,19] For $Ti_2(\mathbf{1})_2(O^iPr)_4$ only small crystals were isolated (0.08 × 0.05 × 0.02 mm) and it was necessary to use synchrotron radiation to determine the structure. Analysis of the bulk solid from a stoichiometric reaction *via* elemental analysis was consistent with the major product being $Ti_2(\mathbf{1})(O^iPr)_6$ but this was not the crystalline product. For ligands $\mathbf{2}H_2$–$\mathbf{8}H_2$ complexes of the form $Ti_2(\mathbf{L})(O^iPr)_6$ were observed in the solid-state. The titanium centres are trigonal bipyramidal with one phenoxide, a nitrogen and three isopropoxide moieties coordinating to each metal centre.

It is clear from analysis of the room temperature ^1H NMR spectra for the products isolated from the reaction of $\mathbf{1}H_2$ and $\mathbf{2}H_2$ with $Ti(O^iPr)_4$ that there are multiple species present in solution. On careful examination of the spectra and VT NMR spectroscopic studies it was concluded that they are consistent with a dynamic equilibrium in solution: 2 $Ti_2(\mathbf{L})(O^iPr)_6$ ⇔ $Ti_2(\mathbf{L})_2(O^iPr)_4$ + 2 $Ti(O^iPr)_4$ (Scheme 1). Analogous equilibria have been observed by Sharpless and Boyle in tartrate and binaphtholate Ti(IV) complexes respectively.[20] Significantly, in this work we have solid-state evidence for both species being formed. The ^1H NMR spectrum from the product with $\mathbf{1}H_2$ has two isopropoxide resonances at 4.89 and 4.47 ppm respectively. From

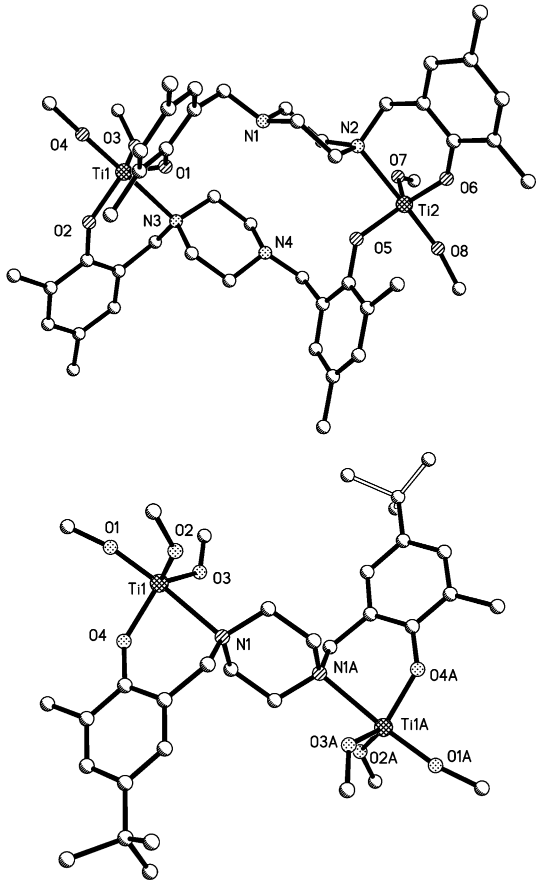


Fig. 1 **Top**: Solid-state structure of $Ti_2(\mathbf{1})_2(O^iPr)_4$. **Bottom**: Solid-state structure of $Ti_2(\mathbf{2})(O^iPr)_6$. See Table 1 for selected bond lengths and angles. The atoms labelled with the suffix A are related by the −x+1,−y,−z+1 symmetry operation.

DOSY NMR spectroscopic measurements and from comparison with neat Ti(O^{i}Pr)$_4$ it is clear that the resonance at 4.47 ppm arises from Ti(O^{i}Pr)$_4$ as this has a significantly higher diffusion rate than the other two species. The resonance at 4.89 ppm originates from Ti$_2$(**L**)(O^{i}Pr)$_6$ and Ti$_2$(**L**)$_2$(O^{i}Pr)$_4$ present in solution. The equilibrium has been further investigated by studying the variation of K (the equilibrium constant) with temperature, see Fig. 2 for the van't Hoff plot for the complexes isolated with **1–2**H$_2$, in CDCl$_3$. For the complexes formed with **3–5**H$_2$ the solution-state NMR spectra are consistent with one major species present in solution, which is the Ti$_2$(**L**)(O^{i}Pr)$_6$ form. In these examples it is hypothesised that the bulky group (^{t}Bu or amyl) in the *ortho* position (R^1) hinders the formation of the Ti$_2$**L**$_2$(O^{i}Pr)$_4$ species. It must be noted that the methylene region of the ^{1}H NMR spectra of the titanium dimers are non trivial due to a multitude of peaks, indicative of a species with low-symmetry coupled with fluctionality on the NMR timescale. Extensive variable temperature NMR spectroscopic investigations were attempted, which showed complex diastereomeric coupling in the methylene region.† However, from analysis of the aromatic and isopropoxide regions it is clear that the Ti$_2$(**L**)(O^{i}Pr)$_6$ form is prevalent in solution.† Elemental analysis supports the formation of the Ti$_2$(**L**)(O^{i}Pr)$_6$ species in the solid-state.

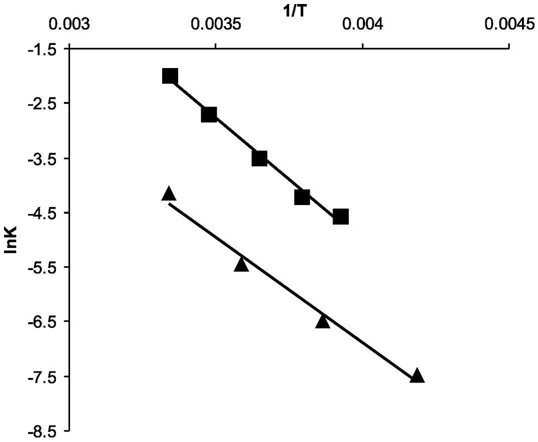


Fig. 2 van't Hoff plots for the equilibrium described in the text and Scheme 1. Squares ligand = **1**H$_2$ (concentration 17.4 mg ml^{-1}) ΔG = 5.1 kJ mol^{-1}, ΔH = 37.3 kJ mol^{-1} and ΔS = 108 J K^{-1} mol^{-1} Triangles ligand = **2**H$_2$ (concentration = 19.5 mg ml^{-1}) ΔG = 10.9 kJ mol^{-1}, ΔH = 30.7 kJ mol^{-1} and ΔS = 66.2 J K^{-1} mol^{-1}. Solvent = CDCl$_3$.

For ligands (**6–7**H$_2$) where R$_3$ = Me, two resonances for the isopropoxides are observed in the ^{1}H NMR spectrum, as expected due to the asymmetry in this ligand system. For the homopiperazine complex Ti$_2$(**8**)(O^{i}Pr)$_6$ was again the dominant species observed in the solution-state.

Polymerisation results

The complexes were tested for the ROP of *rac*-lactide under both solution (Table 2) and melt conditions (Table 3). Under solution conditions high conversions were observed after 24 h. However, relatively low molecular weight material was formed with a broad PDI and a very slight isotactic bias. It is probable that more than one polymer chain is growing per metal centre and this is the cause for the reduction in molecular weights compared to the theoretical values. From VT NMR spectroscopic studies (C$_6$D$_5$CD$_3$ at 80 °C) for complexes Ti$_2$(**3–8**)(O^{i}Pr)$_6$ the 2Ti:1 L dimer was the major moiety and this is presumably the catalytically active species. For complexes with ligands **1**H$_2$–**2**H$_2$ this is not the case from VT NMR the major form is Ti$_2$(**L**)$_2$(O^{i}Pr)$_4$. The presence of multiple species in solution could also be responsible for the broad range of molecular weights. Low molecular weights were formed, however, if the monomer:complex ratio was increased higher molecular weights could be produced.

Table 2 Solution polymerisation data

Ligand	Conv.[a]	M_n[b]	M_n[c]	PDI[c]	P_m[d]
1	96	7000	1800	1.72	0.5
1[e]	95	20600	12950	1.38	0.55
2	96	7000	1500	1.51	0.5
3	95	6900	5900	1.37	0.55
3[e]	96	20800	11300	1.48	0.55
4	95	6900	5600	1.37	0.6
5	94	6850	4200	1.34	0.6
6	91	6600	1200	2.21	0.55
7	96	7000	3700	1.28	0.55
8	94	6850	1200	2.31	0.5

Conditions: Monomer:complex ratio 100 : 1 solvent toluene, T = 80 °C, time = 24 h. [a] determined from ^{1}H NMR analysis; [b] Calculated M_n = (Conv/100 × 144 × 50) + 60. [c] determined from GPC analysis using THF as the solvent and reference to polystyrene standards; [d] determined from the analysis of the methine region of the ^{1}H homonuclear decoupled NMR spectrum. [e] Monomer:complex ratio 300 : 1.

Table 3 Melt polymerisation data

Ligand	Conv.[a]	M_n[b]	M_n[c]	PDI[c]	P_m[d]
1	96	20800	15900	1.86	0.5
1[e]	97	62900	55450	1.56	0.5
2	97	21000	23900	1.53	0.5
3	95	20600	20900	2.01	0.5
3[e]	97	62900	56750	1.57	0.5
4	99	21450	23700	2.01	0.5
5	95	20600	13200	1.56	0.5
6	96	20800	13600	1.53	0.55
7	95	20600	20400	1.63	0.55
8	99	21450	14200	2.03	0.5

Conditions: Monomer:complex ratio 300 : 1, T = 130 °C, time = 30 min. [a] determined from ^{1}H NMR analysis; [b] Calculated M_n = (Conv/100 × 144 × 150) + 60. [c] determined from GPC analysis using THF as the solvent and reference to polystyrene standards; [d] determined from the analysis of the methine region of the ^{1}H homonuclear decoupled NMR spectrum. [e] Monomer:complex ratio 900 : 1.

Attempts then turned to the polymerisation under melt conditions, where a much closer correlation between calculated and experimental molecular weights was seen. Complexes were seen to be incredibly active under these conditions and quantitative conversions were observed after only 30 min. In this case reasonably high molecular weights were obtained and again the PDIs were relatively large. Interestingly, these complexes are more active than traditional amine bis(phenolates) based on Ti(IV) – for example those with a -MeN(CH)$_2$NMe- back bone afforded a 70% yield after 2 h.[21] This is compared to a near quantitative conversion after 2 h in this work, under analogous conditions.

Table 4 X-ray crystallographic parameters

Complex	$Ti_2(1)_2(O^iPr)_4$	$Ti_2(2)(O^iPr)_6$	$Ti_2(3)(O^iPr)_6$	$Ti_2(4)(O^iPr)_6$	$Ti_2(5)(O^iPr)_6$	$Ti_2(6)(O^iPr)_6$	$Ti_2(7)(O^iPr)_6$	$Ti_2(8)(O^iPr)_6$
Empirical formula	$C_{59}H_{91}N_4O_8Ti_2$	$C_{46}H_{82}N_2O_8Ti_2$	$C_{52}H_{94}N_2O_8Ti_2$	$C_{52}H_{96}N_2O_8Ti_2$	$C_{62}H_{116}N_2O_8Ti_2$	$C_{53}H_{96}N_2O_8Ti_2$	$C_{47}H_{83}N_2O_8Ti_2$	$C_{56}H_{103}N_2O_8Ti_2$
Formula weight	1080.16	886.94	971.09	973.11	1113.37	985.12	449.98	1028.20
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic	Triclinic	Monoclinic	Triclinic	Triclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/n$	$P\bar{1}$	$P\bar{1}$	$P2_1/n$	$P\bar{1}$	$P\bar{1}$
a/Å	23.224(6)	9.5960(5)	10.8260(6)	9.4410(3)	11.0450(10)	9.2460(1)	9.4140(4)	14.2220(3)
b/Å	16.478(5)	23.1890(14)	18.8930(9)	10.0110(3)	13.2550(11)	24.3060(3)	9.9250(4)	15.3740(4)
c/Å	31.844(9)	11.4210(8)	14.5330(10)	15.1580(5)	13.9140(14)	26.2840(3)	13.9710(12)	17.4080(4)
α (°)	90	90	90	79.509(1)	115.990(5)	90	92.550(2)	69.6250(10)
β (°)	96.782(3)	91.398(3)	104.050(2)	84.676(1)	109.683(5)	91.5990(10)	94.4870(10)	89.943(2)
γ (°)	90	90	90	87.797(1)	91.805(5)	90	92.879(3)	62.866(1)
Volume/Å^3	12101(6)	2540.7(3)	2883.6(3)	1402.28(8)	1685.0(3)	5904.59(12)	1298.18(13)	3118.09(13)
Z	8	2	2	1	1	4	1	2
Dcalc/g cm^{-3}	1.186	1.159	1.118	1.152	1.097	1.108	1.151	1.095
μ/mm^{-1}	0.317	0.362	0.324	0.334	0.285	0.318	0.355	0.303
Refns collected	102329	27064	42193	19702	33515	67951	18880	53817
θ range/°	2.83–25.17	3.68–27.48	3.54–24.00	3.72–27.48	4.09–27.52	3.53–24.99	4.51–27.48	3.75–27.50
Indep. refns (R_{int})	23430, 0.0710	5764, 0.0931	4506. 0.1040	6423, 0.0458	7641, 0.0614	10306, 0.0726	5909, 0.0247	14138, 0.0624
Goodness-of-fit	1.061	1.049	1.064	1.025	1.017	1.049	1.137	1.006
R_1, wR_2 [$I > 2\sigma(I)$]	0.0727, 0.1800	0.0572, 0.1373	0.0434, 0.0873	0.0599, 0.1525	0.0590, 0.1504	0.0851, 0.2225	0.0604, 0.1663	0.0607, 0.1579
R_1, wR_2 [all data]	0.1017, 0.2005	0.0852, 0.1525	0.0682, 0.0985	0.0796, 0.1701	0.0903, 0.1713	0.10550.2403	0.0677, 0.1747	0.0976, 0.1847
Max, min difference/e Å^{-3}	0.644, –0.472	0.575, –0.539	0.233, –0.354	1.352, –0.653	0.761, –0.626	0.887, –0.504	0.942, –0.723	0.680, –0.630

Conclusion

In conclusion eight new piperazine Ti(IV) complexes have been prepared and characterised *via* single crystal X-ray diffraction. Two dimeric species have been isolated in the solid-state. In solution three species have been observed, however increasing the steric bulk facilitates the formation of one species in solution. The complexes have also been shown to be active for the ROP of *rac*-lactide with high molecular weights being produced under the industrially preferred melt conditions.

Experimental

For the preparation and characterisation of metal complexes, all reactions and manipulations were performed under an inert atmosphere of argon using standard Schlenk or glovebox techniques. $Ti(O^iPr)_4$ (97% Aldrich) was purified by vacuum distillation prior. *rac*-LA (Aldrich) was recrystallised from toluene and sublimed twice prior to use. All other chemicals were purchased from Aldrich. All solvents used in the preparation of metal complexes and polymerisation reactions were dry and obtained *via* SPS (solvent purification system). ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on a Bruker 250, 300 or 400 MHz instrument and referenced to residual solvent peaks. Coupling constants are given in Hertz. Elemental analyses were performed by Mr. A. K. Carver at the Department of Chemistry, University of Bath. The ligands were prepared according to standard literature procedures and the purity confirmed *via* ^1H/$^{13}C\{^1H\}$ NMR and HR-MS prior to use.

Polymerisation procedure:

For solvent-free polymerisations the monomer: complex ratio employed was 300 : 1 at a temperature of 130 °C, in all cases 1 g of *rac*-lactide was used. After the reaction time methanol (20 ml) was added to quench the reaction and the resulting solid was dissolved in dichloromethane. The solvents were removed in-vacuo and the resulting solid washed with methanol (3 × 50 ml) to remove any unreacted monomer. For solution polymerisations a monomer:complex ratio of 100 : 1 was used. In all cases 1 g of lactide and the appropriate amount of initiator were dissolved in toluene (10 ml) these were placed in a preheated oil bath and heated for the desired amount of time. The reaction was quenched by the addition of methanol (20 ml). ^1H NMR spectroscopy ($CDCl_3$) and GPC (THF) were used to determine tacticity and molecular weights (M_n and M_w) of the polymers produced; $P_{r/m}$ (the probability of heterotactic/isotactic linkages) were determined by analysis of the methine region of the homonuclear decoupled ^1H NMR spectra. The equations used to calculate $P_{r/m}$ are given by Coates.[2b] Gel Permeation Chromatography (GPC) analyses were performed on a Polymer Laboratories PL-GPC 50 integrated system using a PLgel 5 μm MIXED-D 300 × 7.5 mm column at 35 °C, THF solvent (flow rate 1.0 ml min^{-1}). The polydispersity index (PDI) was determined from M_w/M_n where M_n is the number average molecular weight and M_w the weight average molecular weight. The polymers were referenced to polystyrene standards.

Single crystal diffraction

All data {except those for $Ti_2(\mathbf{1})_2(O^iPr)_4$ which were recorded using Synchrotron radiation, $\lambda = 0.68890$ Å} were collected on a Nonius kappa CCD diffractometer with Mo-Kα radiation, $\lambda = 0.71073$ Å, see Table 4. $T = 150(2)$ K throughout and all structures were solved by direct methods and refined on F^2 data using the SHELXL-97 suite of programs.[22] Hydrogen atoms, were included in idealised positions and refined using the riding model. Refinements were generally straightforward with the following exceptions and points of note. In certain cases disorder was rife and in those cases it was deemed prudent to leave disordered groups isotropic on merit, in all cases the structures are unambiguously determined. In $Ti_2(\mathbf{2})(O^iPr)_6$ one ^{t}Bu group was disordered in a 60 : 40 ratio; $Ti_2(\mathbf{4})(O^iPr)_6$ contained two isopropoxide groups that were disordered in ratios of 50 : 50 and 60 : 40; these were treated anisotropically but their ADPs were less than ideal; $Ti_2(\mathbf{6})(O^iPr)_6$

the isopropoxide groups adorning Ti2 are disordered over two positions in a 55 : 45 ratio. The methyl groups of two ^{t}Bu (C20, C50) functionalities are disordered over two positions again in a 55 : 45 ratio. In addition the methyl group of the piperazine ring is disordered on three (C26–28) of the ring carbons in a 60 : 20 : 20 ratio. The disordered moieties have been refined isotropically. Only one H-atom has been added to each carbon C26–28; Ti$_2$(**7**)(O^{i}Pr)$_6$ two isopropoxide groups were disordered in ratios of 70 : 30 and 80 : 20, these were refined isotropically. Lastly, in Ti$_2$(**8**)(O^{i}Pr)$_6$ two isopropoxide groups were disordered in a 60 : 40 ratio.

Ligand and complex preparation

Typical procedures are as follows, see supporting information for the characterisation of ligands **2**H$_2$–**8**H$_2$ and their complexes.

1H$_2$ 2,4-di-methylphenol (8.50 g, 69.6 mmol), piperazine anhydrous (3.00 g, 34.8 mmol), and formaldehyde (38% in H$_2$O) (5.78 ml, 2.35 g, 78.1 mmol) were refluxed in MeOH (40 ml) for 24 h. During which time a white precipitate was observed this was filtered and washed with cold MeOH and dried to yield a white solid (5.64 g, 15.9 mmol, 46%). ^{1}H NMR (CDCl$_3$) 2.22 (6H, s, CH$_3$), 2.23 (6H, s, CH$_3$), 2.30–3.20 (8H, br, CH$_2$), 3.67 (4H, s, CH$_2$), 6.65 (2H, d, J = 1.5 Hz, ArH), 6.85 (2H, d, J = 1.5 Hz, ArH), 10.54 (2H, br, OH). ^{13}C{^{1}H} NMR (CDCl$_3$) 15.7 (CH$_3$), 20.5 (CH$_3$), 52.4 (CH$_2$), 61.4 (CH$_2$), 119.9 (Ar), 124.7 (Ar), 126.9 (Ar–H), 127.9 (Ar), 138.8 (Ar–H), 153.4 (Ar–O). Calc. m/z [C$_{22}$H$_{30}$N$_2$O$_2$ + H]$^+$ 355.2385. Found 355.2488.

Ti$_2$(**1**)(O^{i}Pr)$_6$ **1**H$_2$ (0.50 g, 1.41 mmol) and Ti(O^{i}Pr)$_4$ (0.85 ml, 2.87 mmol) were dissolved in CH$_2$Cl$_2$ (30 ml) and stirred (16 h). The solvent was removed *in-vacuo* and recrystallised from hot hexane (40 ml) to yield a pale yellow crystals (0.51 g, 0.64 mmol, 45%). The NMR was a mixture of Ti$_2$(**1**)(O^{i}Pr)$_6$ and Ti$_2$(**1**)$_2$(O^{i}Pr)$_4$ and Ti(O^{i}Pr)$_4$ as discussed in the text. The NMRs for the individual components are: Ti$_2$(**1**)(O^{i}Pr)$_6$ ^{1}H NMR (CDCl$_3$) (233 K) 1.26 (36H, d, J = 6.0 Hz, CH$_3$), 2.13 (6H, s, CH$_3$), 2.15 (3H, s, CH$_3$), 2.16 (3H, s, CH$_3$), 2.30–3.90 (8H, br, CH$_2$), 4.09 (4H, m, N–CH$_2$–Ar), 4.89 (6H, br, CH), 6.69 (2H, s Ar–H), 6.83 (2H, s, ArH). Ti$_2$(**1**)$_2$(O^{i}Pr)$_4$ ^{1}H NMR (233 K) 0.94 (3H, d, J = 6.0 Hz, CH$_3$), 0.97 (3H, d, J = 6.0 Hz, CH$_3$), 1.16 (6H, d, J = 6.0 Hz, Me), 1.20–1.40 (12H, br, CH$_3$), 2.08 (3H, s, Me), 2.10–2.25 (18H, br, CH$_3$), 2.28 (3H, s, CH$_3$), 2.30–3.90 (16H, br, CH$_2$), 4.09 (8H, m, CH$_2$), 4.89 (4H, b, CH), 6.57 (2H, s, Ar–H), 6.76 (2H, s, Ar–H), 6.84 (2H, s, Ar–H), 6.92 (2H, s, Ar–H). Ti(O^{i}Pr)$_4$ ^{1}H NMR (CDCl$_3$) (233 K) 1.26 (24H, d, J = 6.0 Hz, CH$_3$), 4.47 (4H, sept, J = 6.0 Hz, CH). ^{13}C{^{1}H} NMR (CDCl$_3$) 16.8 (CH$_3$), 20.5 (CH$_3$), 26.7 (CH$_3$), 52.0 (CH$_2$), 77.8 (CH), 122.7 (Ar), 124.8 (Ar), 127.0 (Ar), 127.7 (Ar–H), 130.8 (Ar–H), 158.2 (Ar–O). Calc.(%) for C$_{40}$H$_{70}$N$_2$O$_8$Ti$_2$: C 59.85, H 8.79, N 3.49. Found (%); C 59.3, H 8.80, N 3.72.

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