Influence of ligand backbone flexibility in group 4 metal complexes of tetradentate mixed tertiary amine/alkoxide ligands†

Joanna K. Day,[ab] Rebecca E. Baghurst,[a] Robert R. Strevens,[a] Mark E. Light,[c] Michael B. Hursthouse,[c] Bruno F. Stengel,[d] Ian A. Fallis*[a] and Simon Aldridge*[ab]

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Simple epoxide ring opening chemistry using the cyclic secondary amine 1,4-diazacycloheptane or the related linear species *N*,*N*′-dimethylethylenediamine, and racemic (±)−3,3-dimethyl-1,2-epoxybutane gives access to the pendant alcohol functionalised ditertiary amine pro-ligands $[HOCH(^tBu)CH_2N(R)CH_2]_2$ ($H_2\mathbf{L^1}$: $R_2 = CH_2CH_2CH_2$; $H_2\mathbf{L^2}$: $R_2 = Me_2$). The contrasting reactions of $H_2\mathbf{L^1}$ and $H_2\mathbf{L^2}$ towards homoleptic group 4 alkoxides highlight the crucial role of ligand backbone flexibility in complex formation. Thus, the chemistry of the more conformationally rigid system $(\mathbf{L^1})^{2-}$ appears to be constrained by the cyclic ligand core, such that it adopts a bridging (μ_2:η^2,η^2) mode of coordination towards Ti(IV), leading to dinuclear metal systems [*e.g.* $\mathbf{L^1}Ti_2(O^iPr)_6$]. By contrast, the more flexible linear system $(\mathbf{L^2})^{2-}$ binds to both Ti(IV) and Zr(IV) in a chelating fashion leading, for example, to the synthesis of the C_2 symmetric mononuclear complex *rac*-$\mathbf{L^2}Ti(O^iPr)_2$. Thus, a simple synthesis of diastereomerically pure, C_2 symmetric, geometrically *cis* octahedral Ti(IV) complexes from racemic precursors is presented.

Introduction

The design and synthesis of ancillary ligand frameworks offering an alternative to cyclopentadienyl-based systems in early transition metal olefin polymerisation catalysts remains an area of intense research activity.[1] Within this field, ligands featuring anionic oxygen or nitrogen donors (*e.g.* alkoxides/aryloxides, amides or imides) are particularly attractive targets given their π-donor capabilities and the strong electrostatic component to the metal–ligand interaction typically found with electropositive metals. For anionic oxygen ligands, RO^-, the avoidance of secondary bridging interactions has led to the exploitation of a number of strategies in complex synthesis, *e.g.* the incorporation of steric bulk, chelating ligand frameworks and/or additional neutral donor atoms.[2] Hence, for example chelating, sterically encumbered or heteroatom-functionalized bis(*aryl*oxide) complexes of titanium and zirconium have been shown to be highly active olefin polymerisation catalysts,[3–5] and *alk*oxide systems bearing ancillary N-donors have also been the subject of a number of recent studies.[6]

The use of metal complexes in asymmetric transformations, *e.g.* C_2 symmetric (or pseudo-C_2 symmetric) species in the isotactic polymerisation of propylene, has led to the development of a number of strategies for the synthesis of such complexes. Tetradentate bis(aryloxide) ligands featuring a linear array of donor atoms (Scheme 1) have featured prominently among these, with examples of both pre-constructed C_2 symmetric pro-ligands[4b,f,g,5m] and coordination induced C_2 symmetry having been reported.[4d,k,u,5p,6b,7] Within this area we have been interested in developing synthetic routes to sterically encumbered bis(tertiary amine) bis(alkoxide) ligand frameworks, through the ring opening of (±)-3,3-dimethyl-1,2-epoxybutane (Scheme 2). It was envisaged that the use of racemic precursors and the separation of diastereomers by simple crystallization at either the pro-ligand or complex stage would provide a convenient route to C_2 symmetric species.

Experimental

(i) General considerations

Unless otherwise stated, all manipulations were carried out under a nitrogen or argon atmosphere using standard Schlenk line or dry-box techniques. Solvents were pre-dried over sodium wire (hexanes, toluene) or molecular sieves (acetonitrile) and purged with nitrogen prior to distillation from the appropriate drying agent (hexanes: potassium, toluene: sodium, acetonitrile: calcium hydride). Benzene-d_6 and chloroform-*d* (both Goss) were degassed and dried over potassium (benzene-d_6) or molecular sieves (chloroform-*d*) prior to use.

[a] *Cardiff School of Chemistry, Main Building, Park Place, Cardiff, UK CF10 3AT. E-mail: simon.aldridge@chem.ox.ac.uk; Fax: (029) 20874030; Tel: (029) 20875495*
[b] *Inorganic Chemistry, University of Oxford, South Parks Road, Oxford, UK OX1 3QR*
[c] *EPSRC National Crystallography Service, University of Southampton, Highfield, Southampton, UK SO17 1BJ*
[d] *Johnson Matthey Catalysts, Billingham, PO Box 1, Belasis Avenue, Cleveland, UK TS23 1LB*

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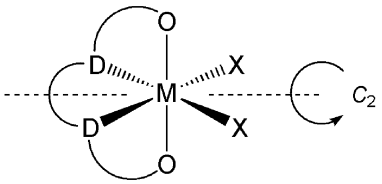
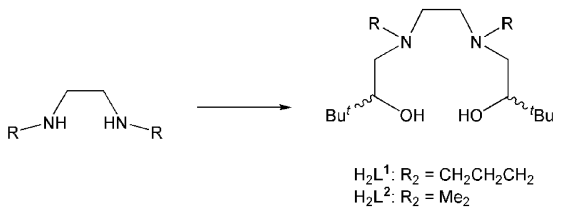


Scheme 1 Target C_2 symmetric, geometrically *cis*, octahedral complexes featuring tetradentate bis(donor) bis(aryl/alkoxide) ligands.



Scheme 2 Syntheses of ligand precursors $H_2\mathbf{L^1}$ and $H_2\mathbf{L^2}$. Reagents and conditions: excess (±)-3,3-dimethyl-1,2-epoxybutane, acetonitrile, sealed tube, 100 °C, 72 h, yield *ca.* 40% for $H_2\mathbf{L^1}$ [obtained as the *rac* (*R*,*R*/*S*,*S*) diastereomers], 59% for $H_2\mathbf{L^2}$ [obtained as a mixture of the *rac* (*R*,*R*/*S*,*S*) and *meso* (*R*,*S*) diastereomers].

Ligand precursors [1,4-diazacycloheptane (Lancaster), 1,4-diazacyclohexane (Avocado), *N*,*N*′-dimethylethylenediamine (Aldrich) and (±)-3,3-dimethyl-1,2-epoxybutane (Lancaster)] and metal reagents [$Ti(O^iPr)_4$ (Lancaster), $Ti(OEt)_4$ and $Zr(O^nPr)_4$ (all Aldrich)] were used as received. NMR spectra were measured on a Bruker AM-400 or JEOL 300 Eclipse Plus FT-NMR spectrometer. Residual signals of solvent were used as reference for ^{1}H and ^{13}C NMR. Infrared spectra were measured for each compound pressed into a disk with an excess of dried KBr or as a solution in an appropriate solvent on a Nicolet 500 FT-IR spectrometer. Mass spectra were measured by the EPSRC National Mass Spectrometry Service Centre, University of Wales, Swansea. Perfluorotributylamine was used as a standard for high resolution EI mass spectra. Elemental microanalysis was performed by Warwick Analytical Services or by the departmental service. Abbreviations: br = broad, s = singlet, d = doublet, t = triplet, q = quartet, sept = septet, m = multiplet.

(ii) Ligand syntheses

***N*,*N*′-Bis(2-hydroxy-3,3-dimethylbutyl)-1,4-diazacycloheptane ($H_2\mathbf{L^1}$).** To a solution of 1,4-diazacycloheptane (0.90 g, 8.99 mmol) in acetonitrile (10 ml), contained in a pressure tube, was added excess (±)-3,3-dimethyl-1,2-epoxybutane (2.69 g, 26.86 mmol). The reaction mixture was stirred at 100 °C for 24 h, and the white crystals which formed on cooling of the reaction mixture were filtered off and washed with cold acetonitrile. Although single crystals suitable for X-ray diffraction could not be obtained, the ^{1}H and ^{13}C NMR data for crystalline samples re-dissolved in chloroform-*d* imply that only one set of diastereomers is present; the crystal structures of nickel(II) and titanium(IV) complexes obtained by further reaction chemistry indicate that this is the *rac* (*R*,*R*/*S*,*S*) pair. Yield: 1.15 g, 43%. ^{1}H NMR ($CDCl_3$, 25 °C): δ 0.85 (s, 18 H, ^{t}Bu), 1.85 (m, 2H, $NCH_2CH_2CH_2N$), 2.20 (m, 2H, C(H)(*H*)CHOH), 2.50 (m, 2H, C(*H*)(H)CHOH), 2.55 (m, 4H, NCH_2), 2.82 (m, 4H, NCH_2), 3.22 (m, 2H, C*H*OH), 3.82 (br s, 2H, O*H*). ^{13}C NMR ($CDCl_3$, 25 °C): δ 25.7 (CH_3 of ^{t}Bu), 28.2 ($NCH_2CH_2CH_2N$), 33.2 (^{t}Bu quaternary), 54.4 (NCH_2), 56.2 (NCH_2), 59.5 (CH_2CHOH), 73.7 (*C*HOH). IR (KBr disk, cm^{-1}) 3417, 2955, 2855, 1653, 1467, 1410, 1362, 1244, 1154, 1088, 1013, 944, 863, 821. Mass spectrum (APCI): 301.6 $(M + H)^+$. Elemental analysis. Calc. for $C_{17}H_{36}N_2O_2$: C, 67.95; H, 12.08; N, 9.32. Found: C, 68.31; H, 12.55; N, 8.99%. In an analogous manner, the corresponding reaction using 1,4-diazacyclo*hexane* generates crystalline samples of *N*,*N*′-bis(2-hydroxy-3,3-dimethylbutyl)-1,4-diazacyclohexane which can be shown by a combination of NMR and X-ray crystallographic studies to contain solely the meso (*R*,*S*) isomer.[8]

***N*,*N*′-Bis(2-hydroxy-3,3-dimethylbutyl)dimethylethylenediamine ($H_2\mathbf{L^2}$).** $H_2\mathbf{L^2}$ was synthesized in an analogous manner to $H_2\mathbf{L^1}$, using *N*,*N*′-dimethylethylenediamine (0.50 g, 5.67 mmol) and isolated after removal of volatiles from the reaction mixture *in vacuo* as a clear oil containing a mixture of *rac* (*R*,*R*/*S*,*S*) and *meso* (*R*,*S*) diastereoisomers at room temperature (waxy solid at −25 °C). Yield: 0.63 g, 59%. ^{1}H NMR ($CDCl_3$, 25 °C): δ 0.85 (s, 36 H, coincident ^{t}Bu groups of both pairs of diastereomers), 2.23, 2.26 (s, each 6H, NCH_3), 2.31–2.68 (br overlapping m, 16H, overlapping NCH_2 groups of both diastereomers), 3.24, 3.27 (m, each 2H, C*H*OH), 4.31, 4.53 (br s, each 2H, O*H*). ^{13}C NMR ($CDCl_3$, 25 °C): δ 25.87, 25.89 (CH_3 of ^{t}Bu), 33.4 (coincident ^{t}Bu quaternary carbons of both pairs of diastereomers), 42.5, 43.5 (NCH_3), 54.7, 55.8 (NCH_2), 58.6, 59.2 (CH_2CHOH), 74.6, 74.7 (*C*HOH). IR (KBr disk, cm^{-1}) 2957, 1463, 1363, 1217, 1090, 1017, 937. Mass spectrum (APCI): 289.1 $(M + H)^+$. Exact mass. Calc. for $C_{16}H_{36}N_2O_2$: 289.2855. Found: 289.2859. Accurate elemental analysis proved impossible for this oil.

(iii) Complex syntheses

$\mathbf{L^1}Ti_2(O^iPr)_6$. Neat titanium tetrakis(isopropoxide) (0.50 ml, 1.76 mmol) was added to a $H_2\mathbf{L^1}$ (0.50 g, 1.66 mmol) and the reaction mixture stirred until it became solid (*ca.* 4 h). Isopropanol formed during the reaction was then removed *in vacuo* and the resulting solid redissolved in dry hexanes. Colourless crystals suitable for X-ray diffraction were grown by cooling the hexanes solution to −30 °C. Variation in reaction conditions (stoichiometry of reaction, order of reagent addition, temperature) did not result in the isolation of alternative products containing a different Ti : $\mathbf{L^1}$ ratio. The yield of $\mathbf{L^1}Ti_2(O^iPr)_6$ was optimised by consideration of the 2 : 1 Ti : $\mathbf{L^1}$ ratio to 64% (*ca.* 0.75 g scale). ^{1}H NMR (C_6D_6, 25 °C): δ 1.00 (s, 18H, ^{t}Bu), 1.37 (d, J = 6.0 Hz, 36H, CH_3 of ^{i}Pr), 1.85 (m, 2H, $NCH_2CH_2CH_2N$), 2.55 (m, 2H, C*H*(H)CHO), 2.84 (m, 2H, C*H*(H)CHO), 3.50 (br overlapping m, 8H, NCH_2 of diazacycloheptane), 4.08 (m, 2H, C(*H*)O), 4.92 (septet, J = 6.0 Hz, 6H, CH of ^{i}Pr). ^{13}C NMR: δ 26.3 (CH_3 of ^{t}Bu), 27.8 (CH_3 of ^{i}Pr), 31.1 ($NCH_2CH_2CH_2N$), 35.6 (^{t}Bu quaternary), 58.1 ($NCH_2CH_2CH_2N$), 60.1 (NCH_2CH_2N), 62.3 ($CH_2C(H)O$), 77.4 (CH of ^{i}Pr), 83.1 (CHO). Mass spectrum (FAB): 747.3 $(M - H)^+$. Elemental

analysis. Calc. for $C_{35}H_{76}N_2O_8Ti_2$: C, 56.15; H, 10.23; N, 3.74. Found: C, 55.81; H, 10.01; N, 3.89%.

$[L^1Ti(OEt)]_2(\mu_2\text{-O})$. $[L^1Ti(OEt)]_2(\mu_2\text{-O})$ was prepared from titanium tetrakis(ethoxide) (0.40 ml, 1.75 mmol) and H_2L^1 (0.50 g, 1.66 mmol) using the method detailed above for $L^1Ti_2(O^iPr)_6$. The product was isolated in very low yield (<5%) as colourless crystals obtained from hexanes solution at −30 °C. Complete characterization was frustrated in this case by the small amount of compound obtained. ^{1}H NMR (C_6D_6, 25 °C): δ 0.99 (s, 36H, ^{t}Bu), 1.21 (t, J = 8.0 Hz, 6H, OCH_2CH_3), 1.88 (m, 4H, $NCH_2CH_2CH_2N$), 2.68 (br m, 4H, CH(H)CHO), 2.78 (m, 4H, CH(H)CHOH), 3.20–3.68 (br overlapping m, 16H, NCH_2 of diazacycloheptane), 3.91 (q, J = 8.0 Hz, 4H, OCH_2CH_3), 4.15 (m, 4H, CHO). Mass spectrum (FAB): 799.6 $(M - H)^+$.

$L^2Ti(O^iPr)_2$. $L^2Ti(O^iPr)_2$ was prepared from titanium tetrakis(isopropoxide) (0.50 ml, 1.76 mmol) and H_2L^2 (0.50 g, 1.74 mmol) using the method detailed above for $L^1Ti_2(O^iPr)_6$, and isolated as colourless crystals after two recrystallizations from concentrated hexanes solution (yield: 44%, *ca.* 1 g scale). Although the oily ligand precursor H_2L^2 was used as a mixture of *rac* (*R*,*R*/*S*,*S*) and *meso* (*R*,*S*) isomers, X-ray diffraction analysis of the crystalline titanium complex reveals it has approximate (non-crystallographically imposed) C_2 symmetry and contains the *rac* (*R*,*R*/*S*,*S*) isomers of the ligand. The oily hexanes-soluble residue remaining after recrystallization can be shown by ^{1}H and ^{13}C NMR to be the C_1 symmetric complex derived from the *meso* (*R*,*S*) ligand precursor. Attempts to obtain this second isomer in pure form for comparative structural and catalytic studies were frustrated by its oily nature and the difficulty in removing the last traces of the C_2 isomer. Characterizing data for crystalline product (*R*,*R*/*S*,*S*): ^{1}H NMR (C_6D_6, 25 °C): δ 1.15 (s, 18H, ^{t}Bu), 1.32 (d, J = 6.3 Hz, 6H, CH_3 of ^{i}Pr), 1.38 (d, J = 9.0 Hz, 2H, NCH_2CH_2N), 1.50 (d, J = 6.0 Hz, 6H, CH_3 of ^{i}Pr), 2.14 (dd, J = 10.7, 4.1 Hz, 2H, NCH_2CHO), 2.22 (s, 6H, NCH_3), 2.74 (d, J = 9.0 Hz, 2H, NCH_2CH_2N), 3.09 (virtual t, J = 11.0 Hz, 2H, CH_2CHO), 3.84 (dd, J = 10.6, 4.1 Hz, 2H, NCH_2CHO), 5.14 (sept, J = 6.0 Hz, 2H, CH of ^{i}Pr). ^{13}C NMR (C_6D_6, 25 °C): δ 26.0, 26.7 (CH_3 of ^{i}Pr), 26.4 (CH_3 of ^{t}Bu), 36.5 (^{t}Bu quaternary), 45.3 (NCH_3), 51.9 (NCH_2 backbone), 62.8 (NCH_2 ligand arm), 74.6 (CH of ^{i}Pr), 84.2 (CHO). Mass spectrum (EI): 452.4 M^+. Exact mass. Calc. for $TiC_{22}H_{48}N_2O_4$ 452.3088: Found: 452.3079. Elemental analysis. Calc. for $TiC_{22}H_{48}N_2O_4$: C, 58.40; H, 10.69; N, 6.19. Found: C, 58.01; H, 10.14; N, 6.24%. ^{1}H and ^{13}C NMR data for oily product (*R*,*S*): ^{1}H NMR (C_6D_6, 25 °C): δ 0.93 (s, 9H, ^{t}Bu), 1.03 (s, 9H, ^{t}Bu), 1.29 (d, J = 6.0 Hz, 3H, CH_3 of ^{i}Pr), 1.33 (d, J = 6.0 Hz, 3H, CH_3 of ^{i}Pr), 1.39 (d, J = 3.0 Hz, 6H, CH_3 of ^{i}Pr), 1.44 (d, J = 3.0 Hz, 6H, CH_3 of ^{i}Pr), 1.71 (dd, J = 12.4, 4.1 Hz, 1H, NCH_2CHO), 1.85 (dd, J = 14.0, 4.0 Hz, 1H, NCH_2CHO), 2.16 (m, 2H, NCH_2CH_2N), 2.41 (s, 3H, NCH_3), 2.42 (s, 3H, NCH_3), 2.75 (m, 2H, NCH_2CH_2N), 3.06 (virtual t, J = 11.0 Hz, 1H, CH_2CHO), 3.13 (virtual t, J = 11.0 Hz, 1H, CH_2CHO), 3.79 (dd, J = 10.8, 4.4 Hz, 1H, NCH_2CHO), 4.33 (dd, J = 9.8, 5.2 Hz, 1H, NCH_2CHO), 4.96 (sept, J = 6.0 Hz, 2H, coincident CH of ^{i}Pr). ^{13}C NMR (C_6D_6, 25 °C): δ 26.0, 26.2 (CH_3 of ^{t}Bu), 25.9, 26.2, 26.6, 26.9 (CH_3 of ^{i}Pr), 34.6 (coincident ^{t}Bu quaternary carbons), 47.9, 50.2 (NCH_3), 56.7, 59.2 (NCH_2 backbone), 59.4, 66.0 (NCH_2 ligand arm), 74.7, 74.8 (CH of ^{i}Pr), 84.8, 85.1 (CHO).

$(L^2)_2Zr$. $(L^2)_2Zr$ was prepared from zirconium tetrakis (propoxide) (0.78 ml of a 70% wt solution in propanol, 1.74 mmol) and H_2L^2 (0.50 g, 1.74 mmol) using the method detailed above for $L^1Ti_2(O^iPr)_6$, and isolated as colourless crystals from a concentrated hexanes solution. In contrast to the crude reaction mixture, the crystalline product gives rise to relatively simple ^{1}H and ^{13}C NMR spectra indicating only two distinct ^{t}Bu and NMe resonances, with subsequent crystallographic analysis revealing both $(L^2)^{2-}$ ligands to be of *meso* (*R*,*S*) stereochemistry. The yield was subsequently optimised by consideration of the 1 : 2 Zr : L^2 ratio to 39% (*ca.* 1.00 g scale). ^{1}H NMR (C_6D_6, 25 °C): δ 1.08 (s, 18H, ^{t}Bu), 1.10 (s, 18H, ^{t}Bu), 1.81 (m, 4H, NCH_2CHO), 2.14 (s, 6H, NCH_3), 2.34 (m, 4H, NCH_2CH_2N), 2.80 (m, 4H, NCH_2CH_2N), 2.91 (s, 6H, NCH_3), 3.14 (t, J = 12.0 Hz, 2H, CH_2CHO), 3.29 (t, J = 11.6 Hz, 2H, CH_2CHO), 3.78 (dd, J = 2.6, 11.1 Hz, 2H, NCH_2CHO), 4.09 (dd, J = 5.1, 11.4 Hz, 2H, NCH_2CHO). ^{13}C NMR (C_6D_6, 25 °C): δ 26.9, 27.2 (CH_3 of ^{t}Bu), 35.2, 35.3 (^{t}Bu quaternary), 43.4, 48.6 (NCH_3), 57.2, 58.9 (NCH_2CH_2N), 60.4, 64.5 (NCH_2), 78.9, 83.9 (CHO). Mass spectrum (FAB): 661.3 $(M - H)^+$. Exact mass. Calc. for $ZrC_{32}H_{68}N_4O_4$: 661.4204. Found: 661.4187. Elemental analysis. Calc. for $ZrC_{32}H_{68}N_4O_4$: C, 57.87; H, 10.32; N, 8.44. Found: C, 57.41; H, 10.00; N, 8.59%.

(iv) Crystallographic method

Data for $L^1Ti_2(O^iPr)_6$, $L^1{}_2Ti_2(OEt)_2(\mu\text{-O})$, $L^2Ti(O^iPr)_2$ and $L^2{}_2Zr$ were collected on an Bruker Nonius Kappa CCD diffractometer. Data collection and cell refinement were carried out using DENZO and COLLECT; structure solution and refinement used SHELXS-97 and SHELXL-97, respectively; absorption corrections were performed using SORTAV.[9] Details of each data collection, structure solution and refinement can be found in Table 1. Relevant bond lengths and angles are included in the figure captions and complete details of each structure have been deposited with the CCDC (numbers as listed in Table 1). In addition, complete details for each structure have been included in the supporting information. The two OEt ligands in $L^1{}_2Ti_2(OEt)_2(\mu\text{-O})$ are disordered and were modeled over two orientations (70 : 30 and 53 : 47 occupancy factors) and refined isotropically. The structure was treated as a racemic twin with the BASF parameter refining to 0.4.

CCDC reference numbers 286913–286916.

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b608680b

Results and discussion

(i) Ligand precursors

The ligand precursors H_2L^1 and H_2L^2 have been synthesised *via* the nucleophilic ring opening of racemic (±)-3,3-dimethyl-1,2-epoxybutane by the cyclic secondary amine 1,4-

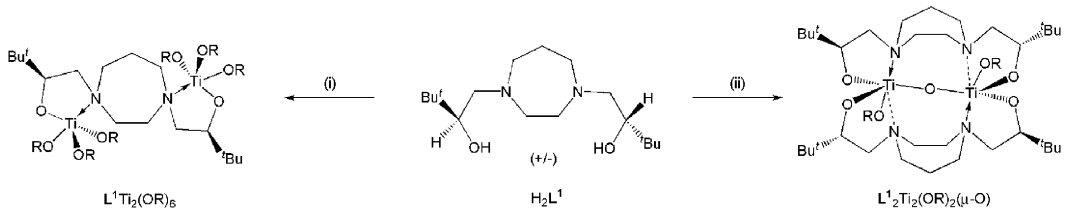
diazacycloheptane, or the related linear species *N*,*N*′-dimethylethylenediamine (to give $H_2\mathbf{L^1}$ and $H_2\mathbf{L^2}$, respectively; Scheme 2). Forcing conditions (excess epoxide, acetonitrile solution at 100 °C in a pressure tube) are required to drive the reaction to completion, the analogous chemistry in ethanol at room temperature leading to incomplete conversion. Similar chemistry can be also applied to 1,4-diazacyclo*hexane* to yield the related compound *N*,*N*′-bis(2-hydroxy-3,3-dimethylbutyl)-1,4-diazacyclohexane.[8] $H_2\mathbf{L^1}$ (like its diaminocyclohexane analogue) is a white crystalline solid which has been characterised by multinuclear NMR and IR spectroscopies, mass spectrometry and elemental analysis. In both cases, the ^{1}H and ^{13}C NMR spectra (in chloroform-*d*) of crystalline ligand samples obtained by direct cooling of the acetonitrile reaction mixture, show single resonances for the *tert*-butyl methyl groups, indicating the presence of only one pair of diastereomers [*i.e.* either *rac* (*R*,*R*/*S*,*S*) or *meso* (*R*,*S*)]. In the case of *N*,*N*′-bis(2-hydroxy-3,3-dimethylbutyl)-1,4-diazacyclohexane, a crystallographic study reveals a centrosymmetric space group, in which each molecule lies on a centre of inversion coincident with the centre of the 1,4-diazacyclohexane ring. Consequently, this ligand necessarily features the *meso* (*R*,*S*) stereochemistry.[8] Although crystalline $H_2\mathbf{L^1}$ can also be obtained by direct cooling of the acetonitrile reaction mixture, the crystals so obtained are not suitable for X-ray diffraction. In this case, however, crystallographic studies (i) of alkoxo-titanium complexes formed by reaction of $H_2\mathbf{L^1}$ with $Ti(OR)_4$ (R = ^{i}Pr, Et) (*vide infra*); and (ii) of the complex $[trans\text{-}(H_2\mathbf{L^1})Ni(OH_2)_2]^{2+}$ isolated as the bis(perchlorate) salt from the subsequent reaction of crystalline $H_2\mathbf{L^1}$ with $Ni(ClO_4)_2 \cdot 6H_2O$ in ethanol,[10] confirm that $H_2\mathbf{L^1}$ crystallises from the reaction mixture as the *rac* (*R*,*R*/*S*,*S*) pair of diastereomers. Yields of crystalline *rac*-$H_2\mathbf{L^1}$ and *meso*-*N*,*N*′-bis(2-hydroxy-3,3-dimethylbutyl)-1,4-diazacyclohexane are typically of the order of 40%, reflecting the fact that in each case the alternative pair of diastereomers remains in solution. In contrast, $H_2\mathbf{L^2}$ can only be obtained as an oily liquid at room temperature (cooling to a waxy solid at −25 °C). ^{1}H and ^{13}C NMR spectra clearly indicate the presence of both pairs of diastereoisomers, the separation of which by fractional crystallisation proves impossible. Consequently, separation of diastereomeric species at the metal complex stage, making use of the differential solubilities of more tractable derivatives was thought to offer a more practical methodology (*vide infra*).

(ii) Complexes of group 4 metals

The coordination chemistries of ligands $(\mathbf{L^1})^{2-}$ and $(\mathbf{L^2})^{2-}$ with respect to group 4 metal centres have been investigated *via* the reactions of $H_2\mathbf{L^1}$ and $H_2\mathbf{L^2}$ with homoleptic titanium and zirconium tetrakis(alkoxide) precursors (Schemes 3 and 4).

Table 1 Details of data collection, structure solution and refinement for $\mathbf{L^1}Ti_2(O^iPr)_6$, $\mathbf{L^1}_2Ti_2(OEt)_2(\mu\text{-}O)$, $\mathbf{L^2}Ti(O^iPr)_2$ and $\mathbf{L^2}_2Zr$ (refinement method: full-matrix least squares (F^2))

Compound	$\mathbf{L^1}Ti_2(O^iPr)_6$	$\mathbf{L^1}_2Ti_2(OEt)_2(\mu\text{-}O)$	$\mathbf{L^2}Ti(O^iPr)_2$	$\mathbf{L^2}_2Zr$
Empirical formula	$C_{35}H_{76}N_2O_8Ti_2$	$C_{38}H_{78}N_4O_7Ti_2$	$C_{22}H_{48}NO_4Ti$	$C_{32}H_{68}N_4O_4Zr$
M_r	748.78	798.84	452.52	664.12
T/K	150(2)	120(2)	120(2)	120(2) K
CCDC no.	286 915	286 913	286 916	286 914
λ/Å	0.71073	0.71073	0.71073	0.71073
Crystal system	Triclinic	Orthorhombic	Triclinic	Triclinic
Space group	$P\bar{1}$	$Pca2_1$	$P\bar{1}$	$P\bar{1}$
a/Å	11.0190(5)	19.7850(10)	8.830(5)	10.762(2)
b/Å	14.3144(6)	11.7253(4)	9.726(5)	12.115(2)
c/Å	15.7604(8)	19.6134(7)	17.047(5)	15.963(3)
α/°	70.240(3)	90	93.801(5)	76.68(3)
β/°	88.145(2)	90	98.098(5)	72.59(3)
γ/°	71.787(2)	90	112.844(5)	68.58(3)
V/Å^3	2214.83(18)	4550.0(3)	1323.9(11)	1831.5(6)
D_c/Mg m^{-3}	1.123	1.166	1.135	1.204
Z	2	4	2	2
μ/mm^{-1}	0.404	0.397	0.349	0.337
F(000)	816	1736	496	720
Crystal size/mm	0.20 × 0.18 × 0.15	0.20 × 0.15 × 0.05	0.30 × 0.20 × 0.02	0.20 × 0.20 × 0.20
θ Range/°	3.05–25.39	2.92–25.02	2.98–25.03	2.92–27.45
Index ranges *hkl*	−13 to 13, −17 to 17, −18 to 19	−23 to 18, −10 to 13, −23 to 21	−10 to 10, −11 to 11, −20 to 20	−13 to 13, −15 to 15, −10 to 20
Reflections collected	31 559	22 572	13 694	36 431
Independent reflections (R_{int})	8020 (0.1319)	7502 (0.0809)	4583 (0.0501)	8322 (0.0562)
Completeness to θ_{max} (%)	98.5	99.2	97.8	99.4
Absorption correction	SORTAV	Semi-empirical from equivs	Semi-empirical from equivs	SORTAV
Max., min. transmission	0.9419, 0.9236	0.9804, 0.9249	0.9930, 0.9025	0.9356, 0.8956
Data/restraints/parameters	8020/0/442	7502/9/471	4583/0/275	8322/0/407
Goodness-of-fit on F^2	1.002	1.008	1.030	1.032
Final R indices [$I > 2\sigma(I)$]	$R1$ = 0.0684, $wR2$ = 0.1524	$R1$ = 0.0607, $wR2$ = 0.1248	$R1$ = 0.0416, $wR2$ = 0.0881	$R1$ = 0.0373, $wR2$ = 0.0851
R Indices (all data)	$R1$ = 0.1451, $wR2$ = 0.1758	$R1$ = 0.1033, $wR2$ = 0.1410	$R1$ = 0.0538, $wR2$ = 0.0932	$R1$ = 0.0458, $wR2$ = 0.0886
$\Delta\rho_{max,\ min}$/e Å^{-3}	0.451, −0.427	0.618, −0.314	0.209, −0.366	1.117, −0.520

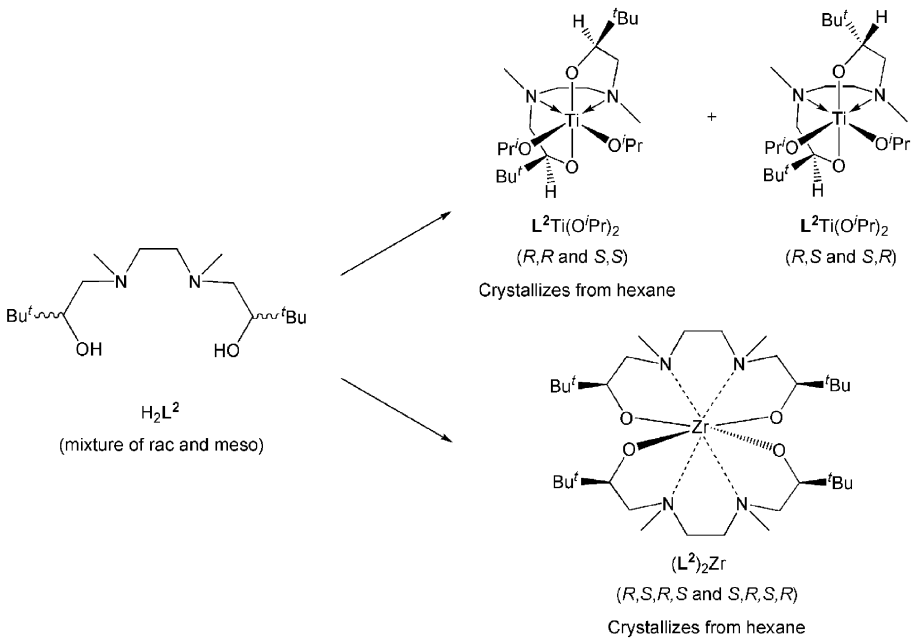


Scheme 3 Syntheses of dinuclear titanium complexes $\mathbf{L^1}Ti_2(O^iPr)_6$ and $\mathbf{L^1}_2Ti_2(OEt)_2(\mu\text{-}O)$. Reagents and conditions: (i) $Ti(O^iPr)_4$ (2 equiv.), neat reagents, 20 °C, 4 h, 64%; (ii) $Ti(OEt)_4$ (1.05 equiv.), neat reagents, adventitious water, 20 °C, 4 h, <5%.

(a) Coordination chemistry of $(\mathbf{L^1})^{2-}$. The reactions of $H_2\mathbf{L^1}$ with titanium alkoxides lead to the formation of dinuclear complexes in which the tetradentate ligand bridges between two Ti(IV) centres. Thus, the reaction of *rac*-$H_2\mathbf{L^1}$ with titanium tetrakis(isopropoxide) at room temperature in the absence of solvent gives a white crystalline solid, for which the integration of ^{t}Bu and ^{i}Pr ^{1}H NMR signals (1 : 2) implies an $\mathbf{L^1}$: O^{i}Pr ratio of 1 : 6. The formulation $\mathbf{L^1}Ti_2(O^iPr)_6$ is given further credence by the results of mass spectrometry experiments and has been confirmed crystallographically (Fig. 1 and Table 1).

The X-ray crystal structure of $\mathbf{L^1}Ti_2(O^iPr)_6$ shows that the complex contains two $Ti(O^iPr)_3$ fragments linked by a single bridging $(\mathbf{L^1})^{2-}$ ligand which binds to each metal centre through one alkoxide and one tertiary amine donor. Each titanium centre is thus five coordinate, with three isopropoxide ligands being retained from the starting material. The geometry around each titanium atom appears to be a distorted trigonal bipyramid with the $\mathbf{L^1}$ amine donor and one isopropoxide ligand occupying the axial sites [O(2)–Ti(1)–N(1) 171.0(1)°, O(6)–Ti(2)–N(2) 170.4(1)°]. The $\mathbf{L^1}$-derived alkoxide donor and the two remaining isopropoxides occupy the three equatorial sites [O(1)–Ti(1)–O(3) 119.3(1)°, O(1)–Ti(1)–O(4) 118.4(1)°; O(3)–Ti(1)–O(4) 115.9(1)°]. In general terms, the Ti–O distances are within the bounds expected for five-coordinate titanium complexes of this type, with the Ti–N distance [2.385 Å (mean)] being, if anything, slightly longer than those found in comparable systems. Thus, for example, a useful comparison can be made with the corresponding bond lengths found in the complexes $N[CH_2(3,5\text{-}Me_2C_6H_2)O]_3$-TiOR [R = $C_6H_3{}^iPr_2$-2,6, *d*(Ti–O) = 1.833 Å (mean), *d*(Ti–N) = 2.305(2) Å; R = ^{i}Pr, *d*(Ti–O) = 1.831 Å (mean), *d*(Ti–N) = 2.295(3) Å] and $N[CH_2(3,5\text{-}Me_2C_6H_2)O]_2(CH_2\text{-}CH_2O)$TiOR [R = $C_6H_3{}^iPr_2$-2,6, *d*(Ti–O) = 1.822 (mean), *d*(Ti–N) = 2.288(3) Å], each of which features an analogous (approximately trigonal bipyramidal) $Ti(OR)_4(NR_3)$ unit, with the amine donor occupying one of the axial positions.[11]

In a bid to obtain a complex of the desired composition, *i.e.* $\mathbf{L^1}_2Ti(OR)_2$, the reaction stoichiometry was varied (using a large excess of $H_2\mathbf{L^1}$ under more forcing conditions); the same dinuclear complex was isolated. Reduction in the steric bulk of the alkoxide co-ligands was therefore investigated in order to probe whether this would allow for the coordination of more than one $(\mathbf{L^1})^{2-}$ moiety. Reaction of $H_2\mathbf{L^1}$ with titanium tetrakis(ethoxide) under similar conditions yields colourless crystals in low yield after recrystallisation from hexane.



Scheme 4 Syntheses of mononuclear group 4 complexes $\mathbf{L^2}Ti(O^iPr)_2$ and $\mathbf{L^2}_2Zr$. Reagents and conditions: $Ti(O^iPr)_4$ or $Zr(O^nPr)_4$ (1 equiv.), neat reagents, 20 °C, 4 h, separation of isomers by recrystallization from hexanes, 44 and 39%, respectively (for crystalline products).

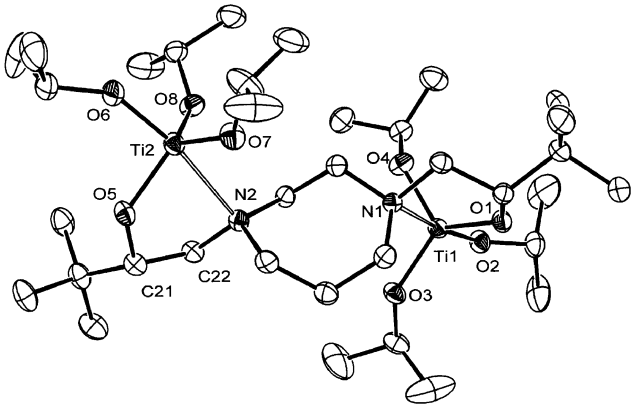


Fig. 1 Structure of $\mathbf{L^1}Ti_2(O^iPr)_6$; hydrogen atoms have been omitted for clarity and ORTEP ellipsoids set at the 30% probability level. Important bond lengths (Å) and angles (°): Ti(1)–O(1) 1.853(3), Ti(1)–O(2) 1.784(3), Ti(1)–O(3) 1.821(3), Ti(1)–O(4) 1.820(3), Ti(1)–N(1) 2.378(3), Ti(2)–N(2) 2.391(3); O(1)–Ti(1)–O(3) 119.3(1), O(1)–Ti(1)–O(4) 118.4(1); O(3)–Ti(1)–O(4) 115.9(1), O(2)–Ti(1)–N(1) 171.0(1), O(6)–Ti(2)–N(2) 170.38(12).

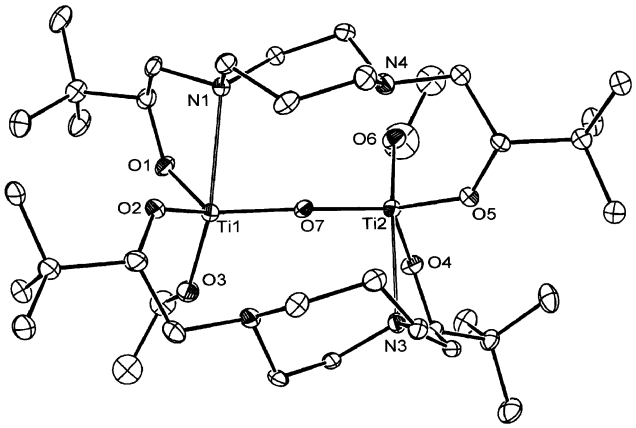


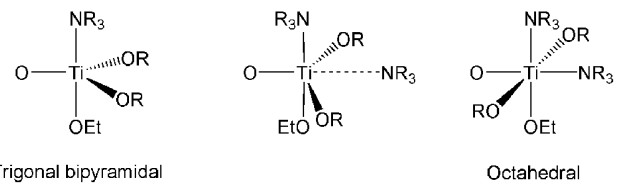
Fig. 2 Structure of $\mathbf{L^1}_2Ti_2(OEt)_2(\mu\text{-}O)$; hydrogen atoms have been omitted for clarity and ORTEP ellipsoids set at the 30% probability level. Important bond lengths (Å) and angles (°): Ti(1)–O(7) 1.826(4), Ti(2)–O(7) 1.818(4), Ti(1)–O(1) 1.860(4), Ti(1)–O(2) 1.860(4), Ti(1)–O(3) 1.835(3), Ti(2)–O(4) 1.852(3), Ti(2)–O(5) 1.840(4), Ti(2)–O(6) 1.827(4), Ti(1)–N(1) 2.506(4), Ti(1)–N(2) 2.757(4), Ti(2)–N(3) 2.443(4), Ti(2)–N(4) 2.962(4); O(6)–Ti(2)–N(3) 165.3(2), O(4)–Ti(2)–O(5) 109.4(2), O(4)–Ti(2)–O(7) 116.6(2), O(5)–Ti(2)–O(7) 125.0(2).

Integration of the ^{t}Bu and Et ^{1}H NMR signals implies an $\mathbf{L^1}$: OEt ratio of 1 : 1, and the formulation $\mathbf{L^1}_2Ti_2(OEt)_2(\mu\text{-}O)$ demonstrated by mass spectrometry has been confirmed crystallographically (Fig. 2 and Table 1).

The crystal structure of $\mathbf{L^1}_2Ti_2(OEt)_2(\mu\text{-}O)$ confirms that a 1 : 1 ratio of $(\mathbf{L^1})^{2-}$ to Ti(IV) can be achieved, albeit with the ligand still adopting a bridging, rather than chelating mode of binding. Noteworthy is the linking of the two titanium centres *via* a symmetrically bridging oxo ligand [Ti(2)–O(7) 1.818(4) Å, Ti(1)–O(7) 1.826(4) Å], which is presumably derived from conversion of titanium-bound OEt ligands to OH (by adventitious water) followed by a condensation step. The coordination sphere at each titanium also features one ethoxide ligand remaining from the starting material and two alkoxide linkages (one from each $\mathbf{L^1}$ ligand). Each metal centre is also engaged in two disparate Ti–N interactions [*e.g.* Ti(2)–N(3) 2.443(4), Ti(2)–N(4) 2.962(4) Å]. The shorter Ti–N distance is relatively long for a N→Ti donor/acceptor interaction featuring a $Ti(OR)_4$ type Lewis acid,[11] whereas the longer Ti–N distance falls outside the sum of conventional covalent radii for N and Ti.[12] The geometry at each titanium centre can therefore probably best be considered as intermediate between trigonal bipyramidal and octahedral, being formally derived from a regular trigonal bipyramid by approach of the weakly bound sixth donor in the equatorial plane (Scheme 5). The axial positions are occupied by the more tightly bound amine donor and the ethoxide ligand [O(6)–Ti(2)–N(3) 165.3(2)°]. The two remaining $\mathbf{L^1}$ alkoxide donors and the bridging oxygen constitute the trigonal plane (sum of the O–Ti–O angles 351.0°) in which distortions from 120° angles presumably reflect, at least in part, the approach of the second, weakly-bound amine donor [O(4)–Ti(2)–O(5) 109.4(2)°; O(4)–Ti(2)–O(7) 116.6(2)°; O(5)–Ti(2)–O(7) 125.0(2)°].

Preliminary results therefore imply that the relatively rigid ligand backbone in $(\mathbf{L^1})^{2-}$ prevents it from binding in a chelating fashion to small transition metal centres such as Ti(IV). Furthermore, although the formation of a Ni(II) complex containing the diprotonated ligand $H_2\mathbf{L^1}$ has demonstrated the possibility of chelation with larger metals, the ancillary water ligands in $[(H_2\mathbf{L^1})Ni(OH_2)_2][ClO_4]_2$ are co-ordinated in the undesirable trans orientation.[10] The Ti(IV) and Zr(IV) coordination chemistries of the more flexible system $(\mathbf{L^2})^{2-}$ were therefore targeted.

(b) Coordination chemistry of $(\mathbf{L^2})^{2-}$. In the case of ligand $(\mathbf{L^2})^{2-}$, the precursor $H_2\mathbf{L^2}$ is obtained as an inseparable mixture of *rac* and *meso* diastereomers and utilised as such for reactions with $Ti(O^iPr)_4$ and $Zr(O^nPr)_4$ (see Scheme 5). The reaction of $H_2\mathbf{L^2}$ with titanium tetrakis(isopropoxide) gives two products, as determined from the ^{1}H and ^{13}C NMR spectra of the crude reaction mixture. Careful recrystallization from hexanes (twice) allows the isolation of a colourless crystalline solid, for which ^{1}H and ^{13}C NMR and mass spectrometry indicate a formulation as $\mathbf{L^2}Ti(O^iPr)_2$. The ^{13}C NMR spectrum (see ESI†) shows only nine signals, indicating that in this complex the two halves of the ligand are symmetry related. This inference is confirmed by the results of a single-crystal X-ray diffraction study (Fig. 3 and Table 1) which



Scheme 5 Schematic representation of the coordination environment at titanium in $\mathbf{L^1}_2Ti_2(OEt)_2(\mu\text{-}O)$.

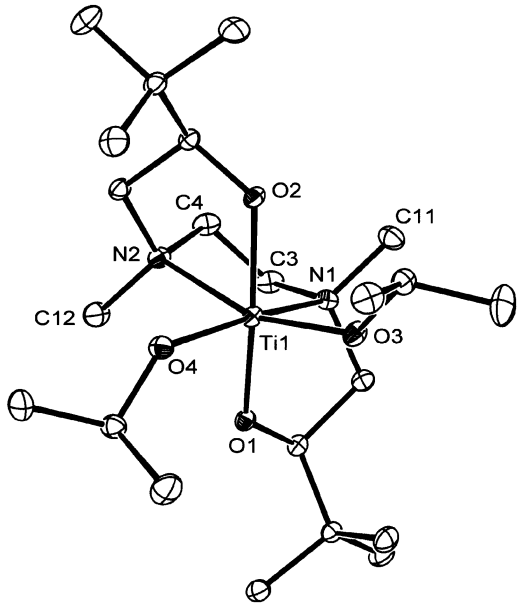


Fig. 3 Structure of $\mathbf{L^2}$Ti(OiPr)$_2$; hydrogen atoms have been omitted for clarity and ORTEP ellipsoids set at the 30% probability level. Important bond lengths (Å) and angles (°): Ti(1)–O(1) 1.906(2), Ti(1)–O(2) 1.901(2), Ti(1)–O(3) 1.836(2), Ti(1)–O(4) 1.834(2), Ti(1)–N(1) 2.325(2), Ti(1)–N(2) 2.313(2); O(1)–Ti(1)–O(2) 163.03(6), O(3)–Ti(1)–O(4) 107.70(7), N(1)–Ti(1)–N(2) 76.20(6).

confirms local (non-crystallographic) C_2 symmetry and that the coordinated ligands are of *rac* stereochemistry (both *R*,*R* and *S*,*S* enantiomers being present in the crystal lattice). Overall, the titanium centre is six-coordinate (a distorted octahedron) and bound to a single $\mathbf{L^2}$ ligand, with two mutually *cis* isopropoxide ligands remaining from the starting material. Thus it would appear that the greater flexibility of the linear $(\mathbf{L^2})^{2-}$ ligand [*cf.* cyclic analogue $(\mathbf{L^1})^{2-}$] allows for a chelating mode of coordination, even for Ti(IV), and that the simple synthesis/isolation of *rac*-$\mathbf{L^2}$Ti(O^{i}Pr)$_2$ from wholly racemic precursors offers a convenient route to C_2 symmetric geometrically *cis* complexes.

The molecular structure of *rac*-$\mathbf{L^2}$Ti(O^{i}Pr)$_2$ contains general structural features characteristic of Ti(IV) complexes of chelating bis(tertiary amine) bis(phenolate) ligands,[4] and closely resembles the complexes $\mathbf{L^{CF_3}}$MX$_2$ (M = Ti, X = Cl; M = Zr, X = CH$_2$Ph) recently synthesized by Carpentier and co-workers containing a diaminodialkoxo ligand system derived from the related but achiral diol [HOC(CF$_3$)$_2$CH$_2$N(Me)CH$_2$]$_2$ ($\mathbf{H_2L^{CF_3}}$).[6b] Thus the transoid O(1)–Ti(1)–O(2) and cisoid N(1)–Ti(1)–N(2) angles associated with the $\mathbf{L^2}$Ti unit [163.03(6) and 76.20(6)°, respectively] and the related Ti–O and Ti–N distances [1.903 (mean) and 2.319 Å (mean)] are essentially identical to the corresponding parameters for $\mathbf{L^{CF_3}}$TiCl$_2$.[6b] Encouraged by the reported synthesis of complexes of the type $\mathbf{L^{CF_3}}$ZrX$_2$ we also examined the reactivity of $\mathbf{H_2L^2}$ towards Zr(IV) precursors. Reaction with zirconium tetrakis(propoxide), however, yields the 1 : 2 complex, Zr($\mathbf{L^2}$)$_2$ irrespective of reaction stoichiometry, which crystallizes from hexane solution with both $\mathbf{L^2}$ ligands of *meso* (*R*,*S*) stereochemistry (Fig. 4). Similar reactivity to generate eight coordinate Zr(IV) complexes of the type ZrL$_2$ is well precedented,[13] with slight lengthening in the Zr–O [2.056(2)–2.073(1) Å] and Zr–N bonds [2.595(2)–2.621(2) Å] with respect to $\mathbf{L^{CF_3}}$Zr(CH$_2$Ph)$_2$ presumably reflecting increases in steric crowding at the metal centre.[6b]

Conclusions

Epoxide ring opening chemistry using 1,4-diazacycloheptane (or its cyclic six-membered analogue 1,4-diazacyclohexane), or the related linear species *N*,*N*′-dimethylethylenediamine, and racemic (±)-3,3-dimethyl-1,2-epoxybutane gives single-step access to pendant alcohol functionalised ditertiary amine pro-ligands. Thus, [HOC(H)^{t}BuCH$_2$N(R)CH$_2$]$_2$ [R$_2$ = CH$_2$CH$_2$CH$_2$ ($\mathbf{H_2L^1}$) and CH$_2$CH$_2$] can be isolated as diastereomerically pure crystalline materials from the reaction

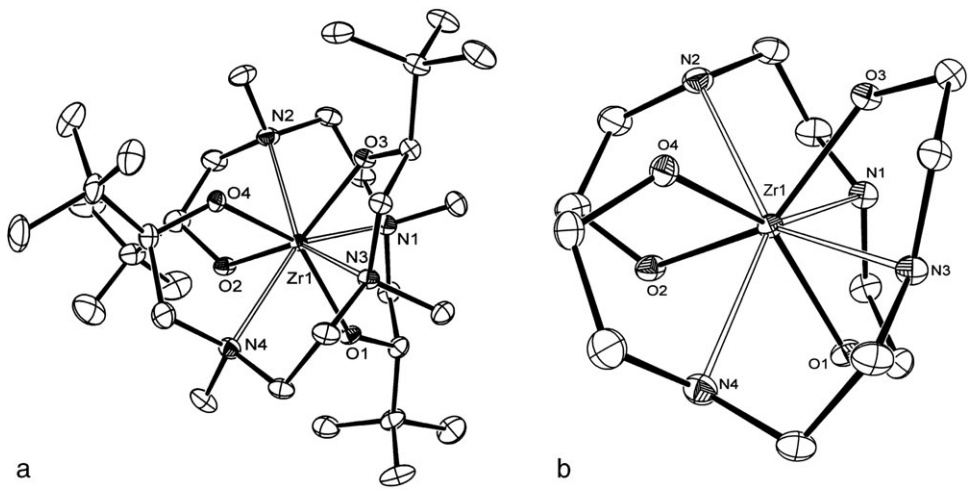


Fig. 4 (a) Structure of $\mathbf{L^2}_2$Zr; hydrogen atoms have been omitted for clarity and ORTEP ellipsoids set at the 30% probability level. Important bond lengths (Å) and angles (°): Zr(1)–O(1) 2.060(2), Zr(1)–O(2) 2.057(2), Zr(1)–O(3) 2.073(2), Zr(1)–O(4) 2.056(2), Zr(1)–N(1) 2.620(2), Zr(1)–N(2) 2.621(2), Zr(1)–N(3) 2.595(2), Zr(1)–N(4) 2.616(2); O(1)–Ti(1)–O(2) 88.99(6), O(3)–Ti(1)–O(4) 87.69(6), N(1)–Ti(1)–N(2) 67.43(6), N(3)–Ti(1)–N(4) 67.62(6); (b) structure of $\mathbf{L^2}_2$Zr emphasizing the coordination geometry at the metal centre.

mixture, while oily $H_2\mathbf{L^2}$ (R_2 = Me_2) is obtained as a mixture of *rac* and *meso* isomers. The contrasting reactions of $H_2\mathbf{L^1}$ and $H_2\mathbf{L^2}$ towards homoleptic group 4 alkoxides highlight the crucial role of ligand backbone flexibility in complex formation. Thus, the chemistry of the more conformationally rigid system $(\mathbf{L^1})^{2-}$ appears to be constrained by the cyclic ligand core, such that it adopts a bridging (μ_2:η^2,η^2) mode of coordination towards Ti(IV), leading to dinuclear metal systems [*e.g.* $\mathbf{L^1}Ti_2(O^iPr)_6$]. By contrast, the more flexible linear system $(\mathbf{L^2})^{2-}$ binds to both Ti(IV) and Zr(IV) in a chelating fashion leading, for example, to the syntheses of the mononuclear 1 : 1 complex $\mathbf{L^2}Ti(O^iPr)_2$ and the 1 : 2 Zr(IV) complex $Zr(\mathbf{L^2})_2$. Although $H_2\mathbf{L^2}$ is necessarily employed as a mixture of *rac* and *meso* diastereomers in its reaction with $Ti(O^iPr)_4$, simple crystallization yields solely the C_2 symmetric isomer of $\mathbf{L^2}Ti(O^iPr)_2$, featuring the *rac* form of the ligand. A simple procedure for the synthesis and isolation of diastereomerically pure C_2 symmetric Ti(IV) complexes of *cis* geometry from racemic precursors is therefore presented.

Acknowledgements

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